

SYNTHESIS AND CHARACTERIZATION OF WELL-DEFINED POLY(1,3- CYCLOHEXADIENE) HOMOPOLYMERS AND COPOLYMERS

David Thomas Williamson

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Approved by

Timothy E. Long, Chair

James E. McGrath

David G. I. Kingston

Alan R. Esker

Carl L. Willis

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Blacksburg Virginia

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David Thomas Williamson

(Abstract)

Polymers containing poly(1,3-cyclohexadiene) were synthesized using a novel pre-formed initiator comprised of an alkyllithium and a tertiary diamine. The use of a pre-formed initiator at moderate temperatures (25°C) enabled the synthesis of high molecular weight poly(1,3-cyclohexadiene) homopolymers ($\langle M_n \rangle = 50000$) with narrow molecular weight distributions ($\langle M_w \rangle / \langle M_n \rangle = 1.20$). In contrast, the use of a conventional anionic initiation approach resulted in polymerizations that lacked significant degrees of livingness, which limited the polymer molecular weights to approximately 10000. Use of the preformed initiator resulted in a reduction in the degree of both chain termination and chain transfer. In addition, the livingness of the polymerization was shown to be a function of the monomer concentration and the polymerization temperature. The regiochemistry of the polymers were shown to be dependent on the tertiary amine used in the polymerization, which provided a route for the synthesis of polymers with a microstructure rich in either high 1,2-addition (70%) or high 1,4-addition (90%). A range of analytical methods were employed to determine the stereo and regiochemistry of poly(1,3-cyclohexadiene). These methods included ^1H NMR, ^{13}C NMR, and endgroup functionalization of the propagating center with chlorotrimethylsilane. The impact of regiochemistry on the thermal properties was examined using differential scanning calorimetry. In addition, the thermooxidative properties of these poly(1,3-cyclohexadiene) polymers were characterized in a series of oxidative studies and the onset of oxidative degradation occurred at 110°C. Perfectly alternating copolymers of poly(1,3-cyclohexadiene-*alt*-styrene) were synthesized, and the reactivity ratios for these copolymers ($r_{1,3\text{CHD}} =$

0.022, $r_{\text{styrene}} = 0.024$) were determined using a conventional Mayo-Lewis approach. The effect of aromatization and hydrogenation on the thermal properties of these copolymers was determined using thermal gravimetric analysis and differential scanning calorimetry. The synthesis of poly(1,3-cyclohexadiene) DVB coupled star-shaped polymers was performed using a convergent arm-first approach in combination with a divinylbenzene coupling agent (PDI = 1.25). Well-defined poly(1,3-cyclohexadiene-*block*-isoprene)-star shaped polymers were synthesized and utilized for the development of novel high temperature thermoplastic elastomers, with excellent elastomeric properties (percent elongation = 745 %, tensile strength = 7.2 MPa). Atomic force microscopy in combination with differential scanning calorimetry verified the presence of microphase separation between the blocks.

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CHAPTER 1

Dissertation Overview

This dissertation examines the synthesis and characterization of poly(1,3-cyclohexadiene) polymers. Chapter two is a review of the relevant literature pertaining to the synthesis of poly(1,3-cyclohexadiene) homopolymers and block copolymers. A critical review of living polymerizations with a focus on anionic polymerizations and the defining characteristics of a living anionic polymerization are also discussed here. In the following chapters, the polymerization of 1,3-cyclohexadiene, the properties of poly(1,3-cyclohexadiene) containing polymers, and the post-polymerization modification of poly(1,3-cyclohexadiene) containing polymers are discussed.

Chapter three describes regiochemical and stereochemical properties of poly(1,3-cyclohexadiene) using three corroborating approaches involving either ^1H NMR spectroscopy, ^{13}C NMR spectroscopy, or end-group functionalization with a ^{29}Si tag. Chapter four explores the synthesis and characterization of poly(1,3-cyclohexadiene) divinyl benzene coupled star-shaped polymers. These polymers were synthesized via the convergent coupling of the living poly(1,3-cyclohexadienyllithium) with divinyl benzene. The utilization of living anionic polymerization methodologies was further explored in chapter five with the synthesis of poly(1,3-cyclohexadiene-*block*-isoprene) diblock copolymers. The synthesis and characterization of these diblock copolymers is discussed. Also in this chapter, the presence of microphase separation between poly(1,3-cyclohexadiene) domains and polyisoprene domains is introduced.

Chapter six explores the synthesis of high molecular weight poly(1,3-cyclohexadiene) containing polymers. In this chapter, a preformed *n*BuLi/TMEDA adduct is introduced and its efficacy for the synthesis of high molecular weight poly(1,3-cyclohexadiene) polymers is discussed. A fundamental study exploring the livingness of poly(1,3-cyclohexadiene) polymerizations is described and the role of chain termination and chain transfer is explored. The well-defined polymerization of 1,3-cyclohexadiene using the preformed *n*BuLi/TMEDA initiator was utilized in chapter seven for the synthesis of poly(1,3-cyclohexadiene-*block*-isoprene) divinyl benzene coupled elastomers. The thermal and mechanical properties of these elastomers is discussed.

In chapter eight, the copolymerization of styrene and 1,3-cyclohexadiene is explored. The reactivity ratios of the monomers were determined using the classical Mayo-Lewis approach. The hydrogenation and aromatization of these copolymers is discussed and a description of the resulting polymer properties is provided. The oxidative sensitivity of poly(1,3-cyclohexadiene) homopolymers is examined in chapter nine. The epoxidation of residual olefin in the polymer repeat unit is also described in this chapter. In chapter ten, the feasibility and controllability of the ozonolysis of poly(1,3-cyclohexadiene) containing polymers is discussed.

CHAPTER 2

Literature Review

2.1 Introduction

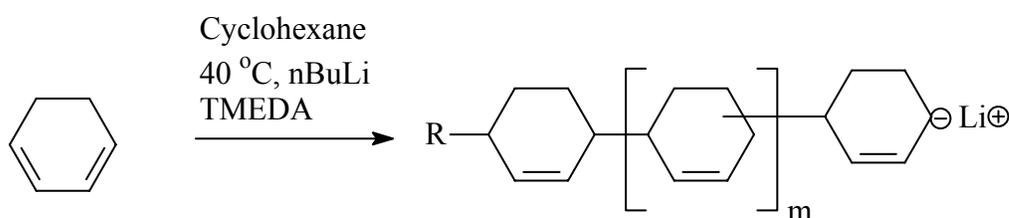
The first anionic polymerization of butadiene was reported using lithium-1-butanide (n-BuLi) by Ziegler in 1929, however, the living nature of the polymerization was not realized until 1956.¹ In 1956, Scwarz et al. demonstrated the living nature of the anionic polymerization of styrene and described the utility of the polymerization in the synthesis of block copolymers. Anionic polymerizations were subsequently used extensively for the production of polydienes. Isoprene and butadiene constitute the majority of the monomers utilized commercially and have been the subject of an extensive body of research. These acyclic dienes have been polymerized via a multitude of different reaction conditions. These conditions included the use of various initiators and the incorporation of numerous additives in an attempt to control the polymer regiochemistry, degree of branching, and degree of termination. Cyclic dienes, such as 1,3-cyclohexadiene, received some attention during the late 1970's, but interest in the polymerization dwindled due to a number of deleterious side reactions that limited the achievable molecular weight. Natori reported in 1997 the first example of a living anionic polymerization of 1,3-cyclohexadiene.² The polymerization was reported

¹ Szwarc, M, M Levy, and R. Milkovich. "Polymerization initiated by electron transfer to monomer. A new method of formation of block polymers." *J. Am. Chem. Soc.* **1956**, 78, 2656. Szwarc, M.. *Carbanions, Living Polymers and Electron Transfer Processes*. Interscience Publishers:

New York, 1968. Ziegler, K., L. Jakob, and A. Wenz. "Alkali organic compounds. XIII. The first reaction products of alkali metals upon butadiene." *Ann.* **1934**, 511, 64. Ziegler, K, H. Colonius, and O. Schafer. "Alkali organic compounds. II. Study of Schlenk's addition of alkali metals to unsaturated hydrocarbons." *Ann.* **1929**, 473, 36.

² Natori, I.. "Synthesis of Polymers with an Alicyclic Structure in the Main Chain. Living Anionic Polymerization of 1,3-Cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System." *Macromolecules* **1997**, 30, 3696.

to proceed in a living fashion in the presence of the additive tetramethylethylenediamine (TMEDA) with the initiator nBuLi (Scheme 1). Due to their cyclic nature, cyclic dienes are potentially a difficult monomer to anionically polymerize due to the electron donation of the cyclic aliphatic structure. The donation of electron density destabilizes the propagating carbanion. However, cyclic dienes represent an interesting and potentially useful family of monomers due to the incorporation of a cyclic unit into the polymer backbone.



Scheme 2-1. Synthesis of poly(1,3-cyclohexadiene) using TMEDA/nBuLi initiator.

A survey of the pertinent literature regarding living anionic polymerizations is explored in the following sections. From the inception of the idea of a living anionic polymerization by Szwarc in 1956 to the current efforts by Hadjichristidis, Long, Mays, McGrath³ and others, the field of living anionic polymerization has a deep and rich history. The following sections attempt to review the mechanistic, synthetic, and morphological characteristics of living anionic polymerizations and the properties of the resulting macromolecules. In the early sections, the mechanistic properties of living anionic polymerizations is reviewed with a focus on the definition of a living system and its synthetic ramifications. Following this, a detailed review of the efforts to synthesize poly(1,3-cyclohexadiene) is performed. This review includes both anionic

³ Long, T.E., A.D. Broske, D.J. Bradley, and J.E. McGrath. "Synthesis and Characterization of Poly(t-butyl Methacrylate -b-Isoprene-b-t-butyl Methacrylate) Block Copolymers by Anionic Techniques." *J. Polym. Sci.* **1989**, 27, 4001. Pispas, Stergios, Marinos Pitsikalis, N. Hadjichristidis, Patrizia Dardani, and Francesco Morandi. "Anionic polymerization of isoprene, butadiene, and styrene with 3-dimethylaminopropyllithium." *Polymer* **1995**, 36, 3005.

and non-anionic efforts. The last sections examine the synthesis of complex macromolecules, including diblock, star-shaped and multiblock copolymers. The morphological characteristics of these copolymers is also explored in this section.

2.2 Living Anionic Polymerization

2.2.1 Introduction

Studies examining anionic polymerizations initially dealt with the reaction of diene and styrene monomers using alkali metals.⁴ Early studies of these reactions indicated the formation of radical anions during the initiation steps, which suggested that the propagating species was also a radical. It was not until Higginson and Wooding published their work exploring the potassium amide initiated polymerization of styrene in liquid ammonia that the anionic nature of the propagating species was clearly evident.⁵ However, it was the pioneering work of Szwarc and coworkers that brought anionic vinyl polymerizations into the forefront of polymer science.⁶ A few years prior to the work by Szwarc, Scott and Hansley demonstrated that lithium initiators were capable of producing polyisoprene having a structure very similar to natural rubber.⁷ The studies by Szwarc and coworkers were based on the studies by Lipkin et al. that explored the reaction of various aromatic hydrocarbons with alkali metals.⁸ In these studies, colored complexes were found after the reaction of aromatic hydrocarbons with alkali metals and these complexes were capable of initiating the polymerization of

⁴ Ziegler, K., L. Jakob, and A. Wenz. "Alkali organic compounds. XIII. The first reaction products of alkali metals upon butadiene." *Ann.* **1934**, 511, 64. Ziegler, K, H. Colonius, and O. Schafer. "Alkali organic compounds. II. Study of Schlenk's addition of alkali metals to unsaturated hydrocarbons." *Ann.* **1929**, 473, 36.

⁵ Higginson, W.C.E., and N.S. Wooding. "Anionic polymerization. I. The polymerization of styrene in liquid ammonia solution catalyzed by potassium amide." *J. Chem. Soc.* **1952**, 774.

⁶ Szwarc, M, M Levy, and R. Milkovich. "Polymerization initiated by electron transfer to monomer. A new method of formation of block polymers." *J. Am. Chem. Soc.* **1956**, 78, 2656.

⁷ Scott, N.D., J. F Walker, and V.L. Hansley. "Sodium naphthalene. I. New method for the preparation of addition compounds of alkali metals and polycyclic aromatic hydrocarbons." *J. Am. Chem. Soc.* **1936**, 58, 2442.

⁸ Lipkin, D., D.E. Paul, and S.I. Weissman. "Reactions of sodium metal with aromatic hydrocarbons." *J. Am. Chem. Soc.* **1953**, 534.

styrene and butadiene.⁹ Later work proved that these complexes were radical anions formed via a single electron transfer from the alkali metal to the lowest unoccupied molecular orbital (LUMO) of the aromatic hydrocarbon.¹⁰ The ease of formation of these radical anions was shown to be a function of the electron affinity of the aromatic hydrocarbon. In addition, Lipkin and coworkers demonstrated that a new red colored species formed immediately after the addition of styrene to a green naphthalene radical anion solution. The new red colored species was initially believed to be the radical anion of styrene.¹¹ However, upon reinvestigation by Szwarc and coworkers, the red colored species was shown to be the styrene dianion, which formed after dimerization of the initially formed styrene radical anion (Scheme 2-2).¹² These styrene dicarbanions were demonstrated to be capable of adding additional styrene leading to the formation of high molecular weight polystyrene. Under rigorous experimental conditions where oxygen, water, and active acidic protons were excluded, these carbanion ends were shown to remain active and capable of polymerizing a second monomer, upon completion of the polymerization of the first monomer.¹³ The absence of termination during polymerization inspired Szwarc to call these “living polymers”.

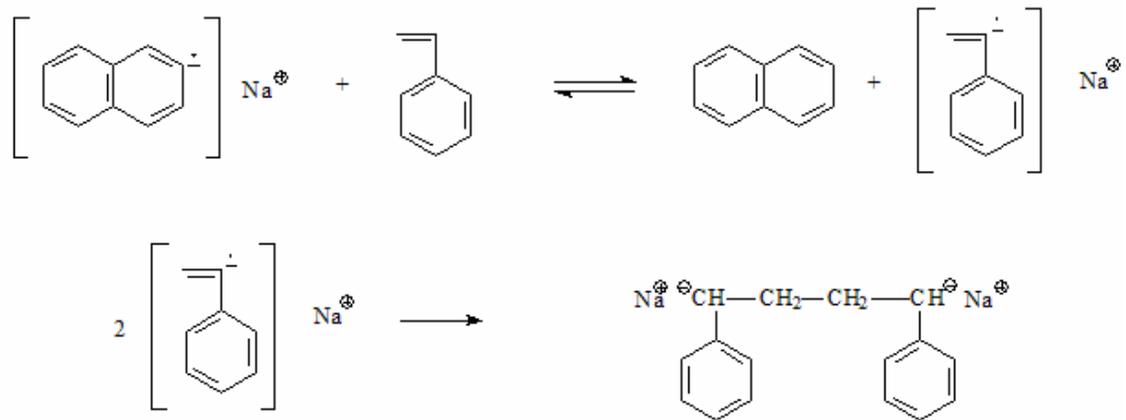
⁹ Lipkin, D., D.E. Paul, and S.I. Weissman. "Reactions of sodium metal with aromatic hydrocarbons." *J. Am. Chem. Soc.* **1953**, 534. Paul, D.E., D. Lipkin, and S.I. Weissman. "Reactions of sodium metal with aromatic hydrocarbons." *J. Am. Chem. Soc.* **1956**, 78, 116.

¹⁰ Ebersson, L., and F. Radner. "Electron-transfer mechanisms in electrophilic aromatic nitration." *Acc. Chem. Res.* **1987**, 20, 53.

¹¹ Lipkin, D., D.E. Paul, and S.I. Weissman. "Reactions of sodium metal with aromatic hydrocarbons." *J. Am. Chem. Soc.* **1953**, 534. Paul, D.E., D. Lipkin, and S.I. Weissman. *J. Am. Chem. Soc.* **1953**, 78, 116.

¹² Szwarc, M, M Levy, and R. Milkovich. "Polymerization initiated by electron transfer to monomer. A new method of formation of block polymers." *J. Am. Chem. Soc.* **1956**, 78, 2656.

¹³ Szwarc, M.. *Carbanions, Living Polymers and Electron Transfer Processes*. Interscience Publishers: New York, 1968.



Scheme 2-2. Formation of styrene dicarbanion from sodium naphthalene.

In addition to the aforementioned electron transfer mechanism described above, living polymers can also be synthesized by using soluble organometallics, such as organolithiums and certain Grignard reagents. The advantage that organometallics have over aromatic complexes is their improved solubility in hydrocarbon solvents. Aromatic complexes are normally only soluble in highly polar solvents, such as tetrahydrofuran. However, organometallics exhibit excellent solubility in a wide range of hydrocarbon solvents including hexane, cyclohexane, and pentane.¹⁴ These initiators function through the direct nucleophilic attack of the monomer, and generate a monofunctional propagating chain. Since the polymer propagates at only one end, the stoichiometric number average molecular weight is given by:

$$\text{Equation 2-1} \quad M_n = \frac{\text{grams of monomer}}{\text{moles of initiator}}$$

In contrast, aromatic complexes, such as sodium naphthalene, yield difunctional carbanionic initiators and propagation can proceed at both ends of the polymer chain. This results in a stoichiometric number average molecular weight given by:

$$\text{Equation 2-2} \quad M_n = \frac{\text{grams of monomer}}{0.5 \text{ moles of initiator}}$$

The characteristics of living anionic polymerizations are a result of the highly reactive nature of the propagating carbanion terminus and its interaction with its counterion.¹⁵ As is found in small molecule carbanion chemistry, carbanion reactivity

¹⁴ Margerison, D., and J.P. Newport. "Degree of association of butyllithium in hydrocarbon media." *Trans. Faraday Soc.* **1963**, 59, 2058. Margerison, D., and J.D. Pont. "Degrees of association of n-pentyllithium and n-octyllithium in benzene." *Trans. Faraday Soc.* **1971**, 67, 353.

¹⁵ Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996. Morton, M., J.E. McGrath, and P.C. Juliano. "Structure-Property Relationships for Styrene-Diene Thermoplastic Elastomers." *J. Polym. Sci.* **1969**, 26, 99.

is greatly affected by the nature of the counterion.¹⁶ Surprisingly, most metal carbon bonds exhibit a significant degree of covalent character.¹⁷ For example, a sodium-carbon bond exhibits approximately 55% covalent character and an aluminum-carbon bond exhibits 78% covalent character. The degree of covalent character is even more pronounced for carbon-lithium bonds, where the degree of covalent character is 83%. It is this highly covalent character coupled with the tendency to undergo hyperconjugation that increases the strength of the carbon lithium bond. Recent studies examining the bond strength of a carbon and lithium bond using both ⁷Li and ¹³C NMR spectroscopy reported that the carbon lithium bond actually exhibits approximately 90% ionic character.¹⁸ The differences in the reported percentages of covalent character were attributed to the formation of alkyllithium aggregates in solution. In the study by Bauer et al., the organolithium species were studied in a THF solution, which was previously shown to interact strongly with lithium cations driving the dissociation of the alkyllithium aggregate. The dissociation of the aggregate was believed to improve the accuracy of the carbon lithium bond measurements.

In hydrocarbon solvents, the Li⁺ cations and the associated carbanions are associated in a putative aggregate.¹⁹ This aggregate can be envisioned as a cluster comprised of the lithium cations and the polymeric carbanions, with the growing polymer chains extending from the small ionic core. The number of propagating chains

¹⁶ Smid, J. "Historical Perspectives on Living Anionic Polymerization." *J. Polym. Sci., Part A: Polym. Chem* **2002**, 40, 2101.

¹⁷ Negishi, E. *Organometallics in Organic Syntheses, Vol. 1: General Discussions and Organometallics of Main Group Metals in Organic Synthesis*. John Wiley and Sons: New York, 1980.

¹⁸ Bauer, W., W.R. Winchester, and von Rague Schleyer P. "Monomeric Organolithium Compounds in Tetrahydrofuran:tert-Butyllithium, sec-Butyllithium, "Supermesityllithium", Mesityllithium, and Phenyllithium. Carbon-Lithium Coupling Constants and the Nature of Carbon Lithium Bonding." *Organometallics* **1987**, 6, 2371.

¹⁹ Wardell, J.L. "Alkali Metals." In *Comprehensive Organometallic Chemistry; The Synthesis, Reactions and Structures of Organometallic Compounds*, edited by G. Wilkinson, F. Gordon, A. Stone and E.W. Abel, 43. Oxford: Pergamon Press, 1982. Brown, T.L. "Mechanism of organolithium reactions in hydrocarbon solution." *Organomet. Chem.* **1966**, 3, 365. Brown, T.L. "Structures and reactivities of organolithium compounds." *Pure Appl. Chem.* **1970**, 23, 447. Wakefield, B.L. *The Chemistry of Organolithium Compounds* Pergamon Press: Oxford, 1974.

in the aggregate is typically defined as the degree of aggregation (n), which is dependent upon the carbanionic species.²⁰ The less sterically hindered n-butyllithium species tend to be found as hexamers at 25°C in cyclohexane. In contrast, more sterically hindered carbanions, such as secondary carbanions, exhibited a decrease in aggregation and formed tetramers or dimers.²¹ Poly(styryllithium) species were shown to be dimers in solution.²² Outlined in Table 1 is the degree of association for a wide range of organometallics species in hydrocarbon solvents. A number of other factors also affect the degree of aggregation. Some of these factors are delocalization of charge, concentration effects, temperature effects, and the role of a polar solvent in place of an aliphatic solvent. Polar solvents decrease the degree of aggregation by solvating the organometallics species.²³ For example, n-BuLi is present as hexamers in both benzene and cyclohexane (Table 2-1), however in THF or diethyl ether, n-BuLi has a degree of aggregation value of 4 and 2.4, respectively.²⁴ Neutron and light scattering studies on solutions containing polymers with alkyllithium chain ends have suggested the presence of polymeric aggregates such as dimers or tetramers, and also the presence species with higher degrees of aggregation.²⁵ The presence of aggregates with a degree of association greater than four or five was disputed and the evidence

²⁰ Lewis, H.L., and T.L. Brown. "Association of alkyllithium compounds in hydrocarbon media. Alkyllithium-base interactions." *J. Am. Chem. Soc.* **1970**, 92, 4664. Bywater, S., and D.J. Worsfold. "Alkyllithium anionic polymerization initiators in hydrocarbon solvents." *J. Organomet. Chem.* **1967**, 10, 1. Weiner, M., C. Vogel, and R. West. "Physical properties and structure of tert-butyllithium." *Inorg. Chem.* **1962**, 1, 654.

²¹ Glaze, W.H., and C.H. Freeman. "Cyclohexylmetal compounds. IV. The effect of aggregate size on the reactivity of alkyllithium compounds." *J. Am. Chem. Soc.* **1969**, 91, 7198. Morton, M., and L.J. Fetters. "Homogeneous anionic polymerization. V. Association phenomena in organolithium polymerization." *J. Polym. Sci.* **1964**, 2, 3311.

²² Wardell, J.L. "Alkali Metals." In *Comprehensive Organometallic Chemistry; The Synthesis, Reactions and Structures of Organometallic Compounds*, edited by G. Wilkinson, F. Gordon, A. Stone and E.W. Abel, 43. Oxford: Pergamon Press, 1982.

²³ Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996.

²⁴ Weiner, M., C. Vogel, and R. West. "Physical properties and structure of tert-butyllithium." *Inorg. Chem.* **1962**, 1, 654. West, P., and Waack. "Colligative property measurements on oxygen- and moisture-sensitive compounds. I. Organolithium reagents in donor solvents at 25°." *J. Am. Chem. Soc.* **1967**, 89, 4395.

²⁵ Bywater, S. "Active Center Aggregation in Lithium Based Anionic Polymerization. Are Very Large Aggregates Present." *Macromolecules* **1999**, 31, 6010.

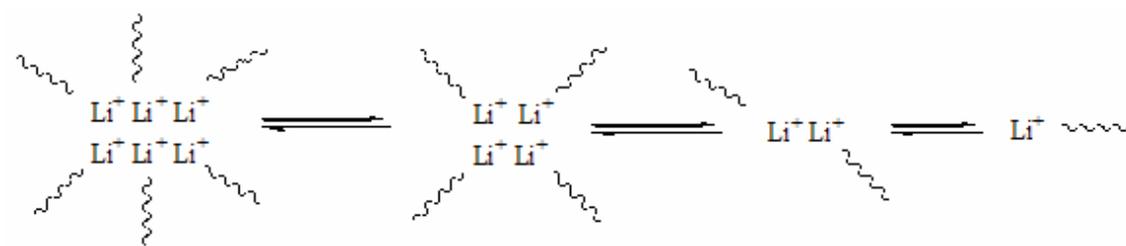


Figure 2-1. The aggregates composed of the clustered lithium cations and the polymer anions are typically found in an equilibrium state. For example, the hexamers are in equilibrium with the tetramers, dimers, and the single propagating polymer chain.

Table 2-1. Aggregation States of Organolithium Compounds in Hydrocarbon Solvents

Compound	Solvent	Degree of Association (n)	Reference
C ₂ H ₅ Li	Benzene	6	26
	Benzene	4.5-6.0	27
	Cyclohexane	6.0	28
n-C ₄ H ₉ Li	Benzene	6.3	29
	Cyclohexane	6.2	29
n-C ₅ H ₁₁ Li	Benzene	6.0	30
n-C ₈ H ₁₇ Li	Benzene	6.0	30
sec-C ₄ H ₉ Li	Cyclohexane	4	31
	Benzene	4	31
t-C ₄ H ₉ Li	Benzene	4	32
	Cyclohexane	4	32

²⁶ Brown, T.L., and M.T. Rogers. "Preparation and properties of crystalline lithium alkyls." *J. Am. Chem. Soc.* **1957**, 79, 1859.

²⁷ Brown, T.L., D.W. Dickerhoff, and D.A. Braffrus. "Infrared and nuclear magnetic resonance [N.M.R.] spectra of ethyllithium." *J. Am. Chem. Soc.* **1962**, 84, 1371.

²⁸ Brown, T.L., J.A. Ladd, and G.N. Newman. "Interaction of alkyllithium compounds with base. Complex formation between ethyllithium and lithium ethoxide in hydrocarbon solvents." *J Organomet. Chem.* **1965**, 3, 1.

²⁹ Margerison, D., and J.P. Newport. "Degree of association of butyllithium in hydrocarbon media." *Trans. Faraday Soc.* **1963**, 59, 2058.

³⁰ Margerison, D., and J.D. Pont. "Degrees of association of n-pentyllithium and n-octyllithium in benzene." *Trans. Faraday Soc.* **1971**, 67, 353.

³¹ Bywater, S., and D.J. Worsfold. "Alkyllithium anionic polymerization initiators in hydrocarbon solvents." *J. Organomet. Chem.* **1967**, 10, 1.

³² Weiner, M., C. Vogel, and R. West. "Physical properties and structure of tert-butyllithium." *Inorg. Chem.* **1962**, 1, 654.

supporting the presence of aggregates with very large degrees of association was attributed to experimental errors.

2.2.2 Criteria for a Living Polymerization.

A living polymerization has been operationally defined as chain growth polymerization devoid of chain transfer or termination.³³ The absence of chain termination or transfer events during the polymerization allows the propagating anions to persist in a quantitative fashion throughout the polymerization. Quantitative persistence of the anions subsequently allows for quantitative functionalization and synthesis of well-defined block copolymers. The recent advent of controlled polymerization methodologies for free radical polymerizations, such as nitroxide mediated polymerization (NMP) or atom transfer radical polymerization (ATRP), has necessitated the introduction of a more flexible definition. Therefore, a living polymerization was recently re-defined as systems in which active centers remain after complete polymerization and subsequent monomer additions will subsequently add to the existing chains and increase their degree of polymerization.³⁴ A more definitive description was put forth by Matyjaszewski that describes the livingness of a polymerization in terms of the rate of propagation relative to termination ($k_{\text{propagation}}/k_{\text{termination}}$).³⁵ In spite of these recent advances in the development of controlled macromolecules using free radical strategies, all living polymerizations must follow a series of diagnostic criteria to be defined as a living polymerization.³⁶ A synopsis of these criteria are described in the following section.

³³ Szwarc, M. *Carbanions, Living Polymers and Electron Transfer Processes*. Interscience Publishers:

New York, 1968. Szwarc, M, M Levy, and R. Milkovich. "Polymerization initiated by electron transfer to monomer. A new method of formation of block polymers." *J. Am. Chem. Soc.* **1956**, 78, 2656. Szwarc, M.. "Living Polymers and Mechanisms of Anionic Polymerization." *Advances in Polymer Science* **1983**, 49, 1.

³⁴ Hawker, C.J., A.W. Bosman, and E. Harth. "New Polymer Synthesis by Nitroxide Mediated Living Radical Polymerizations." *Chem. Rev.* **2001**, 101, 3661.

³⁵ Matyjaszewski, K. "Criteria for living systems with a special emphasis on living cationic polymerization of alkenes." *J. Polym. Sci. Part A: Polym. Chem.* **1993**, 31, 995.

³⁶ Quirk, R. P., and B. Lee. "Experimental criteria for living polymerizations." *Polymer Int.* **1992**, 27, 359.

Criteria for a Living Anionic Polymerization

Criterion 1. The polymerization proceeds until the monomer is quantitatively polymerized and further monomer addition results in the continued polymerization of all the chains. Quantitative monomer consumption is not a defining characteristic of a living polymerization, free radical polymerizations and step growth polymerizations both are capable of quantitative monomer consumption. However, the quantitative persistence of the anions during the polymerization is a defining characteristic of a living polymerization. The livingness of the system is highlighted by the continued polymerization of all the polymer chains, when additional monomer is added. This is often considered the most defining criteria of a living polymerization.

Criterion 2. The number average molecular weight (M_n) exhibits a linear relationship with monomer conversion. This criterion is often used to demonstrate that a polymerization is living because it is experimentally straightforward to determine.³⁷ This is not a rigorous criterion because a plot of molecular weight versus monomer conversion will not detect the presence of termination. If termination occurs during the polymerization, then the remaining polymer chains will continue to propagate thereby consuming monomer. Studies have demonstrated that this criterion will be met even in the presence of low levels of intentional continuous termination.³⁸

Criterion 3. The number of polymer molecules is constant and independent of conversion. This criterion is sensitive to chain transfer because the number of polymer molecules will increase. This criterion is limited by its experimental sensitivity because the detection of low levels of termination or chain transfer can be difficult.³⁹

Criterion 4. The molecular weight of the polymer is a function of the grams of monomer and moles of initiator. The molecular weight of the polymer can be predicted after the monomer is quantitatively consumed. This criterion is sensitive to the presence of protic impurities present in the reaction prior to initiation, which would

³⁷ Natori, I. "Synthesis of Polymers with an Alicyclic Structure in the Main Chain. Living Anionic Polymerization of 1,3-Cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System." *Macromolecules* **1997**, 30, 3696.

³⁸ Quirk, R. P., and B. Lee. "Experimental criteria for living polymerizations." *Polymer Int.* **1992**, 27, 359.

³⁹ Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996.

change the number of active chain ends. However, this method is limited by the error associated with the determination of the molecular weight.

Criterion 5. Polymers with narrow molecular weight distributions are produced.

This is one the most widely used methods for describing a polymerization as being living. Historically, the requirements for a Poisson molecular weight distribution were first described by Flory and Henderson, and Szwarc.⁴⁰ First, the polymerization must be a chain growth polymerization and each propagating site must be equally reactive towards the incoming monomer molecule. The polymerization must also be free of termination or transfer and propagation must be irreversible. Another factor that was outlined by Gold, was the effect of initiation rate relative to propagation rate (k_p/k_i).⁴¹ While polymers with narrow molecular weight distributions have been produced with living systems, slow initiation events were shown to result in broad molecular weight distributions.⁴²

Criterion 6. Block copolymers can be prepared using sequential monomer addition. Due to the persistence of the living anions, block copolymers can be prepared through sequential monomer addition. This is often considered to be one of the best criterion for a living polymerization.⁴³

Criterion 7. End-functionalized polymers can be prepared in quantitative yield. This feature of living polymerization systems was used by Milkovich to produce macromonomers. Unfortunately, most end-functionalization reactions do not proceed quantitatively and statistical error associated with the analytical methods used to determine the degree of functionalization limits the practicality of this method.⁴⁴

⁴⁰ Flory, P.J. "Molecular size distribution in ethylene oxide polymers." *J. Am. Chem. Soc.* **1940**, 62, 1561. Szwarc, M.. *Carbanions, Living Polymers and Electron Transfer Processes*. Interscience Publishers: New York, 1968.

⁴¹ Gold, L. "Statistics of polymer molecular size distributions for an invariant number of propagating chains." *J. Chem. Phys.* **1958**, 28, 91.

⁴² Hsieh, H.L., and O.F. McKinney. "Relation between the heterogeneity index and the kinetic ratio of anionically polymerized polymers." *Polym. Lett.* **1966**, 4, 842.

⁴³ Quirk, R. P., and B. Lee. "Experimental criteria for living polymerizations." *Polymer Int.* **1992**, 27, 359.

⁴⁴ Quirk, R. P., R. T. Mathers, C. Wesdemiotis, and M. A. Arnould. "Investigation of Ethylene Oxide Oligomerization during Functionalization of Poly(styryl)lithium Using MALDI-TOF MS and NMR." *Macromolecules* **2002**, 35, 2912.

Typically, the functional group present on a low molecular weight species can be well characterized.

Criterion 8. The polymerization exhibits pseudo-first order kinetics.⁴⁵ A living anionic polymerization has been shown to exhibit pseudo-first order kinetics as described by equation 3.⁴⁶

Equation 2-3.
$$\ln \frac{[M_0]}{[M]} = k_{\text{obs}} t$$

M_0 = monomer concentration at the beginning of the polymerization

M = monomer concentration during the polymerization

k_{obs} = the rate constant of the polymerization

t = the time of the polymerization

This plot will detect termination reactions, however, it is insensitive to the presence of chain transfer because the number of propagating centers will not change. Therefore, the rate constant (k_{obs}) will remain constant. Long et al. demonstrated the feasibility of monitoring living anionic polymerizations using real time near infrared (NIR) spectroscopy. Direct manipulation of the NIR spectroscopic data enabled the authors to generate a pseudofirst order rate plot for the living anionic polymerization of styrene and isoprene in cyclohexane at 60 °C (Figure 2-2). Although the living nature of both styrene and isoprene were well understood, this study highlights the efficacy of real time spectroscopy in determining the livingness of an anionic polymerization.

⁴⁵ Long, T.E., H.Y. Lui, D.M. Schell, D.M. Teegarden, and D.S. Uerz. "Determination of Solution Polymerization Kinetics by Near-Infrared Spectroscopy. 1. Living Anionic Polymerization Process." *Macromolecules* **1993**, 26, 6237.

⁴⁶ Quirk, R. P., and B. Lee. "Experimental criteria for living polymerizations." *Polymer Int.* **1992**, 27, 359.

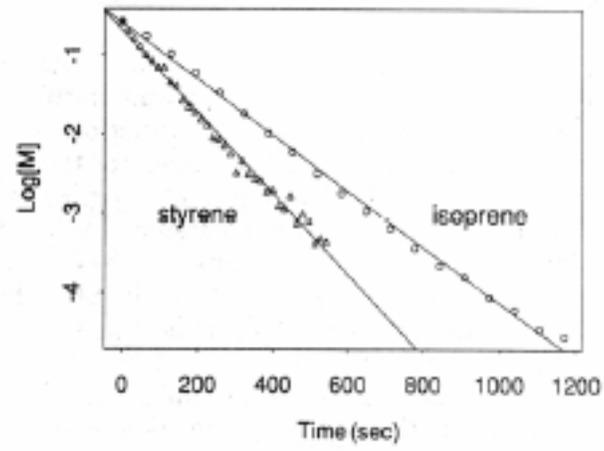


Figure 2-2. Pseudo-first order kinetic plot for the polymerization of styrene and isoprene.

In addition, common sampling techniques used for measuring the rate of reaction are not rapid enough to measure anionic polymerizations when performed in the presence of polar solvents. The rapid data collection associated with real time spectroscopy increases the sensitivity of the method and subtle changes in the kinetics of the polymerization can be detected.

Criterion 9. A plot of equation 2-4 will be linear.⁴⁷

Equation 2-4
$$\ln\left(1 - \frac{[I_0]}{[M_0]} DP_n\right) = -k_p[I_0]t$$

M_0 = monomer concentration at the beginning of the polymerization

I_0 = initiator concentration the beginning of the polymerization

k_p = the rate constant of the polymerization

t = the time of the polymerization

DP_n = Number average degree of polymerization

This technique, advanced by Penczek in 1991, was shown to be sensitive to both chain transfer and termination events. Unlike criteria two, three, or eight, this method was shown to be sensitive to small levels of termination or transfer.

⁴⁷ Penczek, S., P. Kubisa, and R. Szymanski. "On the diagnostic criteria of the livingness of polymerizations." *Makromol. Chem., Rapid Commun.* **1991**, 12, 77.

2.3 General Characteristics of Living Anionic Polymerizations

There are three defined mechanistic stages in anionic polymerizations. These stages are initiation, propagation, and termination. Initiation is defined by the reaction of a highly reactive alkyllithium with the monomer, beginning the chain growth polymerization. The behavior of the propagating polymer chain end with the remaining monomer characterizes the propagation step. If the polymerization meets the above defined criteria for a living anionic polymerization, then the number of active chain ends at the end of the reaction will match the moles of alkyllithium charged to the reaction. The conservation of the reactive chain ends allows the polymerization to be controllably terminated, which is the last stage in an anionic polymerization. The following sections describe these stages in detail, with a focus on the mechanistic details of each stage. In addition, any recent synthetic advances are discussed

2.3.1 Initiation Reactions Involving Alkyllithium Reagents

A significant body of research has explored the initiation of dienes and styrene in hydrocarbon solvents. An early example of such a study was performed by Worsfold and Bywater in 1960, which studied the reaction of styrene with *n*-BuLi in benzene.⁴⁸ In this study, the reaction was determined to follow the relationship.

$$R_i = k[n\text{-C}_4\text{H}_9\text{Li}]^{1/6}[\text{M}_0]$$

Equation 2-5. Relationship between the rate of initiation and the concentration of *n*-BuLi.

The fractional dependence was attributed to the hexameric association of *n*-BuLi in benzene, which was putatively assumed to fully dissociate to the monomeric species to

⁴⁸ Worsfold, D.J., and S. Bywater. "Anionic polymerization of styrene." *Can. J. of Chem.* **1960**, 38, 1891.

react. However, no direct evidence exists supporting the presence of monomeric *n*-BuLi species in hydrocarbon solutions.⁴⁹ Large dissociation enthalpies were associated with the dissociation of *n*-BuLi to a monomeric state, suggesting that any initiation mechanism that only utilizes a monomeric alkyllithium species is not entirely valid.⁵⁰ Brown et al. suggested that aggregated alkyllithium species are reactive toward olefinic and diolefinic monomers rendering a monomeric alkyllithium species unnecessary.⁵¹ The complexation of ethylene with an etherated *n*-BuLi tetramer further supports this proposal.⁵² A number of studies have suggested mechanisms where the alkyllithium species are present in both a monomeric and an associated state.⁵³ An example of this phenomenon was found in the *t*-BuLi initiated polymerization of styrene. A percentage of the *t*-BuLi initiated the polymerization rapidly, however, the remaining *t*-BuLi was determined to be an inefficient initiator and persisted throughout the duration of the reaction.⁵⁴ Studies following these suggested that alkyllithium species are present in a continuous dynamic equilibrium and therefore are constantly re-associating with a new

⁴⁹ Beckelmann, D., and F. Bandermann. "Classification of Polar Additives with Respect to Their Influence on the Microstructure in Anionic Polymerization of Isoprene with Butyllithium by Transition Energy Measurements." *J. Appl. Polym. Sci.* **1999**, 73, 1533.

⁵⁰ Beckelmann, D., and F. Bandermann. "Classification of Polar Additives with Respect to Their Influence on the Microstructure in Anionic Polymerization of Isoprene with Butyllithium by Transition Energy Measurements." *J. Appl. Polym. Sci.* **1999**, 73, 1533. Young, R. N., R. P. Quirk, and L.J. Fetters. "Anionic polymerizations of nonpolar monomers involving lithium." *Advances in Polymer Science* **1984**, 1.

⁵¹ Brown, T.L. "Mechanism of organolithium reactions in hydrocarbon solution." *Organomet. Chem.* **1966**, 3, 365.

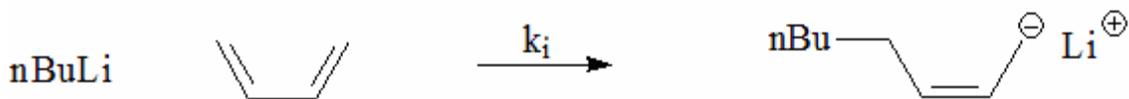
⁵² Bartlett, P.D., C.V. Goebel, and W.P. Webber. "Ethylenation of secondary and tertiary alkyllithiums. II. Its kinetics and the nature of the active species." *J. Am. Chem. Soc.* **1969**, 91, 7425.

⁵³ Hsieh, H.L. "Molecular weight and molecular weight distribution of polymers prepared from butyllithiums." *J. Polym. Sci.* **1965**, A3, 163. Roovers, J.E.L., and S. Bywater. "Reaction of tert-butyllithium with styrene and isoprene. Comparison of chain initiation with the isomers of butyllithium." *Macromolecules* **1975**, 8, 251.

⁵⁴ Hsieh, H.L. "Molecular weight and molecular weight distribution of polymers prepared from butyllithiums." *J. Polym. Sci.* **1965**, A3, 163.

aggregate species.⁵⁵ The exception to this finding is *t*-BuLi, which proceeds through a slow intermolecular exchange in hydrocarbon solvents.⁵⁶

Other factors were shown to further complicate the process of initiation. These include the effect of excess monomer relative to alkyllithium, alkyllithium concentration, and use of aliphatic versus aromatic solvents. The effect of monomer concentration on the reaction order was attributed to the π -complexation of the monomer with the alkyllithium species.⁵⁷ In spite of the large body of fundamental research that was performed, no single mechanism has fully described the initiation of a living anionic polymerization. All the above described studies generally examined concentrated alkyllithium solutions and are not necessarily an appropriate model for what occurs in a living anionic polymerization, which is normally performed under dilute conditions (alkyllithium concentrations less than 5×10^{-2} M). Although the exact mechanism of the initiation event remains unclear, initiation of the polymerization must involve the nucleophilic reaction of the alkyllithium with the double bond present on the monomer (Scheme 2-3).



Scheme 2-3. Initiation step in the anionic polymerization of butadiene.

⁵⁵ Lewis, H.L., and T.L. Brown. "Association of alkyllithium compounds in hydrocarbon media. Alkyllithium-base interactions." *J. Am. Chem. Soc.* **1970**, 92, 4664.

⁵⁶ Darensbourg, M.Y., B.Y. Kimura, G.D. Hartell, and T.L. Brown. "Organometallic exchange reactions. X. Cross-association of tert-butyllithium. Kinetics of tert-butyllithium dissociation." *J. Am. Chem. Soc.* **1970**, 92, 1237.

⁵⁷ Smart, J.A., R. Hogan, P.A. Scherr, and M.T. Emerson. "Metal-double bond interactions. IV. Study of lithium- π -electron interactions in 3-butenyllithium by lithium-7 and proton NMR spectroscopy." *J Organomet. Chem.* **1974**, 64, 1. Smart, J.B., M.T. Emerson, and J.P. Oliver. "Lithium- π -electron interactions in but-3-enyllithium." *J. Am. Chem. Soc.* **1966**, 88, 4101.

2.3.1.1 Use of Novel Initiators

Recent advances in the field of anionic chemistry have utilized initiators that contain a protected functional group. Monofunctional, telechelic, and heterotelechelic macromolecules were synthesized using alkyllithium initiators with protected functionalized hydroxyl groups.⁵⁸ The highly reactive nature of an anionic polymerization requires that the functional group on the initiator be protected with a suitable protecting group. Hydroxyl groups present on the initiator were commonly protected using a trialkylsilyl chloride species, which can be readily removed under acidic conditions.⁵⁹ Other functional groups, such as amine or carboxy, have also been utilized. There are five criteria critical for the evaluation of a protected hydroxyl-functionalized initiator. These criteria are:

Criterion 1. Initiator solubility. A number of the early protected functionalized initiators exhibited poor solubility in aromatic and hydrocarbon solvents and required the use of ethereal solvents. As such, these early functionalized initiators resulted in poly(dienes) with a high percentage of 1,2-microstructure.⁶⁰ The synthesis of poly(dienes) containing a high percentage of 1,4-addition required the use of initiators with excellent solubility in aromatic and hydrocarbon solvents. 3-(*tert*-butyldimethylsilyloxy)-1-propyllithium and similar protected functionalized initiators were shown to have excellent solubility in aromatic and hydrocarbon solvents and

⁵⁸Quirk, R. P., S.H. Jang, H. Yang, and Y Lee. "Anionic synthesis of hydroxyl-functionalized polymers using protected, functionalized alkyllithium and isoprenyllithium initiators." *Macromol. Symp.* **1998**, 132, 281.

⁵⁹Quirk, R. P., J.J. Ma, G. Lizarrage, H. Hasegawa, Y. K. Kim, S.H. Jang, and Y. Lee. "Anionic Synthesis of Hydroxy-Functionalized Polymers Using Functionalized Initiators and Electrophilic Termination." *Macromolecular Symposia* **2000**, 161, 37.

⁶⁰Schulz, D.N., A.F. Halasa, and A.E. Oberster. "Anionic polymerization initiators containing protected functional groups and functionally terminated diene of polymers." *J. Polym. Sci. Part A: Polym. Chem. Ed.* **1974**, 15, 2401. Schulz, D.N., J.C. Sanda, and B.G. Willoughby. "Functionally Terminal Polymers Via Anionic Methods." In *ACS Symposium Series*, edited by J.E. McGrath. Washington DC: The American Chemical Society, 1981.

polymers synthesized using these initiators exhibited a high percentage of 1,4-addition (90%).⁶¹

Criterion 2. Initiator Efficiency. As described above, the rate of initiation must be rapid relative to the rate of propagation for an alkyllithium initiator to be effective for an anionic polymerization. For the 3-(tert-butyldimethylsilyloxy)-1-propyllithium, early studies suggested that during the initiation of the polymerization only a percentage of the alkyllithium species reacted with styrene in a solution of cyclohexane. The remainder of the alkyllithium species were unable to react due to their cross association with the poly(styryllithium) species in the alkyllithium aggregate. Subsequent studies demonstrated that this initiator was efficient for the polymerization of isoprene in cyclohexane.⁶²

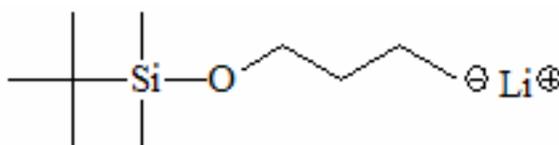


Figure 2-3.-(tert-butyldimethylsilyloxy)-1-propyllithium.

Criterion 3. Rate of initiation relative to propagation. If the rate of initiation relative to propagation is slow, then the polymers will exhibit a broad molecular weight distribution. For the polymerization of styrene, the 3-(tert-butyldimethylsilyloxy)-1-propyllithium initiator suffered from a slow rate of initiation⁶³ and as expected the polymers exhibited a broad molecular weight distribution.⁶⁴

⁶¹ Quirk, R. P., S.H. Jang, H. Yang, and Y Lee. "Anionic synthesis of hydroxyl-functionalized polymers using protected, functionalized alkyllithium and isoprenyllithium initiators." *Macromol. Symp.* **1998**, 132, 281.

⁶² Hudelson, C.L., K. Yamauchi, and T. E. Long. "Unique combinations of macromolecular topology and functionality." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **2002**, 43, 485.

⁶³ Quirk, R. P., S.H. Jang, H. Yang, and Y Lee. "Anionic synthesis of hydroxyl-functionalized polymers using protected, functionalized alkyllithium and isoprenyllithium initiators." *Macromol. Symp.* **1998**, 132, 281.

⁶⁴ Hsieh, H.L., and O.F. McKinney. "Relation between the heterogeneity index and the kinetic ratio of anionically polymerized polymers." *Polym. Lett.* **1966**, 4, 843.

Criterion 4. The protected functional groups are stable during an anionic polymerization. Due to the highly reactive nature of the propagating carbanion in anion polymerizations, it is critical that the protected functional group remain stable during the polymerization. Protected functionalized initiators containing a hydroxyl carrying mixed acetal exhibited a minor loss of functionality during the polymerization.⁶⁵ More recent initiators, such as 3-(tert-butyldimethylsilyloxy)-1-propyllithium, exhibited improved stability during the polymerization and were utilized in the synthesis of well-defined telechelic polyisoprene.⁶⁶

Criterion 5. The protected functional group must be easily deprotected. Typical deprotection strategies utilized mildly acidic conditions, such as the use of one molar equivalent of hydrochloric acid at 65 °C. This method was determined to be effective in the removal of both the tert-butyldimethylsilyl group and the acetal group used by Quirk or Halasa, respectively.^{63,65} Tetrabutylammonium fluoride (TBAF) was also effective in removing the tert-butyldimethylsilyl group from the functionalized initiator.⁶⁷

2.3.2 Propagation Steps in a Living Anionic Polymerization

Analogous to the initiation reaction of living anionic polymerizations, the propagation reaction for both styrene and diene containing monomers in hydrocarbon solvents is effected by the association of the chain end. Uncoupling the propagation reaction from the initiation reaction simplifies the kinetic analysis, but requires the quantitative consumption of the initiator species. The *n*-BuLi initiated polymerization

⁶⁵Schulz, D.N., A.F. Halasa, and A.E. Oberster. "Anionic polymerization initiators containing protected functional groups and functionally terminated diene of polymers." *J. Polym. Sci. Part A: Polym. Chem. Ed.* **1974**, 15, 2401.

⁶⁶Handlin, D.L., R.C. Bening, and C.L. Willis. "Preparation of low viscosity terminally functionalized isoprene polymers." Shell Oil Company, U.S. 5376745 (1994).

⁶⁷Shepard, N., and M.J. Stewart. "Functional anionic initiators." *Macromolecular Reports* **1994**, A31, 835.

of styrene in benzene was one of the first polymerizations studied.⁶⁸ In this study, it was shown that the initiator persists during the beginning of the reaction unless the monomer concentration was in excess of 1.08 M. Additional studies demonstrated that at an *n*-BuLi concentration in excess of millimolar, residual initiator was present at the end of the polymerization.⁶⁹ In contrast to the results for *n*-BuLi, *sec*-BuLi was determined to be consumed rapidly in the early stages of styrene polymerizations.⁶⁸ Therefore, the majority of the studies examining the propagation step have used *sec*-BuLi. The kinetics of diene and styrene polymerizations were found to be complex due to the association phenomenon of the propagating chain-end. For styrene polymerizations it has been repeatedly assumed that the propagating center exists as a dimer in hydrocarbon solutions.⁷⁰ These studies examined the degree of association using light scattering, UV-visible spectroscopy, and viscometry. As shown in similar studies, the degree of association for poly(butadienyllithium) was 4.⁷¹ Unlike the reaction order for the initiation step, the reaction order dependence of the propagating step is independent of the polymerization solvent.⁷² However, the relative rate of polymerization is a function of the solvent or any additives present.

⁶⁸Worsfold, D.J., and S. Bywater. "Anionic polymerization of styrene." *Can. J. of Chem.* **1960**, 38, 1891.

⁶⁹Hsieh, H.L. "Molecular weight and molecular weight distribution of polymers prepared from butyllithiums." *J. Polym. Sci.* **1965**, A3, 163.

⁷⁰Johnson, A.F., and D.J. Worsfold. "Anionic polymerization of butadiene and styrene." *J. Polym. Sci., A* **1965**, 3, 449. Morton, M., R.A. Pett, and L.J. Fetters. "Cross-association of polyisoprenyllithium with ethyllithium." *Macromolecules* **1970**, 333.

⁷¹Worsfold, D.J., and S. Bywater. "Degree of association of polystyryl-, polyisoprenyl-, and polybutadienyllithium in hydrocarbon solvents." *Macromolecules* **1972**, 5, 593.

⁷²Young, R. N., R. P. Quirk, and L.J. Fetters. "Anionic polymerizations of nonpolar monomers involving lithium." *Advances in Polymer Science* **1984**, 1.

2.3.2.1 *Polar Additives*

One of the most often used methods of tuning ion-pair interactions in a polymerization is the utilization of polar solvents or Lewis bases.⁷³ Understanding the effects of Lewis bases or polar solvents on an anionic reaction is critical to controlling the reaction rate and stereochemical selectivity. Highly polar solvents, such as THF or 1,2-dimethoxyethane, were demonstrated to solvate the ionic cluster and increase the percentage of free ion pairs in solution.⁷⁴ The addition of small percentages of polar additives to a nonpolar solution was shown to dramatically affect the percentage of free ions in solution. Common additives utilized in anionic polymerization include THF, diethyl ether, tetramethylethylenediamine (TMEDA), and dipiperidinoethane (dipip).⁷⁵ Tertiary amines, such as TMEDA, were shown to strongly interact with lithium and destabilize the hyperconjugated form, resulting in reduced carbon lithium bond strength.⁷⁶ This increases the reactivity of the carbanion and typically results in increased polymerization rates.⁷⁷ In addition, the nature of the ion pair affects both the degree of 1,2 versus of 1,4-addition and the resulting degree of cis or trans isomers of

⁷³Beckelmann, D., and F. Bandermann. "Classification of Polar Additives with Respect to Their Influence on the Microstructure in Anionic Polymerization of Isoprene with Butyllithium by Transition Energy Measurements." *J. Appl. Polym. Sci.* **1999**, 73, 1533. Schoenberg, E., T. Lambertson, B. Schubert, J.K. Cockcroft, and A. Wiedenmann. "Metal alkyl and aryl compounds. 40. Structure refinement of methyllithium by neutron diffraction of (LiCD₃)₄ at 1.5 and 290 K." *Chem. Ber.* **1990**, 123, 79. Richards, D.H. "The polymerization and copolymerization of butadiene." *Chem. Soc. Rev.* **1977**, 2, 197.

⁷⁴West, P., and Waack. "Colligative property measurements on oxygen- and moisture-sensitive compounds. I. Organolithium reagents in donor solvents at 25°." *J. Am. Chem. Soc.* **1967**, 89, 4395.

⁷⁵Beckelmann, D., and F. Bandermann. "Classification of Polar Additives with Respect to Their Influence on the Microstructure in Anionic Polymerization of Isoprene with Butyllithium by Transition Energy Measurements." *J. Appl. Polym. Sci.* **1999**, 73, 1533.

⁷⁶Negishi, E. *Organometallics in Organic Syntheses, Vol. 1: General Discussions and Organometallics of Main Group Metals in Organic Synthesis*. John Wiley and Sons: New York, 1980.

⁷⁷Smid, J.. "Historical Perspectives on Living Anionic Polymerization." *J. Polym. Sci., Part A: Polym. Chem* **2002**, 40, 2101.

the poly(diene).⁷⁸ These effects arise from the interaction of the propagating chain end with the counterion and the strength of the interaction between the solvent/Lewis base with the alkyllithium species. The size of the ion pair aggregate is not only a function of the solvent polarity but is also affected by the temperature. The ion-pair aggregate in the non-polar hydrocarbon solvents exhibits an increase in aggregation number as the temperature is decreased.⁷⁹ In contrast, the ion pair aggregate exhibits a counter-intuitive relationship to temperature in polar solvents; as the temperature decreases the degree of aggregation becomes lower in polar solvents.⁸⁰ Reduction in solution temperatures increases the percentage of loose ion pairs due to the exothermic nature of ion pair formation. Increasing the percentage of loose ion pairs was shown to have dramatically increased the rate of initiation.

Understanding the role of a Lewis base in determining regiochemistry of the polymerization is critical to recognizing the loss of stereospecificity associated with the lithium counterion, which results in greater than 90% 1,4-addition. The addition of a Lewis base increases the percentage of 1,2-addition during the polymerization, with an increasing percentage of 1,2-addition occurring with Lewis bases that have higher associations with the lithium cation.⁸¹ Lewis bases which have a degree of

⁷⁸Young, R. N., R. P. Quirk, and L.J. Fetters. "Anionic polymerizations of nonpolar monomers involving lithium." *Advances in Polymer Science* **1984**, 1.

⁷⁹Fraenkel, G., W.E. Beckenbaugh, and P.P. Yang. "Exchange and inversion in 2-methylbutyllithium: proton nuclear magnetic resonance line shapes at 300 MHz." *J. Am. Chem. Soc.* **1976**, 98, 6878.

⁸⁰Bauer, W., W.R. Winchester, and von Rague Schleyer P. "Monomeric Organolithium Compounds in Tetrahydrofuran:tert-Butyllithium, sec-Butyllithium, "Supermesityllithium", Mesityllithium, and Phenyllithium. Carbon-Lithium Coupling Constants and the Nature of Carbon Lithium Bonding." *Organometallics* **1987**, 6, 2371. Bauer, w., W.R. Winchester, and von Rague Schleyer P. "Monomeric Organolithium Compounds in Tetrahydrofuran:tert-Butyllithium, sec-Butyllithium, "Supermesityllithium", Mesityllithium, and Phenyllithium. Carbon-Lithium Coupling Constants and the Nature of Carbon Lithium Bonding." *Organometallics* **1987**, 6, 2371. Fraenkel, G., A. Chow, and W.R. Winchester. "Structure and dynamic behavior of solvated neopentyllithium monomers, dimers, and tetramers: proton, carbon-13 and lithium-6 NMR." *J. Am. Chem. Soc.* **1990**, 112, 6190. Bauer, w., and D Seebach. "Determination of the degree of aggregation of organolithium compounds by cryoscopy in tetrahydrofuran." *Helv. Chem. Acta* **1984**, 67, 1972.

⁸¹Quirk, R. P., and D. McFay. "Solvation of polymeric organolithium compounds. Stoichiometry and heats of interaction of N,N,N',N'-tetramethylethylenediamine (TMEDA) with poly(styryl)lithium and poly(isoprenyl)lithium." *J. Polym. Sci., Part A: Polym. Chem.*

complexation greater than monodentate have greater associations with the Li^+ cation.⁸² The strength of the interaction between the lithium counterion and the Lewis base has been measured using enthalpy data. In these studies it was found that the enthalpy of the interaction follows the order depicted in Figure 2-4.⁸³ Recently a broad spectrum of ligation agents have been examined for the ability to induce a high degree of cis enchainment in polyisoprene, and the transition energies.⁸⁴ These authors found a strong correlation between the transition energy and the degree of cis enchainment for monodentate additives. However, bidentate additives did not correlate well and the authors concluded that the bidentate additives, such as TMEDA, form more stable stoichiometric complexes. More recent studies support this conclusion but further discriminate between mono and bidentate additives. In addition to increasing solution polarity, bidentate additives, such as TMEDA and dipiperidinoethane, were shown to interact directly with the alkyllithium species and form almost exclusively dimers (dimer/tetramer 20:1) in hydrocarbon solutions.⁸⁵

1983, 24, 827. Quirk, R. P., and D. McFay. "Solvation of polymeric organolithium compounds. Heats of interaction of tetrahydrofurans and N,N,N',N'-tetramethylethylenediamine (TMEDA) with poly(butadienyl)lithium." *J. Polym. Sci., Part A: Polym. Chem. Ed.* **1986**, 24, 827.

⁸²Quirk, R. P., D.E. Kester, and R.D. Delaney. "Solvation of alkyllithium compounds. Heats of interaction of Lewis bases with butyllithium." *J. Organomet. Chem.* **1973**, 59, 45. Quirk, R. P., and D.E. Kester. "Solvation of alkyllithium compounds. Steric effects on heats of interaction of bases with trimethylsilylmethylithium versus butyllithium." *J. Organomet. Chem.* **1974**, 72, C23. Quirk, R. P., and D.E. Kester. "Solvation of alkyllithium compounds. Steric effects on heats of interaction of bases with hexameric versus tetrameric alkyllithiums." *J. Organomet. Chem.* **1977**, 127, 111.

⁸³Quirk, R. P., and D. McFay. "Solvation of alkyllithium compounds. Heats of interaction of tetrahydrofurans with poly(isoprenyl)lithium and poly(styryl)lithium." *Makromol Chem* **1980**, 1, 71. Young, R. N., R. P. Quirk, and L.J. Fetters. "Anionic polymerizations of nonpolar monomers involving lithium." *Advances in Polymer Science* **1984**, 1.

⁸⁴Beckelmann, D., and F. Bandermann. "Classification of Polar Additives with Respect to Their Influence on the Microstructure in Anionic Polymerization of Isoprene with Butyllithium by Transition Energy Measurements." *J. Appl. Polym. Sci.* **1999**, 73, 1533.

⁸⁵Rennels, R.A., A.J. Maliakal, and D.B. Collum. "Ortholithiation of Anisole by n-BuLi-TMEDA: Reaction via Disolvated Dimers." *J. Am. Chem. Soc.* **1998**, 120, 421. Remenar, J.F., B. L. Lucht, and D.B. Collum. "Lithium Diisopropylamide Solvated by Monodentate and Bidentate Ligands: Solution Structures and Ligand Binding Constants." *J. Am. Chem. Soc.* **1997**, 119, 5567.

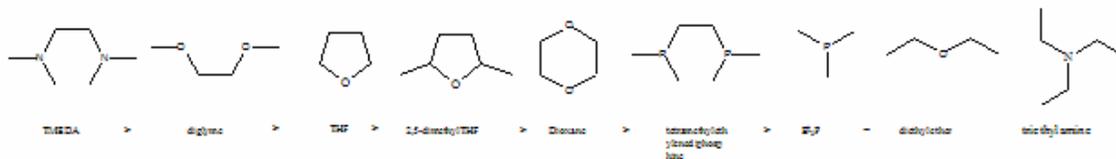


Figure 2-4. The order of the enthalpy interaction between the various ligating agents.

Direct interaction of the bidentate additive dipiperidinoethane (dppe) with the propagating center of the polymerization is believed to be responsible for the higher percentage of 1,2-addition in butadiene polymerizations (99%) than in isoprene polymerizations (97%). The difference in microstructure between these polymerizations was attributed to the steric interaction between the bulky dppe species and the pendant methyl group present in polyisoprenyllithium, that is absent in polybutadienyllithium.⁸⁶ Therefore, the close association of the polymeric alkyl lithium chain end and the bidentate additive in the aggregate present in hydrocarbon solvents was demonstrated to have a strong impact on the polymerization mechanism and the resulting polymer product.

⁸⁶Beckelmann, D., and F. Bandermann. "Classification of Polar Additives with Respect to Their Influence on the Microstructure in Anionic Polymerization of Isoprene with Butyllithium by Transition Energy Measurements." *J. Appl. Polym. Sci.* **1999**, 73, 1533.

2.3.2.2 *Impact of Alkoxides on Anionic Polymerizations*

Alkoxides in anionic polymerizations are not typically considered as Lewis bases but exhibit the ability to alter the regiochemistry,⁸⁷ rate,⁸⁸ and degree of 1,2 versus 1,4-addition. These effects are typically termed "salt effects". Although termed differently, the origin of their interaction with the propagating anion is the same as the Lewis base: the ability to donate a lone pair of the electrons to the complex aggregate of the propagating anion. For the *n*-BuLi initiation of styrene in cyclohexane, the rate of initiation is increased at low concentrations of lithium alkoxide.⁸⁹ Lithium alkoxides were shown repeatedly to slow the rate of the polymerization of styrene, butadiene, and isoprene. The lithium alkoxides occupy a face of the aggregate through electron donation. This complex interaction was explained in terms of equilibrium between the propagating chain end and the alkoxide. The lithium alkoxide complexes with the propagating chain aggregate resulting in a less reactive chain end.⁹⁰ However, the use of other cations in the alkoxide was shown to accelerate the rate of the reaction by 8-100 fold.⁹¹ The increased rates of polymerization exhibited by the addition of other alkali cations (Na, K, Rb) was attributed to the interaction of the propagating anion with the associated alkoxide cation. In addition to increasing the polymerization rate, the polymeric product exhibits a concomitant increase in the percentage of 1,2 enchainment. This increase in 1,2 enchainment is not found when using lithium alkoxides or lithium hydroxides.

⁸⁷Hsieh, H. L., and C.F. Wofford. "Copolymerization of butadiene and styrene by initiation with alkyllithium and alkali metal tert-butoxides." *J. Polym. Sci.* **1969**, 7, 449. Quirk, R. P., and J.J. Ma. "Dilithium initiators based on 1,3-bis(1-phenylethenyl)benzene. Tetrahydrofuran and lithium sec-butoxide effects." *Polymer Int.* **1991**, 24, 197.

⁸⁸Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996.

⁸⁹Hsieh, H.L. "Effect of lithium alkoxide and hydroxide on polymerization initiated with alkyllithium." *J. Polym. Sci., Part A-1* **1970**, 8, 533.

⁹⁰Roovers, J.E.L., and S. Bywater. "Butyl lithium-initiated polymerization of styrene. Effect of lithium butoxide." *Trans. Faraday Soc.* **1966**, 62, 1876.

An alternative to altering the properties of the macromolecule using a polar additive is the use of a counterion other than lithium. As previously mentioned, the lithium counterion exhibits the ability to control the regiochemistry of diene polymerizations. Typically, when dienes are polymerized using lithiated initiators, the resulting polymers exhibit high degrees of 1,4 enchainment. The use of sodium based initiators for the polymerization of dienes is not a well-studied area due to the poor yields obtained with sodium-based initiators.⁹² Studies using soluble organosodium based initiators have been performed, the most notable of these initiators is 2-ethylhexylsodium (2EHS).⁹³ 2EHS was found to initiate the polymerization of isoprene and the initiation rate exhibited a first order dependence on the initiator concentration. Extensive chain transfer was found to occur for the polymerization of isoprene and butadiene when using 2EHS as the initiator. In contrast to polymerizations using lithium-based initiators, 2EHS exhibited a lesser degree of chain transfer when a Lewis base is added to the reaction. The use of 2EHS also resulted in a higher degree of cis enchainment in the polymer backbone. The authors postulated that the behavior of 2EHS initiated polymerizations is a result of a dimeric association of the active centers and it is through these dimeric centers that these events occur. The use of sodium and lithium based reagents in anionic polymerizations has been precluded by the poor solubility of the sodium based reagents in hydrocarbon solvents. The ability of 2EHS to remain soluble in hydrocarbon solvents renders it ideal for these mixed metal reactions. It was determined that the polymerizations initiated with either 2-ethylhexylsodium or ethylhexyllithium resulted in different degrees of 1,2 versus 1,4 addition. When both initiators were used to initiate the polymerization, the ratio of 1,2 versus 1,4 addition varied between the high 1,4 associated with lithium and the high 1,2 associated with sodium based initiators. The authors concluded that the resulting microstructure of this

⁹² Yakbovich-Arest, A.A., N.I. Pakuro, I.V. Zolotareva, E. V. Kristal, and R. Basova. "Polymerization of Conjugated Dienes Initiated by Soluble Organosodium Compounds in Hydrocarbon Solvents." *Polymer Int.* **1995**, 37, 165.

⁹³ Pakuro, N.I., A.A. Arest-Yakbovich, and L.V. Shcheglova. "Investigation of the initiation reaction of isoprene polymerization with 2-ethylhexylsodium in Heptane." *Macromol. Chem. Phys.* **1995**, 198, 3855. Yakbovich-Arest, A.A., N.I. Pakuro, I.V. Zolotareva, E. V. Kristal, and R. Basova. "Polymerization of Conjugated Dienes Initiated by Soluble Organosodium Compounds in Hydrocarbon Solvents." *Polymer Int.* **1995**, 37, 165.

mixed metal initiating system was a function of a mixed metal active center and not simply a result of the kinetic balance between propagation via a lithium cation or a sodium cation. The rate of exchange between sodium and lithium cations was faster than the rate of chain propagation. Other metals, such as barium, have also been employed in anionic polymerizations resulting in altered polymer microstructures.⁹⁴ Studies have reported the use of barium alkoxide-hydroxide or barium dialkoxide salts in the anionic polymerization of butadiene. These polymerizations resulted in polybutadiene with a high percentage of trans 1,4-microstructure (79%). These polymers exhibited sufficient stereoregularity to undergo strain-induced crystallinity. The effect of magnesium cations were also explored by Defieux et al. in the attempt to retard the rate of styrene polymerizations at elevated temperatures.⁹⁵ In these studies, the alkyllithium and alkylmagnesium species were found to form mixed metal aggregates with the alkyl anions taking part in a slow exchange with the metal cations. Due to the slow alkyl anion exchange, secondary alkyl anions associated with the magnesium species were shown to initiate styrene polymerizations.

⁹⁴ Aggarwal, S.L., T.G. Hargis, R.A. Livigni, H.J. Fabris, and L.F. Marker. "Structure and properties of tire rubbers prepared by anionic polymerization." In *Advances in Elastomers and Rubber Elasticity*, edited by J. Lal and J.E. Mark. New York: Plenum, 1986.

⁹⁵ Defieux, A., S. Menoret, S. Carlotti, P. Desbois, C. Schade, and M. Fontanille. "Retarded Anionic Polymerization: Influence of alkyl Substituents in R₂Mg/PSLi Systems on the Characteristics of High Temperature Styrene Polymerization." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **2000**, 41, 1386.

2.3.3 Termination and Functionalization of Living Anionic Polymerizations

In a living polymerization, no termination occurs during the polymerization allowing for a quantitative reaction of the polymer chain end with the terminating reagent.⁹⁶ The living nature of these chain growth polymerizations renders them unique due to the ability to controllably react an appropriate electrophile with the polymer chain end (Scheme 2-4). Typically, the termination reaction simply consists of a proton transfer from the terminating reagent, such as methanol, to the propagating carbanion. However, in recent years the termination step has been viewed as an opportunity to tune physical properties of the macromolecule using a small endcapping molecule.⁹⁷ These reactions have often been optimized by controlling the solvent, temperature, concentration, stoichiometry, and the addition of polar additives. One of the most common electrophiles used for end-functionalization is ethylene oxide, which places a hydroxyl functionality on the polymer chain end. Hydroxyl terminated polystyrene oligomers (1300-9900) were synthesized in this fashion by Quirk et al., who used an excess of ethylene oxide relative to poly(styryllithium).⁹⁸ In this study, the authors did not observe any ether linkages, which would have indicated the presence of ethylene oxide polymerization. The steric strain and intrinsic reactivity of ethylene oxide toward nucleophiles renders this result surprising, however, previous studies demonstrated that

⁹⁶Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996.

⁹⁷Yamauchi, K., J.R. Lizotte, D.M. Hercules, M.J. Vergne, and T.E. Long. "Combinations of Microphase Separation and Terminal Multiple Hydrogen Bonding in Novel Macromolecules." *J. Am. Chem. Soc.* **2002**, 124, 8599. Marsitzky, D., T. Brand, Y. Geerts, M. Klapper, and K. Mullen. "Synthesis of rod-coil block copolymers via end-functionalized poly(p-phenylene)s." *Macromol. Rapid Commun.* **1998**, 19, 385. Masamoto, J., K. Yalima, S. Aida, M. Ueda, and S. Nomura. "Microphase separation in polyoxymethylene end-capped with long-chain alkyl groups." *Polymer* **2000**, 41, 7283. Jiang, Xiquin, K. Tanaka, A. Takahara, and T. Kajiyama. "Effect of chain end group hydrophobicity on surface aggregation structure of poly(styrene-block-4-vinylpyridine) symmetric diblock copolymer films." *Polymer* **1998**, 39, 2615.

⁹⁸Quirk, R. P., and J.J. Ma. "Characterization of the functionalization reaction product of poly(styryl)lithium with ethylene oxide." *J. Polym. Sci., Part A: Polym. Chem.* **1988**, 26, 2031.

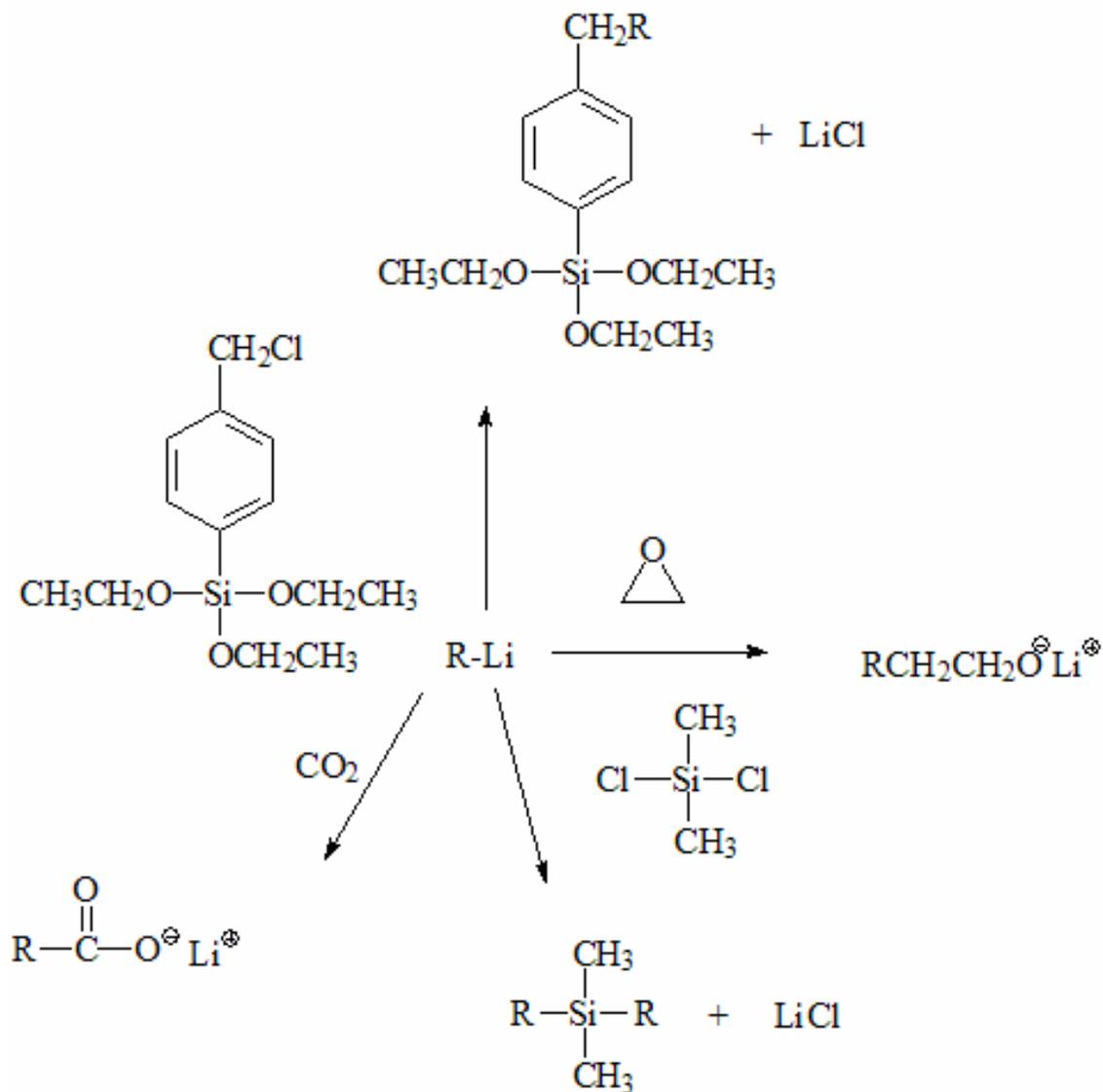
lithium alkoxides are the least reactive alkali metal alkoxides for anionic polymerizations.⁹⁹ Due to the number of well understood reactions utilizing hydroxyl functionalities, ethylene oxide functionalization is ideal for subsequent polymer modification reactions. Recently, studies by Yamauchi and coworkers demonstrated the synthesis of a thermally-responsive, end-functionalized polyisoprene macromolecule, which contained hydrogen bonding moieties attached to the polymer chain end by an ethylene oxide linker.¹⁰⁰ Other applications for functionalized macromolecules included the synthesis of a well defined star polymer via a sol-gel process or the introduction of a polymerizable olefin on the polymer chain end. More broadly, these functional groups have been shown to participate in reversible hydrogen bonding, ionic association, chain extension, branching, or crosslinking reactions. From a historical perspective, one of the most notable uses of polymer functionalization was the synthesis of macromonomers as pioneered by Milkovich and coworkers.¹⁰¹ Studies following the work by Milkovich et al. included the synthesis of novel polymers such as star-shaped macromonomers.¹⁰² This seminal work was based on the presumption that the polymerization was living, thereby facilitating quantitative functionalization of the polymer chain ends.

⁹⁹St. Pierre, L.E., and C.C. Price. "Room temperature polymerization of propylene oxide." *J. Am. Chem. Soc.* **1956**, 78, 3432.

¹⁰⁰Yamauchi, K., J.R. Lizotte, D.M. Hercules, M.J. Vergne, and T.E. Long. "Combinations of Microphase Separation and Terminal Multiple Hydrogen Bonding in Novel Macromolecules." *J. Am. Chem. Soc.* **2002**, 124, 8599.

¹⁰¹Schulz, G.O., and R. Milkovich. "Graft polymers with macromonomers. I. Synthesis from methacrylate-terminated polystyrene." *J. Appl. Polym. Sci.* **1982**, 27, 4773. Milkovich, R. "Synthesis of controlled polymer structures." *Polymer Preprints* **1980**, 21, 40. Milkovich, R. "Synthesis of Controlled Polymer Structures." In *Anionic Polymerization, Kinetics, Mechanisms, and Synthesis*, edited by J.E. McGrath, 41. Washington D.C.: American Chemical Society, 1981.

¹⁰²Xie, H., and W. Sun. "Synthesis and Copolymerization of Epoxy Ether Terminated Polystyrene Macromer." In *Advances in Polymer Synthesis*, edited by B. M. Culbertson and J.E. McGrath. New York: Plenum Press, 1985. Rempp, P., and E. Franta. "Macromonomers: Synthesis, Characterization and Applications." In *Advances in Polymer Science*, 1. New York: Springer-Verlag, 1984. Ishizu, Koji, Hideki Kitana, Tomohiro Ono, and Satoshi Uchida. "Synthesis and Characterization of Polyfunctional Star-Shaped Macromonomers." *Polymer* **1999**, 40, 3229. Ishizu, Koji, and Kenro Sunahara. "Synthesis of Star Polymers by Organized Polymerization of Macromonomers." *Polymer* **1995**, 36, 4155.



Scheme 2-4. Functionalization of the living chain end using a functional group containing electrophile.¹⁰³

¹⁰³Schulz, G.O., and R. Milkovich. "Graft polymers with macromonomers. I. Synthesis from methacrylate-terminated polystyrene." *J. Appl. Polym. Sci.* **1982**, 27, 4773. Quirk, R. P., Y. Jian, and L.J. Fetters. "Carbonation and related reactions of poly(styryl)lithium." *Macromolecules* **1989**, 22, 85. Long, T. E., L. W. Kelts, R.S. Turner, J.A. Wesson, and T.H. Mourey. "Synthesis and characterization of well-defined star polymers via a controlled sol-gel process." *Macromolecules* **1991**, 24, 1431.

2.4 Mechanism of Diene Polymerizations

Linear diene monomers have been extensively studied in an attempt to determine the kinetics of the polymerization. It was initially believed that the cisoid form of the diene is stabilized by the attacking carbanion and the associated lithium counterion to form a six-membered transition state (Figure 2-5).¹⁰⁴

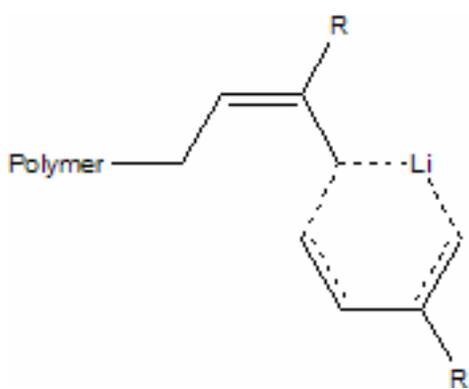


Figure 2-5. Complex of poly(isoprenyllithium) with the diene monomer to form a stabilized cis isomer in the transition state.

This theory was discarded due to its inability to explain the effect of the monomer concentration on the regiochemistry of the polymer. In addition, the regiochemistry of the chain end is fixed only upon the addition of the next monomer unit, and the chain end may isomerize prior to the addition of the next monomer unit. Currently, it is believed that the initially formed cis poly(dienyllithium) chain end can isomerize to the

¹⁰⁴Natori, I. "Synthesis of Polymers with an Alicyclic Structure in the Main Chain. Living Anionic Polymerization of 1,3-Cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System." *Macromolecules* **1997**, 30, 3696.

trans form.¹⁰⁵ This isomerization occurs in competition with the addition of a monomer unit. The equilibrium is shown below (Figure 2-6).

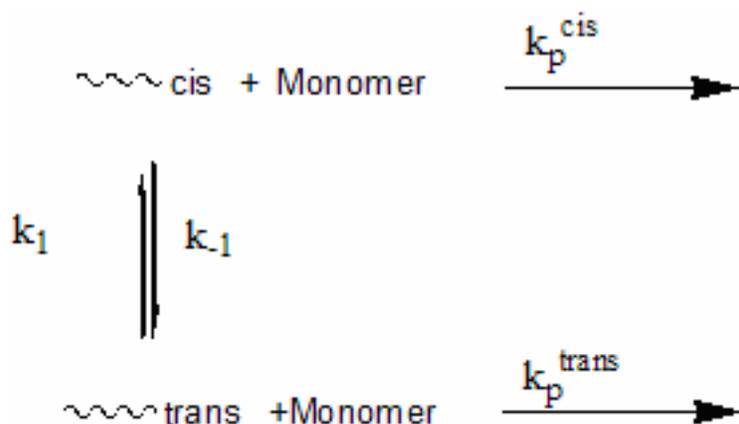


Figure 2-6. Equilibrium relationship between the cis and trans isomers of the propagating anion.

Therefore, at low monomer concentrations, the equilibrium would lie toward the isomerization from the cis to the trans, and significant quantities of the trans form would result. In contrast, in the presence of high monomer concentrations, the cis form of the polymer chain end would rapidly react with the monomer. Therefore, high monomer concentrations would result in high degrees of cis enchainment. This model does not consider the role of the aggregate on the regiochemistry. A postulated mechanism for the rotation of the dienyl anion occurring through the aggregated state would enable the facile cis to trans isomerization to occur without the formation of a charge separated species.¹⁰⁶ Compounds such as 1,3-cyclohexadiene that are locked into the cis isomer should exhibit increased polymerization rates if the model is accurate.

¹⁰⁵Worsfold, D.J., and S. Bywater. "Lithium alkyl initiated polymerization of isoprene. Effect of cis/trans isomerization of organolithium compounds on polymer microstructure." *Macromolecules* **1978**, 11, 582.

¹⁰⁶Worsfold, D.J., and S. Bywater. "Lithium alkyl initiated polymerization of isoprene. Effect of cis/trans isomerization of organolithium compounds on polymer microstructure." *Macromolecules* **1978**, 11, 582.

2.5 Synthesis of Polymers Composed of Cyclic Conjugated Dienes.

2.5.1 Introduction

Ziegler first described the synthesis of polymers prepared via an anionic polymerization in 1929, in which he described the polymerization of butadiene initiated with nBuLi. In this description, a mechanism was outlined that consisted of initiation and propagation, and it was mentioned that the termination and transfer steps may not play a major role.¹⁰⁷ As research continued, the thrust of the work was focused on the non-living polymerization of butadiene. In 1955, Firestone reported a new polymer based on isoprene, which exhibited the characteristics of natural rubber.¹⁰⁸ The initiating system utilized an insoluble lithium metal added to the monomer.

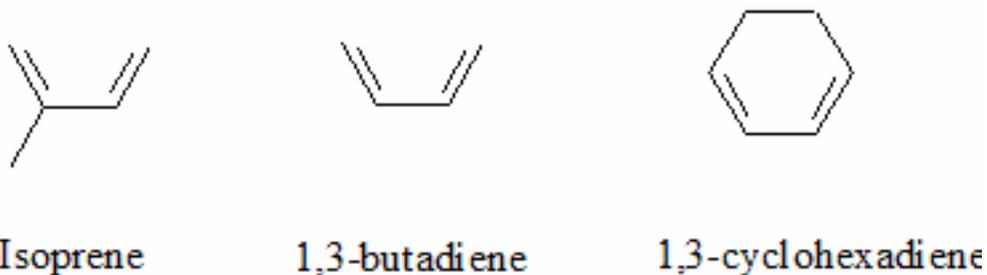


Figure 2-7. Anionically polymerizable diene monomers.

Szwarc coined the term "living" in his seminal work in 1956.¹⁰⁹ In addition to describing the nature of a living anionic polymerization, Szwarc also recognized the utility of the living chain end for the synthesis of more complex architectures. Since that time, much of the research for the anionic polymerization of dienes has focused on

¹⁰⁷Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996.

¹⁰⁸Foster, F.C., and J.L. Binder. *Advances in Chemistry Series No 19* American Chemical Society, 1957.

¹⁰⁹Szwarc, M, M Levy, and R. Milkovich. "Polymerization initiated by electron transfer to monomer. A new method of formation of block polymers." *J. Am. Chem. Soc.* **1956**, 78, 2656.

the monomers of butadiene and isoprene. This is due to the fact that anionic polymerizations are dependent upon the stability of the anion. Since cyclic dienes are destabilized by the electron donating ability of the ring, the resulting cyclic diene anions are less stable than their linear counterparts. The reduced anion stability resulted in decreased polymerization control and less attention was devoted in the following years to these dienes, in spite of the possible advantages of an increase in the thermal stability, chemical stability, and mechanical strength.¹¹⁰

2.5.2 Synthesis of 1,3-cyclohexadiene

A variety of synthetic routes were explored in the attempt to synthesize 1,3-cyclohexadiene, the majority of which were explored industrially. The primary route examined was the oxidation of cyclohexene to cyclohexene oxide and the subsequent dehydration in the presence of a silicon oxide/titanium oxide catalyst.¹¹¹ These routes were typically preferred over halogenation of cyclohexene and subsequent dehydrohalogenation, due to the preferred formation of 1,4-cyclohexadiene.¹¹² The preferential formation of 1,4-cyclohexadiene relative to 1,3-cyclohexadiene also plagued the Birch reduction of benzene, rendering this approach unusable. Recent reports by researchers at Asahi Corporation reported the preparation of high purity 1,3-cyclohexadiene (>99.74%) via the reaction of 2-cyclohexene-1-ol with a zeolite catalyst system at 100 °C.¹¹³ 2-cyclohexene-1-ol was prepared via the oxidation of cyclohexene with a Lindlar catalyst and 11 atm of hydrogen (Scheme 2-5).¹¹⁴

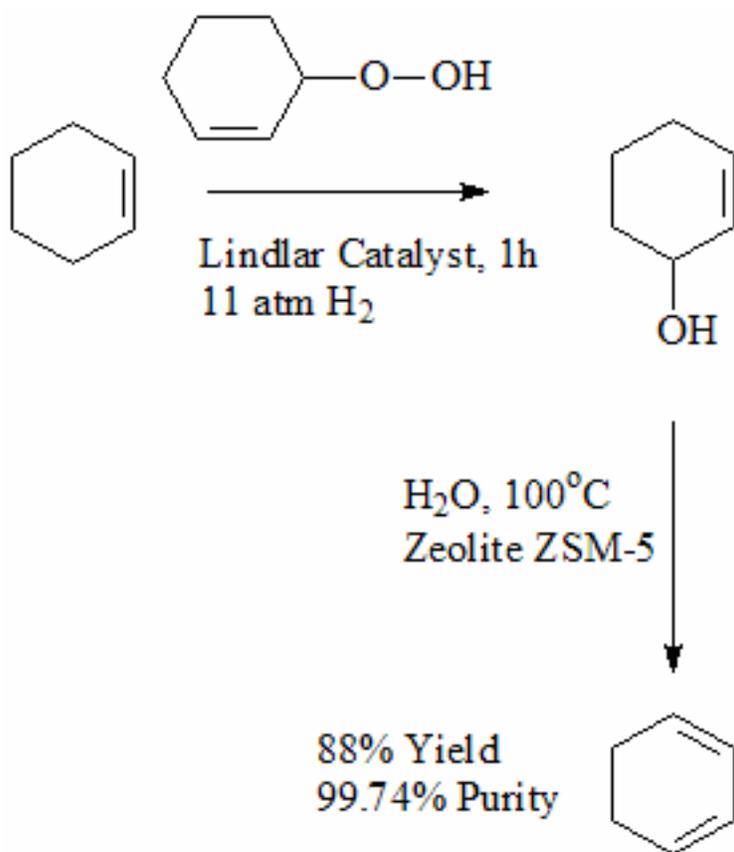
¹¹⁰ Natori, I., and S. Inoue. "Living Anionic Polymerization of 1,3-cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System. Copolymerization and Block Copolymerization with Styrene, Butadiene, and Isoprene." *Macromolecules* **1998**, 31, 982.

¹¹¹"1,3-Cyclohexadiene." Mitsubishi Chemical Industries Co.,JP 57026628 (1982).

¹¹²Fritz, H.E., and D.W. Peck. "Process for the Production of Cyclohexadiene." Union Carbide Corporation,U.S. 3284521 (1964).

¹¹³Mitsuji, O., and H. Ishida. "Preparation of 1,3-cyclohexadiene by catalytic dehydration of 2-cyclohexene-1-ol." Asahi Chemical Ind.,JP 08253435 (1996).

¹¹⁴Mitsuji, O., and H. Ishida. "Preparation of 1,3-cyclohexadiene by catalytic dehydration of 2-cyclohexene-1-ol." Asahi Chemical Ind.,JP 08253435 (1996). Ishida, H., and M. Ono. "Preparation of high Purity 1,3-cyclohexadiene." Asahi Chemical Ind.,JP 07165624 (1996).



Scheme 2-5. Preparation of 1,3-cyclohexadiene from cyclohexene

2.5.3 Polymerization of Cyclic Dienes Using Non-anionic Polymerization Methodologies

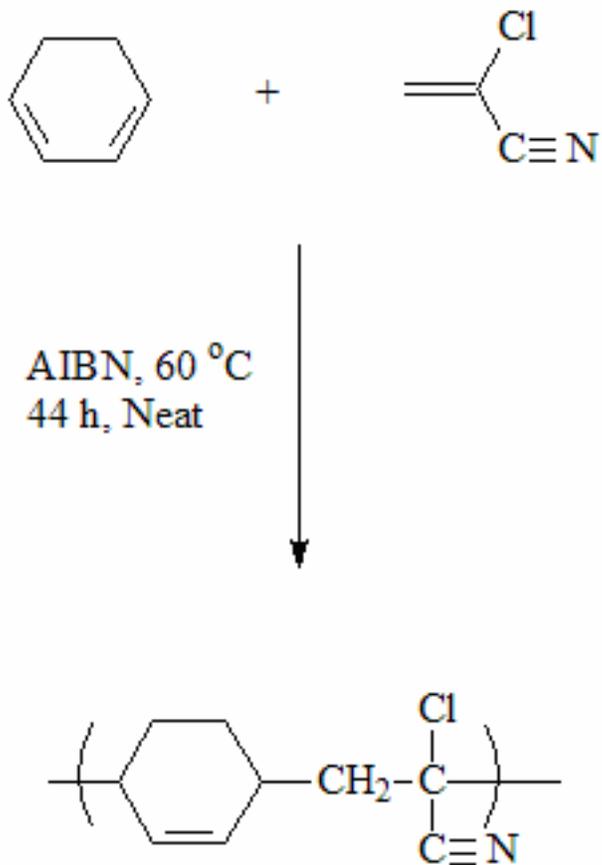
The polymerization of conjugated cyclic dienes has previously been pursued with great difficulty. In addition to the anionic polymerization of 1,3-cyclohexadiene, other routes employed to polymerize conjugated cyclic dienes included free radical, cationic and, metal coordinated mechanisms.¹¹⁵ In general, all early attempts to free radically polymerize cyclic conjugated dienes resulted in low yields (> 10%) and low molecular weight oligomers.¹¹⁶ Later efforts by Reynolds et al. focused on the copolymerization of the monomer pairs chloroacrylonitrile and 1,3-cyclohexadiene¹¹⁷ or fluoroacrylonitrile and 1,3-cyclohexadiene.¹¹⁸ It was proposed that these polymerizations proceeded through a charge transfer complex due to the electron rich-electron poor character of the 1,3-cyclohexadiene-fluoroacrylonitrile monomers, respectively. In general, the yields of these polymerizations varied from 0-93% with the maximum polymerization yields occurring at a 1:1 monomer ratio.

¹¹⁵ Gin, D. L., V. P. Conticello, and R.H. Grubbs. "Heteroatom-Functionalized Cyclohexadienes: Stereoregular Transition-Metal-Catalyzed Polymerization of Precursor to Poly(p-phenylene)." *J. Am. Chem. Soc.* **1992**, 114, 3167. Kohjiya, S., T. Tsuda, K. Nakamura, K. Yamazaki, and S. Yamashita. "Polymerization of 1,3-cycloheptadiene and the structure of poly(1,3-cycloheptadiene)s obtained by anionic initiators." *Macromol. Chem. Phys.* **1981**, 182, 215. Imanishi, Y., K. Matsuzaki, T. Yamane, K. Tadayuki, S. Kohjiya, and S. Okamura. "Cationic Polymerization of Cyclic Dienes." *J. Macromol. Sci., Chem.* **1969**, 3, 249. Nagai, K., and S. Machida. "Spontaneous Copolymerization of 1,3-cyclohexadiene with acrylonitrile in the presence of Zinc Chloride." *J. Polym. Sci. Part A: Polym. Chem.* **1981**, 19, 571.

¹¹⁶ Kohjiya, S., T. Tsuda, K. Nakamura, K. Yamazaki, and S. Yamashita. "Polymerization of 1,3-cycloheptadiene and the structure of poly(1,3-cycloheptadiene)s obtained by anionic initiators." *Macromol. Chem. Phys.* **1981**, 182, 215.

¹¹⁷ Reynolds, J. R., and V. Panchalingam. "Poly(1,3-cyclohexadiene-alt-fluoroacrylonitrile): Synthesis and Characterization of a new alternating copolymer." *J. Polym. Sci. Part A: Polym. Chem.* **1992**, 30, 967.

¹¹⁸ Reynolds, J. R., and V. Panchalingam. "Structural analysis of the alternating copolymer Poly(chloroacrylonitrile-alt-cyclohexadiene)." *Macromolecules* **1988**, 21, 960.



Scheme 2-6. Alternating Copolymerization of 1,3-cyclohexadiene and chloroacrylonitrile

As expected, the major side reaction of these polymerizations was the formation of a Diels-Alder adduct. 1,4-addition was the predominate mechanism of radical addition to the conjugated diene system of 1,3-cyclohexadiene. These polymers were subsequently derivatized to form a more highly saturated polymer via a base catalyzed elimination reaction. Prior work by Nagai et al. in 1981 demonstrated that 1,3-cycloheptadiene spontaneously copolymerized with acrylonitrile in the presence of zinc chloride.¹¹⁹ The copolymerization proceeded to high yields with a small amount of Diels-Alder adduct formed. As found by Reynolds et al. in their copolymerization studies, Nagai et al. found that the predominant manner of addition across the double bond was 1,4-addition. Other copolymerization systems have also been studied, such as the copolymerization of 1,3-cycloheptadiene with maleic anhydride or sulfur dioxide.¹²⁰

Cationic polymerization methods were used extensively to polymerize cyclic conjugated dienes. In contrast to living anionic polymerization methodologies, electron rich monomers are preferred in cationic polymerizations. Typical monomers include THF, isobutylene, cyclopentadiene, and terpenes. For example, C5 resins, which are commonly used as tackifiers in the adhesive industry, are prepared via the cationic polymerization of terpenes. Cyclopentadiene has also received significant attention due to its possible uses as a new hydrocarbon-polymeric material and the low cost of the monomer. In spite of these efforts, the polymerizations exhibited poor molecular weight control and the control over the microstructure was not well understood.¹²¹ Recent studies by Sawamoto et al. examined the polymerization of cyclopentadiene

¹¹⁹Nagai, K., and S. Machida. "Spontaneous Copolymerization of 1,3-cyclohexadiene with acrylonitrile in the presence of Zinc Chloride." *J. Polym. Sci. Part A: Polym. Chem.* **1981**, 19, 571.

¹²⁰Yamaguchi, T., K. Nagai, and O. Itabashi. "Polymerization of cycloolefins. 9. Copolymerization of 1,3-cycloheptadiene." *Kobunshi Kagaku* **1973**, 30, 464.

¹²¹Aso, C., T. Kunitake, and Y. Ishimoto. *J. Polym. Sci. Part A: Polym. Chem. Ed.* **1968**, 6, 1175. Aso, C., T. Kunitake, and Y. Ishimoto. "Polymers from cyclic dienes. V. Cationic polymerization of cyclopentadiene, influence of polymerization conditions on the polymer structure." *J. Polym. Sci. Part A: Polym. Chem.* **1968**, 6, 1175.

using a variety of initiators and additives.¹²² These polymerizations exhibited improved polymerization control, however, the reaction was limited to low molecular weight polymers (<10000) and the molecular weight distributions were broad (>1.3). Previous studies also examined the cationic polymerization of other cyclic conjugated dienes, such as cycloheptadiene, 1,3-cyclooctadiene, and 1,5-cyclooctadiene.¹²³ The polymerization of these cyclic diolefins was rapid when using cationic systems, such as boron trifluoride or titanium tetrachloride. The resulting polymers exhibited some degree of branching, although, the polymerization of cis, cis-1,3-cyclooctadiene was linear when polymerized in dichloromethane. The mechanical properties of the resulting polymers were similar to those exhibited by poly(1,3-cyclohexadiene), for example, they exhibited a softening temperature of 130-180 °C.¹²³

Metal-coordinated mechanisms have also been used to polymerize cyclic conjugated olefins.¹²⁴ Predominately, these studies have focused on the polymerization of 1,3-cyclohexadiene, although Po et al. examined the copolymerization of 1,3-cyclooctadiene and 1,3-cyclohexadiene. The addition of 1,3-cyclooctadiene to the polymerization reduced the polymerization yields and the molecular weights. Poly(1,3-cyclohexadiene) homopolymers prepared using bis(cyclopentadienyl)nickel /methylaluminumoxane systems exhibited a high degree of stereoregularity and were highly crystalline. These highly crystalline systems were insoluble in all common organic solvents and exhibited a melting temperature of 322 °C.¹²⁴ In addition to the

¹²² Ouchi, M., M. Kamigaito, and M. Sawamoto. "Control of Regioselectivity and Main-Chain Microstructure in Cationic Polymerization of Cyclopentadiene." *Macromolecules* **2001**, 34, 6586.

¹²³ Imanishi, Y., K. Matsuzaki, T. Yamane, K. Tadayuki, S. Kohjiya, and S. Okamura. "Cationic Polymerization of Cyclic Dienes." *J. Macromol. Sci., Chem.* **1969**, 3, 249. Imanishi, Y., K. Matsuzaki, S. Kohjiya, and S. Okamura. "Kinetic observations on the polymerization of cis,cis-1,3-cyclooctadiene." *J. Macromol. Sci., Chem.* **1969**, 3, 237. Kohjiya, S., T. Tsuda, K. Nakamura, K. Yamazaki, and S. Yamashita. "Polymerization of 1,3-cycloheptadiene and the structure of poly(1,3-cycloheptadiene)s obtained by anionic initiators." *Macromol. Chem. Phys.* **1981**, 182, 215.

¹²⁴ Dolgoplosk, B.A., S.I. Beilin, Y.V. Korshak, L.M. Chernenko, L.M. Vardanyan, and M. Teterina. "Copolymerization of dienes under influence of p-allyl complexes of nickel." *Eur. Polym. J.* **1973**, 9, 895. Po, R., R. Santi, and M.A. Cardaci. "Polymerization of 1,3-cyclohexadiene with Nickel MAO Catalytic System." *J. Polym. Sci., Part A: Polym. Chem.* **2000**, 38, 3004.

nickel systems, tungsten tetrachloride was coupled with a methyl carbene to polymerize cycloolefins over a range of temperatures. This system was less reactive than an nBuLi initiated anionic system that was examined for comparative purposes.¹²⁴ The research efforts described above focused on the polymerization of cyclic conjugated dienes and resulted in linear polymers where the cyclic repeat unit was directly derived from the cyclic monomer. The polymerization of cyclic olefins has also been performed using metathesis polymerization strategies, which typically result in highly branched polymers.¹²⁵

2.5.4 Living Anionic Polymerization of 1,3-Cyclohexadiene

A number of methods have been utilized to anionically polymerize 1,3-cyclohexadiene and all of these attempts resulted in low molecular weight material and poor yields.¹²⁶ Subsequent findings indicated the ability to polymerize 1,3-cyclohexadiene in a living manner.¹²⁷ In these initial reports, the authors describe the polymerization of 1,3-cyclohexadiene using nBuLi in cyclohexane at various temperatures and found that they were able to minimize the degree of deleterious side reactions by performing the polymerization at low monomer concentrations.

In order to understand the origin and importance of the various factors on the polymerization of 1,3-cyclohexadiene, previous studies have examined the potential

¹²⁵ Ellis, M.J., and B.S. King. "Ring-opening cross metathesis of 1,3-cyclopentadiene-heterodienophile cycloadducts to produce cyclic hydrazines and hydroxylamines." *Tet. Lett.* **2002**, 43, 5833.

¹²⁶ Lefebvre, G, and F. Dawans. "1,3-Cyclohexadiene polymers. I. Preparation and aromatization of poly-1,3-cyclohexadiene." *J. Polym. Sci.* **1964**, A2, 3277. Cassidy, P.E., C.S. Marvel, and S. Ray. "Preparation and aromatization of poly-1,3-cyclohexadiene and subsequent cross-linking. III." *Journal of Polymer Science* **1965**, A3, 1553. Mango, L.A., and R.W. Lenz. "Organometallic reactions which control molecular weight in the anionic polymerization of 1,3-cyclohexadiene." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **1971**, 12, 402.

¹²⁷ Francois, B., and X. Zhong. "Kinetics of 1,3-cyclohexadiene polymerization initiated by organolithium compounds in a non-polar medium." *Makromol. Chem.* **1990**, 191, 2743. Zhong, X., and B. Francois. "Kinetics of 1,3-cyclohexadiene polymerization by organolithium compounds in a non-polar medium. 1." *Makromol Chem* **1990**, 191, 2735.

steps that occur during the polymerization. An outline of these steps is provided in Figures 2-8 through 2-10. The first step is the dimerization of the propagating chain end into an aggregate. As previously described, the propagating end of the polymer is typically associated in the form of an aggregate. The free poly(1,3-cyclohexadienyllithium) chain end is in equilibrium with the aggregated form. The dissociation constant (K_{dis}) describes

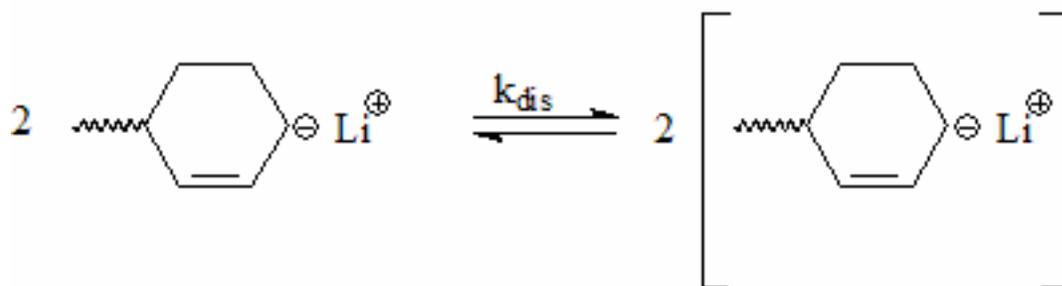


Figure 2-8. The equilibrium between the free polymer chain and the aggregate is related by the dissociation constant

the equilibrium between the two forms. It is commonly believed that the polymerization proceeds through an un-aggregated free chain end,¹²⁸ although evidence has been presented in which styrene was believed to polymerize via an insertion mechanism into the aggregate.¹²⁹ Further support for the presence of an active polymerization site in the aggregate was found in gas phase butadiene polymerizations.¹³⁰ The unassociated poly(1,3-cyclohexadienyllithium) chain end is then free to react with an incoming 1,3-

¹²⁸ Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996.

¹²⁹ Defieux, A., S. Menoret, S. Carlotti, P. Desbois, C. Schade, and M. Fontanille. "Retarded Anionic Polymerization: Influence of alkyl Substituents in R2MG/PSLi Systems on the Characteristics of High Temperature Styrene Polymerization." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **2000**, 41, 1386.

¹³⁰ Young, R. N., L.J. Fetters, J.S. Huang, and R. Krishnamoorti. "Some Light on the Concept of Unreactivity Arising from Active Center Association in Anionic Polymerization." *Polymer International* **1994**, 33, 217.

cyclohexadiene monomer. Two different reactions are believed to occur at this point, which are either chain propagation by nucleophilic attack of poly(1,3-cyclohexadienyllithium) to 1,3-cyclohexadiene or chain transfer to monomer (Figure 2-9). Addition of a monomer unit to the chain end results in an increase in the degree of polymerization (DP), after which the polymeric chain end is free to re-equilibrate with the aggregate.

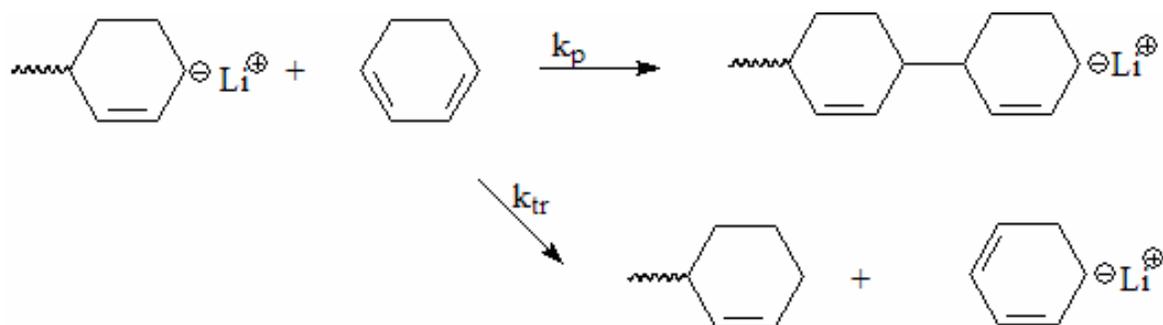


Figure 2-9. The reactions that are available to the free propagating chain end of poly(1,3-cyclohexadienyllithium).

The other available kinetic option is chain transfer to monomer, via a proton transfer step. If the propagating chain end acts as a base and extracts a proton from the monomer, then the polymer chain is terminated and the reactivity of the anion is transferred to the monomer. The reactivity of the monomer anion is not clearly understood and depending upon the reactivity, three different reactions are available to the monomer anion (Figure 2-10). The first option is an elimination reaction which would result in the aromatization of the metallated 1,3-cyclohexadiene species forming benzene and lithium hydride as the product.¹³¹ The second is the isomerization of 1,3-cyclohexadiene forming 1,4-cyclohexadiene. This reaction proceeds through the resonance form of the anionic monomer. The 1,4-cyclohexadiene anion can extract a proton from 1,3-cyclohexadiene forming 1,4-cyclohexadiene and regenerating the 1,3-cyclohexadiene anion. The last option available to the 1,3-cyclohexadiene anion is the addition of the anion to the double bonds of the monomer. This last reaction would result in the reinitiation of the 1,3-cyclohexadiene polymerization.¹³² The importance of the third step is not clear from the current literature. Mango and Lenz reported the reinitiation of the polymerization by the conjugated diene anion to be unimportant and the predominant limitation to achieving high molecular weight is formation of benzene.¹³³ In contrast, Zhong and Francois concluded that the anion formed was stable in the absence of monomer, therefore precluding the formation of benzene as the only termination step. These authors also found a change in the concentration of benzene after the addition of a second charge of 1,3-cyclohexadiene was added to a living completed polymerization of 1,3-cyclohexadiene. If the initiator is essential for the

¹³¹ Natori, I., and S. Inoue. "Anionic Polymerization of 1,3-cyclohexadiene with Alkylolithium/Amine Systems. Characteristics of n-Butyllithium/N,N,N',N'-Tetramethylethylenediamine System for Living Anionic Polymerization." *Macromolecules* **1998**, 31, 4687.

¹³² Francois, B., and X. Zhong. "Kinetics of 1,3-cyclohexadiene polymerization initiated by organolithium compounds in a non-polar medium." *Makromol. Chem.* **1990**, 191, 2743. Zhong, X., and B. Francois. "Kinetics of 1,3-cyclohexadiene polymerization by organolithium compounds in a non-polar medium. 1." *Makromol Chem* **1990**, 191, 2735.

¹³³ Mango, L.A., and R.W. Lenz. "Mechanism and stereochemistry in the anionic polymerization of 1,3-cyclohexadiene and the diimide hydrogenation of polymers." *U.S. Nat. Tech. Inform. Serv.* **1972**, 12, 402.

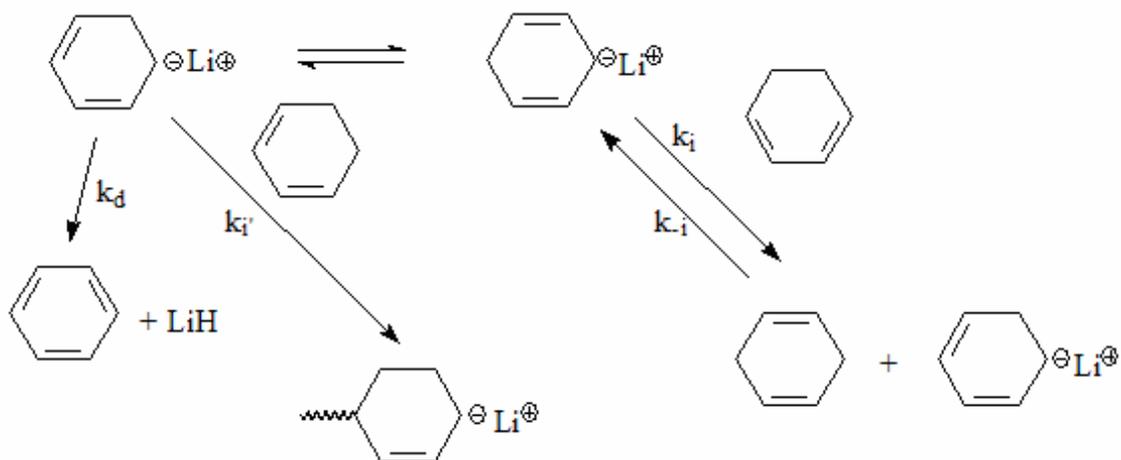


Figure 2-10. Reaction options available to the 1,3-cyclohexadienyllithium. The anion is formed via the extraction of the allylic proton on the monomer.

metallation and subsequent aromatization of 1,3-cyclohexadiene, then the increase in benzene formation would have been found to occur only during the first polymerization and not during the polymerization of the second 1,3-cyclohexadiene charge. Benzene formation is dependent upon the presence of 1,3-cyclohexadiene. Additionally, Zhong and Francois also demonstrated that hydride formation did not occur in the absence of the monomer and the active polymer chain ends were stable in the absence of monomer under the reaction conditions. These reactions were performed at -10 °C in a cyclohexane/heptane solution. In contrast to Mango and Lenz, Zhong and Francois demonstrated that the 1,3-cyclohexadiene anion is capable of reinitiating the polymerization of 1,3-cyclohexadiene. These authors fractionated the polymeric products formed from the polymerization of 1,3-cyclohexadiene via a poly(styryllithium) initiator. A fraction of the poly(1,3-cyclohexadiene) did not contain the polystyrene chain end, therefore indicating the ability of the anion formed via chain transfer to initiate the polymerization. The reaction conditions appear to greatly affect the relative importance of the individual kinetic steps. Polymers have been produced in a living manner in which the degree of transfer has been limited by performing the polymerization at 10 °C under monomer-starved conditions.¹³⁴ The authors postulated that the low ratio of monomer to initiator minimized the chain transfer to monomer step. In 1997, Natori and coworkers reported the first successful living anionic homopolymerization of 1,3-cyclohexadiene.¹³⁵ The reported polymer exhibited a linear relationship between percent conversion and molecular weight. Additionally, the resulting polymer exhibited a narrow molecular weight distribution (PDI=1.09) at a number average molecular weight of 12,400. This initial work was followed by a series of papers indicating the preferred method of polymerizing 1,3-cyclohexadiene in order to achieve a living anionic polymerization. A ratio of TMEDA/nBuLi of 5/4 allowed

¹³⁴ Zhong, X., and B. Francois. "Kinetics of 1,3-cyclohexadiene polymerization by organolithium compounds in a non-polar medium. 1." *Makromol Chem* **1990**, 191, 2735. Francois, B., and X. Zhong. "Kinetics of 1,3-cyclohexadiene polymerization initiated by organolithium compounds in a non-polar medium." *Makromol. Chem.* **1990**, 191, 2743.

¹³⁵ Natori, I. "Synthesis of Polymers with an Alicyclic Structure in the Main Chain. Living Anionic Polymerization of 1,3-Cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System." *Macromolecules* **1997**, 30, 3696.

the polymerization to proceed in a living fashion.¹³⁶ Additionally, it was found that the polymerization rate was increased in the presence of TMEDA. All the polymerizations were performed at 40 °C in cyclohexane. The choice of the ligating agent may play a critical role in the polymerization of 1,3-cyclohexadiene. Previous studies have utilized a broad spectrum of ligating agents.¹³⁷ The results of these experiments are shown below in Table 2-2 and Table 2-3. The role that TMEDA plays in controlling the polymerization is evident in these experiments. As can be seen from Table 2-2, the use of TMEDA was essential to obtaining high molecular weight polymer with narrow molecular weight distributions. The ratio of TMEDA to propagating anion is also critical in controlling the polymerization. The yield of the polymerization is 100% when the TMEDA/nBuLi ratio is maintained at level of 1/1 or higher, and the molecular weight distribution is minimized at these same TMEDA/nBuLi ratios. Researchers have also examined a variety of different amine based ligating additives. Table 2 shows the results of these experiments. It is clear that the nature of the interaction of the additive with the propagating terminus of the polymer is critical, since those ligating agents that provided the correct degree of interaction resulted in a controlled polymerization. In the amine based additive family, only TMEDA and DABCO were effective in controlling the polymerization. The remaining additives either resulted in poorer yields or broader molecular weight distributions. It is typically expected that initiators only affect the polymerization in two ways.

¹³⁶ Natori, I., and S. Inoue. "Living Anionic Polymerization of 1,3-cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System. Copolymerization and Block Copolymerization with Styrene, Butadiene, and Isoprene." *Macromolecules* **1998**, 31, 982.

¹³⁷ Natori, I., and S. Inoue. "Anionic Polymerization of 1,3-cyclohexadiene with Alkylolithium/Amine Systems. Characteristics of n-Butyllithium/N,N,N',N'-Tetramethylethylenediamine System for Living Anionic Polymerization." *Macromolecules* **1998**, 31, 4687.

Table 2-2 The role of TMEDA in controlling the polymerization of 1,3-cyclohexadiene.

Initiator	Yield(%)	$\langle M_n \rangle^a$	$M_{\text{theoretical}}$	$\langle M_w \rangle / \langle M_n \rangle$	%	
					1,2	1,4
nBuLi	33	3500	6600	2.27	2	98
nBuLi/TMEDA(4/0.5)	77	16300	15400	2.42	21	79
nBuLi/TMEDA(4/2)	72	16000	7200	1.52	43	67
nBuLi/TMEDA(4/3)	100	11100	10000	1.12	48	52
nBuLi/TMEDA(4/4)	100	10600	10000	1.07	51	49
nBuLi/TMEDA(4/5)	100	11600	10000	1.06	54	46
nBuLi/TMEDA(4/8)	100	11300	10000	1.07	54	46

Reactions Conditions: 40 °C, Cyclohexane¹³⁸ ^aGPC Conditions: CHCl₃, DRI

¹³⁸ Natori, I., and S. Inoue. "Anionic Polymerization of 1,3-cyclohexadiene with Alkylolithium/Amine Systems. Characteristics of n-Butyllithium/N,N,N',N'-Tetramethylethylenediamine System for Living Anionic Polymerization." *Macromolecules* **1998**, 31, 4687.

These include the initiation efficiency and the role of the cation on the regiochemistry and rate of polymerization. If the initiator is an efficient initiator of the polymerization, then all of the polymer chains will begin propagation at the same time. Assuming the reaction is controlled, all the chains essentially achieve the same molecular weight at the point of termination.¹³⁹ Table 2-3 indicates that the initiator plays a role in the polymerization of 1,3-cyclohexadiene. The role of TMEDA in controlling the polymerization of 1,3-cyclohexadiene in the presence of TMEDA resulted in an apparent controlled polymerization of 1,3-cyclohexadiene, but utilization of the other initiators secBuLi, t-BuLi, or poly(styryllithium) resulted in decreased control of the polymerization.

The polymerization of 1,3-cyclohexadiene is also dependent upon the initiating species. In addition to the increase in molecular weight distribution and some decrease in yield, use of these three initiators resulted in an alteration of the degree of 1,2 versus 1,4 addition from the reported 51% 1,2 and 49% 1,4 found for nBuLi initiated reactions. This change in 1,2 versus 1,4 addition occurs even in the presence of the same cation (lithium), the same additive (TMEDA), and the same ratio of the additive to cation (5/4). Recently work has demonstrated the role of the initiator on the degree of 1,2 versus 1,4 addition. These studies utilized the initiator 3-dimethylaminopropylolithium as an effective initiator for the polymerization of isoprene, butadiene, and styrene.¹⁴⁰ It was found that the degree of 3,4 enchainment increased as the initiator concentration increased. For the polymerization of isoprene, the degree of 3,4 enchainments was found to be 38% for a number average molecular weight of 4300 compared to 15% for a M_n of 38,200. This increase in 3,4 enchainment correlates with the increase in the concentration of the tertiary amine present in the initiator. This is the behavior expected for the increase in percentage of an amine based ligating agent, such as TMEDA or 3-

¹³⁹ Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996.

¹⁴⁰ Pispas, Stergios, Marinos Pitsikalis, N. Hadjichristidis, Patrizia Dardani, and Francesco Morandi. "Anionic polymerization of isoprene, butadiene, and styrene with 3-dimethylaminopropylolithium." *Polymer* **1995**, 36, 3005.

dimethyl propylolithium.¹⁴¹ In addition to the increase in 1,2 enchainment, TMEDA confers a degree of livingness to the polymerization of 1,3-cyclohexadiene. However, the use of TMEDA as a ligating agent introduces a possible deleterious side reaction. TMEDA was previously shown to act as a metallating agent for use in small molecule synthesis and also in the synthesis of low molecular weight dienes.¹⁴² The utility of a metallation reaction has been used extensively for the production of low molecular weight butadienes (10,000 - 40,000) otherwise known as liquid butadienes. Metallating agents such as TMEDA are used to facilitate the exchange of a lithium cation for a hydrogen, thus allowing a chain transfer step to occur. Typically the chain transfer step is performed with an acidic hydrogen, such as the benzylic proton on toluene. Under conditions where the monomer concentration is low for butadiene polymerizations, TMEDA facilitates an intramolecular back biting reaction. This back biting reaction results in the formation of appreciable levels of 4-vinylcyclopentane (Figure 2-11). Recently, the efficacy of the ligating agents 1,4-diazabicyclo[2,2,2] octane (DABCO) and 1,2-dipiperdinoethane (DPPE) have been examined.¹⁴³ It was found that DPPE, when used in combination with either nBuLi, SecBuLi, and t-BuLi, resulted in the formation of poly(1,3-cyclohexadiene) that was either insoluble or the M_n determined via GPC did not match the theoretical M_n . In the cases where the molecular weight deviated from the theoretical molecular weight, the molecular weight achieved was less than the

¹⁴¹ Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996.

¹⁴² Bunting, W., and A.W. Langer. "Telomerization of conjugated diolefines with aromatics and olefins using chelated organosodium catalysts." In *Polyamine Chelated Alkali Metal Compounds*, edited by A.W. Langer. Washington DC: American Chemical Society, 1974.

¹⁴³ Hong, K., and J.W. Mays. "1,3-Cyclohexadiene Polymers. 1. Anionic Polymerization." *Macromolecules* **2001**, 34, 782.

Table 2-3. Effect of Initiator and Tertiary Amine on the Polymerization Control

Initiator	Yield(%)	$\langle M_n \rangle^c$	$M_{\text{theoretical}}$	$\langle M_w \rangle / \langle M_n \rangle$	% 1,2	% 1,4
nBuLi/DABCO ^a	100	11300	10000	1.69	21	79
secBuLi ^a	8	4800	800	1.53	2	98
secBuLi/TMEDA ^a	99	10800	9900	1.53	41	59
secBuLi/DABCO ^b	100	20100	14000	1.04	7	93
secBuLi/DABCO ^a	99	11900	9900	1.79	2	98
tBuLi/TMEDA ^a	91	14700	9100	1.59	46	54
tBuLi/DABCO ^a	100	12600	10000	1.40	1	99
PStLi/TMEDA ^a	100	13600	10510	1.29	64	34
PStLi/DABCO ^a	100	13000	10510	1.14	25	75

^aPolymerization Conditions: 40 °C, Cyclohexane¹⁴⁴ ^bPolymerization Conditions: 20 °C, Benzene¹⁴⁵ ^cGPC Conditions: CHCl₃, DRI

¹⁴⁴ Natori, I., and S. Inoue. "Anionic Polymerization of 1,3-cyclohexadiene with Alkylolithium/Amine Systems. Characteristics of n-Butyllithium/N,N,N',N'-Tetramethylethylenediamine System for Living Anionic Polymerization." *Macromolecules* **1998**, 31, 4687.

¹⁴⁵ Hong, K., and J.W. Mays. "1,3-Cyclohexadiene Polymers. 1. Anionic Polymerization." *Macromolecules* **2001**, 34, 782.

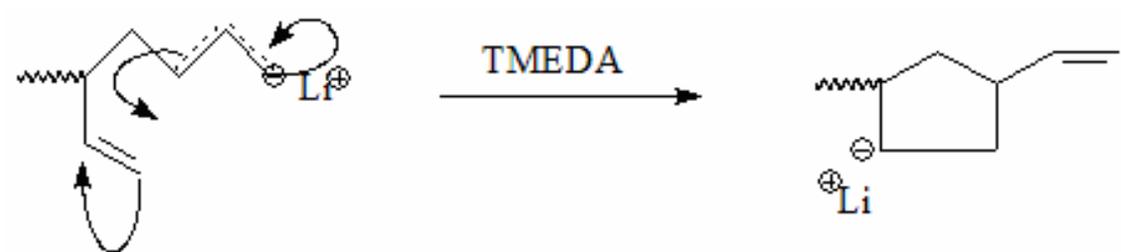


Figure 2-11. The backbiting reaction resulting in the formation of 4-vinylcyclopentane during the synthesis of liquid polybutadienes.

expected molecular weight. Indicating that the active mechanism was a chain transfer from the polymer to the monomer, followed by a subsequent reinitiation of a new propagating chain. The polymerizations were performed at 20 °C in benzene. In contrast, DABCO was found to be effective for the polymerization of poly(1,3-cyclohexadiene) with high 1,4-microstructure. These results vary with the original studies performed by Natori et al.¹⁴⁶ Mays et al. also demonstrated that poly(1,3-cyclohexadiene) can be synthesized using dimethoxyethane (DME). DME was effective in synthesizing poly(1,3-cyclohexadiene) with molecular weights of 40000 (Table 2-4). Unfortunately, these polymerizations exhibited a broad molecular weight distribution ($\langle M_w \rangle / \langle M_n \rangle = 1.51$) at increased polymer molecular weights (35000). These polymerizations were performed at 0 °C using benzene as the polymerization solvent, which is a departure from previous studies that used cyclohexane as the polymerization solvent. The ratio of DME to nBuLi was not maintained at a constant value for all the polymerizations and varied from 1.7 to 4.89. Additional charges of 1,3-cyclohexadiene to the polymerization resulted in broadening of the molecular weight distribution while the molecular weight of the polymer remained nearly unchanged (18400 versus 19700). Therefore, the polymerization did not demonstrate a high degree of livingness when DME was used.

¹⁴⁶ Natori, I.. "Synthesis of Polymers with an Alicyclic Structure in the Main Chain. Living Anionic Polymerization of 1,3-Cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System." *Macromolecules* **1997**, 30, 3696.

Table 2-4. Effect of DME/nBuLi on Polymerization of 1,3-cyclohexadiene

Initiator (Initiator/DME) ^a	M _{theoretical}	<M _n > ^b	<M _w >/<M _n >
nBuLi/DME(1.7)	4700	4000	1.13
nBuLi/DME(1.45)	13800	9500	1.07
nBuLi/DME(2.09)	21100	16300	1.19
nBuLi/DME(2.15)	36500	28700	1.51
nBuLi/DME(4.89)	52000	Not soluble	Not soluble

^aPolymerization Conditions: 20 °C, Benzene ^bGPC Conditions: CHCl₃, DRI

Table 3. Polymerization of 1,3-cyclohexadiene using DME

2.5.5 Synthesis of Polymer Systems Via the Post-Polymerization Modification of Poly(1,3-cyclohexadiene)

Facile chemical modification reactions that are directed at the residual double bond in the repeat unit provide for straightforward synthetic routes to PCHD derived polymers. Epoxidation,¹⁴⁷ hydrogenation,¹⁴⁸ and maleation¹⁴⁹ are a few examples of the modification reactions that were performed on conventional polydienes, such as polyisoprene and poly(1,3-butadiene).¹⁵⁰ In contrast to other polydienes, poly(1,3-cyclohexadiene) was previously demonstrated as a well-defined precursor for the synthesis of new families of poly(phenylene) containing polymers.¹⁵¹ Unfortunately, conventional poly(phenylene) homopolymers are typically intractable and insoluble, and generally exhibit poor polymer processability.¹⁵²

¹⁴⁷ Nor, H., and J.R. Ebdon. "Telechelic Liquid Natural Rubber." *Prog. Polym. Sci.* **1998**, 23, 143. Sakai, T., N. Kihara, and T. Endo. "Polymer Reaction of Epoxide and Carbon Dioxide. Incorporation of Carbon Dioxide into Epoxide Polymers." *Macromolecules* **1995**, 28, 4701. Roland, C.M., J.K. Kallitsis, and K.G. Gravalos. "Plateau Modulus of Epoxidized Polybutadiene." *Macromolecules* **1993**, 26, 6474.

¹⁴⁸ Nor, H., and J.R. Ebdon. "Telechelic Liquid Natural Rubber." *Prog. Polym. Sci.* **1998**, 23, 143.

¹⁴⁹ Odian, George. *Principles of Polymerization* John Wiley and Sons Inc: New York, 1991. Nor, H., and J.R. Ebdon. "Telechelic Liquid Natural Rubber." *Prog. Polym. Sci.* **1998**, 23, 143.

¹⁵⁰ Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996.

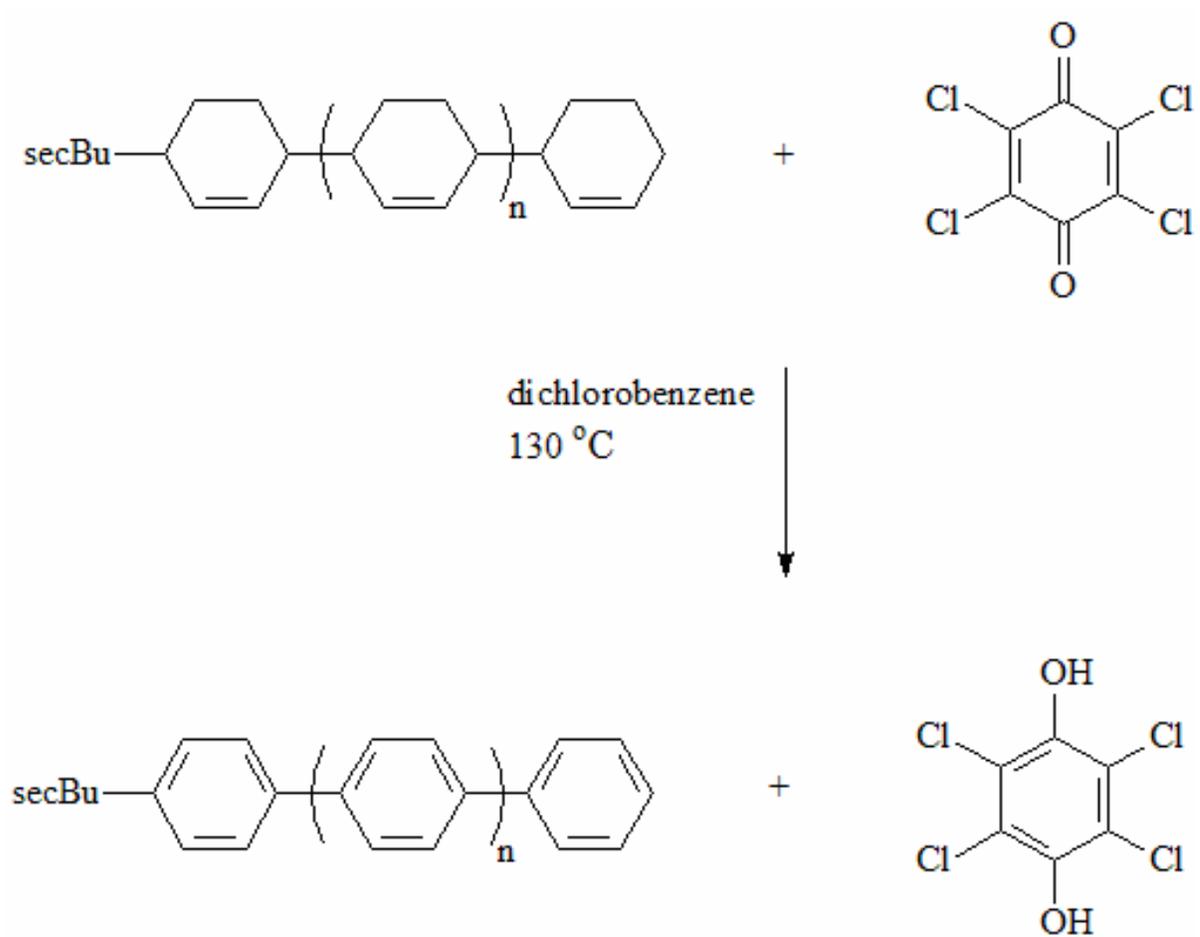
¹⁵¹ Francois, B., and X. Zhong. "Kinetics of 1,3-cyclohexadiene polymerization initiated by organolithium compounds in a non-polar medium." *Makromol. Chem.* **1990**, 191, 2743. Zhong, X., and B. Francois. "Kinetics of 1,3-cyclohexadiene polymerization by organolithium compounds in a non-polar medium. 1." *Makromol Chem* **1990**, 191, 2735. Mignard, E., C. Tachon, and B. Francois. "Neutron scattering analysis of a block copolymer poly(1,4-phenylene)-block-polystyrene-block-poly(phenylene)." *Synth. Met.* **1999**, 102, 1246. Francois, B., S. Izzillo, and P. Iratcabal. "Substituted PPV block copolymer from anionically prepared precursor." *Synth. Met.* **1999**, 102, 1211. Francois, B., G. Widawski, M. Rawiso, and B. Cesar. "Block-copolymers with conjugated segments: Synthesis and structural characterization." *Synth. Met.* **1995**, 69, 463.

¹⁵² Odian, George. *Principles of Polymerization* John Wiley and Sons Inc: New York, 1991.

A variety of synthetic strategies were investigated to improve the solubility of poly(phenylene)-based polymers. First, the incorporation of pendant aliphatic groups on the polymer backbone was performed in an attempt to improve solubility without disrupting the conjugated backbone.¹⁵³ However, this method required the tedious synthesis of novel alkyl substituted aromatic monomers. A more direct and cost effective method involved the synthesis of diblock copolymers, wherein the poly(phenylene) block was attached to a more soluble block such as polystyrene.¹⁵⁴ This approach has typically employed PCHD blocks and a second solubilizing block, such as polystyrene. The PCHD block was subsequently aromatized at high temperatures (130 °C) in the presence an aromatizing agent, such as chloranil (Scheme 2-7). Francois and coworkers have extensively studied the synthesis and performance of poly(styrene-*block*-phenylene) copolymers. The reaction conditions used in these studies resulted in the undesirable oxidation of both the cyclohexene repeat unit and the main chain benzylic position in the polystyrene repeat units. However, these copolymers exhibited interesting optical and electrical properties that were attributed to extended conjugation in the 1,4-substituted poly(phenylene) repeat unit.

¹⁵³ Marsitzky, D., T. Brand, Y. Geerts, M. Klapper, and K. Mullen. "Synthesis of rod-coil block copolymers via end-functionalized poly(p-phenylene)s." *Macromol. Rapid Commun.* **1998**, 19, 385.

¹⁵⁴ Francois, B., G. Widawski, M. Rawiso, and B. Cesar. "Block-copolymers with conjugated segments: Synthesis and structural characterization." *Synth. Met.* **1995**, 69, 463. Mignard, E., C. Tachon, and B. Francois. "Neutron scattering analysis of a block copolymer poly(1,4-phenylene)-block-polystyrene-block-poly(phenylene)." *Synth. Met.* **1999**, 102, 1246. Francois, B., S. Izzillo, and P. Iratcabal. "Substituted PPV block copolymer from anionically prepared precursor." *Synth. Met.* **1999**, 102, 1211.



Scheme 2-7. Synthesis of Polyphenylene via the aromatization of poly(1,3-cyclohexadiene)

A third method that is typically employed to improve the solubility of highly rigid polymers involves the addition of comonomers; however, this approach disrupts the desirable conjugation length.¹⁵⁵ The synthesis of polyphenylene polymers via the aromatization of poly(1,3-cyclohexadiene) was recently described as one of the most convenient routes to high molecular weight, highly conjugated polyphenylene homopolymers and copolymers.¹⁵⁶

Recent studies have utilized star copolymers consisting of poly(1,3-cyclohexadiene) arms coupled to a fullerene core as precursors for star shaped poly(phenylene) polymers, which were expected to improve the physicochemical properties of poly(phenylene). In general, these star-shaped polymers were not well defined and exhibited broad molecular weight distribution due to the presence of multiple species. The aromatized star-shaped copolymers were characterized using UV-visible spectrometry and exhibited an effective conjugation length of approximately eight phenylene units and was unaffected by the presence of the fullerene core. The star-shaped polymers exhibited poor stability and degraded in the presence of UV light. The presence of the fullerene core was suggested to improve the quantum efficiency of the polyphenylene arms.

Another method utilized to improve the thermal and mechanical properties of poly(1,3-cyclohexadiene) was saturation of the polymeric chain via hydrogenation.¹⁵⁷ Hydrogenated poly(1,3-cyclohexadiene) polymers were reported as containing excellent heat, weather, impact, abrasion, and chemical resistance.¹⁵⁸ Furthermore, these

¹⁵⁵ Rusanov, A. L., M. L. Keshtov, and N. M. Belomoina. "New synthetic approach to the preparation of polyphenyleneethynylenes and polyheteroaryleneethynylenes." *High Performance Polymers* **2001**, 13, 153.

¹⁵⁶ Mignard, E., R.C. Hiorns, and B. Francois. "Synthesis and Characterization of Star Copolymers Consisting of Fullerene and Conjugated Poly(phenylene)." *Macromolecules* **2002**, 35, 6132.

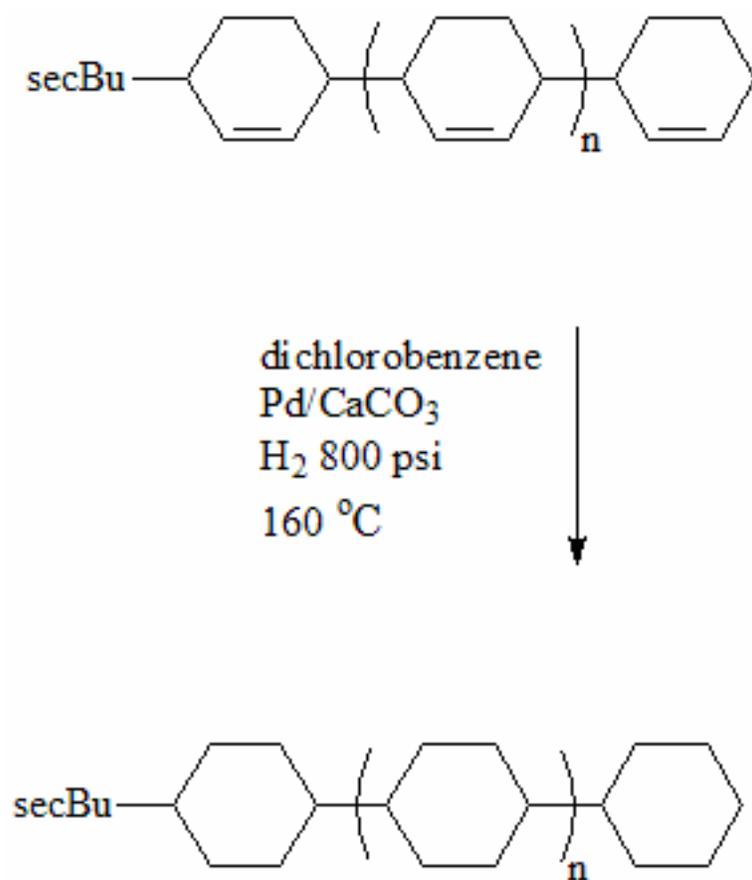
¹⁵⁷ Natori, I., K. Imaizumi, H. Yamagishi, and M. Kazunori. "Hydrocarbon Polymers Containing Six-Membered Rings in the Main Chain. Microstructure and Properties of Poly(1,3-cyclohexadiene)." *J. Polym. Sci., Part B: Polym. Phys.* **1998**, 36, 1657.

¹⁵⁸ Hong, K., and J.W. Mays. "1,3-Cyclohexadiene Polymers. 1. Anionic Polymerization." *Macromolecules* **2001**, 34, 782.

polymers were proposed to be excellent optical materials due to their excellent transparency, rigidity, and low birefringence. Hydrogenation was performed using the heterogeneous catalyst Pd/CaCO₃ with 800 psi of hydrogen at 160 °C. Earlier studies also described the chemical hydrogenation of poly(1,3-cyclohexadiene) using diimide strategies.¹⁵⁹ Saturation of the double bond improves the thermo-oxidative stability of the polymer and increases the glass transition temperature from 150 °C to 225 °C. This method was utilized in the synthesis of miktoarm star copolymers containing both polyethylene and poly(cyclohexylene) arms.¹⁶⁰

¹⁵⁹ Mango, L.A., and R.W. Lenz. "Hydrogenation of unsaturated polymers with diimide." *Makromol Chem* **1973**, 163, 13.

¹⁶⁰ Tsoukatos, T., and N. Hadjichristidis. "Synthesis of Model Polycyclohexylene/polyethylene Miktoarm Star Copolymers with Three and Four Arms." *J. Polym. Sci. Part A: Polym. Chem.* **2002**, 40, 2575.



Scheme 2-8. Hydrogenation of Poly(1,3-cyclohexadiene)

2.6 Synthesis of Complex Architectures

2.6.1 Block Copolymers

2.6.1.1 Introduction

Block copolymers are defined as being "macromolecules composed of linear arrangements of blocks in which a block is defined as being composed of units which are chemically different from the adjacent portions of the macromolecule".¹⁶¹ In general, the notation for a block copolymer is to name each corresponding block in sequential order. For example the correct nomenclature for a block copolymer composed of AAAAAAAAAABBBBBBBB would be polyA-Block-polyB or more commonly polyA-*b*-polyB. Since multiple blocks may be attached the materials can vary from a diblock to a triblock or a multiblock. Table 2-5, shown below, outlines the typical block copolymer nomenclature.¹⁶¹

Table 2-5. Block Copolymer Notations

Polymer Structure	Notation	Copolymer
-AAAA-BBBB-	A-B	Diblock
-AAAA-BBBB-AAAA-	A-B-A	Triblock
-AAAA-BBBB-CCCC-	A-B-C	Triblock
-AAA-BBB-(AAA-BBB) _n -AAA-BBB-	(A-B) _n	Multiblock
(AAAAA-BBBBB) _n -X	(A-B) _n -X	Star

This section describes the various methods used to polymerization block copolymers, including anionic, cationic, group transfer, and controlled radical polymerization methodologies.

¹⁶¹ Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996.

2.6.1.2 *Anionic Synthesis of Block Copolymers.*

A variety of monomer addition strategies have been examined in the attempt to efficiently synthesize block copolymers. The first of these methods is sequential addition, which involves the synthesis of a block consisting of monomer A followed by the addition of monomer B after the complete synthesis of the first block.¹⁶² Additional blocks can be added if the pKa of the conjugate acid of the propagating anion of the subsequent block is lower than the pKa of the conjugate acid of the propagating anion of the previous block.¹⁶³ This was previously shown to be a limiting factor for the synthesis of a variety of block copolymers.¹⁶⁴ In an attempt to overcome this limitation, researchers have developed difunctional agents that are capable of coupling the blocks. This approach represents an effective method to convergently couple the living polymers and synthesize polymer that would not be efficiently synthesized using sequential addition methodologies. In addition, the reaction time is reduced since only half of the triblock polymer needs to be polymerized prior to the coupling reaction. However, there are disadvantages to the coupling methodology. Low coupling efficiencies is a drawback of this approach. A poor coupling reaction results in the presence of uncoupled polymer present with the coupled macromolecule, which can decrease the desired mechanical properties.¹⁶⁵ In addition, precise control of the

¹⁶² Morton, M., and L.J. Fetters. "Anionic polymerization of vinyl monomers." *Rubber Chem and Tech* **1975**, 48, 359. Richards, R.W., and J.L. Thomason. "A simplified apparatus for the preparation of block copolymers with low polydispersity ratios." *Polymer* **1982**, 23, 1988. Falk, J.C., M.A. Benedetto, J. Van Fleet, and L. Ciaglia. "Polystyrene-polyisoprene-polystyrene { α -hydro-w-1-sec-butyl[poly(1-phenylethylene)-poly-(2-methyl-2-butenylene)-poly(1-phenylethylene)]}." *Macromol. Syn.* **1982**, 8, 61.

¹⁶³ Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996. Noshay, A., and J.E. McGrath "Block Copolymers" Academic Press New York 1977.

¹⁶⁴ Long, T.E., A.D. Broske, D.J. Bradley, and J.E. McGrath. "Synthesis and Characterization of Poly(t-butyl Methacrylate -b-Isoprene-b-t-butyl Methacrylate) Block Copolymers by Anionic Techniques." *J. Polym. Sci.* **1989**, 27, 4001.

¹⁶⁵ Lovisi, H.R., L.F. Nicolini, A.A. Ferreira, and M.L.S. Martins. "The Influence of Uncoupled Styrene-Butadiene Diblock Copolymer on the Physical Properties of SBS Thermoplastic Elastomers." In *Application of Anionic Polymerization Research*, edited by R. P. Quirk, 90.

reaction stoichiometry was shown to be difficult in some systems.¹⁶⁶ The stoichiometry of the reaction is dependent upon the presence of trace protic impurities found in either the second monomer charge or the addition of the coupling agent. The presence of trace impurities in these charges can alter the concentration of active anion species present in the reaction. A third methodology is the utilization of a difunctional initiator and this allows the chain to propagate from both ends of the chain. Common examples of difunctional initiators are 1,3-bis(1-phenylethenyl) benzene (DDPE) and sodium naphthalene.¹⁶⁷ The disadvantage of sodium naphthalene is the requirement that the polymerization must proceed in a polar solvent, which tends to result in the formation of a high percentage of 1,2-addition in the resulting macromolecule.¹⁶⁶ Using this methodology one can polymerize the ABA triblock material from the inside out such as for the synthesis of a poly(t-butylmethacrylate)-b-polyisoprene-b-poly(t-butylmethacrylate) triblock material.¹⁶⁸ The utilization of a difunctional initiator enables the synthesis of ABA triblock copolymers that exhibit an inefficient crossover from the A block to the B block. One of the disadvantages of using a difunctional initiator is the insolubility of the initiator in hydrocarbon solvents. Polar solvents are commonly used to accommodate the solubility requirements of the difunctional initiator. Polymerization of a diene monomer such as isoprene or butadiene in a polar solvent typically results in high degree of vinyl enchainment.

Washington D.C.: American Chemical Society, 1998. Fetters, L.J., B.H. Meyer, and McIntyre. "Effect of diblock and homopolymer impurities on the morphology of triblock polymers." *Journal of Applied Polymer Science* **1972**, 16, 2079.

¹⁶⁶ Fetters, L.J. *Block Copolymers: Science and technology*. Edited by D.J. Meier Harwood: New York, 1983.

¹⁶⁷ Szwarc, M. "Living Polymers and Mechanisms of Anionic Polymerization." *Advances in Polymer Science* **1983**, 49, 1.

¹⁶⁸ Long, T.E., A.D. Broske, D.J. Bradley, and J.E. McGrath. "Synthesis and Characterization of Poly(t-butyl Methacrylate -b-Isoprene-b-t-butyl Methacrylate) Block Copolymers by Anionic Techniques." *J. Polym. Sci.* **1989**, 27, 4001.

To overcome this difficulty a number of researchers have developed difunctional initiators that exhibit excellent solubility in nonpolar solvents. The initiators include the product of 1,5-diethylnaphthalene and *sec*BuLi,¹⁶⁹ α,ω -dilithiopolyisoprene,¹⁷⁰ and derivatives of 1,1-diphenylethylene. These initiators have not been well received industrially due to the time and cost associated with their synthesis.

Block Copolymers containing poly(1,3-cyclohexadiene)

Prior to the 1998 study by Natori et al.,¹⁷¹ the amount of research performed that examined the synthesis of polymers composed of 1,3-cyclohexadiene was minimal and these attempts resulted in little success. This study, reporting the first successful living anionic polymerization of 1,3-cyclohexadiene, was followed by series of papers,¹⁷² in which the authors incorporated 1,3-cyclohexadiene into the polymer in a block form. The initial report published by Natori et al.,¹⁷³ involved the synthesis of block copolymers consisting of poly(1,3-cyclohexadiene)-*b*-polystyrene-*b*-poly(1,3-cyclohexadiene), poly(1,3-cyclohexadiene)-*b*-poly(butadiene)-*b*-poly(1,3-cyclohexadiene), and poly(1,3-cyclohexadiene)-*b*-polyisoprene-*b*-poly(1,3-

¹⁶⁹ Nugay, T., and S. Kucukyavuz. "A New Difunctional Anionic Initiator Soluble in Non-Polar Solvents." *Polym. Int.* **1995**, 29, 195.

¹⁷⁰ Madani, A.E., J. Belleney, J. Favier, P. Hemery, and P. Sigwalt. "Polymerization of Isoprene Initiated by Dilithiopolyisoprene." *Polym. Int.* **1993**, 31, 169. Long, T.E., A.D. Broske, D.J. Bradley, and J.E. McGrath. "Synthesis and Characterization of Poly(*t*-butyl Methacrylate -*b*-Isoprene-*b*-*t*-butyl Methacrylate) Block Copolymers by Anionic Techniques." *J. Polym. Sci.* **1989**, 27, 4001.

¹⁷¹ Natori, I., and S. Inoue. "Living Anionic Polymerization of 1,3-cyclohexadiene with the *n*-butyllithium/*N,N,N',N'*-Tetramethylethylenediamine System. Copolymerization and Block Copolymerization with Styrene, Butadiene, and Isoprene." *Macromolecules* **1998**, 31, 982.

¹⁷² Hong, K., J.W. Mays, Y. Wang, and R. Advincula. "Synthesis and Aromatization of Polycyclohexadiene(PCHD) Homo and Block Copolymers: Towards Processible Poly-*p*-Phenylene (PPP) Derivatives." *PMSE Preprints* **1999**, 80, 116. David, J. L., S. P. Gido, K. Hong, Jian Zhou, J. W. Mays, and B.N. Tan. "Core-Shell Cylinder Morphology in Poly(styrene-*b*-1,3-cyclohexadiene) Diblock Copolymers." *Macromolecules* **1999**, 32, 3216. Natori, I., K. Imaizumi, H. Yamagish, and M. Kazunori. "Hydrocarbon Polymers Containing Six-Membered Rings in the Main Chain. Microstructure and Properties of Poly(1,3-cyclohexadiene)." *J. Polym. Sci., Part B: Polym. Phys.* **1998**, 36, 1657.

¹⁷³ Natori, I., K. Imaizumi, H. Yamagish, and M. Kazunori. "Hydrocarbon Polymers Containing Six-Membered Rings in the Main Chain. Microstructure and Properties of Poly(1,3-cyclohexadiene)." *J. Polym. Sci., Part B: Polym. Phys.* **1998**, 36, 1657.

cyclohexadiene). The authors determined the relative reactivities and reaction rates of the monomers by removing aliquots from the living polymerization and measuring the monomer concentration with time. These living polymerizations occurred in a complex environment that consisted of a propagating homopolymer with two different monomers competing with one another during the polymerization. The relative monomer reactivity was determined by measuring concentration of each monomer as a function of time. From these studies, the authors determined that the reactivities of the monomers in cyclohexane in the presence of TMEDA were as follows:

Butadiene > Styrene > Isoprene > 1,3-Cyclohexadiene

The relative rate for the homopolymerization was also determined using identical methods. From these studies, the authors determined that the relative rate of homopolymerization was:

Butadiene > Styrene > Isoprene > 1,3-Cyclohexadiene

Although the rate of homopolymerization followed the same trend as the reactivities of the monomers, the authors found that the difference in the reactivities of the monomers was not found in the rate of homopolymerization. The rate of homopolymerization of isoprene is greater than 1,3-cyclohexadiene, but the difference between the two homopolymerizations is not as great as the difference in the reactivities of the monomers. These studies did not examine the appearance of the resulting polymer in conjunction with the loss of the monomer and were not performed under pure homopolymerization conditions because the system consisted of a mixed solution of monomers. The complex reaction environment renders the results unclear due to the possible complex interplay of factors such as aggregation size, polarity of the solvent, and the role of the efficiency of the crossover from one monomer to the next. In a following study the authors examined the physical properties of the ABA triblock copolymers consisting of poly(1,3-cyclohexadiene)-b-polystyrene-b-poly(1,3-cyclohexadiene) and poly(1,3-cyclohexadiene)-b-polybutadiene-b-poly(1,3-

cyclohexadiene).¹⁷⁴ These polymers were hydrogenated and the resulting physical properties were analyzed. It was found that triblock of the 1,3-cyclohexadiene and butadiene exhibited excellent percent recovery characteristics as compared to SBS thermoplastic elastomers. This study also examined the morphology of the resulting diblock and triblock materials and further studies examined the morphology of the diblock copolymer polystyrene-*b*-poly(1,3-cyclohexadiene) more extensively. From these studies, it appears that the polystyrene-*b*-poly(1,3-cyclohexadiene) diblock tends to arrange itself in a core-shell cylinder morphology¹⁷⁵ and Natori et al. report an excellent phase separation for the associated triblock polymer. A series of studies were performed in the late 1970's in which the reaction was charged with 1,3-cyclohexadiene and either a diene or vinyl aromatic comonomer.¹⁷⁶ The anionic polymerization was initiated with an alkyllithium species. The series of studies did not report the composition of the resulting polymers. It was found that as the charge of 1,3-cyclohexadiene increased the percent yield of the polymerization decreased.

2.6.1.3 *Group Transfer Methodologies*

Early successes by researchers at DuPont Central Research and Development and DuPont Automotive Products in synthesizing poly(methyl methacrylate) polymers at -80 °C created an interest in these polymers for dispersing pigments and rheology

¹⁷⁴ Natori, I., K. Imaizumi, H. Yamagishi, and M. Kazunori. "Hydrocarbon Polymers Containing Six-Membered Rings in the Main Chain. Microstructure and Properties of Poly(1,3-cyclohexadiene)." *J. Polym. Sci., Part B: Polym. Phys.* **1998**, 36, 1657.

¹⁷⁵ David, J. L., S. P. Gido, K. Hong, Jian Zhou, J. W. Mays, and B.N. Tan. "Core-Shell Cylinder Morphology in Poly(styrene-*b*-1,3-cyclohexadiene) Diblock Copolymers." *Macromolecules* **1999**, 32, 3216.

¹⁷⁶ Hsieh, H. L. "Copolymerization of a Linear 1,3-Cyclodiene and a Linear Conjugated Diene." Phillips Petroleum Company, United States 4138356 (1978). Hsieh, H. L. "1,3-Cyclodiene-Acyclic Conjugated Diene Copolymers." Phillips Petroleum Company, United States 4237246 (1977). Hsieh, H. L. "Epoxidized Block Copolymers." Phillips Petroleum Company, United States 40202521 (1978). Hsieh, H. L. "Polymerization of 1,3-Cyclohexadiene With Vinylaromatic Hydrocarbon." Phillips Petroleum Company, United States 4131653 (1979). Hsieh, H. L. "Copolymers of 1,3-cyclohexadienes, Monovinylaromatic Compounds and Polyvinylaromatic Hydrocarbons." Phillips Petroleum Company, United States 4127710 (1980).

control for automotive finishes.¹⁷⁷ Unfortunately, the cost of this process was prohibitive to the development of an industrially viable process, but interest in the poly(methyl methacrylate) block copolymers remained. Further work in the area of methacrylate polymerizations focused on using the Mukiyama reaction, which was known to add a silyl ketene acetal to activated double bonds using a Lewis acid catalyst, such as ZnCl₂. These early studies resulted in the development of Group Transfer Polymerization (GTP). The mechanism of GTP consists of a concerted addition of methyl trimethylsilyl dimethyl ketene acetal to methyl methacrylate (Figure 10).¹⁷⁸ Following the initial GTP studies, a range of viable Lewis acid catalysts were explored, these include bifluoride and fluoride ions coupled with solubilizing reagents such as tri(dimethylamino)sulfonium bifluoride. The introduction of solubilizing reagents led to the introduction of “leave-in-catalysts” for GTP. The synthesis of novel methacrylate based block copolymers followed these early industrial efforts of Webster et al. Block copolymers investigated included poly(methyl methacrylate-block-(dimethylamino) ethyl methacrylate), poly(methyl methacrylate-block-tetrahydropyranyl methacrylate),¹⁷⁹ and poly(2-ethylhexyl acrylate-block-methyl methacrylate).¹⁸⁰ Well-defined polymers with molecular weights in excess of 40000 were synthesized with narrow molecular weight distributions (1.18).

¹⁷⁷ Webster, O.W. "The Discovery and Commercialization of Group Transfer Polymerization." *J. Polym. Sci. Part A: Polym. Chem.* **2000**, 38, 2855.

¹⁷⁸ Hertler, W.R., D.Y. Sogah, and O.W. Webster. "Group-transfer polymerization. 3. Lewis acid catalysis." *Macromolecules* **1984**, 17, 1415.

¹⁷⁹ Patrickios, C.S., A.B. Lowe, S.P. Armes, and N.C. Billingham. "ABC Triblock Polymethacrylates: Group Transfer Polymerization Synthesis of the ABC, ACB, and BAC Topological Isomers and Solution Characterization." *J. Polym. Sci. Part A: Polym. Chem.* **1998**, 36, 617.

¹⁸⁰ Kriz, J., B. Masar, J. Plestil, Z. Tuzar, H. Pospisil, and D. Doskocilova. "Three-Layer Micelles of an ABC Block Copolymer: NMR, SANS, and LS Study of a Poly(2-ethylhexyl acrylate)-block-poly(methyl methacrylate)-block-poly(acrylic acid) Copolymer in D₂O." *Macromolecules* **1998**, 31, 41.

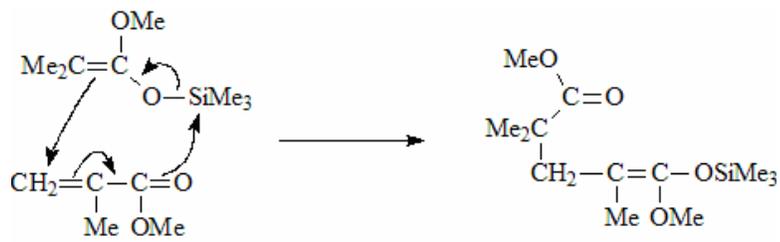
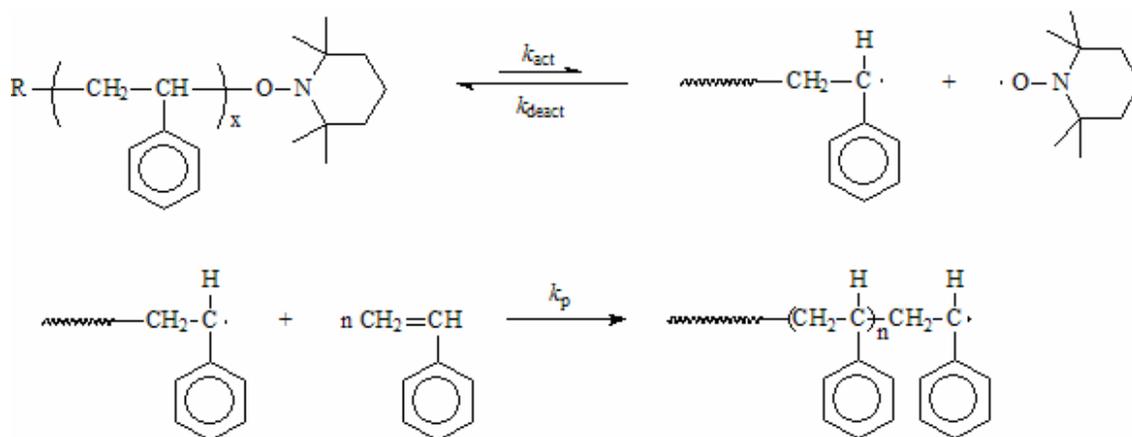


Figure 2-12. Mechanism of Group Transfer Polymerization

2.6.1.4 Controlled Free Radical

Until recently, the synthesis of block copolymers required the use of anionic, cationic or group transfer polymerization methodologies. However, in recent years the need for well-defined, functionalized materials has driven the development of novel end-capping reagents capable of minimizing the degree of termination reactions. The development of iniferters (*initiator-transfer agent-terminator*) by Otsu in 1982 was the first attempt to develop a controlled free radical approach.¹⁸¹ Subsequent studies provided additional strategies to control free radical polymerizations. Of these, nitroxide mediated polymerizations (NMP) and atom transfer radical polymerizations (ATRP) have



Scheme 2-9. Styrene SFRP reaction scheme.

¹⁸¹ Otsu, T, and M. Yoshida. "Role of initiator-transfer agent-terminator (iniferter) in radical polymerizations: polymer design by organic disulfides as iniferters." *Makromol Chem, Rapid Commun.* **1982**, 3, 127.

received the most attention.¹⁸² NMP utilizes a reversible termination of the propagating polymeric chain to reduce the overall concentration of the propagating chain end (Scheme 2-9). Therefore, the concentration of the reactive chain is extremely low and minimizes the degree of irreversible termination reactions, such as combination or disproportionation. The nature of the mediating radical is critical to the success of the living free radical procedure, as such, a range of persistent or stabilized radicals have been investigated. These methods were successful in reducing the concentration and reactivity of the propagating chain end.¹⁸³ These procedures were not successful in completely eliminating deleterious side reactions, which are associated with radical polymerizations, however, the best systems were shown to display the characteristics of a living system. In spite of these advances, some chain end degradation was shown to occur in NMP. One potential pathway is the reduction of the mediating nitroxide forming a hydroxylamine and a terminated polymer chain end. The functional group tolerance exhibited by controlled free radical methodologies has made it the method of choice when synthesizing novel polymeric materials with a high degree of functionality. While the utility of free radical polymerizations has been greatly expanded by the introduction of controlled free radical methodologies, there are still deficiencies in the methodology. These include an inability to control polymer tacticity, the presence of low levels of radical-radical coupling reactions, long reaction times, high reaction temperatures, and less than quantitative polymerization yields.

NMP has received significant interest due to its ability to mediate the synthesis of block copolymers, such polystyrene containing block copolymers. The polymerization of styrene using 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) at elevated temperatures (130 °C) is a well behaved polymerization free of significant termination reactions.¹⁸⁴ As such, many of the early studies examining the synthesis of

¹⁸² Puts, R. D. , and D. Y. Sogah. " Control of Living Free-Radical Polymerization by a New Chiral Nitroxide and Implications for the Polymerization Mechanism." *Macromolecules* **1996**, 29, 3323.

¹⁸³ Hawker, C.J., A.W. Bosman, and E. Harth. "New Polymer Synthesis by Nitroxide Mediated Living Radical Polymerizations." *Chem. Rev.* **2001**, 101, 3661.

¹⁸⁴ Georges, M.K., R.P.N. Veregin, P.M. Kazmaier, and G.K. Hamer. "Narrow molecular weight resins by a free-radical polymerization process." *Macromolecules* **1993**, 26, 2987.

block copolymers used styrene as the first block to ensure adequate molar crossover to the second block. Examples include poly(styrene-block-methyl methacrylate), poly(styrene-block-2-dimethylaminoethyl methacrylate), and poly(styrene-block-t-butyl methacrylate).¹⁸⁵ The functional group tolerance exhibited by controlled free radical methods was utilized in later studies for the synthesis of block copolymers containing a functionalized block. In contrast, these functionalized monomers would have been unusable with living anionic methodologies due to the extraordinarily high reactivity of the propagating carbanion. The synthesis of well-defined poly(styrene-block-4-vinylbenzylphosphonate) using NMP ($\langle M_n \rangle = 22000$, $\langle M_w \rangle / \langle M_n \rangle = 1.2$) further demonstrates the unique ability of controlled radical polymerization strategies to synthesize functionalized block copolymers that would have been impossible to synthesize using anionic methods.¹⁸⁶

¹⁸⁵ Fernandez-Garcia, M., R. Cuervo-Rodriguez, and E.L. Madruga. "Synthesis, Characterization, and Glass Transition Temperature of Poly(styrene-b-butyl methacrylate) Block Copolymers by Stable Free Radical Polymerization." *J. Polym. Sci. Part A: Polym. Chem.* **2001**, 82, 14.

¹⁸⁶ Boutevin, B., Y. Hervaud, A. Boulahna, and M. El. Asri. "Free Radical Polymerization of Dimethyl vinylbenzylphosphonate." *Macromolecules* **2002**, 35, 6511.

2.6.2 Star-Shaped Polymers

Star-shaped polymers have received significant attention due to their highly branched structure which gives rise to their unique properties. A branched structure has been described as nonlinear polymer composed of multiple backbone chains emanating from junction points.¹⁸⁷ Branching results in more compact structure relative to linear analogues, due to high segment density, which in turn effect the crystalline, mechanical, and viscoelastic properties. Star-shaped polymers have generally been synthesized using controlled polymerization pathways, such as anionic,¹⁸⁸ cationic,¹⁸⁹ living free radical,¹⁹⁰ and group transfer polymerization (GTP).¹⁹¹ The two approaches used to synthesize star-shaped polymers are termed “arm-first” and “core-first”. In the “core-first” approach, a multifunctional initiator is used to initiate the polymerization of the monomer (Figure 2-12). The number of arms is controlled by the number of initiating groups on the initiator. The length of the arms is controlled by the ratio of grams of monomer to moles of initiating sites.

¹⁸⁷ Roovers, J. "Branched polymers." In *Encyclopedia of Polymer Science and Engineering*, edited by J. I. Kroschwitz, 478. New York: Wiley, 1985.

¹⁸⁸ Hadjichristidis, N., and L.J. Fetters. "Star Branched Polymers. 4. Synthesis of 18-Arm Polyisoprenes." *Macromolecules* **1980**, 13, 193. Bywater, S. "Preparation and properties of star-branched polymers." *Adv. Polym. Sci.* **1979**, 30, 89. Tsoukatos, T., and N. Hadjichristidis. "Synthesis of Model Polycyclohexylene/polyethylene Miktoarm Star Copolymers with Three and Four Arms." *J. Polym. Sci. Part A: Polym. Chem.* **2002**, 40, 2575.

¹⁸⁹ Storey, R. F., and K. A. Shoemake. "Poly(Styrene-*b*-Isobutylene) Multiarm Star Block Copolymers." *J. Polym. Sci., Part A: Polym. Chem* **1999**, 37, 1629. Asthana, Siddhartha, and J. P. Kennedy. "Star Block Polymers of Multiple Polystyrene-*b*-Polyisobutylene Arms Radiating from a Polydivinylbenzene Core." *J. Polym. Sci.* **1999**, 37, 2235.

¹⁹⁰ Pasquale, A. J., and T. E. Long. "Synthesis of star-shaped polystyrenes via nitroxide-mediated stable free-radical polymerization." *J. Polym. Sci. Part A: Polym. Chem.* **2000**, 39, 216.

¹⁹¹ Webster, O.W. "The use of group transfer polymerization for the control of polymethacrylate molecular structure." *Makromol Chem* **1990**, 33, 133.

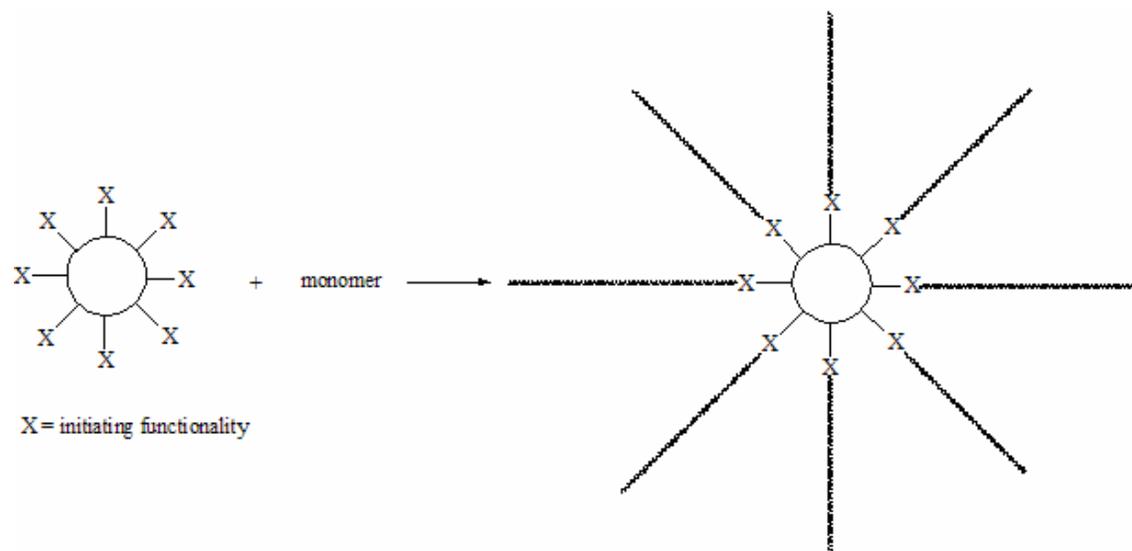


Figure 2-13. Synthesis of star-shaped polymers using the "core-first" approach.

If the initiation is rapid relative to propagation and the activity of the initiator is high, the well-defined star-shaped polymers can be obtained. This method was employed in the first cationic synthesis of star-shaped polymers, which contained three or four arms per star.¹⁹² This approach has a tendency to generate polymers with a broad molecular weight distribution.¹⁹³ The alternative approach, generally termed the "arm-first" method is commonly used for both living anionic and cationic syntheses of star-shaped polymers (Figure 2-13).¹⁹⁴ In this approach, the number of polymer arms is dictated by the ratio of initiating species relative to coupling agent.

Anionic polymerization methods are ideal for the synthesis of complex polymeric structures via the coupling of reactive end groups. Precise control of molecular weight and polydispersity is a distinguishing feature of anionic polymerizations. Furthermore, anionic polymerization methods also provide excellent control of the functionality of controlled architectures such as star-shaped polymers.¹⁹⁵ Typically, the "arm-first" method in combination with a living anionic polymerization was used in the syntheses of star-shaped polymers. An advantage of this approach is the facile synthesis of a homogenous population of star-shaped polymers.

¹⁹² Mishra, M., B. Wang, and J.P. Kennedy. "Living carbocationic polymerization. IX. Three-arm star telechelic polyisobutylenes by $C_6H_3(C(CH_3)_2OCH_3)_3/BCl_3$ complexes." *Polym. Bull.* **1987**, 17, 307.

¹⁹³ Meneghetti, S.P., P.J. Lutz, and D. Rein. "Star-Shaped Polymers via Anionic Polymerization Methods." In *Star and Hyperbranched Polymers*, edited by Munmaya Mishra and Shiro Kobayashi, 27. New York: Marcel Dekker, 1999.

¹⁹⁴ Ishizu, Koji, and Kenro Sunahara. "Synthesis of Star Polymers by Organized Polymerization of Macromonomers." *Polymer* **1995**, 36, 4155. Storey, R. F., and K. A. Shoemake. "Poly(Styrene-*b*-Isobutylene) Multiarm Star Block Copolymers." *J. Polym. Sci., Part A: Polym. Chem* **1999**, 37, 1629. Hadjichristidis, N., and L.J. Fetters. "Star Branched Polymers. 4. Synthesis of 18-Arm Polyisoprenes." *Macromolecules* **1980**, 13, 193. Hadjichristidis, N., and L.J. Fetters. "Star-Branched Polymers. 4. Synthesis of 18-Arm Polyisoprenes." *Macromolecules* **1980**, 13, 193. Storey, R. F., K. A. Shoemake, and B. J. Crisholm. "Synthesis and Characterization of Multi-Arm Star-Branched Polyisobutylenes." *J. Polym. Sci. Part A: Polym. Chem.* **1996**, 34, 2003.

¹⁹⁵ Ishizu, Koji, and Kenro Sunahara. "Synthesis of Star Polymers by Organized Polymerization of Macromonomers." *Polymer* **1995**, 36, 4155. Storey, R. F., K. A. Shoemake, and B. J. Crisholm. "Synthesis and Characterization of Multi-Arm Star-Branched Polyisobutylenes." *J. Polym. Sci. Part A: Polym. Chem.* **1996**, 34, 2003.

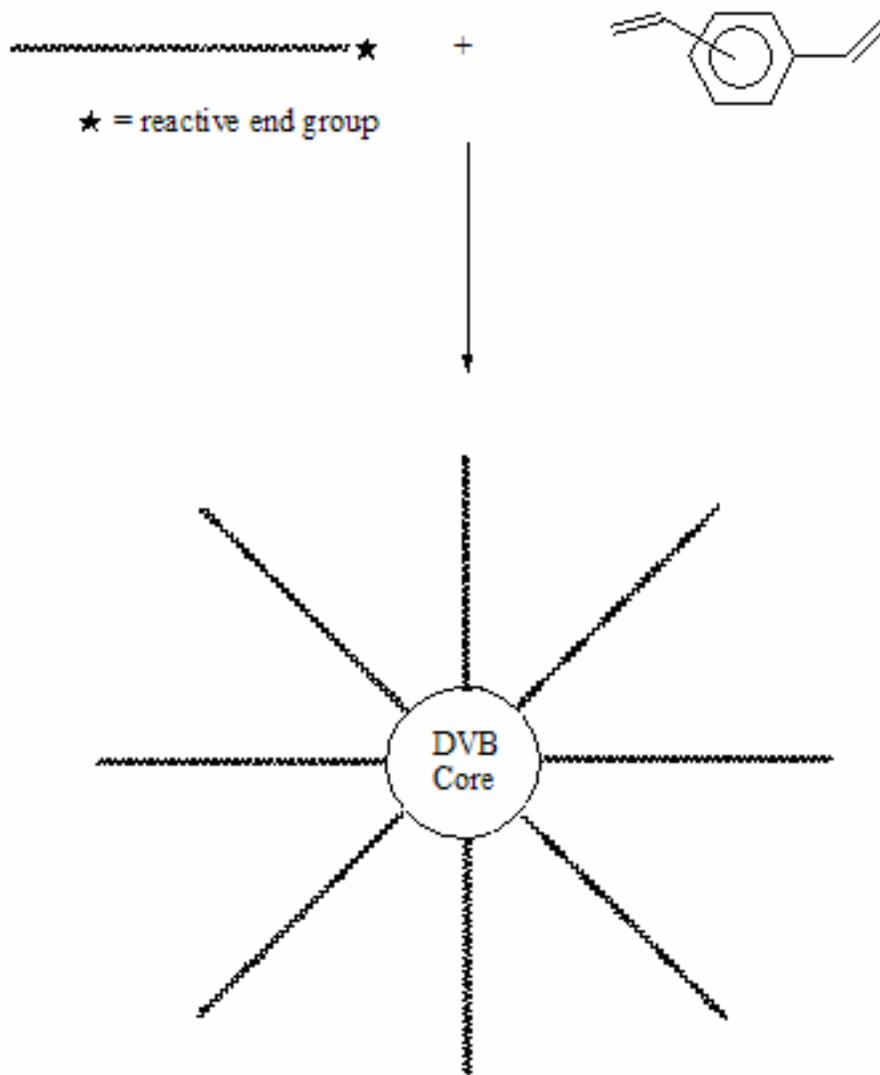


Figure 2-14. Synthesis of star-shaped polymers using the "arm-first" approach.

This method has been employed using a variety of linking agents, where each linking agent exhibits a different theoretical functionality. A limiting factor for a number of possible linking agents is the equal reactivity and accessibility of all the sites on the coupling agents. These factors are limiting for silicon tetrachloride¹⁹⁶ and other coupling agents such as chloromethylated benzenes.¹⁹⁷ Some of the other linking agents are dimethyl phthalate, trisallyloxytriazines, and para and meta divinylbenzene.¹⁹⁸ The theoretical functionality of linking agents such as trichloromethylsilane and tetrachlorosilane dictates the number of arms formed per star. In contrast, divinyl compounds undergo homopolymerization and form star polymers where the number of arms is greater than the functionality of a single divinyl compound.¹⁹⁹ This approach was immediately commercially successful and was utilized to synthesize poly(ethylene-co-propylene) star-shaped polymers, which were used as a viscosity improver in motor oil.²⁰⁰ Although functionalization of the outer end of the arms has been demonstrated it typically requires a specialized initiator.²⁰¹ This method has been utilized for the modification of hydroxyl groups to sulfozwitterionics.²⁰²

¹⁹⁶ Morton, M., T.E. Helminiak, S.D. Gadkary, and F. Bueche. "Preparation and properties of monodisperse branched polystyrene." *J. Polym. Sci.* **1962**, 11, 668.

¹⁹⁷ Wenger, F., and S. P.S. Yen. "A simple process for controlled anionic polymerization. The preparation of monodisperse polystyrene." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **1961**, 2, 295. Nguyen, T.G., and H.H. Kausch. *Makromol Chem, Rapid Commun.* **1985**, 6, 391.

¹⁹⁸ Rempp, P., and D. Decker. "Preparation of macromolecular compounds with a star-shaped structure." *Compt. Rend.* **1965**, 26, 1977. Zilliox, J.G., D. Decker, and P. Rempp. "Polydispersion of star polymers prepared by an anionic method in a homogeneous phase." *Acad. Sci., Paris* **1966**, 262, 726. Zilliox, J.G., P. Rempp, and J. Parrod. "Preparation of star-shaped macromolecules by anionic copolymerization." *J. Polym. Sci. Part A.* **1968**, 22, 145. Worsfold, D.J., J.G. Zilliox, and P. Rempp. "Preparation of star-shaped polymers by anionic block copolymerization and their characterization." *Can. J. of Chem.* **1969**, 47, 3379. Young, R. N., and L.J. Fetters. "Star-branched polymers. 2. The reaction of dienyllithium chains with the isomers of divinylbenzene." *Macromolecules* **1978**, 11, 899.

¹⁹⁹ McGrath, J.E., ed. *Anionic Polymerization: Kinetics, Mechanisms, and Synthesis*. Vol. 166, *ACS Symposium Series* American Chemical Society: Washington D.C., 1981.

²⁰⁰ Kennedy, J.P., and S. Jacob. "Cationic Polymerization Astronomy: Synthesis of Polymer Star by Cationic Means." *Acc. Chem. Res.* **1998**, 31, 835.

²⁰¹ Burchard, W., and G. Merkle. "Acid-base-induced association of amino-terminated polystyrenes. 1. Linear chains and ring formation." *J. Phys. Chem.* **1992**, 96, 3915.

²⁰² Meneghetti, S.P., P.J. Lutz, and D. Rein. "Star-Shaped Polymers via Anionic Polymerization Methods." In *Star and Hyperbranched Polymers*, edited by Munmaya Mishra and Shiro Kobayashi, 27. New York: Marcel Dekker, 1999.

The alternate method, termed "core-first", involves the generation of the reactive core prior to the addition of arm forming monomers.²⁰³ One of the major disadvantages of the core first method is the tendency of the core to couple. The tendency to couple decreases as the arms of the star grow and protect the core. The advantage of the core first method is the ability to functionalize the outer chain ends of the star-shaped macromolecule. Although the outer chain ends of star-shaped polymers synthesized using the arm-first approach can be functionalized, this typically requires a specialized initiator. A functionalized exterior can then be utilized in the generation of networks or star-shaped polymers containing copolymeric branches.²⁰⁴ Recently, a number of studies have combined both the "core-first" and the "arm-first" method in a single synthesis to generate stars with mixed arm lengths in what is termed the "in-out" method.²⁰⁵

Recently, a number of variations of the aforementioned methods have been utilized to synthesize new macromolecular structures. Among these methods is the incorporation of cationic polymerization methodology in concert with anionic polymerization methods to generate well-defined star-shaped macromolecules.²⁰⁶ For the synthesis of the star-shaped polymers the authors initiated the polymerization of isobutylene with 1,3,5-tricumyl chloride. The polyisobutylene chains were then

²⁰³ Lutz, P.J., and P. Rempp. "New developments in star polymer synthesis: star-shaped polystyrenes and star-block copolymers." *Makromol Chem* **1988**, 189, 1051.

²⁰⁴ Mendes, E., P.J. Lutz, J. Bastide, and F. Boue. "Soft Order in High-Functionality Star Polymer Solutions and Gels: A Small-Angle Neutron Scattering Study." *Macromolecules* **1995**, 28, 174. Lutz, P.J., C. Picot, G. Hild, and P. Rempp. "Some considerations about the structure of polystyrene model-networks." *Brit. Polym. J.* **1977**, 9, 151. Meneghetti, S.P., P.J. Lutz, and D. Rein. "Star-Shaped Polymers via Anionic Polymerization Methods." In *Star and Hyperbranched Polymers*, edited by Munmaya Mishra and Shiro Kobayashi, 27. New York: Marcel Dekker, 1999.

²⁰⁵ Hadjichristidis, N. "Synthesis of Miktoarm Star (u-Star) Polymers." *J. Polym. Sci., Part A: Polym. Chem* **1999**, 37, 857. Frater, D. J., J.W. Mays, and C. Jackson. "Synthesis and Dilute Solution Properties of Divinylbenzene-Linked Polystyrene Stars with Mixed Arm Lengths: Evidence for Coupled Stars." *J. Polym. Sci., Part A: Polym. Chem* **1997**, 35, 141.

²⁰⁶ Feldthusen, Jesper, Bela Ivan, and Axel H.E Muller. "Synthesis of linear and Star-Shaped Block Copolymers of Isobutylene and Methacrylates by Combination of Living Cationic and Anionic Polymerizations." *Macromolecules* **1998**, 31, 578.

terminated by the addition of diphenylethylene and methanol, forming a diphenylethylene methoxy moiety (DPOMe) on the polymer chain end. The DPOMe group was then transformed into an initiator for the anionic polymerization of methyl methacrylate via a metalation reaction that utilized the highly reactive K/Na alloy. Novel trifunctional initiators have been developed for the synthesis of star-shaped poly(caprolactams).²⁰⁷ A more controlled method for the generation of star-shaped polymers utilized a combination of the arm-first approach in concert with a novel difunctional diphenylethylene derivative and subsequent re-initiation of a second monomer for the generation of an A₂B₂ star-shaped macromolecule.²⁰⁸ In the development of a less defined core, a number of alternative methods for the generation of the core have been investigated. These included the use of a bromomethylbenzene derivative for the generation of the t-butylmethacrylate star-shaped polymers,²⁰⁹ hyperbranched cores,²¹⁰ the use of epoxide functionality on the main chain as the coupling site for preformed arms,²¹¹ and use of convergent coupling of the arms to dendritically branched polystyrene.²¹²

²⁰⁷ Chang, W.L., K.C. Frisch, and K. Ashida. "Anionic Polymerization of Star-Shaped Nylon with a Trifunctional Initiator." *Journal of Polymer Science: Part A* **1989**, 27, 3637.

²⁰⁸ Fernyhough, C.M., R. N. Young, and R.D. Tack. "Synthesis and Characterization of Polyisoprene-Poly(methylmethacrylate) AB Diblock and A₂B₂ Heteroarm Star Copolymers." *Macromolecules* **1999**, 32, 5760.

²⁰⁹ Pitsikalis, M., S. Sioula, S. Psipas, N. Hadjichristidis, D.C. Cook, J. Li, and J. W. Mays. "Linking Reactions of Living Polymers with Bromomethylbenzene Derivatives: Synthesis and Characterization of Star Homopolymers and Graft Copolymers with Polyelectrolyte Branches." *J. Polym. Sci., Part A: Polym. Chem* **1999**, 37, 4337. Hogen-Esch, T.E., and W. Toreki. "Synthesis of macrocyclic- and star-vinyl polymers." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **1989**, 30, 129.

²¹⁰ Knischka, R., P.J. Lutz, A. Sunder, R. Mulhaupt, and H. Frey. "Functional Poly(ethylene oxide) Multiarm Star Polymers: Core-First Synthesis Using Hyperbranched Polyglycerol Initiators." *Macromolecules* **2000**, 33, 315.

²¹¹ Zhang, H., and E. Ruckenstein. "Graft, Block-Graft and Star Shaped Copolymers by an in Situ Coupling Reaction." *Macromolecules* **1998**, 31, 4753.

²¹² Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996.

2.6.3 Morphology of Block Copolymer Systems

Multiphase materials have been the focus of a significant body of research over the past two or three decades. Multiphase polymer systems can take the form of blends, block and graft copolymers, and interpenetrating networks.²¹³ These multiphase systems are typically characterized by the presence of multiple phases in the solid state. The presence of multiple phases in the solid state was recognized by Schollenberger in 1958. In this study, Schollenberger recognized that in the solid state, linear polyurethanes are comprised of both a soft and a hard segment. The soft portion was due to the polyester segment and the hard portion was due to the polyurethane segment. A variety of synthetic methods have been reported that are capable of producing block copolymers which exhibit phase separation. One example is the polymerization of ring opening oligomers in combination with step growth monomers. The methodology has been utilized for the synthesis of commercial polymer "Hytrel". The ability to anionically synthesize block copolymers was first recognized by Szwarc in his seminal 1956 paper.²¹⁴ Following that study, a variety of different block copolymers were synthesized and characterized.²¹⁵ In spite of numerous studies examining the morphological differences between diblock and triblock copolymers, it was not until Milkovich that the ability of triblock materials to form virtual crosslinks was discovered. As discussed previously, living anionic polymerizations represent an excellent avenue for the synthesis of macromolecules with varying architectures. This precise control over the architecture of the macromolecule is ideal for the study of the structure property relationship of block copolymers. Architecture is a critical parameter in determining the morphological properties of a block copolymer. Block copolymers have been found to arrange into a variety of different morphologies as a function of the volume fraction of each block. These morphologies can consist of lamellae, hexagonal

²¹³ McGrath, J.E. "An Introductory Overview of Block Copolymers." In *Block Copolymers: Science and Technology*, edited by D.J. Meier. New York: Harwood Academic Publishers, 1979.

²¹⁴ Szwarc, M, M Levy, and R. Milkovich. "Polymerization initiated by electron transfer to monomer. A new method of formation of block polymers." *J. Am. Chem. Soc.* **1956**, 78, 2656.

²¹⁵ Morton, M., J.E. McGrath, and P.C. Juliano. "Structure-Property Relationships for Styrene-Diene Thermoplastic Elastomers." *J. Polym. Sci.* **1969**, 26, 99.

close packed cylinders, body-centered-cubic packed spheres, and highly complex structures such as gyroid and metastable perforated lamellae phases (Figure 2-14).²¹⁶

The segregation of the blocks into separate domains is a result of the thermodynamic incompatibility of the segments (as indicated by the Flory-Huggins interaction parameter χ) as well as the length of the block N. For most block copolymer systems, the interaction between the two different blocks, termed the A and B blocks, is repulsive. The repulsive interaction between the two blocks provides the necessary driving force for the formation of domains resulting in a reduction in the surface to volume ratio. As the domains are formed, the polymer chains assume chain conformations that minimize the formation of a density deficiency at the core of the domain. The formation of tightly packed domains limits the number of available states and results in a reduction of the conformational entropy. The loss of conformational entropy acts to limit the growth of the domains. Additionally, the growth of the domain size results in a decrease in the entropy due to a decrease in the interphase. These three factors, the thermodynamic incompatibility, the loss of conformational entropy, and the loss of entropy due to a decreasing interphase, determine the domain size in the solid state.

²¹⁶ Hanley, K.J., T.P. Lodge, and Ching-I Huang. "Phase Behavior of a Block Copolymer in Solvent of Varying Selectivity." *Macromolecules* **2000**, 33, 5918.



Figure 2-15. Different classes of microphase-separated structures in block copolymers.

These factors are a function of the molecular parameters of the block copolymer, such as the molecular weight, chemical composition, and molecular architecture.²¹⁷ The relationship between the molecular weight and the domain size of the resulting material as described by the function:²¹⁸

$$D \propto M^a$$

D is the domain spacing of the material, M is molecular weight of the block, and the exponent (a) is approximately 2/3 if the blocks strongly segregate from one another.²¹⁹ The domain size resulting from the phase separation occurring in block copolymers is also a function of the number of blocks occurring in the multiblock copolymer. Typically the domain size becomes smaller as the number of blocks increases, assuming a constant block size, with diblock copolymers having larger domain sizes than multiblock copolymers. Annealing also reduces the size of the domain. Transmission electron microscopy in concert with staining techniques were used to image these domains (Figure 2-15). Thermoplastic elastomers (TPE) represent an application of the phase separation phenomenon. TPE are formed from ABA triblock copolymers, such as poly(styrene-*block*-isoprene-*block*-styrene) (SIS). As previously described, ABA triblock copolymers can be formed through several different methods. These are sequential addition, coupling, and use of a difunctional initiator. All of these synthetic methods have been used for the synthesis of a TPE. To be a TPE, the block copolymer must exhibit microphase separation and two widely different glass transition temperatures (ie -50 and 100 °C). The phase that exhibits the higher T_g is considered the hard phase and the phase with the lower T_g is considered the soft phase.

²¹⁷ Stroble, G. *The Physics of Polymers*. 2nd^{ed} Springer-Verlag: Berlin, 1997.

²¹⁸ Matsushita, Y., Y. Mogi, H. Mukai, and J. Watanabe. "Preparation and the Morphology of Multiblock Copolymers of the (AB)_n Type." *Polymer* **1994**, 35, 246.

²¹⁹ Helfand, E., and A.R. Wasserman. "Block copolymer theory. 4. Narrow interphase approximation." *Macromolecules* **1976**, 9, 879. Ohta, T., and K. Kawasaki. "Equilibrium morphology of block copolymer melts." *Macromolecules* **1986**, 19, 2621.

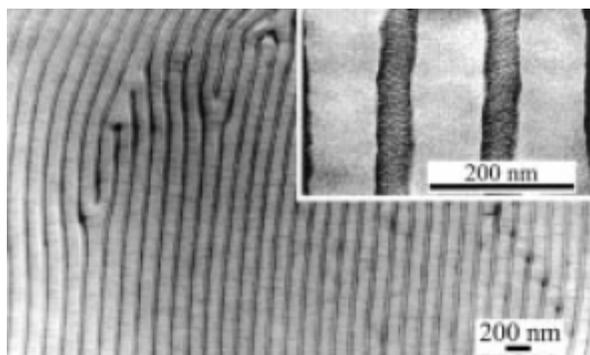


Figure 2-16. TEM micrograph of a stained poly(styrene-block-4-vinylpyridine) blended with dodecyl phenol (taken from Ikkala et al.²²⁰)

²²⁰ Ruokolainen, J., Saariaho, M., Ikkala, O. "Supramolecular Routes to Hierarchical Structures" *Macromolecules*, **1999**, 32, 1152.

Below the lower T_g , the polymer behaves as a glass and above the higher T_g , the polymer behaves as a liquid. In the region between the two glass transitions the TPE behaves as an elastic material. The presence of two glass transitions can be found using differential scanning calorimetry, rheology, and dynamic mechanical analysis.²²¹ The elastic behavior is a result of the interaction between the glassy phase and the liquid phase (Figure 2-16). The glassy phase of the material behaves as a crosslinking site between the rubbery phase.

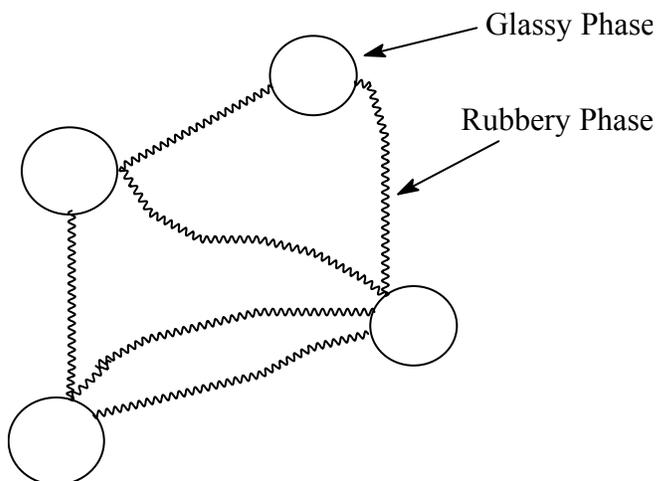


Figure 2-17. Depiction of the phase separation occurring in a thermoplastic elastomer.

A number of studies have been performed that examined the effects of composition and block molecular weight on the morphology of the TPE. These early studies focused on the block copolymers poly(styrene-*block*-isoprene-*block*-styrene) (SIS) or poly(styrene-*block*-butadiene-*block*-styrene) (SBS). Morton et al., in a comprehensive study of the morphologies of SIS and SBS, examined the effects of three factors on TPE.²²² These factors were the role of composition, block length and block length distribution. These authors found that the stress values and the ultimate strength were dependant upon the polystyrene content and not upon the block length. These authors also found that polymers with 40% polystyrene content exhibited a yield point

²²¹ Iekeda, R.M., M.L. Wallach, and R.J. Angelo. "Multiple Glass Transitions of Block Copolymers. II Differential Scanning Calorimetry of Styrene-Diene Block Copolymers." In *Block Copolymers*, edited by S.L. Aggarwal, 43. New York: Plenum Press, 1970.

²²² Morton, M., J.E. McGrath, and P.C. Juliano. "Structure-Property Relationships for Styrene-Diene Thermoplastic Elastomers." *J. Polym. Sci.* **1969**, 26, 99.

that is irreversible below the glass transition temperature of the polymer. The morphology was found to consist of a semicontinuous polystyrene domain. These authors also examined the morphology of the block copolymers and found the polystyrene domain size was approximately 300 to 400 angstroms for a SBS block copolymer with block lengths of 13,000 for the polystyrene block and 80,000 for the butadiene block. The morphology of both diblock and ABA triblock copolymers is a function of the percent composition of the various blocks. At low percentages of A, the polymer morphology consists of spheres of A suspended in a matrix of B. As the percentage of A increases the polymer morphology proceeds from spheres of A suspended in a matrix of B to cylinders of A suspended in matrix of B to lamellae of A and B. As the percentage of A increases, a phase inversion occurs, this phase inversion results in A being the continuous matrix and B taking the form of either a cylinder or a sphere. The boundary between the two phases is not a sharp division that occurs between the phases. Instead, there is a degree of overlap between the two phases. An examination of the role of polymer structure on the morphology of the boundary has been performed.²²³ The synthesis of block copolymers with graded regions of the polymer chain, where at the end of the A block and beginning of the B block there is a region where both monomers are copolymerized. The presence of graded regions results in the formation of a more diffuse boundary in the solid state. The role of processing can also affect the resulting polymer morphology. It has been found that annealing a SBS the polystyrene domains become smaller and closer together.²²⁴ For SBS systems with a higher weight percentage of styrene, approximately 25 wt%, the extrusion of the TPE will result in the formation of anisotropy. At this weight percent, the typical morphology found for SBS is cylinders of polystyrene suspended in a matrix of polybutadiene. When the polymer is extruded, the polystyrene cylinders align with the direction of the polymer flow during the processing. The net result is presence of

²²³ Aggarwal, S.L. "Introduction and Overview." In *Processing, Structure, and Properties of Block Copolymers*, edited by M.J. Folkes, 1. New York: Elsevier Applied Science Publishers, 1985.

²²⁴ Harpell, G.A., and C.E. Wilkes. "Relationship of Morphology to Physical Properties of Styrene-Butadiene Block Copolymers." In *Block Copolymers*, edited by S.L. Aggarwal, 31. New York: Plenum Press, 1970.

continuous polystyrene cylinders along one direction of the processed material with polystyrene layers separated by polybutadiene layers along the perpendicular direction.²²⁵ The anisotropy of the polymeric material results in a different modulus along the different axis of the material, with the higher modulus along the axis with the continuous polystyrene cylinders. When the material is elongated, the material behaves differentially along the two different axis. Extension along the axis with the continuous polystyrene domains resulted in irreversible plastic yielding of the polystyrene domains at low strain values. The yielding was typically found to occur at the center of the cylinder. In contrast, extension along the perpendicular axis results in elastomeric behavior. Phase separation has also been found for graft copolymers, where the size of the grafted block is of sufficient size.²²⁶ Furthermore, there must be a high degree of control of the grafting chemistry for the grafted materials to exhibit properties similar to the properties found in standard TPE.²²⁶

Thermoplastic elastomers containing poly(1,3-cyclohexadiene) have been prepared previously by Natori et al.²²⁷ These polymers were comprised of poly(1,3-cyclohexadiene) and butadiene. The first ABA triblock TPE was synthesized via sequential addition methodology, where the poly(1,3-cyclohexadiene) block was synthesized first, then butadiene block and finally the last poly(1,3-cyclohexadiene) block. The polymers exhibited relatively narrow molecular weight distributions and the polymers exhibited to T_g , indicative of a phase separation. The polymers exhibited a tensile strength at the point of fracture of approximately 10 MPa. The tensile elongation was found to be proportional with the percentage of butadiene present in the

²²⁵ Odell, J. A., and A. Keller. "The Interrelation between Microstructure and Properties of Block Copolymers." In *Processing, Structure, and Properties of Block Copolymers*, edited by M.J. Folkes, 29. New York: Elsevier Applied Science Publishers, 1985.

²²⁶ Campbell, D.S. "Thermoplastic Elastomeric Block Copolymers." In *Developments in Block Copolymers II*, edited by I. Goodman, 203. New York: Elsevier Science Publishers, 1982.

²²⁷ Imaizumi, K., Tomohiro Ono, I. Natori, Shinichi Sakuri, and Kunihiko Takedo. "Microphase-Separated Structure of 1,3-Cyclohexadiene/Butadiene Triblock Copolymers and Its Effect on Mechanical and Thermal Properties." *J. Polym. Sci., Part B: Polym. Phys.* **2001**, 39, 13. Natori, I., K. Imaizumi, H. Yamagishi, and M. Kazunori. "Hydrocarbon Polymers Containing Six-Membered Rings in the Main Chain. Microstructure and Properties of Poly(1,3-cyclohexadiene)." *J. Polym. Sci., Part B: Polym. Phys.* **1998**, 36, 1657.

macromolecule and varied from 450% to 130% at 70% and 50% butadiene, respectively. The authors also utilized a difunctional initiator in the presence of TMEDA to initiate the polymerization of butadiene. Following the polymerization of butadiene, the authors added 1,3-cyclohexadiene and allowed the reaction to proceed for five hours.²²⁸ These polymers exhibited relatively narrow molecular weight distributions (1.26-1.09) with broader distributions occurring with larger percentages of poly(1,3-cyclohexadiene). The authors found that the tensile elongation varied from 3 to 380%, again dependent upon the percentage of butadiene. The authors selectively hydrogenated the butadiene block only, and also hydrogenated the entire polymer. Analysis of the hydrogenated polymer via SEM found the phase separations disappeared upon hydrogenation, however, both SAXS and dynamical mechanical analysis (DMA) indicated that the ABA triblock polymer remained phase separated in the solid phase.

Phase separation can also be found in the solution state, where the solvent has a higher degree of affinity for one block as opposed to the other.²²⁹ The behavior of block copolymers in solution can be represented in an isothermal phase diagram. In phase one the block copolymers is found as a true solution, however, as the concentration of the block copolymer is increased the molecules form micelles. Upon formation of the aggregates in solution, localized order is generated in solution. This localized structure does not extend throughout the solution, it is not until the polymer concentration is increased further that long-range order or periodic structure in solution is formed. At the appropriate concentration the solvated diblock results in the formation of micelles. This situation typically results in the reorganization of the material, forming a core-shell structure with the shell being comprised of the more solvated

²²⁸ Imaizumi, K., Tomohiro Ono, I. Natori, Shinichi Sakuri, and Kunihiko Takedo. "Microphase-Separated Structure of 1,3-Cyclohexadiene/Butadiene Triblock Copolymers and Its Effect on Mechanical and Thermal Properties." *J. Polym. Sci., Part B: Polym. Phys.* **2001**, 39, 13.

²²⁹ Cowie, J.M.G. "Carbon-chain Block Copolymers and their Relationship with Solvents." In *Developments in Block Copolymers I.*, edited by I. Goodman, 1. New York: Elsevier Science Publishers, 1982.

block.²³⁰ The architecture of the macromolecule impacts the resulting polymer morphology. This structure property relationship is evident in the critical micellar concentration (CMC) of polymers with identical monomer compositions but different architectures. The CMC for a block copolymer is three orders of magnitude higher than the CMC of the analogous star-shaped polymer. In these studies, the composition of the arms of the star and the composition of the diblock copolymer were identical.²³¹ This difference is believed to be the result of the decreased combinatorial entropy of the star polymer arms.²³² Star-shaped architectures provide a rich venue for the investigation of the structure-morphology relationship, as the star-shaped macromolecules can exhibit differing morphologies compared to their diblock analogues.²³³ Star-shaped macromolecules are not only effected by the presence of the diblock arms but also by the presence of the core.²³⁴ As the core increases in size relative to the arms, the morphology of the material becomes more dependant upon the core structure. In contrast, some systems exhibit morphologies independent of the architecture, where both the star and block copolymers exhibited the same morphology and lamellar spacing.²³⁵ Nevertheless, star-shaped architectures are unique in that the architecture provides the opportunity to examine the effect of having three or more homopolymers that are coupled together at a single point. Several interesting morphologies have been exhibited by materials containing different homopolymeric arms²³⁶ and arms comprised

²³⁰ Alexandridis, P., and T.A. Hatton. *Colloids Surf., A* **1995**, 96, 1.

²³¹ Voulgaris, D., C. Tsitsilianis, F.J. Esselink, and G. Hadziioannou. "Polystyrene/poly(2-vinyl pyridine) heteroarm star copolymer micelles in toluene: morphology and thermodynamics." *Polymer* **1998**, 39, 6429.

²³² Voulgaris, D., C. Tsitsilianis, F.J. Esselink, and G. Hadziioannou. "Polystyrene/poly(2-vinyl pyridine) heteroarm star copolymer micelles in toluene: morphology and thermodynamics." *Polymer* **1998**, 39, 6429.

²³³ Matsushita, Y., H. Momose, Y. Yoshida, and I. Noda. "Lamellar domain spacing of the ABB graft copolymers." *Polymer* **1997**, 38, 149.

²³⁴ Gorda, K.R., and D.G. Pfeiffer. "Star-Shaped Condensation Polymers: Synthesis, Characterization, and Blend Properties." *J. Polym. Sci.* **1993**, 50, 1977.

²³⁵ Matsushita, Y., Y. Mogi, H. Mukai, and J. Watanabe. "Preparation and the Morphology of Multiblock Copolymers of the (AB)_n Type." *Polymer* **1994**, 35, 246.

²³⁶ Okamoto, S., H. Hasegawa, T. Hashimoto, T. Fujimoto, H. Zhang, H. Takeo, T. Kazama, A. Takano, and Y. Isono. "Morphology of model three-component three-arm star shaped copolymers." *Polymer* **1997**, 38, 5275.

of the same monomer but of different lengths²³⁷ or a combination of both. Some of these morphologies include 3-fold axis of periodicity and an ordered tricontinuous domain. The self-organization of the block copolymers can also be impacted by the presence of a terminal moiety endcapping the outside block. The phase separation of block copolymers can be driven by the presence of a long alkyl group on the end of the hydrophobic block of the block copolymer.²³⁸ Indicating that phase separation can be favored by a large χ value even when the number of repeat units (N) is small, under the condition that the endcapping molecule induces a larger χ value. It has also been found that the addition of a capping group containing a fluorinated methyl group at the end is sufficient to alter the surface aggregation state of a block polymer comprised of poly(styrene-*block*-poly-4-vinylpyridine).²³⁹ In this research, it was found that after annealing, the styrene block preferentially migrated to the surface if the block copolymer was not end capped with perfluorinated methyl containing molecule. However, capping the 4-vinyl pyridine block with the fluorinated methyl group resulted in no change in the surface composition occurring in the sample after annealing. The ability to alter the surface morphology in response to an external stimulus such as heating, as previously mentioned, or the exposure to altered solvent environments provides the opportunity to create smart materials.²⁴⁰ Smart materials are materials which altered their surface morphology in response an external stimulus, such as water exposure.²⁴¹ This reversible response was dependant upon the architecture of the macromolecule, only block copolymers exhibited a reversible response to the water

²³⁷ Zhang, H., Z. Gao, K. Khougaza, and A. Eisenberg. "Solubilization equilibria of water in nonaqueous solutions of block ionomer reverse micelles: an NMR study." *Macromolecules* **1992**, 25, 3002. Iatrou, H, and N. Hadjichristidis. "Synthesis of a model 3-miktoarm star terpolymer." *Macromolecules* **1992**, 25, 4649.

²³⁸ Masamoto, J., K. Yalima, S. Aida, M. Ueda, and S. Nomura. "Microphase separation in polyoxymethylene end-capped with long-chain alkyl groups." *Polymer* **2000**, 41, 7283.

²³⁹ Jiang, Xiquin, K. Tanaka, A. Takahara, and T. Kajiyama. "Effect of chain end group hydrophobicity on surface aggregation structure of poly(styrene-*block*-4-vinylpyridine) symmetric diblock copolymer films." *Polymer* **1998**, 39, 2615.

²⁴⁰ Russel, T.P., T.E. Karis, Gallot Y., and A.M. Mayes. "A Lower Critical Ordering Transition in a Diblock Copolymer Melt." *Nature* **1994**, 368, 729.

²⁴¹ Senshu, K., S. Tamashita, M. Ito, A. Hirao, and S. Nakahama. "Surface Characterization of Hydroxyethyl Methacrylate Styrene Block Copolymers by TEM observation and Contact Anyle Measurement." *Langmuir* **1995**, 11, 2293.

exposure. Random copolymers exhibited an irreversible surface aggregation in response to the hydrophilic environment. These random copolymers, that exhibited the irreversible response, were composed of the same monomer composition as their block copolymer counterparts. The sequential block copolymer synthesized anionically exhibited a reversible surface response.²⁴²

2.7 Monitoring of Polymerization Processes

Historically, the determination of the kinetics of polymerization was determined using careful sampling techniques followed by gravimetric and molecular weight analysis. On the other hand, the polymerization can be sampled and the concentration of residual monomer can be analyzed using gas chromatography or spectroscopic techniques. Unfortunately, many polymerization methodologies are sensitive to trace levels of oxygen, water, or other contaminants. The rigorous requirement of living anionic polymerization methodologies renders these sampling techniques cumbersome.

Nevertheless, a number of methods have been utilized to determine the reaction kinetics of anionic polymerizations. These methods include reaction sampling,²⁴³ dilatometry, stopflow,²⁴⁴ capillary flow, and in-situ spectroscopy.²⁴⁵ In dilatometry the reaction mixture is added to the bulb affixed to a graduated capillary. After the bulb has been charged it is immersed into a constant temperature bath. The polymerization progress is monitored by following the height of column of liquid in the capillary until the polymerization is complete.²⁴⁶ The stopped flow technique consists of an apparatus

²⁴² Senshu, K., S. Tamashita, M. Ito, A. Hirao, and S. Nakahama. "Surface Characterization of Hydroxyethyl Methacrylate Styrene Block Copolymers by TEM observation and Contact Angle Measurement." *Langmuir* **1995**, 11, 2293.

²⁴³ Ding, Jifeng, Colin Price, and Colin Booth. "Use of Crown Ether in the Anionic Polymerization of Propylene Oxide-1 Rate of Polymerization." *Eur. Polym. J.* **1991**, 27, 891.

²⁴⁴ Szwarc, M.. *Carbanions, Living Polymers and Electron Transfer Processes*. Interscience Publishers:New York, 1968.

²⁴⁵ Long, T.E., H.Y. Lui, D.M. Schell, D.M. Teegarden, and D.S. Uerz. "Determination of Solution Polymerization Kinetics by Near-Infrared Spectroscopy. 1. Living Anionic Polymerization Process." *Macromolecules* **1993**, 26, 6237.

²⁴⁶ Ding, Jifeng, Colin Price, and Colin Booth. "Use of Crown Ether in the Anionic Polymerization of Propylene Oxide-1 Rate of Polymerization." *Eur. Polym. J.* **1991**, 27, 891.

with two reservoirs, a mixing chamber, and a capillary that is contained in a spectrophotometer. The sample is ejected from the reservoirs and flows into the mixing chamber. After the reagents have been mixed in the mixing chamber and the reaction initiated the reaction solution flows into the capillary. The length of the capillary from the mixing chamber to the spectrophotometer dictates the length of time the reaction proceeds prior to data sampling. Thus obtainment of a series of time points requires a large number of experiments as the length of the capillary must be altered for each time point. Furthermore, application of this methodology requires meticulously clean reaction conditions with a complex equipment setup.

Recently, Long and coworkers described the utility of *in situ* near-infrared spectroscopy in the analysis of the well-defined living anionic polymerization of styrene and isoprene. These studies were performed using various organic solvents and at various polymerization conditions. *In situ* infrared spectroscopy is a state-of-the-art, real-time, monitoring technique well suited to obtain real-time structural and kinetic information about polymerization processes. Advantages of *in situ* reaction monitoring include evaluating reaction variables for the determination of reaction performance and optimization of reaction conditions, analyzing reactions that use hazardous or air-sensitive reagents, and elimination of experimental uncertainties associated with reactor sampling. Furthermore, *in situ* monitoring facilitates monitoring instantaneous changes in reactants, intermediates, and products, essentially allowing one to “watch” a reaction as it proceeds. This allows for the facile tracking of reaction trends, concentration changes, reaction end-points, and percent conversions for a wide range of reactions. Kinetic information can easily be obtained and evaluated from the concentration monitoring of key reaction components. Deleterious side reactions can be followed and evaluated without the use of invasive sampling techniques. In addition, the time normally required to acquire analytical results is minimized and the data is more comprehensive (*i.e.* more data points). All of the information of a reaction obtained by *in situ* monitoring can be combined and evaluated to provide an in-depth understanding of reaction pathways.

In situ spectroscopy was previously utilized to explore the reaction kinetics of the living anionic polymerization of a mixed monomer system, i.e. styrene and para-substituted styrenes (where $R = \text{Si}(\text{CH}_3)_2\text{C}(\text{CH}_3)_3$), in a polar solvent. Despite the insertion of the near-infrared probe, the living nature of the anionic propagating intermediate was not affected as evidenced by the preservation of a narrow molecular weight distribution and predictable molecular weight (as determined using GPC). First-order polymerization kinetics were determined for the homopolymerization of each monomer and the kinetics agreed well with many of the earlier comprehensive studies using more complicated analyses. A typical plot of absorbance versus time is shown in Figure 2-17.

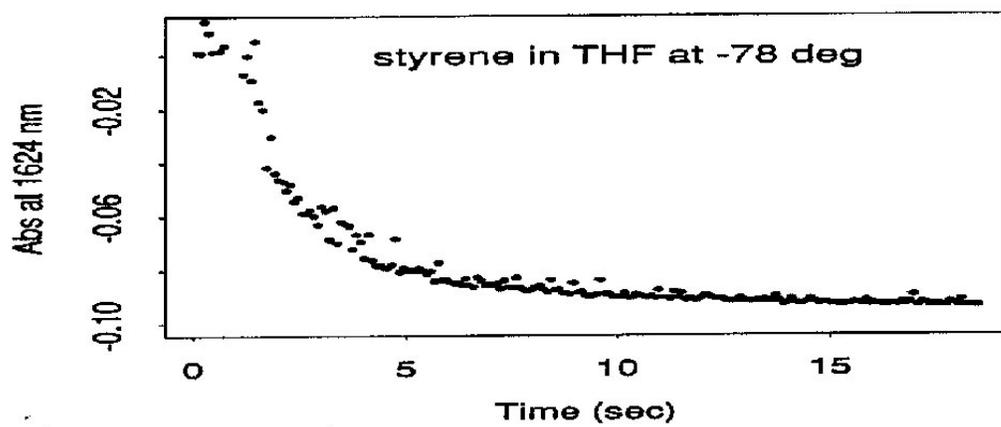


Figure 2-18 Absorbance at 1624 nm (NIR) vs. time for a styrene polymerization in THF at -78°C .

CHAPTER 3

Determination of the Regiochemistry of Poly(1,3-cyclohexadiene) via Endgroup Functionalization

Taken From:

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3.1 Abstract

The regiochemical and stereochemical characterization of both 6000 and 9980 trimethylsilyl end-capped poly(1,3-cyclohexadiene)s are reported. ^1H NMR and ^{29}Si NMR spectra were utilized to determine the percentage of 1,2- and 1,4-addition in poly(1,3-cyclohexadiene). ^1H NMR spectral analysis using the olefinic and allylic regions indicated that the 6000 polymer backbone contained 70% 1,2-addition and 30% 1,4-addition. Similar analysis for the 9980 homopolymer backbone indicated 76% 1,2- and 24% 1,4-addition. Two different poly(1,3-cyclohexadiene) polymers containing either 70% 1,2-addition or 90% 1,4-addition were synthesized. Juxtaposition of the ^{13}C NMR spectra of these polymers was performed and the resonances associated with 1,2-addition or 1,4-addition were determined. The ^{13}C NMR analysis indicated that these polymers contained 26% 1,2-addition or 10% 1,2-addition, in good agreement with the values measured using ^1H NMR spectroscopy. In addition, analysis of the trimethylsilyl (TMS) endgroup of the 6000 homopolymer via ^1H NMR and ^{29}Si NMR indicated that the chain end regiochemistry was 76% 1,2- and 24% 1,4-addition. It was proposed, based on ^1H NMR spectral analysis of the trimethylsilyl endgroup, that the 6000 homopolymer contained 6% trans and 18% cis-1,4 units at the chain end. For the range

of molecular weights studied, the regiochemistry was determined to be independent of the poly(1,3-cyclohexadiene) molecular weight.

3.2 Introduction

The polymerization of cyclic dienes, such as 1,3-cyclohexadiene, received minor attention during the late 1970's,²⁴⁷ but interest dwindled due to a number of deleterious side reactions that limited the attainable molecular weights.²⁴⁸ In 1997, Natori reported the first example of a living anionic polymerization of 1,3-cyclohexadiene.²⁴⁹ The polymerization was reported to proceed in a living fashion in the presence of the additive tetramethylethylenediamine (TMEDA) with the initiator n-butyllithium (nBuLi). The regiochemistry was determined using ¹H NMR at elevated temperatures (160 °C) in dichlorobenzene.²⁵⁰ The homopolymer was reported to contain approximately 50% 1,2 and 50% 1,4 repeating units. More recent studies have reported the regiochemistry to be approximately 70% 1,2-addition and 30% 1,4-addition.²⁵¹ The degree of 1,2-addition versus 1,4-addition is a critical factor that dictates the mechanical

²⁴⁷ Gin, D. L., V. P. Conticello, and R.H. Grubbs. "Heteroatom-Functionalized Cyclohexadienes: Stereoregular Transition-Metal-Catalyzed Polymerization of Precursor to Poly(p-phenylene)." *J. Am. Chem. Soc.* **1992**, 114, 3167. Sharaby, Z., M. Martan, and J. Jagur-Grodzinski. "Stereochemistry of Poly(1,3-cyclohexadienes). NMR Investigation of Effects Due to the Solvent Medium and to the Mechanism of Polymerization." *Macromolecules* **1982**, 15, 1167. Sharaby, Z., J. Jagur-Grodzinski, M. Martan, and D. Vofsi. "Kinetics and Mechanism of the Anionic Polymerization of Cyclohexadienes Initiated by Naphthalene Radical Anions and Dianions." *J. Polym. Sci., Polym. Chem. Ed.* **1982**, 20, 901. Mango, L.A., and R.W. Lenz. "Organometallic reactions which control molecular weight in the anionic polymerization of 1,3-cyclohexadiene." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **1971**, 12, 402. Mango, L.A., and R.W. Lenz. "Mechanism and stereochemistry in the anionic polymerization of 1,3-cyclohexadiene and the diimide hydrogenation of polymers." *U.S. Nat. Tech. Inform. Serv.* **1972**, 12, 402.

²⁴⁸ Francois, B., and X. Zhong. "Kinetics of 1,3-cyclohexadiene polymerization initiated by organolithium compounds in a non-polar medium." *Makromol. Chem.* **1990**, 191, 2743. Zhong, X., and B. Francois. "Kinetics of 1,3-cyclohexadiene polymerization by organolithium compounds in a non-polar medium. 1." *Makromol Chem* **1990**, 191, 2735.

²⁴⁹ Natori, I. "Synthesis of Polymers with an Alicyclic Structure in the Main Chain. Living Anionic Polymerization of 1,3-Cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System." *Macromolecules* **1997**, 30, 3696.

²⁵⁰ Natori, I., and S. Inoue. "Living Anionic Polymerization of 1,3-cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System. Copolymerization and Block Copolymerization with Styrene, Butadiene, and Isoprene." *Macromolecules* **1998**, 31, 982.

²⁵¹ Williamson, D.T., J.F. Elman, P.H. Madison, A.J. Pasquale, and T.E. Long. "Synthesis and Characterization of Poly(1,3-cyclohexadiene) Homopolymers and Star-shaped Polymers." *Macromolecules* **2001**, 34, 2108.

and thermal properties of diene based polymers.²⁵² Typically, poly(dienes) containing high degrees of 1,2-addition exhibit higher glass transition temperatures and higher moduli, as compared to polymers containing high degrees of 1,4-addition.

In a more recent study, Mays et al. described the synthesis of poly(1,3-cyclohexadiene) homopolymers with a variety of different additives²⁵³ in addition to the TMEDA/nBuLi initiator adduct studied by Natori and coworkers. The bidentate additive dimethoxyethane (DME) and 1,4-diazobicyclooctadiene (DABCO) were determined to be similarly effective in the controlled polymerization of 1,3-cyclohexadiene. However, the effect of the ratio of these additives to alkyllithium was not studied and a wide range of ratios were utilized. Furthermore, the broadening of the molecular weight distribution (1.34) at higher molecular weights indicated the polymerization control decreased as higher molecular weights were targeted (46000).

In light of conflicting results and the critical role of 1,2-addition versus 1,4-addition on polymer properties, poly(1,3-cyclohexadiene) homopolymers were prepared in the presence of the ligating agent TMEDA and the initiator nBuLi at 40 °C. The regiochemistry and chain isomerization of the resulting polymers were determined via complementary NMR techniques. The living nature of the 1,3-cyclohexadiene polymerization also ensured a novel quantitative endcapping reaction with chlorotrimethylsilane (TMSCl). Thus, a terminal spectroscopic tag suitable for ¹H, ¹³C, and ²⁹Si NMR studies was quantitatively introduced. These endgroup studies were also corroborated with ¹H NMR studies examining the regiochemistry of the polymer repeating unit.

²⁵² Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996.

²⁵³ Hong, K., J.W. Mays, Y. Wang, and R. Advincula. "Synthesis and Aromatization of Polycyclohexadiene(PCHD) Homo and Block Copolymers: Towards Processible Poly-p-Phenylene (PPP) Derivatives." *PMSE Preprints* **1999**, 80, 116.

3.3 Experimental Section

Materials. 1,3-Cyclohexadiene (Aldrich) was degassed several times and vacuum distilled (0.13-0.16 mmHg, 10 °C) from dibutylmagnesium (DBM). n-Butyllithium (FMC Corporation Lithium Division, 1.35 M in n-hexane) was used without further purification. TMEDA (Aldrich) and Chlorotrimethylsilane (Aldrich 98%) were vacuum distilled (0.13-0.16 mmHg, 10 °C) from calcium hydride and stored under nitrogen at – 25 °C. DABCO (Aldrich, 98%) was sublimed under reduced pressure (0.13 - 0.16 mmHg, 25 °C) three times and diluted into cyclohexane. Cyclohexane was stirred over sulfuric acid (10:1 cyclohexane:sulfuric acid) for 7-10 days, decanted, and distilled from a sodium dispersion under nitrogen immediately prior to use. All reagents were transferred using syringe and cannula techniques under ultrapure (99.999%) nitrogen.

Polymer Synthesis. A 100 mL round-bottomed flask containing anhydrous cyclohexane (60 mL, 0.54 mol), 1,3-cyclohexadiene (5.95 mL, 62.4 mmol), and TMEDA (0.094 mL, 0.625 mmol) was heated to 40 °C. The initiator nBuLi (0.31 mL, 0.5 mmol) was added by syringe and the solution was heated at 40 °C for 25 minutes. Upon completion of the 1,3-cyclohexadiene polymerization, excess chlorotrimethylsilane (0.5 mL, 2.5 mmol) was added by syringe to ensure quantitative capping of the living polymer chain ends with trimethylsilyl (TMS) endgroups. The resulting endcapped polymer was precipitated into isopropanol (600 mL), filtered, and dried at 50 °C in vacuo for 12-18 hours. Precipitation ensured complete removal of excess TMSCl and hydrolyzed products, and ¹H and ²⁹Si NMR confirmed the absence of appreciable TMSCl. An antioxidant such as Irganox 1010 (0.10 weight % compared to the polymer) was added to the precipitation solvent to retard oxidative degradation during subsequent storage. In order to control the product molecular weight, both TMEDA and nBuLi concentrations were varied. However, the ratio of TMEDA/nBuLi was maintained at 5/4 and the monomer concentration was maintained at 10 wt%.

Polymer Characterization. Molecular weights were determined using size exclusion chromatography (SEC) with a Waters Alliance SEC system equipped with a Viscotek

150R viscosity detector. SEC measurements were performed at 25 °C in chloroform at a flow rate of 1.0 mL/min. The determination of molecular weights using universal calibration based on polystyrene standards is well established.²⁵⁴ In addition, a Waters 717plus equipped with a Waters 2410 refractive index detector and a Wyatt Technology Minidawn MALLS detector was utilized for absolute molecular weight measurements. The dn/dc values were determined on-line using the calibration constant for the RI detector and the mass of the polymer sample. SEC measurements were performed at 40 °C in chloroform at a flow rate of 1.0 mL/min. For all samples, it was assumed that 100% of the polymer eluted from the column during the measurement.

NMR Measurements. ¹H and ¹³C NMR high resolution NMR spectra were obtained at 400 and 100 MHz, respectively, using a Varian NMR spectrometer equipped with a 10 mm and 5 mm broad band probe and standard pulse decoupling. ¹H NMR samples were referenced to the residual signal of the deuterated solvent. The samples were dissolved in dichlorobenzene and chromium(III) acetylacetonate was added to reduce the relaxation time for the ¹³C and ²⁹Si NMR studies. The ¹³C and ²⁹Si spectra were obtained at 80 °C using an inverse gated, double filtered, broadband decoupling sequence. Our earlier studies involving the oxidation of poly(1,3-cyclohexadiene)s demonstrated that oxidative degradation did not occur under these conditions.²⁵⁵ The error associated with the NMR measurements was determined as outlined earlier.²⁵⁶

3.4 Results and Discussion

The trimethylsilyl terminated poly(1,3-cyclohexadiene)s were synthesized as depicted in Scheme 3-1. In order to examine the effect of chain length on the regiochemistry, TMS endcapped poly(1,3-cyclohexadiene) homopolymers were

²⁵⁴ Yau, W.W., and S.W. Rementer. "Polymer Characterization by SEC-Viscometry: Molecular Weight, Size, and Intrinsic Viscosity Distribution." *J. Chromatogr.* **1990**, 13, 627.

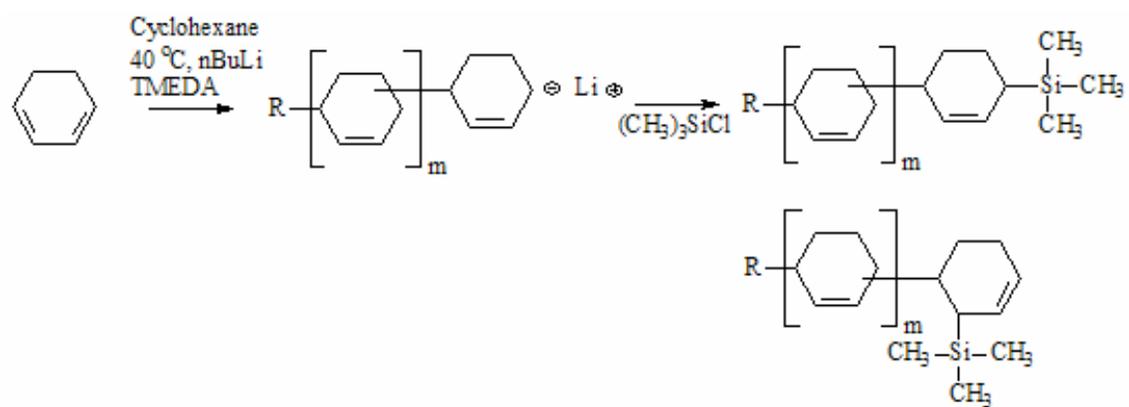
²⁵⁵ Williamson, D.T., K. Brazhnik, A.J. Pasquale, and T.E. Long. "Synthesis and Characterization of Hydrogenated Poly(1,3-cyclohexadiene) Star-Shaped Polymers." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **2000**, 41, 1544.

²⁵⁶ Popov, A. I., and K. Hallenga, eds. *Modern NMR Techniques and Their Application in Chemistry, Practical Spectroscopy Series* Marcel Dekker: New York, 1991.

synthesized with calculated number average molecular weights of 10000 and 5000. The resulting polymers exhibited narrow molecular weight distributions ($M_w/M_n = 1.01-1.06$) and controlled number average molecular weights (9980 and 6000 respectively). In addition, the number average molecular weight, as determined via ^1H NMR analysis of the trimethylsilyl endgroup, agreed well (6200) with the GPC value (6000). This indicated quantitative endcapping and the absence of significant protonation via acidic impurities in the chlorosilane reagent. The polymers were spectroscopically characterized using both the polymer repeating unit and the TMS endgroup. Two different ^1H NMR methods were utilized to determine the polymer regiochemistry.

The first method (Method A) compared the olefinic integration with the allylic integration, and the second method (Method B) compared the allylic integration with the aliphatic integration. Both of the methods have been widely employed throughout the literature.²⁵⁷ These assignments are based on a previous study by Natori et al., which

²⁵⁷ Natori, I., and S. Inoue. "Living Anionic Polymerization of 1,3-cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System. Copolymerization and Block Copolymerization with Styrene, Butadiene, and Isoprene." *Macromolecules* **1998**, 31, 982. Natori, I., and S. Inoue. "Anionic Polymerization of 1,3-cyclohexadiene with Alkylolithium/Amine Systems. Characteristics of n-Butyllithium/N,N,N',N'-Tetramethylethylenediamine System for Living Anionic Polymerization." *Macromolecules* **1998**, 31, 4687. Natori, I., K. Imaizumi, H. Yamagish, and M. Kazunori. "Hydrocarbon Polymers Containing Six-Membered Rings in the Main Chain. Microstructure and Properties of Poly(1,3-cyclohexadiene)." *J. Polym. Sci., Part B: Polym. Phys.* **1998**, 36, 1657. Hong, K., and J.W. Mays. "1,3-Cyclohexadiene Polymers. 1. Anionic Polymerization." *Macromolecules* **2001**, 34, 782. Williamson, D.T., J.F. Elman, P.H. Madison, A.J. Pasquale, and T.E. Long. "Synthesis and Characterization of Poly(1,3-cyclohexadiene) Homopolymers and Star-shaped Polymers." *Macromolecules* **2001**, 34, 2108.



Scheme 3-1. Synthetic methodology for the preparation of trimethylsilyl terminated poly(1,3-cyclohexadiene) homopolymers.

describes the deconvolution of the allylic from the aliphatic region at 1.8 ppm.²⁵⁸ The approximation of the chemical shift by deconvolution was determined using 2D-NMR spectroscopy.²⁵⁹ The following set of linear equations was utilized to determine the regiochemistry using method A, which compares the allylic integration with the olefin integration (Equation 3-1).

$$\begin{aligned} \text{Equation 3-1. } \text{Area}_{\text{olefinic}} &= 2x+2y & x &= \text{relative amount of 1,2-addition} \\ \text{Area}_{\text{allylic}} &= 3x+2y & y &= \text{relative amount of 1,4-addition} \end{aligned}$$

Using method A, the percentage of 1,2 versus 1,4 was reproducibly determined to be 70% 1,2 and 30% 1,4 for the 9980 homopolymer and 76% 1,2 and 24% 1,4 for the 6000 homopolymer (Figure 3-1). Method B, which utilizes the aliphatic and allylic proton integrations, was also used to determine the regiochemistry of poly(1,3-cyclohexadiene) homopolymers. Characterization of the homopolymer using method B to determine the regiochemistry resulted in 52% 1,2-addition and 48% 1,4-addition. These values agreed well with previous literature references.²⁶⁰

²⁵⁸ Natori, I., and S. Inoue. "Anionic Polymerization of 1,3-cyclohexadiene with Alkylolithium/Amine Systems. Characteristics of n-Butyllithium/N,N,N',N'-Tetramethylethylenediamine System for Living Anionic Polymerization." *Macromolecules* **1998**, 31, 4687.

²⁵⁹ Natori, I., and S. Inoue. "Living Anionic Polymerization of 1,3-cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System. Copolymerization and Block Copolymerization with Styrene, Butadiene, and Isoprene." *Macromolecules* **1998**, 31, 982.

²⁶⁰ Natori, I., and S. Inoue. "Living Anionic Polymerization of 1,3-cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System. Copolymerization and Block Copolymerization with Styrene, Butadiene, and Isoprene." *Macromolecules* **1998**, 31, 982. Natori, I., and S. Inoue. "Anionic Polymerization of 1,3-cyclohexadiene with Alkylolithium/Amine Systems. Characteristics of n-Butyllithium/N,N,N',N'-Tetramethylethylenediamine System for Living Anionic Polymerization." *Macromolecules* **1998**, 31, 4687. Natori, I., K. Imaizumi, H. Yamagish, and M. Kazunori. "Hydrocarbon Polymers Containing Six-Membered Rings in the Main Chain. Microstructure and Properties of Poly(1,3-cyclohexadiene)." *J. Polym. Sci., Part B: Polym. Phys.* **1998**, 36, 1657. Hong, K., J.W. Mays, Y. Wang, and R. Advincula. "Synthesis and Aromatization of Polycyclohexadiene(PCHD) Homo and Block Copolymers: Towards Processible Poly-p-Phenylene (PPP) Derivatives." *PMSE Preprints* **1999**, 80, 116. Hong, K., and J.W. Mays. "1,3-Cyclohexadiene Polymers. 1. Anionic Polymerization." *Macromolecules* **2001**, 34, 782.

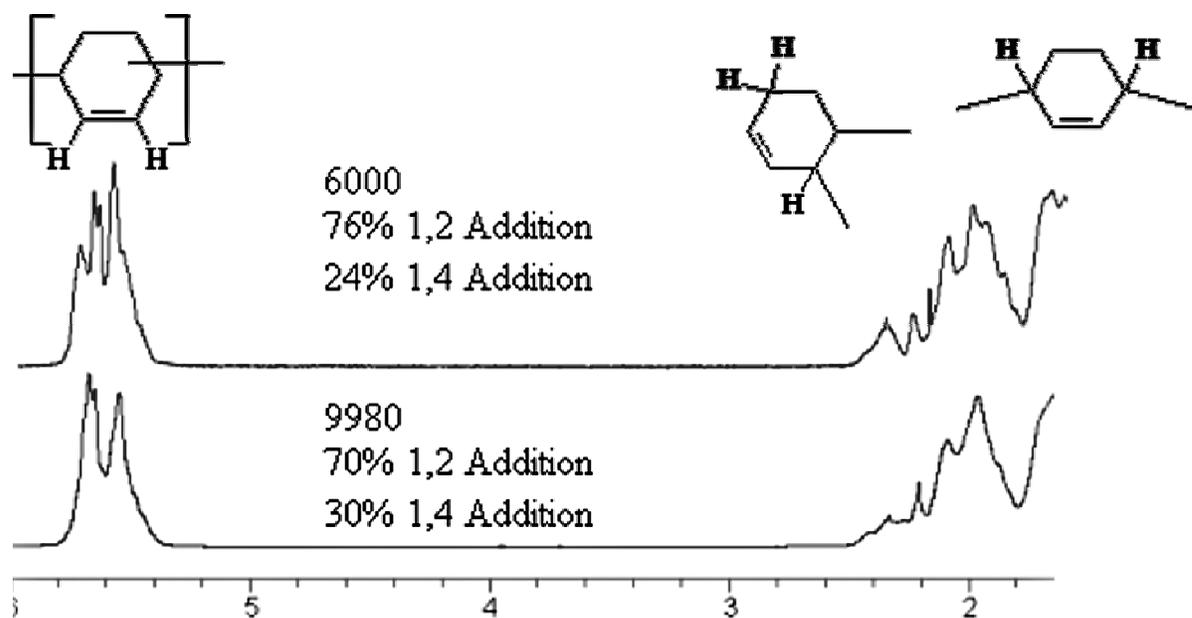


Figure 3-1. ^1H NMR spectra of the 9980 (bottom spectrum) and the 6000 (top spectrum) homopolymer. Regiochemistry was determined by comparing the integration of the allylic region (1.8-2.4) with the olefinic integration (5.4-5.8 ppm).

The lack of agreement between these two apparently complementary methods has resulted in some confusion in determining the correct regiochemistry of poly(1,3-cyclohexadiene). Previous studies have reported that the presence of cyclohexane or cyclohexadiene rings in the polymer backbone will render method B inaccurate.²⁶¹ The presence of chain transfer and chain termination were proposed to provide a potential avenue for both hydrogenation or dehydrogenation reactions. However, the excellent agreement between the molecular weight determined by GPC and the theoretical molecular weight based on the ratio of grams of monomer to moles of initiator in combination with the narrow molecular weight distribution determined by GPC suggests that these side reactions were not significant. Furthermore, the narrow molecular weight distribution indicates any branching reactions that occurred were minimized. Previous studies have demonstrated that ¹³C NMR spectroscopy is the preferred method for the characterization of polyisoprene and polybutadiene microstructure.²⁶² Typically, ¹³C NMR will observe the specific resonances for each type of microstructure and also show splitting that occurs due to sequence distribution. Unfortunately, the rich range of stereochemistries present in poly(1,3-cyclohexadiene) renders the ¹³C NMR spectrum extremely complex. For example, a variety of tacticities are present in poly(1,3-cyclohexadiene), which include erythro diisotactic, threo diisotactic, disyndiotactic, and isosyndiotactic. Previous studies examining the tacticity of a poly(1,3-cyclohexadiene) sample prepared using nBuLi in the absence of additives demonstrated four allylic carbon signals at 40.65, 39.81, 39.52, and 39.18 ppm.²⁶³ However, the authors did not conclusively identify all the resonances and only suggested assignments were made.

²⁶¹ Sharaby, Z., M. Martan, and J. Jagur-Grodzinski. "Stereochemistry of Poly(1,3-cyclohexadienes). NMR Investigation of Effects Due to the Solvent Medium and to the Mechanism of Polymerization." *Macromolecules* **1982**, 15, 1167.

²⁶² Van der Velden, G, C Didden, T Veermans, and J. Beulen. "A new method for the microstructure determination of polybutadiene with cis-1,4, trans-1,4, and vinyl-1,2 units by carbon-13 NMR." *Macromolecules* **1987**, 20, 1252.

²⁶³ Sharaby, Z., M. Martan, and J. Jagur-Grodzinski. "Stereochemistry of Poly(1,3-cyclohexadienes). NMR Investigation of Effects Due to the Solvent Medium and to the Mechanism of Polymerization." *Macromolecules* **1982**, 15, 1167.

A limitation in all the previous attempts to determine the regiochemistry of poly(1,3-cyclohexadiene) was the inability to controllably synthesize polymers with varying microstructures. As a result, only poly(1,3-cyclohexadiene) polymers containing a high percentage of 1,4-addition were studied. However, recent advances in our laboratories in combination with the advances by both Mays et al. and Natori et al. have provided viable synthetic routes for the controlled synthesis of poly(1,3-cyclohexadiene) containing either a high 1,4-microstructure or a high 1,2-microstructure. Therefore, two different poly(1,3-cyclohexadiene) polymers that contained either 90% 1,4-addition or 70% 1,2-addition were synthesized. A narrow molecular weight distribution of 1.06-1.03 in combination with the excellent agreement between the GPC molecular weight (5350 and 5290) and the calculated molecular weight based on the grams of monomer to moles of initiator (5000) indicated that the polymerization was controlled. The livingness of the polymerization ensured the absence of chain transfer or chain termination reactions and any subsequent reactions during the polymerization. The elimination of these side reactions reduced the complexity of the ^{13}C NMR analysis by preventing the introduction of cyclohexane or cyclohexadiene repeat units into the polymer backbone.

The ^{13}C NMR spectra for polymers containing 90% 1,4-addition and 70% 1,2-addition is shown in Figure 3-2. The signals in the allylic region were examined because these carbons were expected to be the most sensitive to microstructural variations and aliphatic contaminants, such as cyclohexane, would not complicate the analysis. The ^{13}C NMR spectra for these polymers were juxtaposed and the resonances were assigned as belonging to either a 1,2-microstructure or a 1,4-microstructure as follows. Signals present in the PCHD9014 sample were assumed to belong to a 1,4-microstructure if that signal was not present in the PCHD7012 sample. Similarly, signals present in the PCHD7012 sample were assumed to belong to a 1,2-microstructure if that signal was not observed in the PCHD9014 sample. If the signal was found in both spectra, then it was assigned as undetermined and both 1,2 and 1,4-microstructures were assigned. The chemical shifts and the assigned microstructures for PCHD7012 and PCHD9014 are outlined in Table 3-1 and Table 3-2, respectively. Using these assigned resonances and their integrations, the degree of 1,4-addition was determined to be 88% 1,4-addition and 12% 1,2-addition for PCHD9014, which agrees well with the methods used to determine the microstructure using ^1H NMR (90% 1,4-addition). For the 70% 1,2-microstructure containing polymer (PCHD7012), the percentage of 1,2-addition was determined to be 74% 1,2-addition and 26% 1,4-addition. Due to the spectral complexity, no attempts were made to further describe the resonances beyond the assignment of 1,2 or 1,4-addition.

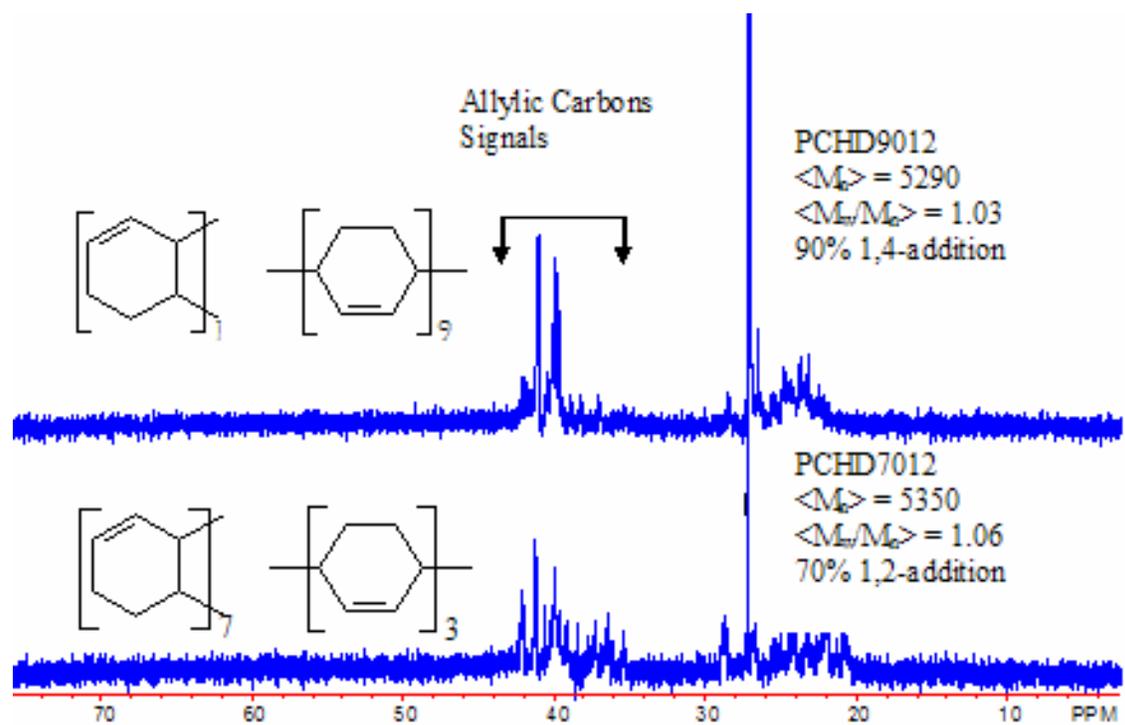


Figure 3-2. ^{13}C NMR spectra of poly(1,3-cyclohexadiene) polymers containing either 70% 1,2-addition (PCHD7012) or 90% 1,4-addition (PCHD9014).

Table 3-1. ¹³CNMR Resonance Assignments for a high 1,2-microstructure containing polymer (PCHD7012).

Signal (ppm)	Assigned Microstructure	Integration
42.2	1,2-addition	2.64
42.0	1,4-addition	2.97
41.2	1,2-addition	5.0
40.6	1,2-addition	1.74
39.9	1,2-addition	2.90
39.86	1,4-addition	2.90
39.5	1,4-addition	4.13
39.1	1,2-addition	4.5
38.4	1,2-addition	1.93
37.3	1,2-addition	3.52
36.4	1,2-addition	4.34
35.4	1,2-addition	2.86

Table 3-2. ¹³CNMR Resonance Assignments for a 1,4-microstructure containing polymer (PCHD9014).

Signal (ppm)	Assigned Microstructure	Integration
41.9	1,4-addition	1.17
41.7	1,4-addition	0.71
41.5	1,4-addition	0.71
40.9	1,4-addition	10.0
40.4	1,4-addition	1.53
40.1	1,4-addition	3.29
39.9	1,4-addition	7.01
39.6	1,4-addition	3.87
38.9	1,4-addition	2.03
38.4	1,2-addition	1.25
36.9	1,2-addition	1.66
35.3	1,2-addition	1.49

In order to ascertain the correct regiochemistry, a trimethylsilyl endgroup was introduced as a spectroscopic tag for both ^1H and quantitative ^{29}Si NMR spectroscopic studies. The NMR endgroups were used to determine the regiochemical and stereochemical structure of the polymer chain end. Due to the reactivity difference between addition of the living poly(1,3-cyclohexadienyllithium) anion to 1,3-cyclohexadiene versus chlorotrimethylsilane, the regiochemistry adjacent to the trimethylsilyl endgroup does not necessarily need to agree with the regiochemistry of the repeating unit. ^1H NMR spectral analysis of the TMS endgroups on the 9980 polymer (Figure 3-3) indicated a ratio of 73% 1,2-addition and 27% 1,4-addition. A similar ^1H NMR spectral analysis of the 6000 polymer (Figure 3-3) resulted in a ratio of 76% 1,2-addition and 24% 1,4-addition. The TMS groups resulting from 1,4-addition are expected to be in a less shielded environment and occur further downfield of the shielded TMS groups arising from a 1,2-addition. The cis-1,4 TMS peak from 0.018 to 0.003 ppm and the trans-1,4 TMS peak at 0.031 to 0.019 ppm were assigned (Figure 3-3). Based on these assignments, the 6000 polymer was proposed to contain 6% trans and 18% cis-1,4 units. In order to further support the ^1H NMR spectroscopy determined 1,2-addition versus 1,4-addition ratio, the silicon methyl chain ends were also characterized using ^{29}Si NMR (Figure 3-4). Analysis of the ^{29}Si NMR spectrum indicated a ratio of 76% 1,2-addition and 24% 1,4-addition. These values, determined by examining the TMS end-groups, corroborated with the percentage of 1,2- versus 1,4-addition as determined by the examination of the ratio of the allylic and olefinic peaks in the ^1H NMR spectrum.

The excellent agreement between regiochemistry of the polymer backbone determined using both ^1H NMR and ^{13}C NMR spectroscopic methods with the silicon chain ends suggested that the reactivity of the polymer chain end towards the monomer and the end-capping reagent was similar. Furthermore, these complimentary spectroscopic techniques suggested that the regiochemistry of poly(1,3-cyclohexadiene) as prepared using TMEDA was 76% 1,2-addition and 24% 1,4-addition. The regiochemistry of the polymer prepared using DABCO was 88% 1,4-addition and 12% 1,2-addition.

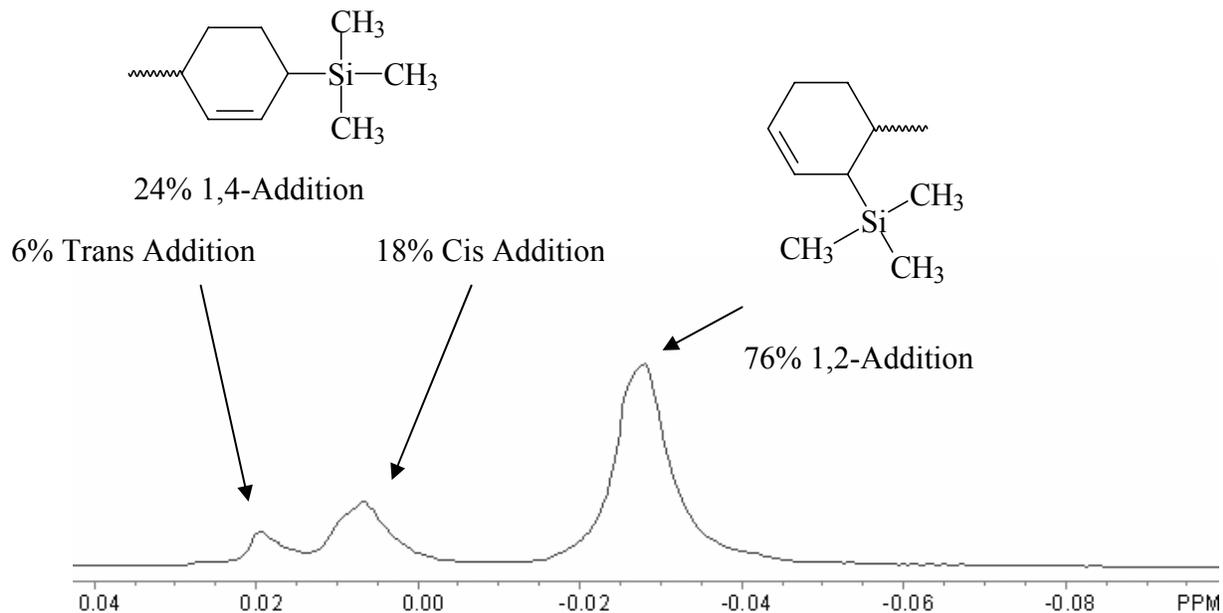


Figure 3-3. ^1H NMR spectra of the trimethylsilyl endgroup on the 6000 homopolymer indicating the presence of 24% 1,4-addition and 76% 1,2-addition. Polymer was synthesized with a TMEDA/nBuLi ratio of 5:4.

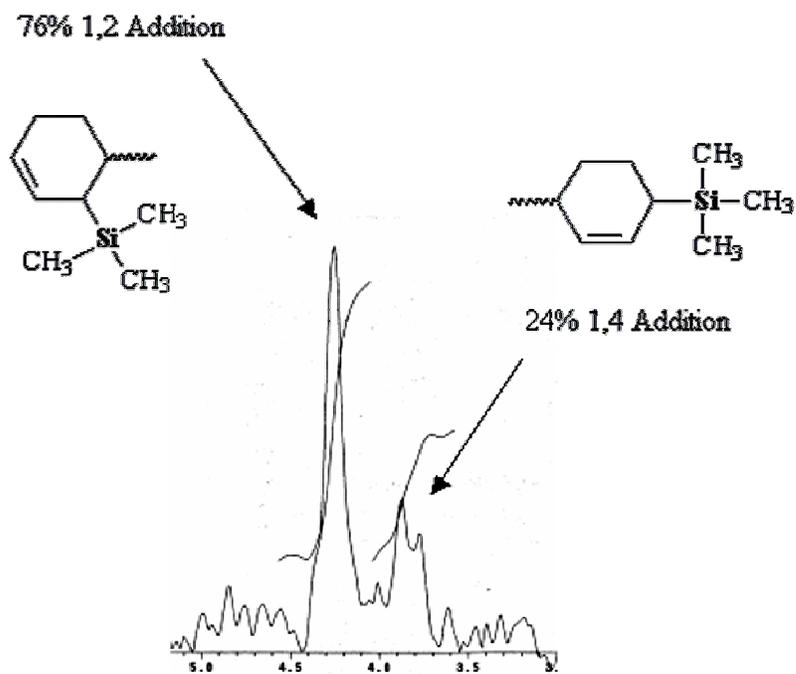


Figure 3-4. ^{29}Si NMR spectrum of the 6000 homopolymer indicating the presence of 24% 1,4-addition and 76% 1,2-addition. Polymer was synthesized with a TMEDA/nBuLi ratio of 5:4.

3.5 Conclusions

The regiochemistry of poly(1,3-cyclohexadiene) was examined through endgroup functionalization with chlorotrimethylsilane. The endgroup studies were compared with a more conventional study of the backbone of the polymer chain. The polymer backbone contained 70% 1,2-addition and 30% 1,4-addition. The regiochemistry of the 6000 trimethylsilyl endcapped chain ends were examined via both ^1H and ^{29}Si NMR spectroscopy. Using endgroup analysis, the homopolymer was found to exhibit 76% 1,2-addition and 24% 1,4-addition. The ratio of the cis versus trans was determined upon ^1H NMR examination of the TMS endgroups and found to be 6% trans and 18% cis of the total 24% 1,4-addition. In addition, these studies demonstrate that comparing the allylic to the aliphatic peaks to determine the polymer regiochemistry leads to erroneous results. Studies examining the nature of the difference between the two apparently complementary methods are currently being performed. This is the first reported determination of the cis versus trans ratio for the polymerization of 1,3-cyclohexadiene and the first reported use of an endcapping approach to study the regiochemistry of the cyclohexene containing poly(1,3-cyclohexadiene) backbone. These complimentary methods represent a significant improvement over the previously reported methods used to study the regiochemistry of poly(1,3-cyclohexadiene).

CHAPTER 4

Synthesis and Characterization of Poly(1,3-Cyclohexadiene) Homopolymers and Star-shaped Polymers

Taken From:

Williamson, D.T., J.F. Elman, P.H. Madison, A.J. Pasquale, T.E. Long. "Synthesis and Characterization of Poly(1,3-Cyclohexadiene) Homopolymers and Star-shaped Polymers" *Macromolecules* **2001**, *34*, 2108.

4.1 Abstract

The synthesis of high molecular weight star-shaped polymers comprising poly(1,3-cyclohexadiene) arms coupled to a divinyl benzene (DVB) core is reported. In-situ FTIR spectroscopy was used to verify first order polymerization kinetics for 1,3-cyclohexadiene at 40 °C in cyclohexane with a 10 wt% monomer concentration using a tetramethylethylenediamine (TMEDA) to n-butyllithium (nBuLi) ratio of 5/4. The propagation rate constant was determined to be $0.31 \text{ l mol}^{-1} \text{ s}^{-1}$. The degree of 1,2-addition (70%) versus 1,4-addition (30%) for 1,3-cyclohexadiene was determined using ^1H NMR spectroscopy. The molecular weights of the preformed arms were 10,000 and 5,000 and the ratio of DVB to nBuLi was systematically varied from 6:1 to 24:1. Gel permeation chromatography coupled with light scattering detection was utilized to detect the formation of star-shaped polymers and the presence of star-star coupling. In-situ spectroscopy and obvious color changes indicated that the addition of DVB to poly(1,3-cyclohexadienyllithium) was rapid. The molecular weight distribution (M_w/M_n) of the star polymers ranged from 1.40 to 1.90. The polymeric materials were thermally stable to 330 °C under a nitrogen environment. The refractive indices of both the homopolymers and star polymers were 1.572 at 600 nm and remained relatively constant from 1600 nm to 550 nm. The T_g of the high molecular weight star-shaped polymers was 150 °C.

4.2 Introduction

Living polymerization strategies permit the synthesis of macromolecules with well defined architectures.²⁶⁴ These resulting macromolecules exhibit narrow molecular weight distributions and predictable molecular weights.²⁶⁵ Furthermore, these methods can be utilized to synthesize a myriad of complex polymer architectures including block copolymers, star shaped polymers, and graft copolymers. In recent years, a number of radical based polymerization methods have evolved which are capable of producing macromolecules with relatively narrow molecular weight distributions and varied architectures. These methods include stable free radical polymerization (SFRP), atom transfer radical polymerization (ATRP), and reversible atom fragment transfer (RAFT). The greatest advantage of these methods is the functional group tolerance exhibited during the polymerization as compared to conventional organolithium initiated processes. However, compared to living anionic polymerization, slower reaction rates and lower monomer conversions are problematic for the synthesis of block copolymers. In contrast, living anionic polymerizations exhibit rapid reaction times and high monomer conversions. Living anionic polymerization is a commercially viable approach to prepare a vast number of hydrocarbon polymers based on polyisoprene, poly(butadiene), and polystyrene homo and block copolymers.²⁶⁶ A large number of potential commercial applications exist for hydrocarbon polymers due to their

²⁶⁴ Morton, M. *Anionic Polymerization: Principles and Practice* Academic Press: New York, 1983. Bywater, S. *Encyclopedia of Polymer Science and Engineering*. Edited by J.I. Kroschwitz. Vol. 2 Wiley-Interscience: New York, 1985. Rempp, P., E. Franta, and J.E. Herz. "Macromolecular engineering by anionic methods." *Advances in Polymer Science* **1988**, 86, 145.

²⁶⁵ Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996.

²⁶⁶ Billmeyer, Fred W. *Textbook of Polymer Science*. 3rd ed John Wiley and Sons: New York, 1984.

potentially desirable thermal resistance, chemical stability, and superior mechanical strengths.²⁶⁷

Various polymerization techniques were utilized in the mid-1960's and early 1970's in an attempt to find a viable polymerization methodology for 1,3-cyclohexadiene.²⁶⁸ Additionally, in the late 1970's a series of patents were issued to Phillips Petroleum that described the process and composition of 1,3-cyclohexadiene containing polymers.²⁶⁹ The effects of various ligating agents on the resulting composition were also investigated. The ligating agents investigated were TMEDA, dimethoxyethane (DME), and tetrahydrofuran (THF). The compositions were limited to "random" copolymers containing poly(1,3-cyclohexadiene), polystyrene, polyisoprene, or polybutadiene and prepared using various ligating agents. Despite these early attempts to polymerize 1,3-cyclohexadiene in a controlled fashion, the resulting polymers exhibited unpredictable molecular weights and broad molecular weight distributions. Natori and coworkers recently reported the successful living anionic polymerization of 1,3-cyclohexadiene utilizing n-butyllithium (nBuLi) in

²⁶⁷ Natori, I., K. Imaizumi, H. Yamagishi, and M. Kazunori. "Hydrocarbon Polymers Containing Six-Membered Rings in the Main Chain. Microstructure and Properties of Poly(1,3-cyclohexadiene)." *J. Polym. Sci., Part B: Polym. Phys.* **1998**, 36, 1657.

²⁶⁸ Sharaby, Z., J. Jagur-Grodzinski, M. Martan, and D Vofsi. "Kinetics and Mechanism of the Anionic Polymerization of Cyclohexadienes Initiated by Naphthalene Radical Anions and Dianions." *J. Polym. Sci., Polym. Chem. Ed.* **1982**, 20, 901. Lefebvre, G, and F. Dawans. "1,3-Cyclohexadiene polymers. I. Preparation and aromatization of poly-1,3-cyclohexadiene." *J. Polym. Sci.* **1964**, A2, 3277. Sharaby, Z., M. Martan, and J. Jagur-Grodzinski. "Stereochemistry of Poly(1,3-cyclohexadienes). NMR Investigation of Effects Due to the Solvent Medium and to the Mechanism of Polymerization." *Macromolecules* **1982**, 15, 1167. Mango, L.A., and R.W. Lenz. "Mechanism and stereochemistry in the anionic polymerization of 1,3-cyclohexadiene and the diimide hydrogenation of polymers." *U.S. Nat. Tech. Inform. Serv.* **1972**, 12, 402. Mango, L.A., and R.W. Lenz. "Organometallic reactions which control molecular weight in the anionic polymerization of 1,3-cyclohexadiene." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **1971**, 12, 402.

²⁶⁹ Hsieh, H. L. "1,3-Cyclodiene-Acyclic Conjugated Diene Copolymers." Phillips Petroleum Company, United States 4237246 (1977). Hsieh, H. L. "Copolymerization of a Linear 1,3-Cyclodiene and a Linear Conjugated Diene." Phillips Petroleum Company, United States 4138356 (1978). Hsieh, H. L. "Epoxidized Block Copolymers." Phillips Petroleum Company, United States 40202521 (1978). Hsieh, H. L. "Polymerization of 1,3-Cyclohexadiene With Vinylaromatic Hydrocarbon." Phillips Petroleum Company, United States 4131653 (1979). Hsieh, H. L. "Copolymers of 1,3-cyclohexadienes, Monovinylaromatic Compounds and Polyvinylaromatic Hydrocarbons." Phillips Petroleum Company, United States 4127710 (1980).

combination with a single ligation agent (tetramethylethylenediamine (TMEDA)).²⁷⁰ The resulting homopolymers exhibited relatively narrow molecular weight distributions and modest molecular weights. In addition to the elucidation of the relative reactivities of the monomer pairs, Natori and coworkers also reported the synthesis of di- and tri-block copolymers composed of various combinations of styrene, butadiene, and isoprene.²⁷¹ Mays and coworkers have studied the morphologies of poly(styrene-*b*-1,3-cyclohexadiene) diblock copolymers.²⁷² In addition, poly(1,3-cyclohexadiene) was utilized as a precursor for the synthesis of poly(phenylene)s via aromatization with the chloranil dehydrogenating agent.²⁷³

Living anionic polymerizations have been utilized widely in the synthesis of star-shaped polymers. The living nature of the polymerization allows for the linking of preformed arms to a linking agent such as divinylbenzene (DVB). This approach, generally termed the “arm-first” method is commonly used for both living anionic and cationic syntheses of star-shaped polymers.²⁷⁴ “Arm-first” methods can be employed

²⁷⁰ Natori, I. "Synthesis of Polymers with an Alicyclic Structure in the Main Chain. Living Anionic Polymerization of 1,3-Cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System." *Macromolecules* **1997**, 30, 3696.

²⁷¹ Natori, I., and S. Inoue. "Living Anionic Polymerization of 1,3-cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System. Copolymerization and Block Copolymerization with Styrene, Butadiene, and Isoprene." *Macromolecules* **1998**, 31, 982. Natori, I. "Synthesis of Polymers with an Alicyclic Structure in the Main Chain. Living Anionic Polymerization of 1,3-Cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System." *Macromolecules* **1997**, 30, 3696. Natori, I., and S. Inoue. "Anionic Polymerization of 1,3-cyclohexadiene with Alkylolithium/Amine Systems. Characteristics of n-Butyllithium/N,N,N',N'-Tetramethylethylenediamine System for Living Anionic Polymerization." *Macromolecules* **1998**, 31, 4687.

²⁷² David, J. L., S. P. Gido, K. Hong, Jian Zhou, J. W. Mays, and B.N. Tan. "Core-Shell Cylinder Morphology in Poly(styrene-*b*-1,3-cyclohexadiene) Diblock Copolymers." *Macromolecules* **1999**, 32, 3216.

²⁷³ Hong, K., J.W. Mays, Y. Wang, and R. Advincula. "Synthesis and Aromatization of Polycyclohexadiene(PCHD) Homo and Block Copolymers: Towards Processible Poly-p-Phenylene (PPP) Derivatives." *PMSE Preprints* **1999**, 80, 116.

²⁷⁴ Ishizu, Koji, and Kenro Sunahara. "Synthesis of Star Polymers by Organized Polymerization of Macromonomers." *Polymer* **1995**, 36, 4155. Storey, R. F., and K. A. Shoemake. "Poly(Styrene-*b*-Isobutylene) Multiarm Star Block Copolymers." *J. Polym. Sci., Part A: Polym. Chem* **1999**, 37, 1629. Hadjichristidis, N., and L.J. Fetters. "Star Branched Polymers. 4. Synthesis of 18-Arm Polyisoprenes." *Macromolecules* **1980**, 13, 193. Hadjichristidis, N., and L.J. Fetters. "Star-Branched Polymers. 4. Synthesis of 18-Arm Polyisoprenes." *Macromolecules* **1980**, 13, 193. Storey, R. F., K. A. Shoemake, and B. J. Crisholm. "Synthesis

with various linking agents. Two common linking agents are silicon tetrachloride, and *p*- and *m*-divinylbenzene. In favorable cases, the functionality of a chlorosilane based linking agent dictates the number of arms in the star polymer. However, divinyl compounds undergo homopolymerization and form star polymers where the number of arms is greater than the functionality of a single divinyl compound. An advantage of the arm first method is the facile synthesis of narrow molecular weight distribution star-shaped polymers. An alternate method, termed “core-first”, involves the generation of a reactive core prior to the addition of arm forming monomers. The advantage of the core first method is the ability to functionalize the outer chain ends of the star-shaped macromolecule using various termination agents. Although the outer chain ends of a star can be functionalized using the arm first route, this route requires the use of protected functional initiators. The functionalized periphery can subsequently be utilized for the preparation of networks or star-shaped polymers containing copolymeric branches.²⁷⁵ The disadvantage of the core first method is the generation of a relatively large molecular weight distribution.²⁷⁶ Recently, a number of researchers have combined both the “core-first” and the “arm-first” methods in a single synthesis to generate stars with two different types of polymer arms in what is termed the “in-out” method.²⁷⁷ Additionally, star-shaped macromolecules have been used extensively in a number of commercial applications including adhesives, coatings, dispersants, membranes, compatibilizers, thermoplastic elastomers, viscosity-index and melt-strength modifiers, and as vehicles for drug delivery.²⁷⁸

and Characterization of Multi-Arm Star- Branched Polyisobutylenes." *J. Polym. Sci. Part A: Polym. Chem.* **1996**, 34, 2003.

²⁷⁵ Meneghetti, S.P., P.J. Lutz, and D. Rein. "Star-Shaped Polymers via Anionic Polymerization Methods." In *Star and Hyperbranched Polymers*, edited by Munmaya Mishra and Shiro Kobayashi, 27. New York: Marcel Dekker, 1999.

²⁷⁶ Meneghetti, S.P., P.J. Lutz, and D. Rein. "Star-Shaped Polymers via Anionic Polymerization Methods." In *Star and Hyperbranched Polymers*, edited by Munmaya Mishra and Shiro Kobayashi, 27. New York: Marcel Dekker, 1999.

²⁷⁷ Hadjichristidis, N. "Synthesis of Miktoarm Star (u-Star) Polymers." *J. Polym. Sci., Part A: Polym. Chem.* **1999**, 37, 857. Frater, D. J., J.W. Mays, and C. Jackson. "Synthesis and Dilute Solution Properties of Divinylbenzene-Linked Polystyrene Stars with Mixed Arm Lengths: Evidence for Coupled Stars." *J. Polym. Sci., Part A: Polym. Chem.* **1997**, 35, 141.

²⁷⁸ Pitsikalis, M., S. Sioula, S. Psipas, N. Hadjichristidis, D.C. Cook, J. Li, and J. W. Mays. "Linking Reactions of Living Polymers with Bromomethylbenzene Derivatives: Synthesis

These research efforts involve the synthesis via the “arm-first” method of novel star-shaped polymers consisting of poly(1,3-cyclohexadiene) arms coupled to a divinyl benzene core. In addition, in-situ FTIR spectroscopy was utilized to examine the kinetics of the homopolymerization and the rate of crossover upon addition of DVB. The physical performance of the resulting polymers were examined with a special focus on the thermal and optical properties.

4.3 Experimental Section

Materials. 1,3-cyclohexadiene (Aldrich) was degassed several times and vacuum distilled (0.10 mmHg, 10 °C) from dibutylmagnesium (DBM). Divinylbenzene (DVB) (Aldrich, 80% divinylbenzene comprising a mixture of isomers, 20% ethylvinylbenzene) was distilled under vacuum (0.10 mmHg, 25 °C) from calcium hydride and dibutylmagnesium immediately prior to use. No attempts to remove the ethylvinylbenzene were made and all further references to DVB assume the presence of the ethylvinylbenzene. n-Butyllithium (FMC Corporation Lithium Division, 1.35 M in n-hexane) was used without further purification. TMEDA (Aldrich) was vacuum distilled from calcium hydride and stored under nitrogen at –25 °C until ready for use. Cyclohexane was stirred over sulfuric acid (10:1 cyclohexane:sulfuric acid) for 7-10 days, decanted, and distilled from a sodium dispersion under nitrogen immediately prior to use.

Polymer Synthesis. The anionic polymerization of 1,3-cyclohexadiene was initiated using nBuLi/TMEDA (4/5) in cyclohexane at 40 °C for 45 minutes for the 10,000 M_n arms and 25 minutes for 5,000 M_n arms to ensure quantitative conversion of the monomer. In-situ FTIR was utilized to confirm the quantitative disappearance of monomer. Polymerizations were performed under a nitrogen atmosphere at monomer concentrations of approximately 10 wt%. A typical polymerization involved charging a 100 mL round-bottomed flask with anhydrous cyclohexane (60 mL, 0.54 mol) and 1,3-

cyclohexadiene (5.95 mL, 62.4 mmol). The solution was allowed to reach 40 °C. TMEDA (0.094 mL, 0.625 mmol) was charged to the vessel. The initiator nBuLi (0.31 mL, 0.5 mmol) was charged to initiate polymerization. The living poly(1,3-cyclohexadienyllithium) anions in cyclohexane were yellow and appeared to be slightly heterogeneous at 40 °C. Upon completion of the 1,3-cyclohexadiene polymerization, the flask was charged with a predetermined amount of DVB. The reaction solution immediately changed from a yellow to a deep red color upon the addition of DVB. DVB was allowed to react for two hours, as confirmed via in-situ FTIR to ensure complete conversion. The polymerization was terminated with degassed methanol (1.0 mL) and the resulting star polymer was precipitated into isopropanol (600 mL), filtered, and dried at 50 °C in vacuo overnight. An antioxidant such as Irganox 1010 (0.10 wt% compared to polymer) was added to the precipitation solvent to retard oxidative degradation during subsequent storage.

In-situ FTIR Spectroscopy. The in-situ FTIR spectroscopic studies were performed using a ReactIR 1000 (ASI Applied Systems) reaction analysis system equipped with a light conduit and DiComp (diamond composite) insertion probe. The specifics of the ReactIR based on attenuated total reflectance (ATR) have been described in detail previously.²⁷⁹

Polymer Characterization. ¹H and ¹³C NMR spectra were determined in CDCl₃ at 400 MHz with a Varian Spectrometer. Glass transition temperatures were determined using a Perkin-Elmer Pyris 1 DSC at a heating rate of 10 °C/min under nitrogen. Glass transition temperatures are reported as the inflection point of the change in heat capacity during the second heat. Molecular weights were determined using size exclusion chromatography (SEC) with a Water Alliance SEC system equipped with a Viscotek 150R viscosity detector. In addition, a Waters 717plus equipped with a Waters 2410

²⁷⁹ Storey, R. F., A.B. Donnalley, and T.L. Maggio. "Real-time monitoring of carbocationic polymerization of isobutylene using in situ FTIR-ATR spectroscopy with conduit and diamond-composite sensor technology." *Macromolecules* **1998**, 31, 1523. Pasquale, A.J., and T.E. Long. "Real-Time Monitoring of the Stable Free Radical Polymerization of Styrene via in-Situ Mid-Infrared Spectroscopy." *Macromolecules* **1999**, 32, 7954.

refractive index detector and a Wyatt Technology Minidawn MALLS detector was utilized for absolute molecular weight measurements. The dn/dc values were determined on-line using the calibration constant for the RI detector and the mass of the polymer sample. For all samples, it was assumed that 100% of the polymer eluted from the column during the measurement. SEC measurements were performed at 25 °C in chloroform at a flow rate of 1.0 mL/min. TGA measurements were performed on a TA Instruments Hi-Res TGA 2950 thermogravimetric analyzer (TGA) under nitrogen with a heating rate of 10 °C per minute.

Thin Film Optical Characterization. The complex refractive index of the material was determined using variable angle spectroscopic ellipsometry (VASE, Tompkins). To determine these optical constants in the deep ultraviolet region a VUV-VASE (J. A. Woollam Co.) instrument was utilized. The star polymer was dissolved in dichlorobenzene and spun cast onto silicon substrates. The solvent was removed with mild heating, and x-ray photoelectron spectroscopy (XPS) (PHI 5600) was performed to ensure the removal of the dichlorobenzene. Spectra were acquired from 145 to 1700 nm using three angles of incidence (65°, 70°, 75°). Spectra were then modeled using WVASE32 software. A Herzinger-Johs™ parametric layer has been used to estimate η and k of the polymer as this imposes a Kramers-Kronig formalism onto the optical constants.²⁸⁰

²⁸⁰ Tompkins, H.G., and W.A. McGahan, eds. *Spectroscopic Ellipsometry and Reflectometry: A User's Guide*. Edited by H.G. Tompkins and W.A. McGahan Wiley Interscience: New York, 1999.

4.4 Results and Discussion

The synthesis of a 5000 g/mol poly(1,3-cyclohexadiene) homopolymer was monitored using in-situ FTIR spectroscopy. The resulting polymer was characterized using SEC and found to be a single peak with a molecular weight of 5,200 g/mol and a molecular weight distribution of 1.01. In-situ near-FTIR spectroscopy has been previously employed for determination of the kinetics of the anionic homopolymerization of styrene and isoprene.²⁸¹ However, this is the first reported use of in-situ mid-FTIR spectroscopy to study the kinetics of a living anionic polymerization. The monomer and polymer peaks in the spectrum must be clearly resolved as shown in Figure 4-1 in order to ensure accurate analysis. The decrease in the absorbance of the monomer peak found at 657 cm⁻¹ and the increase in the absorbance of the polymer peak at 703 cm⁻¹ resulting from the out of plane bending vibration of the carbon to hydrogen bond of the alkene are shown in Figure 4-1. The polymer was synthesized using a 10 wt% monomer/cyclohexane solution at 40 °C using the TMEDA/nBuLi ratio of 5/4. The polymerization was then initiated with nBuLi and the solution became heterogeneous within five minutes. Despite the heterogeneity of the polymerization solution, molecular weights are predictable and molecular weight distributions are relatively narrow. Figure 4-2 is a waterfall plot of the polymerization indicating that complete conversion of the monomer occurred within 13 minutes.

²⁸¹ Long, T.E., H.Y. Lui, D.M. Schell, D.M. Teegarden, and D.S. Uerz. "Determination of Solution Polymerization Kinetics by Near-Infrared Spectroscopy. 1. Living Anionic Polymerization Process." *Macromolecules* **1993**, 26, 6237.

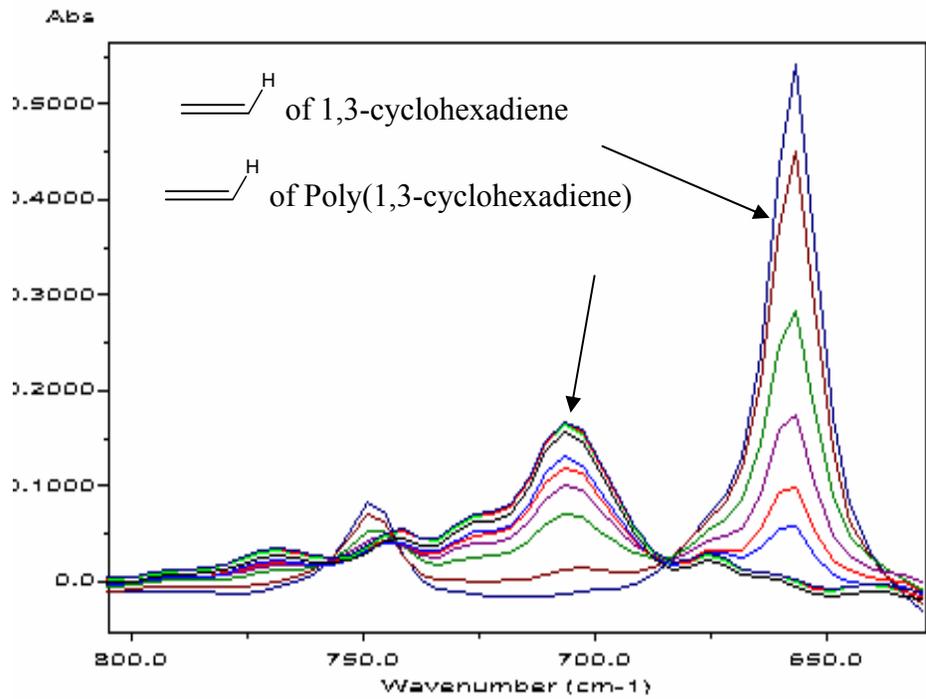


Figure 4-1. In-situ FTIR spectra illustrating the disappearance of the monomer absorption at 657 cm^{-1} and concomitant polymer absorption increase at 703 cm^{-1} for the synthesis of a 5000 poly(1,3-cyclohexadiene) homopolymer.

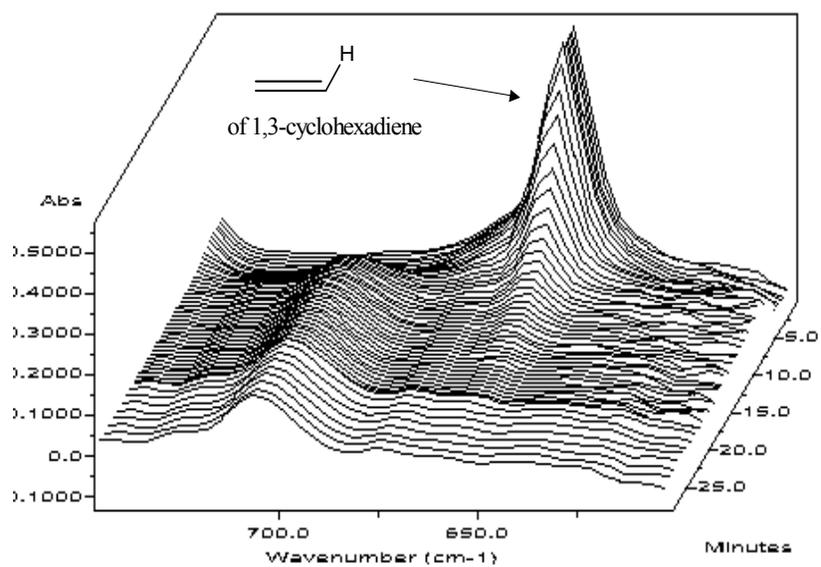


Figure 4-2. Waterfall plot of the polymerization of 1,3-cyclohexadiene indicating that the polymerization was quantitative within 15 minutes. $\langle M_n \rangle = 5200$, $\langle M_w \rangle / \langle M_n \rangle = 1.01$.

The polymerization kinetics did not change as the polymerization proceeded from a homogeneous solution to a heterogeneous solution as is shown in Figure 4-2. Due to the excellent resolution of both the monomer and polymer absorbances, the spectral data was utilized in the generation of a pseudo first order kinetic plot with monomer concentration plotted against time as shown in Figure 4-3. The calculated rate constant for propagation was $0.31 \text{ l mol}^{-1} \text{ s}^{-1}$. Values for the polymerization rate constant of an anionic polymerization are dependant upon the temperature, monomer concentration, and the presence of additives.²⁸² An understanding of the propagation rate facilitated the minimization of any termination/transfer steps occurring after quantitative polymerization of the arms and prior to the addition of the DVB.

Scheme 4-1 illustrates the synthetic methodology used for the preparation of poly(1,3-cyclohexadiene) DVB star-shaped polymers. The convergent linking of poly(1,3-cyclohexadienyllithium) chain ends to the DVB core resulted in the formation of star-shaped polymers. Upon addition of DVB to the poly(1,3-cyclohexadienyllithium) solution, the reaction color immediately changed from yellow to a deep red color indicative of the formation of a highly delocalized benzylic anion resulting from the rapid crossover from the poly(1,3-cyclohexadienyllithium) anion to the DVB monomer. In-situ spectroscopy of the DVB addition also indicated the crossover reaction occurred in a rapid manner. In order to study the effect of arm length and DVB/nBuLi ratio on the resulting star polymer formation, a series of star-shaped polymers were synthesized using a constant arm length of 10,000 g/mol with varying ratios of DVB to nBuLi (Table 4-1).

²⁸² Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996.

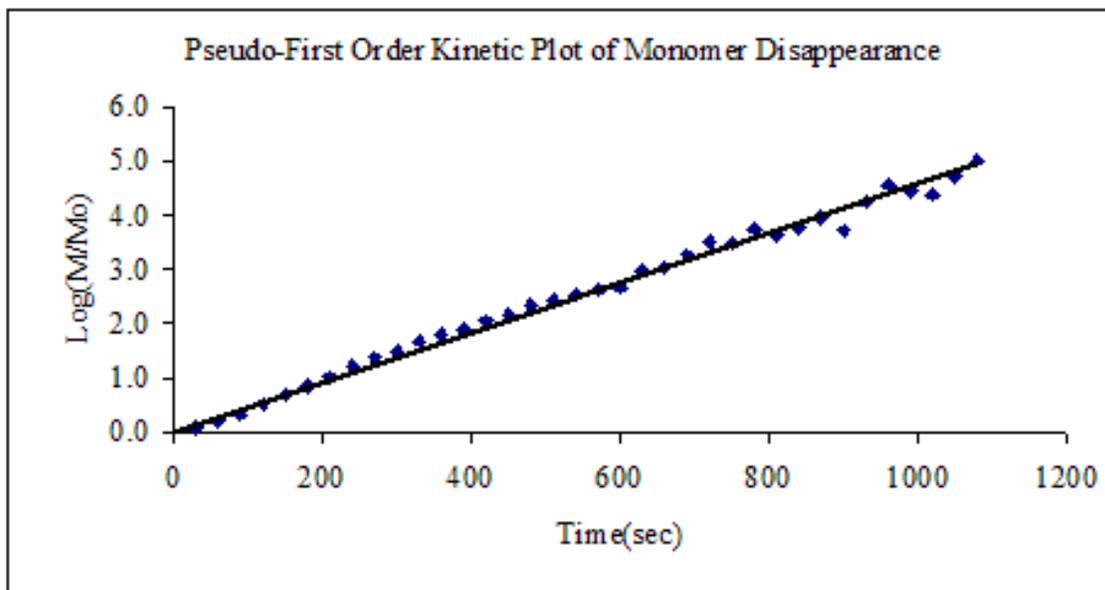
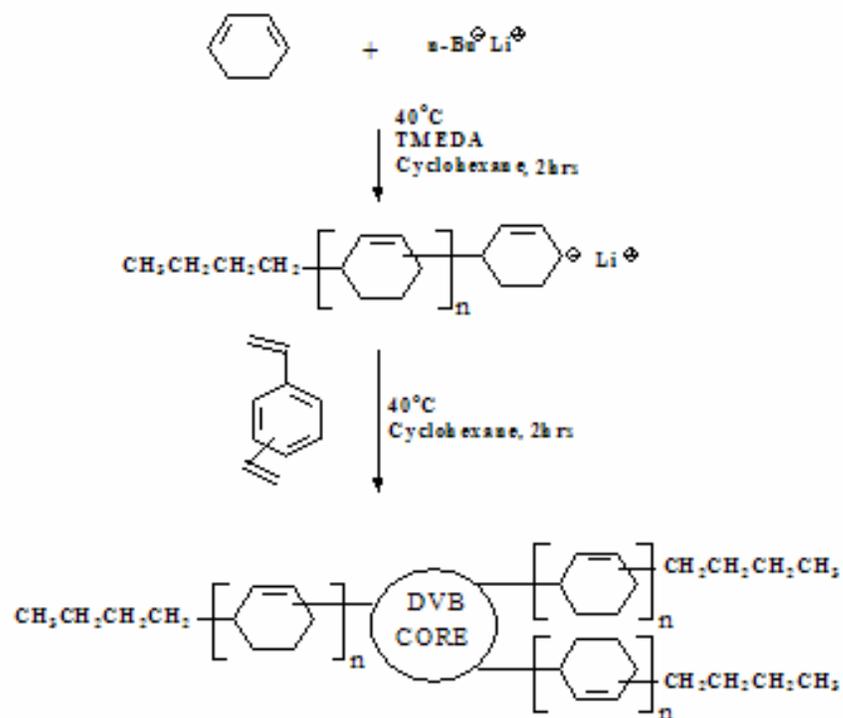


Figure 4-3. Pseudo first order kinetic plot for the homopolymerization of 1,3-cyclohexadiene. The polymerization exhibited excellent molecular weight control ($\langle M_n \rangle = 5200$). Polymerization was performed at 40 °C in cyclohexane with an initiator concentration of 8.33×10^{-3} mol/L.



Scheme 4-1. Synthetic methodology utilized for the synthesis of star-shaped polymers. The coupling reaction was allowed to proceed for 16 h.

Table 4-1. Star-shaped polymers synthesized with 10,000 g/mol, and 5,000 g/mol arms.

DVB/nBuLi	$\langle M_n \rangle^a$ (arm)	$\langle M_n \rangle^a$ (star)	# of arms ^b (calc)	% Conversion ^c	$\langle M_n \rangle / \langle M_n \rangle^d$
8:1	10000 g/mol	760000	67	80%	1.50
14:1	10000 g/mol	1600000	135	80%	1.85
18:1	10000 g/mol	2200000	178	70%	1.87
24:1	10000 g/mol	2800000	214	78%	1.89
8:1	5000 g/mol	490000	82	90%	1.54
14:1	5000 g/mol	1200000	176	89%	2.02

^aThe SEC conditions were as follows: CHCl₃, 25°C, DRI/MALLS (absolute molecular weight). ^bThe number of arms per star was determined by dividing the M_n by the arm M_n after subtraction of the DVB contribution to the molecular weight of the star-shaped polymer. ^cThe percent conversion was determined by dividing the area of the star polymer in the GPC chromatogram by the total area after subtraction of the DVB contribution to the total area. ^dThe molecular weight distribution for the star-shaped polymer, this does not include the uncoupled arms.

The absolute molecular weights of the resulting macromolecules were approximated using the universal calibration as previously described²⁸³ and using multiple angle laser light scattering (MALLS). The molecular weights were determined using MALLS due to the improved accuracy of MALLS compared to viscometric methods for branched polymer architectures. The resulting polymers exhibited high molecular weights and relatively narrow molecular weight distributions. Table 4-1 indicates that the maximum number of 10000 g/mol arms per star occurred using a DVB/nBuLi ratio of 24:1. As expected, an important factor for the control of star polymer molecular weight is the DVB:initiator ratio. It is proposed that the highly rigid nature of the preformed arms may facilitate linking to the core. The average number of arms per star (f) were determined using the following formula, where %DVB is the wt% of the DVB in the star:

Equation 4-1.
$$f = ((M_n^{\text{star}}) - \%DVB * (M_n^{\text{star}})) / M_{n(\text{th})}^{\text{arms}}$$

Star-shaped polymers comprising arms with a number average molecular weight of 10,000 g/mol were prepared at a linking efficiency ranging from 70% to 80%. Increased linking efficiencies were possible for star-shaped polymers synthesized using 5000 arms (Table 4-1). The resulting polymers all exhibited relatively narrow molecular weight distributions and a high percent of conversion of the living anionic arms to the DVB core as shown in Figure 4-4. As the DVB/nBuLi ratio was increased, the core size also increased allowing for a greater number of arms attached to the core. The increase in polydispersity for higher DVB/nBuLi ratios is likely due to the presence of star-star coupling. Characterization of the star shaped polymers using MALLS enabled the identification of the larger molecular weight species. Juxtaposition of the light scattering data for star polymers synthesized from the 10000 preformed arms (Figure 4-5) clearly shows the increasing presence of coupled stars as the DVB/nBuLi ratio is increased.

²⁸³ Gitsov, I, and J.M.J. Frechet. "Solution and Solid-State Properties of Hybrid Linear-Dendritic Block Copolymers." *Macromolecules* **1993**, 26, 6536.

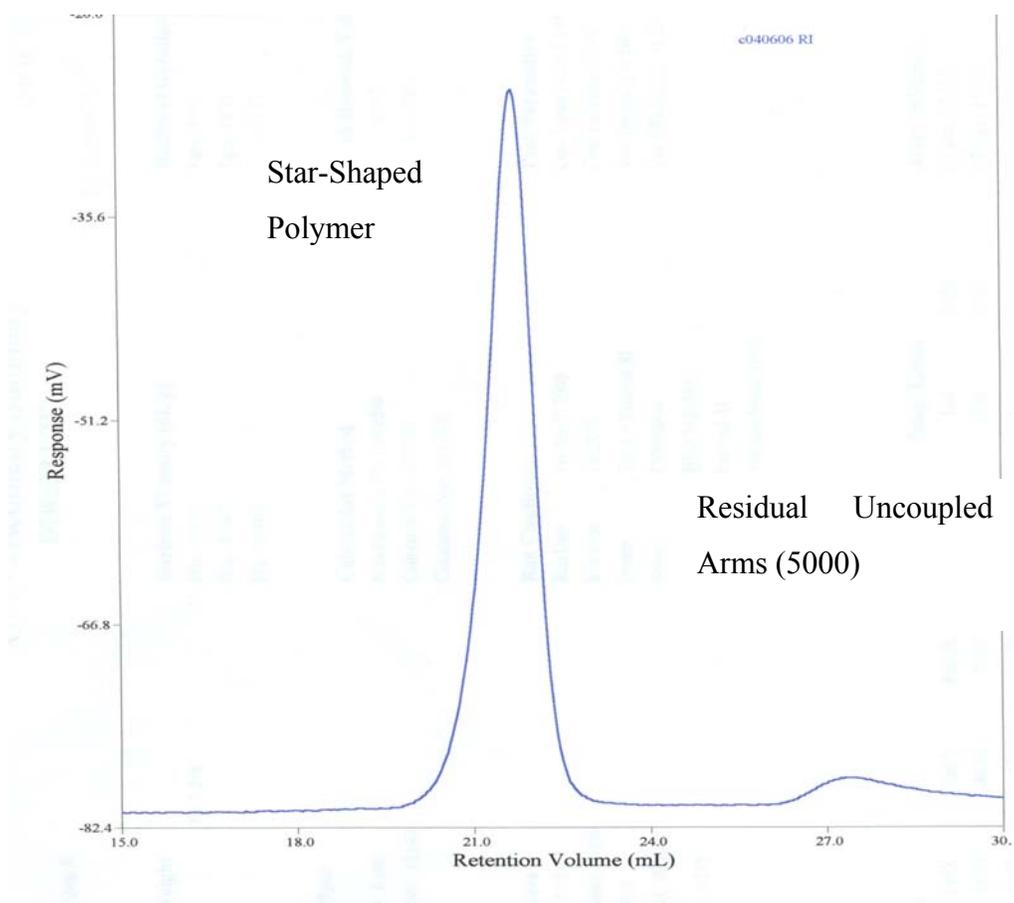


Figure 4-4. SEC of the star shaped polymer with a DVB/nBuLi ratio of 8:1 and an arm length of 5000. SEC conditions: CHCl₃, 25 °C, DRI detector.

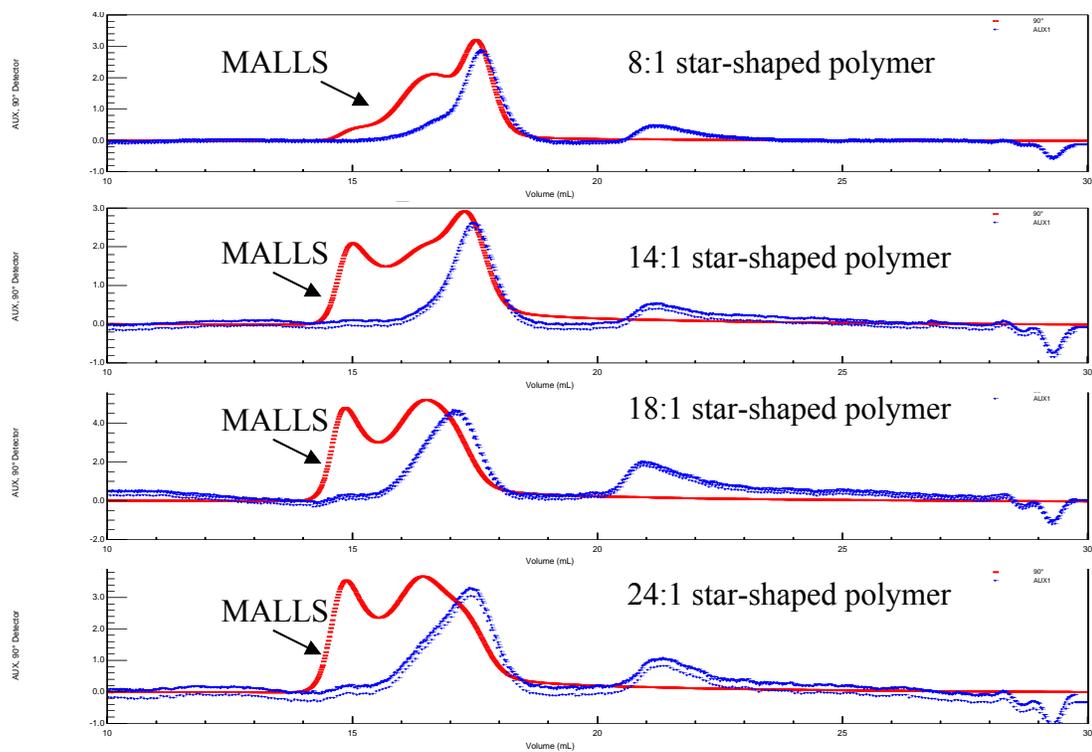


Figure 4-5. SEC of the 10000 series of star-shaped polymers, the light scattering data is superimposed on the refractive index data . SEC conditions: CHCl_3 , 25 °C, MALLS detector.

The length of the preformed arms does not appear to impact the degree of star-star coupling. In contrast, the molecular weight of the arms is an important factor that determines the number of arms coupled to the star core. Table 4-1 clearly indicates for a constant 8:1 DVB/nBuLi ratio that star polymers with an arm length of 5,000 have more arms (approximately 82 arms) than a star polymer with a 10,000 arms (approximately 67 arms). Table 4-1 depicts a similar trend based on arm number-average molecular weight for other DVB/nBuLi ratios. The DVB molar charge to the solution of preformed arms is significantly larger than DVB charges reported earlier in the synthesis of star-shaped polymers. In order to obtain a more comprehensive understanding of the solution properties of the novel star-shaped macromolecules containing poly(1,3-cyclohexadiene), a wide range of DVB/nBuLi ratios was studied. This enabled a more thorough study of the effect of architecture on the radius of gyration. In the study of the macromolecules with 10,000 g/mol arms, the radius of gyration (R_z) increased from 17.6 to 27.5 as the ratio of DVB/nBLi increased from 8:1 to 14.1, as expected for traditional DVB based star-shaped macromolecules. For the macromolecules synthesized with a ratio of DVB/nBuLi of 18:1 and 24:1, the radius of gyration was 33.3 and 33.4. This indicates that the radius of gyration reaches a constant value that is independent of the ratio of DVB/nBuLi. As the ratio exceeds 18:1, the radius of gyration is dependent upon the size of the DVB core. These results suggest that the architecture of the macromolecule changes from a more traditional DVB based star-shaped polymer to a DVB microgel covered with poly(1,3-cyclohexadiene) arms.

The resulting polymers were characterized using both ^{13}C and ^1H NMR. The degree of 1,2- versus 1,4-addition was determined by comparing the integrations of the olefinic protons to the allylic protons in the spectra (Figure 4-6) and solving the following set of linear equations (Equation 4-2).

Equation 4-2.

$$\text{Area}_{\text{olefinic}} = 2x + 2y \quad x = \text{relative amount of 1,2 addition}$$

$$\text{Area}_{\text{allylic}} = 3x + 2y \quad y = \text{relative amount of 1,4 addition}$$

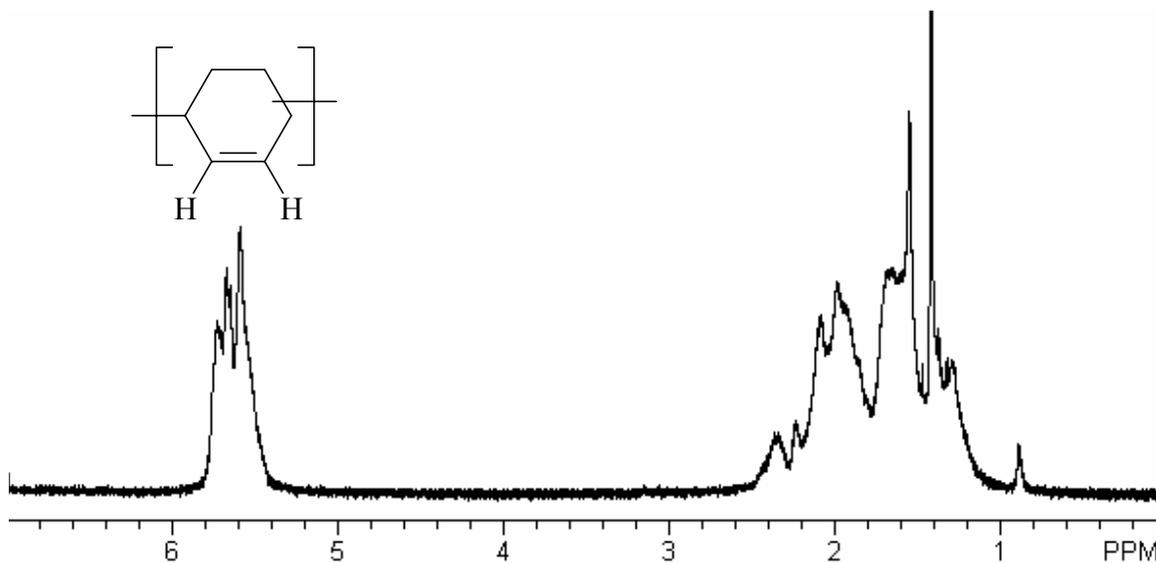


Figure 4-6. ^1H NMR spectra of the poly(1,3-cyclohexadiene) homopolymer with a molecular weight of 10000. The polymer exhibited approximately 70 % 1,2-addition and 30 % 1,4-addition.

The ratio of 1,2 versus 1,4 was found to be 70 % 1,2 and 30 % 1,4 using this method. Previous researchers have reported that the ratio of 1,2 to 1,4 in poly(1,3-cyclohexadiene) homopolymers) is approximately 50% 1,2 and 50% 1,4.²⁸⁴ However, a different synthetic strategy was employed and the NMR measurements were performed at 150 °C in deuterated m-dichlorobenzene. Our earlier efforts have demonstrated that these NMR conditions may promote oxidation of poly(1,3-cyclohexadiene) altering the ratio of the allylic to olefinic protons.²⁸⁵

The thermal stabilities and transition temperatures of the resulting star-shaped polymers were determined using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) respectively. Figure 4-7 illustrates that the onset of weight loss for the star polymers occurs at 330 °C under nitrogen, which is consistent with earlier studies on block copolymers comprising poly(1,3-cyclohexadiene)s.²⁸⁶ Differential scanning calorimetry indicated the presence of a single glass transition temperature at approximately 150 °C (Figure 4-8) for all star-shaped polymers. The DVB core size did not influence the glass transition temperature.

²⁸⁴ Natori, I., and S. Inoue. "Anionic Polymerization of 1,3-cyclohexadiene with Alkylolithium/Amine Systems. Characteristics of n-Butyllithium/N,N,N',N'-Tetramethylethylenediamine System for Living Anionic Polymerization." *Macromolecules* **1998**, 31, 4687.

²⁸⁵ Williamson, D.T., K. Brazhnik, A.J. Pasquale, and T.E. Long. "Synthesis and Characterization of Hydrogenated Poly(1,3-cyclohexadiene) Star-Shaped Polymers." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **2000**, 41, 1544.

²⁸⁶ David, J. L., S. P. Gido, K. Hong, Jian Zhou, J. W. Mays, and B.N. Tan. "Core-Shell Cylinder Morphology in Poly(styrene-b-1,3-cyclohexadiene) Diblock Copolymers." *Macromolecules* **1999**, 32, 3216.

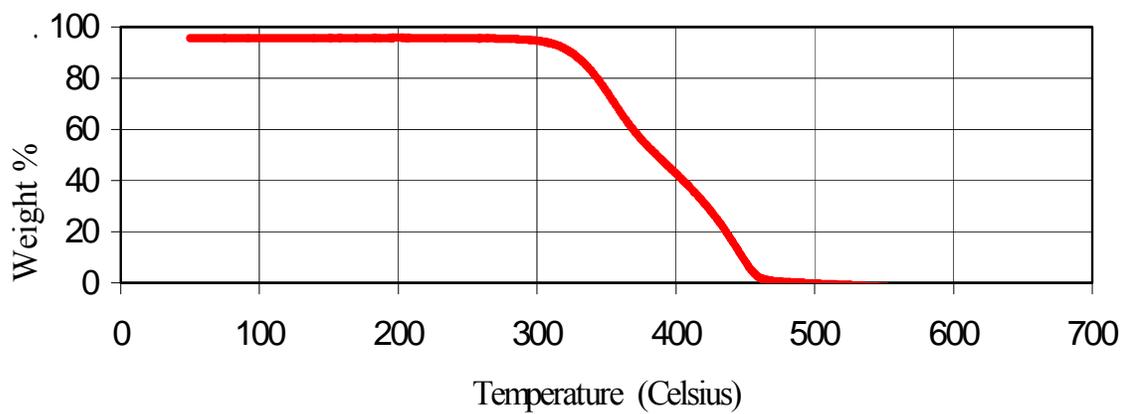


Figure 4-7. TGA of the star shaped polymer with a DVB/nBuLi ratio of 8:1 and an arm length of 5000.

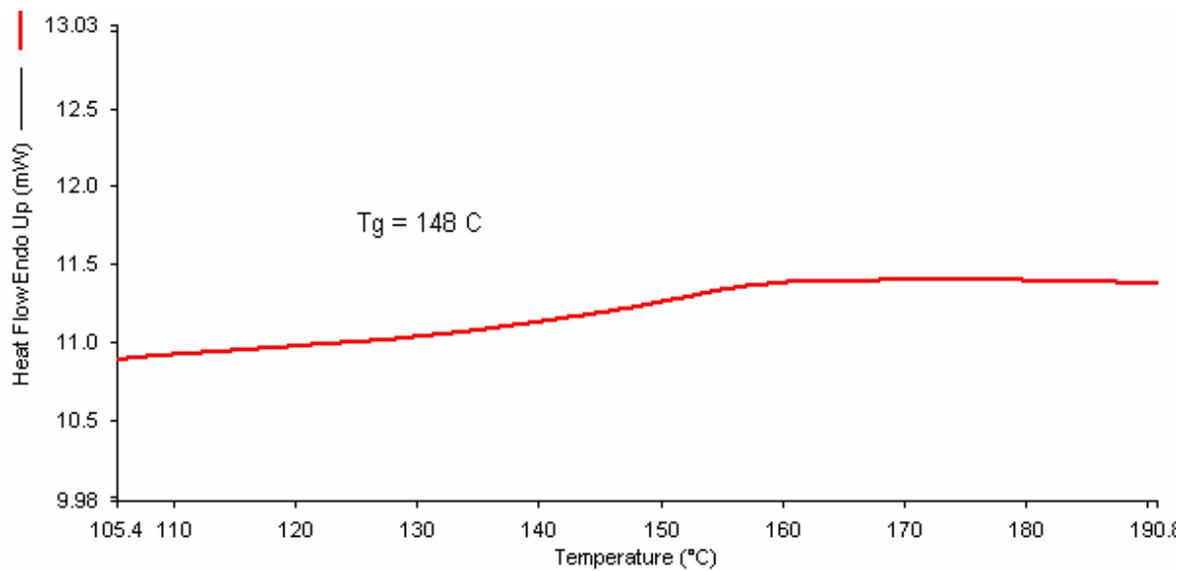


Figure 4-8. DSC analysis of the star-shaped polymer with a DVB/nBuLi ratio of 18:1 and an arm molecular weight of 10000. DSC Conditions: 10 °C/min, Nitrogen.

Optical Properties.

In order to determine the optical properties of the resulting star polymers, the refractive indices were determined using ellipsometry as described earlier. As shown in Figure 4-9, both the star and homopolymers exhibited a large constant refractive index of 1.572 over a broad range of wavelengths from 1700 nm to 550 nm. The large absorbance of the polymer found below 600 nm is attributed to the aromatic core of the star and the olefinic sites in the repeating units. The homopolymer arms in the absence of aromatic inhibitor and the DVB core exhibit less absorbance in the aromatic region of the spectrum (approximately 250 nm).

4.5 Conclusions

These investigations demonstrate the utility of living anionic polymerization for the synthesis of novel poly(1,3-cyclohexadiene) DVB star-shaped polymers with various arm lengths using various DVB/nBuLi ratios. In-situ FTIR spectroscopy was useful for the determination of polymerization kinetics ($k_p = 0.31 \text{ l mol}^{-1} \text{ s}^{-1}$) ensuring complete monomer conversion and optimization of DVB coupling. NMR spectroscopic studies indicated that the degree of 1,2-addition versus 1,4-addition was 70% 1,2-addition and 30% 1,4-addition. In-situ spectroscopy and obvious color changes indicated that the addition of DVB to poly(1,3-cyclohexadienyllithium) was rapid. The linking of the arms to the DVB core was improved at lower arm molecular weights of 5000. Although increased molecular weights were achieved as the DVB/nBuLi ratio was increased, it is presumed that the architecture changes from a conventional star at low ratios to a poly(1,3-cyclohexadiene)-coated microgel. The resulting star-shaped polymers were thermally stable to 330 °C in a nitrogen environment and exhibited a T_g value of 150 °C and a refractive index of 1.572 at 600 nm. The size of the DVB core did not affect the glass transition temperature.

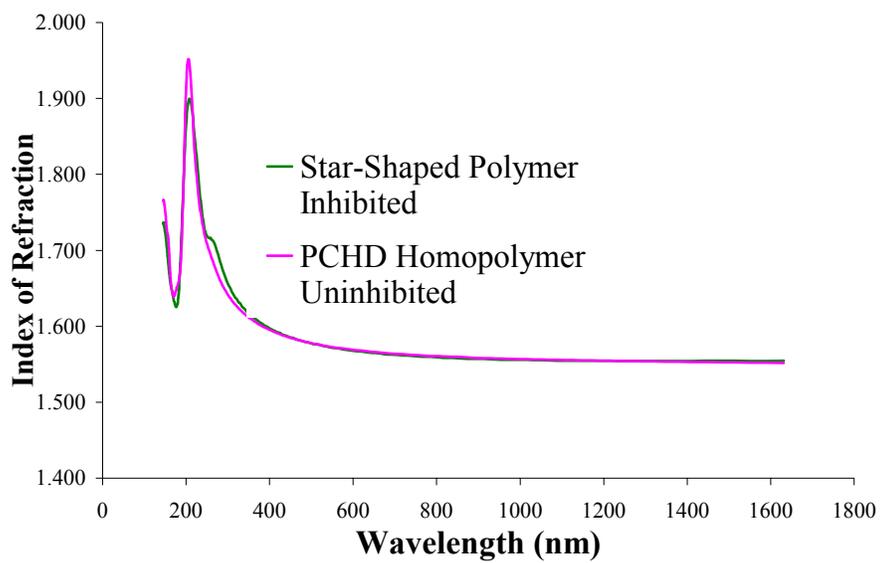


Figure 4-9. Refractive index of the star-shaped polymer and un-inhibited homopolymer as a function of wavelength. Measured using ellipsometry at 25 °C.

CHAPTER 5

Synthesis and Characterization of Poly(1,3-cyclohexadiene-block-isoprene) Diblock Copolymers.

Taken From:

Williamson, D.T., and T.E.Long. "Combining Statistical Design of Experiments with In-parallel Polymerization Methodologies" *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **2001**, 42, 634

Williamson, D.T., J.R. Lizotte, and T.E. Long. "Facile Living Anionic Polymerization Process: New Monomer and Polymer Architectures Containing 1,3-cyclohexadiene without a High Vacuum Line" *PMSE Preprints* **2001**, 87.

5.1 Abstract

Statistically designed experimentation was used to study the effect of monomer concentration and temperature on the polymerization of 1,3-cyclohexadiene in the presence of tetramethylethylenediamine (TMEDA). The reaction yield and polymer molecular weight were determined to be dependent on both monomer concentration and reaction temperature. On the basis of these results, well defined poly(1,3-cyclohexadiene)-block-polyisoprene diblock copolymers with narrow molecular weight distributions (1.06) and high molecular weights (50000) were synthesized. Phase separation between PCHD blocks and polyisoprene blocks occurred at block number average molecular weights in excess of 500. Poly(1,3-cyclohexadienyllithium) exhibited an efficient crossover to isoprene. A series of star-shaped thermoplastic elastomers were synthesized with the coupling agent divinyl benzene (DVB). High molecular weight (80000 - 100000) star-shaped thermoplastic elastomers with relatively narrow molecular weight distributions (1.28 - 1.36) were synthesized. A range of PCHD content from 16% to 38% was introduced into the thermoplastic elastomers.

5.2 Introduction

Poly(1,3-cyclohexadiene) polymers were prepared using a variety of different synthetic methods, including free radical, coordination and anionic polymerization strategies.²⁸⁷ The polymerization of 1,3-cyclohexadiene is of considerable interest as poly(1,3-cyclohexadiene) exhibits a unique combination of physical properties including excellent optical (index of refraction = 1.572) and thermal properties ($T_g = 150\text{ }^\circ\text{C}$).²⁸⁸ In addition, these polymers can be chemically modified to form a variety of unique polymeric derivatives, such as poly(cyclohexane) and poly(phenylene).²⁸⁹ Unfortunately, a number of molecular weight limiting side reactions plague the polymerization of 1,3-cyclohexadiene.²⁹⁰ Despite previous attempts to polymerize 1,3-

²⁸⁷ Sharaby, Z., M. Martan, and J. Jagur-Grodzinski. "Stereochemistry of Poly(1,3-cyclohexadienes). NMR Investigation of Effects Due to the Solvent Medium and to the Mechanism of Polymerization." *Macromolecules* **1982**, 15, 1167. Sharaby, Z., J. Jagur-Grodzinski, M. Martan, and D Vofsi. "Kinetics and Mechanism of the Anionic Polymerization of Cyclohexadienes Initiated by Naphthalene Radical Anions and Dianions." *J. Polym. Sci., Polym. Chem. Ed.* **1982**, 20, 901. Lefebvre, G, and F. Dawans. "1,3-Cyclohexadiene polymers. I. Preparation and aromatization of poly-1,3-cyclohexadiene." *J. Polym. Sci.* **1964**, A2, 3277. Mango, L.A., and R.W. Lenz. "Organometallic reactions which control molecular weight in the anionic polymerization of 1,3-cyclohexadiene." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **1971**, 12, 402. Mango, L.A., and R.W. Lenz. "Mechanism and stereochemistry in the anionic polymerization of 1,3-cyclohexadiene and the diimide hydrogenation of polymers." *U.S. Nat. Tech. Inform. Serv.* **1972**, 12, 402.

²⁸⁸ Williamson, D.T., K. Brazhnik, A.J. Pasquale, and T.E. Long. "Synthesis and Characterization of Hydrogenated Poly(1,3-cyclohexadiene) Star-Shaped Polymers." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **2000**, 41, 1544. Williamson, D.T., J.F. Elman, P.H. Madison, A.J. Pasquale, and T.E. Long. "Synthesis and Characterization of Poly(1,3-cyclohexadiene) Homopolymers and Star-shaped Polymers." *Macromolecules* **2001**, 34, 2108.

²⁸⁹ Williamson, D.T., T.E. Glass, and T.E. Long. "Aromatization of poly(1,3-cyclohexadiene-co-styrene): A novel route to soluble poly(phenylene-co-styrene) copolymers." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **2002**, 43, 1201. Williamson, D.T., and T.E. Long. "Self-assembled poly(phenylene) containing macromolecules via the controlled anionic polymerization of 1,3-cyclohexadiene." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **2002**, 43, 330. Hong, K., J.W. Mays, Y. Wang, and R. Advincula. "Synthesis and Aromatization of Polycyclohexadiene(PCHD) Homo and Block Copolymers: Towards Processible Poly-p-Phenylene (PPP) Derivatives." *PMSE Preprints* **1999**, 80, 116.

²⁹⁰ Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996. Hong, K., and J.W. Mays. "1,3-Cyclohexadiene Polymers. 1. Anionic Polymerization." *Macromolecules* **2001**, 34, 782.

cyclohexadiene in a controlled fashion, the molecular weight of the resulting polymers was unpredictable and the molecular weight distributions were broad.²⁹¹

Recently, Natori and coworkers reported the synthesis of a series of poly(1,3-cyclohexadiene) polymers using a TMEDA/nBuLi initiator adduct at 40 °C in cyclohexane.²⁹² This adduct was reported to be efficient for the synthesis of a range of polymer molecular weights and polymer systems containing poly(1,3-cyclohexadiene), such a poly(1,3-cyclohexadiene-block-butadiene) and poly(1,3-cyclohexadiene-block-isoprene). A ratio of TMEDA/nBuLi of 5/4 was necessary to synthesize poly(1,3-cyclohexadiene) homopolymers with narrow molecular weight distributions (1.10). When higher molecular weight polymers were synthesized (40000) the molecular weight distribution broadened (1.30) due the occurrence of deleterious side reactions, such as chain transfer to monomer.

The living nature of this polymerization enables novel block copolymer systems containing poly(1,3-cyclohexadiene) to be developed, including diblock, triblock, and star-shaped polymers. Block copolymers consist of different polymers that are chemical connected that form microdomain structures, which arise from the thermodynamic incompatibility of the constituent blocks.²⁹³ The behavior of block copolymers was extensively studied over the past three decades due to the presence of commercially and academically relevant properties.²⁹⁴ The commercial applications for

²⁹¹ Mango, L.A., and R.W. Lenz. "Organometallic reactions which control molecular weight in the anionic polymerization of 1,3-cyclohexadiene." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **1971**, 12, 402. Mango, L.A., and R.W. Lenz. "Mechanism and stereochemistry in the anionic polymerization of 1,3-cyclohexadiene and the diimide hydrogenation of polymers." *U.S. Nat. Tech. Inform. Serv.* **1972**, 12, 402.

²⁹² Natori, I. "Synthesis of Polymers with an Alicyclic Structure in the Main Chain. Living Anionic Polymerization of 1,3-Cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System." *Macromolecules* **1997**, 30, 3696. Natori, I., and S. Inoue. "Living Anionic Polymerization of 1,3-cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System. Copolymerization and Block Copolymerization with Styrene, Butadiene, and Isoprene." *Macromolecules* **1998**, 31, 982.

²⁹³ Stroble, G. *The Physics of Polymers*. 2nd ed Springer-Verlag: Berlin, 1997.

²⁹⁴ Aggarwal, S.L. "Introduction and Overview." In *Processing, Structure, and Properties of Block Copolymers*, edited by M.J. Folkes, 1. New York: Elsevier Applied Science Publishers, 1985. Campbell, D.S. "Thermoplastic Elastomeric Block Copolymers." In *Developments in*

block copolymers have been far-reaching and include elastomer, adhesive, and compounding additive applications.²⁹⁵ Triblock and star-shaped polymers have received significant commercial attention due to their ability to exhibit elastomeric properties at ambient temperatures while remaining melt-processable at elevated temperatures. Diblock copolymers have also received commercial attention, most notably due to their adhesive properties. From an academic perspective, block copolymers have received significant attention due to the rich morphological variations exhibited by block copolymers and the high regularity exhibited within the specific morphologies. Recently Hashimoto et al. explored the interaction between blends of diblock copolymers and either homopolymers or another diblock copolymer.²⁹⁶ In these blending studies, one of the constituent blocks present in the first diblock copolymer was also present as either a homopolymer or a constituent block in the other diblock copolymer. The authors were able to modulate the interface between the microdomains and ultimately force the formation of macrophase separation. In addition, the authors demonstrated the presence of a novel morphology, a hexagonally perforated layer, through the introduction of varying volume fractions of the second diblock. This novel morphology was shown to extend to temperatures 100 °C below the order-disorder transition temperature.

In light of the numerous studies examining the interactions between diblock copolymers and the combination of properties exhibited by poly(1,3-cyclohexadiene),

Block Copolymers II, edited by I. Goodman, 203. New York: Elsevier Science Publishers, 1982. Quirk, R. P. "New block copolymers for higher temperature applications." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **1985**, 26, 14.

²⁹⁵ Lutz, P.J., and P. Rempp. "New developments in star polymer synthesis: star-shaped polystyrenes and star-block copolymers." *Makromol Chem* **1988**, 189, 1051.

²⁹⁶ Kimishima, K., H. Jinnai, and T. Hashimoto. "Control of Self Assembled Structures in Binary Mixtures of A-B Diblock Copolymer by Changing the Interaction between B and C block chains." *Macromolecules* **1999**, 32, 2585. Yamaguchi, D., M. Takenaka, H. Hasegawa, and T. Hashimoto. "Macro and Microphase Transitions in Binary Blends of Block Copolymers with Complementary Asymmetric Compositions." *Macromolecules* **2001**, 34, 1707. Hashimoto, T., K. Yamasaki, S. Koizumi, and H. Hasegawa. "Ordered structure in blends of block copolymers. 1. Miscibility criterion for lamellar block copolymers." *Macromolecules* **1993**, 26, 2895. Hashimoto, T., H. Tanaka, and H. Hasegawa. "Ordered structure in mixtures of a block copolymer and homopolymers. 2. Effects of molecular weights of homopolymers." *Macromolecules* **1990**, 23, 4378.

the synthesis of poly(1,3-cyclohexadiene) containing block copolymers is expected to represent a fascinating new family of block copolymers. In addition, the synthesis of poly(1,3-cyclohexadiene) containing block copolymers could provide access to the development of high temperature thermoplastic elastomers. Natori et al. recently described the synthesis of novel diblock copolymers containing poly(1,3-cyclohexadiene).²⁹⁷ Diblock copolymers with a constituent polymer block of polystyrene, polyisoprene, and polybutadiene were synthesized. Unfortunately, the percentage of poly(1,3-cyclohexadienyllithium) that reacted with the second monomer charge was not described. In addition, the effect of anion concentration and polymerization temperature was also not described in the studies.

These research efforts focused on the synthesis and characterization of poly(1,3-cyclohexadiene-block-isoprene) block copolymers. In order to study the synthesis of well-defined block copolymers, a statistically sound experimental design approach was used to understand the effect of reaction temperature and monomer concentration. In addition, the crossover efficiency from poly(1,3-cyclohexadienyllithium) to isoprene and poly(isoprenyllithium) to 1,3-cyclohexadiene was examined. The kinetics of these polymerizations were monitored using in-situ FTIR spectroscopy. The thermal characteristics of these diblock copolymers were characterized using differential scanning calorimetry (DSC) and the microphase separation between poly(1,3-cyclohexadiene) and polyisoprene was demonstrated using atomic force microscopy in the tapping mode (TMAFM). In addition, the feasibility of the synthesis of poly(1,3-cyclohexadiene-block-isoprene) divinyl benzene coupled star-shaped polymer was studied.

²⁹⁷ Natori, I., and S. Inoue. "Anionic Polymerization of 1,3-cyclohexadiene with Alkylolithium/Amine Systems. Characteristics of n-Butyllithium/N,N,N',N'-Tetramethylethylenediamine System for Living Anionic Polymerization." *Macromolecules* **1998**, 31, 4687.

5.3 Experimental Section

Materials. 1,3-cyclohexadiene (Aldrich, 98 %) and isoprene (Aldrich, 99%) were degassed several times and distilled at reduced pressure (0.10 mm Hg, 10 °C) from dibutylmagnesium (DBM, 0.84 M). Divinylbenzene (DVB) (Aldrich, 80% divinylbenzene comprising a mixture the meta and para isomers and 20 wt% ethylvinylbenzene) was distilled under reduced pressure (0.10 mm, 25 °C) from calcium hydride (Aldrich 95%) and dibutylmagnesium immediately prior to use. The ethylvinylbenzene was not removed and all further references to DVB assume the presence of the ethylvinylbenzene (20 mol%). Dichlorodimethyl silane (Aldrich, 99.9%) was distilled from calcium hydride under reduced pressure (0.10 mm Hg, 10 °C). n-Butyllithium (FMC Corporation, Lithium Division, 1.35 M in n-hexane) was used without further purification. TMEDA (Aldrich, 99%) was distilled at reduced pressure (0.13-0.16 mmHg, 10 °C) from calcium hydride and stored under nitrogen at -25 °C until ready for use. Cyclohexane (Burdick-Jackson, HPLC grade) was stirred over sulfuric acid (10:1 cyclohexane:sulfuric acid) for 7-10 days, decanted, and distilled from a sodium dispersion under nitrogen immediately prior to use. All reagents were transferred using syringe and cannula techniques under ultrapure (99.999%) nitrogen.

Synthesis of Poly(1,3-cyclohexadiene). A 100-mL round-bottomed flask containing anhydrous cyclohexane (60 mL, 0.54 mol), 1,3-cyclohexadiene (5.95 mL, 62.4 mmol), and TMEDA (0.094 mL, 0.625 mmol) was heated to the prescribed temperature. The initiator, n-BuLi (0.31 mL, 0.5 mmol), was added using a syringe and the polymerization was allowed to proceed for 25 minutes. The polymerization was terminated using degassed methanol (Burdick-Jackson, HPLC grade). The resulting polymer was precipitated into isopropanol (600 mL), filtered, and dried at 50 °C in vacuo for 12-18 hours. An antioxidant such as Irganox 1010 (0.10 weight % compared to the polymer) was added to the precipitation solvent to retard oxidative degradation during subsequent storage.

Synthesis of Poly(1,3-cyclohexadiene)-*block*-Polyisoprene. A 250-mL round-bottomed flask containing anhydrous cyclohexane (60 mL, 0.54 mol) and 1,3-cyclohexadiene (6.7 mL, 62.5 mmol) was maintained at 25 °C. The TMEDA:nBuLi initiator (0.56 mmol) was added using a syringe and the polymerization was maintained at the prescribed temperature for 120 minutes. Following the polymerization of 1,3-cyclohexadiene, isoprene (17 mL, 78 mmol) and cyclohexane (300 mL, 1.71 mol) was added to the reaction. Upon addition of isoprene, the polymerization immediately changed to a light green color, indicative of the poly(isoprenyllithium) species in the presence of TMEDA. The isoprene polymerization was allowed to proceed for 120 minutes. The polymerization was terminated using degassed methanol (Burdick-Jackson, HPLC grade). The resulting polymer was precipitated into isopropanol (600 mL), filtered, and dried at 50 °C in vacuo for 12-18 hours. An antioxidant such as Irganox 1010 (0.10 weight % compared to the polymer) was added to the precipitation solvent to retard oxidative degradation during subsequent storage.

Atomic Force Microscopy. Atomic force microscopy (AFM) was performed on a Nanoscope III microscope from Digital Instruments Inc. operated at room temperature in the tapping mode in air using microfabricated cantilevers provided by the manufacturer (spring constant of 30 N m⁻¹). Digital Instruments image processing software was used for image analysis. The set point and tapping amplitude was 1.80 and 2.80 V, respectively. Silicon wafers were prepared by sonication in methanol and were subsequently dried under nitrogen. Polymer samples were prepared for AFM analysis by dissolving the polymer in toluene (4 wt%) and spin coating on prepared silicon wafers at 2000 rpm. The samples were annealed at 120 °C for 12 h. The samples were characterized by performing AFM in the tapping mode (TMAFM) as previously described²⁹⁸

²⁹⁸ Leclere, Ph., R. Lazzaroni, J.L. Bredas, J.M. Yu, P. Dubois, and R. Jerome. "Microdomain Morphology Analysis of Block Copolymers by Atomic Force Microscopy with Phase Detection Imaging." *Langmuir* **1996**, 12, 4317.

In situ mid-FTIR. In situ mid-FTIR spectra were collected with a ReactIR 1000 (MCT detector, S/N = 7500, resolution = 4 cm⁻¹) (ASI Applied Systems, Millersville, MD, www.asirxn.com) reaction system equipped with a light conduit and DiComp (diamond-composite) insertion probe. Reaction data was analyzed using ASI ReactIR software. The details and capabilities of the ReactIR 1000 reaction analysis system based on total attenuated reflectance (ATR) were described in detail previously.²⁹⁹

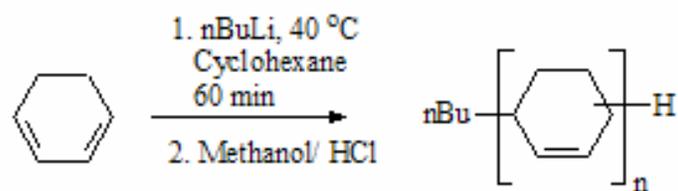
Polymer Characterization. ¹H NMR spectra were determined in CDCl₃ at 400 MHz with a Varian Spectrometer. Glass transition temperatures were determined using a Perkin-Elmer Pyris 1 DSC at a heating rate of 10 °C/min under nitrogen. Glass transition temperatures are reported as the midpoint of the change in heat capacity during the second heat. Molecular weights were determined using size exclusion chromatography (SEC) with a Water Alliance SEC system equipped with a Viscotek 150R viscosity detector. In addition, a Waters 717plus equipped with a Waters 2410 refractive index detector and a Wyatt Technology Minidawn MALLS detector was utilized for absolute molecular weight measurements. The dn/dc values were determined on-line using the calibration constant for the RI detector and the mass of the polymer sample. For all samples, it was assumed that 100% of the polymer eluted from the column during the measurement. SEC measurements were performed at 40 °C in chloroform at a flow rate of 1.0 mL/min.

²⁹⁹ Pasquale, A.J., and T.E. Long. "Real-Time Monitoring of the Stable Free Radical Polymerization of Styrene via in-Situ Mid-Infrared Spectroscopy." *Macromolecules* **1999**, 32, 7954.

5.4 Results and Discussion

Initial attempts to polymerize PCHD at a monomer concentration of two percent resulted in yields of less than 10% (Scheme 5-1). It is well documented that living anionic polymerization methods exhibit near quantitative yields at low monomer concentrations.³⁰⁰ Therefore, these results were unexpected, based on earlier reports. Statistically designed experimentation was performed to examine the nature of these anomalous results in an efficient manner. The effect of monomer concentration and temperature were simultaneously investigated. During these studies, the monomer concentration was varied from 0.8 to 20 wt% and the temperature was varied from 10 to 60 °C. Percent yield, molecular weight, and molecular weight distribution were determined for each reaction performed. A number of variables were held constant, which is necessary when performing a series of statistically designed experiments. The constants were: stirring rate, degree of protic impurities, ratio of TMEDA/nBuLi (5/4), ratio of monomer/nBuLi (125/1), and polymerization time (120 min). The levels of protic impurities were minimized through rigorous distillation procedures and titration of each reaction prior to initiating the polymerization. The results of these experiments are shown in Table 5-1. Figure 5-1 depicts the relationship between the reaction yield, monomer concentration, and reaction temperature. Both monomer concentration and temperature affected the reaction yield.

³⁰⁰ Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996.



Scheme 5-1. Synthesis of poly(1,3-cyclohexadiene).

Table 5-1. Results of the statistically designed experimentation examining the effect of temperature and monomer concentration on the polymerization of 1,3-cyclohexadiene.

Experiment	Monomer Wt%	Polymerization Temperature (°C)	$\langle M_n \rangle$ (GPC ^a)	$\langle M_w \rangle / \langle M_n \rangle^a$	Yield ^b %
1	0.80	10	734	1.49	14
2	18.0	60	23900	1.05	53
3	18.0	10	20700	1.40	96
4	0.80	60	450	1.18	1.6
5	10.4	40	9980	1.02	95
6	10.4	60	11800	2.10	65
7	0.80	30	1730	1.50	21
8	10.4	10	14800	1.03	36
9	27.0	30	27700	1.22	98
10	10.4	30	12100	1.09	98

^aThe SEC conditions were as follows: CHCl₃, 25 °C, DRI/Viscometric Analysis.

^bDetermined by gravimetric analysis

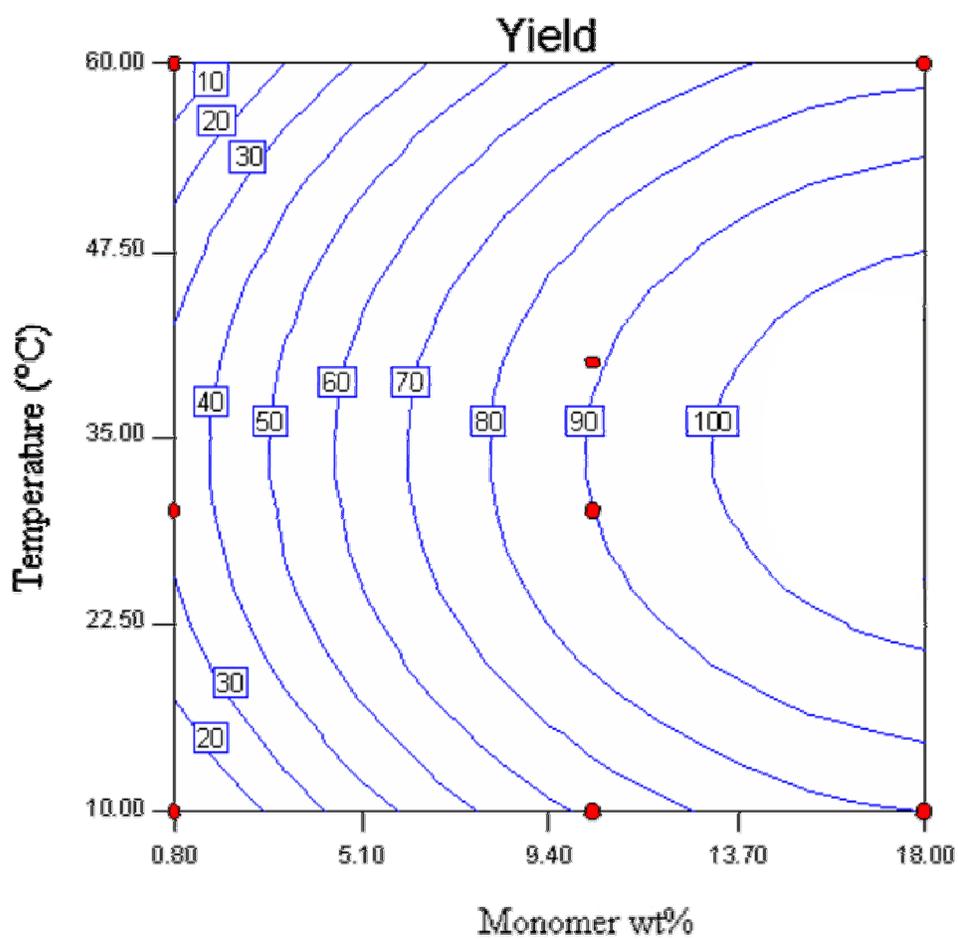


Figure 5-1. Topographical map illustrating the effect of reaction temperature and monomer weight percent on the yield of an anionic PCHD polymerization. Model was determined using the data from Table 5-1 utilizing a central composite model.

The equation describing the reaction yield as a function of both temperature and monomer weight percent is shown below (Equation 5-1).

Equation 5-1. Yield = -30.18829+8.31520*X+3.34640*Y+-0.20962*X²-0.048916*Y²

X= Monomer Weight Percent (%)

Y= Polymerization Temperature (°C)

A control experiment was performed at 40 °C with 10 wt% 1,3-cyclohexadiene concentration to verify the statistically derived equation. The polymerization exhibited a 95% yield, which is within the 95% confidence interval of the model. The effect of temperature and monomer concentration on the molecular weight of the resulting polymers is shown in Figure 5-3. The moles of nBuLi were held constant throughout the analysis, as previously noted above. The molecular weight of the polymer was described with the following equation (Equation 5-2).

Equation 5-2 M_n=1005.96+1112.41X

X= Monomer Weight Percent (%)

Under these polymerization conditions, the molecular weight of the macromolecule was not only dependant on the ratio of nBuLi to 1,3-cyclohexadiene, but also dependent on the weight percent of monomer. Equation 2 outlines the linear relationship between the molecular weight and the monomer concentration. A control experiment performed at 40 °C with a 15 wt% monomer concentration verified equation 5-2. The experiment resulted in a polymer with a number average molecular weight of 17,100 and a molecular weight distribution of 1.05, both values were within the 95% confidence interval of the model. These results indicate that the anionic polymerization of 1,3-cyclohexadiene was not a true living polymerization, when performed under the conditions described above. These results were attributed to deleterious side reactions associated with the polymerization of 1,3-cyclohexadiene (Scheme 5-2).

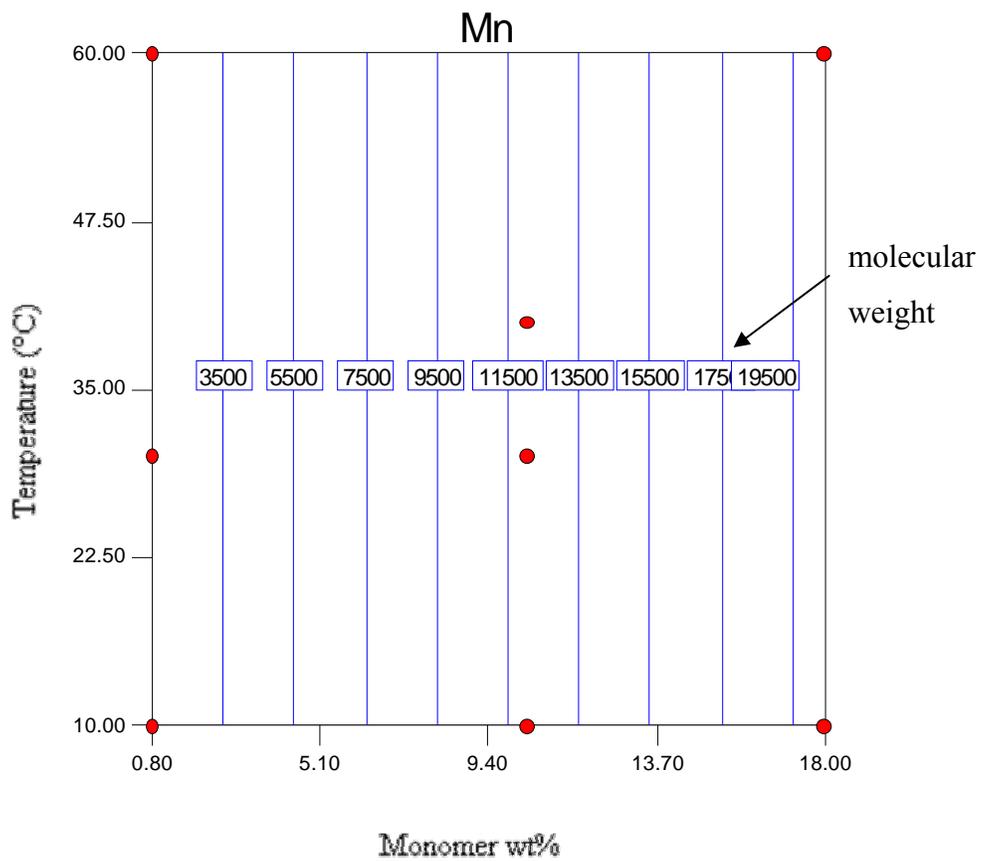
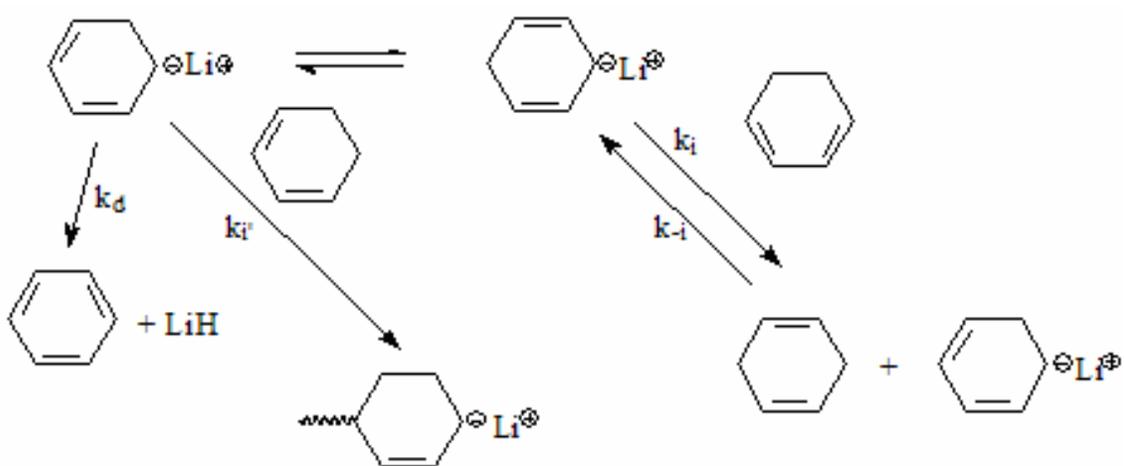


Figure 5-2 Topographical map illustrating the effect of reaction temperature and monomer weight percent on the yield of an anionic PCHD polymerization. Model was determined using the data from Table 5-1 utilizing a central composite model.



Scheme 5-2. Side reactions associated with the anionic polymerization of 1,3-cyclohexadiene. The metallated 1,3-cyclohexadiene species can proceed to form benzene, 1,4-cyclohexadiene, or reinitiate the polymerization.

These side reactions arise from chain transfer to monomer, resulting in a metallated 1,3-cyclohexadiene species. The metallated monomer species can proceed to form 1,4-cyclohexadiene,³⁰¹ benzene, or act as an initiator for the polymerization of 1,3-cyclohexadiene.³⁰² Statistical analysis of these results indicated there is less than a 1% chance these results were due to noise. Due to these results, all further polymerizations of 1,3-cyclohexadiene were performed at monomer concentrations of 8 wt% to 12 wt%. In addition, equations 1 and 2 were used to predict molecular weight and reaction yield.

A series of diblock copolymers containing PCHD and polyisoprene were synthesized via sequential addition. The molecular weight, molecular weight distribution, and glass transition temperatures of the macromolecules were determined (Table 5-2). The glass transition temperatures for these diblock elastomers were approximately -10 °C for the polyisoprene blocks and 140 °C for the PCHD blocks. The residual PCHD homopolymer present is attributed to the deleterious side reactions and similar results were described in previous studies.³⁰³ At the start of these experiments, the miscibility of the PCHD and polyisoprene blocks was studied and a series of multiblock copolymers were synthesized with various block molecular weights. The molecular weight of the blocks for these polymers were varied from 500 to 5000 and the polymers were characterized via DSC analysis.

³⁰¹ Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996. Francois, B., and X. Zhong. "Kinetics of 1,3-cyclohexadiene polymerization initiated by organolithium compounds in a non-polar medium." *Makromol. Chem.* **1990**, 191, 2743. Zhong, X., and B. Francois. "Kinetics of 1,3-cyclohexadiene polymerization by organolithium compounds in a non-polar medium. 1." *Makromol Chem* **1990**, 191, 2735. Hong, K., and J.W. Mays. "1,3-Cyclohexadiene Polymers. 3. Synthesis and characterization of Poly(1,3-cyclohexadiene-block-styrene)." *Macromolecules* **2001**, 34, 3540.

³⁰² Venkatsubramanian, N., and S. Siegel. "Aromatization and Disproportionation of 1,3-Cyclohexadiene by Potassium 3-Aminopropylamide." *J. Am. Chem. Soc.* **1988**, 53, 5972.

³⁰³ Hong, K., and J.W. Mays. "1,3-Cyclohexadiene Polymers. 3. Synthesis and characterization of Poly(1,3-cyclohexadiene-block-styrene)." *Macromolecules* **2001**, 34, 3540. Williamson, D.T., J.F. Elman, P.H. Madison, A.J. Pasquale, and T.E. Long. "Synthesis and Characterization of Poly(1,3-cyclohexadiene) Homopolymers and Star-shaped Polymers." *Macromolecules* **2001**, 34, 2108.

Table 5-2 Results for the synthesis of the PCHD-block-polyisoprene diblocks and alternating block copolymer study.

Polymer	PCHD Block $\langle M_n \rangle$ (GPC) ^a	Diblock $\langle M_n \rangle$ (Theoretical)	Diblock $\langle M_n \rangle$ (GPC) ^a	$\langle M_w \rangle / \langle M_n \rangle$
Poly(CHD)-b-(PI), 10K-20K	11100	30000	38400	1.03
Poly(CHD)-b-(PI), 15K-25K	12300	40000	55930	1.02
Poly(CHD)-b-(PI), (500-500)12	ND	12500	12600 ^b	1.50
Poly(CHD)-b-(PI), 10K-10K	ND	20000	22800 ^c	1.12 ^c
Poly(I)-b-P(CHD), 10K-10K	ND	20000	18900 ^c	1.75 ^c

^aThe SEC conditions were as follows: CHCl₃, 25 °C, DRI/Polystyrene Standards. ^bThe SEC conditions were as follows: CHCl₃, 25 °C, DRI/Viscometric Analysis. ^cThe SEC conditions were as follows: CHCl₃, 40 °C, MALLS.

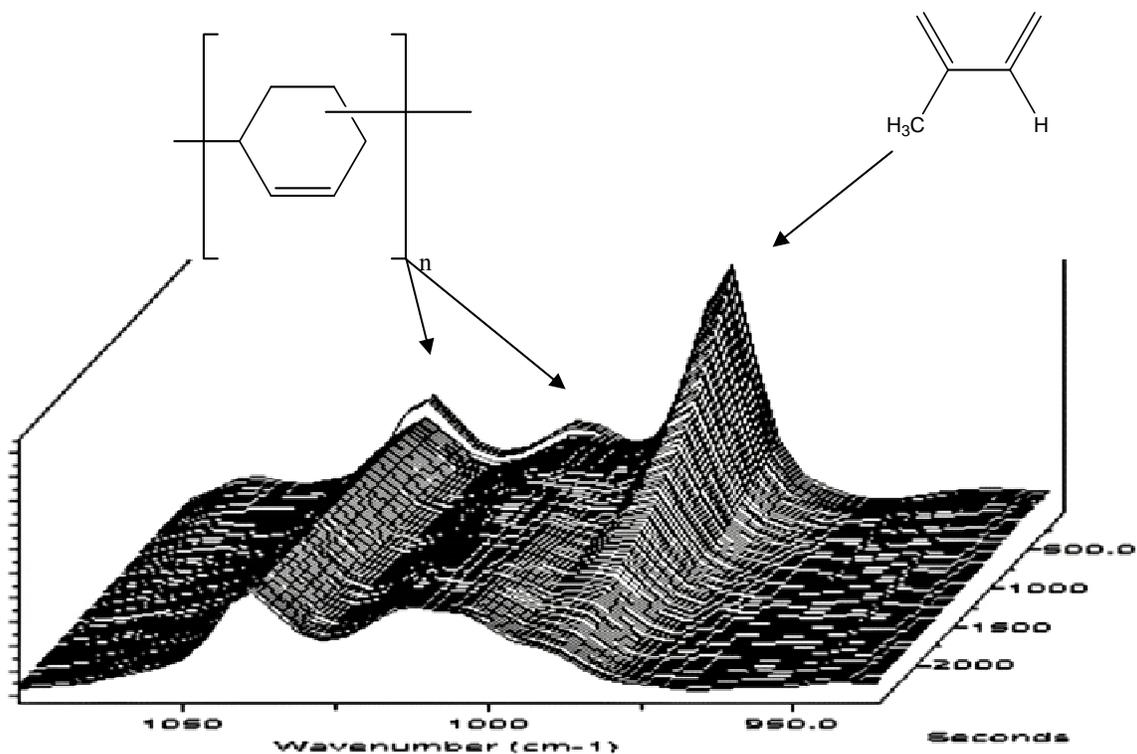


Figure 5-3 Waterfall plot of the polymerization of isoprene after the polymerization of 1,3-cyclohexadiene. Note the rapid consumption of the isoprene monomer (20 min) following the polymerization of 1,3-cyclohexadiene. The molecular weight of the poly(1,3-cyclohexadiene) block was 10000 and the molecular weight of the isoprene block was 10000.

Only copolymers with a block molecular weight of 500 exhibited a single intermediate T_g of 47 °C, which was attributed to a phase-mixing of the copolymer blocks. In contrast, the block copolymers with higher molecular weight blocks exhibited two transitions. The first lower temperature transition was associated with the isoprene blocks (-10 °C) and the higher transition was associated with PCHD blocks (130-140 °C).

In addition to the miscibility studies, the polymerization was monitored via in situ FTIR to determine the kinetics of the polymerization and the efficiency of the crossover. The polymerization rate of isoprene under these reaction conditions was determined to be 0.40 l mol⁻¹ s⁻¹ and polymerization rate of 1,3-cyclohexadiene was determined to be 0.31 l mol⁻¹ s⁻¹. The crossover efficiency from poly(1,3-cyclohexadienyllithium) to isoprene and the poly(isoprenyllithium) to 1,3-cyclohexadiene was determined in an in situ FTIR study. The crossover from 1,3-cyclohexadiene to isoprene was found to be rapid and efficient (Figure 5-3), with the rate of the isoprene polymerization in the diblock synthesis (0.37 l mol⁻¹ s⁻¹) closely matching the rate of an isoprene homopolymerization (0.40 l mol⁻¹ s⁻¹), under identical reaction conditions. However, the crossover from poly(isoprenyllithium) to 1,3-cyclohexadiene was determined to be inefficient, as demonstrated by the reduced rate of the 1,3-cyclohexadiene polymerization. Here, the polymerization of 1,3-cyclohexadiene was reduced (0.18 l mol⁻¹ s⁻¹) relative to the rate of a 1,3-cyclohexadiene homopolymerization (0.31 l mol⁻¹ s⁻¹).

These in situ results were corroborated with a series of classical crossover experiments. Poly(1,3-cyclohexadiene-*block*-isoprene) and poly(isoprene-*block*-1,3-cyclohexadiene) diblock copolymers with identical compositions were synthesized (Figure 5-4). The molecular weight distribution of the poly(1,3-cyclohexadiene-*block*-isoprene) (1.12) was narrower than that of the poly(isoprene-*block*-1,3-cyclohexadiene) (1.75). In addition, the molecular weight of the poly(1,3-cyclohexadiene-*block*-isoprene) diblock copolymer was controlled. The rapid crossover from the poly(1,3-cyclohexadienyllithium) to isoprene was attributed to the physical structure of

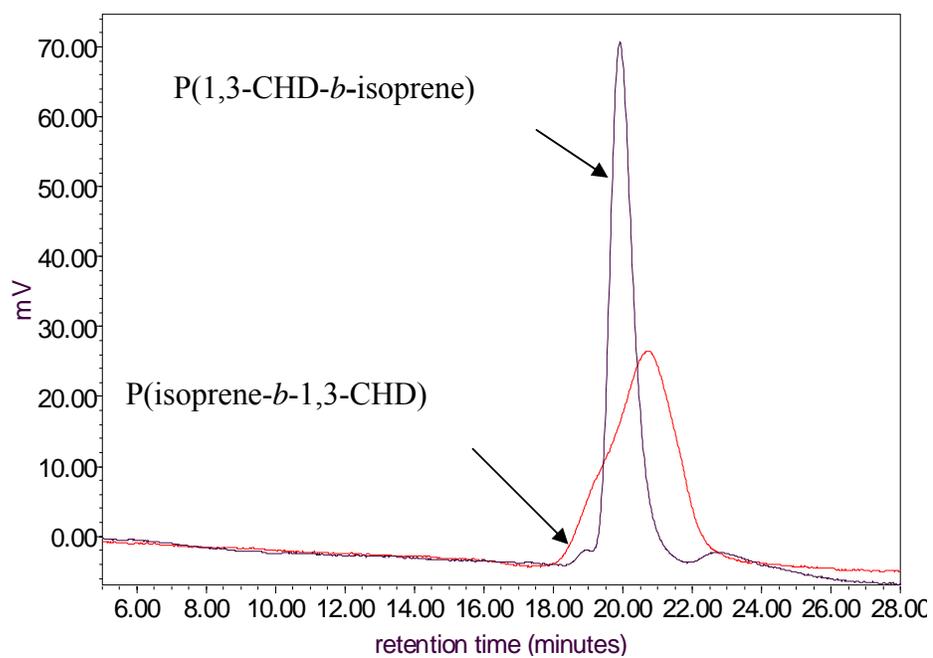


Figure 5-4 SEC of the poly(1,3-cyclohexadiene-*block*-isoprene) (PDI = 1.12) and poly(isoprene-*block*-1,3-cyclohexadiene) (PDI = 1.75) diblock copolymers. SEC conditions: CHCl₃, 40 °C, MALLS.

propagating carbanions.³⁰⁴ The primary allylic carbanion of poly(isoprenyllithium) is expected to be more stable than the secondary allylic carbanion of poly(1,3-cyclohexadienyllithium).

Multiple glass transition temperatures suggested that the poly(1,3-cyclohexadiene) block phase separates from the polyisoprene block. Classically, the presence of microphase separation has been verified using transmission electron microscopy in combination with selective chemical imaging techniques. Imaging the microphase separation present in these poly(1,3-cyclohexadiene) containing diblocks represented a unique challenge due to the similarity of the polymer blocks. The polyisoprene and the poly(1,3-cyclohexadiene) blocks were both susceptible to the classical osmium or ruthenium staining approaches. In previous studies, the polyisoprene block was selectively hydrogenated and the poly(1,3-cyclohexadiene) block was stained with osmium tetroxide. Unfortunately, the hydrogenation of the polyisoprene block alters the interaction between the poly(1,3-cyclohexadiene) and the polyisoprene block, thereby effecting both the domains sizes and the degree of microphase separation. To avoid this difficulty, we employed atomic force microscopy in the tapping mode (TMAFM) to examine the microphase separation between the poly(1,3-cyclohexadiene) block and the polyisoprene block. Silicon wafers were spin coated with a 4 wt% solution of the elastomer in toluene and the samples were annealed at 120 °C for 12 h under vacuum. The presence of microphase separation between the poly(1,3-cyclohexadiene) block and the polyisoprene block was readily apparent (Figure 5-5). The image on the left is a topographical image of the surface and the image on the right is the phase contrast image of the surface. Previous studies have described the utility of the phase contrast image for the detection of microdomains based on the differences in the viscoelastic response of the various blocks. The reduced interaction time of the AFM tip with the poly(1,3-cyclohexadiene) domains was expected produce near zero phase lag values causing these domains to appear darker (Figure 5-5, right). The polyisoprene domains were expected to remain in contact with the AFM tip forcing a

³⁰⁴ Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996.

delay in the tip motion and an increase in the phase lag, which would give rise to the brighter areas in the image. In spite of the smoothness of the surface, domains were also apparent in the topographical image (Figure 5-5, left). Previous studies suggested that the height difference between the different domains arises from the ability of the low T_g domains to relax by protruding out of the surface of the film. Therefore, the lighter regions in image were attributed to the protruding domains of the polyisoprene blocks. The regions in the AFM image were also assigned based on the composition of the star-shaped elastomer, which was 30% poly(1,3-cyclohexadiene) and 70% polyisoprene. Using this similar analysis, the dark regions of the phase contrast image that represented approximately 30% of the image were attributed to the hard domains of the poly(1,3-cyclohexadiene) blocks. These block copolymer studies were utilized in the efficient synthesis a series of triblock copolymers.

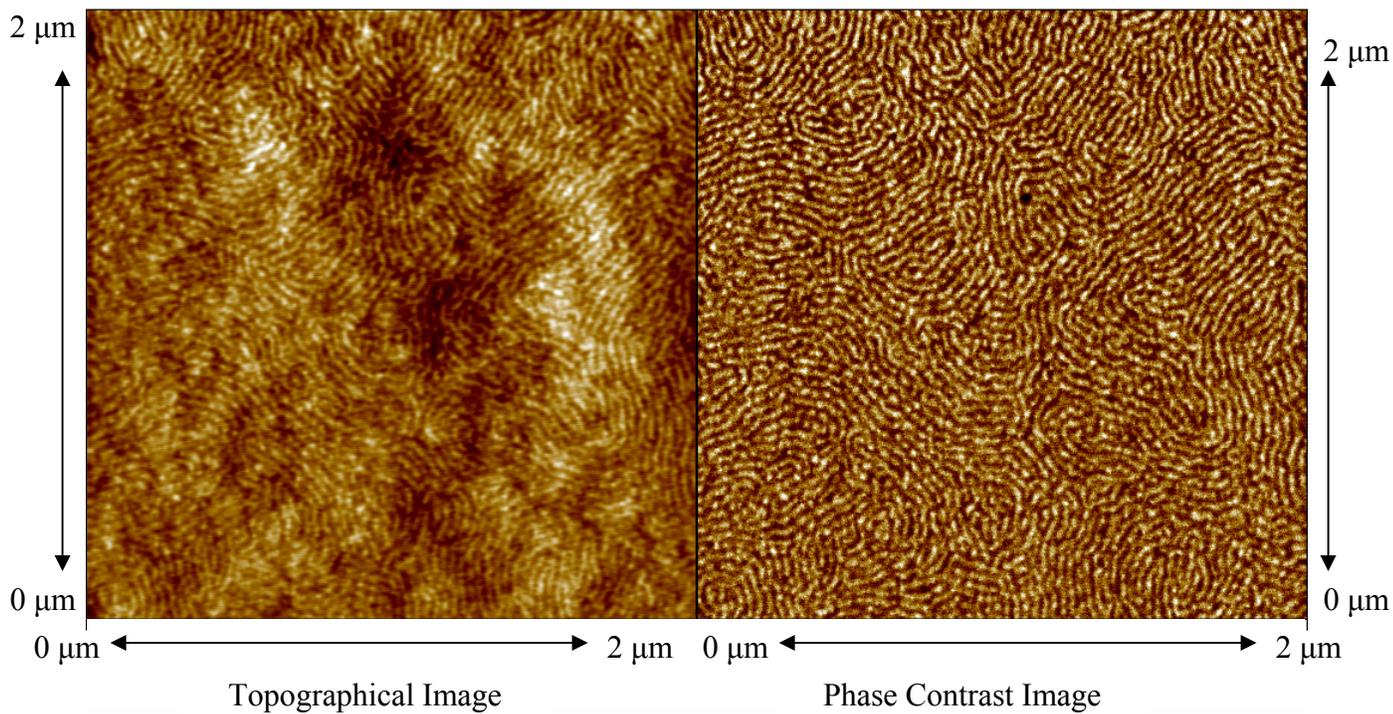
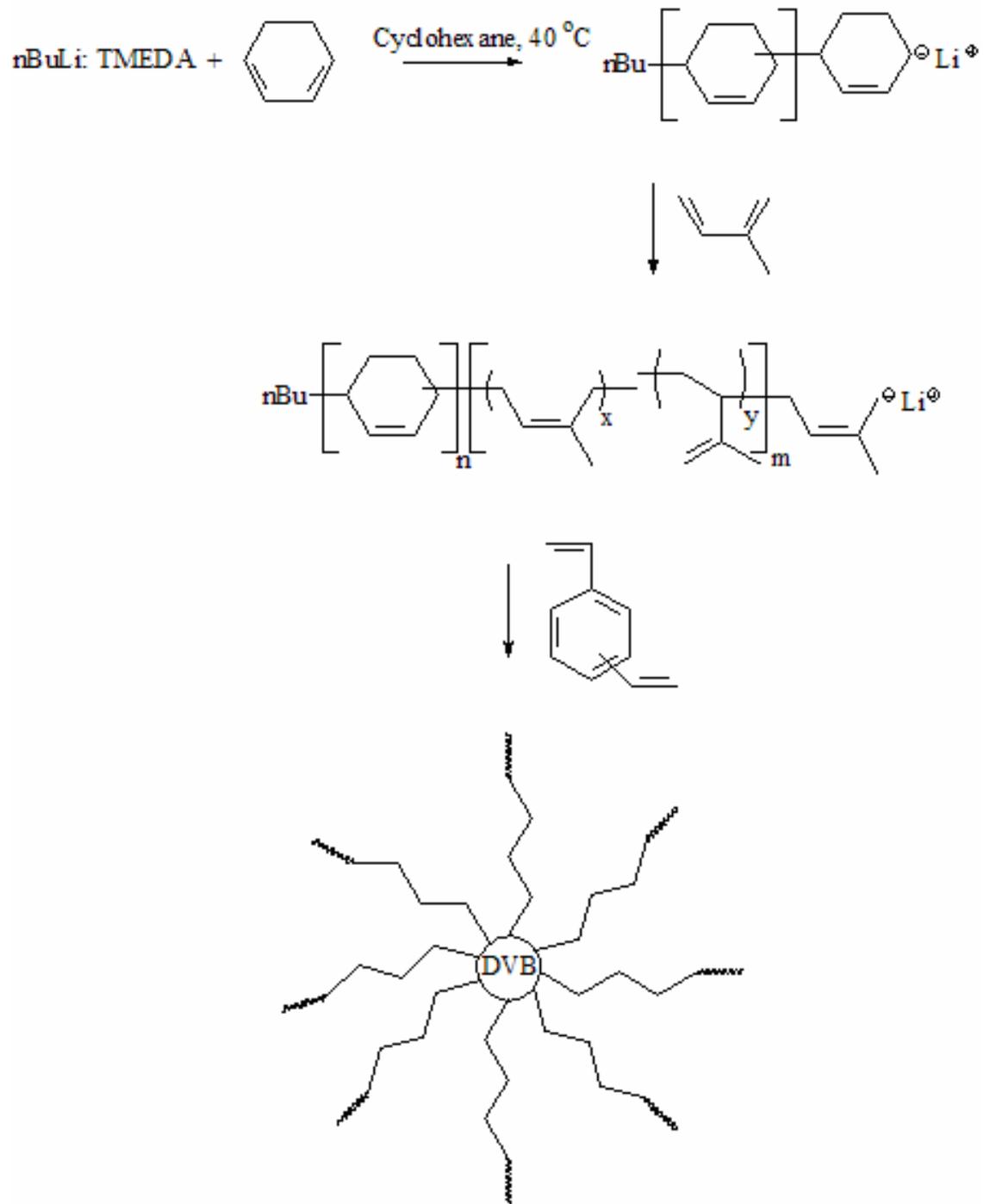


Figure 5-5 TMAFM analysis of poly(1,3-cyclohexadiene-*block*-isoprene) containing 30% poly(1,3-cyclohexadiene) indicating the presence of microphase separation between poly(1,3-cyclohexadiene) and polyisoprene.

A series of thermoplastic elastomers containing PCHD were synthesized (Scheme 5-2). These thermoplastic elastomers were synthesized via the coupling of poly(1,3-cyclohexadiene-*block*-isoprene) diblock copolymers together with divinyl benzene (DVB). The PCHD blocks were synthesized at a monomer concentration of 10 wt%. After completion of the 1,3-cyclohexadiene polymerization, the poly(1,3-cyclohexadienyllithium) chain ends were seeded with isoprene and the reaction solution was diluted with additional cyclohexane. After dilution, the remaining isoprene monomer was added to the reaction solution. These steps were found necessary to reduce the reaction solution viscosity and maintain the reactivity of the chain ends. The isoprene polymerization was allowed to proceed for approximately eight half-lives prior to the addition of the coupling agent. The elastomers synthesized are outlined in Table 5-4. The ratio of moles of DVB to moles of n-butyllithium was maintained at 3:1 for all of the elastomers synthesized. The PCHD content was varied from 26% to 70%. The molecular weight distributions varied from 1.36 to 1.28, as expected for DVB coupled star-shaped macromolecules (Figure 5-5). The narrow molecular weight distributions confirmed the persistence and high reactivity of poly(1,3-cyclohexadienyllithium) species. Unfortunately, a large percentage of the poly(1,3-cyclohexadiene) homopolymers and poly(1,3-cyclohexadiene-*block*-isoprene) diblock copolymers were present with the star-shaped elastomers. These polymers formed clear elastomeric films, when cast from a chloroform solution. These films were characterized for their elastomeric properties (Table 5-4).



Scheme 5-3 Synthetic methodology utilized to synthesize poly(1,3-cyclohexadiene-*block*-isoprene) star-shaped polymers.

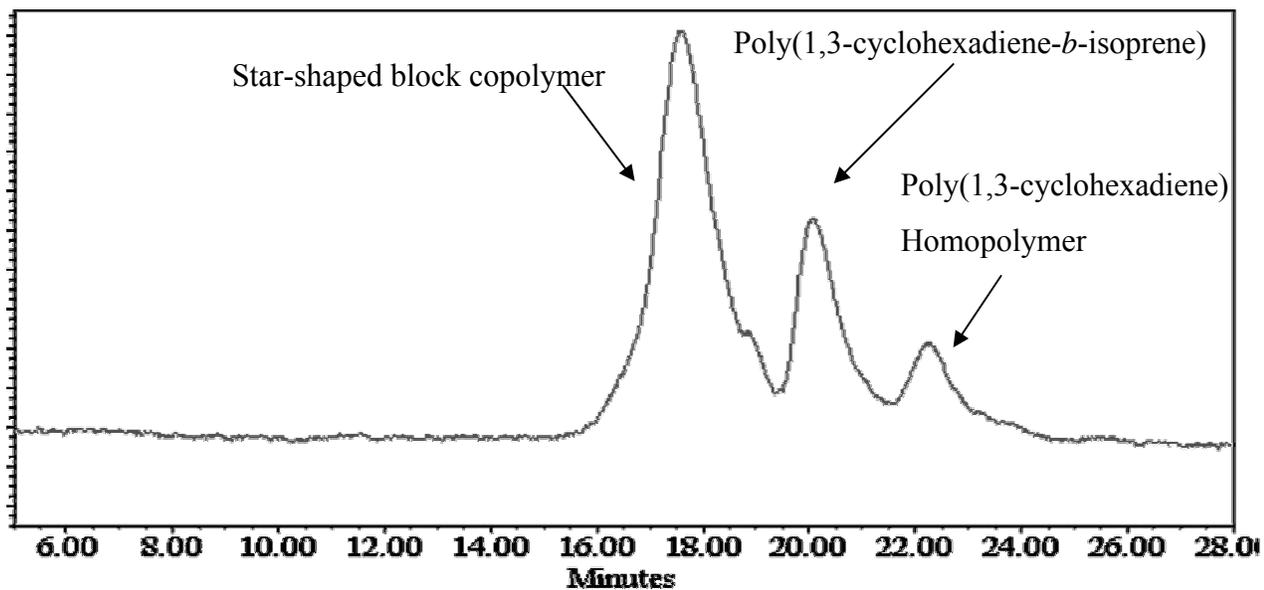


Figure 5-6 SEC of the star shaped polymer with a DVB/nBuLi ratio of 3:1 and an arm length of 40000 g/mol. SEC conditions: CHCl₃, 40 °C, MALLS.

Table 5-3 Star-shaped thermoplastic elastomers synthesized using DVB. The DVB/nBuLi ratio maintained at 3/1.

1,3-CHD wt %	$\langle M_n \rangle$ poly(1,3-CHD) Theoretical	$\langle M_n \rangle$ Arm Theoretical	$\langle M_w \rangle$ Star *	Star $\langle M_w \rangle / \langle M_n \rangle^*$
16 %	10,000	50,000	110,000	1.28
26 %	10,000	40,000	82,000	1.36
38 %	10,000	26,000	100,000	1.35

*SEC conditions: 40 °C, Chloroform, MALLS. All star-shaped polymers were synthesized at a DVB/nBuLi of 3:1.

Table 5-4 Mechanical properties of poly(1,3-cyclohexadiene-block-isoprene) star-shaped macromolecules.

1,3-CHD wt %	T _g polyisoprene	T _g Poly(1,3- cyclohexadiene)	Peak Stress (MPa)*	Percent Strain at Break (%)*
21 %	1 °C	140 °C	4.5	1195
25 %	-10 °C	140 °C	15	735
39 %	-7 °C	140 °C	17	541
100%	NA	138 °C	23	1.8

Determined according to ASTM #D412

As expected increased percentages of poly(1,3-cyclohexadiene) resulted in an increased peak stress and a decreased percent strain at break.

5.5 Conclusion

The effect of various factors on the polymerization of 1,3-cyclohexadiene was examined. The monomer concentration and reaction temperature affected the polymer molecular weight and reaction yield. Higher concentrations of monomer resulted in higher molecular weights and increased reaction yields. The presence of deleterious side reactions is believed to be responsible for these effects. These results were utilized to synthesize a series of poly(1,3-cyclohexadiene-*block*-isoprene) diblock copolymers with narrow molecular weight distributions (1.06) and high molecular weights (50000). Phase separation between PCHD blocks and polyisoprene blocks occurred at block sizes in excess of 500. Poly(1,3-cyclohexadienyllithium) exhibited an efficient crossover isoprene. A series of star-shaped thermoplastic elastomers were synthesized with the coupling agent divinyl benzene (DVB). High molecular weight (80000 - 100000) star-shaped thermoplastic elastomers with relatively narrow molecular weight distributions (1.28 - 1.36) were synthesized. A range of PCHD content from 16% to 38% was introduced into the thermoplastic elastomers.

CHAPTER 6

Influence of Tertiary Diamines in the Synthesis of High Molecular Weight Poly(1,3-cyclohexadiene)

Taken From:

D. T. Williamson, and T.E. Long “Influence of Tertiary Diamines in the Synthesis of High Molecular Weight Poly(1,3-cyclohexadiene)” *J. Polym. Sci., Part A. Polym. Chem.* **2003**, accepted for publication.

6.1 Abstract

The synthesis of high molecular weight poly(1,3-cyclohexadiene) homopolymers was examined. Use of a pre-formed initiator adduct facilitated the synthesis of high molecular weight poly(1,3-cyclohexadiene) ($\langle M_n \rangle = 40000$ g/mol) of narrow molecular weight distribution ($\langle M_w \rangle / \langle M_n \rangle = 1.12$). A plot of kinetic chain length versus time indicated termination steps were minimized and chain transfer steps were eliminated when a pre-formed initiator adduct was used. The polymerization was highly sensitive to both temperature and choice of tertiary diamine. Use of bulky tertiary diamines, such as spartiene or dipiperidinoethane, resulted in poor polymerization control and reduced polymerization rates ($7.0 \times 10^{-5} \text{ sec}^{-1}$) as compared to tetramethylethylenediamine (TMEDA) mediated polymerizations ($1.5 \times 10^{-4} \text{ sec}^{-1}$). A series of poly(1,3-cyclohexadiene-*block*-isoprene) diblock copolymers were synthesized to determine the molar crossover efficiency of the polymerization. Polymerizations performed at 25 °C exhibited improved molar crossover efficiencies (93%) versus polymerizations performed at 40 °C (80%). The improved crossover efficiency was attributed to the reduction of termination events at reduced polymerization temperatures. The microstructure of these polymers was calculated using ^1H NMR spectroscopy and the relationship between molecular weight and glass

transition temperature at infinite molecular weight was determined for polymers containing 70% 1,2-addition (150 °C) and 80% 1,4-addition (138 °C).

6.2 Introduction

Poly(1,3-cyclohexadiene) polymers were prepared using a variety of different synthetic methods, including free radical, coordination and anionic polymerization strategies.³⁰⁵ The polymerization of 1,3-cyclohexadiene is of considerable interest as poly(1,3-cyclohexadiene) exhibits a unique combination of physical properties including excellent optical (index of refraction = 1.572) and thermal properties ($T_g = 150\text{ }^\circ\text{C}$).³⁰⁶ In addition, these polymers can be chemically modified to form a variety of unique polymeric derivatives, such as poly(cyclohexylene) and poly(phenylene).³⁰⁷ Unfortunately, a number of molecular weight limiting side reactions plague the polymerization of 1,3-cyclohexadiene.³⁰⁸ Despite previous attempts to polymerize 1,3-

³⁰⁵ Sharaby, Z., M. Martan, and J. Jagur-Grodzinski. "Stereochemistry of Poly(1,3-cyclohexadienes). NMR Investigation of Effects Due to the Solvent Medium and to the Mechanism of Polymerization." *Macromolecules* **1982**, 15, 1167. Sharaby, Z., J. Jagur-Grodzinski, M. Martan, and D Vofsi. "Kinetics and Mechanism of the Anionic Polymerization of Cyclohexadienes Initiated by Naphthalene Radical Anions and Dianions." *J. Polym. Sci., Polym. Chem. Ed.* **1982**, 20, 901. Lefebvre, G, and F. Dawans. "1,3-Cyclohexadiene polymers. I. Preparation and aromatization of poly-1,3-cyclohexadiene." *J. Polym. Sci.* **1964**, A2, 3277. Mango, L.A., and R.W. Lenz. "Organometallic reactions which control molecular weight in the anionic polymerization of 1,3-cyclohexadiene." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **1971**, 12, 402. Mango, L.A., and R.W. Lenz. "Mechanism and stereochemistry in the anionic polymerization of 1,3-cyclohexadiene and the diimide hydrogenation of polymers." *U.S. Nat. Tech. Inform. Serv.* **1972**, 12, 402.

³⁰⁶ Williamson, D.T., K. Brazhnik, A.J. Pasquale, and T.E. Long. "Synthesis and Characterization of Hydrogenated Poly(1,3-cyclohexadiene) Star-Shaped Polymers." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **2000**, 41, 1544. Williamson, D.T., J.F. Elman, P.H. Madison, A.J. Pasquale, and T.E. Long. "Synthesis and Characterization of Poly(1,3-cyclohexadiene) Homopolymers and Star-shaped Polymers." *Macromolecules* **2001**, 34, 2108.

³⁰⁷ Williamson, D.T., T.E. Glass, and T.E. Long. "Aromatization of poly(1,3-cyclohexadiene-co-styrene): A novel route to soluble poly(phenylene-co-styrene) copolymers." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **2002**, 43, 1201. Williamson, D.T., and T.E. Long. "Self-assembled poly(phenylene) containing macromolecules via the controlled anionic polymerization of 1,3-cyclohexadiene." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **2002**, 43, 330. Hong, K., J.W. Mays, Y. Wang, and R. Advincula. "Synthesis and Aromatization of Polycyclohexadiene(PCHD) Homo and Block Copolymers: Towards Processible Poly-p-Phenylene (PPP) Derivatives." *PMSE Preprints* **1999**, 80, 116.

³⁰⁸ Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996. Hong, K., and J.W. Mays. "1,3-Cyclohexadiene Polymers. 1. Anionic Polymerization." *Macromolecules* **2001**, 34, 782.

cyclohexadiene in a controlled fashion, the molecular weight of the resulting polymers was unpredictable and the molecular weight distributions were broad.³⁰⁹

In 1997, Natori reported the first living anionic polymerization of 1,3-cyclohexadiene in the presence of the ligating agent tetramethylethylenediamine (TMEDA).³¹⁰ The polymerization of 1,3-cyclohexadiene in the presence of TMEDA exhibited a linear relationship between the number average molecular weight and the percent conversion, which the authors attribute to a living polymerization. Natori et al. evaluated a range of tertiary amine/organolithium combinations for their efficacy in maintaining a controlled anionic polymerization of 1,3-cyclohexadiene.³¹¹ Of the combinations studied, TMEDA/nBuLi adducts were the most effective in controlling the polymerization and use of a pre-formed initiator was critical to controlling the polymerization.

³⁰⁹ Mango, L.A., and R.W. Lenz. "Organometallic reactions which control molecular weight in the anionic polymerization of 1,3-cyclohexadiene." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **1971**, 12, 402. Mango, L.A., and R.W. Lenz. "Mechanism and stereochemistry in the anionic polymerization of 1,3-cyclohexadiene and the diimide hydrogenation of polymers." *U.S. Nat. Tech. Inform. Serv.* **1972**, 12, 402.

³¹⁰ Natori, I. "Synthesis of Polymers with an Alicyclic Structure in the Main Chain. Living Anionic Polymerization of 1,3-Cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System." *Macromolecules* **1997**, 30, 3696. Natori, I., and S. Inoue. "Living Anionic Polymerization of 1,3-cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System. Copolymerization and Block Copolymerization with Styrene, Butadiene, and Isoprene." *Macromolecules* **1998**, 31, 982. Natori, I., and S. Inoue. "Anionic Polymerization of 1,3-cyclohexadiene with Alkylolithium/Amine Systems. Characteristics of n-Butyllithium/N,N,N',N'-Tetramethylethylenediamine System for Living Anionic Polymerization." *Macromolecules* **1998**, 31, 4687. Natori, I., K. Imaizumi, H. Yamagish, and M. Kazunori. "Hydrocarbon Polymers Containing Six-Membered Rings in the Main Chain. Microstructure and Properties of Poly(1,3-cyclohexadiene)." *J. Polym. Sci., Part B: Polym. Phys.* **1998**, 36, 1657. Imaizumi, K., Tomohiro Ono, I. Natori, Shinichi Sakuri, and Kunihiro Takedo. "Microphase-Separated Structure of 1,3-Cyclohexadiene/Butadiene Triblock Copolymers and Its Effect on Mechanical and Thermal Properties." *J. Polym. Sci., Part B: Polym. Phys.* **2001**, 39, 13.

³¹¹ Natori, I., and S. Inoue. "Anionic Polymerization of 1,3-cyclohexadiene with Alkylolithium/Amine Systems. Characteristics of n-Butyllithium/N,N,N',N'-Tetramethylethylenediamine System for Living Anionic Polymerization." *Macromolecules* **1998**, 31, 4687.

Previous studies have also demonstrated that alkyllithium species are present as aggregates in hydrocarbon solutions.³¹² These aggregates exist in various degrees of association from hexamers of nBuLi in hexane, to the putative polystyryllithium dimers found in cyclohexane.³¹³ While early studies suggested that these aggregates do not play a role in organolithium chemistry and simply serve as a reservoir for reactive alkyllithium species,³¹⁴ recent studies have clearly demonstrated the role of the alkyllithium aggregates in the direct mediation of alkyllithium chemistry. For example, a fully associated poly(styryllithium) species was shown to react with gaseous butadiene below the glass transition temperature of polystyrene verifying the ability of an aggregated anion to react with monomer.³¹⁵ In addition, recent reports by Collum and coworkers suggested that the interaction of various modifiers with both nBuLi and lithium diisopropylamide (LDA) resulted in well-defined adducts consisting of both the alkyllithium and the modifier species.³¹⁶ A well-defined dimeric TMEDA/nBuLi adduct was shown to occur in a hydrocarbon solution, which was further implicated in a mechanism involving the pre-complexation of anisole and the adduct during ortholithiation.³¹⁷

³¹² Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996. Bywater, S., and D.J. Worsfold. "Alkyllithium anionic polymerization initiators in hydrocarbon solvents." *J. Organomet. Chem.* **1967**, 10, 1.

³¹³ Bywater, S., and D.J. Worsfold. "Alkyllithium anionic polymerization initiators in hydrocarbon solvents." *J. Organomet. Chem.* **1967**, 10, 1. Glaze, W.H., and C.H. Freeman. "Cyclohexylmetal compounds. IV. The effect of aggregate size on the reactivity of alkyllithium compounds." *J. Am. Chem. Soc.* **1969**, 91, 7198. Lewis, H.L., and T.L. Brown. "Association of alkyllithium compounds in hydrocarbon media. Alkyllithium-base interactions." *J. Am. Chem. Soc.* **1970**, 92, 4664.

³¹⁴ Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996.

³¹⁵ Young, R. N., L.J. Fetters, J.S. Huang, and R. Krishnamoorti. "Some Light on the Concept of Unreactivity Arising from Active Center Association in Anionic Polymerization." *Polymer International* **1994**, 33, 217.

³¹⁶ Hoffman, D., and D.B. Collum. "Binding of Diamines to nButyllithium Dimers: Relative Solvation Energies and Evidence of Correlated Solvation." *J. Am. Chem. Soc.* **1998**, 120, 5810. Rennels, R.A., A.J. Maliakal, and D.B. Collum. "Ortholithiation of Anisole by n-BuLi-TMEDA: Reaction via Disolvated Dimers." *J. Am. Chem. Soc.* **1998**, 120, 421. Remenar, J.F., B. L. Lucht, and D.B. Collum. "Lithium Diisopropylamide Solvated by Monodentate and Bidentate Ligands: Solution Structures and Ligand Binding Constants." *J. Am. Chem. Soc.* **1997**, 119, 5567.

³¹⁷ Rennels, R.A., A.J. Maliakal, and D.B. Collum. "Ortholithiation of Anisole by n-BuLi-TMEDA: Reaction via Disolvated Dimers." *J. Am. Chem. Soc.* **1998**, 120, 421.

In early studies, the impact of polar modifiers, such as tetrahydrofuran, diethyl ether, and triethyl amine was attributed to an increase in the solution polarity. More recent studies support this conclusion but also discriminate between mono and bidentate additives.³¹⁸ In addition to increasing solution polarity, bidentate additives, such as TMEDA and dipiperidinoethane, were shown to interact directly with the alkylolithium species and form almost exclusively dimers in hydrocarbon solutions.³¹⁹ Direct interaction of the bidentate additive dipiperidinoethane (dipip) with the propagating center of the polymerization is believed to be responsible for the higher percentage of 1,2-addition in butadiene polymerizations (97%) than in isoprene polymerizations (80%).³²⁰ The difference in microstructure between these polymerizations was attributed to the steric interaction between the bulky dipip species and the pendant methyl group present in polyisoprenyllithium, that is absent in polybutadienyllithium. Therefore, the close association of the polymeric alkylolithium chain end and the bidentate additive in the aggregate present in hydrocarbon solvents was demonstrated to have a strong impact on the polymerization mechanism and the resulting polymer product.

Recently, Natori and coworkers reported the synthesis of a series of poly(1,3-cyclohexadiene) polymers using a TMEDA/nBuLi initiator adduct at 40 °C in cyclohexane.³²¹ This adduct was reported to be efficient for the synthesis of a range of

³¹⁸ Beckelmann, D., and F. Bandermann. "Classification of Polar Additives with Respect to Their Influence on the Microstructure in Anionic Polymerization of Isoprene with Butyllithium by Transition Energy Measurements." *J. Appl. Polym. Sci.* **1999**, 73, 1533.

³¹⁹ Rennels, R.A., A.J. Maliakal, and D.B. Collum. "Ortholithiation of Anisole by n-BuLi-TMEDA: Reaction via Disolvated Dimers." *J. Am. Chem. Soc.* **1998**, 120, 421. Remenar, J.F., B. L. Lucht, and D.B. Collum. "Lithium Diisopropylamide Solvated by Monodentate and Bidentate Ligands: Solution Structures and Ligand Binding Constants." *J. Am. Chem. Soc.* **1997**, 119, 5567.

³²⁰ Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996.

³²¹ Natori, I. "Synthesis of Polymers with an Alicyclic Structure in the Main Chain. Living Anionic Polymerization of 1,3-Cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System." *Macromolecules* **1997**, 30, 3696. Natori, I., and S. Inoue. "Living Anionic Polymerization of 1,3-cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System. Copolymerization and Block Copolymerization with Styrene, Butadiene, and Isoprene." *Macromolecules* **1998**, 31, 982.

polymer molecular weights and polymer systems containing poly(1,3-cyclohexadiene), such as poly(1,3-cyclohexadiene-*block*-butadiene) and poly(1,3-cyclohexadiene-*block*-isoprene). A ratio of TMEDA/nBuLi of 5/4 was necessary to synthesize poly(1,3-cyclohexadiene) homopolymers with narrow molecular weight distributions (1.10). When higher molecular weight polymers were synthesized (40000) the molecular weight distribution broadened (1.30) due the occurrence of deleterious side reactions, such as chain transfer to monomer.

In a more recent study, Mays et al. described the synthesis of poly(1,3-cyclohexadiene) homopolymers with a variety of different additives³²² In addition to the TMEDA/nBuLi initiator adduct studied by Natori and coworkers. The bidentate additive dimethoxyethane (DME) and 1,4-diazobicyclooctadiene (DABCO) were determined to be similarly effective in the controlled polymerization of 1,3-cyclohexadiene. However, the effect of the ratio of these additives to alkyllithium was not systematically studied and a wide range of ratios were utilized. Furthermore, the broadening of the molecular weight distribution (1.34) at higher molecular weights indicated the polymerization control decreased as higher molecular weights were targeted (46000).

Poly(1,3-cyclohexadiene) typically exhibits poor solubility in a wide range of solvents and often precipitates during the polymerization when the reaction is performed in cyclohexane.³²³ In order to improve polymer solubility and polymerization control, Mays et al. utilized benzene as the polymerization solvent while performing the polymerizations at reduced temperatures (0 – 20 °C).³²⁴ Despite the significant advances of both Natori and Mays, the polymerization of 1,3-cyclohexadiene still

³²² Hong, K., J.W. Mays, Y. Wang, and R. Advincula. "Synthesis and Aromatization of Polycyclohexadiene(PCHD) Homo and Block Copolymers: Towards Processible Poly-p-Phenylene (PPP) Derivatives." *PMSE Preprints* **1999**, 80, 116.

³²³ Williamson, D.T., J.F. Elman, P.H. Madison, A.J. Pasquale, and T.E. Long. "Synthesis and Characterization of Poly(1,3-cyclohexadiene) Homopolymers and Star-shaped Polymers." *Macromolecules* **2001**, 34, 2108.

³²⁴ Hong, K., and J.W. Mays. "1,3-Cyclohexadiene Polymers. 1. Anionic Polymerization." *Macromolecules* **2001**, 34, 782.

suffered from deleterious side reactions at higher targeted molecular weights. In addition, the polymerizations required more polar polymerization solvents, such as benzene, due to reduced polymer solubility. These earlier studies did not fully examine the degree of livingness of the polymerization or examine the effect of various amines on the degree of termination or chain transfer.

We report herein the improved polymerization of 1,3-cyclohexadiene in the presence of a *pre-formed* TMEDA/nBuLi initiator adduct in an industrially feasible and non-polar solvent. Use of these polymerization conditions resulted in reduced molecular weight distributions (1.12) even at higher molecular weights (42000). In addition to the TMEDA/nBuLi initiator adduct, a range of other additives were studied to assess their viability as polymerization initiators for 1,3-cyclohexadiene. The degree of livingness of the polymerization processes were evaluated by examining the molecular weight distribution, the molar crossover efficiency to isoprene, and degree of chain transfer.

6.3 Experimental Section

Materials. 1,3-cyclohexadiene (Aldrich, 98%) was degassed several times and distilled at reduced pressure (0.10 mmHg, 10 °C) from dibutylmagnesium (DBM, 0.84 M). TMEDA (Aldrich, 99%), dipip (Aldrich, 98%), and sparteine (Aldrich, 98%) were distilled at reduced pressure (0.13 - 0.16 mmHg, 10 °C) from calcium hydride and stored under nitrogen at -25 °C until ready for use. DABCO (Aldrich, 98%) was sublimed under reduced pressure (0.13 - 0.16 mmHg, 25 °C) three times and diluted into cyclohexane. Cyclohexane (Burdick-Jackson, HPLC grade) was stirred over sulfuric acid (10:1 cyclohexane:sulfuric acid) for 7 - 10 days, decanted, and distilled from a sodium dispersion under nitrogen immediately prior to use. All reagents were transferred using syringe and cannula techniques under ultrapure (99.999%) nitrogen.

Polymer Synthesis

Synthesis of a Pre-formed TMEDA/nBuLi Adduct. A 25-mL round-bottomed flask that contained cyclohexane was charged with nBuLi (5.0 mL, 8 mmol) and cooled to -20 °C. The tertiary diamine TMEDA (0.59 mL, 4 mmol) was added drop-wise. Upon addition of the tertiary diamine, a white TMEDA/nBuLi adduct rapidly precipitated. Prior to initiation of the polymerization, the adduct was re-dissolved by heating to 67 °C and used to initiate the polymerization. It was observed that the pre-formed complex precipitate became soluble in the cyclohexane solution at 67 °C.

Synthesis of Poly(1,3-cyclohexadiene). A 100-mL round-bottomed flask containing anhydrous cyclohexane (60 mL, 0.54 mol) and 1,3-cyclohexadiene (5.95 mL, 62.4 mmol), was heated to 25°C. A Corning temperature controller was used during the kinetics experiments to ensure the temperature was maintained at $25 \pm 1^\circ\text{C}$. The solubilized TMEDA/nBuLi initiator adduct (0.125 mmol nBuLi, 0.080 mL) was added using a syringe to initiate the polymerization and the solution remained homogenous throughout the duration of the polymerization. The polymerization was terminated using degassed methanol (Burdick-Jackson, HPLC grade). The resulting polymer was precipitated into isopropanol (600 mL), filtered, and dried at 50 °C in vacuo for 12-18 hours. An antioxidant such as Irganox 1010 (0.10 weight % compared to the polymer) was added to the precipitation solvent to retard oxidative degradation during subsequent storage.

Synthesis of Poly(1,3-cyclohexadiene)-*block*-Polyisoprene. A 250-mL round-bottomed flask containing anhydrous cyclohexane (60 mL, 0.54 mol) and 1,3-cyclohexadiene (6.7 mL, 62.5 mmol) was maintained at 25 °C. The preformed TMEDA:nBuLi initiator (0.56 mmol) was added using a syringe and the polymerization temperature was maintained at 25 °C for 120 minutes. Following the polymerization of 1,3-cyclohexadiene, isoprene (17 mL, 78 mmol) and cyclohexane (300 mL, 1,71 mol) was added to the reaction. Upon addition of isoprene, the polymerization immediately changed to a light green color, indicative of the poly(isoprenyllithium) species in the presence of TMEDA. The isoprene polymerization was allowed to proceed for 120 minutes. The polymerization was terminated using degassed methanol (Burdick-

Jackson, HPLC grade). The resulting polymer was precipitated into isopropanol (600 mL), filtered, and dried at 50 °C in vacuo for 12-18 hours. An antioxidant such as Irganox 1010 (0.10 weight % compared to the polymer) was added to the precipitation solvent to retard oxidative degradation during subsequent storage.

⁷Li NMR spectra. ⁷Li NMR spectra of the initiator adducts were measured in cyclohexane at the prescribed temperature using a Varian Spectrometer operating at 155 MHz. A LiCl solution (1.0 M) in deuterated water (D₂O) was used as a reference (0 ppm). Solutions of the initiator adducts in cyclohexane were transferred via a syringe to well dried NMR tubes under dry nitrogen at 25 °C. The solutions were further diluted with cyclohexane to generate 0.01 mM nBuLi solutions.

Polymer Characterization. ¹H NMR spectra were determined in CDCl₃ at 400 MHz with a Varian Spectrometer. Glass transition temperatures were determined using a Perkin-Elmer Pyris 1 DSC at a heating rate of 10 °C/min under nitrogen. Glass transition temperatures are reported as the midpoint of the change in heat capacity during the second heat. Molecular weights were determined using size exclusion chromatography (SEC) with a Waters SEC system. A Waters 717plus equipped with a Waters 2410 refractive index detector and a Wyatt Technology Minidawn MALLS detector was utilized for absolute molecular weight measurements. The dn/dc values were determined on-line using the calibration constant for the DRI detector and the mass of the polymer sample. SEC measurements were performed at 40 °C in chloroform at a flow rate of 1.0 mL/min. For all samples, it was assumed that 100% of the polymer eluted from the column during the measurement.

6.4 Results and Discussion

A broad range of polar additives, such as tertiary diamines, were evaluated for use in the controlled synthesis of poly(1,3-cyclohexadiene).³²⁵ It was previously

³²⁵ Natori, I., and S. Inoue. "Living Anionic Polymerization of 1,3-cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System. Copolymerization and Block

reported that the use a tertiary amine/nBuLi initiator adduct reduced the degree of 1,3-cyclohexadiene metallation, which is prevalent during *sec*BuLi initiated 1,3-cyclohexadiene polymerizations.³²⁶ Furthermore, the metallation of 1,3-cyclohexadiene was reduced through the use of lower polymerization temperatures.³²⁷ In an effort to reduce the degree of 1,3-cyclohexadiene metallation and subsequently improve the polymerization control, a series of tertiary diamine/nBuLi initiator adducts were studied at reduced polymerization temperatures (Table 6-1).

Although tertiary amine/nBuLi initiator adducts utilizing dipip and spartiene enabled the synthesis of low molecular weight polymers (10000), only adducts containing TMEDA and DABCO were viable for the synthesis of polymers with molecular weights exceeding 10000. DABCO/nBuLi or DABCO/*sec*BuLi adducts were effective for the synthesis of poly(1,3-cyclohexadiene) polymers that contained a high percentage of 1,4-addition (80%). These polymerizations remained homogenous during the reaction. In contrast, polymerizations using the TMEDA adducts exhibited a high percentage of 1,2-addition (70%). TMEDA/nBuLi (1/2) initiator adducts systems were utilized in the synthesis of well-defined high molecular weight poly(1,3-cyclohexadiene) polymers with narrow molecular weight distributions (1.19). Previous authors have reported the synthesis of high molecular weight polymers (40000), however, these polymers exhibited broader molecular weight distributions (1.30) and were synthesized at a higher temperature (40 °C) with a higher TMEDA/nBuLi ratio (5/4). As previously mentioned, use of elevated polymerization temperatures typically

Copolymerization with Styrene, Butadiene, and Isoprene." *Macromolecules* **1998**, 31, 982. Natori, I. "Synthesis of Polymers with an Alicyclic Structure in the Main Chain. Living Anionic Polymerization of 1,3-Cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System." *Macromolecules* **1997**, 30, 3696. Hong, K., and J.W. Mays. "1,3-Cyclohexadiene Polymers. 1. Anionic Polymerization." *Macromolecules* **2001**, 34, 782.

³²⁶ Natori, I., and S. Inoue. "Anionic Polymerization of 1,3-cyclohexadiene with Alkylolithium/Amine Systems. Characteristics of n-Butyllithium/N,N,N',N'-Tetramethylethylenediamine System for Living Anionic Polymerization." *Macromolecules* **1998**, 31, 4687.

³²⁷ Zhong, X., and B. Francois. "Kinetics of 1,3-cyclohexadiene polymerization by organolithium compounds in a non-polar medium. 1." *Makromol Chem* **1990**, 191, 2735. Francois, B., and X. Zhong. "Kinetics of 1,3-cyclohexadiene polymerization initiated by organolithium compounds in a non-polar medium." *Makromol. Chem.* **1990**, 191, 2743.

Table 6-1. Characterization of the poly(1,3-cyclohexadiene) homopolymers prepared via anionic polymerization. All polymerizations were performed at 25 °C in cyclohexane.

Initiator	Additive	$\frac{\text{Additive (mol)}}{\text{Initiator (mol)}}$	Isolated Yield (%)	$\langle M_n \rangle^a$ (Calc)	$\langle M_n \rangle^b$ (MALLS)	$\langle M_w \rangle / \langle M_n \rangle$	Addition (% 1,4) ^c
secBuLi	N/A	N/A	45	20000	45380	1.03	86%
nBuLi	spartiene	1/1	100	10000	12300	1.38	60%
nBuLi	spartiene	1/2	98	10000	15300	1.16	83%
nBuLi	DABCO	1/2	89	10000	7700	1.31	80%
secBuLi	DABCO	4/5	99	20000	29000	1.33	79%
nBuLi	dipip	1/2	98	10000	9800	1.28	78%
nBuLi	TMEDA	1/2	100	10000	10100	1.01	35%
nBuLi	TMEDA	1/2	99	50000	50700	1.19	30%
nBuLi	TMEDA	1/2 ^d	54	50000	16700	1.74	54%

^aBased on grams of monomer/mole of initiator ^bGPC Conditions: chloroform, 40°C, MALLS. ^cDetermined via ¹H NMR spectroscopy. ^dInitiator adduct generated in-situ
[†] Additive (mol) / initiator ratio (mol).

results in increased metallation of 1,3-cyclohexadiene, therefore it was assumed that the high TMEDA/nBuLi ratio was necessary to reduce monomer metallation and maintain a controlled polymerization.³²⁸ In our studies, the ability to control the polymerization at TMEDA/nBuLi ratios of 1/2 was attributed to the reduced polymerization temperatures (25 °C), which presumably decreased the incidence of monomer metallation.³²⁹

As described in previous studies, the method of preparation used to synthesize the TMEDA/nBuLi initiator systems was a critical factor with an excess of TMEDA relative to nBuLi being required to maintain a controlled polymerization. At smaller ratios of TMEDA/nBuLi, the polymerization exhibited poor control and the polymers had broad molecular weight distributions. In addition, the degree of chain transfer or chain termination was not explored in these studies and the relationship between additive structure and polymerization was not systematically examined. Furthermore, the effect of initiator preparation on the polymerization kinetics was not studied. In order to study the effect of initiator preparation on the livingness of the polymerization, high molecular weight poly(1,3-cyclohexadiene) polymers (50000) were synthesized using two different TMEDA/nBuLi preparations. A pre-formed initiator adduct was prepared as described in the experimental section. An in-situ initiator adduct was prepared by adding the TMEDA and nBuLi to the polymerization solvent containing 1,3-cyclohexadiene. The polymers synthesized using the pre-formed TMEDA/nBuLi initiator adducts exhibited improved molecular weight control and narrower molecular weight distributions (50700, 1.19) relative to the polymer synthesized using the in-situ initiator adduct (16700, 1.74) (Table 6-1). The use of an in-situ generated initiator adduct resulted in poor molecular weight control, broad molecular weight distributions, and reduced polymer yield. Thus, the pre-formed initiator provided a route to a controlled anionic polymerization at a 0.5 molar ratio of TMEDA/nBuLi.

³²⁸ Natori, I., and S. Inoue. "Living Anionic Polymerization of 1,3-cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System. Copolymerization and Block Copolymerization with Styrene, Butadiene, and Isoprene." *Macromolecules* **1998**, 31, 982.

³²⁹ Francois, B., and X. Zhong. "Kinetics of 1,3-cyclohexadiene polymerization initiated by organolithium compounds in a non-polar medium." *Makromol. Chem.* **1990**, 191, 2743.

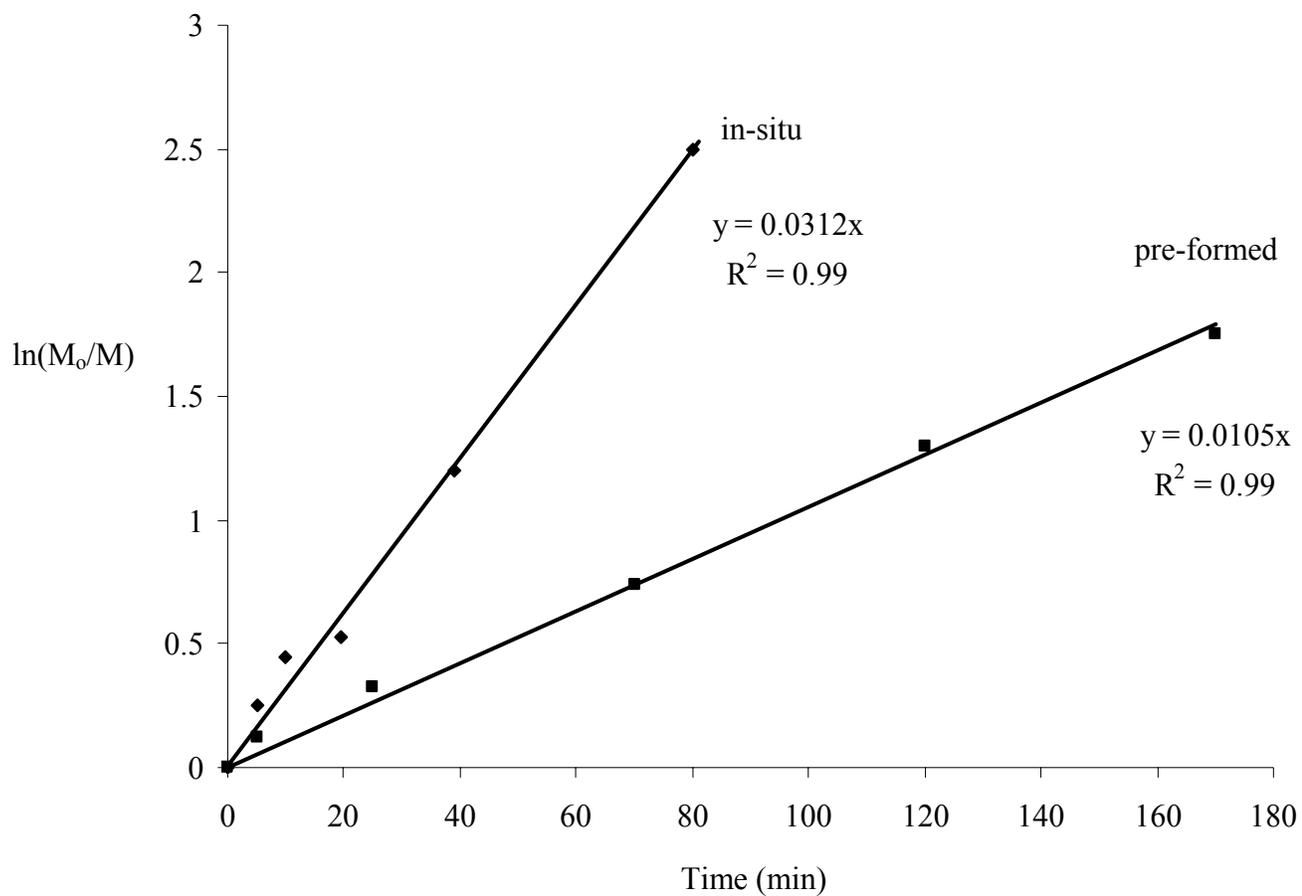


Figure 6-1. Pseudo first order rate plot of the polymerization of 1,3-cyclohexadiene using either the in-situ generated initiator adduct (left plot) of the pre-formed initiator adduct (right plot) at 25 °C in cyclohexane.

The effect of initiator adduct preparation on the kinetics of the polymerization of 1,3-cyclohexadiene was also determined (Figure 6-1). Reactions performed using the in-situ initiator exhibited an observed rate constant of $5.2 \times 10^{-4} \text{ sec}^{-1}$, which was nearly three times the value of the polymerization rate when the pre-formed initiator adduct ($1.7 \times 10^{-4} \text{ sec}^{-1}$) was used at identical reaction conditions. The kinetic plots all exhibited excellent goodness of fit values ($R^2 = 0.99$) and the linear regression plot passed through the zero intercept. Therefore, it was concluded that these polymerizations proceeded in the absence of termination reactions.³³⁰ A number of previous studies have utilized similar pseudo first order rate analyses to indicate that the polymerization of 1,3-cyclohexadiene was living.³³¹

A number of studies have examined the metallation of 1,3-cyclohexadiene to determine if monomer metallation resulted in termination or chain transfer.³³² If the monomer metallation resulted in chain termination, then the pseudo first order rate plot would not be linear. Based on the linear pseudo first order rate plots obtained (Figure 6-1), it was concluded that the anionic polymerization of 1,3-cyclohexadiene using both the in-situ and pre-formed initiator adducts occurred in the absence of significant termination (Figure 6-1). However, a linear pseudo first order rate plot does not preclude the possibility of chain transfer to monomer and subsequent re-initiation. In order to demonstrate the presence of chain transfer via a metallated 1,3-cyclohexadiene species, a plot of the degree of polymerization versus time was generated (Figure 6-2). This plot would clearly indicate any deviation from a truly living polymerization

³³⁰ Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996.

³³¹ Natori, I., and S. Inoue. "Living Anionic Polymerization of 1,3-cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System. Copolymerization and Block Copolymerization with Styrene, Butadiene, and Isoprene." *Macromolecules* **1998**, 31, 982.

³³² Zhong, X., and B. Francois. "Kinetics of 1,3-cyclohexadiene polymerization by organolithium compounds in a non-polar medium. 1." *Makromol Chem* **1990**, 191, 2735. Francois, B., and X. Zhong. "Kinetics of 1,3-cyclohexadiene polymerization initiated by organolithium compounds in a non-polar medium." *Makromol. Chem.* **1990**, 191, 2743.

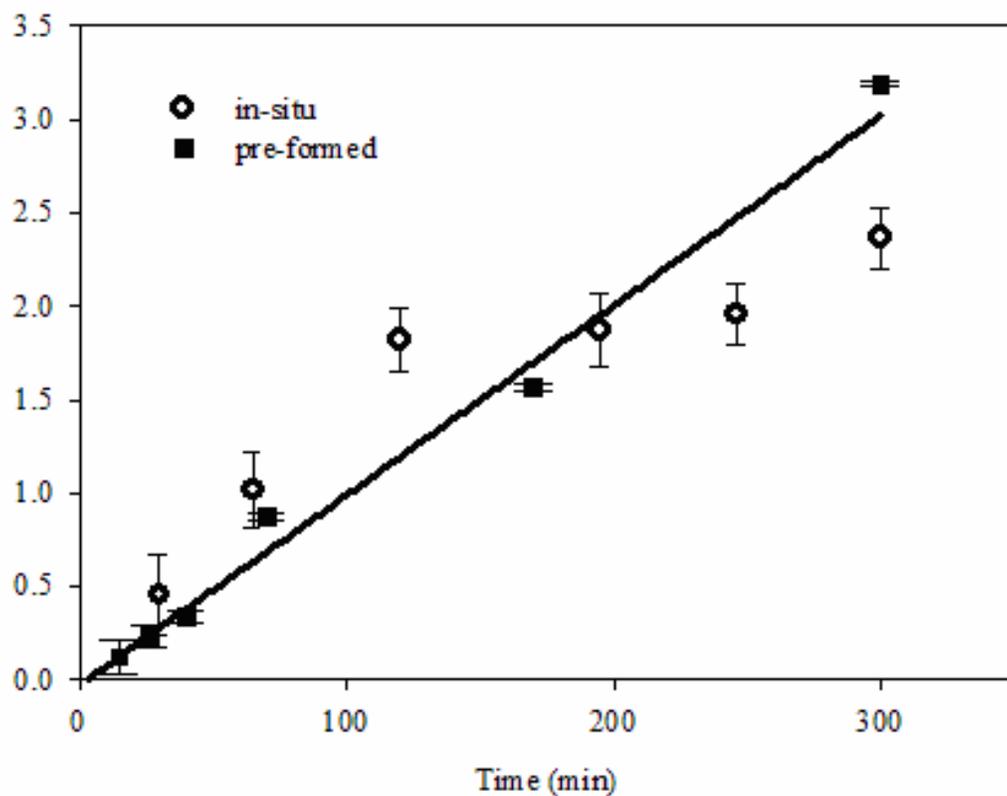


Figure 6-2. A plot of the natural log of degree of polymerization versus time for both the pre-formed initiator adduct (top line) and the in-situ generated initiator adduct (bottom curve). A linear plot indicates the polymerization proceeded in the absence of both termination and chain transfer.

system, either through termination or chain transfer events,³³³ and a linear plot indicates that the polymerization proceeds in the absence of both chain transfer and termination. As supported in Figure 6-2, the polymerization of 1,3-cyclohexadiene using the pre-formed initiator adduct proceeded in the absence of significant chain transfer or termination events over the molecular weight range studied. In sharp contrast, the use of the in-situ initiator adduct exhibited a non-linear plot. Therefore, the non-linearity of this plot for the in-situ generated initiator adduct was attributed to chain transfer events as the polymerization was previously shown to be free of termination events (Figure 6-1). This is the first report that clearly demonstrates that metallated 1,3-cyclohexadiene will reinitiate the polymerization of 1,3-cyclohexadiene under these polymerization conditions. Furthermore, the reduced degree of chain transfer present when using the pre-formed initiator adducts as compared to the in-situ initiator adduct accounts for the ability to synthesize high molecular weight poly(1,3-cyclohexadiene) homopolymers only when using the pre-formed initiator adduct.

The ability to synthesize well-defined block copolymers via sequential addition is often considered the most defining and critical characteristic of a living polymerization. Previous studies have demonstrated the synthesis of block copolymers that contain a poly(1,3-cyclohexadiene) block.³³⁴ However, the molar efficiency of crossover from poly(1,3-cyclohexadienylithium) to a second block was not examined. A crossover study unequivocally confirms the true living nature of the polymerization, as it will reveal low levels of chain termination which may occur during polymerization of the first block.

A series of diblock copolymers consisting of poly(1,3-cyclohexadiene-*block*-isoprene) were synthesized using both the pre-formed and in-situ generated initiator adducts (Table 6-2). The poly(1,3-cyclohexadiene) block was sampled prior to the

³³³ Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996.

³³⁴ Natori, I., K. Imaizumi, H. Yamagishi, and M. Kazunori. "Hydrocarbon Polymers Containing Six-Membered Rings in the Main Chain. Microstructure and Properties of Poly(1,3-cyclohexadiene)." *J. Polym. Sci., Part B: Polym. Phys.* **1998**, 36, 1657.

Table 6-2. Characterization of poly(1,3-cyclohexadiene-*block*-isoprene) prepared using a variety of conditions.

Polymer	Block Sizes (calc)	Polymerization Temperature (°C)	Initiation System	$\langle M_n \rangle$ ($\langle M_w \rangle / \langle M_n \rangle$)*	Crossover Efficiency (mol %)**
PCHD-b-PI-1	10K-20K	25	preformed	29000 (1.02)	91
PCHD-b-PI-2	10K-20K	25	in-situ	34000 (1.03)	85
PCHD-b-PI-3	10K-20K	40	preformed	54200 (1.02)	80
PCHD-b-PI-4	20K-40K	25	preformed	69000 (1.04)	80
PCHD-b-PI-5	20K-40K	25	in-situ	82900 (1.29)	56

*GPC Conditions: Chloroform, 40°C, MALLS. **Determined using DRI

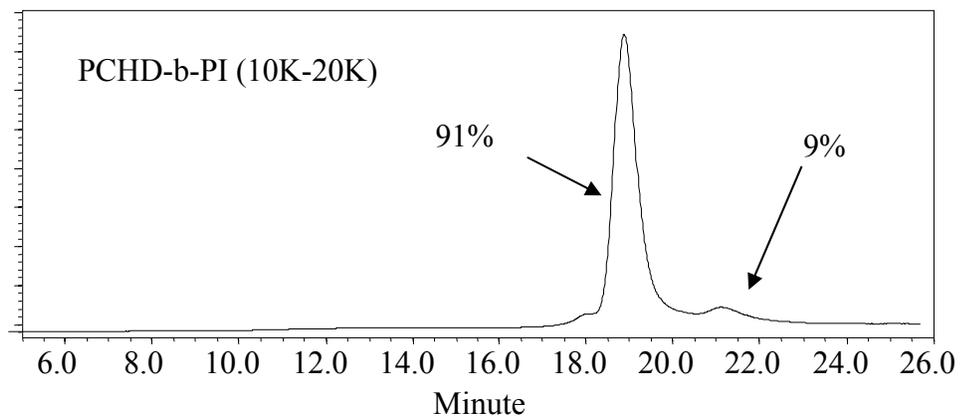


Figure 6-3. Characterization of a poly(1,3-cyclohexadiene-*block*-isoprene) diblock copolymer with a $\langle M_n \rangle = 10000$ poly(1,3-cyclohexadiene) block synthesized using the TMEDA/nBuLi pre-formed initiator.

addition of the isoprene charge and was determined to have a number average molecular weight of 9780. All of the diblock copolymers were well-defined as determined by SEC (Figure 6-3).

The molar crossover efficiency was determined as described in equation 1.

$$\text{Crossover Efficiency (mol \%)} = \frac{((R \times M_1) - M_2)}{((R \times M_1) + M_1)} \times 100\%$$

Equation 3

$$R = \frac{\text{weight fraction of poly(1,3-Cyclohexadiene - block - isoprene)}}{\text{weight fraction of poly(1,3-cyclohexadiene)}}$$

M_1 = grams of 1,3-cyclohexadiene charged to the reaction
 M_2 = grams of isoprene charged to the reaction

The weight ratio of the diblock copolymer compared to the poly(1,3-cyclohexadiene) homopolymer (R) was determined using the DRI values from the GPC. In the synthesis of these diblock systems, the pre-formed initiator adducts exhibited significantly higher molar crossover efficiencies (93%) compared to the in-situ generated initiator adducts (85%). Temperature also impacted the molar efficiency of crossover. At a temperature of 40 °C, the molar crossover efficiency for reactions using the pre-formed initiator adducts was reduced (80%). The reduction in molar crossover efficiency was attributed to the increased frequency of termination events at elevated temperatures. The difference in molar crossover efficiency between these two different initiator adducts was more dramatic when higher molecular weight poly(1,3-cyclohexadiene) blocks were synthesized. For a constant poly(1,3-cyclohexadiene) block with a molecular weight of 20000, the crossover efficiency of the pre-formed initiator was 80%, while the crossover efficiency of the in-situ generated system was only 56%. Therefore, use of the pre-formed initiator greatly reduced the degree of chain termination events. While the use of the pre-formed initiator improved the anionic polymerization of 1,3-cyclohexadiene by reducing termination and eliminating chain transfer, the reaction still suffered from some degree of termination as indicated by non-quantitative molar

Table 6-3. Characterization of poly(1,3-cyclohexadiene) homopolymers prepared using a variety of conditions. All polymerizations were performed in cyclohexane.

Initiator System	Temperature (°C)	TMEDA/nBuLi	$\langle M_n \rangle^a$ (calc)	Isolated Yield (%)	$\langle M_n \rangle^b$	$\langle M_w \rangle / \langle M_n \rangle^b$
pre-formed	25	1/2	50000	99	50700	1.19
pre-formed	25	1/2	40000	93	43200	1.13
pre-formed	40	1/2	60000	57	40000	1.30
in-situ	25	1/2	50000	54	16700	1.74
in-situ	25	5/4	50000	20	23800	1.50

^aBased on grams of monomer/mole of initiator ^bGPC Conditions: chloroform, 40°C, MALLS.

crossover efficiencies. Furthermore, as higher molecular weights were targeted the degree of chain termination increased.

In light of the dramatic differences in polymerization control for the pre-formed TMEDA/nBuLi initiator adducts relative to in-situ adducts, fundamental studies were performed to further explore the effect of initiator preparation and polymerization temperature on polymerization control (Table 6-3). As expected, polymerizations performed using the pre-formed initiator at 25 °C were controlled, resulting in well-defined macromolecules. Use of the in-situ initiator adduct resulted in poorly controlled polymerizations at all ratios of TMEDA/nBuLi investigated and the polymer precipitated significantly during the polymerization. In contrast, the polymers synthesized using the pre-formed initiator adducts exhibited improved solubility in the polymerization solvent and improved polymerization control.

As shown in Table 6-3, an elevated reaction temperature reduced polymer yield and increased molecular weight distribution. In previous studies, polymerizations using a TMEDA/nBuLi pre-formed initiator adducts were performed at 40 °C with ratios of TMEDA/nBuLi of 5/4 to maintain polymerization control. To investigate the effect of reaction temperature on the structure of the pre-formed initiator, variable temperature ⁷Li NMR spectroscopy studies were performed at 25 °C and 40 °C. Previous reports examined the pre-formed initiator adduct using ⁷Li NMR spectroscopy, however, these studies were performed at sub-ambient conditions (-50 °C), which was significantly below the polymerization temperature (40 °C).³³⁵ In addition, previous studies demonstrated that the complexation of alkyllithium species with TMEDA shifted the ⁷Li NMR resonance upfield.³³⁶

³³⁵ Natori, I., and S. Inoue. "Anionic Polymerization of 1,3-cyclohexadiene with Alkylolithium/Amine Systems. Characteristics of n-Butyllithium/N,N,N',N'-Tetramethylethylenediamine System for Living Anionic Polymerization." *Macromolecules* **1998**, 31, 4687.

³³⁶ Wehman, E., T.B.H. Jastrzebski, J. Ernsting, D.M. Grove, and G. Van Koten. "Structural Investigation of Aryllithium Clusters in Solution." *J Organomet. Chem.* **1988**, 353, 133.

The spectrum of the pre-formed initiator adduct at 25 °C (middle spectrum) exhibited three resonances, two signals centered around 3 ppm and another signal centered at 4 ppm. The upfield resonances at 3 ppm were attributed to lithium cations present in a more highly shielded environment due to a tight association with TMEDA. In a similar fashion, the less shielded resonance at 4 ppm was proposed to be due to a less tightly associated TMEDA/nBuLi species. When this system was heated to 40 °C (top spectrum), the upfield resonances shifted downfield to 4 ppm due to the reduced association of TMEDA with the lithium cation. The downfield shift of the resonances (3 ppm to 4 ppm) as the temperature increased suggested that the change in chemical shift was due to the interaction with TMEDA and not due to a change in aggregation state (i.e. a tetramer to dimer equilibrium). Previous studies demonstrated that increased temperatures increased the percentage of alkyllithium dimers, which occurred upfield from the alkyllithium tetramers.³³⁷ As a control, the ⁷Li NMR spectrum of an in situ generated initiator adduct (bottom spectrum) was studied at 25 °C. The spectrum exhibited a single resonance at 4 ppm matching the signal present in the pre-formed initiator adduct at 40 °C, which supports the assumption that at 40 °C the nBuLi species dissociates from TMEDA resulting in the same degree of interaction with TMEDA as the in-situ generated initiator. Therefore, the poorer polymerization control of the pre-formed initiator adduct at 40 °C relative to that at 25 °C was due to the absence of the more associated alkyllithium species. As shown in Figure 6-5, the propagating anion was also examined using UV-visible spectroscopy. Two absorptions were present in the spectra (310, 390 nm) which suggested the presence of at least two species of propagating anions.

³³⁷ Wang, J.S., R. Jerome, R. Warin, and Ph. Teyssie. "Anionic Polymerization of Acrylic Monomers. 10. ¹³C and ⁷Li NMR Studies of the Monomeric Model of Living Poly(methyl methacrylate)." *Macromolecules* **1993**, 26, 1402.

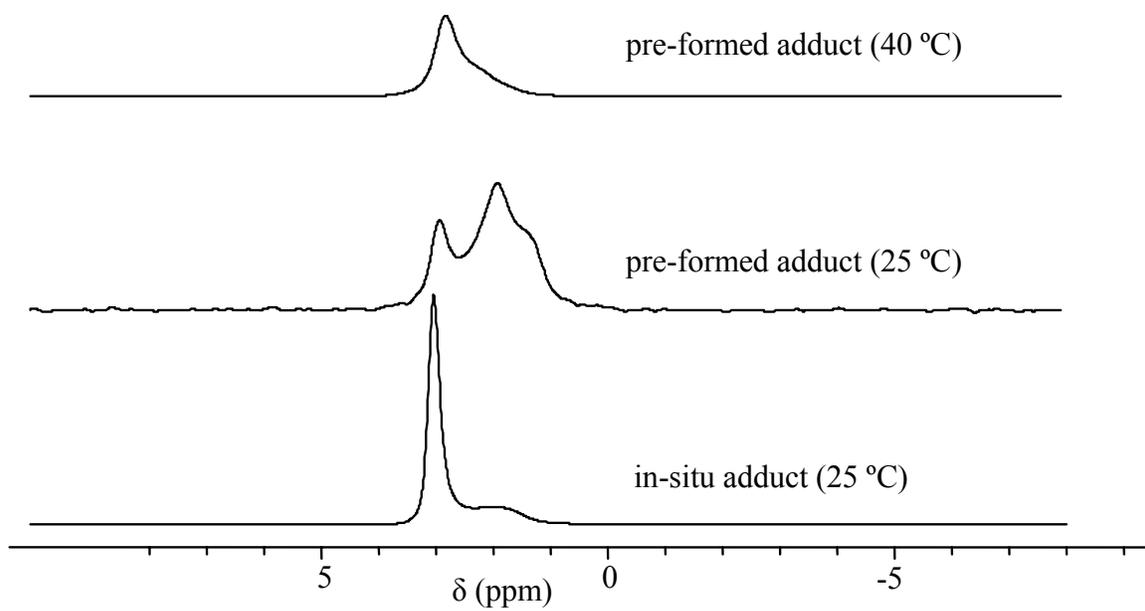


Figure 6-4. ${}^7\text{Li}$ NMR of the TMEDA/nBuLi complexes. The upfield resonances (3 ppm) present in the pre-formed complex at 25 °C (middle spectrum) shift downfield to 4 ppm when the complex is heated to 40 °C (top spectra).

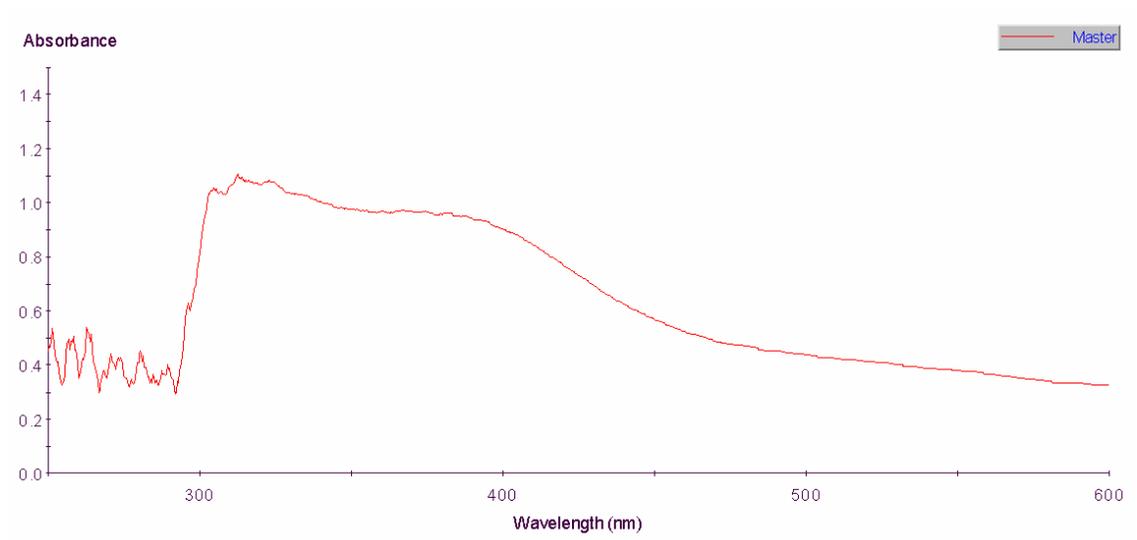


Figure 6-5. UV-visible spectra of a poly(1,3-cyclohexadienyllithium) anion in cyclohexane at 25 °C.

To further elucidate the effect of the various tertiary diamines on polymerization control, the kinetics of the reaction of various tertiary diamine/nBuLi initiator adducts were studied (Figure 6-6). Based on earlier literature, the tertiary amines studied (TMEDA, dipip, and sparteine) all exhibit a similar degree of affinity for the lithium cation present in alkyllithiums.³³⁸ The polymerization rate constant using the TMEDA/nBuLi pre-formed initiator adduct was $1.5 \times 10^{-4} \text{ sec}^{-1}$, which was twice the polymerization rate constant when using a sparteine/nBuLi initiator adduct ($7.0 \times 10^{-5} \text{ sec}^{-1}$). These polymerizations exhibited a linear relationship between molecular weight and percent conversion in the range of molecular weights examined in these kinetic studies. The dramatic difference in the rate constant between these two tertiary amines was attributed to the cyclohexane rings on the tertiary amine in sparteine. The constrained nature of the cyclohexane rings in sparteine enabled the lone pair of electrons present on the tertiary amine to interact with the lithium cation. These cyclohexane rings are locked into place due to their direct attachment to the bicyclo[3,3,1]nonane molecule core. The deleterious effect of steric bulk on the propagating center was further exhibited by the dipip/nBuLi initiator adduct, which did not polymerize in a controlled fashion under the conditions employed in these studies. The difference between the sparteine and dipip systems was attributed to the unique constrained nature of the tertiary amines present in sparteine. These results agree well with previous studies by Mays et al., who found that dipip modified polymerizations resulted in insoluble material.³³⁹

³³⁸ Beckelmann, D., and F. Bandermann. "Classification of Polar Additives with Respect to Their Influence on the Microstructure in Anionic Polymerization of Isoprene with Butyllithium by Transition Energy Measurements." *J. Appl. Polym. Sci.* **1999**, 73, 1533.

³³⁹ Hong, K., and J.W. Mays. "1,3-Cyclohexadiene Polymers. 1. Anionic Polymerization." *Macromolecules* **2001**, 34, 782.

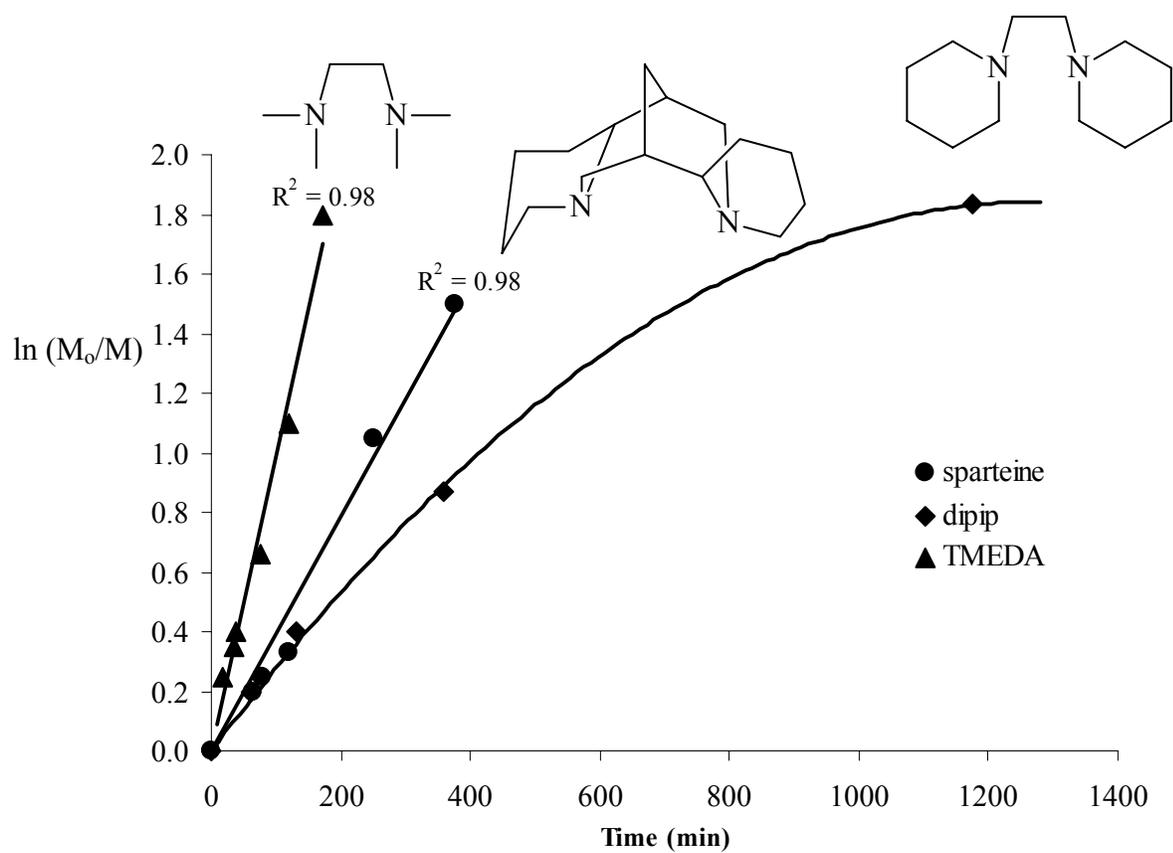


Figure 6-6. Kinetic analysis of the polymerization of 1,3-cyclohexadiene using the tertiary diamines TMEDA (left plot), sparteine (middle plot), and dppe (right plot). Polymerizations were performed at 25 °C in cyclohexane with an amine/nBuLi ratio of 1:2.

However, the use of 1,2-dimethoxyethane, which exhibits a similar degree of affinity for the lithium cation,³⁴⁰ was previously shown to result in a controlled polymerization.³⁴¹ Therefore, small chelating additives, such as TMEDA or 1,2-dimethoxyethane, facilitate the controlled polymerization of 1,3-cyclohexadiene by providing the correct amount of carbon lithium bond polarization while reducing the steric bulk of the additive. While these studies strongly suggest the structure of the initiating species affects the resulting polymerization, it is understood that the structure of the propagating alkyllithium polymer chain end may differ significantly from the structure of the preformed initiator.

DABCO is unique among the tertiary amines studied, because the nitrogen lone pairs do not interact with the lithium cation in a bidentate fashion. Previous studies classified DABCO as exhibiting a medium level of interaction with the lithium cations, similar to the level of interaction between lithium cations and THF.³⁴² As such, DABCO was not considered with the other additives studied, which are bidentate and classified as exhibiting a high level of interaction with the lithium cation. However, DABCO did provide a considerable level of polymerization control and was adequate for the controlled synthesis of poly(1,3-cyclohexadiene) homopolymers containing 80% 1,4-addition (Table 6-1).

³⁴⁰ Beckelmann, D., and F. Bandermann. "Classification of Polar Additives with Respect to Their Influence on the Microstructure in Anionic Polymerization of Isoprene with Butyllithium by Transition Energy Measurements." *J. Appl. Polym. Sci.* **1999**, 73, 1533.

³⁴¹ Hong, K., and J.W. Mays. "1,3-Cyclohexadiene Polymers. 1. Anionic Polymerization." *Macromolecules* **2001**, 34, 782.

³⁴² Beckelmann, D., and F. Bandermann. "Classification of Polar Additives with Respect to Their Influence on the Microstructure in Anionic Polymerization of Isoprene with Butyllithium by Transition Energy Measurements." *J. Appl. Polym. Sci.* **1999**, 73, 1533.

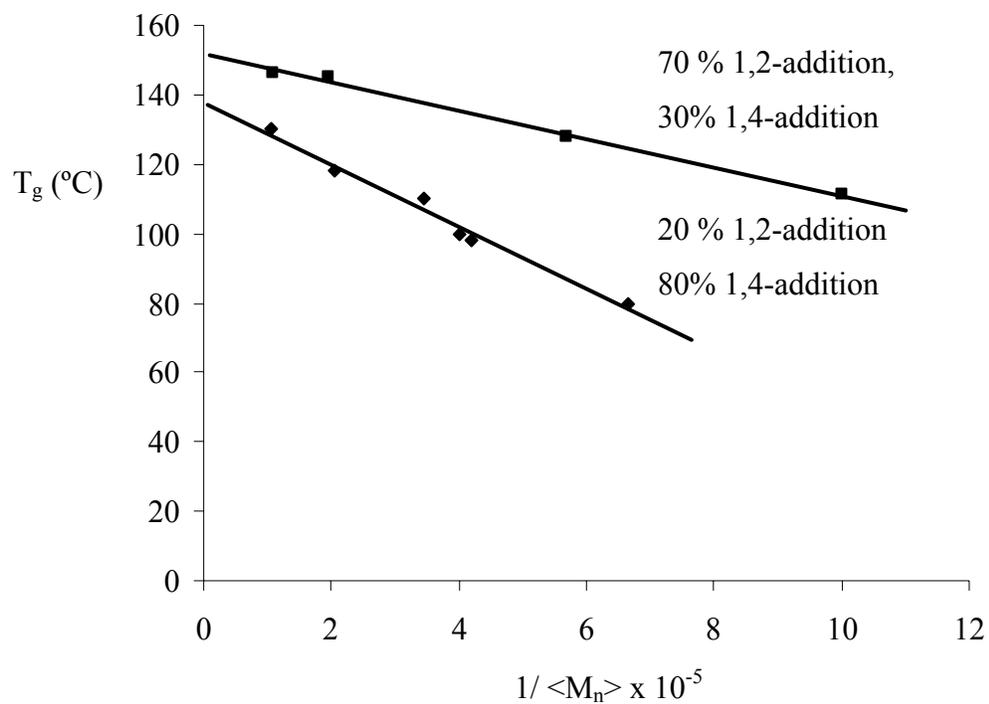


Figure 6-7. Characterization of the glass transition temperature using a Fox-Flory treatment for poly(1,3-cyclohexadiene) with both 70% 1,2-addition (top line) and 20% 1,2-addition (bottom line). DSC Conditions: 10 °C/min, N₂.

In light of the ability to controllably synthesize poly(1,3-cyclohexadiene) polymers with a range of microstructures, a series of polymers containing a high 1,2-microstructure and a high 1,4-microstructure were synthesized over a range of molecular weights. Using the method we have previously described, the microstructure of the polymers was determined using ^1H NMR spectroscopy.³⁴³ Polymers with 80% 1,4-addition were synthesized using a pre-formed DABCO/nBuLi initiator adduct at 25 °C in cyclohexane. The DABCO/nBuLi pre-formed initiator was prepared similarly as the TMEDA/nBuLi preformed initiator and was heated to 55 °C to solubilize the adduct prior to initiation. The polymers were prepared in cyclohexane at 25 °C and the polymerization was allowed to proceed for 12 hours. These polymers exhibited relatively narrow molecular weight distributions (< 1.30) over a broad range of molecular weights (1500 - 94000). In a similar fashion, poly(1,3-cyclohexadiene) homopolymers with 70% 1,2-addition were synthesized using a pre-formed TMEDA/nBuLi initiator adduct at 25 °C in cyclohexane. The glass transition temperature (T_g) of these polymers was determined using DSC analysis and plotted versus number average molecular weight (Figure 6-7)

The glass transition temperature at infinite molecular weight ($T_{g\infty}$) for these polymers was determined using the Fox-Flory equation, which describes the relationship between the number average molecular weight (M_n) and glass transition temperature (T_g) as follows,

$$\text{Equation 4} \quad T_g = T_{g\infty} - K_g M_n^{-1}$$

where K_g is a polymer dependant constant. The plots for both the polymer with 70% 1,2-microstructure and 80% 1,4-microstructure exhibited excellent goodness of fit values with an R^2 of 0.98 and 0.99, respectively.

The $T_{g\infty}$ for the poly(1,3-cyclohexadiene) with 70% 1,2-microstructure was determined to be 150 °C. In contrast, the $T_{g\infty}$ for poly(1,3-cyclohexadiene) with 80%

³⁴³ Williamson, D.T., T.E. Glass, and T.E. Long. "Determination of the Stereochemistry of Poly(1,3-cyclohexadiene) Via End-group Functionalization." *Macromolecules* **2001**, 34, 6144.

1,4-microstructure was 138 °C. As expected, the $T_{g\infty}$ for poly(1,3-cyclohexadiene) with a high percentage of 1,2-microstructure was higher than the $T_{g\infty}$ for poly(1,3-cyclohexadiene) with a high percentage of 1,4-microstructure.³⁴⁴ Anionically prepared polydienes, such as polyisoprene and polybutadiene, exhibit a strong dependency of $T_{g\infty}$ on 1,2 versus 1,4-addition, with the T_g increasing as the percentage of 1,2-addition increases.³⁴⁵ The $T_{g\infty}$ for poly(1,3-cyclohexadiene) with a high percentage of 1,2-addition was previously shown to be approximately 170 °C,³⁴⁶ however, a different ratio of TMEDA/nBuLi (5/4) and a higher polymerization temperature (40 °C) were used. The K_g values for poly(1,3-cyclohexadiene) with 80 % 1,4-addition and 70 % 1,2-addition were $9.3 \times 10^{-5} \text{ g}^{-1}\text{mol}$ and $4.0 \times 10^{-5} \text{ g}^{-1}\text{mol}$, respectively. In addition, plots of the glass transition temperature versus number average molecular weight were generated for poly(1,3-cyclohexadiene) polymers with either a high 1,2-microstructure or a high 1,4-microstructure (Figure 6-8 and Figure 6-9). The critical molecular weight (M_c) for the polymers containing 70% 1,2-addition was determined as approximately 78000, which agrees well with previous studies by Natori et al. The critical molecular weight for polymers containing 80% 1,4-addition was estimated at 98000, which appeared to occur at the onset of the plateau of the glass transition temperature versus molecular weight plot. Attempts to synthesize polymers with molecular weights exceeding the critical molecular weight were unsuccessful. The glass transition temperature of a poly(1,3-cyclohexadiene) homopolymer with a 100% 1,4-addition microstructure was estimated using the microstructure composition for the 90000 and 94000 samples with 70% 1,2-addition and the 80% 1,4-addition, accordingly. The glass transition temperature was determined to be 125 °C for a polymer with 100% 1,4-microstructure. In a similar fashion, the glass transition temperature for a polymer with 100% 1,2-microstructure was estimated as 157 °C.

³⁴⁴ Bywater, S., Y. Firat, and P.E. Black. "Microstructures of polybutadienes prepared by anionic polymerization in polar solvents. Ion-pair and solvent effects." *J. Polym. Sci. Part A*. **1984**, 22, 669.

³⁴⁵ Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996.

³⁴⁶ Natori, I., K. Imaizumi, H. Yamagishi, and M. Kazunori. "Hydrocarbon Polymers Containing Six-Membered Rings in the Main Chain. Microstructure and Properties of Poly(1,3-cyclohexadiene)." *J. Polym. Sci., Part B: Polym. Phys.* **1998**, 36, 1657.

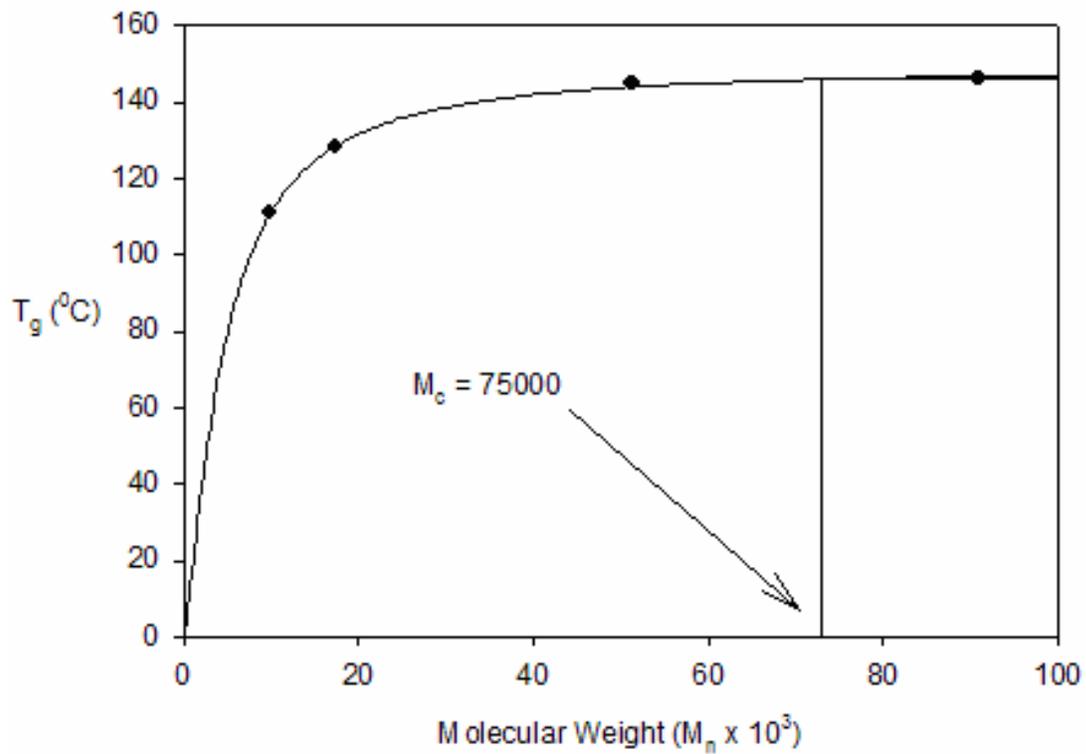


Figure 6-8. A plot of the glass transition temperature for poly(1,3-cyclohexadiene) homopolymers containing 70% 1,2-addition. The critical molecular weight was determined to be approximately 75000.

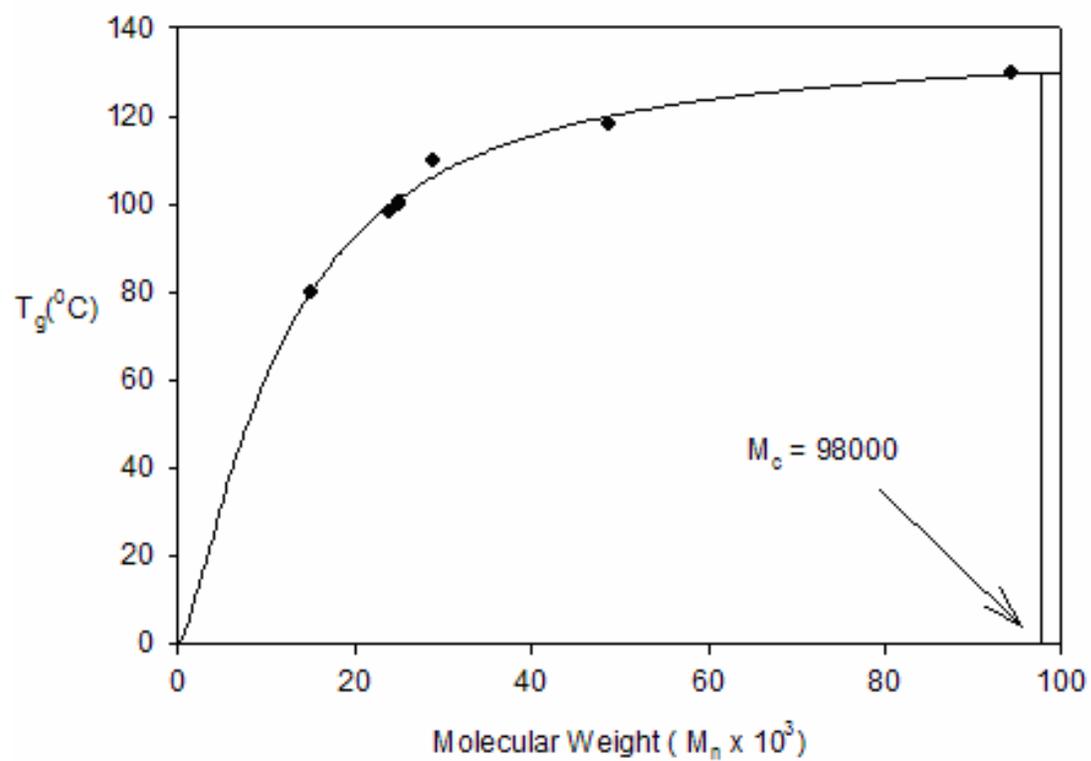


Figure 6-9. A plot of the glass transition temperature for poly(1,3-cyclohexadiene) homopolymers containing 80% 1,4-addition. The M_c was estimated at 98000, which appeared to be the onset of the plateau region for the glass transition temperature.

6.5 Conclusion

The synthesis of high molecular weight poly(1,3-cyclohexadiene) homopolymers was demonstrated and an improved synthetic method using a pre-formed TMEDA/nBuLi or DABCO/nBuLi adduct was developed. The use of a pre-formed initiator adduct decreased the number of termination events and eliminated chain transfer events as compared to an in-situ generated initiator system. These polymerizations were determined to be highly sensitive to both reaction temperature and the choice of tertiary diamine. Use of bulky tertiary diamines, such as spartiene or dipip, resulted in poor polymerization control and reduced polymerization rates. Use of a lower polymerization temperature (25 °C) improved molecular weight control and reduced the molecular weight distribution. Polymer microstructure was calculated using ¹H NMR spectroscopy and the relationship between molecular weight and glass transition temperature was determined.

CHAPTER 7

Synthesis of Poly(1,3-cyclohexadiene) Containing Star-shaped Elastomers

Taken From:

D.T. Williamson, and T.E. Long “Synthesis of Poly(1,3-cyclohexadiene) Containing Star-shaped Elastomers” *Makromol. Chem.* **2003**, Submitted for publication.

7.1 Abstract.

The synthesis of high molecular weight star-shaped polymers comprising poly(1,3-cyclohexadiene-block-isoprene) diblock arms coupled to a divinyl benzene (DVB) core is reported. The molecular weights of the diblock arms were varied from 30000 to 50000 and the ratio of DVB to nBuLi was systematically varied from 3:1 to 12:1. Gel permeation chromatography coupled with light scattering detection was utilized to detect the formation of star-shaped polymers and the presence of star-star coupling. The molecular weight distribution ($\langle M_w \rangle / \langle M_n \rangle$) of the star polymers ranged from 1.25 to 1.50. The effect of poly(1,3-cyclohexadiene) content on the mechanical properties of these novel elastomers is reported. Elastic modulus, elongation at break, and tensile strength were all found to be a function of the percentage of poly(1,3-cyclohexadiene). The glass transition temperatures were determined using both differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). Atomic force microscopy was performed in the tapping mode (TMAFM) to verify the presence of microphase separation.

7.2 Introduction

Poly(styrene-*block*-butadiene-*block*-styrene) (SBS) and poly(styrene-*block*-isoprene-*block*-styrene) (SIS) triblock copolymers are well known to exhibit an excellent combination of elasticity and thermoplasticity. These triblock copolymers are multiphase materials, wherein the polystyrene blocks microphase separate from the polydiene blocks. The microphase-separated domains are responsible for the remarkable elastomeric properties of these macromolecules. This behavior persists over a wide range of temperatures and the lower and the upper temperature limits are dictated by the T_g of the polybutadiene (-90 °C) and polystyrene (100 °C) blocks, accordingly.³⁴⁷ The polystyrene domains lose physical integrity and are unable to maintain their elastomeric properties, when the temperature approaches 100 °C.³⁴⁸ Numerous studies were performed to increase the upper use temperature of thermoplastic elastomers in order to compete with vulcanized rubber.³⁴⁹ Jerome and coworkers recently synthesized triblock copolymers of poly(isobornyl methacrylate)-*block*-poly(1,3-butadiene)-*block*-poly(isobornyl methacrylate).³⁵⁰ These elastomers exhibited improved tensile strength (30 MPa), high percent elongation (1000 %), and a high upper use temperature of 160 °C. In addition, earlier efforts involved the preparation of thermoplastic elastomers containing poly(α -methylstyrene),³⁵¹ poly(ethylene sulfide),³⁵² and poly(*p*-methylstyrene).³⁵³ In spite of exhibiting a higher

³⁴⁷ McGrath, J.E. "An Introductory Overview of Block Copolymers." In *Block Copolymers: Science and Technology*, edited by D.J. Meier. New York: Harwood Academic Publishers, 1979. Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996.

³⁴⁸ Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996.

³⁴⁹ Ming Yu, Jian, P. Dubois, and Robert Jerome. "Synthesis and Properties of Poly(isobornyl methacrylate-*b*-butadiene-*b*-isobornyl methacrylate) Copolymers: New Thermoplastic Elastomers of a large service Temperature Range." *Macromolecules* **1996**, 29, 7316.

³⁵⁰ Morton, M., and S.L. Mikesell. "ABA block copolymers of dienes and cyclic sulfides." *J. Macromol. Sci., Chem.* **1993**, A7, 1391.

³⁵¹ Quirk, R. P. "New block copolymers for higher temperature applications." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **1985**, 26, 14.

³⁵² Morton, M., and S.L. Mikesell. "ABA block copolymers of dienes and cyclic sulfides." *J. Macromol. Sci., Chem.* **1993**, A7, 1391.

glass transition temperature, these polymers exhibited either a low ceiling temperature or poor ultimate mechanical properties.

In contrast to other polydienes, poly(1,3-cyclohexadiene) PCHD exhibits a remarkably high T_g (150 °C), which is 50 °C higher than the T_g of polystyrene.³⁵⁴ Unfortunately, the polymerization of 1,3-cyclohexadiene is plagued by a number of molecular weight limiting side reactions. Previous studies in the mid-1960's and early 1970's involved a wide variety of polymerization techniques to identify a viable polymerization methodology for 1,3-cyclohexadiene.³⁵⁵ Despite these early attempts to polymerize 1,3-cyclohexadiene in a controlled fashion, the resulting polymers exhibited unpredictable molecular weights and broad molecular weight distributions. In 1997, Natori reported the first living anionic polymerization of 1,3-cyclohexadiene in the presence of the ligating agent N,N,N',N'-tetramethylethylenediamine (TMEDA). As an indication of the living nature of the reaction, the polymerization exhibited a linear relationship between number average molecular weight and percent conversion. A series of studies were reported following this initial study.³⁵⁶ In these studies, the

³⁵³ Quirk, R. P. "New block copolymers for higher temperature applications." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **1985**, 26, 14.

³⁵⁴ Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996.

³⁵⁵ Sharaby, Z., J. Jagur-Grodzinski, M. Martan, and D Vofsi. "Kinetics and Mechanism of the Anionic Polymerization of Cyclohexadienes Initiated by Naphthalene Radical Anions and Dianions." *J. Polym. Sci., Polym. Chem. Ed.* **1982**, 20, 901. Lefebvre, G, and F. Dawans. "1,3-Cyclohexadiene polymers. I. Preparation and aromatization of poly-1,3-cyclohexadiene." *J. Polym. Sci.* **1964**, A2, 3277. Sharaby, Z., M. Martan, and J. Jagur-Grodzinski. "Stereochemistry of Poly(1,3-cyclohexadienes). NMR Investigation of Effects Due to the Solvent Medium and to the Mechanism of Polymerization." *Macromolecules* **1982**, 15, 1167. Mango, L.A., and R.W. Lenz. "Mechanism and stereochemistry in the anionic polymerization of 1,3-cyclohexadiene and the diimide hydrogenation of polymers." *U.S. Nat. Tech. Inform. Serv.* **1972**, 12, 402. Mango, L.A., and R.W. Lenz. "Organometallic reactions which control molecular weight in the anionic polymerization of 1,3-cyclohexadiene." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **1971**, 12, 402.

³⁵⁶ Natori, I., and S. Inoue. "Living Anionic Polymerization of 1,3-cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System. Copolymerization and Block Copolymerization with Styrene, Butadiene, and Isoprene." *Macromolecules* **1998**, 31, 982. Natori, I., and S. Inoue. "Anionic Polymerization of 1,3-cyclohexadiene with Alkylolithium/Amine Systems. Characteristics of n-Butyllithium/N,N,N',N'-Tetramethylethylenediamine System for Living Anionic Polymerization." *Macromolecules* **1998**, 31, 4687. Natori, I., K. Imaizumi, H. Yamagish, and M. Kazunori. "Hydrocarbon

synthesis and characterization of poly(1,3-cyclohexadiene)-block-poly(1,3-butadiene)-block-poly(1,3-cyclohexadiene) triblock copolymers was examined. These polymers exhibited relatively narrow molecular weight distributions with varying percentages of 1,3-cyclohexadiene. Increased incorporation of 1,3-cyclohexadiene broadened the molecular weight distributions. The presence of TMEDA during the polymerization increased the T_g of the poly(1,3-butadiene) block. In later studies, Natori et al. altered the synthetic strategy and utilized a difunctional initiator.³⁵⁷ A difunctional initiator was utilized, in the presence TMEDA, to initiate the polymerization of the polybutadiene block. Following the synthesis of the polybutadiene blocks, 1,3-cyclohexadiene was added to synthesize the PCHD blocks. This synthetic methodology utilized both a difunctional initiator and sequential addition. In sequential addition, the last block of a triblock copolymer does not typically exhibit the same molecular weight as the first block.³⁵⁸ It is therefore a concern that the asymmetric triblock structure will affect the elastomeric properties and corresponding morphologies.³⁵⁹ An alternative approach to PCHD containing thermoplastic elastomers involves coupling strategies which permit the synthesis of highly branched polymeric structures, such as star-shaped polymers.³⁶⁰

Star-shaped polymers, wherein the arms of the star are nearly identical in chain length, are readily prepared using living anionic polymerization methodologies.

Polymers Containing Six-Membered Rings in the Main Chain. Microstructure and Properties of Poly(1,3-cyclohexadiene)." *J. Polym. Sci., Part B: Polym. Phys.* **1998**, 36, 1657. Imaizumi, K., Tomohiro Ono, I. Natori, Shinichi Sakuri, and Kunihiko Takedo. "Microphase-Separated Structure of 1,3-Cyclohexadiene/Butadiene Triblock Copolymers and Its Effect on Mechanical and Thermal Properties." *J. Polym. Sci., Part B: Polym. Phys.* **2001**, 39, 13.

³⁵⁷ Imaizumi, K., Tomohiro Ono, I. Natori, Shinichi Sakuri, and Kunihiko Takedo. "Microphase-Separated Structure of 1,3-Cyclohexadiene/Butadiene Triblock Copolymers and Its Effect on Mechanical and Thermal Properties." *J. Polym. Sci., Part B: Polym. Phys.* **2001**, 39, 13.

³⁵⁸ Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996.

³⁵⁹ Matsen, M.W. "Equilibrium Behavior of Asymmetric triblock copolymer melts." *Polymer Science* **2000**, 113, 5539.

³⁶⁰ Meneghetti, S.P., P.J. Lutz, and D. Rein. "Star-Shaped Polymers via Anionic Polymerization Methods." In *Star and Hyperbranched Polymers*, edited by Munmaya Mishra and Shiro Kobayashi, 27. New York: Marcel Dekker, 1999.

Typically two methods are utilized for the synthesis of star-shaped macromolecules. These approaches are the "core-first" and the "arm-first" methods. In the "arm-first" method, a living monofunctional arm of known length is reacted with a plurifunctional compound. "Arm-first" methods can be employed with various linking agents such as silicon tetrachloride, and *p*- and *m*-divinylbenzene.³⁶¹ In favorable cases, the functionality of a chlorosilane based linking agent dictates the number of arms in the star polymer. However, divinyl compounds undergo homopolymerization and form star polymers with a DVB core.³⁶² These star-shaped polymers exhibit a greater number of arms than the functionality of a single divinyl compound.³⁶³ An advantage of the arm first method is the facile synthesis of star-shaped polymers with narrow molecular weight distributions. In contrast to the "arm-first" method, "core-first" methods generate a reactive core prior to the addition of arm forming monomers. The arm forming monomers then polymerize in a radial fashion from the core in a living manner. This enables the outer chain ends of the star-shaped macromolecule to be functionalized using various termination agents.³⁶¹ The outer chain ends of a star can be functionalized using the arm first route, however, this approach requires the use of protected functionalized initiators. The functionalized periphery can subsequently be utilized for the preparation of networks or star-shaped polymers containing copolymeric branches. The disadvantage of the core first method is the generation of polymers with relatively large molecular weight distributions.³⁶⁴ Recently, a number of researchers have combined both the "core-first" and the "arm-first" methods in a single synthesis to generate stars with two different types of polymer arms via the "in-out" method.³⁶⁵

³⁶¹ Meneghetti, S.P., P.J. Lutz, and D. Rein. "Star-Shaped Polymers via Anionic Polymerization Methods." In *Star and Hyperbranched Polymers*, edited by Munmaya Mishra and Shiro Kobayashi, 27. New York: Marcel Dekker, 1999.

³⁶² Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996.

³⁶³ McGrath, J.E., ed. *Anionic Polymerization: Kinetics, Mechanisms, and Synthesis*. Edited by Joan Comstock. Vol. 166, *ACS Symposium Series* American Chemical Society: Washington D.C., 1981.

³⁶⁴ Meneghetti, S.P., P.J. Lutz, and D. Rein. "Star-Shaped Polymers via Anionic Polymerization Methods." In *Star and Hyperbranched Polymers*, edited by Munmaya Mishra and Shiro Kobayashi, 27. New York: Marcel Dekker, 1999.

³⁶⁵ Hadjichristidis, N. "Synthesis of Miktoarm Star (u-Star) Polymers." *J. Polym. Sci., Part A: Polym. Chem* **1999**, 37, 857. Frater, D. J., J.W. Mays, and C. Jackson. "Synthesis and Dilute

Star-shaped polymers exhibit useful rheological properties³⁶⁶ and were used as viscosity improvers. Recent studies examining the synthesis of PCHD star-shaped polymers were reported.³⁶⁷ These polymers exhibited relatively narrow molecular weight distributions and were synthesized using either divinylbenzene or silicon based coupling agents.

Herein, the synthesis of poly(1,3-cyclohexadiene-*block*-isoprene) DVB coupled, star-shaped elastomers via the arm-first method is reported. The molecular weight characteristics of these novel elastomers were examined using gel permeation chromatography in combination with multiple angle laser light scattering (MALLS). The effect of poly(1,3-cyclohexadiene) content on the elastomeric properties was examined and the presence of microphase separation was verified using atomic force microscopy.

7.3 Experimental Section

Materials. 1,3-cyclohexadiene (Aldrich, 98%) and isoprene (Aldrich, 99%) were degassed several times and distilled at reduced pressure (0.10 mm Hg, 10 °C) from dibutylmagnesium (DBM, 0.84 M). Divinylbenzene (DVB) (Aldrich, 80% divinylbenzene comprising a mixture the meta and para isomers and 20 wt% ethylvinylbenzene) was distilled under reduced pressure (0.10 mm, 25 °C) from calcium hydride (Aldrich 95%) and dibutylmagnesium immediately prior to use. The ethylvinylbenzene was not removed and all further references to DVB assume the presence of the ethylvinylbenzene (20 mol%). n-Butyllithium (FMC Corporation,

Solution Properties of Divinylbenzene-Linked Polystyrene Stars with Mixed Arm Lengths: Evidence for Coupled Stars." *J. Polym. Sci., Part A: Polym. Chem* **1997**, 35, 141.

³⁶⁶ Fetters, L.J., Andrea D. Kiss, and Dale S. Pearson. "Rheological Behavior of Star-Shaped Polymers." *Macromolecules* **1993**, 25, 647. Knischka, R., P.J. Lutz, A. Sunder, R. Mulhaupt, and H. Frey. "Functional Poly(ethylene oxide) Multiarm Star Polymers: Core-First Synthesis Using Hyperbranched Polyglycerol Initiators." *Macromolecules* **2000**, 33, 315.

³⁶⁷ Hong, K., and J.W. Mays. "1,3-Cyclohexadiene Polymers. 1. Anionic Polymerization." *Macromolecules* **2001**, 34, 782. Williamson, D.T., J.F. Elman, P.H. Madison, A.J. Pasquale, and T.E. Long. "Synthesis and Characterization of Poly(1,3-cyclohexadiene) Homopolymers and Star-shaped Polymers." *Macromolecules* **2001**, 34, 2108.

Lithium Division, 1.35 M in n-hexane) was used without further purification. TMEDA (Aldrich, 99%) was distilled at reduced pressure (0.13-0.16 mmHg, 10 °C) from calcium hydride and stored under nitrogen at -25 °C until ready for use. Cyclohexane (Burdick-Jackson, HPLC grade) was stirred over sulfuric acid (10:1 cyclohexane:sulfuric acid) for 7-10 days, decanted, and distilled from a sodium dispersion under. The cyclohexane was then vacuum distilled from poly(styryllithium) immediately prior to use. All reagents were transferred using syringe and cannula techniques under ultrapure (99.999%) nitrogen.

Synthesis of a Pre-formed TMEDA/nBuLi Adduct. A 25-mL round-bottomed flask was charged with nBuLi (5 mL, 8 mmol) and cooled to -20 °C. The tertiary diamine TMEDA (0.59 mL, 4 mmol) was added drop-wise. Upon addition of the tertiary diamine, the white TMEDA/nBuLi adduct formed rapidly. Prior to initiation of the polymerization, the adduct was re-dissolved by heating to 67 °C and used to initiate the polymerization.

Polymer Synthesis. Synthesis of poly(1,3-cyclohexadiene)-*block*-polyisoprene-*block*-DVB. A 500-mL round-bottomed flask containing anhydrous cyclohexane (60 mL, 0.54 mol) and 1,3-cyclohexadiene (6.70 mL, 62.5 mmol) was maintained at 25 ± 3 °C. The preformed TMEDA:nBuLi initiator (0.56 mmol) was added using a syringe and the polymerization was maintained at the prescribed temperature for 120 minutes. Following the polymerization of 1,3-cyclohexadiene, isoprene (17 mL, 78 mmol) and cyclohexane (300 mL, 1.71 mol) was added to the reaction. Upon addition of isoprene, the polymerization immediately changed to a light green color, indicative of the poly(isoprenyllithium) species in the presence of TMEDA. The isoprene was polymerized for 2h prior to the addition of DVB (0.72 mL, 3.51 mmol). Upon addition of DVB, the polymerization immediately changed to a deep red color, indicative of the divinylbenzyl lithium species. The DVB coupling reaction was allowed to proceed for 12h at 40 °C. The polymerization was terminated using degassed methanol (Burdick-Jackson, HPLC grade). The resulting polymer was precipitated into isopropanol (2.5 L), filtered, and dried at 50 °C in vacuo for 12-18 hours. An antioxidant such as

Irganox 1010 (0.10 weight % compared to the polymer) was added to the precipitation solvent to retard oxidative degradation during subsequent storage.

Polymer Characterization. ^1H NMR spectra were determined in CDCl_3 at 400 MHz with a Varian Spectrometer. Glass transition temperatures were determined using a Perkin-Elmer Pyris 1 DSC at a heating rate of 10 $^\circ\text{C}/\text{min}$ under nitrogen. Glass transition temperatures are reported as the midpoint of the change in heat capacity during the second heat. Molecular weights were determined using size exclusion chromatography (SEC) with a Water Alliance SEC system equipped with a Viscotek 150R viscosity detector. In addition, a Waters 717plus equipped with a Waters 2410 refractive index detector and a Wyatt Technology Minidawn MALLS detector was utilized for absolute molecular weight measurements. The dn/dc values were determined on-line using the calibration constant for the RI detector and the mass of the polymer sample. For all samples, it was assumed that 100% of the polymer eluted from the column during the measurement. SEC measurements were performed at 40 $^\circ\text{C}$ in chloroform at a flow rate of 1.0 mL/min.

Film Preparation. Samples for viscoelastic measurements were prepared by dissolving the block copolymers in chloroform (10 wt%) in the presence of an antioxidant (Irganox 1010, Ciba-Geigy Group). The polymer solution was poured into a Petri dish and the solvent was allowed to slowly evaporate over 5-7 days at 25 $^\circ\text{C}$. The films were then dried at 40 $^\circ\text{C}$ for 4 h and finally dried at 80 $^\circ\text{C}$ for 24 h to a constant weight. These films were clear, colorless and elastomeric.

Dynamic Mechanical Analysis. Dynamic mechanical analysis (DMA) was performed of a TA-instruments 2988 dynamic mechanical analyzer. The storage modulus (G') and loss modulus (G'') were measured at a fixed frequency and strain (110%). Samples were prepared from solution cast films and cut to a constant size (1 X 8 X 0.25 mm) and were deformed at a constant rate (1hz) at a heating rate of 5 $^\circ\text{C}/\text{min}$. The glass transition temperature for the polyisoprene block was determined by measuring the peak in the loss modulus. The glass transition temperature for the poly(1,3-

cyclohexadiene) block was estimated by measuring the temperature where the elastomer mechanically failed. It was assumed that at this elevated temperature the onset of the T_g for poly(1,3-cyclohexadiene) resulted in the failure of the poly(1,3-cyclohexadiene) domains and subsequent mechanical failure of the elastomer.

Tensile Measurements. The tensile properties of the polymers were determined using a Texture Analyzer, (Texture Analysis Inc). Films samples were solution cast as described above, cut into microdumbbells (10 x 2.70 x 0.25 mm), and characterized as outlined in ASTM D 882-01. Data are reported as the average of 3 or more measurements.

Atomic Force Microscopy. Atomic force microscopy (AFM) was performed on a Nanoscope III microscope from Digital Instruments Inc. operated at room temperature in the tapping mode in air using microfabricated cantilevers provided by the manufacturer (spring constant of 30 N m⁻¹). Digital Instruments image processing software was used for image analysis. The set point and tapping amplitude was 1.80 and 2.80 V, respectively. Silicon wafers were prepared by sonication in methanol and were subsequently dried under nitrogen. Polymer samples were prepared for AFM analysis by dissolving the polymer in toluene (4 wt%) and spin coated on prepared silicon wafers at 2000 rpm. The samples were annealed at 120 °C for 12 h. The samples were characterized by performing AFM in the tapping mode (TMAFM) as previously described.³⁶⁸

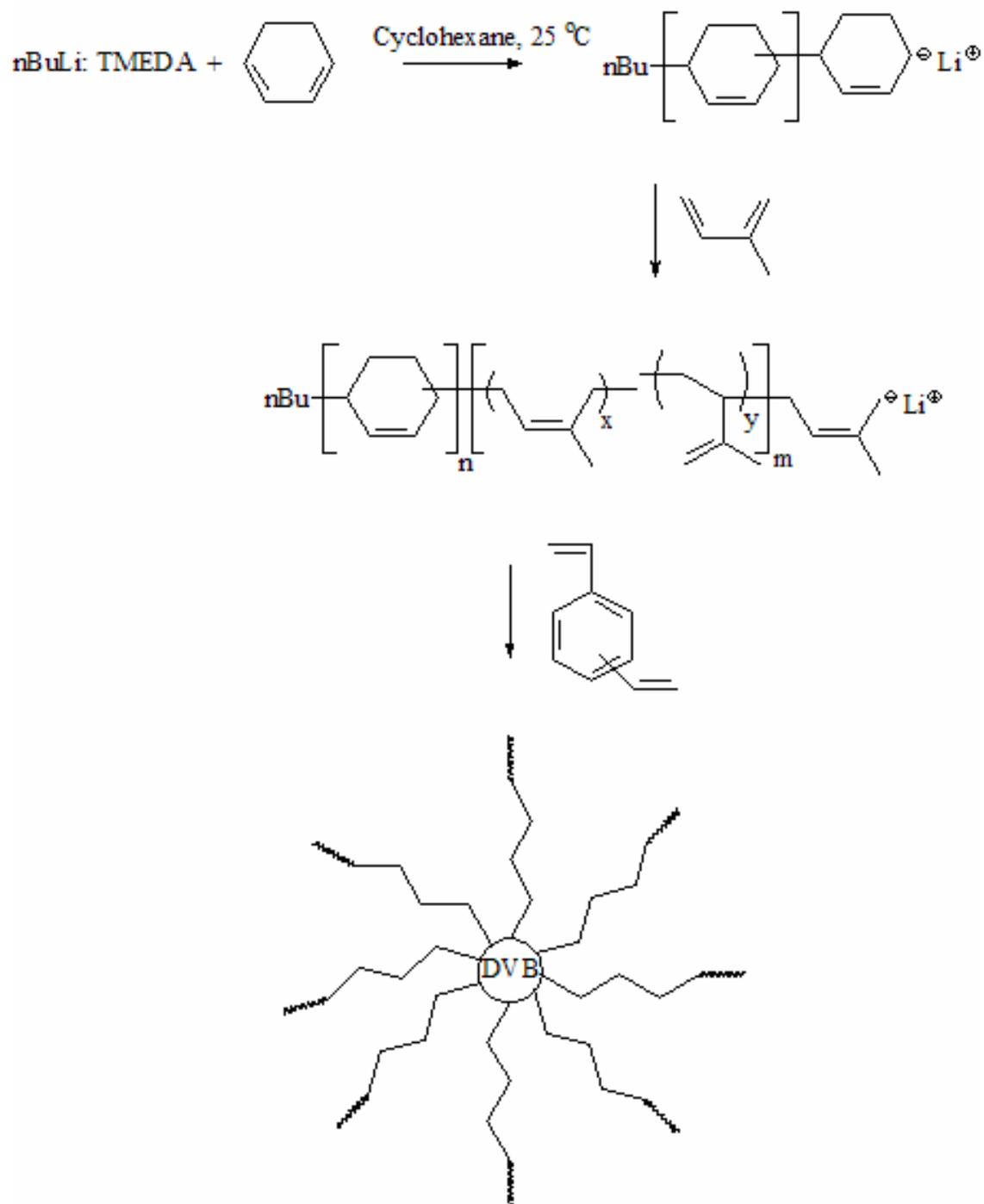
³⁶⁸ Leclere, Ph., R. Lazzaroni, J.L. Bredas, J.M. Yu, P. Dubois, and R. Jerome. "Microdomain Morphology Analysis of Block Copolymers by Atomic Force Microscopy with Phase Detection Imaging." *Langmuir* **1996**, 12, 4317.

7.4 Results and Discussion

Star-shaped polymers with poly(1,3-cyclohexadiene-*block*-isoprene) arms were prepared using the arm-first method and divinylbenzene as the coupling agent (Scheme 7-1). The poly(1,3-cyclohexadiene-*block*-isoprene) arms were prepared via sequential addition of the monomers and the viscosity of the reaction solution remained low during the synthesis of the arms. The poly(1,3-cyclohexadiene) block remained soluble during the polymerization and the crossover to isoprene was efficient, as indicated by the rapid color change (yellow to green). Previously we have demonstrated that monomer concentration effects the livingness of 1,3-cyclohexadiene polymerizations.³⁶⁹ As such, the synthesis of the poly(1,3-cyclohexadiene) block was performed at a monomer concentration of 10 wt%. To minimize the reaction viscosity during the synthesis of the diblocks, the reaction was diluted to a total polymer concentration of 8 wt% when the isoprene charge was added. In addition, if the reaction was performed in the absence of the dilution step, then the polymerization exhibited a large exotherm (approximately 80 °C) and the polymer product was no longer usable. The highly sensitive nature of living anionic polymerizations required the dilution step to be performed under highly rigorous conditions. In some cases, the dilution step resulted in the termination of the poly(1,3-cyclohexadienyllithium) species rendering the reaction unusable. The success rate of the synthesis was approximately 25%. However, the successful reactions exhibited remarkable reproducibility, with the molecular weight distributions remaining relatively constant ($\langle M_w \rangle / \langle M_n \rangle = 1.36 \pm 0.15$). The majority of this error was attributed to the inherent error associated with the molecular weight determination, which is typically 10%. As described in chapter 5, the polymerization of the polyisoprene block was monitored with in-situ FTIR spectroscopy to verify the near quantitative conversion (>95%) of the isoprene prior to the addition of the DVB coupling agent.

³⁶⁹ Williamson, D.T., and T.E. Long. "Combining statistical design of experiments with in-parallel polymerization methodologies." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **2001**, 42, 634.

Upon addition of DVB to the poly(1,3-cyclohexadiene)-*block*-poly(isoprenyllithium) solution, the reaction color immediately changed from green to a deep red color indicative of the formation of a highly delocalized benzylic anion resulting from the rapid crossover from the poly(1,3-cyclohexadiene)-*block*-poly(isoprenyllithium) anion to the DVB monomer. The molecular weight characterization of a star-shaped polymer with poly(1,3-cyclohexadiene-*block*-isoprene) arms (sample # 30TPE81) is shown in Figure 7-1. The coupling efficiency was estimated from the GPC-DRI measurements, although in some cases the peak from the residual uncoupled diblock could not be deconvoluted from the star polymer peak and no attempts to isolate the star-shaped elastomers by fractionation were made.



Scheme 7-1. Synthetic approach used to synthesize poly(1,3-cyclohexadiene-*block*-isoprene) DVB coupled star-shaped elastomers.

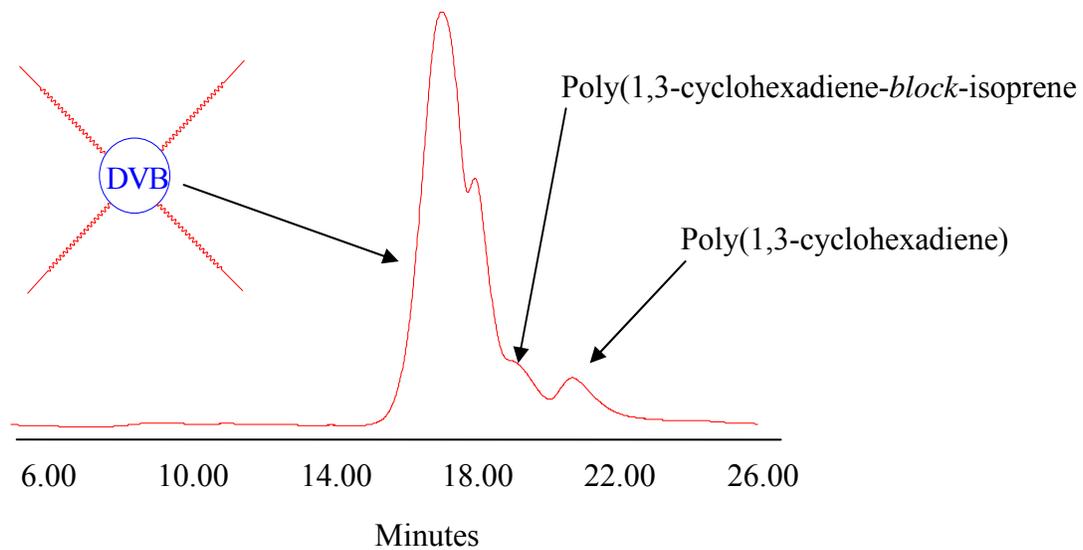


Figure 7-1. GPC characterization of a poly(1,3-cyclohexadiene-*block*-isoprene) DVB coupled star-shaped copolymer with a $\langle M_n \rangle = 192000$ and a $\langle M_w \rangle / \langle M_n \rangle = 1.25$ (Sample # 30TPE81).

For all samples synthesized in this study, the degree of coupling of the poly(1,3-cyclohexadiene-*block*-isoprene) arms to the DVB core was approximately 90-95%.

To study the effect of the DVB/nBuLi ratio on the coupling efficiency and number of arms per star, a series of star-shaped polymers were synthesized using a constant diblock arm length of 30000 g/mol with varying ratios of DVB to nBuLi (Table 7-1). The molecular weights were determined using MALLS due to the improved accuracy of MALLS compared to viscometric methods for branched polymer architectures. The resulting polymers exhibited high molecular weights (80000 to 192000) and narrow molecular weight distributions (1.25 to 1.31). As expected, an important factor for the control of the star polymer molecular weight was the DVB/initiator ratio. The average number of arms per star (f) were determined using the following formula, where %DVB is the weight percent of the DVB in the star:

$$\text{Equation 7-1} \quad f = ((M_n^{\text{star}}) - \% \text{DVB} * (M_n^{\text{star}})) / M_{n(\text{th})}^{\text{arms}}$$

Star-shaped polymers comprising arms with a number average molecular weight of 30,000 g/mol were prepared at a linking efficiency of approximately 90-95%. The resulting polymers all exhibited relatively narrow molecular weight distributions and a high percent of conversion of the living anionic arms to the DVB core as shown in Table 7-1. At low ratio of DVB/nBuLi of 3:1 (sample # 30TPE31), the number of arms per star (f) was 2.7, which indicated that approximately 30% of the coupled diblocks were dimers. The remaining 70% was comprised of three arm stars. As the DVB/nBuLi ratio was increased, the core size also increased allowing for a greater number of arms attached to the core. Surprisingly, when the DVB/nBuLi ratio was further increased from 8/1 (sample # 30TPE81) to 12/1 (sample # 30TPE121), the number of arms decreased from 6.4 to 4.7.

Table 7-1. Characterization of poly(1,3-cyclohexadiene-*block*-isoprene) DVB coupled star-shaped polymers synthesized with varying ratios of DVB/nBuLi. Coupling efficiency was determined using the DRI signal and the number of arms was determined using Equation 7-1.

Polymer	Block size	DVB/nBuLi	$\langle M_n \rangle^{**}$	$\langle M_w \rangle / \langle M_n \rangle^{**}$	Coupling Efficiency (%) [*]	Number of Arms (f)
30TPE31	10K-30K	3:1	800000	1.27	98	2.7
30TPE61	10K-30K	6:1	120000	1.27	98	4.0
30TPE81	10K-30K	8:1	192000	1.25	95	6.4
30TPE121	10K-30K	12:1	140000	1.31	96	4.7

GPC Conditions: 40 °C, Chloroform, *DRI signal used, **MALLS signal used

Previous studies have demonstrated that at increased ratios of DVB/nBuLi, the molecular weight increased due to star-star coupling.³⁷⁰ Characterization of the star-shaped polymers using MALLS enabled the identification of these larger molecular weight species. As shown in Figure 7-2, when the ratio of DVB/nBuLi increased, then the relative amount of higher molecular weight species increased. This was attributed to star-star coupling, which was shown to occur in polyisoprene based star-shaped polymers using DVB as the coupling agent. In spite of the introduction of these higher molecular weight species, the molecular weight distribution of these star-shaped, elastomeric polymers did not increase significantly when the DVB/nBuLi ratio was increased. A ratio of DVB/nBuLi of 8/1 (sample # 30TPE81) resulted in elastomeric, star-shaped materials with the highest molecular weight (192000) and smallest molecular weight distribution (1.25). As such, a ratio of DVB/nBuLi of 8/1 was used to synthesize a series of polymers containing varying compositions of 1,3-cyclohexadiene.

The relative volume fractions of the component blocks in a block copolymer were previously shown to determine the morphology presented by the block copolymers, in both the solid state and in solution.³⁷¹ These morphologies in turn impact the thermal and mechanical properties of the elastomeric material. A series of poly(1,3-cyclohexadiene) star-shaped elastomers were synthesized with varying volume fractions of 1,3-cyclohexadiene to investigate the effect of the polymer composition on mechanical properties. The ratio of DVB/nBuLi was 8/1 for all the polymers synthesized and the volume fraction of poly(1,3-cyclohexadiene) varied from 15% (sample # 15TPE81) to 50% (sample # 50TPE81). The molecular weight characterization of these polymers is reported in Table 7-2.

³⁷⁰ McGrath, J.E., ed. *Anionic Polymerization: Kinetics, Mechanisms, and Synthesis*. Edited by Joan Comstock. Vol. 166, *ACS Symposium Series* American Chemical Society: Washington D.C., 1981.

³⁷¹ McGrath, J.E. "An Introductory Overview of Block Copolymers." In *Block Copolymers: Science and Technology*, edited by D.J. Meier. New York: Harwood Academic Publishers, 1979.

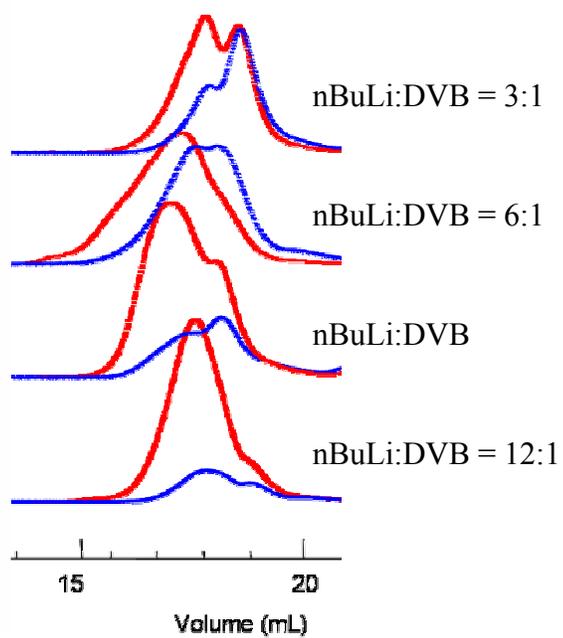


Figure 7-2. Molecular weight characterization of the series of star-shaped polymers with varying ratios of DVB/nBuLi, the light scattering data (top curves) is superimposed on the refractive index data (bottom curves).

Table 7-2. Characterization of poly(1,3-cyclohexadiene-*block*-isoprene) DVB coupled star-shaped polymers synthesized with varying percentage of poly(1,3-cyclohexadiene). Coupling efficiency was determined using the DRI signal and the number of arms was determined using Equation 7-1.

Polymer	Block Size PCHD-b-PI	DVB/nBuLi	$\langle M_n \rangle^{**}$	$\langle M_w \rangle / \langle M_n \rangle^{**}$	Coupling Efficiency (%) [*]
15TPE81	10K-40K	8:1	350000	1.50	75
30TPE81	10K-30K	8:1	192000	1.25	95
50TPE81	10K-10K	8:1	120000	1.28	85

GPC Conditions: 40 °C, Chloroform, *DRI signal used, **MALLS signal used

The composition of these polymers was determined using ^1H NMR spectroscopy and agreed well with the relative monomer amounts that were charged to the reactions. The resulting polymers exhibited high molecular weights and narrow molecular weight distributions. During the synthesis of sample # 15TPE81, the viscosity of the polymer sample increased upon DVB addition and stirring efficiency was reduced. These factors were believed to be responsible for the broad molecular weight distribution and reduced coupling efficiency. Reaction viscosity remained low for the rest of the polymers samples synthesized and the star-shaped polymers were well-defined.

These polymers were characterized using both differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) (Table 7-3). DSC analysis of these star-shaped polymers was effective in determining the glass transition temperature (T_g) of the polyisoprene block. These T_g s ranged from $-15\text{ }^\circ\text{C}$ to $-13\text{ }^\circ\text{C}$. These elevated glass transition temperatures relative to high 1,4 polyisoprene were attributed to the high percentage of 3,4-addition that resulted from the presence of TMEDA in the polymerization solution. The average percentage of 3,4-addition was 53% and was estimated using ^1H NMR (Figure 7-3). As expected, the volume fraction of the poly(1,3-cyclohexadiene) block was too small to accurately measure the T_g using DSC analysis. A poly(1,3-cyclohexadiene) homopolymer control was synthesized ($\langle M_n \rangle = 10000$, $\langle M_w \rangle / \langle M_n \rangle = 1.05$) and the glass transition temperature was measured. The T_g for this polymer was $138\text{ }^\circ\text{C}$, which was expected based on our earlier studies.³⁷² The star-shaped elastomers were also characterized using DMA (Figure 7-4), which was expected to be effective for measuring the T_g for both the poly(1,3-cyclohexadiene) and polyisoprene blocks. The glass transition temperature for the polyisoprene block was determined by examining the peak in the loss modulus. These T_g s varied from -5 to $-8\text{ }^\circ\text{C}$, which was within the error of the measurement. The glass transition temperature for the poly(1,3-cyclohexadiene) block was also measured effectively using the DMA.

³⁷² Williamson, D.T., C.L. Hudelson, and T.E. Long. "Synthesis of Telechelic High Molecular Weight Poly(1,3-cyclohexadienes)." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **2002**, 43, 502.

Table 7-3. Thermal analysis of poly(1,3-cyclohexadiene-*block*-isoprene) DVB coupled star-shaped polymers synthesized with varying ratios of DVB/nBuLi.

Polymer	T _g polyisoprene*	T _g polyisoprene**	T _g poly(1,3-cyclohexadiene)*	T _g poly(1,3-cyclohexadiene)**
PCHD(10K)			138 °C	Not Determined
30TPE31	-15 °C	-5 °C	Not Detected	146 °C
30TPE61	-14 °C	-2 °C	Not Detected	148 °C
30TPE81	-13 °C	-3 °C	Not Detected	145 °C
30TPE121	-14 °C	-1 °C	Not Detected	151 °C

DSC Conditions: 20 °C/min, second heat, Nitrogen environment

DMA Conditions: 5 °C/min, second heat, Nitrogen environment, 1hz

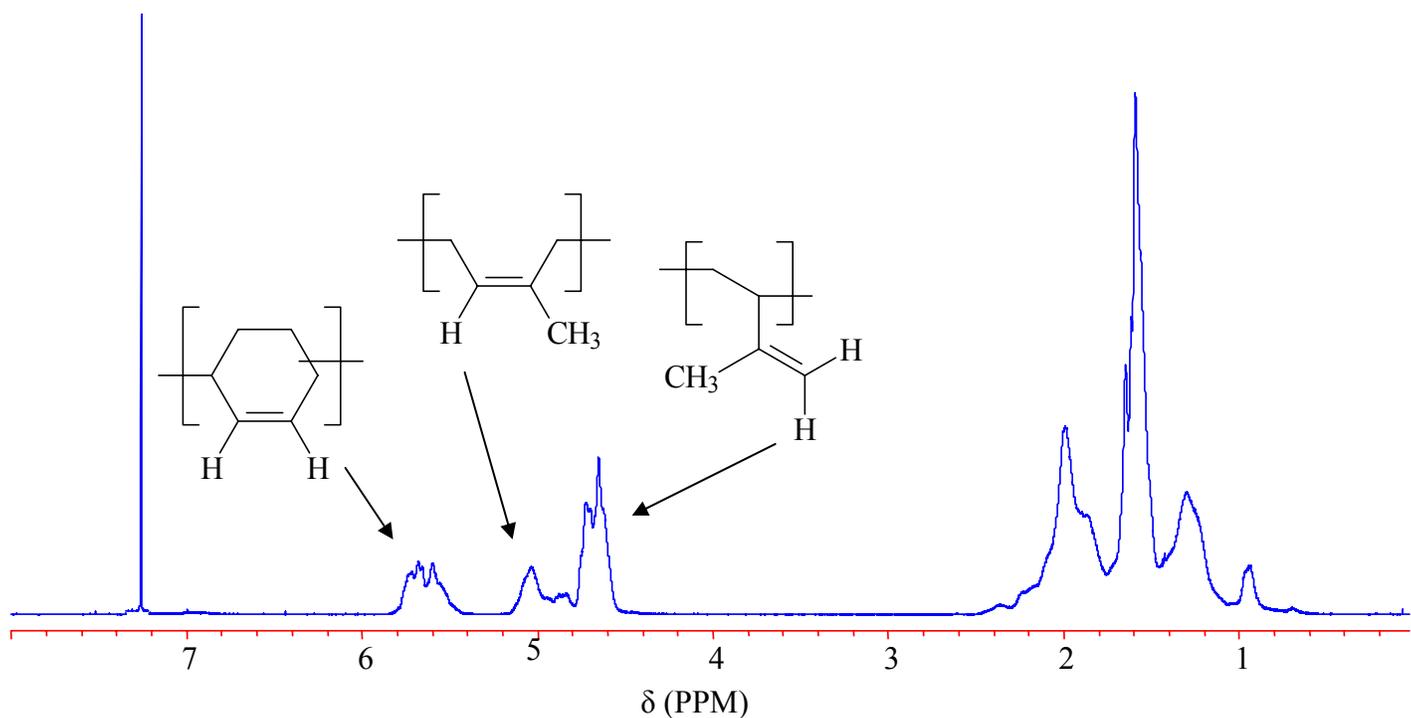


Figure 7-3. ¹H NMR characterization of a poly(1,3-cyclohexadiene-*block*-isoprene) DVB coupled elastomer (30TPE31). The polymer composition and degree of 3,4 versus 1,4-addition were determined by examining the absorbances at 5.6 ppm (poly(1,3-cyclohexadiene)), 5.1 ppm (polyisoprene, 1,4 microstructure), and 4.75 (polyisoprene, 1,2 microstructure).

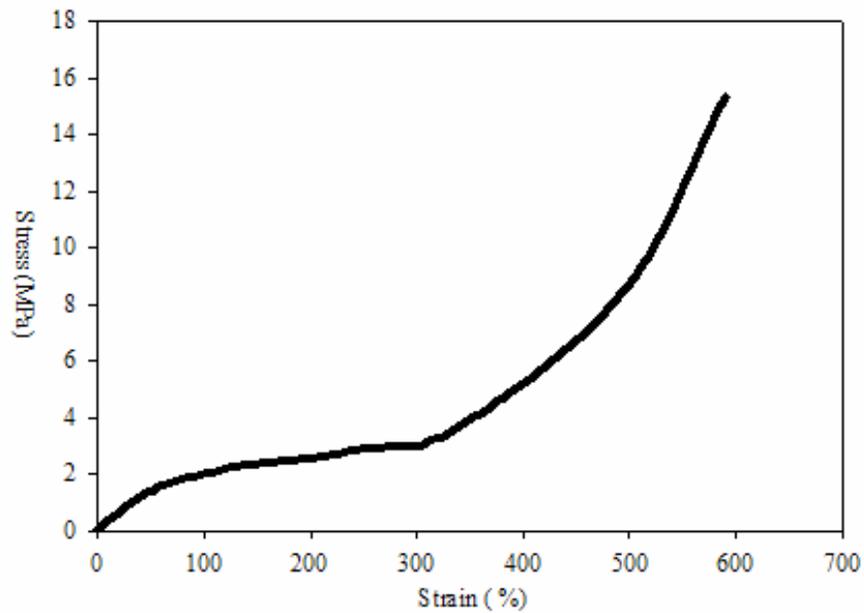


Figure 7-4. Mechanical analysis of a poly(1,3-cyclohexadiene-*block*-isoprene) DVB coupled star-shaped elastomer (Sample # 30TPE81). Instron testing was performed according to ASTM D-882-01.

These samples exhibited a glass transition temperature of approximately 148 °C. This T_g agreed well with the T_g measured by DSC analysis for the poly(1,3-cyclohexadiene) homopolymer control (sample # pCHD10K). As expected, the presence of two different glass transition temperatures indicated that the polyisoprene blocks phase separated from the poly(1,3-cyclohexadiene) blocks.

Elastomeric properties were expected to arise from the phase separation between the high T_g poly(1,3-cyclohexadiene) blocks and the low T_g polyisoprene blocks. Instron analysis was performed to measure the elastomeric properties of the polymers. The polymers were solution cast from chloroform into clear films. These films were dried under vacuum for 28 h to ensure the quantitative removal of the solvent. The films were then cut into microdumbbells and their tensile properties were measured according to ASTM D-882-01 (Figure 7-5). The effect of the ratio of DVB/nBuLi was examined by comparing the tensile properties of samples that were synthesized with a DVB/nBuLi ratio of 3:1, 6:1, 8:1, and 12:1. These polymers exhibited an average elongation at break of 633% and an average tensile strength of 17.0 MPa. As expected, the ratio of DVB did not affect the elastic modulus, elongation at break, or the tensile strength of the polymers. However, a number of previous studies have shown the impact of composition on the tensile properties of the polymer.³⁷³ The presence of increasing percentages of the high T_g component was shown to alter the polymer morphology and in turn impact the tensile properties of the polymer. Instron analysis was performed on elastomers with varying poly(1,3-cyclohexadiene) content (15%, 30%, and 50%) to examine the effect of polymer composition (Table 7-4). As the percentage of poly(1,3-cyclohexadiene) increased, the elongation at break decreased and the tensile strength increased. The elastic modulus also increased as the percentage of 1,3-cyclohexadiene increased.

³⁷³ McGrath, J.E. "An Introductory Overview of Block Copolymers." In *Block Copolymers: Science and Technology*, edited by D.J. Meier. New York: Harwood Academic Publishers, 1979.

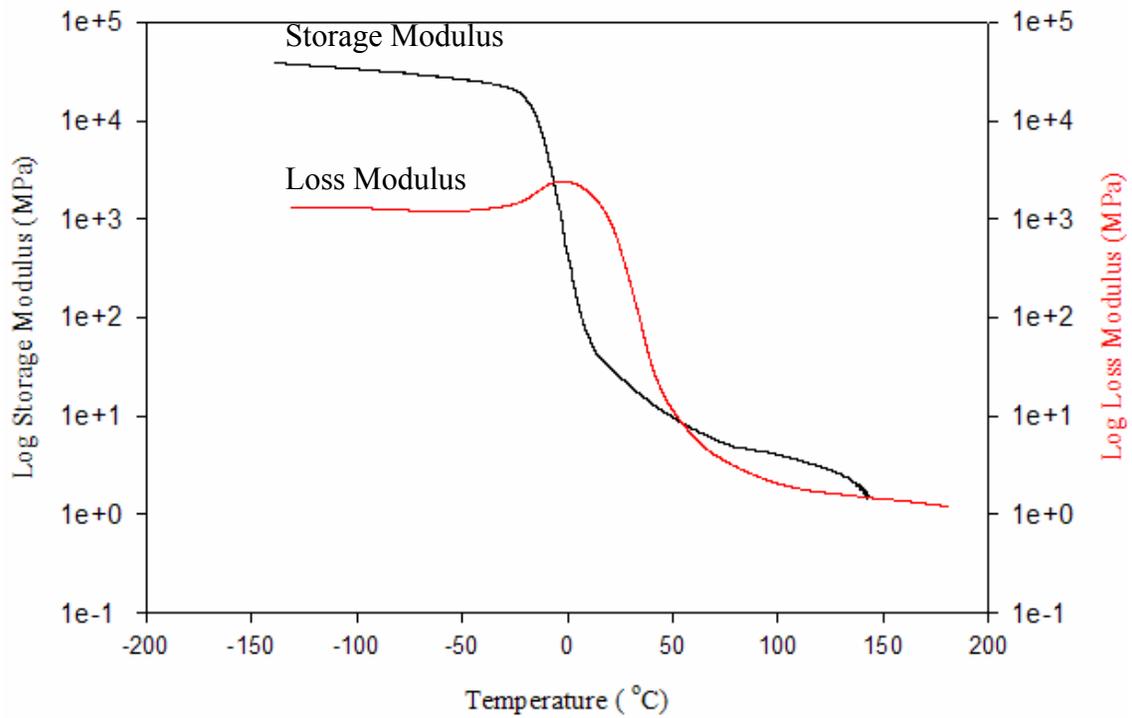


Figure 7-5. Characterization of a poly(1,3-cyclohexadiene-*block*-isoprene) DVB coupled star-shaped elastomer (Sample # 30TPE81) using DMA.

Table 7-4. Mechanical analysis of poly(1,3-cyclohexadiene-*block*-isoprene) DVB coupled star-shaped polymers synthesized with varying percentages of poly(1,3-cyclohexadiene). Instron analysis was performed according to ASTM D-882-01.

Polymer	Elastic Modulus (MPa)	Elongation at Break (%)	Tensile Strength (MPa)
15TPE81	0.5 ± 0.1	745 ± 81	7.2 ± 0.2
30TPE81	2.2± 0.1	650 ± 24	15.1 ± 0.1
50TPE81	9.1± 0.1	212 ± 39	17.0 ± 0.1
Poly(1,3-CHD)	23.0± 0.1*	1.8 ± 0.1	Not Determined

Instron analysis performed according to ASTM D-882-01

* Youngs' Modulus

Previous studies by Natori et al. reported the synthesis poly(1,3-cyclohexadiene-*block*-butadiene-*block*-1,3-cyclohexadiene) that were prepared via sequential addition with approximately 30% poly(1,3-cyclohexadiene) content.³⁷⁴ These polymers typically exhibited a tensile strength of 20-25 MPa and a percent elongation of 700%. Therefore, the star-shaped elastomers prepared in this study exhibit similar mechanical properties to linear polymers with a similar composition.

Multiple glass transition temperatures in combination with excellent elastomeric properties strongly indicated that the poly(1,3-cyclohexadiene) domains phase separated from the polyisoprene domains.³⁷⁵ The presence of microphase separation is generally verified using transition electron microscopy in combination with selective chemical imaging techniques.³⁷⁵ Imaging the microphase separation in poly(1,3-cyclohexadiene) containing elastomers represented a unique challenge due to the chemical similarity of the polymer blocks. The polyisoprene and the poly(1,3-cyclohexadiene) blocks were both susceptible to the classical osmium or ruthenium staining approaches.³⁷⁶ In previous studies, the polyisoprene block was selectively hydrogenated and the poly(1,3-cyclohexadiene) block was subsequently stained with osmium tetroxide.³⁷⁷ Unfortunately, the hydrogenation of the polyisoprene block alters the interaction between the poly(1,3-cyclohexadiene) and the polyisoprene block, thereby affecting both the domain sizes and the degree of microphase separation.

³⁷⁴ Imaizumi, K., Tomohiro Ono, I. Natori, Shinichi Sakuri, and Kunihiko Takedo. "Microphase-Separated Structure of 1,3-Cyclohexadiene/Butadiene Triblock Copolymers and Its Effect on Mechanical and Thermal Properties." *J. Polym. Sci., Part B: Polym. Phys.* **2001**, 39, 13.

³⁷⁵ Stroble, G. *The Physics of Polymers*. 2nd ed Springer-Verlag: Berlin, 1997.

³⁷⁶ Natori, I., K. Imaizumi, H. Yamagishi, and M. Kazunori. "Hydrocarbon Polymers Containing Six-Membered Rings in the Main Chain. Microstructure and Properties of Poly(1,3-cyclohexadiene)." *J. Polym. Sci., Part B: Polym. Phys.* **1998**, 36, 1657.

³⁷⁷ Imaizumi, K., Tomohiro Ono, I. Natori, Shinichi Sakuri, and Kunihiko Takedo. "Microphase-Separated Structure of 1,3-Cyclohexadiene/Butadiene Triblock Copolymers and Its Effect on Mechanical and Thermal Properties." *J. Polym. Sci., Part B: Polym. Phys.* **2001**, 39, 13.

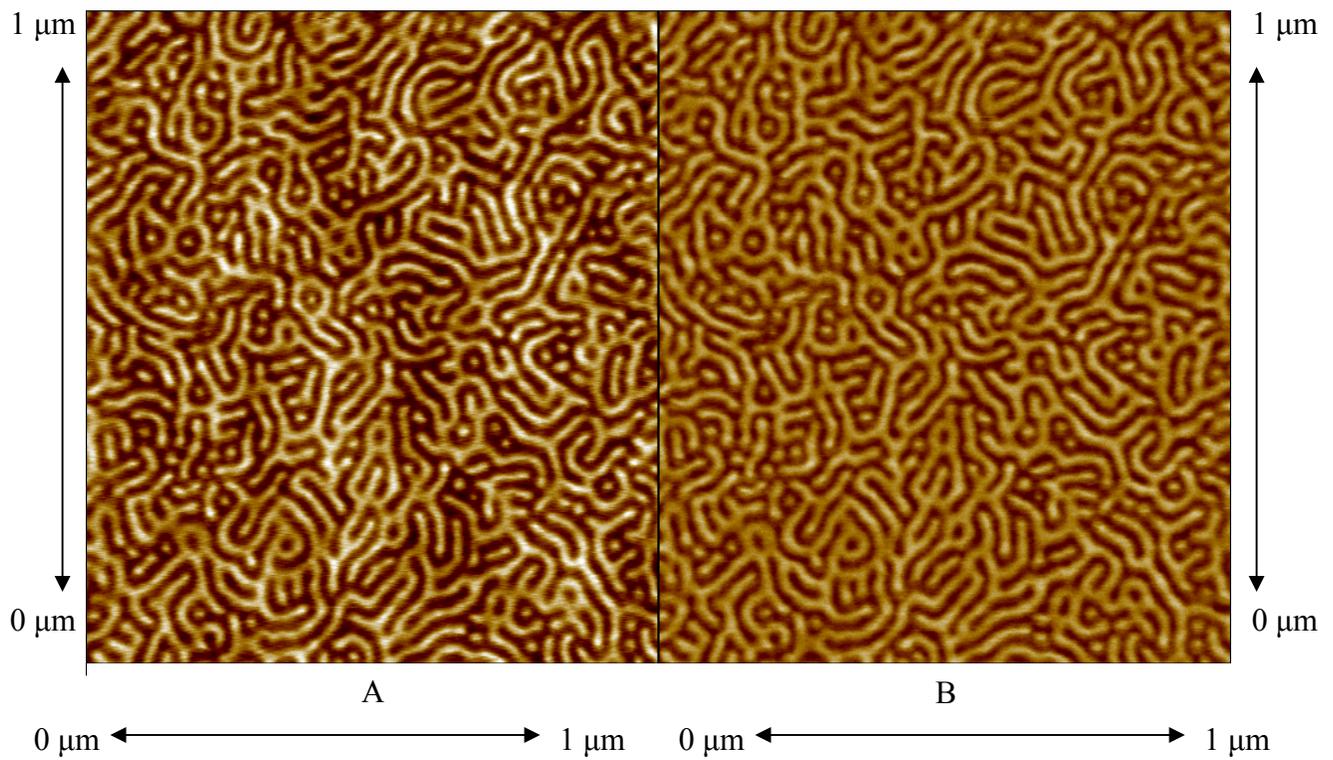


Figure 7-6. Microphase separation present in a poly(1,3-cyclohexadiene-block-isoprene) DVB coupled star-shaped elastomer by TMAFM (Sample # 30TPE81). The poly(1,3-cyclohexadiene) domains appear darker than the polyisoprene domains in both the (A) topographical image and (B) the phase contrast image.

To avoid this complication, tapping mode atomic force microscopy (TMAFM) was used to examine the microphase separation of the poly(1,3-cyclohexadiene) and the polyisoprene blocks (Figure 7-6). Silicon wafers were spin coated with a 4 wt% solution of the elastomer (30TPE81) in toluene and the samples were annealed at 120 °C for 12 h under vacuum. The presence of microphase separation between the poly(1,3-cyclohexadiene) block and the polyisoprene block was readily apparent (Figure 7-6A and B). The image on the left is a topographical image of the surface (Figure 7-6A) and the image on the right is the phase contrast image of the surface (Figure 7-6B). Previous studies described the utility of the phase contrast image for the detection of microphases based on the differences in the viscoelastic response of the various blocks.³⁷⁸ The reduced interaction time of the AFM tip with the poly(1,3-cyclohexadiene) domains resulted in near zero phase lag values causing the poly(1,3-cyclohexadiene) domains to appear darker (Figure 7-6B). The polyisoprene domains remained in contact with the AFM tip forcing a delay in the tip motion and an increase in the phase lag, giving rise to the brighter areas in the image (Figure 7-6B). The topographical image of the surface was also used to characterize the polymer surface (Figure 7-6A). Previous studies suggested that the height difference between the different domains arises from the ability of the lower T_g domains to relax by protruding out of the surface of the film. Accordingly, the lighter regions in the image were attributed to the protruding domains of the polyisoprene blocks, which constituted approximately 70% of the TMAFM image. The relative percentages of the two domains in the AFM image (30% poly(1,3-cyclohexadiene) and 70% polyisoprene) agreed well with the composition of the star-shaped elastomer, which was 30% poly(1,3-cyclohexadiene) and 70% polyisoprene. To our knowledge, this is the first report verifying the presence of microphase separation in poly(1,3-cyclohexadiene-*block*-isoprene) block copolymers using atomic force microscopy.

³⁷⁸ Leclere, Ph., R. Lazzaroni, J.L. Bredas, J.M. Yu, P. Dubois, and R. Jerome. "Microdomain Morphology Analysis of Block Copolymers by Atomic Force Microscopy with Phase Detection Imaging." *Langmuir* **1996**, 12, 4317.

7.5 Conclusions

A novel series of poly(1,3-cyclohexadiene-block-isoprene) star-shaped elastomers were successfully synthesized using a convergent “arm-first” approach with DVB. These star-shaped elastomers exhibited controlled molecular weights and narrow molecular weight distributions indicative of a controlled living anionic polymerization. As expected, increased ratios of DVB/nBuLi resulted in elevated levels of star-star coupling. The tensile strength, elongation at break, and elastic modulus were dependent on the percentage of poly(1,3-cyclohexadiene) present in the elastomer. Microphase separation of the poly(1,3-cyclohexadiene) and polyisoprene blocks was verified using both DMA and TMAFM analysis. TMAFM was performed and the presence of both poly(1,3-cyclohexadiene) and polyisoprene domains was verified. The domains in the TMAFM image were assigned based on the percent composition of the polymer sample and the relative differences in the viscoelastic response between the poly(1,3-cyclohexadiene) and polyisoprene blocks.

CHAPTER 8

Synthesis of Block Copolymers Based on the Alternating Anionic Copolymerization of Styrene and 1,3-Cyclohexadiene

Taken From:

D.T. Williamson, T.D. Buchanan, and T.E. Long. "Synthesis of Block Copolymers Based on the Alternating Anionic Copolymerization of Styrene and 1,3-Cyclohexadiene" *Macromolecules* **2003**, Submitted for Publication.

8.1 Abstract

A series of poly(1,3-cyclohexadiene-*alt*-styrene) containing block copolymers that exhibited predictable molecular weights and narrow molecular weight distributions were synthesized with various 1,3-cyclohexadiene contents (10-50 mol%). In situ spectroscopy in combination with the Mayo-Lewis graphical method was employed to determine the reactivity ratios for the copolymerization of styrene and 1,3-cyclohexadiene. The reactivity ratios for 1,3-cyclohexadiene and styrene were 0.022 and 0.024, accordingly. The alternating copolymers served as suitable precursors for chemical modification and were either quantitatively aromatized or hydrogenated in a controlled fashion. The thermal stabilities of the modified copolymers were determined, and as expected, the hydrogenated copolymers exhibited improved thermal stability compared to poly(1,3-cyclohexadiene-*alt*-styrene) containing block copolymers. However, the aromatized copolymers unexpectedly exhibited reduced thermal stability in both nitrogen and oxygen environments.

8.2 Introduction

The synthesis of polymers containing poly(1,3-cyclohexadiene) (PCHD) has recently received significant interest.³⁷⁹ These polymers exhibited excellent thermal properties due to a high glass transition temperature for both high 1,4-PCHD (80%) and 1,2-PCHD (70%) of approximately 100 and 150°C, respectively.³⁸⁰ The T_g for high 1,2-PCHD is over 200°C higher than the T_g for high cis 1,4-polyisoprene, which demonstrates that poly(1,3-cyclohexadiene) is unique in the polydiene family. This unusually high T_g was attributed to the cyclic structure of the repeat unit of poly(1,3-cyclohexadiene), which obviously increases the degree of polymer rigidity relative to

³⁷⁹ Williamson, D.T., J.F. Elman, P.H. Madison, A.J. Pasquale, and T.E. Long. "Synthesis and Characterization of Poly(1,3-cyclohexadiene) Homopolymers and Star-shaped Polymers." *Macromolecules* **2001**, 34, 2108. Williamson, D.T., K. Brazhnik, A.J. Pasquale, and T.E. Long. "Synthesis and Characterization of Hydrogenated Poly(1,3-cyclohexadiene) Star-Shaped Polymers." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **2000**, 41, 1544. Hong, K., and J.W. Mays. "1,3-Cyclohexadiene Polymers. 1. Anionic Polymerization." *Macromolecules* **2001**, 34, 782. Imaizumi, K., Tomohiro Ono, I. Natori, Shinichi Sakuri, and Kunihiko Takedo. "Microphase-Separated Structure of 1,3-Cyclohexadiene/Butadiene Triblock Copolymers and Its Effect on Mechanical and Thermal Properties." *J. Polym. Sci., Part B: Polym. Phys.* **2001**, 39, 13. Natori, I., and S. Inoue. "Living Anionic Polymerization of 1,3-cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System. Copolymerization and Block Copolymerization with Styrene, Butadiene, and Isoprene." *Macromolecules* **1998**, 31, 982. Natori, I., and S. Inoue. "Anionic Polymerization of 1,3-cyclohexadiene with Alkylolithium/Amine Systems. Characteristics of n-Butyllithium/N,N,N',N'-Tetramethylethylenediamine System for Living Anionic Polymerization." *Macromolecules* **1998**, 31, 4687. Williamson, D.T., T.E. Glass, and T.E. Long. "Determination of the Stereochemistry of Poly(1,3-cyclohexadiene) Via End-group Functionalization." *Macromolecules* **2001**, 34, 6144. Williamson, D.T., B.D. Mather, and T.E. Long. "Oxidation and Epoxidation of Poly(1,3-cyclohexadiene)." *J. Polym. Sci., Part A: Polym. Chem.* **2002**, 41, 84. Hong, K., and J.W. Mays. "1,3-Cyclohexadiene Polymers. 3. Synthesis and characterization of Poly(1,3-cyclohexadiene-block-styrene)." *Macromolecules* **2001**, 34, 3540.

³⁸⁰ Williamson, D.T., and T.E. Long. "Self-assembled poly(phenylene) containing macromolecules via the controlled anionic polymerization of 1,3-cyclohexadiene." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **2002**, 43, 330. Imaizumi, K., Tomohiro Ono, I. Natori, Shinichi Sakuri, and Kunihiko Takedo. "Microphase-Separated Structure of 1,3-Cyclohexadiene/Butadiene Triblock Copolymers and Its Effect on Mechanical and Thermal Properties." *J. Polym. Sci., Part B: Polym. Phys.* **2001**, 39, 13. Natori, I., K. Imaizumi, H. Yamagish, and M. Kazunori. "Hydrocarbon Polymers Containing Six-Membered Rings in the Main Chain. Microstructure and Properties of Poly(1,3-cyclohexadiene)." *J. Polym. Sci., Part B: Polym. Phys.* **1998**, 36, 1657.

other dienes.³⁸¹ In addition, the cyclic nature of the repeat unit and the presence of a residual double bond renders poly(1,3-cyclohexadiene) as an ideal precursor for the synthesis of a broad range of functionalized polymers.³⁸²

Most anionic copolymerizations are “blocky copolymerizations”, where one monomer is preferentially polymerized prior to the polymerization of the second monomer. Due to the living nature of these chain growth polymerizations, the compositional heterogeneity is incorporated along the polymer chain, forming a tapered block copolymer. The synthesis of tapered copolymers from the copolymerization of styrene and butadiene is a classical example of this effect. In addition, Long et al. used this straightforward approach to synthesize tapered block copolymers of polystyrene and polyisoprene, while monitoring the copolymerization using *in situ* near IR spectroscopy.³⁸³ Various polar additives were shown to increase the randomness of certain anionic copolymerizations, such as styrene and butadiene.³⁸⁴ Tetramethylethylenediamine is one of the most effective polar additives at randomizing the copolymerization of styrene and butadiene. While blocky and random copolymerizations have been shown for anionic reactions, there are very few reports describing alternating, alkyllithium-initiated, copolymerizations. Recent reports suggested that the copolymerization of styrene and 1,1-diphenylethylene was potentially alternating under ideal polymerization conditions.³⁸⁵ However, Bates et al. were unable to synthesize a copolymer with a mole ratio of DPE/styrene of 1:1.

³⁸¹ Natori, I., K. Imaizumi, H. Yamagishi, and M. Kazunori. "Hydrocarbon Polymers Containing Six-Membered Rings in the Main Chain. Microstructure and Properties of Poly(1,3-cyclohexadiene)." *J. Polym. Sci., Part B: Polym. Phys.* **1998**, 36, 1657.

³⁸² Williamson, D.T., K. Brazhnik, A.J. Pasquale, and T.E. Long. "Synthesis and Characterization of Hydrogenated Poly(1,3-cyclohexadiene) Star-Shaped Polymers." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **2000**, 41, 1544.

³⁸³ Long, T.E., H.Y. Lui, D.M. Schell, D.M. Teegarden, and D.S. Uerz. "Determination of Solution Polymerization Kinetics by Near-Infrared Spectroscopy. 1. Living Anionic Polymerization Process." *Macromolecules* **1993**, 26, 6237.

³⁸⁴ Antkowiak, T.A., A.E. Oberster, A.F. Halasa, and D.P. Tate. "Temperature and concentration effects on polar-modified alkyllithium polymerizations and copolymerizations." *J. Polym. Sci., Part A: Polym. Chem.* **1972**, 10, 1319.

³⁸⁵ Xu, J.J., and F.S. Bates. "Synthesis and Thermal Properties of Hydrogenated Poly(styrene-co-1,1-diphenylethylene) Copolymers." *Macromolecules* **2003**, 36, 5432.

In contrast, the mechanism of most free radical copolymerizations lies between being an “ideal copolymerization” or an “alternating copolymerization”. In an ideal copolymerization, the product of the reactivity ratios (r_1r_2) is 1.0 and the distribution of monomers in the polymer chain at any time during the polymerization is random. In contrast, the product of the reactivity ratios in an alternating copolymerization is zero and the polymer composition is 1:1, independent of the composition of the monomer feed. The polymerization mechanism becomes increasingly alternating as the r_1r_2 product approaches zero. Determining accurate reactivity ratios is critical to understanding the reaction mechanism and predicting the approximate copolymer composition from the monomer composition.

Traditional approaches for determining accurate polymerization reaction data include gravimetric and molecular weight analysis or reaction sampling followed by chromatographic or spectroscopic sampling. Reaction sampling techniques are plagued by the introduction of oxygen or other impurities during sampling, and these impurities are particularly harmful to anionic polymerizations. Previous studies have shown *in situ* spectroscopy to be a viable alternative, state-of-the-art, real-time, monitoring technique that is well suited to obtain monomer conversion data for polymerization processes.³⁸⁶ This robust technique was also used to characterize a number of anionic processes including the living anionic polymerization of 1,3-cyclohexadiene.³⁸⁷ A number of recent reports have described the application of *in situ* mid-IR spectroscopy for the measurement of monomer conversion and subsequent determination of the reactivity ratios. These studies included the determination of acrylonitrile/methyl acrylate and norbornene/maleic anhydride reactivity ratios.³⁸⁸

³⁸⁶ Pasquale, A.J., and T.E. Long. "Real-Time Monitoring of the Stable Free Radical Polymerization of Styrene via in-Situ Mid-Infrared Spectroscopy." *Macromolecules* **1999**, 32, 7954.

³⁸⁷ Williamson, D.T., J.F. Elman, P.H. Madison, A.J. Pasquale, and T.E. Long. "Synthesis and Characterization of Poly(1,3-cyclohexadiene) Homopolymers and Star-shaped Polymers." *Macromolecules* **2001**, 34, 2108.

³⁸⁸ Pasquale, A. J., J.R. Lizotte, D.T. Williamson, and T. E. Long. "The allure of "molecular videos": In-situ infrared spectroscopy of polymerization processes." *Polymer News* **2002**, 27,

Facile chemical modification reactions that are directed at the residual double bond in the repeat unit provide for straightforward synthetic routes to PCHD derived polymers. Epoxidation,³⁸⁹ hydrogenation,³⁹⁰ and maleation³⁹¹ are a few examples of the modification reactions that were performed on conventional polydienes, such as polyisoprene and poly(1,3-butadiene).³⁹² Recent studies in our laboratories have examined the synthesis and characterization of epoxidized poly(1,3-cyclohexadiene).³⁹³ In contrast to other polydienes, poly(1,3-cyclohexadiene) was also previously demonstrated as a well-defined precursor for the synthesis of new families of poly(phenylene) containing polymers.³⁹⁴ Unfortunately, conventional poly(phenylene) homopolymers are typically intractable and insoluble, and generally exhibit poor polymer processability.³⁹⁵

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272. Wiles, K.B., V.A. Bhanu, A. J. Pasquale, T. E. Long, and J.E. McGrath. "Determination of reactivity ratios for acrylonitrile/methyl acrylate radical copolymerization via non-linear methodologies using real time FTIR." *J. Polym. Sci. Part A*. **2003** accepted for publication
- ³⁸⁹ Nor, H., and J.R. Ebdon. "Telechelic Liquid Natural Rubber." *Prog. Polym. Sci.* **1998**, 23, 143. Sakai, T., N. Kihara, and T. Endo. "Polymer Reaction of Epoxide and Carbon Dioxide. Incorporation of Carbon Dioxide into Epoxide Polymers." *Macromolecules* **1995**, 28, 4701. Roland, C.M., J.K. Kallitsis, and K.G. Gravalos. "Plateau Modulus of Epoxidized Polybutadiene." *Macromolecules* **1993**, 26, 6474.
- ³⁹⁰ Nor, H., and J.R. Ebdon. "Telechelic Liquid Natural Rubber." *Prog. Polym. Sci.* **1998**, 23, 143.
- ³⁹¹ Odian, George. *Principles of Polymerization* John Wiley and Sons Inc: New York, 1991. Nor, H., and J.R. Ebdon. "Telechelic Liquid Natural Rubber." *Prog. Polym. Sci.* **1998**, 23, 143.
- ³⁹² Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996.
- ³⁹³ Williamson, D.T., B.D. Mather, and T.E. Long. "Oxidation and Epoxidation of Poly(1,3-cyclohexadiene)." *J. Polym. Sci., Part A: Polym. Chem.* **2002**, 41, 84.
- ³⁹⁴ Francois, B., and X. Zhong. "Kinetics of 1,3-cyclohexadiene polymerization initiated by organolithium compounds in a non-polar medium." *Makromol. Chem.* **1990**, 191, 2743. Zhong, X., and B. Francois. "Kinetics of 1,3-cyclohexadiene polymerization by organolithium compounds in a non-polar medium. 1." *Makromol Chem* **1990**, 191, 2735. Mignard, E., C. Tachon, and B. Francois. "Neutron scattering analysis of a block copolymer poly(1,4-phenylene)-block-polystyrene-block-poly(phenylene)." *Synth. Met.* **1999**, 102, 1246. Francois, B., S. Izzillo, and P. Iratcabal. "Substituted PPV block copolymer from anionically prepared precursor." *Synth. Met.* **1999**, 102, 1211. Francois, B., G. Widawski, M. Rawiso, and B. Cesar. "Block-copolymers with conjugated segments: Synthesis and structural characterization." *Synth. Met.* **1995**, 69, 463.
- ³⁹⁵ Odian, George. *Principles of Polymerization* John Wiley and Sons Inc: New York, 1991.

A variety of synthetic strategies were investigated to improve the solubility of poly(phenylene)-based polymers. First, the incorporation of pendant aliphatic groups on the polymer backbone was performed in an attempt to improve solubility without disrupting the conjugated backbone.³⁹⁶ However, this method required the tedious synthesis of novel alkyl substituted aromatic monomers. A more direct and cost effective method involved the synthesis of diblock copolymers, wherein the poly(phenylene) block was attached to a more soluble block such as polystyrene.³⁹⁷ This approach has typically employed PCHD blocks and a second solubilizing block, such as polystyrene. The PCHD block was subsequently aromatized at high temperatures (130°C) in the presence an aromatizing agent, such as chloranil. Francois and coworkers have extensively studied the synthesis and performance of poly(styrene-*block*-phenylene) copolymers.³⁹⁸ The reaction conditions used in these studies resulted in the undesirable oxidation of both the cyclohexene repeat unit and the main chain benzylic position in the polystyrene repeat units. However, these copolymers exhibited interesting optical and electrical properties that were attributed to extended conjugation in the 1,4-substituted poly(phenylene) repeat unit. A third method that is typically employed to improve the solubility of highly rigid polymers involves the addition of comonomers; however, this approach disrupts the desirable conjugation length.³⁹⁹

³⁹⁶ Marsitzky, D., T. Brand, Y. Geerts, M. Klapper, and K. Mullen. "Synthesis of rod-coil block copolymers via end-functionalized poly(p-phenylene)s." *Macromol. Rapid Commun.* **1998**, 19, 385.

³⁹⁷ Francois, B., G. Widawski, M. Rawiso, and B. Cesar. "Block-copolymers with conjugated segments: Synthesis and structural characterization." *Synth. Met.* **1995**, 69, 463. Mignard, E., C. Tachon, and B. Francois. "Neutron scattering analysis of a block copolymer poly(1,4-phenylene)-*block*-polystyrene-*block*-poly(phenylene)." *Synth. Met.* **1999**, 102, 1246. Francois, B., S. Izzillo, and P. Iratcabal. "Substituted PPV block copolymer from anionically prepared precursor." *Synth. Met.* **1999**, 102, 1211.

³⁹⁸ Francois, B., G. Widawski, M. Rawiso, and B. Cesar. "Block-copolymers with conjugated segments: Synthesis and structural characterization." *Synth. Met.* **1995**, 69, 463. Mignard, E., R.C. Hiorns, and B. Francois. "Synthesis and Characterization of Star Copolymers Consisting of Fullerene and Conjugated Poly(phenylene)." *Macromolecules* **2002**, 35, 6132.

³⁹⁹ Rusanov, A. L., M. L. Keshtov, and N. M. Belomoina. "New synthetic approach to the preparation of polyphenyleneethynylenes and polyheteroaryleneethynylenes." *High Performance Polymers* **2001**, 13, 153.

Poly(phenylenes) exhibit excellent oxidative stability due to the lack of labile hydrogens. On the other hand, polydienes are more sensitive to oxidation due to their ability to form both stable free radicals and peroxy radicals due to the reactivity at the allylic position.⁴⁰⁰ For example, polystyrene, poly(1,3-butadiene), and polyisoprene were shown to readily form the peroxy radical, resulting in poor oxidative stability. In contrast, polymers such as polyethylene and polypropylene do not readily form the peroxy radical and are less sensitive to oxidation. The oxidative behavior of polystyrene has appeared anomalous due to oxidative instability in solution, but demonstrated excellent oxidative stability in the solid state. This unusually high oxidative stability was attributed to the lack of segmental motion in the polymer chain when the polymer was below the glass transition temperature (104°C). However, when polystyrene was heated above 104°C, segmental motion occurred and the polymer oxidatively degraded. Typically, a variety of oxygen containing groups were introduced during the oxidation of polystyrene, including ketones, aldehydes, and ethers. A fundamental understanding of thermo-oxidative stability is not only critical in preventing oxidation, but is also important in the design of novel oxygen scavengers.⁴⁰¹

We report herein the use of *in situ* mid-IR spectroscopy to measure the reactivity ratios for 1,3-cyclohexadiene/styrene anionic copolymerization using the Mayo-Lewis graphical approach. The 1,3-cyclohexadiene unit in alternating copolymers was aromatized using mild conditions (25°C) in the presence of the quinone derivative, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was also performed. The use of DDQ facilitated the use of extremely mild conditions and afforded relatively well-defined poly(phenylene-*alt*-styrene) containing block copolymers. The thermo-oxidative stability of the alternating copolymers was also investigated. In addition, a series of

⁴⁰⁰ Grassie, N., and G. Scott. *Polymer Degradation and Stabilization* Cambridge University: Cambridge, 1985.

⁴⁰¹ Karovicova, J., and P. Simko. "Determination of synthetic phenolic antioxidants in food by high-performance liquid chromatography." *J. Chromatogr., A.* **2000**, 882, 271. Allen, D.W., M.R. Clench, A. Crowson, and D.A. Leathard. "Identification by particle beam liquid chromatography-mass spectroscopy of transformation products of the antioxidant irganox 1330 in food contact polymers subjected to electron beam radiation." *J. Chromatogr.* **1993**, 629, 283.

alternating copolymers that contained hydrogenated poly(1,3-cyclohexadiene) repeat units were synthesized and the thermal stability in both nitrogen and oxygen environments was determined and compared to the aromatized analogs.

8.3 Experimental.

Materials. Styrene (Aldrich, 99%) was dried over calcium hydride (Aldrich, 95%) and distilled under reduced pressure (0.10 mm Hg, 10°C). 1,3-Cyclohexadiene (Acros, 99%) was degassed three times and vacuum distilled (0.10 mm Hg, 10°C) from dibutylmagnesium (DBM, 0.89 M). *sec*-Butyllithium (*sec*BuLi) (FMC Corporation, Lithium Division, 1.78 M in heptane) was used as received. Cyclohexane (Burdick Jackson, HPLC) was stirred over sulfuric acid (10:1 cyclohexane:sulfuric acid) for 7-10 days, decanted, and distilled from a sodium dispersion under nitrogen immediately prior to use. 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, Acros, 98%) and hydrogen (HoloX, 99.99%), were used as received. All reagents were transferred using syringe and cannula techniques under ultrapure (99.999%) nitrogen.

***In situ* mid-FTIR.** *In situ* mid-FTIR spectra were collected with a ReactIR 1000 (MCT detector, S/N = 7500, resolution = 4 cm⁻¹) (ASI Applied Systems, Millersville, MD, www.asirxn.com) reaction system equipped with a light conduit and DiComp (diamond-composite) insertion probe. Reaction data was analyzed using ASI ReactIR software. The details and capabilities of the ReactIR 1000 reaction analysis system based on total attenuated reflectance (ATR) were described in detail previously.⁴⁰²

Polymerization. The anionic copolymerization of styrene and 1,3-cyclohexadiene was initiated with *sec*BuLi in cyclohexane at 25 ±3 °C and allowed to proceed for 2 h to ensure quantitative conversion of styrene and 1,3-cyclohexadiene. Polymerizations were performed under a nitrogen atmosphere at 20 wt% monomer concentrations. A typical polymerization involved the addition of anhydrous cyclohexane (60 mL, 0.54

⁴⁰² Pasquale, A.J., and T.E. Long. "Real-Time Monitoring of the Stable Free Radical Polymerization of Styrene via *in-Situ* Mid-Infrared Spectroscopy." *Macromolecules* **1999**, 32, 7954.

mol), styrene (5.85 g, 0.56 mol), and 1,3-cyclohexadiene (5.85 g, 0.75 mol) to a 100 mL round-bottomed flask. The solution was allowed to reach 25°C, and *sec*BuLi (0.65 mL, 1.15 mmol) was added to initiate the polymerization. The polymerization was allowed to proceed for 2 h and was terminated with degassed methanol (Burdick Jackson, HPLC grade, 1.0 mL). The resulting copolymer was precipitated into isopropanol (600 mL), filtered, and dried at 50°C in vacuo overnight. An antioxidant such as Irganox 1010 (0.10 wt % compared to polymer) was added to the precipitation solvent to retard oxidative degradation during subsequent storage. This antioxidant was present during all subsequent polymer modification reactions.

Aromatization of Poly(1,3-cyclohexadiene-*co*-styrene) Copolymers. A dried, round-bottomed flask was charged with DDQ (18.1 g, 0.80 mol), a poly(1,3-cyclohexadiene-*co*-styrene) copolymer (5.0 g), and 1,2-dichlorobenzene (Aldrich, 99%, 500 mL). The flask was degassed with nitrogen in order to ensure the removal of residual oxygen, and maintained at 25°C for 48 h. The polymer was precipitated into isopropanol (Burdick Jackson, HPLC grade, 500 mL), filtered, and dried in vacuo at 60°C for 12 h.

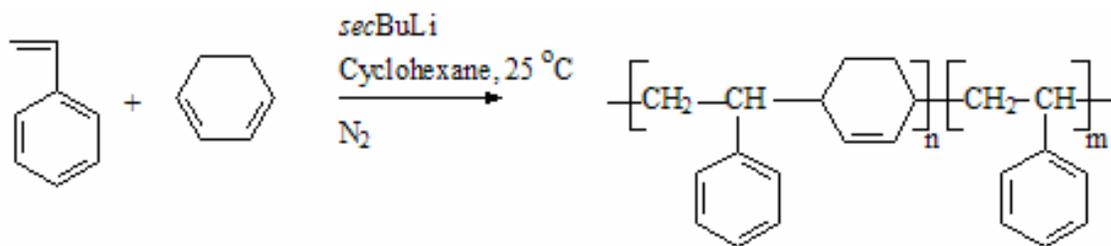
Preparation of the Preformed Nickel Hydrogenation Catalyst. The nickel based hydrogenation catalyst was prepared as previously described.⁴⁰³ Cyclohexane (15 mL) and nickel octoate (Shepard Chemical Company, 0.228 g, 0.66 mmol) were added to a sealed round-bottomed flask. Triethyl aluminum (TEA, 1.36 mL, 1.62 mmol) was added drop-wise to the homogenous nickel solution. An opaque, black colloidal suspension formed immediately and was allowed to stir for 15 min, at 25°C under a nitrogen atmosphere.

Hydrogenation of Poly(1,3-cyclohexadiene-*co*-styrene). The copolymer was hydrogenated as previously described. A typical hydrogenation involved the addition of a poly(1,3-cyclohexadiene-*co*-styrene) copolymer (1.0 g, 0.83 mmol), a preformed

⁴⁰³ Hoover, J. M., T.C. Ward, and J.E. McGrath. "The Influence of Hydrogenation on Star Block Copolymers Based on Tertiary-ButylStyrene-Isoprene-DivinylBenzene." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **1985**, 26, 252.

nickel catalyst (approximately 10 mL, 0.05 mmol), and cyclohexane to a pressure vessel. The pressure vessel was pressurized with hydrogen to 90 psi and vented three times. The vessel was finally pressurized with hydrogen (90 psi) and heated at 50°C for 24 h. After hydrogenation, the nickel catalyst was extracted from the polymer solution using three citric acid (Aldrich, 98%, 500 mL, 50 mmol) washes. The solution was concentrated to 100 mL and precipitated into isopropanol (600 mL), filtered, and dried in vacuo at 60°C for 24 h.

Polymer Characterization. ^1H NMR spectra were determined in CDCl_3 at 400 MHz with a Varian Spectrometer. Glass transition temperatures were determined using a Perkin-Elmer Pyris 1 DSC at a heating rate of 10°C/min under nitrogen. Glass transition temperatures are reported as the midpoint of the change in heat capacity during the second heat. Molecular weights were determined using size exclusion chromatography (SEC) with a Waters 717plus equipped with a Waters 2410 refractive index detector and a Wyatt Technology Minidawn MALLS detector was utilized for absolute molecular weight measurements. The dn/dc values were determined on-line using the calibration constant for the RI detector and the mass of the polymer sample. SEC measurements were performed at 40°C in chloroform at a flow rate of 1.0 mL/min. For all samples, it was assumed that 100% of the polymer eluted from the column during the measurement. TGA measurements were performed on a TA Instruments Hi-Res TGA 2950 thermogravimetric analyzer (TGA) under nitrogen at a heating rate of 10°C per minute. Mass spectra were collected using a Balzers Quadstar 422 which was attached in series to the TGA instrument.



Scheme 8-1. Alternating, anionic copolymerization of 1,3-cyclohexadiene and styrene. Copolymerizations were performed at 25 °C in cyclohexane.

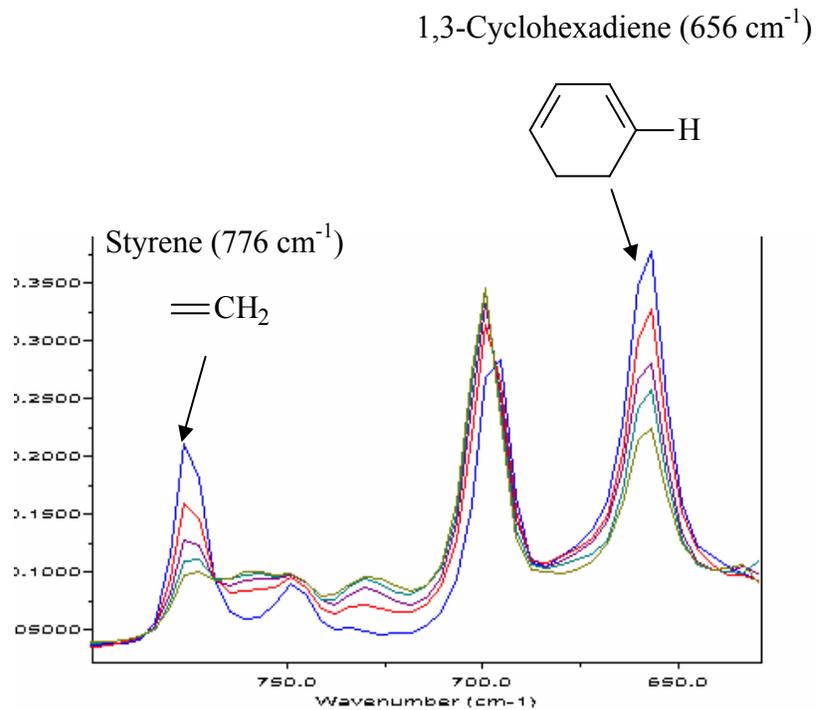


Figure 8-1 In-situ FTIR spectra illustrating the disappearance of the 1,3-cyclohexadiene absorption at 657 cm^{-1} and the disappearance of the styrene absorption at 776 cm^{-1} . Polymerizations were performed at $25\text{ }^{\circ}\text{C}$ and were initiated with secBuLi.

8.4 Results and Discussion

In situ FTIR was used to monitor monomer conversion in real time to determine the reactivity ratio of the 1,3-cyclohexadiene/styrene anionic copolymerization (Scheme 8-1). The reaction flask including the attached ATR based infrared probe was purged with nitrogen and maintained at 5-7 psi. The reactor was initially titrated with poly(styryllithium) to remove any deleterious impurities and subsequently rinsed with cyclohexane prior to the addition of the reactants. Strong vinylene carbon-hydrogen (=C-H) absorbances of the monomers were observed and facilitated the kinetic analysis of the copolymerization (Figure 8-1). The vinylene carbon-hydrogen absorbance for 1,3-cyclohexadiene was observed at 656 cm^{-1} and the vinylene-carbon hydrogen absorbance for styrene was observed at 776 cm^{-1} .

Anionic reactivity ratios for 1,3-cyclohexadiene and styrene were determined via graphical analysis of the rearranged copolymer composition equation developed by Mayo and Lewis. This method relies on the measuring the copolymer composition at low degrees of conversion (0-10%), which ensures that the monomer feed composition does not change significantly during the polymerization. *In situ* mid-FTIR spectroscopy was used to determine the monomer concentration at low degrees of conversion (0-10%) in a real-time fashion. The monomer conversion data was subsequently used to calculate the instantaneous copolymer conversion ($d[\text{styrene}]/d[1,3\text{-cyclohexadiene}]$) that was calculated using the terminal model. In this study, five different styrene:1,3-cyclohexadiene comonomer feed compositions were analyzed: 40:60, 45:55, 50:50, 55:45, and 60:40. $d[\text{styrene}]/d[1,3\text{-cyclohexadiene}]$ values were calculated from the real-time mid-FTIR data and the r_{styrene} and $r_{1,3\text{-cyclohexadiene}}$ values were determined using the instantaneous copolymer equation. Values ranging from -1 to 2.8 were chosen for $r_{1,3\text{-cyclohexadiene}}$ and r_{styrene} values were then calculated for each of the assumed $r_{1,3\text{-cyclohexadiene}}$ values. The r_{styrene} and $r_{1,3\text{-cyclohexadiene}}$ values were then estimated using the Mayo Lewis graphical method (Figure 8-2). The average value of r_{styrene} and $r_{1,3\text{-cyclohexadiene}}$ was 0.024 and 0.022, accordingly. This is the first reported use of *in situ* mid-FTIR spectroscopy to determine the reactivity ratio of an anionic copolymerization.

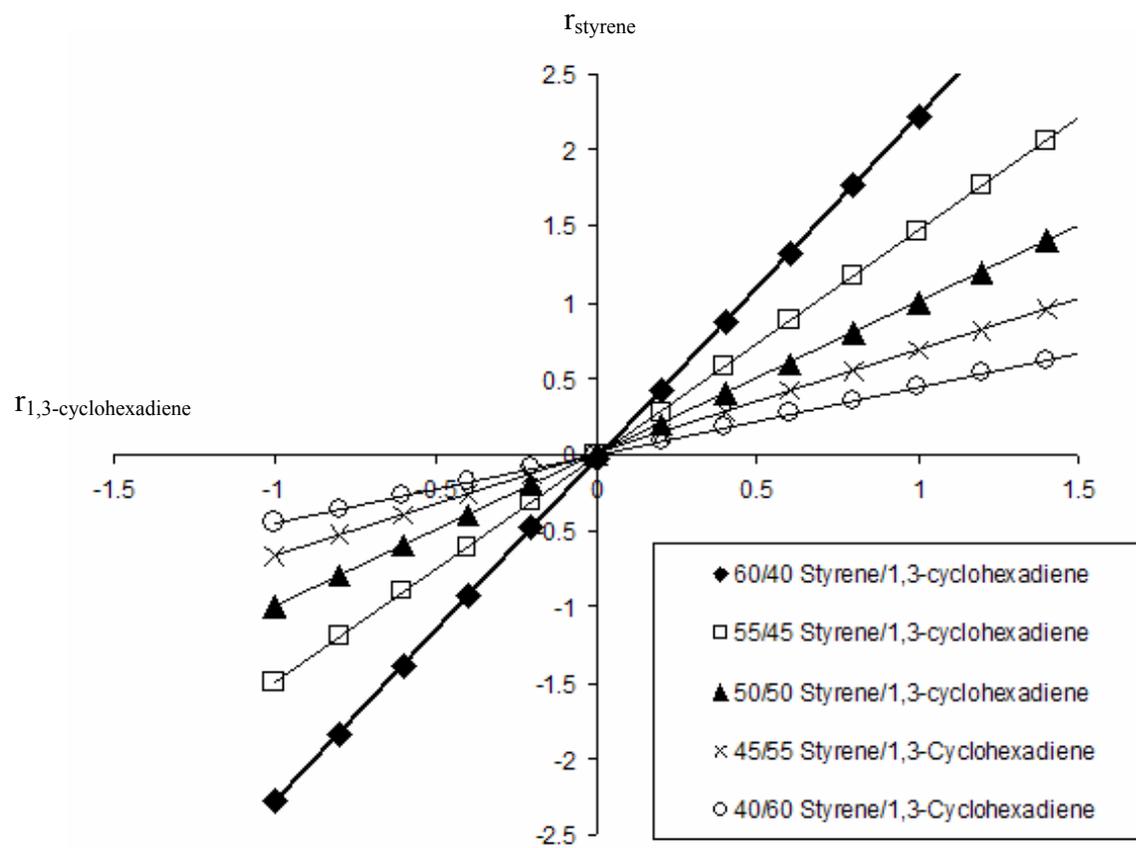


Figure 8-2. Mayo-Lewis graphical evaluation of the reactivity ratios for styrene and 1,3-cyclohexadiene.

Previously, Mays et al. suggested that the copolymerization of styrene and 1,3-cyclohexadiene may be random.⁴⁰⁴ In contrast, reports by Francois et al. concluded that the copolymerization of styrene and 1,3-cyclohexadiene had a tendency to polymerize in alternating fashion.⁴⁰⁵ The studies by Francois utilized polymerization rate constants that were previously reported in the literature or were determined experimentally.⁴⁰⁶ Francois et al. reported r_{styrene} and $r_{1,3\text{-cyclohexadiene}}$ values of 1.86 and 0.11, accordingly. Unfortunately, the methods used in the studies by Francois et al. to determine the values for the crossover from poly(1,3-cyclohexadienyllithium) to styrene and poly(styryllithium) to 1,3-cyclohexadiene were not described. The differences between the classical Mayo Lewis approach used in this study and method used by Francois et al. may account for the disparity in the values for r_{styrene} and $r_{1,3\text{-cyclohexadiene}}$.

A series of poly(1,3-cyclohexadiene-*alt*-styrene) containing block copolymers were synthesized as summarized in Scheme 8-1. These copolymerizations were performed at 25 °C to minimize the occurrence of deleterious side reactions, which are associated with the anionic polymerization of 1,3-cyclohexadiene. These side reactions were attributed earlier to termination and chain transfer of the allylic hydrogens.⁴⁰⁷ Previous studies have utilized similar strategies to ensure the living nature of the homopolymerization of 1,3-cyclohexadiene.⁴⁰⁸ Upon the addition of the *sec*BuLi initiator, the copolymerization solution immediately turned yellow. The polymerization remained homogenous throughout the entire polymerization process. In contrast, previous reports from our laboratories have described the heterogenous nature of 1,3-cyclohexadiene homopolymerizations at 40 °C in the presence of the additive

⁴⁰⁴ Hong, K., and J.W. Mays. "1,3-Cyclohexadiene Polymers. 3. Synthesis and characterization of Poly(1,3-cyclohexadiene-block-styrene)." *Macromolecules* **2001**, 34, 3540.

⁴⁰⁵ Francois, B., S. Izzillo, and P. Iratcabal. "Substituted PPV block copolymer from anionically prepared precursor." *Synth. Met.* **1999**, 102, 1211.

⁴⁰⁶ Francois, B., G. Widawski, M. Rawiso, and B. Cesar. "Block-copolymers with conjugated segments: Synthesis and structural characterization." *Synth. Met.* **1995**, 69, 463.

⁴⁰⁷ Francois, B., and X. Zhong. "Kinetics of 1,3-cyclohexadiene polymerization initiated by organolithium compounds in a non-polar medium." *Makromol. Chem.* **1990**, 191, 2743.

⁴⁰⁸ Zhong, X., and B. Francois. "Kinetics of 1,3-cyclohexadiene polymerization by organolithium compounds in a non-polar medium. 1." *Makromol Chem* **1990**, 191, 2735. Hong, K., and J.W. Mays. "1,3-Cyclohexadiene Polymers. 1. Anionic Polymerization." *Macromolecules* **2001**, 34, 782.

tetramethylethylenediamine.⁴⁰⁹ The improved solubility of the poly(1,3-cyclohexadiene-*alt*-styrene) alternating copolymers relative to poly(1,3-cyclohexadiene) homopolymers was attributed to the presence of the styrene comonomer. A series of copolymers that contained 10 to 50 wt% cyclohexadiene content was prepared to further examine the effect of polymer composition on the thermal properties.

The unique, alternating nature of the styrene/1,3-cyclohexadiene copolymerization enabled the synthesis of a series of tapered block copolymers comprised of a block of poly(1,3-cyclohexadiene-*alt*-styrene) attached to a block of polystyrene. It was expected that following the quantitative conversion of 1,3-cyclohexadiene, the remaining styrene would homopolymerize forming a polystyrene block. The composition, molecular weights, and molecular weight distributions for the various copolymers are summarized in Table 8-1. The targeted molecular weight for all the block copolymers was 10000. The molecular weights for the copolymers agreed well with the molecular weights based on the ratio of the grams of monomer to moles of *sec*BuLi. In general, the molecular weight distributions of the copolymers remained relatively narrow and the polymer yields were quantitative. The molecular weight distribution of the perfectly alternating copolymer of poly(1,3-cyclohexadiene-*alt*-styrene) increased (1.27) relative to the other copolymers (1.09) that contained a smaller poly(1,3-cyclohexadiene-*alt*-styrene) block. Despite an increase in the molecular weight distribution, which was attributed to competitive termination and chain transfer reactions that occurred at higher 1,3-cyclohexadiene levels (> 50%), all polymerizations were quantitative (>95%). Direct determination of the degree of 1,2 versus 1,4 addition in the copolymers was not possible due to the presence of the polystyrene repeat

⁴⁰⁹ Williamson, D.T., J.F. Elman, P.H. Madison, A.J. Pasquale, and T.E. Long. "Synthesis and Characterization of Poly(1,3-cyclohexadiene) Homopolymers and Star-shaped Polymers." *Macromolecules* **2001**, 34, 2108.

Table 8-1. Characterization of the poly(1,3-cyclohexadiene-*alt*-styrene) block copolymers prepared via anionic polymerization.

Polymer	Styrene (Mole %) ^a	Poly(1,3-CHD- <i>alt</i> - styrene) Block Size (calc)	Polystyrene Block Size (calc)	$\langle M_n \rangle^b$ of Block Copolymer	$\langle M_w \rangle / \langle M_n \rangle^b$
PCHDS-PS-1	43	10000	-	12000	1.27
PCHDS-PS-2	70	6000	4000	12100	1.09
PCHDS-PS-3	87	2000	8000	11200	1.05

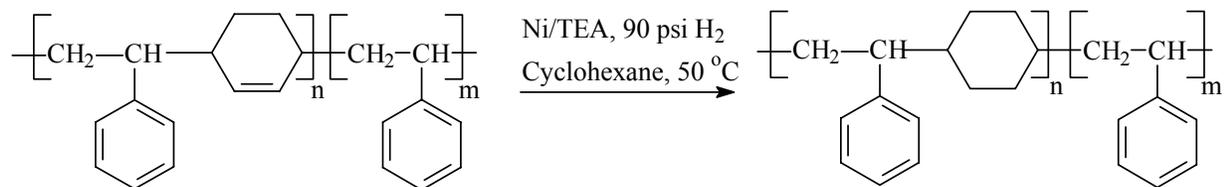
^aDetermined via ¹H NMR spectroscopy ^b GPC conditions: Chloroform, 40°C, MALLS.

unit. Therefore, a poly(1,3-cyclohexadiene) homopolymer control was synthesized under identical synthetic conditions to approximate the percentage of 1,2 versus 1,4 addition in poly(1,3-cyclohexadiene) repeat units. Using the method we previously reported, the control was determined to contain 20% 1,2-addition and 80% 1,4-addition.⁴¹⁰ All polymer structures are assumed to contain approximately 20% 1,2-addition for the cyclohexadiene repeat unit. The residual double bonds that are present in the cyclic 1,3-cyclohexadiene repeat unit were subsequently subjected to aromatization or hydrogenation processes.

A number of previous studies have examined the hydrogenation of poly(1,3-cyclohexadiene) homopolymers and block copolymers for the synthesis of poly(cyclohexane) copolymers.⁴¹¹ As expected, poly(cyclohexane) containing high levels of 1,2-enchainment typically exhibited an exceptionally high T_g (220°C) for a cycloaliphatic polymer. Accordingly, the series of the poly(1,3-cyclohexadiene-*alt*-styrene) containing block polymers were quantitatively hydrogenated (Scheme 8-2), resulting in a series of poly(cyclohexane-*alt*-styrene) containing block copolymers (Table 8-2). It was expected that these novel copolymers would exhibit superior temperature resistance compared to polystyrene. An examination of the integration from 6.0 to 6.2 ppm revealed that the degree of hydrogenation was quantitative (Figure 8-3). These polymers were further characterized using GPC analysis to ensure that the hydrogenation proceeded in the absence of crosslinking or chain scission. The molecular weights of the hydrogenated copolymers agreed well with the molecular weights of the precursor polymers and the molecular weight distributions remained narrow.

⁴¹⁰ Williamson, D.T., T.E. Glass, and T.E. Long. "Determination of the Stereochemistry of Poly(1,3-cyclohexadiene) Via End-group Functionalization." *Macromolecules* **2001**, 34, 6144.

⁴¹¹ Imaizumi, K., Tomohiro Ono, I. Natori, Shinichi Sakuri, and Kunihiko Takedo. "Microphase-Separated Structure of 1,3-Cyclohexadiene/Butadiene Triblock Copolymers and Its Effect on Mechanical and Thermal Properties." *J. Polym. Sci., Part B: Polym. Phys.* **2001**, 39, 13. Natori, I., K. Imaizumi, H. Yamagishi, and M. Kazunori. "Hydrocarbon Polymers Containing Six-Membered Rings in the Main Chain. Microstructure and Properties of Poly(1,3-cyclohexadiene)." *J. Polym. Sci., Part B: Polym. Phys.* **1998**, 36, 1657.



Scheme 8-2. Synthetic methodology that was utilized in the quantitative hydrogenation of poly(1,3-cyclohexadiene-*alt*-styrene)containing block copolymers.

Table 8-2. GPC characterization of poly(cyclohexane-*alt*-styrene) block copolymers prepared via the quantitative, catalytic, hydrogenation of poly(1,3-cyclohexadiene-*alt*-styrene) containing block copolymers using a pre-formed Ni/TEA catalyst.

Precursor Molecular Weight	Poly(cyclohexane- <i>alt</i> -styrene) Block Size ^b	Percent Conversion ^a	$\langle M_n \rangle^b$	$\langle M_w \rangle / \langle M_n \rangle^b$	T _g
12000	13100	99	13100	1.27	131
12100	7440	99	12400	1.11	110
11200	2280	99	11400	1.10	104

^aDetermined via ¹H NMR spectroscopy ^bGPC conditions: Chloroform, 40°C, MALLS.

^cDSC conditions: 10°C/min, nitrogen

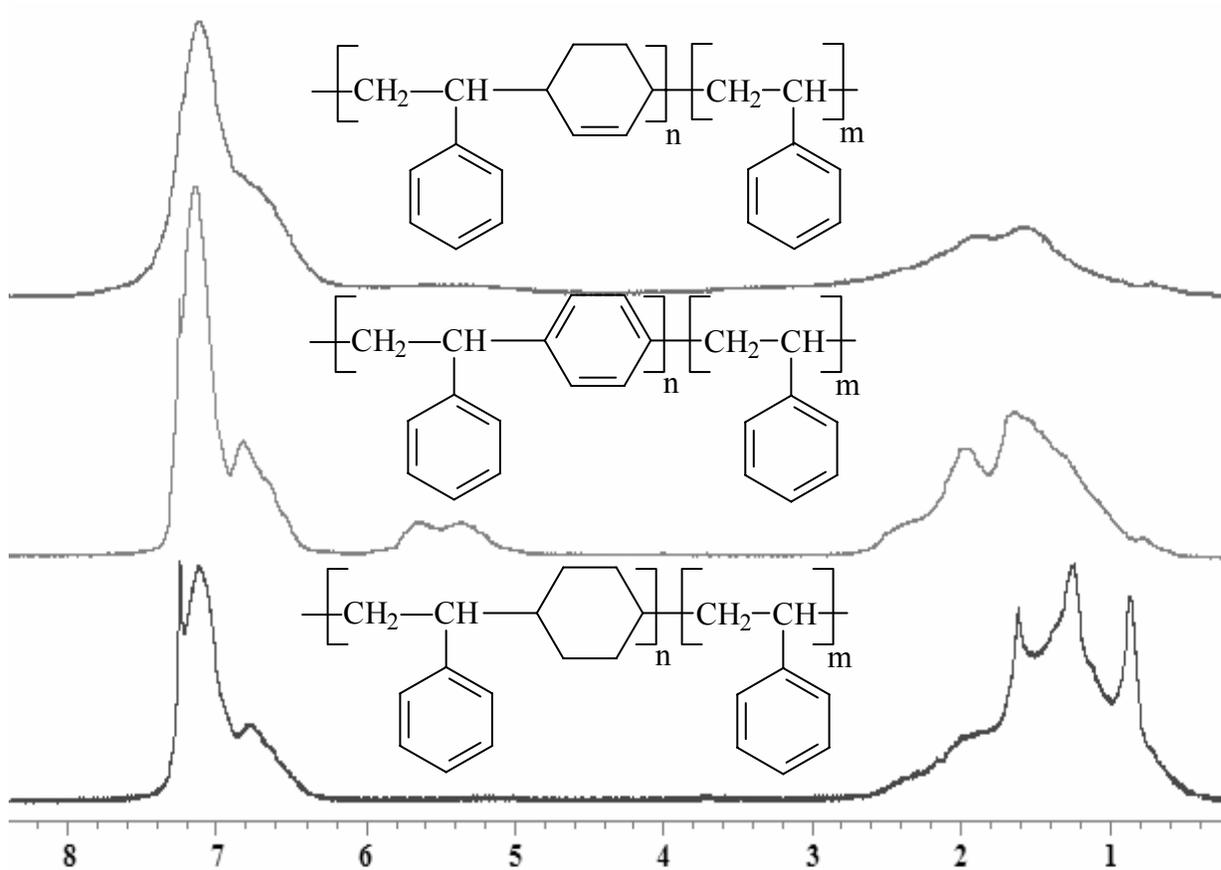


Figure 8-3. ^1H NMR spectra of a poly(phenylene-*alt*-styrene)-*block*-polystyrene (top spectrum), poly(1,3-cyclohexadiene-*alt*-styrene)-*block*-polystyrene (middle spectrum), and poly(cyclohexane-*alt*-styrene)-*block*-polystyrene.

Thus, the quantitative hydrogenation of the copolymers proceeded in the absence of appreciable chain scission or crosslinking. Previous reports using coordination catalysts have described the partial hydrogenation of styrene repeat units in block copolymers.⁴¹²

In order to verify the absence of polystyrene hydrogenation, a comparison of the mole percent of the cyclohexane repeat units to the styrene repeat units was performed to confirm that hydrogenation of the pendant aromatic ring in the styrene repeat unit did not occur. ¹H NMR spectroscopy confirmed the agreement between the mole percent of cyclohexane repeat units and the mole percent of cyclohexadiene repeat units present in the precursor (Table 8-1). As hydrogenation of the polystyrene repeat units would have increased the mole percent of cyclohexane repeat units, it was confirmed that hydrogenation of the copolymer was both selective for the 1,3-cyclohexadiene unit and quantitative.

As previously mentioned, the poly(cyclohexane-*alt*-styrene) containing block copolymers were expected to exhibit a higher T_g than polystyrene. The T_g of the poly(1,3-cyclohexadiene-*alt*-styrene) containing block copolymers were approximately 100°C for all copolymer compositions studied. Table 8-2 indicates that the T_g of the copolymers increased with an increase in the cyclohexane concentration. The T_g of the 10000, perfectly alternating poly(cyclohexane-*alt*-styrene) copolymer was 130°C. The presence of a single glass transition in all the samples tested indicated that poly(cyclohexane-*alt*-styrene) block phase mixed with the polystyrene block, likely due to the low molecular weight of the polymer blocks. A plot of the T_g versus composition exhibited the expected curvature that is characteristic for random copolymers.⁴¹³

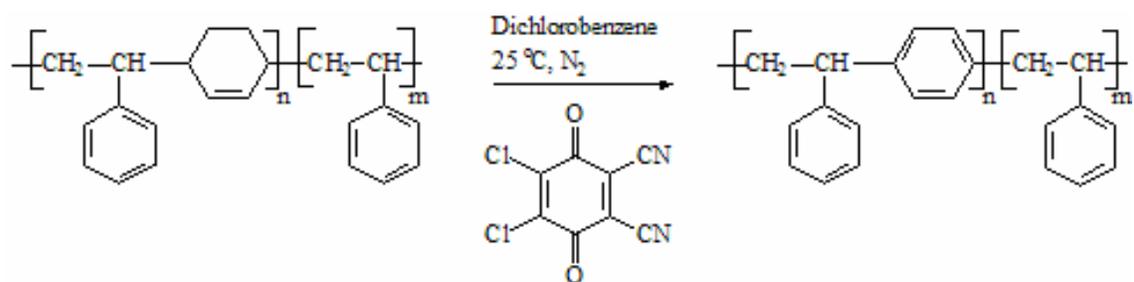
⁴¹² Falk, J.C. "Coordination Catalysts for the Selective Hydrogenation of Polymeric Unsaturation." *J. Polym. Sci., Part A: Polym. Chem* **1971**, *9*, 2617.

⁴¹³ Sperling, L.H. *Introduction to Physical Polymer Science*. 3rd ed Wiley-Interscience: New York, 2001.

The poly(1,3-cyclohexadiene-*alt*-styrene) containing block copolymers were aromatized using DDQ in order to investigate the influence of a doubly benzylic carbon on thermal stability (Scheme 8-3). To minimize the possibility of oxidation at the benzylic position in the styrene unit, the aromatization reaction was performed at 25 °C in the presence of DDQ. Francois and coworkers demonstrated that the aromatization of poly(styrene-*alt*-1,3-cyclohexadiene) copolymers at elevated temperatures resulted in the introduction of an olefin in the styrene repeat unit, due to oxidation at the benzylic position.⁴¹⁴ To avoid oxidation at the polystyrene benzylic position, the aromatization reaction was performed at 25 °C with DDQ. The results of the aromatization of these copolymers are summarized in Table 8-3. Characterization of these copolymers using SEC indicated that the aromatization of the random copolymers was performed in the absence of significant branching or degradation (Figure 8-4). However, preliminary studies indicated that any attempts to perform the aromatization at higher polymer concentrations (>0.02 g/mL) resulted in branching, as indicated by an increase in both the molecular weight and molecular weight distribution. The copolymers that contained 30 and 13 wt% phenylene repeat units were highly soluble in a variety of organic solvents (chloroform, dichlorobenzene). ¹H NMR spectroscopy (Figure 8-3) was used to determine the degree of aromatization, which was determined to be greater than 95%. The introduction of trace levels of DDQ into the polymer during the aromatization reaction was previously described,⁴¹⁵ and no efforts were made in this study to eliminate this minor reaction. ¹H NMR spectroscopy verified that DDQ and any significant related by-products were removed.

⁴¹⁴ Francois, B., G. Widawski, M. Rawiso, and B. Cesar. "Block-copolymers with conjugated segments: Synthesis and structural characterization." *Synth. Met.* **1995**, 69, 463.

⁴¹⁵ Xhong, X. F., and B. Francois. "Soluble polystyrene-block-poly(p-phenylene) block copolymers prepared from polystyrene-block-poly(1,3-cyclohexadiene) precursors. Study of the aromatization process." *Makromol. Chem.* **1991**, 192



Scheme 8-3. Synthetic methodology that was utilized in the quantitative hydrogenation of poly(1,3-cyclohexadiene-*alt*-styrene) containing block copolymers.

Table 8-3. GPC characterization of poly(phenylene-*alt*-styrene) containing block copolymers prepared via the controlled and quantitative aromatization of poly(1,3-cyclohexadiene-*alt*-styrene)-*block*-polystyrene copolymers via DDQ. .

Precursor Molecular Weight	Poly(phenylene- <i>alt</i> -styrene) Block Size ^b	Percent Conversion ^a	$\langle M_n \rangle^b$	$\langle M_w \rangle / \langle M_n \rangle^b$
12000	*	*	*	*
12100	7200	98	12000	1.13
11200	1880	98	9390	1.08

^aDetermined via ¹H NMR spectroscopy. ^bGPC conditions: Chloroform, 40°C, MALLS

* The polymers were insoluble in CHCl₃

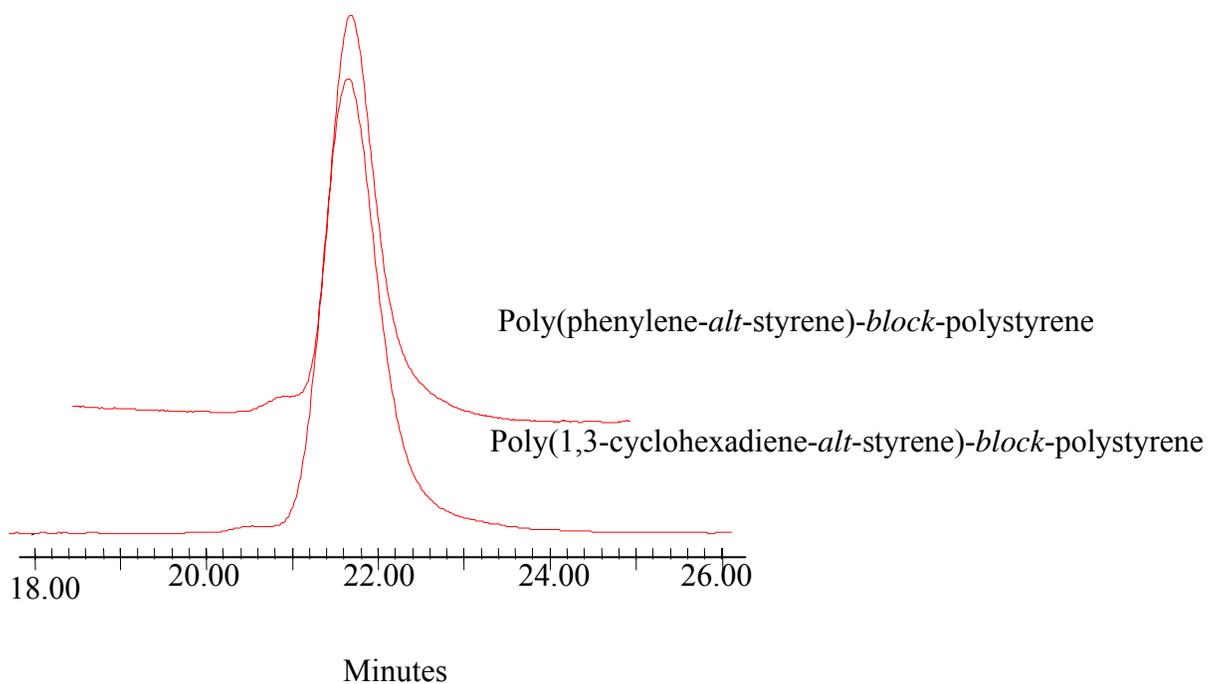


Figure 8-4. GPC traces of poly(phenylene-*alt*-styrene)-*block*-polystyrene (top curve) ($\langle M_n \rangle = 1200$) and poly(1,3-cyclohexadiene-*alt*-styrene)-*block*-polystyrene ($\langle M_n \rangle = 12400$).

The thermal stability of the poly(1,3-cyclohexadiene-*alt*-styrene)-*block*-polystyrene block copolymer and their hydrogenated and aromatized derivatives were determined via thermogravimetric analysis. These samples all had theoretical molecular weights of 10000 and a polystyrene block with a molecular weight of 4000. The thermal stability of these polymers was determined in both nitrogen (Figure 8-5) and oxygen environments (Figure 8-6). In a nitrogen environment, the onset of thermal degradation of poly(1,3-cyclohexadiene-*alt*-styrene) containing block copolymer was 340°C. As expected, the hydrogenated analog, poly(cyclohexane-*alt*-styrene) containing polymer, was stable to higher temperatures (380 °C). This improved thermal stability was attributed to the removal of the reactive allylic hydrogens upon hydrogenation. Surprisingly, the aromatized analog, the poly(phenylene-*alt*-styrene) containing block copolymer, exhibited reduced thermal stability in nitrogen and proceeded through a stepwise degradation mechanism (Figure 8-5). Typically, poly(phenylene) containing polymers exhibit improved thermal stability due to the presence of additional aromatic units. However, the copolymers in this study contained a doubly benzylic linkage that connected a phenylene unit to a styrene unit (Scheme 8-3). The doubly benzylic linkage was proposed to account for the initial degradation step in the multi-step process. The weight loss in the initial step at 210°C was approximately 19 wt%, which correlated well with the percentage of poly(phenylene) present in the polymer (22 wt%). In addition, the production of 4,4'-dimethylbiphenyl resulting from the thermal degradation originating at the doubly benzylic position was monitored using TGA-MS. 4,4'-dimethylbiphenyl production was studied by monitoring key molecule fragments at 89, 115, 152, 167, and 182 amu.⁴¹⁶ Isothermal analysis performed at 210 °C demonstrated that the production of 4,4'-dimethylbiphenyl was associated with the initial 19 wt% loss. These results support the role of the doubly benzylic position in the degradation mechanism, which involves chain scission between the benzylic position of the styrene repeat unit and the phenylene

⁴¹⁶ Stein, S.E. *1,3-Cyclohexadiene Mass Spectrum* [NIST Chemistry WebBook]. NIST Standard Reference Data Base, 2001 [cited June 18 2002].

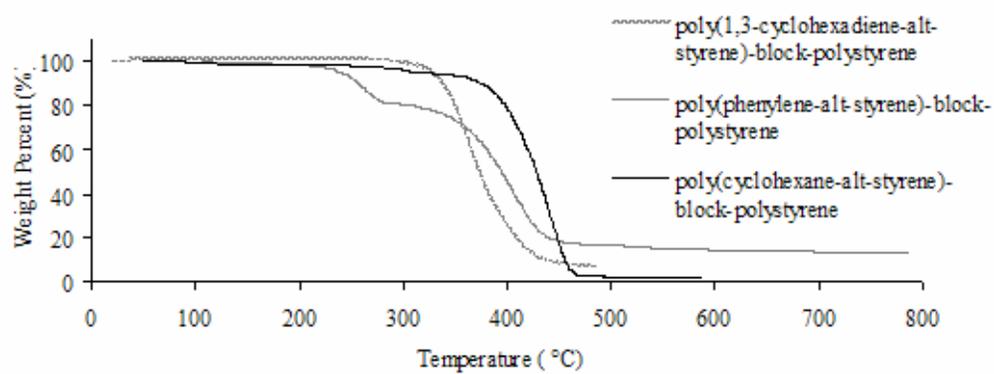


Figure 8-5 Thermogravimetric analysis of poly(1,3-cyclohexadiene-*alt*-styrene)-*block*-polystyrene, poly(cyclohexane-*alt*-styrene)-*block*-polystyrene and poly(phenylene-*alt*-styrene)-*block*-polystyrene in a nitrogen environment. The heating rate was 10 °C/min.

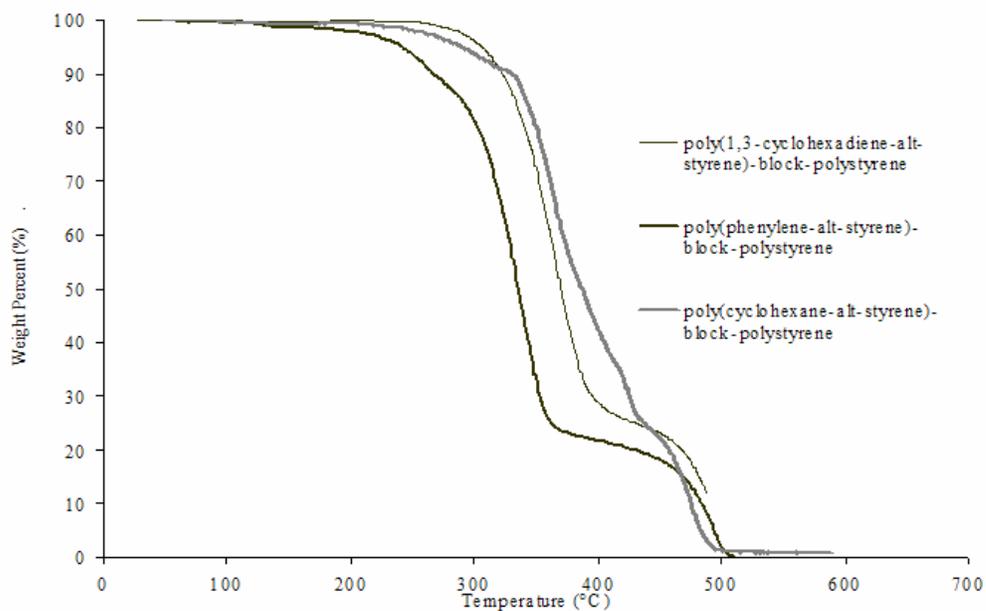


Figure 8-6. Thermogravimetric analysis of poly(1,3-cyclohexadiene-*alt*-styrene)-*block*-polystyrene, poly(cyclohexane-*alt*-styrene)-*block*-polystyrene and poly(phenylene-*alt*-styrene)-*block*-polystyrene in an oxygen environment. The heating rate was 10 °C/min.

repeat unit. The presence of alternative degradation products, such as xylene or a styrene-cyclohexadiene dimer, were not detected. The thermal stability of these copolymers differed in the presence of oxygen, wherein poly(cyclohexane-*alt*-styrene) and poly(1,3-cyclohexadiene-co-styrene) containing block copolymers both initially degraded at approximately 300 °C (Figure 8-6). The poly(phenylene-*alt*-styrene) containing block copolymers were somewhat less thermally stable as compared to the other copolymers, with the onset of degradation occurring at 250 °C. Moreover, the onset of thermal degradation occurred at a higher temperature in an oxygen environment compared to a nitrogen environment.

8.5 Conclusion.

In situ mid-FTIR was successfully used to determine the reactivity ratios for the anionic copolymerization of 1,3-cyclohexadiene and styrene. The real-time data was readily transformed using the classical Mayo Lewis approach and 1,3-cyclohexadiene and styrene exhibited reactivity ratios of 0.022 and 0.024, respectively. Subsequently, the unique, alternating nature of this anionic copolymerization enabled the synthesis of an interesting family of poly(1,3-cyclohexadiene-*alt*-styrene) containing block copolymers. These copolymers were transformed via both hydrogenation and aromatization to novel poly(cyclohexane-*alt*-styrene) and poly(phenylene-*alt*-styrene) containing block copolymers, respectively. These novel copolymers were characterized thermally and were compared to poly(1,3-cyclohexadiene-*alt*-styrene) block copolymer precursors. The poly(cyclohexane-*alt*-styrene) containing block copolymers were the most thermally stable, while the poly(phenylene-*alt*-styrene) block copolymers were the least thermally stable in both a nitrogen and oxygen environment. Future studies will utilize the alternating, anionic copolymerization of 1,3-cyclohexadiene and styrene to prepare a series of novel alternating copolymers with unique polar functionality.

CHAPTER 9

Oxidation and Epoxidation of Poly(1,3-Cyclohexadiene)

Taken From:

D.T. Williamson, B.D. Mather, and T.E. Long “Oxidation and Epoxidation of Poly(1,3-Cyclohexadiene)” *J. Polym. Sci. Part A. Polym. Chem.* **2002**, *41*, 84.

9.1 Abstract

Poly(1,3-cyclohexadiene) (PCHD) derivatives were synthesized via facile chemical modification reactions of the residual double bond in the repeat unit. The oxidation and degradation of PCHD was investigated to enable subsequent controlled epoxidation reactions. PCHD exhibited a 15% weight loss at 110 °C in the presence of oxygen. The oxidative degradation demonstrated using GPC and ¹H NMR spectroscopy was attributed to main chain scission. Aldehyde and ether functional groups were introduced into the polymer during the oxidation process. PCHD was quantitatively epoxidized in the absence of deleterious oxidation with meta-chloroperoxybenzoic acid. ¹H and ¹³C NMR spectroscopy confirmed that polymers with controlled degrees of epoxidation were reproducibly obtained. Epoxidized PCHD exhibited a T_g at 154 °C, which was slightly higher than the PCHD precursor of nearly equivalent molecular weight. Moreover, GPC indicated the absence of undesirable crosslinking or degradation, and molecular weight distributions remained narrow. The thermo-oxidative stability of the fully epoxidized polymer was compared to the PCHD precursor, and the epoxidized PCHD exhibited an initial weight loss at 250 °C in oxygen, which was 140 °C higher than PCHD.

9.2 Introduction

Oxidative degradation is a critical process that determines polymer durability, performance, lifetime, and reliability. A number of external factors significantly affect oxidation and degradation processes in polymer products. Examples include temperature, pH, and the presence of reactive gases such as oxygen.⁴¹⁷ The mechanism of autooxidative degradation of polydienes, such as polyisoprene, is well understood.⁴¹⁸ During the autooxidation of polyisoprene, a variety of functional groups are introduced, including ketones, aldehydes, esters, carboxylic acids, unsaturated ethers, and alcohols.⁴¹⁹ The number average molecular weight is dramatically reduced due to main chain scission during the autooxidative degradation of polyisoprene.⁴²⁰ On the other hand, poly(1,3-butadiene) undergoes crosslinking, and the number average molecular weight increases.⁴²¹ This mechanistic difference between polyisoprene and poly(1,3-butadiene) arises from pendant vinyl groups in the 1,2 units of poly(1,3-butadiene). Pendant vinyl groups in poly(1,3-butadiene) are highly susceptible to radical attack, which results in polymer chain crosslinking. Polyisoprene degradation predominately proceeds through a different radical mechanism, where the allylic hydrogen in the polymer backbone undergoes hydrogen radical abstraction followed by main chain scission. In addition to determining polymer lifetime, understanding the conditions that induce deleterious reactions such as chain scission and crosslinking is critical to

⁴¹⁷ Odian, George. *Principles of Polymerization* John Wiley and Sons Inc: New York, 1991.

⁴¹⁸ Schnabel, W. *Polymer Degradation, Principles and Practical Applications* Macmillan Publishing Co: New York, 1981. Chiantore, O., M. Guaita, M. Lazzari, N. Hadjichristidis, and M. Pitsikalis. "Thermal degradation of model linear and star-shaped polyisoprene molecules." *Polym. Degrad. Stab.* **1995**, 49, 385. Chien, J.C.W., and J.K.Y. Kiang. "Polymer reaction. II. Oxidative pyrolysis of polyisoprene." *Macromolecules* **1979**, 12, 1088. Alam, T. M., M. Celina, R.A. Assink, R.L. Clough, K.T. Gillen, and D.R. Wheeler. "Investigation of Oxidative Degradation in Polymers Using ¹⁷O NMR Spectroscopy." *Macromolecules* **2000**, 33, 1181.

⁴¹⁹ Alam, T. M., M. Celina, R.A. Assink, R.L. Clough, K.T. Gillen, and D.R. Wheeler. "Investigation of Oxidative Degradation in Polymers Using ¹⁷O NMR Spectroscopy." *Macromolecules* **2000**, 33, 1181.

⁴²⁰ Grassie, N., and G. Scott. *Polymer Degradation and Stabilization* Cambridge University: Cambridge, 1985.

⁴²¹ Grassie, N., and G. Scott. *Polymer Degradation and Stabilization* Cambridge University: Cambridge, 1985.

conducting controlled, reproducible polymer modification reactions. Therefore, it is important to understand the reaction conditions where the onset of autooxidation and chain scission occurs prior to performing polymer modification reactions.

Polymer modification reactions enable the chemical and physical properties of an existing polymer to be tailored for specific applications. Polymers containing an unsaturated site in the repeating unit, such as polydienes, are candidates for a vast array of modification reactions. Examples of these post-polymerization modifications include bromination,⁴²² epoxidation,⁴²³ hydrogenation, and maleation.⁴²⁴ However, the allylic hydrogens in the polymer backbone are also highly sensitive to oxidation and degradation under the conditions employed for many polymer modification reactions.⁴²⁵ In addition to tailoring polymer properties, post-polymerization modifications are utilized to incorporate reactive functional groups into the polymer backbone. For example, the introduction of amino functional groups was utilized for additional chemical processes, such as the crosslinking of epoxy resins. Chemical modification reactions were performed in solution, the solid state, and at polymer surfaces through the use of gases and liquids.⁴²⁶ Several factors such as reaction phase, percent crystallinity, conformation, neighboring group effects, and tacticity affect polymer reactivity during chemical modifications. In addition, chemical modification reactions performed at a polymer surface will alter the surface without affecting the bulk

⁴²² Buzdugan, E., P. Ghioca, E.A. Badea, and S. Serban. "Bromination of Some Styrene-Diene Block Copolymers." *Eur. Polym. J.* **1997**, 33, 1713. Nor, H., and J.R. Ebdon. "Telechelic Liquid Natural Rubber." *Prog. Polym. Sci.* **1998**, 23, 143.

⁴²³ Nor, H., and J.R. Ebdon. "Telechelic Liquid Natural Rubber." *Prog. Polym. Sci.* **1998**, 23, 143. Sakai, T., N. Kihara, and T. Endo. "Polymer Reaction of Epoxide and Carbon Dioxide. Incorporation of Carbon Dioxide into Epoxide Polymers." *Macromolecules* **1995**, 28, 4701. Roland, C.M., J.K. Kallitsis, and K.G. Gravalos. "Plateau Modulus of Epoxidized Polybutadiene." *Macromolecules* **1993**, 26, 6474.

⁴²⁴ Odian, George. *Principles of Polymerization* John Wiley and Sons Inc: New York, 1991. Nor, H., and J.R. Ebdon. "Telechelic Liquid Natural Rubber." *Prog. Polym. Sci.* **1998**, 23, 143.

⁴²⁵ Ranby, B, and J.F. Rabek. *Photodegradation, Photo-Oxidation and Photostabilization of Polymers*. Edited by ` John Wiley and Sons: New York, 1975.

⁴²⁶ Billmeyer, Fred W. *Textbook of Polymer Science*. 3rd ed John Wiley and Sons: New York, 1984.

properties, such as T_g . However, the same modification reaction performed in solution will affect the bulk properties.

Various polymerization techniques were utilized in the mid 1960's and early 1970's in an attempt to identify viable polymerization methodologies for 1,3-cyclohexadiene.⁴²⁷ In the late 1970's, a series of patents were issued to Phillips Petroleum describing the preparative process and composition of 1,3-cyclohexadiene containing polymers.⁴²⁸ The compositions were limited to "random" copolymers containing PCHD, polystyrene, polyisoprene, or poly(1,3-butadiene) and were prepared using various ligating agents. Despite these early attempts to polymerize 1,3-cyclohexadiene in a controlled fashion, the resulting polymers exhibited unpredictable molecular weights and broad molecular weight distributions. Natori and coworkers recently reported the successful living anionic polymerization of 1,3-cyclohexadiene utilizing *n*-butyllithium (*n*-BuLi) in combination with a single ligating agent (N,N,N',N'-tetramethylethylenediamine (TMEDA)).⁴²⁹ The resulting homopolymers

⁴²⁷ Sharaby, Z., J. Jagur-Grodzinski, M. Martan, and D Vofsi. "Kinetics and Mechanism of the Anionic Polymerization of Cyclohexadienes Initiated by Naphthalene Radical Anions and Dianions." *J. Polym. Sci., Polym. Chem. Ed.* **1982**, 20, 901. Lefebvre, G, and F. Dawans. "1,3-Cyclohexadiene polymers. I. Preparation and aromatization of poly-1,3-cyclohexadiene." *J. Polym. Sci.* **1964**, A2, 3277. Sharaby, Z., M. Martan, and J. Jagur-Grodzinski. "Stereochemistry of Poly(1,3-cyclohexadienes). NMR Investigation of Effects Due to the Solvent Medium and to the Mechanism of Polymerization." *Macromolecules* **1982**, 15, 1167. Mango, L.A., and R.W. Lenz. "Mechanism and stereochemistry in the anionic polymerization of 1,3-cyclohexadiene and the diimide hydrogenation of polymers." *U.S. Nat. Tech. Inform. Serv.* **1972**, 12, 402. Mango, L.A., and R.W. Lenz. "Organometallic reactions which control molecular weight in the anionic polymerization of 1,3-cyclohexadiene." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **1971**, 12, 402.

⁴²⁸ Hsieh, H. L. "1,3-Cyclodiene-Acyclic Conjugated Diene Copolymers." Phillips Petroleum Company, United States 4237246 (1977). Hsieh, H. L. "Copolymerization of a Linear 1,3-Cyclodiene and a Linear Conjugated Diene." Phillips Petroleum Company, United States 4138356 (1978). Hsieh, H. L. "Epoxidized Block Copolymers." Phillips Petroleum Company, United States 40202521 (1978). Hsieh, H. L. "Polymerization of 1,3-Cyclohexadiene With Vinylaromatic Hydrocarbon." Phillips Petroleum Company, United States 4131653 (1979). Hsieh, H. L. "Copolymers of 1,3-cyclohexadienes, Monovinylaromatic Compounds and Polyvinylaromatic Hydrocarbons." Phillips Petroleum Company, United States 4127710 (1980).

⁴²⁹ Natori, I. "Synthesis of Polymers with an Alicyclic Structure in the Main Chain. Living Anionic Polymerization of 1,3-Cyclohexadiene with the *n*-butyllithium/N,N,N',N'-Tetramethylethylenediamine System." *Macromolecules* **1997**, 30, 3696.

exhibited relatively narrow molecular weight distributions and modest molecular weights. Mays et al. recently described the synthesis of PCHD in the presence of 2,2,2-diazabicyclooctane (DABCO), which was subsequently utilized in the synthesis of well-defined PCHD star-shaped polymers.⁴³⁰ In addition, PCHD star-shaped polymers were prepared in our laboratories using the divinylbenzene coupling agent.⁴³¹ The unsaturated site in the repeat unit of PCHD is readily susceptible to chemical modification which will result in new polymer families, and our previous studies have demonstrated that the chemical modification of PCHD improved the chemical and thermal stability.⁴³² For example, PCHD was aromatized using chloranil and was hydrogenated to form poly(cyclohexane).⁴³³ The hydrogenated polymer exhibited a remarkably high T_g (220 °C) and improved oxidative stability as compared to the PCHD precursor. Despite these initial efforts, limited attention was devoted to the thermal stability and chemical modification of PCHD.

In this study, the thermo-oxidative stability of PCHD in both oxygen and nitrogen environments was examined. The results of these studies were used to develop reaction conditions that avoided deleterious oxidation during subsequent polymer modification studies. Controlled epoxidation of PCHD was performed and the thermal properties of the epoxidized polymer were examined.

⁴³⁰ Hong, K., and J.W. Mays. "1,3-Cyclohexadiene Polymers. 1. Anionic Polymerization." *Macromolecules* **2001**, 34, 782.

⁴³¹ Williamson, D.T., J.F. Elman, P.H. Madison, A.J. Pasquale, and T.E. Long. "Synthesis and Characterization of Poly(1,3-cyclohexadiene) Homopolymers and Star-shaped Polymers." *Macromolecules* **2001**, 34, 2108.

⁴³² Williamson, D.T., and T.E. Long. "Self-assembled poly(phenylene) containing macromolecules via the controlled anionic polymerization of 1,3-cyclohexadiene." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **2002**, 43, 330.

⁴³³ Natori, I., K. Imaizumi, H. Yamagishi, and M. Kazunori. "Hydrocarbon Polymers Containing Six-Membered Rings in the Main Chain. Microstructure and Properties of Poly(1,3-cyclohexadiene)." *J. Polym. Sci., Part B: Polym. Phys.* **1998**, 36, 1657.

9.3 Experimental Section

Materials. 1,3-Cyclohexadiene (Aldrich, 99%) was degassed several times and distilled at reduced pressure (0.13-0.16 mm Hg, 10 °C) from dibutylmagnesium (DBM, Acros, 0.89M). *n*-Butyllithium (*n*-BuLi, FMC Corporation, Lithium Division, 1.35 M in *n*-hexane) was used without further purification. TMEDA (Aldrich, 97%) was distilled under reduced pressure (0.13-0.16 mm Hg, 10 °C) from calcium hydride (Aldrich, 95%) and stored under nitrogen at -25 °C. Cyclohexane (Burdick-Jackson, HPLC grade) was stirred over sulfuric acid (10:1 cyclohexane:sulfuric acid) for 7-10 days, decanted, and distilled from a sodium dispersion under nitrogen immediately prior to use. All reagents were transferred using syringe and cannula techniques under ultrapure (99.999%) nitrogen.

Polymer Synthesis. A 100-mL round-bottomed flask containing anhydrous cyclohexane (60 mL, 0.54 mol), 1,3-cyclohexadiene (5.95 mL, 62.4 mmol), and TMEDA (0.094 mL, 0.625 mmol) was heated to 40 °C. The initiator *n*-BuLi (0.31 mL, 0.5 mmol) was added using a syringe and the polymerization was maintained at 40 °C for 25 minutes. The polymerization was terminated using degassed methanol (Burdick-Jackson, HPLC grade). The resulting polymer was precipitated into isopropanol (600 mL), filtered, and dried at 50 °C in vacuo for 12-18 hours. Typically, an antioxidant such as Irganox 1010 (0.10 weight % compared to the polymer) was added to the precipitation solvent to retard oxidative degradation during subsequent storage. However, Irganox 1010 was not added during precipitation for polymers used in subsequent epoxidation and oxidation studies and the polymer was stored at -10 °C in a nitrogen environment. In order to control the product molecular weight, both TMEDA and *n*BuLi concentrations were varied. However, the ratio of TMEDA/*n*BuLi was maintained at 5/4 and the monomer concentration was maintained at 10 wt%.

Polymer Oxidation. PCHD (1.0 g, 0.017 mmol) was added to a round-bottomed flask charged with 1,2-dichlorobenzene (Aldrich, 99%, 50 mL) forming a homogeneous

solution. The flask was sealed with a rubber septum and the polymer solution was heated in excess nitrogen (10 psi) or oxygen (10 psi) at the prescribed temperature for 4 hours. The solution was cooled and the polymer was precipitated into isopropanol (200 mL), filtered, and collected.

Polymer Epoxidation. Quantitative epoxidation of the homopolymers was conducted using 3-chloroperoxybenzoic acid (MCPBA, Aldrich 95%). PCHD (3.0 g, 0.05 mmol) was added to a round-bottomed flask charged with anhydrous chloroform (Aldrich, Burdick-Jackson, 200 mL), forming a homogeneous solution. MCPBA (0.90 g, 3.5 mmol) was added to the flask. The flask was sealed with a rubber septum and the reaction was allowed to proceed for approximately 2 hours at 0 °C in a nitrogen atmosphere. The epoxidized polymer was precipitated into isopropanol (600 mL) and filtered. The polymer was rinsed repeatedly with water, methanol, and isopropanol. Repeated washings ensured the quantitative removal of residual MCPBA and 3-chlorobenzoic acid. The polymers were dried at 80 °C in vacuo for 12 hours.

Polymer Characterization. Molecular weights were determined using size exclusion chromatography (SEC) with a Waters Alliance GPC system equipped with a Viscotek 150R viscosity detector and an RI concentration detector. The determination of molecular weights using universal calibration based on polystyrene standards is well established.⁴³⁴ GPC measurements were performed at 25 °C in chloroform at a flow rate of 1.0 mL/min. ¹H and ¹³C NMR spectra were obtained in CDCl₃ with a Varian Unity 400 spectrometer. Glass transition temperatures were determined using a Perkin-Elmer Pyris 1 DSC at a heating rate of 10 °C/min under nitrogen. Glass transition temperatures are reported as the midpoints of the heat capacity change during the second heating. TGA measurements were performed on a TA Instruments Hi-Res TGA 2950 thermogravimetric analyzer (TGA) under nitrogen at a heating rate of 10 °C per minute. Mass spectra were collected using a Balzers Quadstar 422 which was attached in series to the TGA instrument.

⁴³⁴ Yau, W.W., and S.W. Rementer. "Polymer Characterization by SEC-Viscometry: Molecular Weight, Size, and Intrinsic Viscosity Distribution." *J. Chromatogr.* **1990**, 13, 627.

9.4 Results and Discussion

A solution of PCHD in 1,2-dichlorobenzene was heated in the presence of oxygen or nitrogen from 60 °C to 143 °C, in order to determine the thermal and oxidative stability of PCHD in the two different environments. The PCHD sample that was used in these studies had an initial molecular weight of 16000 g/mol and a molecular weight distribution of 1.15. The oxidized polymers were characterized using ^1H NMR spectroscopy and the ratio of olefinic to aliphatic protons was determined. When PCHD was heated in the presence of oxygen at temperatures from 60 to 140 °C, the ratio of the olefinic integration to the aliphatic integration deviated from the samples heated in nitrogen (Figure 9-1). As the temperature was increased, the degree of oxidation increased for the samples heated in oxygen resulting in a decreased aliphatic to allylic ratio. In contrast, when the samples were heated in a nitrogen environment, the olefinic to aliphatic ratio did not change over the entire temperature range. Therefore, oxygen was critical to the mechanism of degradation and the increased rate of degradation was presumably due to reactive allylic hydrogens present in an oxygen environment. When heated for only 4 hours at 140 °C under oxygen, the products did not exhibit any significant changes in either the ^1H or the ^{13}C NMR spectra. In order to identify the functional groups introduced during oxidation, PCHD was heated for 40 hours at 147 °C. This oxidized sample exhibited resonances associated with the introduction of oxygen containing functional groups into the polymer repeat unit (Figure 9-2). The new resonances at 4.2 ppm were assigned to protons associated with an alcohol or ether functionality. A smaller resonance at 9.8 ppm was assigned to the protons associated with the introduction of an aldehyde functional group into the polymer. The resonances at 5.1 and 6.0 ppm were attributed to the splitting of the alkene protons via the addition of oxygen to the allylic carbon. These NMR

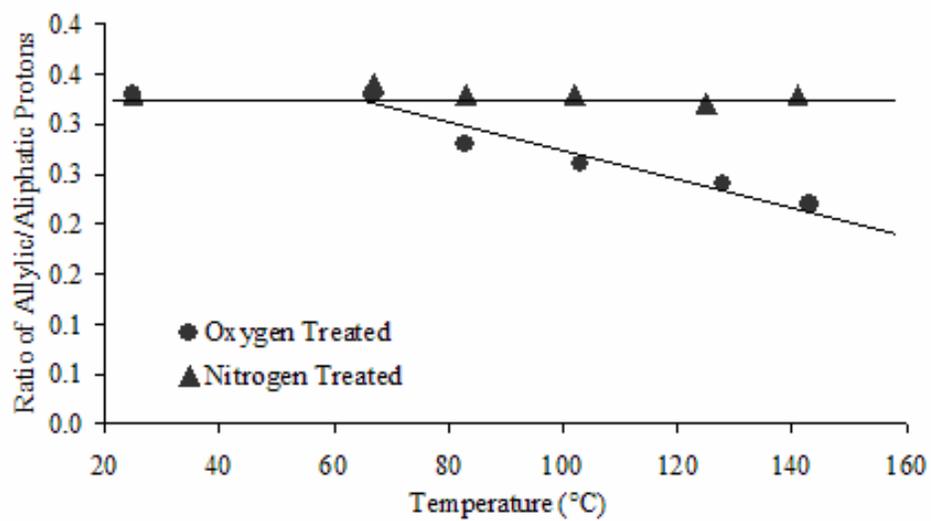


Figure 9-1. ^1H NMR spectrum of PCHD demonstrating the change in the ratio of the integration of the aliphatic and the olefinic protons as a function of temperature.

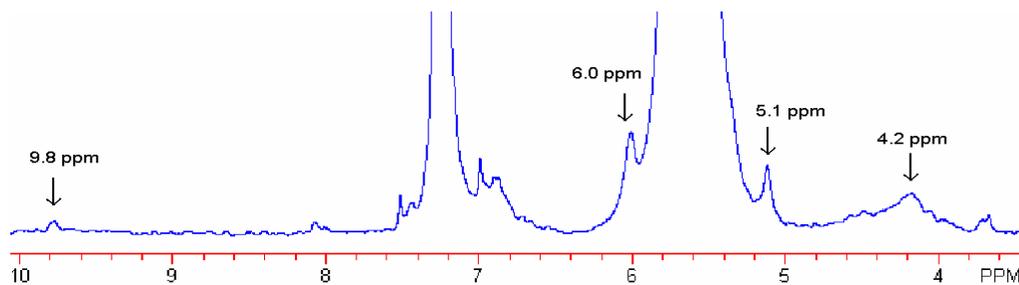


Figure 9-2. ¹H NMR spectrum of PCHD that was heated at 137 °C for 40 hours in the presence of oxygen.

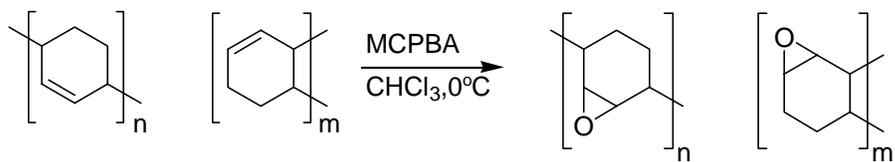
assignments agreed well with previous studies that examined the autooxidation of polyisoprene.⁴³⁵ These studies demonstrated that during the oxidation of polyisoprene, ethers and unsaturated ethers were predominately introduced into the polymer repeat unit.

For other olefin containing polymers such as polyisoprene, autooxidation is typically associated with chain degradation and scission. In order to determine the relationship between oxidation and chain scission for PCHD, the 16000 g/mol PCHD solution was heated in an oxygen environment for 4 hours and characterized using GPC. As shown in Figure 3, the molecular weight of PCHD remained constant until 110 °C. At temperatures above 110 °C, the number average molecular weight of PCHD decreased, which indicated that extensive chain degradation had occurred. In addition, the molecular weight distribution of PCHD increased at 110 °C (Figure 3). As discussed above for PCHD solutions heated in the presence of oxygen, the olefinic to aliphatic ratio deviated from the nitrogen control. Therefore, the incorporation of oxygen containing functional groups into the polymer backbone occurred at a lower temperature than the onset of oxygen mediated chain scission. In order to minimize the degree of both chain scission and the oxidation of the allylic hydrogens, all subsequent polymer modification reactions were performed at temperatures below 50 °C under a nitrogen environment.

PCHD was epoxidized to both improve oxidative stability and introduce a reactive site to the polymer backbone. PCHD homopolymers with molecular weights of 6200, 10000, and 24000 g/mol were prepared as previously described.⁴³⁶ These polymers were epoxidized as outlined in Scheme 9-1 and the resulting epoxidized polymers were characterized.

⁴³⁵ Alam, T. M., M. Celina, R.A. Assink, R.L. Clough, K.T. Gillen, and D.R. Wheeler. "Investigation of Oxidative Degradation in Polymers Using ¹⁷O NMR Spectroscopy." *Macromolecules* **2000**, 33, 1181.

⁴³⁶ Williamson, D.T., J.F. Elman, P.H. Madison, A.J. Pasquale, and T.E. Long. "Synthesis and Characterization of Poly(1,3-cyclohexadiene) Homopolymers and Star-shaped Polymers." *Macromolecules* **2001**, 34, 2108.



Scheme 9-1. Synthetic methodology for the synthesis of epoxidized PCHD.

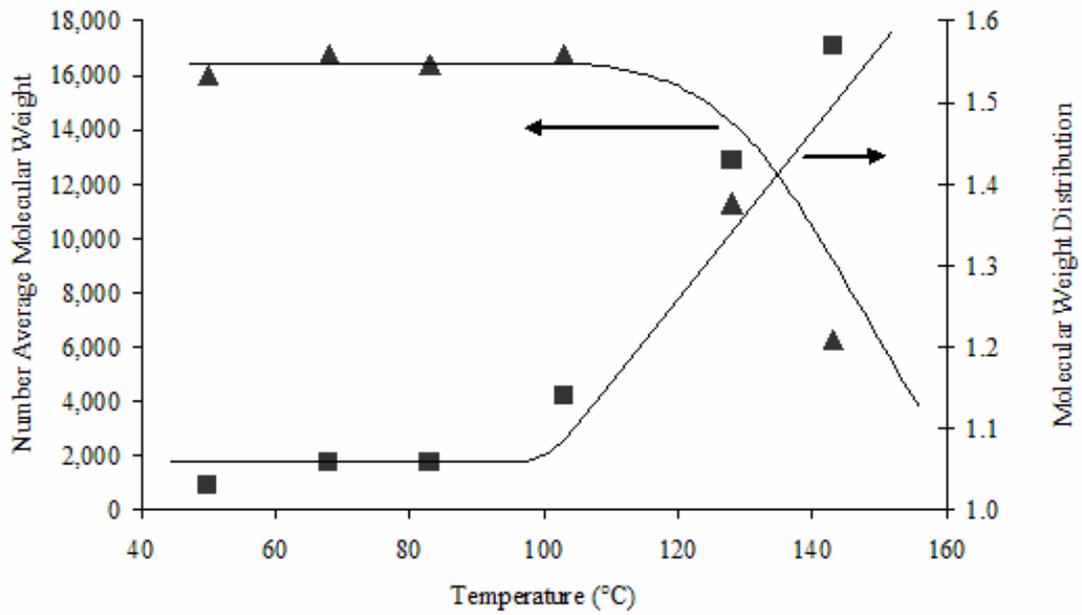


Figure 9-3. The decrease in the molecular weight of PCHD that has been heated in the presence of oxygen (□). The increase in the molecular weight distribution of a sample PCHD that has been heated in an oxygen environment (Δ).

Table 9-1. Epoxidation of PCHD

PCHD*	PCHD	Epoxidized**	Epoxidized
M _n (g/mol)	M _w /M _n	PCHD M _n (g/mol)	PCHD M _w /M _n
6200	1.01	7150	1.01
10000	1.01	11600	1.06
24000	1.06	25000	1.17

* GPC Conditions: Chloroform, 25 °C.** GPC Conditions: THF, 40 °C.

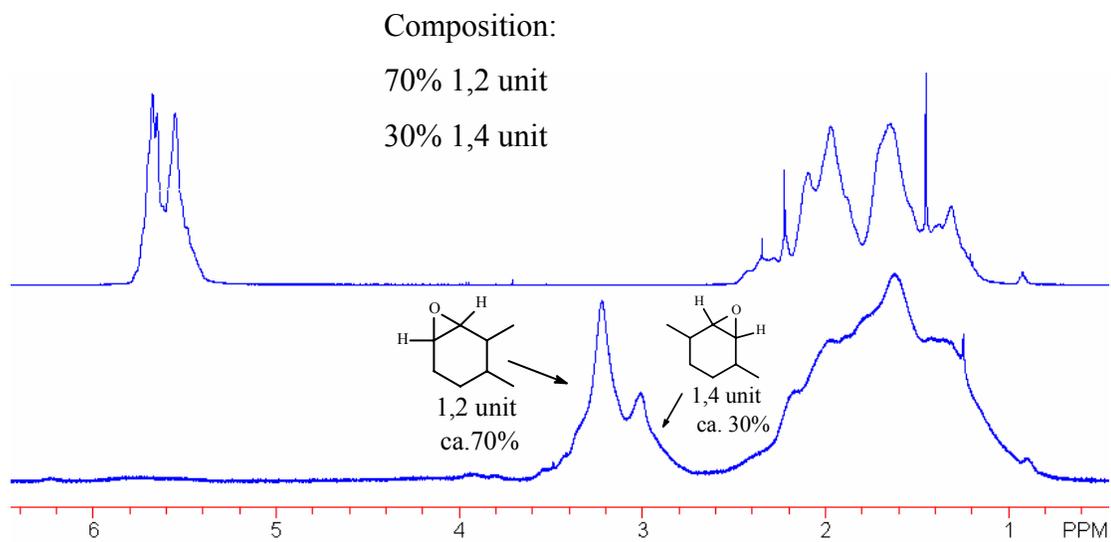


Figure 9-4. ^1H NMR spectrum of PCHD ($\langle M_n \rangle = 10000$) and epoxidized PCHD ($\langle M_n \rangle = 11600$).

Table 9-1 indicates that epoxidation of PCHD occurred in the absence of appreciable crosslinking or chain scission. The narrow molecular weight distribution (1.17) of the 25000 g/mol epoxidized PCHD further exemplified the controlled nature of the epoxidation. The degree of epoxidation of the homopolymers was determined using both ^1H and ^{13}C NMR spectroscopy (Figure 9-4). The disappearance of the olefinic resonances from 5.40 ppm to 5.80 ppm in PCHD was associated with the appearance of the epoxide resonances at 2.80 ppm to 3.60 ppm. Integration of the deconvoluted resonances resulted in a 70:30 ratio. The deconvoluted peak from 3.15 ppm to 3.60 ppm was assigned as the epoxidized form of the 1,2 unit of PCHD and the peak from 2.80 ppm to 3.15 ppm was assigned to epoxidized form of the 1,4 unit of PCHD. The relative values of 1,2 versus 1,4 addition in the PCHD precursor was shown previously to be approximately 70/30. The ^{13}C NMR spectroscopic analysis of both PCHD and the epoxidized PCHD are shown in Figure 9-5. During the epoxidation, the disappearance of the carbon signals from 126 ppm to 130 ppm were associated with the appearance of the signal from 50 to 60 ppm. As shown in both Figures 9-4 and 9-5, the epoxidation reaction resulted in quantitative epoxidation of PCHD. As expected, the epoxidized polymers were soluble in polar solvents, such as THF. In an attempt to control the degree of the epoxidation, a series of partially epoxidized polymers were synthesized with controlled molar ratios of MCPBA to polymer repeat unit. The degree of epoxidation was determined using ^1H NMR spectroscopy (Figure 9-6) by comparing the integration of the olefin region with the integration of the epoxide region. The degree of epoxidation as determined using ^1H NMR spectroscopy exhibited excellent agreement with the theoretical degree of epoxidation that was determined stoichiometrically. The presence of multiple resonances (2.8-3.4 ppm) at lower levels of epoxidation (15-57%) was attributed to the presence of adjacent 1,3-cyclohexadiene units to the epoxidized units. These new resonances shifted when the polymer was quantitatively epoxidized, which supports the assertion that these new resonances arose from the influence of adjacent 1,3-cyclohexadiene units.

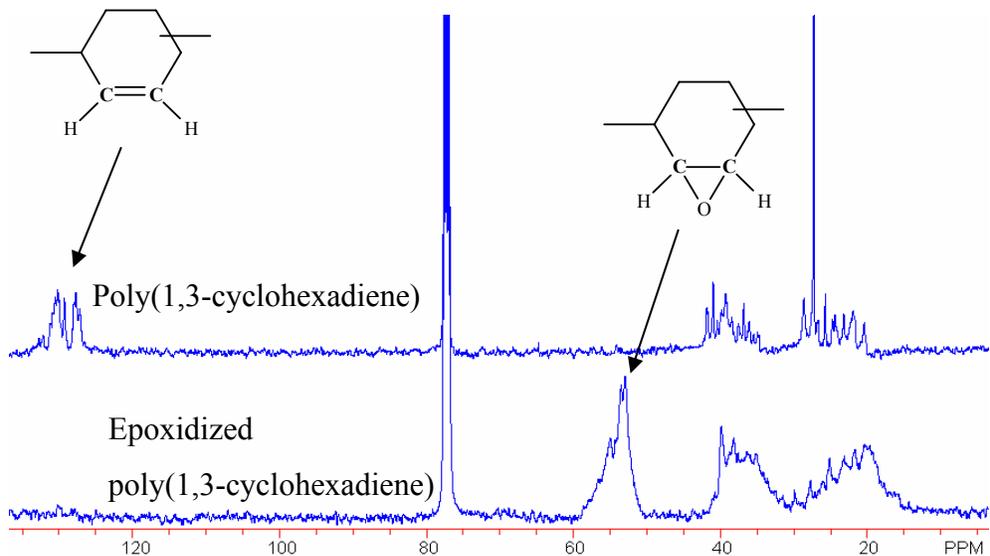


Figure 9-5. ¹³C NMR spectrum of PCHD ($\langle M_n \rangle = 1000$) and epoxidized PCHD ($\langle M_n \rangle = 11600$).

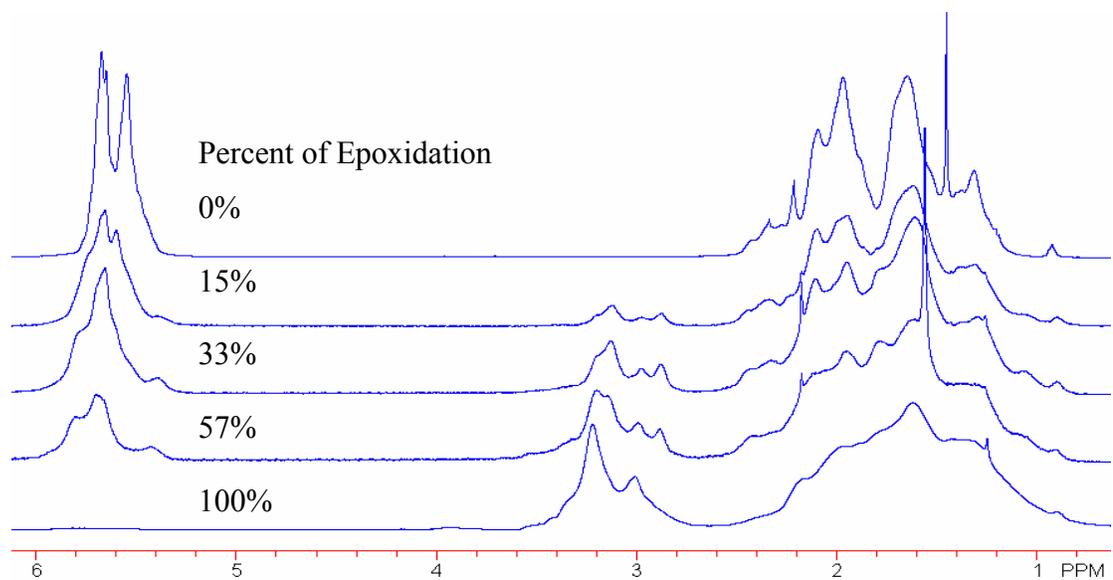


Figure 9-6. ¹H NMR spectrum of the epoxidized PCHD at various levels of epoxidation $\langle M_n \rangle = 24000$ for the precursor.

In addition, the partially epoxidized polymer suggested that the 1,2-units were initially epoxidized more rapidly than the 1,4-units. Previous studies have demonstrated that increased double bond substitution resulted in increased epoxidation rates.⁴³⁷ These results clearly indicated that the epoxidation of PCHD with MCPBA was a controlled modification reaction that occurred in the absence of polymer degradation.

Analysis of the thermal properties of both PCHD and the epoxidized PCHD was performed using thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results of the TGA experiments under nitrogen are shown in Figure 9-7. In a nitrogen environment, PCHD initially degraded at 95 °C with a loss of 12 wt%. Previous studies suggested that this initial weight loss was due to the release of residual solvent trapped in the polymer.⁴³⁸ To elucidate the nature of the initial thermal degradation, PCHD was characterized using TGA-MS (Figure 9-8). The degradation reaction was monitored for the release of 1,3-cyclohexadiene via a chain depolymerization mechanism. All samples were dried under vacuum for 3-5 days at 95 °C and ¹H NMR ensured the absence of residual monomer. The mass spectrometry of 1,3-cyclohexadiene is well understood and the formation of fragments with 39, 51, 65, and 79 amu are typically observed.⁴³⁹ Accordingly, the evolution of 1,3-cyclohexadiene was monitored using mass spectrometry for these fragments. These results indicated the degradation of PCHD occurred in two stages. During the first stage, the polymer proceeded through a chain degradation mechanism at 95 °C, as indicated by the presence of 1,3-cyclohexadiene fragments (Figure 9-8). During this first degradation step, the polymer chain depolymerized resulting in a loss of 12 wt%. After the first stage of degradation, the polymer was thermally stable until 300 °C.

⁴³⁷ Dreyfuss, P., and J. P. Kennedy. "Epoxidation with m-Chloroperbenzoic Acid: An Analytical Method for Determining Unsaturation of Olefins and Polymers." *Anal. Chem.* **1975**, 47, 771.

⁴³⁸ David, J. L., S. P. Gido, K. Hong, Jian Zhou, J. W. Mays, and B.N. Tan. "Core-Shell Cylinder Morphology in Poly(styrene-b-1,3-cyclohexadiene) Diblock Copolymers." *Macromolecules* **1999**, 32, 3216.

⁴³⁹ Stein, S.E. *1,3-Cyclohexadiene Mass Spectrum* [NIST Chemistry WebBook]. NIST Standard Reference Data Base, 2001 [cited June 18 2002].

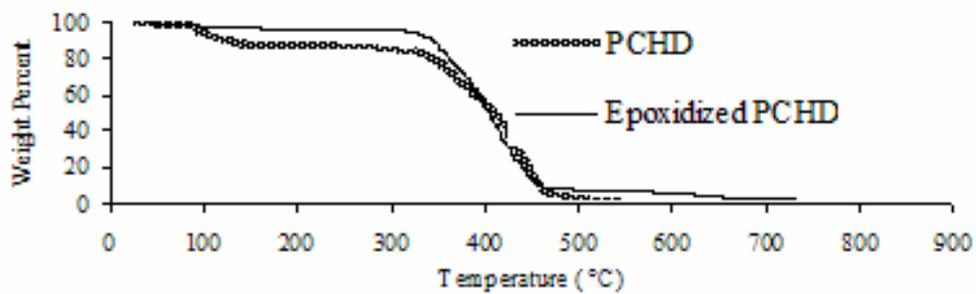


Figure 9-7. Thermo-gravimetric analysis of PCHD ($\langle M_n \rangle = 10000$) and epoxidized PCHD ($\langle M_n \rangle = 11600$) in the presence of nitrogen .

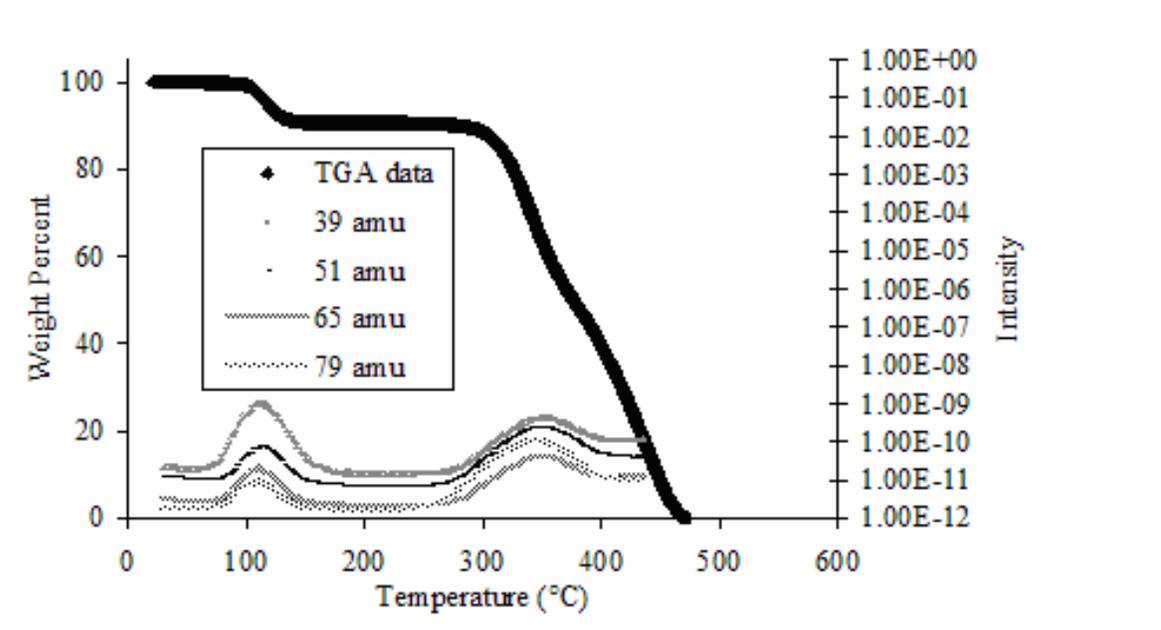


Figure 9-8. Thermo-gravimetric analysis coupled with mass spectrometry of PCHD indicating the two step degradation of PCHD.

A second chain degradation event occurred at 300 °C, forming additional 1,3-cyclohexadiene. These results suggested that at 95 °C the polymer chain depolymerized until a more thermally stable unit on the polymer backbone was reached. The remaining polymer backbone remained thermally stable until 300 °C. In contrast to the PCHD precursor, the epoxidized polymer exhibited excellent thermal stability with the onset of thermal degradation occurring at 380 °C.

The thermal characteristics of the homopolymer and the epoxidized polymer were also determined in an oxygen environment (Figure 9-9). PCHD exhibited a weight loss at 110 °C followed by a rapid increase in weight due to the incorporation of oxygen at 150 °C. The onset of thermal degradation of PCHD in the solid state correlated with the onset of random chain scission in solution, which was demonstrated to occur at 110 °C (Figure 9-3). In contrast to the poor thermal stability of PCHD, the epoxidized polymers did not exhibit weight loss until 250 °C. This observation indicated that the epoxidation of PCHD improved the thermal stability of the polymer in both oxygen and a nitrogen environment.

DSC was used to examine the effect of epoxidation of the homopolymer on the glass transition temperature (T_g). The epoxidation of PCHD resulted in a 15 °C increase in the T_g from 139 °C for the PCHD to 154 °C for the epoxidized polymer. This increase in T_g was attributed to the introduction of the polar epoxide functionality, and not simply due to an increase in molecular weight. Current studies in our laboratories have shown that 154 °C exceeds the $T_{g\infty}$ for PCHD polymers with a 70% 1,2 microstructure.⁴⁴⁰

⁴⁴⁰ Williamson, D.T., T.E. Glass, and T.E. Long. *Macromolecules* **2002**, to be submitted

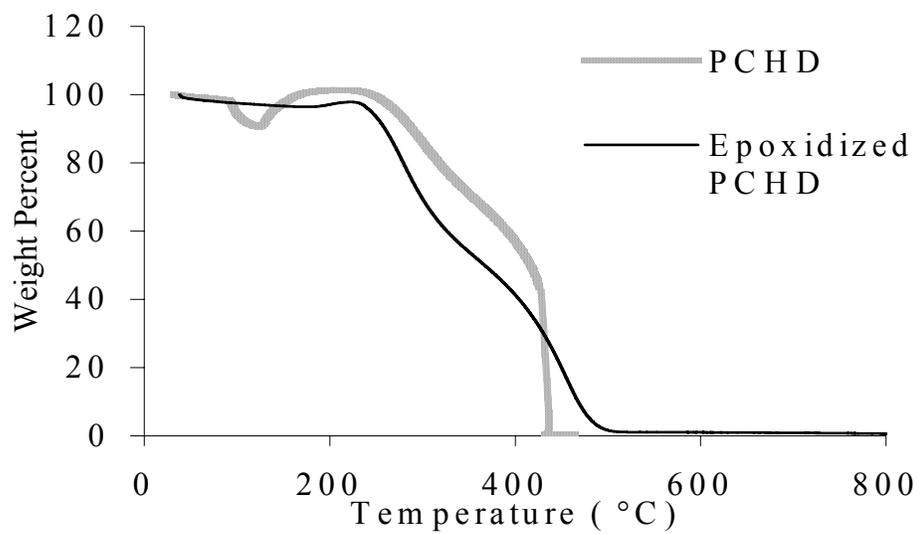


Figure 9-9. Thermo-gravimetric analysis of PCHD ($\langle M_n \rangle = 10000$) and epoxidized PCHD ($\langle M_n \rangle = 11600$) in the presence of nitrogen.

9.5 Conclusions

The thermal and oxidative stability of PCHD was investigated using a combination of size exclusion chromatography and thermo-gravimetric analysis. The onset of oxidative degradation of a PCHD solution occurred at approximately 60 °C, and the introduction of aldehyde and ether groups into the polymer occurred at higher temperatures and increased reaction times. At higher temperatures (110 °C), oxidative degradation involved chain scission resulting in increased molecular weight distributions and decreased molecular weights. TGA-MS analysis of the PCHD in a nitrogen environment indicated a two-step chain degradation mechanism, wherein the initial degradation step resulted in the liberation of 1,3-cyclohexadiene through the depolymerization of PCHD. Epoxidation was conducted at 25 °C with MCBPA, in the absence of deleterious polymer degradation. The resulting polymer exhibited excellent molecular weight control and narrow molecular weight distributions. The epoxidation of PCHD improved both the thermal and oxidative stability. These epoxide containing polymers are suitable precursors to novel macromolecules with highly branched and functionalized architectures.

CHAPTER 10

Ozonolysis of Poly(1,3-cyclohexadiene) Containing polymers

10.1 Abstract

The ozonolysis of poly(1,3-cyclohexadiene) containing polymers was explored. Homopolymers of poly(1,3-cyclohexadiene) were determined to be too reactive towards ozone and an insoluble product was isolated. Decreased polymer concentrations were shown to reduce the degree of branching and the ozonolyzed polymers were soluble at elevated temperatures in DMSO. A series of poly(1,3-cyclohexadiene-*alt*-styrene)-*block*-polystyrene copolymers were synthesized to reduce the concentration of poly(1,3-cyclohexadiene) repeat units in the polymer backbone. These block copolymers exhibited narrow molecular weight distributions ($\langle M_w \rangle / \langle M_n \rangle = 1.05 - 1.03$). Ozonolysis of these block copolymers exhibited improved reaction controllability as demonstrated by the increased polymer solubility and decreased molecular weight distribution ($\langle M_w \rangle / \langle M_n \rangle = 1.18 - 3.79$). The presence of an aldehyde functionality was demonstrated by ^1H NMR spectroscopy and FTIR spectroscopy. These polymers exhibited near quantitative conversion of the double bonds to an aldehyde functional group.

10.2 Introduction

Numerous commercially important polymers are prepared via the living anionic polymerization of isoprene and butadiene, including adhesive systems, thermoplastic elastomers, and oil modifiers.⁴⁴¹ These anionically prepared acyclic poly(dienes) are typified by low glass transition temperatures (T_g), short relaxation times at ambient temperatures, and ease of synthesis.⁴⁴² In contrast to the large body of research examining these acyclic poly(dienes), poly(1,3-cyclohexadiene) polymers have received little attention. A variety of different synthetic methods were studied with little success, these methods included free radical, coordination and anionic polymerization strategies.⁴⁴³ It was concluded in these studies that the polymerization was limited by molecular weight limiting side reactions, such as chain termination and chain transfer.⁴⁴⁴ As a result, the molecular weight of the resulting polymers was unpredictable and the molecular weight distributions were broad.⁴⁴⁵

⁴⁴¹ Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996. Quirk, R. P. "New block copolymers for higher temperature applications." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **1985**, 26, 14.

⁴⁴² Stroble, G. *The Physics of Polymers*. 2nd ed Springer-Verlag: Berlin, 1997. Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996.

⁴⁴³ Sharaby, Z., M. Martan, and J. Jagur-Grodzinski. "Stereochemistry of Poly(1,3-cyclohexadienes). NMR Investigation of Effects Due to the Solvent Medium and to the Mechanism of Polymerization." *Macromolecules* **1982**, 15, 1167. Sharaby, Z., J. Jagur-Grodzinski, M. Martan, and D Vofsi. "Kinetics and Mechanism of the Anionic Polymerization of Cyclohexadienes Initiated by Naphthalene Radical Anions and Dianions." *J. Polym. Sci., Polym. Chem. Ed.* **1982**, 20, 901. Lefebvre, G, and F. Dawans. "1,3-Cyclohexadiene polymers. I. Preparation and aromatization of poly-1,3-cyclohexadiene." *J. Polym. Sci.* **1964**, A2, 3277. Mango, L.A., and R.W. Lenz. "Organometallic reactions which control molecular weight in the anionic polymerization of 1,3-cyclohexadiene." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **1971**, 12, 402. Mango, L.A., and R.W. Lenz. "Mechanism and stereochemistry in the anionic polymerization of 1,3-cyclohexadiene and the diimide hydrogenation of polymers." *U.S. Nat. Tech. Inform. Serv.* **1972**, 12, 402.

⁴⁴⁴ Hsieh, H. L., and R. P. Quirk. *Anionic Polymerization: Principles and Practical Applications* Marcel Dekker: New York, 1996. Hong, K., and J.W. Mays. "1,3-Cyclohexadiene Polymers. 1. Anionic Polymerization." *Macromolecules* **2001**, 34, 782.

⁴⁴⁵ Mango, L.A., and R.W. Lenz. "Organometallic reactions which control molecular weight in the anionic polymerization of 1,3-cyclohexadiene." *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **1971**, 12, 402. Mango, L.A., and R.W. Lenz. "Mechanism and stereochemistry in

Recently, Natori and coworkers reported the synthesis of a series of poly(1,3-cyclohexadiene) polymers using a TMEDA/nBuLi initiator adduct at 40 °C in cyclohexane.⁴⁴⁶ This adduct was reported to be efficient for the synthesis of a range of polymer molecular weights and polymer systems containing poly(1,3-cyclohexadiene), such a poly(1,3-cyclohexadiene-block-butadiene) and poly(1,3-cyclohexadiene-block-isoprene). A ratio of TMEDA/nBuLi of 5:4 was necessary to synthesize poly(1,3-cyclohexadiene) homopolymers with narrow molecular weight distributions (1.10). When higher molecular weight polymers were synthesized (40000) the molecular weight distribution broadened (1.30) due to the occurrence of deleterious side reactions, such as chain transfer to monomer.

Polymer modification reactions enable the chemical and physical properties of an existing polymer to be tailored for specific applications. Polymers containing an unsaturated site in the repeating unit, such as polydienes, are candidates for a vast array of modification reactions. Examples of these post-polymerization modifications include bromination,⁴⁴⁷ epoxidation,⁴⁴⁸ hydrogenation, and maleation.⁴⁴⁹ However, the allylic hydrogens in the polymer backbone are also highly sensitive to oxidation and

the anionic polymerization of 1,3-cyclohexadiene and the diimide hydrogenation of polymers." *U.S. Nat. Tech. Inform. Serv.* **1972**, 12, 402.

⁴⁴⁶ Natori, I. "Synthesis of Polymers with an Alicyclic Structure in the Main Chain. Living Anionic Polymerization of 1,3-Cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System." *Macromolecules* **1997**, 30, 3696. Natori, I., and S. Inoue. "Living Anionic Polymerization of 1,3-cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System. Copolymerization and Block Copolymerization with Styrene, Butadiene, and Isoprene." *Macromolecules* **1998**, 31, 982.

⁴⁴⁷ Buzdugan, E., P. Ghioca, E.A. Badea, and S. Serban. "Bromination of Some Styrene-Diene Block Copolymers." *Eur. Polym. J.* **1997**, 33, 1713. Nor, H., and J.R. Ebdon. "Telechelic Liquid Natural Rubber." *Prog. Polym. Sci.* **1998**, 23, 143.

⁴⁴⁸ Nor, H., and J.R. Ebdon. "Telechelic Liquid Natural Rubber." *Prog. Polym. Sci.* **1998**, 23, 143. Sakai, T., N. Kihara, and T. Endo. "Polymer Reaction of Epoxide and Carbon Dioxide. Incorporation of Carbon Dioxide into Epoxide Polymers." *Macromolecules* **1995**, 28, 4701. Roland, C.M., J.K. Kallitsis, and K.G. Gravalos. "Plateau Modulus of Epoxidized Polybutadiene." *Macromolecules* **1993**, 26, 6474.

⁴⁴⁹ Odian, George. *Principles of Polymerization* John Wiley and Sons Inc: New York, 1991. Nor, H., and J.R. Ebdon. "Telechelic Liquid Natural Rubber." *Prog. Polym. Sci.* **1998**, 23, 143.

degradation under the conditions employed for many polymer modification reactions.⁴⁵⁰ In addition to tailoring polymer properties, post-polymerization modifications are utilized to incorporate reactive functional groups into the polymer backbone. For example, the introduction of amino functional groups was utilized for additional chemical processes, such as the crosslinking of epoxy resins. Chemical modification reactions were performed in solution, the solid state, and at polymer surfaces through the use of gases and liquids.⁴⁵¹ Several factors such as reaction phase, percent crystallinity, conformation, neighboring group effects, and tacticity affect polymer reactivity during chemical modifications. In addition, chemical modification reactions performed at a polymer surface will alter the surface without affecting the bulk properties, such as T_g . However, the same modification reaction performed in solution will affect the bulk properties.

In addition to bromination, epoxidation, and maleation, ozonolysis is a novel type of post-polymerization modification that could be utilized for the introduction of polar functionalities into a non-polar polymer. Previously, ozonolysis of polymers was generally regarded as an unfavorable reaction associated with polymer degradation.⁴⁵² The agent of ozonolysis is ozone, which is a highly reactive allotrope of oxygen that is produced via the passage of oxygen through a silent electric discharge. The reaction of ozone with a double bond is well understood and proceeds via the 1,3-cycloaddition of ozone with a double bond followed by rearrangements that result in the cleavage of the double bond.⁴⁵³ Polymers with a double bond in the polymer backbone were previously demonstrated to be highly sensitive to ozone. As expected, the reaction of ozone with these double bond containing polymers resulted in polymer chain scission, a reduction

⁴⁵⁰ Ranby, B, and J.F. Rabek. *Photodegradation, Photo-Oxidation and Photostabilization of Polymers*. Edited by ` John Wiley and Sons: New York, 1975.

⁴⁵¹ Billmeyer, Fred W. *Textbook of Polymer Science*. 3rd ed John Wiley and Sons: New York, 1984.

⁴⁵² Nor, H.M., and J.R. Ebdon. "Ozonolysis of natural rubber in chloroform solution." *Polymer* **2000**, 41, 2359.

⁴⁵³ Bailey, P.S., H.H Hwang, and C. Chiang. "Mechanisms of Epoxidation during Ozonation of Carbon-Carbon Double Bonds." *J. Org. Chem.* **1985**, 50, 231.

in molecular weight, and a broadening of the molecular weight distribution.⁴⁵⁴ Ozonolysis was also demonstrated to be a powerful analytical tool for the examination of copolymers containing a double bond in one of the repeat units. In this method, ozone was reacted with the polymer chain specifically at the double bond containing repeat units and the polymer chain was cleaved. The size and distribution of the repeat units without a double bond was subsequently determined using size exclusion chromatography (SEC).⁴⁵⁵

Herein, poly(1,3-cyclohexadiene) containing polymers were reacted with ozone and novel polymers containing aldehyde and carboxylic acid functionalities were produced. These novel polymers were characterized using ¹H NMR spectroscopy, FTIR spectroscopy, differential scanning calorimetry (DSC), and size exclusion chromatography.

10.3 Experimental Section

Materials. 1,3-cyclohexadiene (Aldrich, 98%) and styrene (Aldrich, 99%) were degassed several times and distilled at reduced pressure (0.10 mm Hg, 10 °C) from dibutylmagnesium (DBM, 0.84 M). n-Butyllithium (FMC Corporation, Lithium Division, 1.35 M in n-hexane) was used without further purification. TMEDA (Aldrich, 99%) was distilled at reduced pressure (0.13-0.16 mmHg, 10 °C) from calcium hydride and stored under nitrogen at -25 °C until ready for use. Cyclohexane (Burdick-Jackson, HPLC grade) was stirred over sulfuric acid (10:1 cyclohexane:sulfuric acid) for 7-10 days, decanted, and distilled from a sodium dispersion under nitrogen immediately prior to use. All reagents were transferred using syringe and cannula techniques under ultrapure (99.999%) nitrogen.

⁴⁵⁴ Ho, K.W., and J.E. Guthmann. "The ozonolysis of butyl and halobutyl elastomers." *J. Polym. Sci. Part A*. **1989**, 27, 2435.

⁴⁵⁵ Hackathorn, M.J., and M.J. Brock. "Alternating structures in copolymers as elucidated by microozonolysis." *J. Polym. Sci. Part A*. **1975**, 13, 945.

Polymer Synthesis.

Synthesis of Poly(1,3-cyclohexadiene). A 100-mL round-bottomed flask containing anhydrous cyclohexane (60 mL, 0.54 mol), 1,3-cyclohexadiene (5.95 mL, 62.4 mmol), and TMEDA (0.094 mL, 0.625 mmol) was heated to the 40 °C. The initiator, n-BuLi (0.31 mL, 0.5 mmol), was added using a syringe and the polymerization was allowed to proceed for 25 minutes. The polymerization was terminated using degassed methanol (Burdick-Jackson, HPLC grade). The resulting polymer was precipitated into isopropanol (600 mL), filtered, and dried at 50 °C in vacuo for 12-18 hours. An antioxidant such as Irganox 1010 (0.10 weight % compared to the polymer) was added to the precipitation solvent to retard oxidative degradation during subsequent storage.

Polymerization of Poly(styrene-co-1,3-cyclohexadiene). The anionic copolymerization of styrene and 1,3-cyclohexadiene was initiated with secBuLi in cyclohexane at 25°C and allowed to proceed for 2 h to ensure quantitative conversion of styrene and 1,3-cyclohexadiene. Polymerizations were performed under a nitrogen atmosphere at 20 wt% monomer concentrations. A typical polymerization involved the addition of anhydrous cyclohexane (60 mL, 0.54 mol), styrene (5.85 g, 0.56 mol), and 1,3-cyclohexadiene (5.85 g, 0.75 mol) to a 100 mL round-bottomed flask. The solution was maintained at 25 °C, and secBuLi (0.65 mL, 1.15 mmol) was added to initiate the polymerization. The polymerization was allowed to proceed for 2 h and was terminated with degassed methanol (Burdick Jackson, HPLC grade, 1.0 mL). The resulting copolymer was precipitated into isopropanol (600 mL), filtered, and dried at 50°C in vacuo overnight. An antioxidant such as Irganox 1010 (0.10 wt % compared to polymer) was added to the precipitation solvent to retard oxidative degradation during subsequent storage. This antioxidant was present during all subsequent polymer modification reactions.

Ozonolysis Procedure. Ozone was generated by passing dry oxygen (flow rate = 30 mL/min) through an ozone generator (Model OGA/C, Yanco Industries, Ozone Services Division). The concentration of ozone in the ozone/oxygen solution was 147 µg/mL. A

500 μg polymer sample was dissolved in the desired solvent in a glass reactor equipped with a magnetic stirrer, a tube for the oxygen/ozone inlet, and a port used for the exhausting the ozone. The residual ozone in the ozone exhaust was destroyed using the ozone destroyer that was attached to the ozone generator. The polymer solution was cooled to the specified temperature and the ozone/oxygen gas solution was bubbled through the solution. After the reaction was complete, nitrogen was bubbled through the solution to remove any excess ozone. The solution was then treated using either oxidative or reductive conditions.

Oxidative Workup. Formic acid (0.19 mole, 8.8 g, 18.9 mL) and hydrogen peroxide (Aldrich, 0.19 mole, 6.68 g) were added to a solution containing the ozonolyzed polymer product. The solution was heated to 50 °C for 2 h. In some cases, tetrahydrofuran (Aldrich, 100 mL) was added to solubilized the ozonolyzed product.

Reductive Workup. A reducing agent, such as dimethyl sulfide (Aldrich, 1.0 mL, 0.7 mmol) or triphenyl phosphine (Aldrich, 0.18 g, 0.7 mmol), was added to the solution containing the ozonolyzed polymer product). Studies examining the effectiveness of the reductants found both dimethyl sulfide and triphenyl phosphine to be equally efficient reducing agents. The solution was allowed to react for 20 min and subsequently precipitated into hexane.

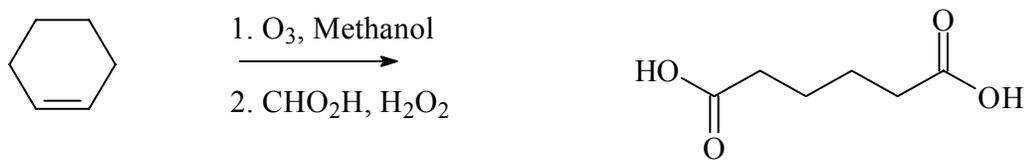
Polymer Characterization. Glass transition temperatures were determined using a Perkin-Elmer Pyris 1 DSC at a heating rate of 10°C/min under nitrogen. Glass transition temperatures are reported as the midpoint of the change in heat capacity during the second heat. Molecular weights were determined using size exclusion chromatography (SEC) with a Waters Alliance SEC system equipped with a Waters 717plus equipped with a Waters 2410 refractive index detector and a Wyatt Technology Minidawn MALLS detector was utilized for absolute molecular weight measurements. The dn/dc values were determined on-line using the calibration constant for the RI detector and the mass of the polymer sample. SEC measurements were performed at

40°C in chloroform at a flow rate of 1.0 mL/min. For all samples, it was assumed that 100% of the polymer eluted from the column during the measurement.

NMR Measurements. ^1H and ^{13}C NMR high resolution NMR spectra were obtained at 400 and 100 MHz, respectively, using a Varian NMR spectrometer equipped with a 10 mm and 5 mm broad band probe and standard pulse decoupling. ^1H NMR samples were referenced to the residual signal of the deuterated solvent. The samples were dissolved in acetone and chromium(III) acetylacetonate was added to reduce the relaxation time for the ^{13}C NMR studies.

10.4 Results and Discussion

Cyclohexene was used in the initial experiments to determine the reaction conditions used in subsequent polymer experiments. Scheme 10-1 outlines the synthetic approach used during the reaction. The ozonolysis was performed in methanol with an ozone concentration of 146 $\mu\text{g/mL}$, and the product was oxidized using a solution containing formic acid and hydrogen peroxide. In order to minimize the occurrence of various side reactions common during ozonolysis, the ozonolysis was performed at reduced temperature (-78°C).



Scheme 10-1. Synthetic approach used to synthesize adipic acid via the reaction between ozone and cyclohexene.

Adipic acid was isolated in high yield (> 80%) and the product was characterized using ^1H NMR (Figure 10-1). As expected, signals for the protons α and β to the carboxylic acid group appeared at 2.35 and 1.56 ppm, respectively. The signal for the carboxylic acids protons appeared at 12.30 ppm, which was confirmed by performing a deuterium exchange experiment. The ozonolysis and subsequent oxidation of cyclohexene was quantitative resulting in high purity adipic acid (>98%). Traces of formic acid were removed by recrystallization from a 40:60 methanol/cyclohexane solution. The formation of side products, such as polymeric peroxides, was not observed. The absence of peroxide forming side reactions was attributed to the low reaction temperature (-78°C). These studies were subsequently utilized as a starting point in an attempt to controllably ozonolysis poly(1,3-cyclohexadiene) containing polymers.

The ozonolysis of cyclohexene was performed in methanol, unfortunately, poly(1,3-cyclohexadiene) and any of the poly(1,3-cyclohexadiene-co-styrene) copolymers used in this study were insoluble in methanol. Therefore, the ozonolysis of the polymers was performed in less polar solvents, such as dichlorobenzene, cyclohexane, chloroform, and dichloromethane. Initial studies also examined the utility of tetrahydrofuran (THF) as a possible solvent, because of its ability to solubilize both the reactant and the product. Unfortunately, the reaction between THF and ozone occurred competitively with the desired reaction between ozone and poly(1,3-cyclohexadiene). THF was previously demonstrated to react with ozone to form a peroxide species that subsequently rearranged in the absence of a reducing agent to form 2,3-dihydro-furan.⁴⁵⁶ The ozonolysis of poly(1,3-cyclohexadiene) was performed as shown in scheme 10-2. The viable solvents for the reaction allowed the ozonolysis to be performed using a range of temperatures. Ozonolysis reactions performed in dichloromethane were performed at -78 °C, however, reactions performed in either chloroform, cyclohexane, or dichlorobenzene required the use of elevated temperatures (15 or 25 °C) due to the freezing point of the solvent.

⁴⁵⁶ Bailey, P.S. *Ozonation in Organic Chemistry*. 2 vols. Vol. 1 Academic Press: New York, 1978.

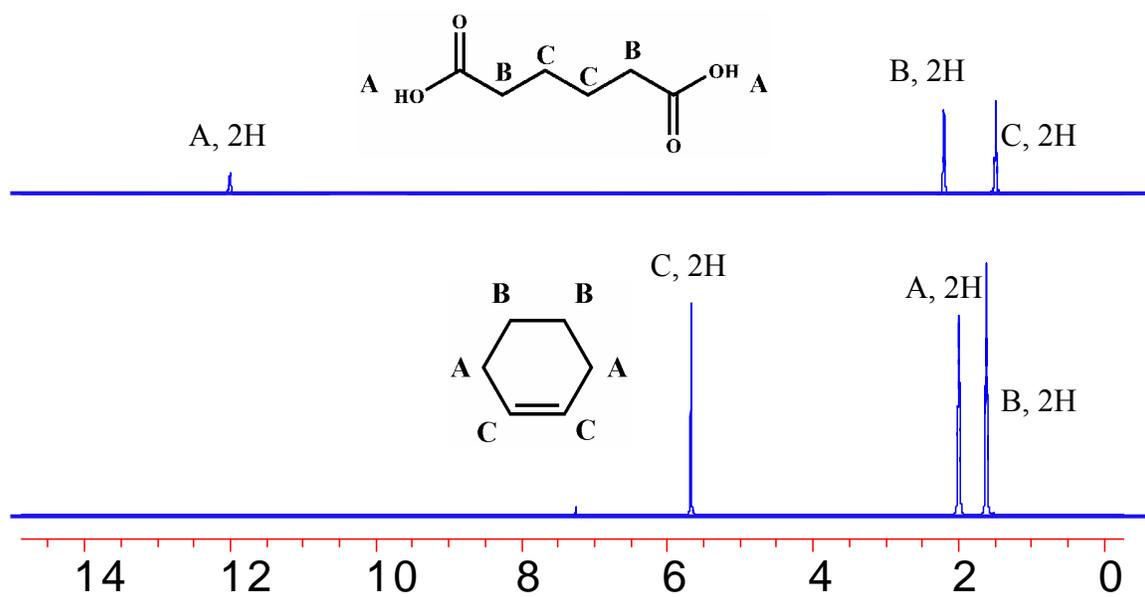
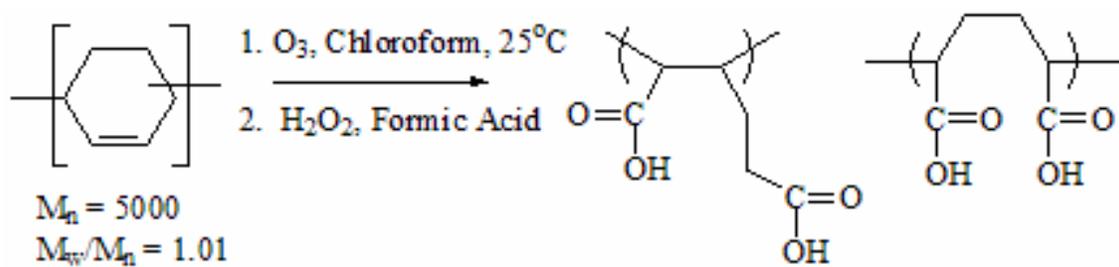


Figure 10-1 ¹H NMR spectra of cyclohexene (bottom spectrum) and adipic acid (top spectrum).



Scheme 10-2 Oxidative ozonolysis reaction of a poly(1,3-cyclohexadiene) homopolymer.

Initial attempts to ozonolyze poly(1,3-cyclohexadiene) resulted in the formation of an insoluble material. The formation of the insoluble material was attributed to an intramolecular reaction and subsequent branching that was favored by the presence of a high concentration of double bonds in the polymer backbone (Figure 10-2). A major side reaction associated with the ozonolysis of double bonds is the reaction of the highly reactive carbonyl oxide and an aldehyde.⁴⁵⁷ When this reaction occurs via an intermolecular attack, then polymeric peroxides are formed. In a polymeric system, the intermolecular attack results in polymer branching. Therefore it was expected that reducing the polymer concentration to 4 mg/mL would decrease the likelihood of branching and increase the product solubility. When the reaction was performed at a concentration of 4 mg/ml, the product exhibited improved solubility and did not precipitate during the ozonolysis reaction, however, the isolated polymer product was only soluble in DMSO at elevated temperatures (120 °C) (Table 10-1).

To decrease the degree of polymer branching during the ozonolysis reaction and improve the solubility of the polymer product, a series of poly(1,3-cyclohexadiene-*alt*-styrene)-block-styrene copolymers were synthesized for subsequent ozonolysis. These polymers were synthesized with a range of poly(1,3-cyclohexadiene) content (2-10 mol %) using a “one-shot-block” technique. We have previously demonstrated that styrene and 1,3-cyclohexadiene copolymerize in an alternating fashion. Therefore, block copolymers comprised of poly(1,3-cyclohexadiene-*alt*-styrene)-block-polystyrene were synthesized via the addition of secBuLi to a solution containing an excess of styrene (Scheme 10-3). GPC and ¹H NMR spectroscopy were used to characterize the block copolymers (Table 10-2). The molecular weights for the copolymers agreed well with the molecular weights based on the ratio of the grams of monomer to moles of secBuLi. The composition of the block copolymers was verified via ¹H NMR spectroscopy.

⁴⁵⁷ Bailey, P.S. *Ozonation in Organic Chemistry*. 2 vols. Vol. 1 Academic Press: New York, 1978.

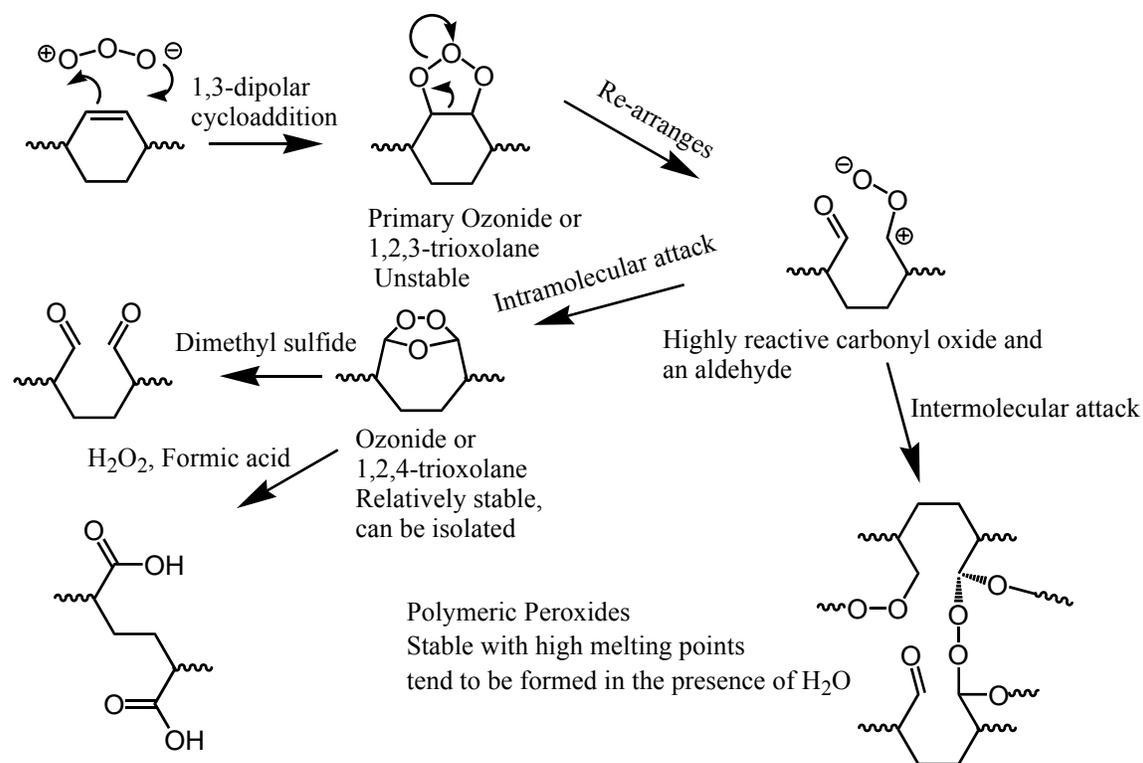
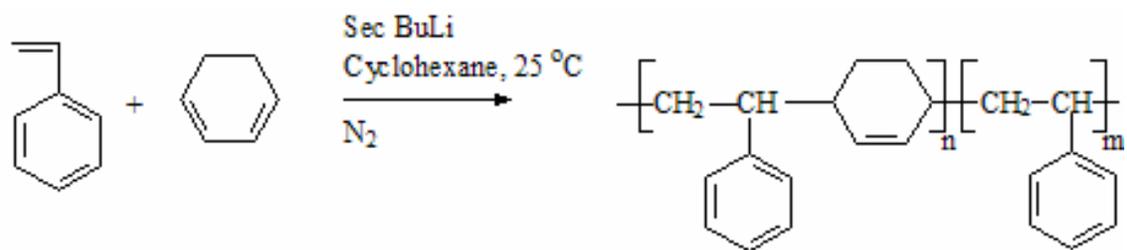


Figure 10-2 Ozonolysis of the poly(1,3-cyclohexadiene) repeat unit (Taken from Bailey et al.⁴⁵⁴).

Table 10-1. Results for the ozonolysis of poly(1,3-cyclohexadiene) homopolymers.

Reaction	Reaction Solvent	Reaction Temperature (°C)	Reaction Concentration	Product Solubility
8-OPCHD	CHCl ₃	25	8 mg/mL	insoluble
6-OPCHD	CHCl ₃	25	6 mg/mL	insoluble
6-OPCHDB	CH ₂ Cl ₂	-78	6 mg/mL	insoluble
6-OPCHDC	cyclohexane	15	6 mg/mL	insoluble
6-OPCHDD	dichlorobenzene	15	6 mg/mL	insoluble
4-OPCHDA	CHCl ₃	25	4 mg/mL	DMSO
4-OPCHDB	CH ₂ Cl ₂	-78	4 mg/mL	DMSO
4-OPCHDC	cyclohexane	15	4 mg/mL	DMSO
4-OPCHDD	dichlorobenzene	15	4 mg/mL	DMSO
4-OPCHDE*	dichlorobenzene	15	4 mg/mL	DMSO

* Polymer was treated with dimethyl sulfide.



Scheme 10-3. Alternating, anionic copolymerization of 1,3-cyclohexadiene and styrene. Copolymerizations were performed at 25 °C in cyclohexane.

Table 10-2. Characterization of the poly(1,3-cyclohexadiene-*alt*-styrene) containing block copolymers prepared via anionic polymerization. All polymerizations were performed at 25 °C for 2 h.

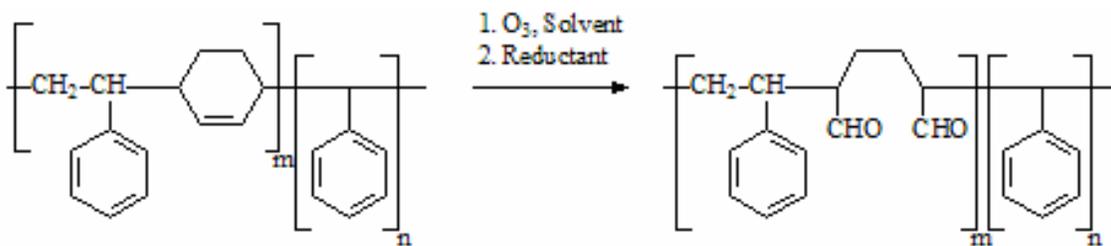
1,3-cyclohexadiene Content (mol %)	M_n (theoretical)	$\langle M_n \rangle$ *	$\langle M_w \rangle / \langle M_n \rangle$ *
2	10000	11500	1.05
6**	10000	9560	1.03
10**	10000	11200	1.05

*GPC conditions: Chloroform, 40°C, MALLS. ** Determined by ^1H NMR spectroscopy

In general, the molecular weight distributions of the copolymers remained relatively narrow and the polymer yields were quantitative. These block copolymers were subsequently reacted with ozone at a polymer concentration of 4 mg/mL. Previous studies suggested that polystyrene formed peroxide containing species and a stable 1,2,4-trioxolane when exposed to ozone at elevated temperatures (60 °C).⁴⁵⁸ However, when a polystyrene control ($\langle M_n \rangle = 8900$, $\langle M_w \rangle / \langle M_n \rangle = 1.03$) was treated with ozone at 15 or 25 °C, the molecular weight and molecular weight distribution remained unchanged ($\langle M_n \rangle = 8800$, $\langle M_w \rangle / \langle M_n \rangle = 1.03$) and ¹H NMR spectroscopy did not show any new resonances.

Ozonolysis of the block copolymers was performed as described in Scheme 10-4. These polymers were dissolved in either dichloromethane or dichlorobenzene at a concentration of 4 mg/mL. The ozone/oxygen solution (ozone concentration = 147 µg/mL) was bubbled through the reaction until the solution turned a light blue color, which indicated that the solution was becoming saturated with ozone. Nitrogen was then bubbled through the solution to remove the excess ozone and the 1,2,4-trioxolane species was reduced with either dimethyl sulfide or triphenyl phosphine. ¹H NMR spectroscopy of the polymer with 6 mol% poly(1,3-cyclohexadiene) after ozonolysis indicated the presence of aldehyde signals between 9-10 ppm (Figure 10-3). The ratio of the integration of the aldehyde signal relative to the aromatic repeat unit was 11.1:480, which agrees well with the degree of expected ratio of 12:470. In addition, the polymer was characterized using quantitative ¹³C NMR spectroscopy. As shown in figure 10-4, the aldehyde signal was at 204 ppm and its relative intensity to the aromatic styrene carbons was 1:48 (B / (A + C + D)). This ratio indicates that the polymer contained approximately 11.9 mol% of aldehyde functionality, which agrees well with the theoretical percentage of aldehyde content of 12 mol%. Analysis of the ozonolyzed polymer using FTIR also indicates the presence of the

⁴⁵⁸ Kefely. *J. Polym. Sci. Part A: Polym. Chem. Ed.* **1981**, 19, 2175.



Scheme 10-4. Synthetic approach used for the ozonolysis of the poly(1,3-cyclohexadiene) containing block copolymers.

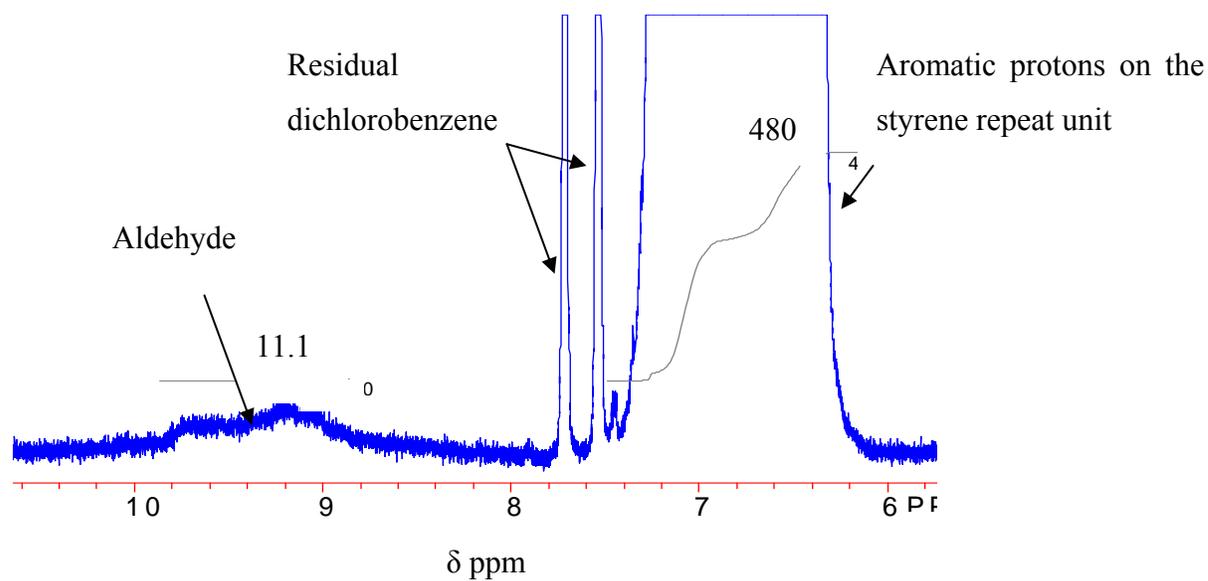


Figure 10-3. ^1H NMR spectroscopic analysis of the ozonolyzed poly(1,3-cyclohexadiene-alt-styrene) containing copolymer indicating the presence of the expected aldehyde resonances between 9 and 10 ppm.

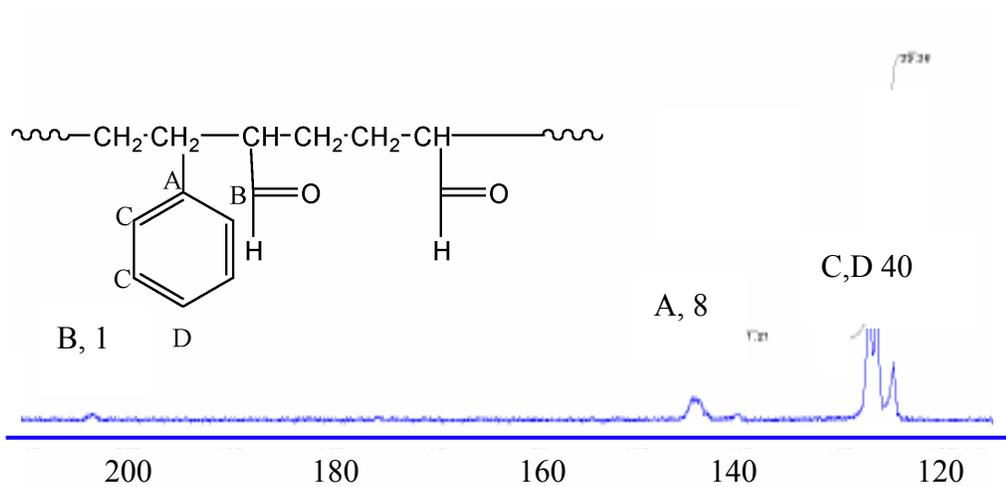


Figure 10-4. ^{13}C NMR spectrum of ozonolyzed poly(1,3-cyclohexadiene) containing block copolymer ($\langle M_n \rangle = 10000$). NMR Conditions: CDCl_3 , 25 °C.

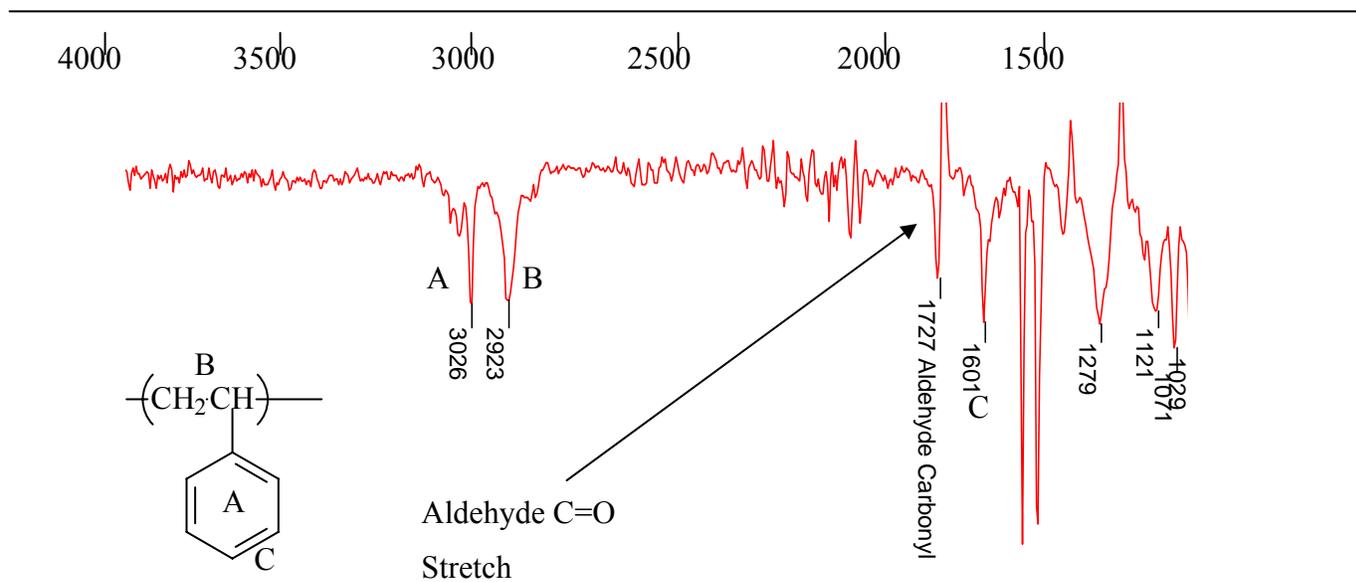


Figure 10-5. FTIR analysis of ozonolyzed poly(1,3-cyclohexadiene) containing block copolymer ($\langle M_n \rangle = 10000$).

aldehyde carbonyl stretch at 1727 cm^{-1} . The remaining absorptions in the spectrum were attributed to the polystyrene repeat units.

Characterization of the ozonolyzed polymer molecular weight and molecular weight distributions was performed using GPC (Table 10-3). As expected, increased percentages of poly(1,3-cyclohexadiene) repeat units resulted in an increased degree of branching during ozonolysis. For example, increasing the percentage of poly(1,3-cyclohexadiene) repeat units from 2 - 10 mol% resulted in an increase in the molecular weight distribution from 1.18 to 3.79 (Figure 10-6). Temperature also affected the controllability of the reaction. The reduced reaction temperatures decreased the solubility of the polymer during the ozonolysis reaction and the polymer precipitated. Typically, if the polymer precipitated during the reaction, then the ozonolyzed product remained insoluble after the 1,2,4-trioxolane species was reduced. This was attributed to a branching reaction that was believed to occur in the precipitated polymer, which further reduced its solubility and ultimately resulted in an intractable, crosslinked material.

10.5 Conclusions

The ozonolysis of poly(1,3-cyclohexadiene) containing polymers was explored. Homopolymers of poly(1,3-cyclohexadiene) were determined to be too reactive towards ozone and significant branching was shown to occur. Decreased polymer concentrations reduced the degree of branching, but, these polymers still exhibited poor solubility. A series of poly(1,3-cyclohexadiene-*alt*-styrene)-*block*-polystyrene copolymers were synthesized to reduce the concentration of poly(1,3-cyclohexadiene) repeat units in the polymer backbone. Ozonolysis of these block copolymers exhibited improved reaction controllability as demonstrated by the increased polymer solubility and decreased molecular weight distribution. The presence of an aldehyde functionality was demonstrated by ^1H and ^{13}C NMR spectroscopy, and FTIR. These polymers exhibited near quantitative conversion of the double bonds to an aldehyde functional group.

Table 10-3. Characterization of ozonolyzed poly(1,3-cyclohexadiene) containing block copolymers.

Solvent	Poly(1,3-cyclohexadiene) content (mol %)	Ozonolysis Temperature (°C)	$\langle M_n \rangle^*$	$\langle M_w \rangle / \langle M_n \rangle$
dichlorobenzene	2	15	14200	1.18
CH ₂ Cl ₂	2	-78	ND	ND
CH ₂ Cl ₂	2	15	13100	1.19
dichlorobenzene	6	15	13500	2.20
CH ₂ Cl ₂	10	-78	ND	ND
dichlorobenzene	10	15	38000	3.79

* GPC conditions: Chloroform, 40°C, MALLS. ND = not determined due to polymer insolubility.

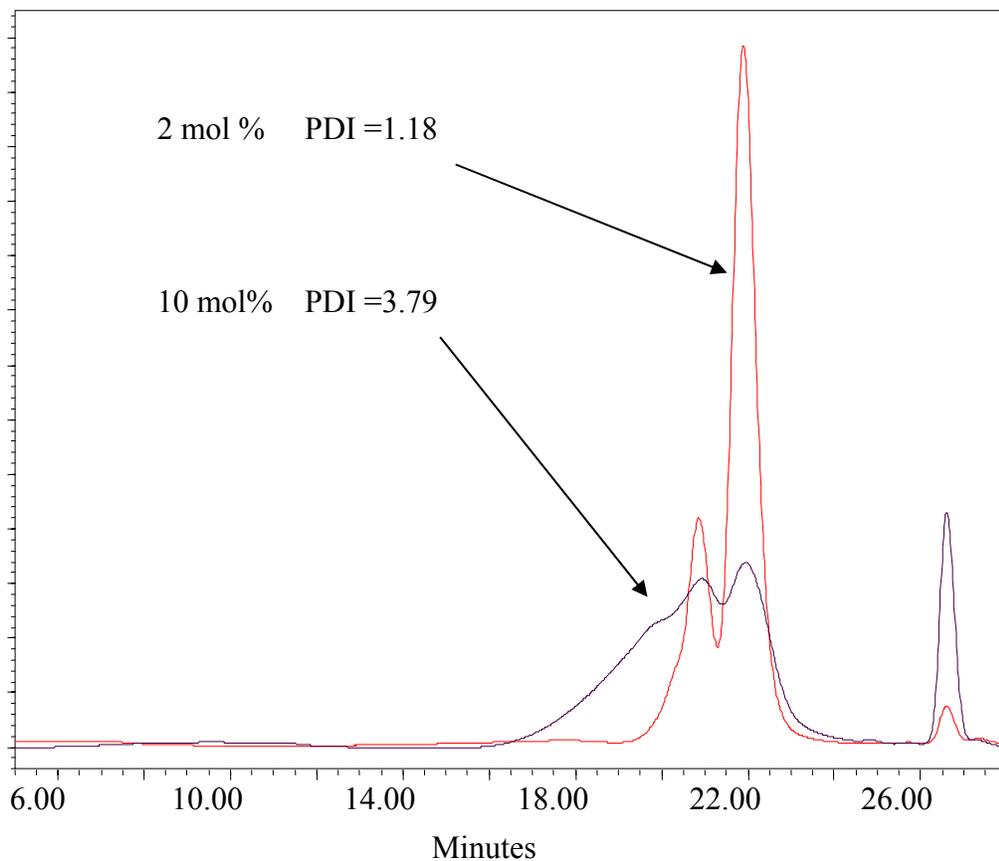


Figure 10-6. GPC analysis of the polymers after ozonolysis for poly(1,3-cyclohexadiene) containing block copolymers with 2 and 10 mol% of poly(1,3-cyclohexadiene).

CHAPTER 11

Synthesis of Glucose Containing Acrylate Copolymers

11.1 Abstract

The synthesis of glucose containing polymers was explored using a recently developed glycosylation technique using a boron trifluoride transesterification catalyst. β -D-glucose pentaacetate was shown to be more a more efficient glycosylating agent than the α -D-glucose pentaacetate. These results were utilized to synthesize 2-(3,4,5,6-tetraacetoxy- β -D-glucopyranose)-ethyl acrylate, which was subsequently copolymerized with methyl acrylate. These polymers exhibited modest molecular weights (5000 – 7000 g/mol) with a molecular weight distribution of 1.50-2.00. The acetyl protecting groups were removed in the absence of methanolysis to synthesize poly(methyl acrylate-*co*-2-(glucose)-ethyl acrylate). The introduction of the hydrogen bonding functionality on the glucose containing repeat unit was shown to increase the glass transition temperature and also induce the polymer chains to associate in chloroform.

11.2 Introduction

Polymers containing mono or disaccharide moieties have recently received significant attention due to the vast array of potential applications for these macromolecules. These applications are derived from the unique properties imbued by saccharides, such as water solubility, biodegradability, hydrophilicity, antigenic activity, and pharmacological activity.⁴⁵⁹ The numerous potential uses for these saccharide containing polymers in combination with the commercial availability of a broad range of saccharides renders these polymer systems as highly attractive research candidates. A limiting factor for a number of these systems is the polyfunctionality of the saccharide, which can complicate the synthesis of monomers bearing a vinyl functionality.⁴⁶⁰

The synthesis of saccharide functionalized monomers often times involves complex multistep synthetic approaches, which deleteriously impacts the atom economy of saccharide containing monomers. The hydroxyl functionality was typically protected using isopropylidene groups, which can be attached via a condensation reaction with acetone in the presence of either a Lewis or Bronsted acid.⁴⁶¹ This approach allows for all of the hydroxyl groups to be protected, except for one. Protection of the hydroxyl functionality was performed to mask its activity, thereby improving the efficiency of the subsequent attachment of a polymerizable group, such as a vinyl moiety. The presence of a single remaining hydroxyl group decreased the complexity of the vinyl group attachment step. Other strategies included the use of acetyl groups, however, this strategy required the use of a 1-halogeno sugar. The halogen was then targeted for the attachment of the polymerizable functionality. A number of different approaches were employed in the attachment of the polymerizable group, which differ primarily in the

⁴⁵⁹ Wulff, G., J. Schmid, and T. Venhoff. "The synthesis of polymerizable vinyl sugars." *Macromol. Chem. Phys.* **1996**, 197, 259.

⁴⁶⁰ Wulff, G., J. Schmid, and T. Venhoff. "The preparation of new types of polymerizable sugars with C-C bonds between sugar and double bond." *Macromol. Chem. Phys.* **1996**, 197, 1285.

⁴⁶¹ Forsyth, S.A., D.R. MacFarlane, R.J. Thomson, and M. Itzstein. "Rapid, Clean, and Mild O-acetylation of alcohols and carbohydrates in an ionic liquid." *Chem. Comm.* **2002**, 714.

functional group used to attach the saccharide to the polymerizable functionality. Ester, ethers, amides, glycosidic bonds, and carbon-carbon bonds have all been explored as possible saccharide-monomer linkages. Each of these approaches presents both advantages and disadvantages in the ease of synthesis and end-use stability of the linkage.⁴⁶² Esters and glycosidic linkages are among the easiest to form but these groups were shown to suffer from hydrolytic instability. Since removal of the hydroxyl protecting groups is typically performed under hydrolytic conditions, careful consideration must be given to the stability of both the ester and glycosidic linkages.⁴⁶³ However, the slow hydrolysis of these linkages provides an avenue for controlled drug delivery applications that is based on the slow release of a saccharide prodrug conjugate.⁴⁶⁴ Ethers and amides were shown to exhibit greater resistance to hydrolysis, but did degrade over time. In contrast, carbon-carbon bonds exhibited excellent stability in a wide range of conditions, but were the most difficult linkages to form. Normally carbon-carbon bond forming strategies employed Grignard reagents.

Recent advances in the glycosidation of alcohols using high yield inexpensive processes have increased the attractiveness of saccharide containing polymers. Although extensive research efforts focused on the chemistry of mono and disaccharides has been performed, these processes were typically limited by their rigorous purification protocols, poor atom efficiency, and poor stereoselectivity. In addition, with the exception of 1,2:5,6-di-O-isopropylidene-glucofuranose, the synthesis of the necessary protected glycosyl donor was hampered by poor yields.⁴⁶⁵ Recently, studies examining the stereoselective α -glycosidation using Lewis acid catalysis has

⁴⁶² Wulff, G., J. Schmid, and T. Venhoff. "The synthesis of polymerizable vinyl sugars." *Macromol. Chem. Phys.* **1996**, 197, 259.

⁴⁶³ Wulff, G., J. Schmid, and T. Venhoff. "The preparation of new types of polymerizable sugars with C-C bonds between sugar and double bond." *Macromol. Chem. Phys.* **1996**, 197, 1285.

⁴⁶⁴ Ouchi, T., F. Hirotoishi, S. Jokei, H. Chikashita, I. Hidenori, and O. Vogl. "Synthesis of acryloyl-type polymer fixing 5-fluorouracil residues through D-glucofuranoses and its antitumor." *J. Polym. Sci. Part A.* **1986**, 24, 2059.

⁴⁶⁵ Chatterjee, S.K., and P. Nuhn. "Stereoselective alpha-glycosylation using FeCl₃ as a Lewis acid catalyst." *Chem. Comm.* **1998**, 1729.

yielded improved stereoselective glycosidation reaction conditions.⁴⁶⁶ Furthermore, these reactions used β -D-Glucose pentaacetate as the glycosyl donor. β -D-Glucose pentaacetate exhibits excellent solubility in a range of solvents, it is inexpensive to synthesize, and the acetyl protecting groups are readily removed using a basic methanol solution. The Lewis acids used in the reactions were FeCl_3 and BF_3 . These reactions exhibited excellent yields (95-68%) and were performed with retention of stereochemical selectivity. For FeCl_3 , the anomeric ratio of the products (α/β) was typically in the range of 100:0 to 90:10. Although the mechanism has not been fully examined, the proposed mechanism involves the anchimeric assistance of the O-acetyl group at the C_2 position of the pyranose ring of glucose.⁴⁶⁷ In contrast, BF_3 catalyzed reactions typically result in the α anomer. As in the FeCl_3 catalyzed reactions, the mechanism for BF_3 has not been fully elucidated, but is believed to involve the complexation of BF_3 with the pyranose ring.⁴⁶⁸ These stereochemically selective glycosidation reactions of peracetylated saccharides provide an avenue to synthesize saccharide containing polymers that are enriched in either the α or β anomer.

Glucose containing polymers have been prepared using a variety of polymerization strategies. Free radical polymerizations were most commonly employed, likely due to the reduced stringency of the polymerization conditions. While free radical polymerizations are sensitive to oxygen and chain transfer events, the reaction conditions are not as stringent as needed for a successful ionic polymerization.⁴⁶⁹ In spite of the experimental difficulties, both cationic and anionic polymerization methods were used in combination with protected saccharide containing

⁴⁶⁶ Doren, H., R. Geest, F. Bolhuis, R.M. Kellog, and H. Wynberg. "The Crystal Structure of Heptyl 1-Thio- α -D-Glucopyranoside. A Member of a New Homologous Series of Mesogenic Carbohydrate Derivatives." *Carbohydr. Res.* **1989**, 194, 79.

⁴⁶⁷ Chatterjee, S.K., and P. Nuhn. "Stereoselective α -glycosylation using FeCl_3 as a Lewis acid catalyst." *Chem. Comm.* **1998**, 1729.

⁴⁶⁸ Doren, H., E. Smits, J.B.F.N. Engberts, and R.M. Kellog. "Mesogenic sugars. From aldoses to liquid crystals and surfactants." *Chem. Soc. Rev.* **2000**, 29, 183.

⁴⁶⁹ Odian, George. *Principles of Polymerization* John Wiley and Sons Inc: New York, 1991.

monomers to synthesize saccharide containing polymers.⁴⁷⁰ The major applications for glucose containing polymers have been in the synthesis of hydrogels, and bioactive polymers. Schaeffer et al. explored the synthesis of hydrogels using a 3-acryloyl-1,2:5,6-di-O-isopropylidene- α -D-glucofuranose monomer copolymerized with hydroxyethyl acrylate.⁴⁷¹ These hydrogels were explored for potential contact lens applications. Polymers containing 4-[N-[2-(2-acetylamino-2-deoxy-3-O-D-glucofuranosyl)propionyl]-L-alanyl-amino] glutamic ester were synthesized in the attempt to instill immunological activity towards a bacterial cell wall in the polymer.⁴⁷² Similar efforts by Nakaya et al. focused on the synthesis of polymeric glycolipid analogs based on the polymerization of (glucofuranosyloxy) alkyl methacrylates with varying alkyl chain lengths. In both of these studies the polymers intended biological activity was derived from the interaction of the polymer bound bioactive sugar moieties with the biological entity. In contrast, Ouchi et al. explored the controlled, hydrolytic, release of 5-fluorouracil from the polymeric carrier. These polymers exhibited antitumor activity when 3-[5-fluorouracilyl)propionic acid was hydrolyzed from the glucofuranose carrier that was attached to the polymer backbone. The use of ionic polymerization techniques for the preparation of saccharide containing polymers has been limited. However, Hirao has explored the anionic polymerization of functionalized styrenic monomers, and functionalized diphenylethylene monomers.⁴⁷³

⁴⁷⁰ Wulff, G., J. Schmid, and T. Venhoff. "The synthesis of polymerizable vinyl sugars." *Macromol. Chem. Phys.* **1996**, 197, 259.

⁴⁷¹ Kossmehl, G., J. Volkheimer, and H. Schaefer. "Hydrogels based on -acryloyl-1,2:5,6-di-O-isopropylidene- α -D-glucofuranose." *Angew. Makromol. Chem.* **1995**, 228, 59.

⁴⁷² Ouchi, T., Y. Sakamoto, S. Jokei, and H. Chikashita. "Synthesis of an acryloyl-type polymer with pendant D-glucose analog of N-acetylmuramyl-L-Alanyl-D-isoglutamine." *Macromol. Chem.* **1984**, 185, 255.

⁴⁷³ Loykulant, S., and A. Hirao. "Protection and Polymerization of Functional Monomers. 30. Anionic Living Anionic Polymerization of 4-alkylstyrenes Containing Acetal-Protected Monosaccharide Residues." *Macromolecules* **2000**, 33, 4757. Loykulant, S., M. Hayashi, and A. Hirao. "Protection and Polymerization of Functional Monomers. 28. Anionic Living Polymerization of Styrene Derivatives Containing Acetal-Protected Monosaccharide Residues." *Macromolecules* **1998**, 31, 9121. Hayashi, M., S. Loykulant, A. Hirao, and S. Nakahama. "Synthesis of End-Functionalized Polymers by Means of Living Anionic Polymerization. 9. Synthesis of Well-defined End-Functionalized Polymers with One, Two, Three, or Four Monosaccharide Residues." *Macromolecules* **1998**, 31, 2057. Loykulant, S., and A. Hirao. "Living Anionic Polymerization of Styrene Derivatives m,m'-Disaccharide with Acetal-Protected Monosaccharide Residues." *Macromol. Chem. Phys.* **2001**, 202, 1791.

These studies explored the synthesis of both linear and well-defined branched copolymers. A different approach to the synthesis of anionically prepared monomers with saccharides was employed by Bosker et al. In these studies, an amino functionalized polystyrene macromolecule was end functionalized with Passelli type maltodextrins via sodium cyanoborohydride.⁴⁷⁴

In this study, the efficacy of FeCl₃ and BF₃ catalysts for the synthesis of saccharide containing polymers were examined. The synthesis of saccharide containing acrylate monomers was performed using glucose pentaacetate. These monomers were subsequently copolymerized with methyl acrylate and the molecular weight of the copolymers was explored. Finally, the thermal properties of these copolymers were explored.

11.3 Experimental Section

Materials. Iron (III) Chloride was purchased from Aldrich at two different degrees of purity (99% and 99.99%) and used as received. Boron trifluoride diethyl etherate (Aldrich) was used as received. β -D-Glucose pentaacetate (Aldrich, 98%) and α -D-Glucose pentaacetate were used as received. Dichloromethane (Burdick Jackson, 99%) and chloroform (Burdick Jackson, 99%) were dried over calcium hydride and distilled under reduced pressure (0.13-0.16 mm Hg, 10 °C). Tetrahydrofuran (Burdick Jackson, HPLC Grade) was dried over sodium/benzophenone and distilled under nitrogen. Hydroxyethyl acrylate (Aldrich, 99%) and methyl acrylate (Aldrich, 99%) were passed through a column of activated alumina (Aldrich, Brockman Type 1) to remove the inhibitor and stored under nitrogen at -20 °C. 2,2'-Azobisisobutyronitrile (Aldrich, 98%) was used as received. All reagents were transferred using syringe and cannula techniques under ultrapure (99.999%) nitrogen.

⁴⁷⁴ Bosker, W.T.E., K. Agosten, M.A. Cohen Stuart, W. Norde, J.W. Timmermans, and T.M. Slaghek. "Synthesis and Interfacial Behavior of Polystyrene-Polysaccharide Block Copolymers." *Macromolecules* **2003**, 36, 1982.

General procedure for the synthesis of 2-(3,4,5,6-tetraacetoxy - β -D-glucopyranose)-ethyl acrylate (TAGA). β -D-Glucose pentaacetate (23.4 g, 60 mmol) was dissolved in chloroform (100 mL) in a clean dried round-bottomed flask. The flask was sealed with a septum and purged with nitrogen. Hydroxyethyl acrylate (8.96 g, 9.08 mL, 80 mmol) was charged to the flask via a syringe. Boron trifluoride diethyl etherate (28 mL, 100 mmol) was added. The reaction was allowed to proceed for 20 min. The reaction was quenched with an aqueous 1 molar sodium bicarbonate solution. The chloroform layer was washed with aqueous HCl (1 M), H₂O, and brine. The chloroform layer was then dried with anhydrous calcium carbonate. The solvent was removed under reduced pressure. ¹H NMR (CDCl₃) δ 6.38-6.48 (m, 1H, =CH), 6.06-6.18 (m, 1H, =CH), 5.85-5.94 (m, 1H, =CH), 5.75 (d, 1H, =CH), 4.95-5.22 (m, 3H, -CH-), 4.57 (d, 1H, -CH-), 4.20-4.40 (m, 2H, -CH₂-), 4.0-4.18 (m, 2H, -CH₂-), 3.83-3.86 (t, 2H, -CH₂-), 1.98-2.10 (m, 12H, -CH₃).

General procedure for the synthesis of acetic acid 3,5-diacetoxy-2-acetoxymethyl-6-dodecyloxy -tetrahydro-pyran-4-yl ester. Dodecanol (1.86 g, 2.2 mL, 10 mmol) and β -D-Glucose pentaacetate (3.9g, 10 mmol) was dissolved in chloroform (50 mL). The reaction was septum sealed and purged with nitrogen. A Lewis acid, such as boron trifluoride diethyl etherate (14 mL, 50 mmol), was added and the reaction was allowed to proceed for 20 min. The reaction was quenched with an aqueous 1 molar sodium bicarbonate solution. The chloroform layer was washed with aqueous HCl (1 M), H₂O, and brine. The chloroform layer was then dried with anhydrous calcium carbonate. The solvent was removed under reduced pressure. ¹H NMR δ 5.02-5.22 (m, 3H, =CH), 4.48 (d, 1H, =CH), 4.22 (m, 1H, =CH₂), 4.05 (m, 2H, -CH₂-), 3.83 (t, 1H, -CH₂-). 1.98-2.10 (m, 12H, -CH₃), 1.47-1.6 (dd, 2H, -CH₂-), 1.2-1.38 (m, 18H, -CH₂-), 0.92 (d, 3H, -CH₃).

Synthesis of poly(methyl acrylate-co-TAGA). TAGA (0.80g, 1.85 mmol) and AIBN (8 mg, 0.05 mmol) was dissolved in THF (50 mL) and added to a clean dried round-bottomed flask. The solution was degassed with nitrogen for 10 min. Methyl acrylate

(7.94 g, 92 mmol) was charged to the reaction solution. The reaction was heated to 65 °C for 16 h. The polymerization was precipitated into a methanol/H₂O (50:50) solution.

Removal of the acetate protecting groups from poly(methyl acrylate-*co*-TAGA). A poly(methyl acrylate-*co*-TAGA) copolymer (3g) was dissolved in a solution of chloroform/methanol (6:1, 30 mL). Potassium carbonate (1g, 9.434 mmol) was added to the solution and the reaction was heated to 45 °C allowed to proceed for 2 h. The solution was washed with H₂O (50 mL, 2X) and brine (50 mL). The solvent was removed in vacuo and the polymer was dried at 50 °C at reduced pressure (0.13-0.16 mmHg).

Polymer Characterization. ¹H NMR spectra were determined in CDCl₃ at 400 MHz with a Varian Spectrometer. Glass transition temperatures were determined using a Perkin-Elmer Pyris 1 DSC at a heating rate of 10 °C/min under nitrogen. Glass transition temperatures are reported as the midpoint of the change in heat capacity during the second heat. Molecular weights were determined using size exclusion chromatography (SEC) with a Waters Alliance SEC system equipped with a Viscotek 150R viscosity detector. SEC measurements were performed at 25 °C in chloroform at a flow rate of 1.0 mL/min. The determination of molecular weights using universal calibration based on polystyrene standards is well established.⁴⁷⁵ In addition, a Waters 717plus equipped with a Waters 2410 refractive index detector and a Wyatt Technology Minidawn MALLS detector was utilized for absolute molecular weight measurements. The dn/dc values were determined on-line using the calibration constant for the RI detector and the mass of the polymer sample. SEC measurements were performed at 40 °C in chloroform at a flow rate of 1.0 mL/min. For all samples, it was assumed that 100% of the polymer eluted from the column during the measurement.

⁴⁷⁵ Yau, W.W., and S.W. Rementer. "Polymer Characterization by SEC-Viscometry: Molecular Weight, Size, and Intrinsic Viscosity Distribution." *J. Chromatogr.* **1990**, 13, 627.

11.4 Results and Discussion

Previous studies have examined the ability of Lewis acids to mediate glycosylation reactions, wherein they have suggested the presence of possible side reactions and the effect of alcohol selection on the reaction efficiency. Therefore, our initial studies examined the glycosylation of an alcohol using a Lewis acid, such as boron trifluoride or ferric chloride. Two ferric chloride grades were examined in this study (99% and 99.99%) for their ability to couple α -D-Glucose pentaacetate with methanol. The results for these coupling studies are shown in Table 11-1. These results represent the average of at least two experiments. The coupling efficiency was determined gravimetrically. When the 99% ferric chloride was used, no coupling was observed. In contrast, limited glycosylation (18%) was observed when the 99.99% ferric chloride was used. Boron trifluoride diethyl etherate was also explored for its efficacy in the glycosylation reaction. Improved glycosylation yields were obtained with boron trifluoride, however, these reactions typically required extended reaction times (80 h). In order to explore the role of stereochemistry on the glycosylation reaction, the glycosylation of methanol with β -D-Glucose pentaacetate was also explored. These reactions were typically exhibited high yields (80-90%) in 30 minutes or less. The difference in the reactivity between the alpha and beta anomers was attributed to the complexation of the boron trifluoride with glucose pentaacetate (Figure 11-1). Previous studies suggested that the boron trifluoride complexed with the oxygen in the ring preventing the methanol nucleophile from attacking from the top of the ring. In the alpha form, the methanol nucleophile is also unable to attack from below due to the axial acetyl group at the 1 position. However, this group is equatorial in the beta form and the methanol is free to attack axially, which after a proton transfer event, results in the formation of methanol and acetic acid.

After completion of the glycosylation reaction, the remaining esters present in glucose pentaacetate are viable candidates for subsequent transesterification reactions. Previous studies described decreased yields in glycosylation reactions using Lewis acids, which was attributed to side reactions that occur after completion of glycosylation

Table 11-1. Effect of Lewis acids on the Glycosylation of Methanol using D-Glucose pentaacetate.

Alcohol	Anomer used	Lewis acid	Ratio of Reagents Alcohol:GPA:Lewis acid	Time (h)	Coupling Efficiency
Methanol	α	FeCl ₃ (99%)	1:1:1	16	ND
Methanol	α	FeCl ₃ (99%+)	1:1:1	16	ND
Methanol	α	FeCl ₃ (99.99%)	1:1:1	16	18%
Methanol	α	BF ₃ Et ₂ O	1:1:1	16	8%
Methanol	α	BF ₃ Et ₂ O	1:1:1	80	63%
Methanol	β	BF ₃ Et ₂ O	1:1:1	0.33	90%
Methanol	β	BF ₃ Et ₂ O	1:1:1	0.5	86%

ND= Not Detected

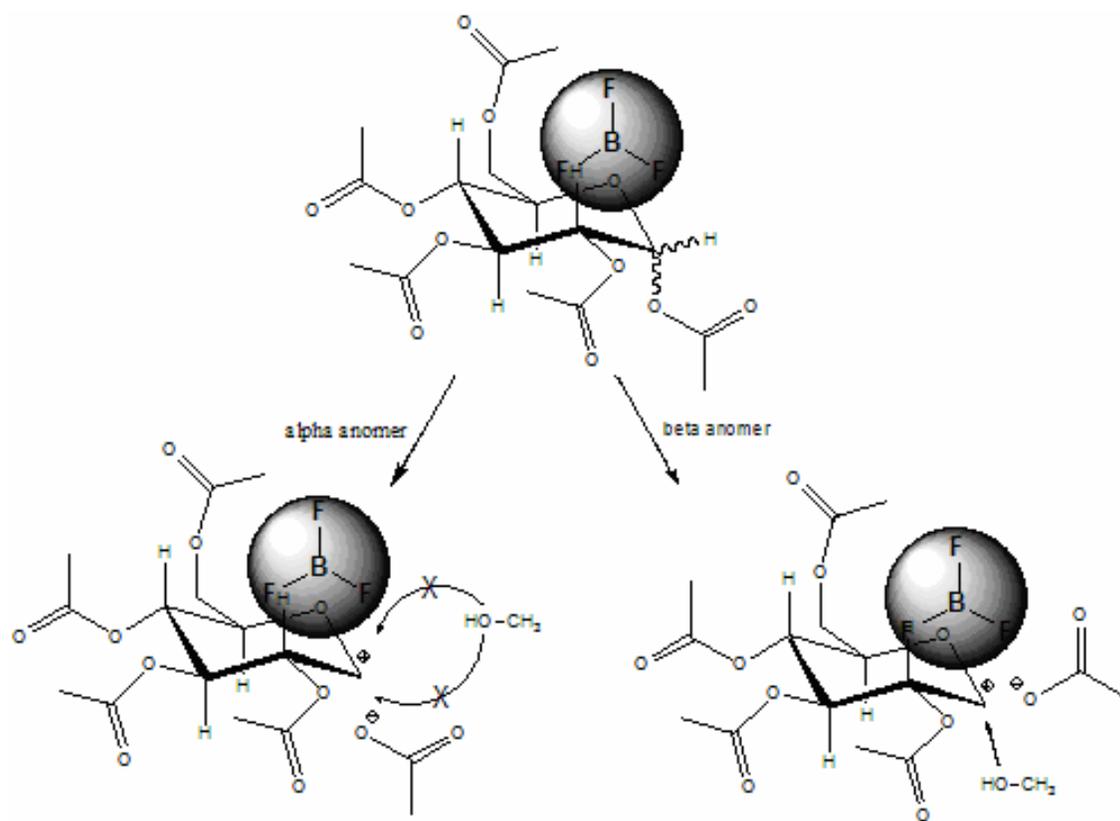


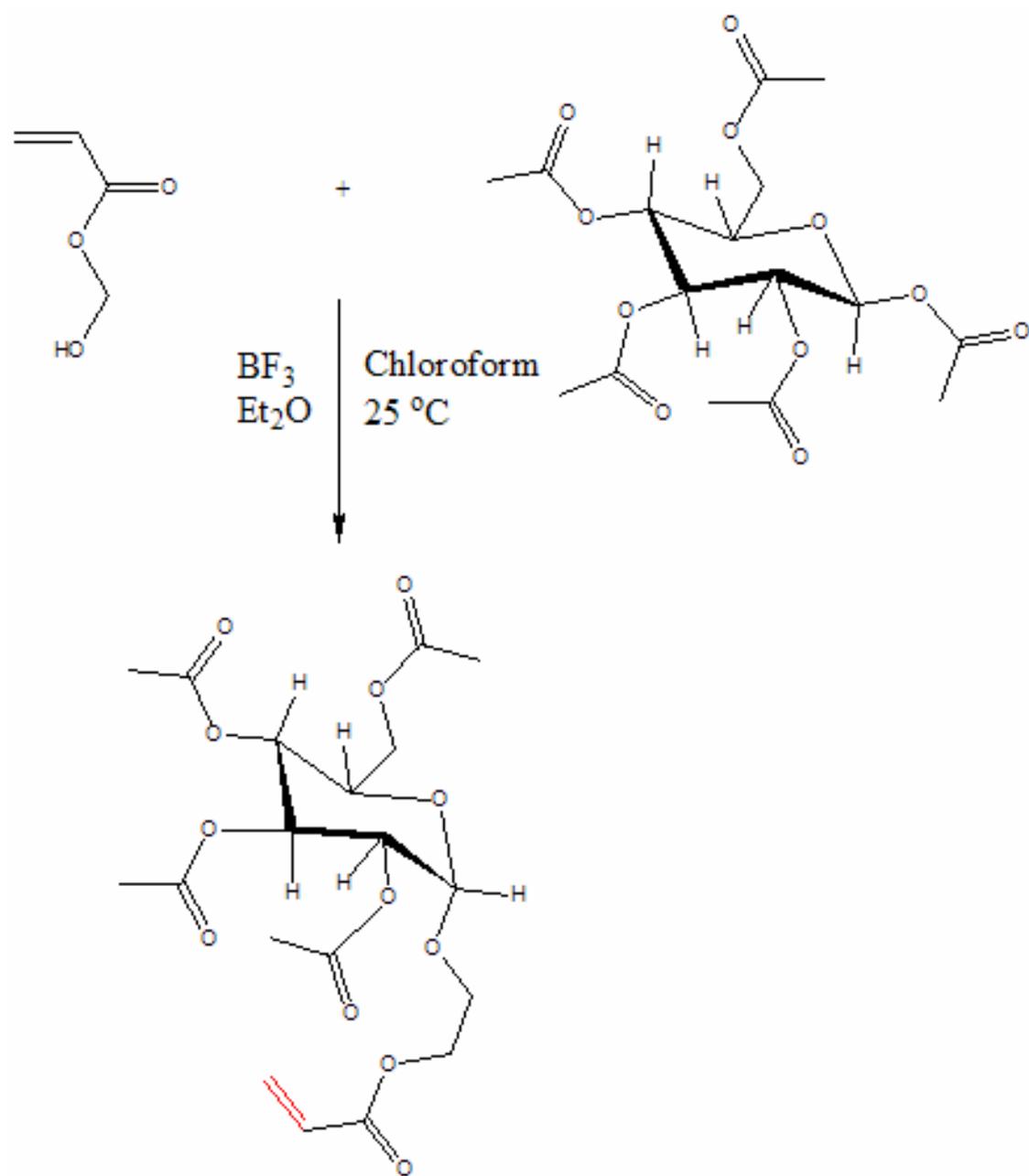
Figure 11-1. Depiction of the role of BF_3 in the reduced reactivity of α -D-glucose pentaacetate with primary alcohols.

reaction.⁴⁷⁶ To determine if transesterification occurred after the glycosidation reaction, a glycosidation reaction was performed using boron trifluoride, eicosanol, and β -D-glucose pentaacetate. Eicosanol was utilized in these experiments due to the ease of isolation of the transesterified product, icosyl acetate. The reaction was allowed to proceed for 6 hours. The transesterified product, icosyl acetate, was isolated using column chromatography. No other major side products were isolated. In light of these results, all subsequent glycosidation reactions were performed for 25 minutes using boron trifluoride, β -D-Glucose pentaacetate, and a primary alcohol.

In order to synthesize a series of polymers containing the protected glucose functionality, hydroxyethyl acrylate was reacted with boron trifluoride diethyl etherate, and β -D-Glucose pentaacetate (Scheme 11-1). No further efforts to purify 2-(3,4,5,6-tetraacetoxy β -D-glucopyranose)-ethyl acrylate (TAGA), were performed. The purity of the TAGA monomer was determined using ^1H NMR spectroscopy and these reactions typically exhibited good yields (70-80%). A series of poly(methyl acrylate-*co*-TAGA) copolymers were synthesized. The composition of the copolymers was determined using ^1H NMR spectroscopy (Figure 11-2). These polymers typically exhibited low molecular weights (5040-7660) with molecular weight distributions expected for a free radical polymerization (1.51-2.02) (Table 11-2). The composition of the copolymers agreed well with the composition of the monomer feed. In spite of the presence of numerous potential chain transfer sites on the TAGA comonomer, the polymers did not exhibit broad molecular weight distributions.

A variety of deprotection strategies were examined in the attempt to remove the acetyl protecting groups. Acidic deprotection strategies only partially deprotected the pendant glucose group. In contrast, basic deprotection strategies that used a chloroform/methanol (6:1) with potassium carbonate resulted in a rapid, quantitative deprotection. These reactions were quantitative in less than 12 hours and ^1H NMR

⁴⁷⁶ Doren, H., R. Geest, R.M. Kellog, and H. Wynberg. "Synthesis and Liquid Crystalline Properties of the n-alkyl 1-thio- α -D-glucopyranosides, A New Homologous Series of Carbohydrate Mesogens." *Carbohydr. Res.* **1989**, 194, 71.



Scheme 11-1. Synthetic strategy utilized in the synthesis of TAGA.

Table 11-2. Molecular Weight Characterization of Poly(methyl acrylate-co-TAGA) Copolymers.

Methyl Acrylate wt%	TAGA wt%	TAGA mol%* (calc %)	$\langle M_n \rangle$	$\langle M_w \rangle / \langle M_n \rangle$
100	0	0 (0)	6330	1.61
96	4	0.8 (0.6)	5280	1.51
92	8	1.6 (1.5)	5040	2.02
80	20	2.8 (2.4)	7660	1.70

GPC Conditions: CHCl₃, 40 °C, MALLS

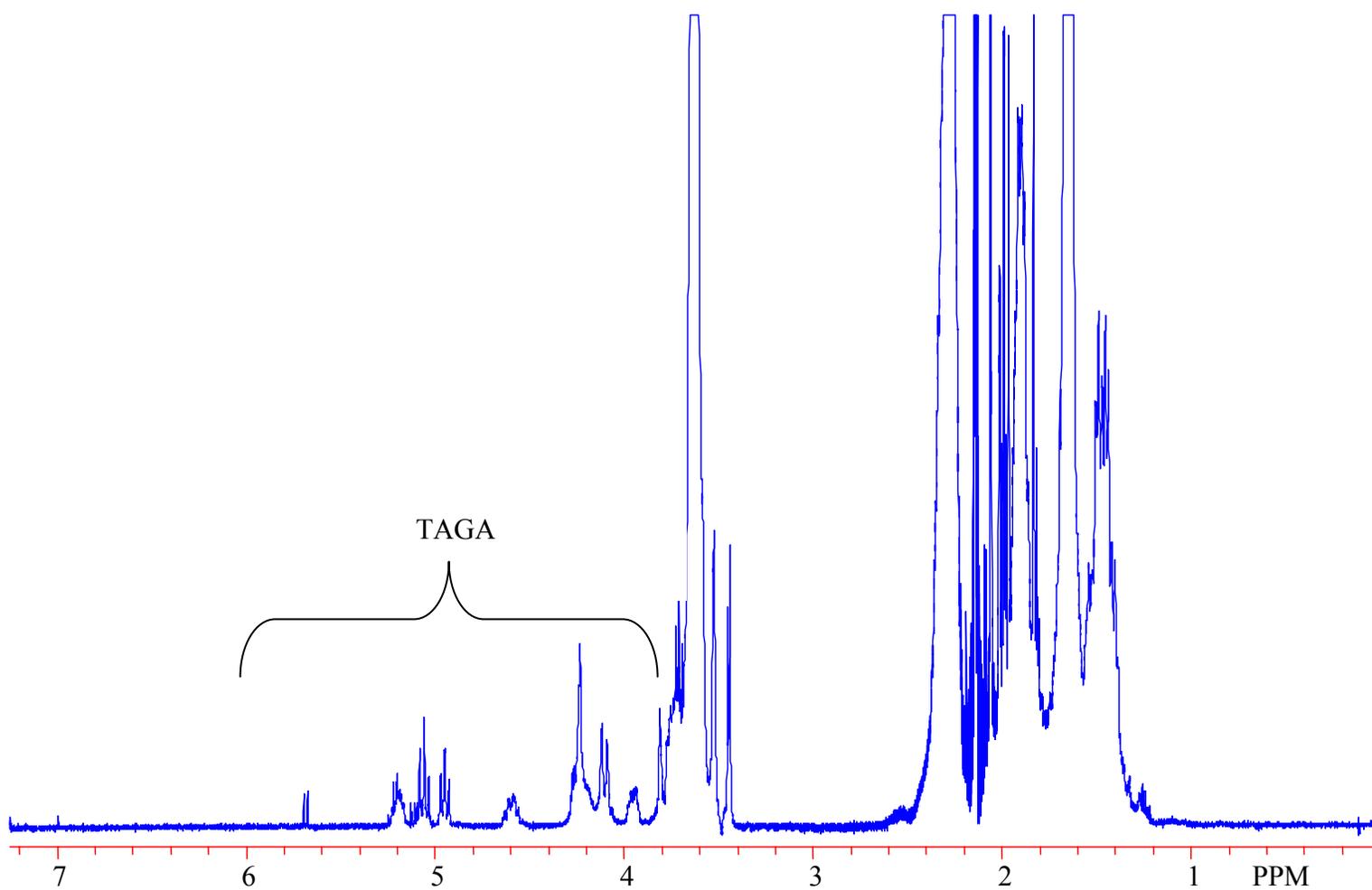


Figure 11-2. ^1H NMR spectrum of poly(methyl acrylate-*co*-TAGA). NMR Conditions : CDCl_3 , 25 °C

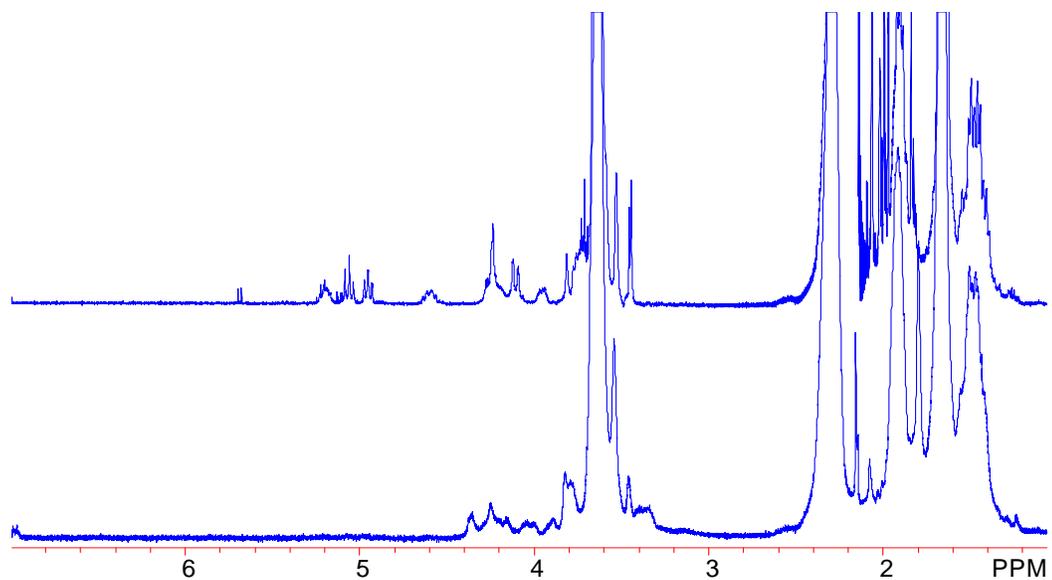


Figure 11-3. ¹H NMR spectrum of poly(methyl acrylate-co-TAGA) (top spectrum) and poly(methyl acrylate-co-2-(glucose)-ethyl acrylate) (bottom spectrum). NMR Conditions : CDCl₃, 25 °C

spectroscopic characterization of the polymers did not indicate any significant reaction of the methyl ester functionality on the poly(methyl acrylate) repeat unit (Figure 11-3). The resonances associated with poly(2-(glucose)-ethyl acrylate) repeat unit shifted upfield, which is in agreement with previous studies.⁴⁷⁷ The poly(methyl acrylate) homopolymer control was not affected by the deprotection conditions, however, the copolymers that contained the poly(TAGA) repeat unit exhibited increased molecular weights with decreased molecular weight distributions (Table 11-3). The increase in molecular weight was attributed to the introduction of the hydrogen bonding functionality on the glucose repeat unit, which induced polymer chain associations between polymer chains in chloroform.

The thermal properties of these polymers were characterized using DSC. As expected, the poly(methyl acrylate-*co*-TAGA) copolymers exhibited a glass transition temperature between 8 °C and -25°C. The glass transition temperature for poly(methyl acrylate) was previously reported as 9 °C, however, this value was for high molecular weight polymers. The poly(methyl acrylate) homopolymers reported in this study were below the critical molecular weight, therefore the glass transition temperature was expected to be strongly dependent on molecular weight. In a similar fashion, the glass transition temperature for the poly(methyl acrylate-*co*-2-(glucose)-ethyl acrylate) copolymers was determined. These polymers exhibited glass transition temperatures between -8 °C and 25 °C. Poly(methyl acrylate) composition was plotted against the glass transition temperature for both the poly(methyl acrylate-*co*-TAGA) and poly(methyl acrylate-*co*-2-(glucose)-ethyl acrylate) copolymers (Figure 11-4). The increase in glass transition temperature was attributed to the introduction of the hydrogen bonding functionality on the glucose repeat unit.

⁴⁷⁷ Hayashi, M., S. Loykulant, A. Hirao, and S. Nakahama. "Synthesis of End-Functionalized Polymers by Means of Living Anionic Polymerization. 9. Synthesis of Well-defined End-Functionalized Polymers with One, Two, Three, or Four Monosaccharide Residues." *Macromolecules* **1998**, 31, 2057. Loykulant, S., M. Hayashi, and A. Hirao. "Protection and Polymerization of Functional Monomers. 28. Anionic Living Polymerization of Styrene Derivatives Containing Acetal-Protected Monosaccharide Residues." *Macromolecules* **1998**, 31, 9121.

Table 11-3. Molecular Weight Characterization of Poly(methyl acrylate-*co*-2-(glucose)-ethyl acrylate) Copolymers.

Composition TAGA %	$\langle M_n \rangle$	$\langle M_w \rangle / \langle M_n \rangle$	$\langle M_n \rangle$	$\langle M_w \rangle / \langle M_n \rangle$
0	6330	1.61	7290	1.29
0.8	5280	1.51	23400	1.56
1.6	5040	2.02	11910	1.22

GPC Conditions: CHCl₃, 40 °C, MALLS

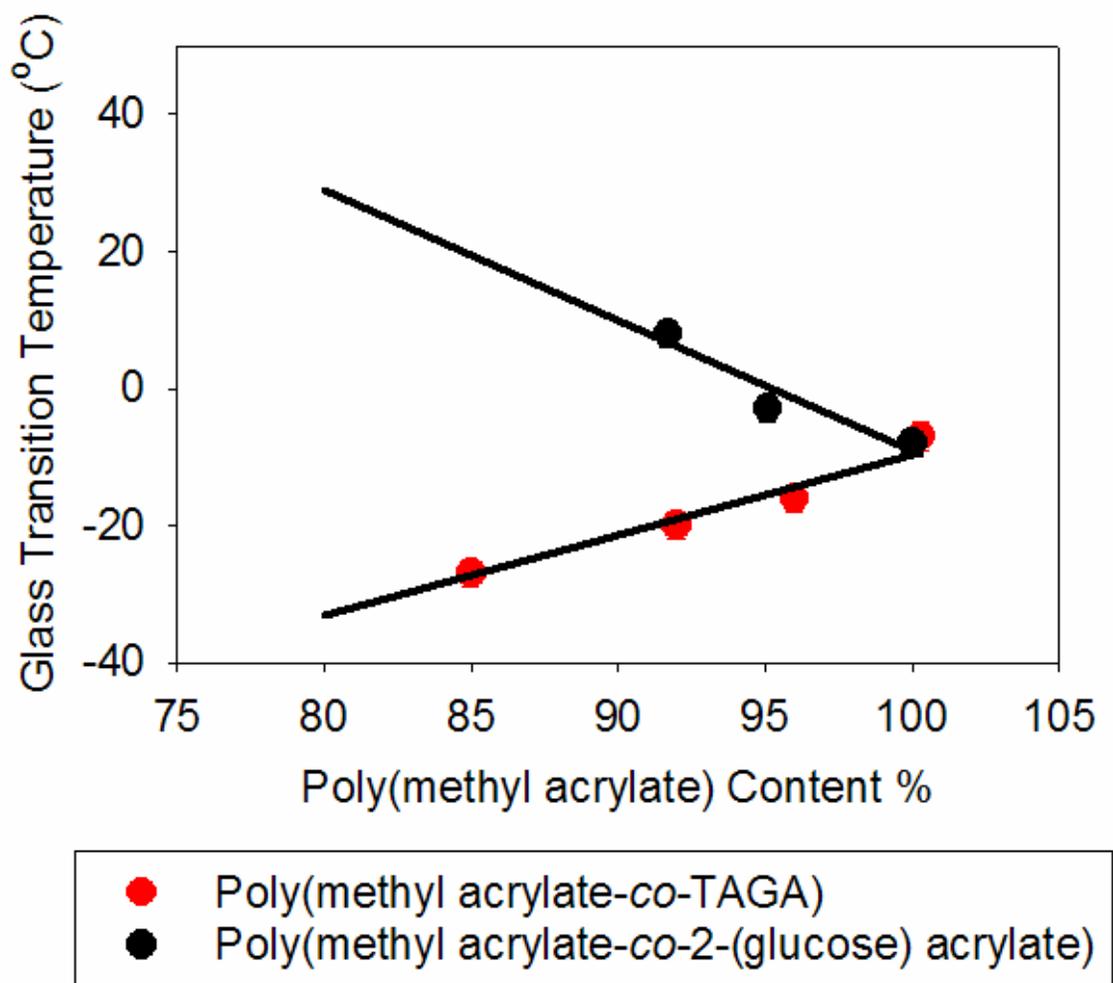


Figure 11-4. Effect of copolymer composition on the glass transition temperature of poly(methyl acrylate-co-TAGA) and poly(methyl acrylate-co-2-(glucose)-ethyl acrylate).

11.5 Conclusions

Boron trifluoride was shown to be effective in the coupling of primary alcohols and glucose acetate. Furthermore, β -D-glucose pentaacetate was shown to be more a more efficient glycosylating agent than the α -D-glucose pentaacetate. This effect was attributed to the ability of the nucleophilic alcohol to attack the anomeric position on the glucose pentaacetate. These results are in agreement with the previously proposed mechanisms for BF_3 catalyzed glycosylation reactions. These results were utilized to synthesize 2-(3,4,5,6-tetraacetoxy- β -D-glucopyranose)-ethyl acrylate, which was subsequently copolymerized with methyl acrylate. The acetyl protecting groups were removed in the absence of methanolysis to synthesize poly(methyl acrylate-*co*-2-(glucose)-ethyl acrylate). The introduction of the hydrogen bonding functionality on the glucose containing repeat unit was shown to increase the glass transition temperature and also induce the polymer chains to associate in chloroform.

Suggested Future Work:

1. Synthesis of higher molecular weight poly(methyl acrylate-*co*-TAGA) copolymers to explore the effect of the glucose functionality on polymers with molecular weights exceeding the critical molecular weight for poly(methyl acrylate).
2. Rheology of the deprotected copolymers to explore the onset of the hydrogen bond dissociation.
3. Synthesis and deprotection of poly(methyl acrylate-*co*-TAGA) copolymers to examine the ability of the pendant glucose functionality to microphase separate from the poly(methyl acrylate) matrix.
4. Synthesis and deprotection of poly(ethyl acrylate-*co*-TAGA) copolymers to examine the effect of hydrogen bonding in the presence of significant polymer chain mobility at room temperature.

CHAPTER 12

Conclusions

The regiochemistry of poly(1,3-cyclohexadiene) was examined through endgroup functionalization with chlorotrimethylsilane and were compared with a more conventional study of the backbone of the polymer chain. A 6000 polymer was determined to contain 70% 1,2-addition and 30% 1,4-addition via the comparison of the olefinic resonances with the allylic resonances. In addition, the regiochemistry of the 6000 trimethylsilyl endcapped chain ends were examined via both ^1H and ^{29}Si NMR spectroscopy. Using endgroup analysis, the homopolymer was found to exhibit 76% 1,2-addition and 24% 1,4-addition. This is the first reported determination of the cis versus trans ratio for the polymerization of 1,3-cyclohexadiene and the first reported use of an endcapping approach to study the regiochemistry of the cyclohexene containing poly(1,3-cyclohexadiene) backbone. The ratio of the cis versus trans was determined upon ^1H NMR examination of the TMS endgroups and found to be 6% trans and 18% cis of the total 24% 1,4-addition. The regiochemistry of the poly(1,3-cyclohexadiene) was also examined using ^{13}C NMR spectroscopy. To identify the resonances present in the ^{13}C NMR spectra, two different polymers containing varying percentages of 1,2 and 1,4-addition were synthesized and characterized. Using the ^1H NMR spectroscopic method, the polymers were shown to contain 90% 1,4 addition for the TMEDA modified polymer and 25% addition for the DABCO modified polymer. Using the ^{13}C NMR spectroscopic method, these were shown to contain 90% 1,4-addition for the TMEDA modified polymer and 10% 1,4-addition for the DABCO modified polymer, respectively. These complimentary methods represent a significant improvement over the previously reported methods used to study the regiochemistry of poly(1,3-cyclohexadiene).

The utility of living anionic polymerization for the synthesis of novel poly(1,3-cyclohexadiene) DVB star-shaped polymers with various arm lengths using various

DVB/nBuLi ratios was also explored. In-situ FTIR spectroscopy was useful for the determination of polymerization kinetics ($k_p = 0.31 \text{ l mol}^{-1} \text{ s}^{-1}$) ensuring complete monomer conversion and optimization of DVB coupling. In-situ spectroscopy and obvious color changes indicated that the addition of DVB to poly(1,3-cyclohexadienyllithium) was rapid. The linking of the arms to the DVB core was improved at lower arm molecular weights of 5000. Although increased molecular weights were achieved as the DVB/nBuLi ratio was increased, it is presumed that the architecture changes from a conventional star at low ratios to a poly(1,3-cyclohexadiene)-coated microgel. The resulting star-shaped polymers were thermally stable to 330 °C in a nitrogen environment and exhibited a T_g value of 150 °C and a refractive index of 1.572 at 600 nm. The size of the DVB core did not affect the glass transition temperature.

Using the polymerization methodology reported by Natori et al.,⁴⁷⁸ the effect of monomer concentration and reaction temperature on the polymer molecular weight and reaction yield was examined. Higher concentrations of monomer resulted in higher molecular weights and increased reaction yields. The presence of deleterious side reactions is believed to be responsible for these effects. These results were utilized to synthesize a series of poly(1,3-cyclohexadiene-*block*-isoprene) diblock copolymers with narrow molecular weight distributions (1.06) and high molecular weights (50000). Phase separation between PCHD blocks and polyisoprene blocks occurred at block sizes in excess of 500. As shown using in situ FTIR spectroscopy, poly(1,3-cyclohexadienyllithium) exhibited an efficient crossover isoprene. A series of star-shaped thermoplastic elastomers were synthesized with the coupling agent divinyl benzene (DVB). High molecular weight (80000 - 100000) star-shaped thermoplastic elastomers with relatively narrow molecular weight distributions (1.28 - 1.36) were synthesized. A range of PCHD content from 16% to 38% was introduced into the thermoplastic elastomers.

⁴⁷⁸ Natori, I. "Synthesis of Polymers with an Alicyclic Structure in the Main Chain. Living Anionic Polymerization of 1,3-Cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System." *Macromolecules* **1997**, 30, 3696.

The synthesis of high molecular weight poly(1,3-cyclohexadiene) homopolymers was demonstrated and an improvement in the synthetic method used by Natori et al.⁴⁷⁹ was developed using a pre-formed TMEDA/nBuLi or DABCO/nBuLi adduct was developed. The use of a pre-formed initiator adduct decreased the number of termination events and eliminated chain transfer events as compared to an in-situ generated initiator system. These polymerizations were determined to be highly sensitive to both reaction temperature and the choice of tertiary diamine. Use of bulky tertiary diamines, such as spartiene or dipip, resulted in poor polymerization control and reduced polymerization rates. Use of a lower polymerization temperature (25 °C) improved molecular weight control and reduced the molecular weight distribution. The polymerizations exhibited improved polymer solubility relative to the in-situ generated initiator.

Using the in-situ generated initiator system, a novel series of poly(1,3-cyclohexadiene-*block*-isoprene) star-shaped elastomers were successfully synthesized using a convergent “arm-first” approach with DVB. These star-shaped elastomers exhibited controlled molecular weights and narrow molecular weight distributions indicative of a controlled living anionic polymerization. As expected, increased ratios of DVB/nBuLi resulted in elevated levels of star-star coupling. The tensile strength, elongation at break, and elastic modulus were dependent on the percentage of poly(1,3-cyclohexadiene) present in the elastomer. Microphase separation of the poly(1,3-cyclohexadiene) and polyisoprene blocks was verified using both DMA and TMAFM analysis. TMAFM was performed and the presence of both poly(1,3-cyclohexadiene) and polyisoprene domains was verified. The domains in the TMAFM image were assigned based on the percent composition of the polymer sample and the relative differences in the viscoelastic response between the poly(1,3-cyclohexadiene) and polyisoprene blocks.

⁴⁷⁹ Natori, I.. "Synthesis of Polymers with an Alicyclic Structure in the Main Chain. Living Anionic Polymerization of 1,3-Cyclohexadiene with the n-butyllithium/N,N,N',N'-Tetramethylethylenediamine System." *Macromolecules* **1997**, 30, 3696.

In situ mid-FTIR was successfully used to determine the reactivity ratios for the anionic copolymerization of 1,3-cyclohexadiene and styrene. The real-time data was readily transformed using the classical Mayo Lewis approach and 1,3-cyclohexadiene and styrene exhibited reactivity ratios of 0.022 and 0.024, respectively. Subsequently, the unique, alternating nature of this anionic copolymerization enabled the synthesis of an interesting family of poly(1,3-cyclohexadiene-*alt*-styrene) containing block copolymers. These copolymers were transformed via both hydrogenation and aromatization to novel poly(cyclohexane-*alt*-styrene) and poly(phenylene-*alt*-styrene) containing block copolymers, respectively. These novel copolymers were characterized thermally and were compared to poly(1,3-cyclohexadiene-*alt*-styrene) block copolymer precursors. The poly(cyclohexane-*alt*-styrene) containing block copolymers were the most thermally stable, while the poly(phenylene-*alt*-styrene) block copolymers were the least thermally stable in both a nitrogen and oxygen environment.

The thermal and oxidative stability of PCHD was investigated using a combination of size exclusion chromatography and thermo-gravimetric analysis. The onset of oxidative degradation of a PCHD solution occurred at approximately 60 °C, and the introduction of aldehyde and ether groups into the polymer occurred at higher temperatures and increased reaction times. At higher temperatures (110 °C), oxidative degradation involved chain scission resulting in increased molecular weight distributions and decreased molecular weights. TGA-MS analysis of the PCHD in a nitrogen environment indicated a two-step chain degradation mechanism, wherein the initial degradation step resulted in the liberation of 1,3-cyclohexadiene through the depolymerization of PCHD. Epoxidation was conducted at 25 °C with MCBPA, in the absence of deleterious polymer degradation. The resulting polymer exhibited excellent molecular weight control and narrow molecular weight distributions. The epoxidation of PCHD improved both the thermal and oxidative stability.

The ozonolysis of poly(1,3-cyclohexadiene) containing polymers was explored. Homopolymers of poly(1,3-cyclohexadiene) were determined to be too reactive towards

ozone and significant branching was shown to occur. Decreased polymer concentrations reduced the degree of branching, but, these polymers still exhibited poor solubility. A series of poly(1,3-cyclohexadiene-*alt*-styrene)-*block*-polystyrene copolymers were synthesized to reduce the concentration of poly(1,3-cyclohexadiene) repeat units in the polymer backbone. Ozonolysis of these block copolymers exhibited improved reaction controllability as demonstrated by the increased polymer solubility and decreased molecular weight distribution. The presence of an aldehyde functionality was demonstrated by ^1H and ^{13}C NMR spectroscopy, and FTIR. These polymers exhibited near quantitative conversion of the double bonds to an aldehyde functional group.

Boron trifluoride was shown to be effective in the coupling of primary alcohols and glucose acetate. Furthermore, β -D-glucose pentaacetate was shown to be more a more efficient glycosylating agent than the α -D-glucose pentaacetate. This effect was attributed to the ability of the nucleophilic alcohol to attack the anomeric position on the glucose pentaacetate. These results are in agreement with the previously proposed mechanisms for BF_3 catalyzed glycosylation reactions. These results were utilized to synthesize 2-(3,4,5,6-tetraacetoxy- β -D-glucopyranose)-ethyl acrylate, which was subsequently copolymerized with methyl acrylate. The acetyl protecting groups were removed in the absence of methanolysis to synthesize poly(methyl acrylate-*co*-2-(glucose)-ethyl acrylate). The introduction of the hydrogen bonding functionality on the glucose containing repeat unit was shown to increase the glass transition temperature and also induce the polymer chains to associate in chloroform.

CHAPTER 13

Suggested Future Work

13.1 Poly(1,3-cyclohexadiene) DVB coupled Star-shaped macromolecules

1. Synthesize a series of poly(1,3-cyclohexadiene) DVB coupled star-shaped macromolecules with different poly(1,3-cyclohexadiene) arm lengths.
 - a. Examine the melt and solution rheology.
 - i. Compare with similar polystyrene based systems.
 - ii. Compare with similar hydrogenated poly(1,3-cyclohexadiene) analogs.
 - b. Examine the polymer as a potential viscosity improver in motor oil.

13.2 Poly(1,3-cyclohexadiene-*block*-isoprene) copolymers

1. Synthesize a series of poly(1,3-cyclohexadiene-*block*-isoprene) copolymers with various compositions and different block molecular weights.
 - a. Utilize melt rheology to determine the order-disorder transition temperature for the various copolymers and then utilize this data to determine the Flory-Huggins interaction parameter (χ).
 - b. Synthesize block copolymers with various poly(1,3-cyclohexadiene) microstructures and compare the rheological properties for these copolymers.

13.3 Poly(1,3-cyclohexadiene) Homopolymers

1. Examine the effect of N,N,N',N'-tetramethyl-cyclohexane-1,2-diamine on the polymerization of 1,3-cyclohexadiene.
2. Synthesize high molecular weight poly(1,3-cyclohexadiene) homopolymers with varying degrees of 1,2 and 1,4-microstructure.
3. Using the procedures developed by Knauss et al. or Hadjichristidis et al. synthesize highly branched poly(1,3-cyclohexadiene) polymers with a range of microstructures.
 - a. Examine the effect of branching in the systems using both melt and solution rheology.
 - b. Examine the role of the microstructure on the ability of these highly branched copolymers to relax in a shear field while in the melt. Compare these results with a more conventional system, such as a highly branched polystyrene system.
4. Introduce a polar functional group into the polymer backbone at a range of levels using epoxidation or hydroboration-oxidation.
 - a. Examine the impact of the polar functional group on the ability to electro-spin these polymers.
 - b. Examine the adhesive properties of these systems.
 - c. Utilize the functional groups to attach a potential self-assembling molecule to the surface.
5. Introduce a sulfonic acid functionality into the polymer repeat unit via sulfonation chemistry
 - a. Explore the utility of these copolymers as a potential fuel cell membrane.

- b. Examine the thermal stability of the sulfonic acid functional group on the cycloaliphatic polymer backbone and compare with the thermal stability of sulfonic acid groups attached to aromatic polymer systems.

Vita

David Thomas Williamson, son of Paul and Janet Williamson, was born on June 21, 1973 in Camp Lejeune, North Carolina. His family traveled often and he spent time growing up in North Carolina, Pennsylvania, Virginia, and in Okinawa, a small island near the country of Japan. He graduated from North Stafford High School in May of 1992. In August of the same year, he started his undergraduate studies at Virginia Polytechnic Institute and State University. In 1993, he joined the U.S. Navy as a machinist mate in the nuclear power program. After finishing his training, he was selected to remain on as an assistant instructor teaching engineering mathematics. From 1995-1997, he attended Virginia Commonwealth University where he completed his B.S. degree in chemistry with a minor in Biology. From 1997 to 1999, he remained at Virginia Commonwealth University to perform research in the Microbiology Immunology Department and the Chemistry Department. In August of 1999, he joined the chemistry department at Virginia Polytechnic Institute and State University to pursue a PhD in Chemistry with Professor Tim Long. Upon completion of his PhD degree in August of 2003, he will join Dupont at the Experimental Station in Wilmington Delaware as a Research Chemist in the Chemical Sciences Division.