LIVING POLYMERIZATION FOR THE INTRODUCTION OF TAILORED HYDROGEN BONDING

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ABSTRACT

In an effort to synthesize macromolecules comprising both covalent and non-covalent bonding to tune ultimate physical properties, a variety of methodologies and functionalization strategies were employed. First, protected functional initiation, namely 3-[(N-benzyl-N-methyl)amino]-1-propyllithium and 3-(t-butyldimethylsilyloxy)-1-propyllithium, in living anionic polymerization of isoprene was used to yield well-defined chain end functional macromolecules. Using both initiating systems, polymers with good molar mass control and narrow molar mass distributions were obtained and well-defined chain end functionality was observed. There was no observed effect on the polymer microstructure from the polar functionality in the initiator, with ~92% 1,4- and 8% 3,4-enchainment observed in each case. Further investigation of the 3-[(N-benzyl-N-methyl)amino]-1-propyllithium initiated polyisoprenes proved that facile deprotection was not possible and residual catalyst was not removable from the polymer. However, polymers initiated with 3-(t-butyldimethylsilyloxy)-1-propyllithium were quantitatively hydrogenated and deprotected under relatively mild conditions to yield hydroxyl functional macromolecules in several architectures, including linear and star-shaped. Excellent conversion from arm polymer to star polymer was observed and well-defined macromolecules were obtained. Subsequently, a series of non-functional, hydroxyl functional, and 2-ureido-4[1H]-pyrimidone (UPy) chain end functional linear and star-shaped poly(ethylene-co-propylene)s were synthesized and characterized. The melt phase properties were investigated using melt rheology and the effect of macromolecular

topology and multiple hydrogen bond functionality was investigated. Linear UPy functional poly(ethylene-*co*-propylene)s exhibited increased viscosity and shear thinning onset at lower frequencies than non-functional polymers of similar molar mass due to interaction of the multiple hydrogen bonding groups. Star-shaped UPy functional poly(ethylene-*co*-propylene)s showed inhibition to terminal flow and the absence of a zero shear viscosity in melt rheological characterization, indicative of a network like structure imparted from the multiple hydrogen bonding interactions.

In addition, the living anionic polymerization of D_3 was controlled using the functionalized initiators   3-[(N-benzyl-N-methyl)amino]-1-propyllithium   and   3-(t-butyldimethylsilyloxy)-1-propyllithium.   Good molar mass control and narrow molar mass distributions were observed. In contrast to the polyisoprene homopolymers, facile deprotection of the 3-(t-butyldimethylsilyloxy)-1-propyllithium was not possible due to the acid sensitivity of the poly(dimethylsiloxane) backbone.   However, facile deprotection of the protected secondary amine was achieved through hydrogenolysis and well-defined terminal amine functionalized poly(dimethylsiloxane) was synthesized, which are then amenable to further functionalization reactions.

In contrast to the well-defined polymers synthesized using living anionic polymerization, free radical polymerizations was used to synthesize free radical copolymers with broader polydispersities and pendant UPy groups. These copolymers were compared with a simple dimeric hydrogen bonding carboxylic acid containing copolymer.   Melt rheological characterization revealed that, at similar concentrations, the effect of the UPy group was much greater than the carboxylic acid, and broadened plateau moduli and increased viscosity for the UPy containing polymers were observed,

while the acid containing polymer exhibited similar results to a non-functional control. The dynamic viscosity was observed to increase systematically with increasing UPyMA incorporation and the quadruple hydrogen bonding interactions were observed to dissociate between ~80-150 °C.

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Table of Contents

List of Figures

List of Tables

List of Schemes

Chapter 1...
Dissertation Overview

This dissertation focuses on the synthesis and characterization of polymers with tailored hydrogen bonding interactions. Chapter two is a review of the literature pertaining to living anionic polymerization and the monomer families of interest, as well as tailored multiple hydrogen bonding interactions. In the following chapters, the synthesis of well-defined polymers with functionality in various architectures will be described.

Chapter three focuses on the living anionic polymerization of D_3 using a protected hydroxyl initiator and a protected amine initiator. The suitability of these initiators to produce well-defined polymers with chain end functionality is discussed. Chapter four discusses the living anionic polymerization of isoprene using the same protected hydroxyl and protected amine initiator. The synthesis of both linear and star-shaped polymers is addressed and the effect of chain end functionality in conjunction with architecture is addressed with melt rheological characterization. Chapter five focuses on the functionalization of poly(ethylene-*co*-propylene)s with 2-ureido-4[1*H*]-pyrimidone (UPy) multiple hydrogen bonding groups. Initial studies were performed on a non-polar long chain alcohol model compound and appropriate reaction conditions were determined. Subsequently, the linear and star-shaped poly(ethylene-*co*-propylene)s were modified with UPy groups and the melt state properties were investigated.

Chapter six focuses on the free radical copolymerization of 2-ethylhexyl methacrylate with a 2-ureido-4[1*H*]-pyrimidone (UPy) containing methacrylate monomer. In contrast to the chain end functionalization achieved using living polymerization, this methodology yielded random UPy functionalization throughout the polymer chain in a random fashion. These polymers were compared with dimeric hydrogen bond containing 2-ethylhexyl methacrylate copolymers and their properties were studied in the melt state. Chapter seven describes the synthesis and characterization of novel A_2 and B_3 type macromonomers based on methyl methacrylate using living anionic polymerization with the functionalized initiator 3-(t-butyldimethylsilyloxy)-1-propyllithium. A novel protected functional diphenylethylene molecule was synthesized and used as a coinitiator with both s-butyllithium and 3-(t-butyldimethylsilyloxy)-1-propyllithium to yield macromolecules with one, two, or three hydroxyl groups at the same chain end. Chapter eight focuses on the synthesis and characterization of hydroxyl terminated polyisobutylene using living cationic polymerization. Chapter nine summarizes overall accomplishments.

Chapter 2 Literature Review

2.1 Introduction

In 1929, Ziegler described the polymerization of butadiene using n-butyllithium.[1]

In this work, Ziegler described a mechanism that consisted of both initiation and propagation, but mentioned that termination and transfer steps did not play a large role. This was the first anionic polymerization system. However, this work was not pursued at the time and the living nature of the polymerization was not realized until 1956. In 1956, Szwarc et al. coined the term "living" for these type of polymerizations.[2] In this seminal work, Szwarc described the nature of the living anionic system, in addition to recognizing the usefulness of the living anionic chain end in the synthesis of more complex architectures. Since that time, anionic polymerization has been widely used in the preparation of polydienes. Isoprene and butadiene have been studied extensively and make up the largest percentage of commercially utilized monomers. These monomers have been polymerized using a range of reaction conditions, including the use of different initiators and the incorporation of additives to tune the polymer stereochemistry, degree of branching, and degree of termination. Functional initiators were first reported in the literature in the 1970's and but have received relatively limited attention since that time.[3] In more recent years, significant attention has again focused on the use of functional

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[1] 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.Ziegler, K., L. Jakob and A. Wenz "Alkali organic compounds. XIII. The first reaction products of alkali metals upon butadiene." *Ann.* **1934**, *511*, 64.
[2] 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.
[3] Schulz, D. N. and A. F. Halasa "Anionic Polymerization Initiators Containing Protected Functional Groups. II." *J. Polym. Sci. Polymer Chemistry Edition* **1977**, *15*, 2401-2410.Schulz, D. N., A. F. Halasa and A. E. Oberster "Anionic Polymerization Initiators Containing Protected Functional Groups and Functionally Terminated Diene Polymers." *J. Polym. Sci. Polymer Chemistry Edition* **1973**, *12*, 153-166.

initiation in anionic polymerization due to advantages over electrophilic termination strategies.[4] A new generation of initiators has provided increased chain-end integrity and facile deprotection strategies to yield well-defined chain end functionality.   These nucleophilic functional groups, typically hydroxyl or amino, then provide the opportunity for diverse functionalization strategies at the polymer chain end.

An overview of the relevant literature relating to living anionic polymerization is presented in the following sections. Living anionic polymerization has a long and well-studied history, starting from its recognition in 1956 by Szwarc. The following segments will attempt to review the mechanistic, synthetic, and morphological aspects of living anionic polymerization and characterization of the properties of the resulting macromolecules. To begin with, the criteria for a living polymerization system and its mechanistic properties are reviewed and the synthetic implications are discussed. A detailed review of the synthetic efforts for isoprene polymerizations will follow, including both anionic and non-anionic methods. The last section will detail the role of multiple hydrogen bonding in macromolecular design.

2.2   Living Anionic Polymerization

2.2.1   Introduction

Although the character of living anionic polymerizations was not recognized until 1956 by Szwarc et al. [5] , investigations were previously conducted on anionic

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[4] Quirk, R. P., S. H. Jang and J. Kim "Recent Advances in Anionic Synthesis of Functionalized Elastomers using Functionalized Alkyllithium Initiators." *Rubber Rev., Rubber Chem. Tech.* **1996**, *69*, 444.
[5] 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.

polymerizations using reaction of diene and styrene monomers with alkali metals.[6] The presence of radical anions was discovered during the initiation steps of these reactions and it was assumed that the propagating species was also radical in nature. The anionic nature of these types of reactions was first clearly demonstrated by Higginson and Wooding with their investigations into the potassium amide initiation polymerization of styrene in liquid ammonia.[7] Scott and Hansley also demonstrated the use of lithium initiators to synthesize polyisoprene having a very similar structure to that of natural rubber.[8] Studies by Lipkin et al. were the basis for the seminal work of Szwarc and coworkers and focused on the reaction of aromatic hydrocarbons with alkali metals.[9] It was found that the reaction of aromatic hydrocarbons with alkali metals yielded colored complexes that were capable of initiating the polymerization of styrene and butadiene. These complexes were later shown to be radical anions formed by a single electron transfer from the alkali metal to the lowest unoccupied molecular orbital (LUMO) of the aromatic hydrocarbon.[10] The formation of the radical anions was controlled by the electron affinity of the aromatic hydrocarbon. Lipkin et al. also discovered that a new red colored species was formed from the addition of styrene to a green naphthalene radical anion solution. At the time, it was assumed that this red colored species was the radical anion of styrene. However, Szwarc and coworkers were able to show that the red colored

[6] 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.Ziegler, K., L. Jakob and A. Wenz "Alkali organic compounds. XIII. The first reaction products of alkali metals upon butadiene." *Ann.* **1934**, *511*, 64.
[7] Higgenson, 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**, 760-774.
[8] 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.
[9] Lipkin, D., D. E. Paul, J. Townsend and S. I. Weissman "Observations on a class of free radicals derived from aromatic compounds." *Science* **1953**, *117*, 535-536.Lipkin, D., D. E. Paul and S. I. Weissman "Reactions of sodium metal with aromatic hydrocarbons." *J. Am. Chem. Soc.* **1956**, *78*, 116-120.
[10] Eberson, L. and F. Radner "Electron-transfer mechanisms in electrophilic aromatic nitration." *Acc. Chem. Res.* **1987**, *20*, 53.

species was in fact the styrene dianion, formed from dimerization of the styrene radical anion.[11] These styrenic dianions were shown to be efficient initiators for styrene polymerization and high molecular weight polymers were obtained. Szwarc and coworkers were also able to exhibit the ability to synthesize block copolymers and demonstrated that under rigorous laboratory conditions excluding oxygen, water, and acidic protons, the chain ends remained active and were able to polymerize a second monomer after consumption of the first.[12] Due to the lack of termination events, Szwarc termed these polymers "living".

While this work led to the discovery of the living anionic polymerization methodology, the use of aromatic initiating complexes is limited due to the solubility of these species. Aromatic complexes are soluble only in polar solvents, such as tetrahydrofuran (THF) and limit their utility in the synthesis of many polymers. In contrast to this, organolithium reagents and certain Grignard reagents are readily soluble in a wide range of hydrocarbon solvents, such as hexane, benzene, cyclohexane, and pentane.[13] These reagents have been shown to be efficient initiators of living polymerizations and operate through nucleophilic attack on the monomer. In this case, a monofunctional propagating chain is generated and the stoichiometric number average molecular weight can be calculated using:

Equation 2-1: M_n = grams of monomer/moles of initiator

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[11] 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.

[12] Szwarc, M. "*Carbanions, Living Polymers and Electron Transfer Processes.*" Interscience Publishers: New York, 1968.

[13] 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.

The aromatic initiating complexes discussed previously are difunctional carbanionic initiators and propagation occurs at both chain ends, thereby changing the stoichiometric number average molecular weight to:

Equation 2-2: M_n = grams of monomer/ 0.5 moles of initiator

The nature of living anionic polymerizations is defined by the highly reactive carbanion and its interaction with its counterion.[14] An understanding of the chemistry of the carbanion terminus is paramount to an understanding of the overall system. It has been found that the counterion greatly affects the reactivity of the carbanion.[15] Therefore, it is believed the lithium counterion in living anionic systems strongly affects the reactivity of the carbanion. The nature of the carbon-lithium bond has been well-studied, however, widely differing conclusions have been reached regarding its character. Negishi reported that the carbon-lithium bond has approximately 83% covalent character, while other carbon-metal bonds have less covalent character, such as sodium (55%) and aluminum (78%).[16] The covalent character of the carbon-lithium bond was also observed in several other cases.[17] In contrast to this, Bauer et al. have reported that the carbon-lithium bond is 90% ionic in nature.[18] The discrepancy between this report and previous

[14] Hsieh, H. L. and R. P. Quirk "*Anionic Polymerization: Principles and Practical Applications*"; Marcel Dekker: New York, 1996.McGrath, J. E. "Anionic Polymerization: Kinetics, Mechanisms, and Synthesis". In *ACS Symposium Series*; American Chemical Society: Washington, D. C., 1981.

[15] Young, R. N., R. P. Quirk and L. J. Fetters "*Advances in Polymer Science*"; Springer-Verlag: Berlin, 1984.Morton, M. "*Anionic Polymerization: Principles and Practice*"; Academic Press: New York, 1983.Bywater, S. "*Encyclopedia of Polymer Science and Engineering*"; Wiley-Interscience: New York, 1985.

[16] 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.

[17] Lambert, C. and P. von Rague Schleyer "Are Polar Organometallic Compounds "Carbanions"? The Gegenion Effect on Structure and Energies of Alkali-Metal Compounds." *Angew. Chem. Int. Ed.* **1994**, *33*, 1129.Coates, G. E., M. L. H. Green and K. Wade "*In Organometallic Compounds*"; 3rd ed.; Methuen: London, 1967.

[18] Bauer, W., W. R. Winchester and P. von Rague Schleyer "Monomeric Organolithium Compounds in Tetrahydrofuran: tert-Butyllithium, sec-Butyllithium, "Supermesityllithium", Mesityllithium, and

findings was attributed to the propensity of these structures to form aggregates in solution. Bauer et al. performed both ^{7}Li and ^{13}C NMR spectroscopy in THF solution, which has been shown to dissociate aggregations of this type. They have therefore concluded that a more accurate description of a single carbon-lithium bond was obtained than previous measurements.

The formation of aggregates plays an important role in living polymerization systems and has been the subject of a large body of literature. The formation of aggregates has been attributed to the ionic character of the carbon-lithium bond.[19] This aggregate can be thought of as a cluster of lithium cations and carbanions with the polymeric chains extending from the ionic core. The number of chains that are found in this cluster are typically referred to as the degree of aggregation.[20] The degree of aggregation is defined by the steric bulk of the participating anionic centers. Under the same conditions, a primary carbanion will have a higher degree of aggregation than a secondary carbanion, which will be higher than a tertiary carbanion. The more sterically hindered secondary and tertiary carbanions generally take the form of a tetramer or dimer due to their larger steric bulk.[21] Primary carbanions such as n-butyllithium are found as hexamers in cyclohexane solution at room temperature, while the larger and more

Phenyllithium. Carbon-Lithium Coupling Constants and the Nature of Carbon-Lithium Bonding." *Organometallics* **1987**, *6*, 2371.

[19] Wardell, J. L. "*In Comprehensive Organometallic Chemistry; The Synthesis, Reactions and Structures of Organometallic Compounds"*; Pergamon Press: Oxford, 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.

[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. Part A* **1964**, *2*, 3311.

sterically hindered poly(styryl)lithium species is found in solution as dimers.[22]   The

degree of association for a range of alkyllithium species is shown in Table 2-1. Several

other factors also influence the degree of aggregation, including delocalization of charge,

concentration effects, temperature effects, and the addition of polar solvents to the system.

It is important to understand aggregation of the ion pairs due to the fact that it is generally

believed that polymerization occurs only in the unaggregated form.[23]   Large aggregates,

such as hexamers, are in equilibrium with their tetramers, dimers, as well as the single

propagating chain end. The use of polar solvents or Lewis bases is one of the most

commonly used methods to tune ion pair interactions in a polymerization.

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[22] Wardell, J. L. "*In Comprehensive Organometallic Chemistry; The Synthesis, Reactions and Structures of Organometallic Compounds*"; Pergamon Press: Oxford, 1982.
[23] Hsieh, H. L. and R. P. Quirk "*Anionic Polymerization: Principles and Practical Applications*"; Marcel Dekker: New York, 1996.

Table 2-1. Aggregation states of organolithium compounds in hydrocarbon solvents.

Compound	Solvent	Degree of Association	Reference
C_2H_5Li	Benzene	6.0	[24]
	Benzene	4.5-6	[25]
	Cyclohexane	6.0	[26]
n-C_4H_9Li	Benzene	6.3	[27]
	Cyclohexane	6.2	[27]
n-$C_5H_{11}Li$	Benzene	6.0	[28]
n-$C_8H_{17}Li$	Benzene	6.0	[28]
sec-C_4H_9Li	Cyclohexane	4	[29]
	Benzene	4	[29]
t-C_4H_9Li	Benzene	4	[30]
	Cyclohexane	4	[30]

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

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

[26] 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.

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

[28] Margerison, D. and J. D. Pont "Degrees of association of n-pentyllithium and n-octyllithium in benzene." Ibid. **1971**, *67*, 353.

[29] Bywater, S. and D. J. Worsfold "Alkyllithium Anionic Polymerization Initiators in Hydrocarbon Solvents." *J. Organomet. Chem.* **1967**, *10*, 1.

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

2.2.2 Criteria for Living Polymerization

A living polymerization is described as a chain polymerization in which the kinetic steps of termination and chain transfer are absent.[31] Polymerizations that proceed in the absence of termination and chain transfer steps provide persistent propagating chain ends throughout the polymerization. Quantitative retention of anionic chain ends provides the subsequent opportunity for quantitative chain end functionalization and synthesis of well-defined block copolymers. While the term living polymerization was used in the past solely for anionic polymerizations, recent advances in controlled radical polymerization, such as nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP), or reversible addition-fragmentation chain transfer (RAFT), technologies have necessitated a redefinition of the term "living". Living polymerizations were recently redefined as systems that retain active centers after complete polymerization and additional monomer will add to the existing chains and increase the degree of polymerization.[32] Matyjaszewski has also recently developed a more quantitative description for living polymerizations in terms of the rate of propagation in relation to termination.[33] Although there have been great strides in controlled polymerization methodologies in recent years, a series of criteria must be

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[31] Hsieh, H. L. and R. P. Quirk "*Anionic Polymerization: Principles and Practical Applications*"; Marcel Dekker: New York, 1996.

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

[33] 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.

fulfilled in order for a polymerization to be classified as living.[34]   These criteria are described in the following section.

Criteria for a Living Polymerization

Criterion 1. *Polymerization proceeds until the monomer is quantitatively consumed and addition of monomer results in the continued polymerization of all chains.* While quantitative consumption of monomer is not a defining characteristic of living polymerizations, quantitative persistence of polymer chain ends is. Both free radical polymerizations and step growth polymerizations are capable of quantitative conversion of monomer to polymer, but only in living systems is chain end reactivity quantitatively maintained throughout the polymerization. When additional monomer is added, all chains continue to consume monomer, and maintain their livingness. This is often considered the most defining criteria of a living polymerization system.

Criterion 2. *The number average molecular weight increases linearly with monomer conversion.* While this criterion is often used as a benchmark of living polymerization, because it is simple to determine experimentally, it is not a rigorous indicator of a living polymerization. A plot of molecular weight versus conversion will not show the presence of termination during the polymerization because the remaining polymer chains will continue to propagate and consume monomer. This criterion was fulfilled even when intentional low levels of termination were introduced during the polymerization.[35]

Criterion 3. *The number of growing polymer chains remains constant throughout the polymerization and is independent of conversion.* This criterion regulates the presence of

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[34] Quirk, R. P. and B. Lee "Experimental criteria for living polymerizations." *Polymer Int.* **1992**, *27*, 359.
[35] Ibid.

chain transfer during the polymization because chain transfer will increase the number of macromolecules in the system. Experimentally, this criterion is often difficult to determine because measurement of low levels of termination and chain transfer is challenging.[36]

Criterion 4. *The number average molecular weight is related to the grams of monomer/moles of initiator ratio.* Assuming quantitative monomer conversion, the number average molecular weight is proportional to the grams of monomer/moles of initiator ratio. This criterion detects low levels of protic impurities prior to initiation that may terminate active chain ends. However, this criterion is limited due to error associated with molecular weight determination.

Criterion 5. *Narrow molecular weight distribution polymers are produced.* This criterion is widely used in defining a polymerization as living. Flory and Szwarc first described the requirements for a Poisson molecular weight distribution.[37] The first requirement is that the polymerization is a chain polymerization and each reactive chain end is equally reaction toward incoming monomer units. Chain transfer and termination must be absent and propagation must be irreversible. The rate of initiation was also described as a factor by Gold, in that the initiation rate relative to the propagation rate

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[36] Hsieh, H. L. and R. P. Quirk "*Anionic Polymerization: Principles and Practical Applications*"; Marcel Dekker: New York, 1996.
[37] 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.

effects the molecular weight distribution.[38] Slow initiation events have been shown to result in broader molecular weight distributions.[39]

Criterion 6. *Sequential monomer addition results in block copolymer formation.* Because the chain ends remain living throughout the polymerization, block copolymers can be prepared by sequential monomer addition. The ability to form block copolymers if often cited as a benchmark of living polymerizations.[40]

Criterion 7. *Preparation of end-functionalized polymers is quantitative.* Due to the living reactive chain end, a variety of functionalization reactions are possible at the ω-chain end. Milkovich utilized this feature of living polymerization to synthesize macromonomers.[41] The use of this criterion to define a living polymerization is limited due to the fact that most end-functionalization reactions are not quantitative and determination of extent of reaction remains difficult.[42] In general, incorporation of chain-end functional groups on low molecular weight polymers is able to be well characterized.

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

[39] 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.

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

[41] Schulz, G. O. and R. Milkovich "Graft polymers with macromonomers. I. Synthesis from methacrylate-terminated polystyrene." *J. Appl. Polym Sci.* **1982**, *27*, 4773-4786.Schulz, G. O. and R. Milkovich "Graft polymers with macromonomers. II. Copolymerization kinetics of methacrylate-terminated polystyrene and predicted graft copolymer structures." *J. Polym. Sci. Polym. Chem. Ed.* **1984**, *22*, 1633-1652.

[42] 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.

Criterion 8. *The polymerization exhibits pseudo-first order kinetics.*[43] Living polymerizations have been shown to exhibit pseudo-first order kinetics as described by equation 2-3.

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

M_0 = initial monomer concentration
M = monomer concentration during the polymerization
k_{obs} = rate constant of polymerization
t = time of the polymerization

This treatment detects termination reactions, but is not sensitive to chain transfer events because the number of propagating chain ends remains constant, leading to a constant rate constant (k_{obs}). Long et al. were able to demonstrate the efficacy of using real time spectroscopy to monitor polymerization processes.[44] Using real time near infrared spectroscopy (NIR) data, the authors generated a pseudo-first order rate plot for the living anionic polymerization of styrene and isoprene in cyclohexane at 60 °C. While the living nature of both styrene and isoprene polymerizations was well-understood, this tool provided a new real time means to monitor the process. Additionally, sampling techniques are oftentimes not able to capture the reaction rate, particularly in the presence of polar solvents, and real time monitoring with rapid data collection increases the sensitivity to subtle changes in the kinetics of the polymerization.

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

$$\textbf{Equation 2-4} \qquad \ln(1 - ([I_o]/[M_o])DP_n) = -k_p[I_o]t$$

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[43] 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." Ibid. **1993**, *26*, 6237.
[44] Ibid.

M_o = initial monomer concentration

I_o = initial initiator concentration

k_p = rate constant of the polymerization

t = time of the polymerization

DP_n = number average degree of polymerization

Penczek et al. reported this technique in 1991 and it was shown that it was sensitive to both chain transfer and termination events.[45] In comparison to criteria two, three, and eight, this criterion is sensitive to small levels of termination and transfer.

[45] 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 Polymerization

The following sections describe the three stages of an anionic polymerization: initiation, propagation, and termination. In the initiation step, a reactive alkyllithium species reacts with a monomer unit, which begins the polymerization process. During the propagation step, the reactive chain end converts the remaining monomer to polymer. As was described previously, in order for the polymerization to be defined as living, the number of reactive anions must remain constant through out the polymerization and the number of reactive chain ends at the end of the polymerization will be equal to the moles of initiator charged. After the monomer has been quantitatively consumes, the living polymer chain ends are then terminated. The mechanistic details of these stages will be detailed in the following sections.

2.3.1   Initiation with Alkyllithium Reagents

The initiation of diene and styrene based monomer families in hydrocarbon solvents has been well-explored in the literature. The initiation of styrene with n-butyllithium in benzene was reported by Worsfold and Bywater in 1960.[46] In this study, the rate of reaction was determined to be proportional to the initiator concentration to the one-sixth power. This fractional dependence was attributed to the hexameric association of n-butyllithium in benzene. It was assumed that in order for polymerization to occur, the aggregate dissociated to a monomeric form. There is, however, no direct evidence to support the existence of monomeric n-butyllithium species in hydrocarbon media.[47] The dissociation of n-butyllithium to a monomeric state was found to have large dissociation

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[46] Worsfold, D. J. and S. Bywater "Anionic polymerization of styrene." *Can. J. of Chem.* **1960**, *38*, 1891.
[47] 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.

enthalpies, which suggests that the assumption of monomeric n-butyllithium as the active initiating species was not entirely valid.[48]   Later, Brown et al. suggested that a monomeric alkyllithium species was unnecessary for initiation because aggregated alkyllithium species were reactive toward olefinic monomers.[49] This theory was further supported by the observation of the complexation of ethylene with an etherated n-butyllithium tetramer.[50] While it is simpler to assume that a monomeric alkyllithium species is the active initiating species in anionic polymerizations, several studies have suggested that both monomeric and associated aggregates are responsible for initiation events.[51]   This was demonstrated using tert-butyllithium in the iniation of styrene polymerization. Some of the t-butyllithium was found to initiate styrene polymerization rapidly, while the remaining portion persisted throughout the polymerization.[52] More recent studies have suggested that alkyllithium species are present in an equilibrium state and are constantly reassociating into different aggregate species.[53]   While this was demonstrated for most alkyllithium species, tert-butyllithium was an exception, exhibiting a slow intermolecular exchange in hydrocarbon media.[54]

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[48] Young, R. N., R. P. Quirk and L. J. Fetters "*Advances in Polymer Science"*; Springer-Verlag: Berlin, 1984.

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

[50] 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.

[51] 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.

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

[53] Lewis, H. L. and T. L. Brown "Association of Alkyllithium Compounds in Hydrocarbon Media. Alkyllithium-Base Interactions." *J. Am. Chem. Soc.* **1970**, *92*, 4664.

[54] 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 dissocation." Ibid., 1237.

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An understanding of the initiation step of anionic polymerizations is further complicated by several additional factors, including effect of excess monomer in relation to alkyllithium, alkyllithium concentration, and effect of aliphatic versus aromatic solvents. Smart et al. probed the effect of monomer concentration on initiation events and attributed the effect to pi-complexation of the monomer to the initiator species.[55] While there is a large body of literature pertaining to the initiation of living anionic polymerizations, no mechanism has yet accurately described the process. Additionally, most fundamental studies have involved concentrated alkyllithium solutions and are not necessarily a good model for living anionic polymerizations, which are typically performed under dilute solution conditions. While the exact mechanism of living anionic polymerization initiation has not yet been elucidated, it is understood that initiation involves the nucleophilic attack of the alkyllithium species on the double bond of the monomer (Scheme 2-1).

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[55] Smart, J. B., M. T. Emerson and J. P. Oliver "Lithium-p-electron interactions in but-3-enyllithium." Ibid. **1966**, *88*, 4101.Smart, J. B., R. Hogan, P. A. Scherr and M. T. Emerson "Metal-double bond interactions. IV. Studey of lithium-p-electron interactions in 3-butenyllithium by lithium-7 and proton NMR spectroscopy." *J. Organomet. Chem.* **1974**, *64*, 1.
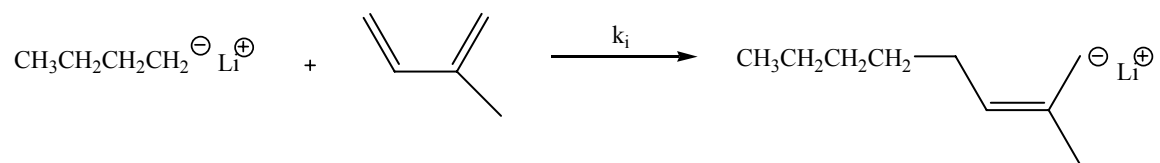
Scheme 2-1. Initiation step in the anionic polymerization of isoprene.

2.3.1.1 Use of Functional Initiators

In general, polymers resulting from anionic polymerizations may be end-functionalized by a variety of post-polymerization reactions with electrophilic agents.[56] However, many of these reactions are not quantitative and produce a number of undesirable side-products.[57] An alternative method to synthesize end-functionalized polymer chains is through the use of functionalized alkyllithium initiators, which provide quantitative chain end functionalization. It is generally necessary to use a protecting group in the initiator because most functionalities of interest, such as hydroxyl, carboxyl, or amino, are not stable in the presence of organolithium reagents.[58] A suitable protecting group should be unreactive toward the alkyllithium initiator, but also be easily removed after the polymerization is complete to generate the desired functional group.[59] A series of criteria have been established to determine viability for functional initiators in living anionic polymerizations.

Criterion 1. *Initiator solubility.* The first criterion is that the functionalized alkyllithium initiator must be soluble in hydrocarbon media. Early investigations into protected functional initiators yielded alkyllithiums with poor solubility in hydrocarbon solvents,

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[56] Hsieh, H. L. and R. P. Quirk "*Anionic Polymerization: Principles and Practical Applications*"; Marcel Dekker: New York, 1996.Goethals, E. J. "Telechelic Polymers: Synthesis and Applications"; CRC Press: Boca Raton, Fl, 1989.

[57] Hsieh, H. L. and R. P. Quirk "*Anionic Polymerization: Principles and Practical Applications*"; Marcel Dekker: New York, 1996.

[58] Schulz, D. N., S. Datta and R. M. Waymouth "Use of protecting groups in polymerization." *Polym. Mater. Sci. Eng.* **1997**, *76*, 3-5.Nakahama, S. and A. Hirao "Protection and polymerization of functional monomers: anionic living polymerization of protected monomers." *Prog. Polym. Sci.* **1990**, *15*, 299-335.Greene, T. W. and P. G. M. Wuts "*Protective Groups in Organic Synthsis*"; 3rd ed.; John Wiley & Sons: New York, 1999.

[59] Quirk, R. P., S. H. Jang, H. Yang and Y. Lee "Polymer Synthesis Using Functionalized Alkyllithium Initiators: Telechelic, heterotelechelic and functionalized star-branched polymers." *Macromol. Symp.* **1998**, *132*, 281-291.

and required solvation in ether-based solvents.[60]   Due to the necessity to solvate the

initiator species in polar media, the resulting polydienes contained high 1,2-enchainment.

In order to achieve polydienes with high 1,4-enchainment, it was necessary to develop

initiators with excellent solubility in hydrocarbon media. 3-(*tert*-butyldimethylsilyloxy)-

1-propyllithium (tBDMSPrLi) and a series of related protected hydroxyl initiators have

excellent solubility in hydrocarbon media and have yielded polydienes with high 1,4-

enchainment (>90%).[61]

Criterion 2. *Initiator Efficiency.*   The second criterion is that the initiator must

efficiently initiate chain growth polymerization.   As described previously, the rate of

initiation must be much greater than the rate of propagation in order to be effective as an

anionic initiator.   Early studies into the polymerization of styrene using tBDMSPrLi

indicated that only a percentage of initiator species reacted with the monomer and the

remainder were unable to react.   More recent studies have shown the efficacy of this

initiator for diene polymerizations.[62]

Criterion 3. *Rate of initiation relative to propagation.* The third criterion is that the rate

of initiation should be faster than the rate of propagation in order to obtain a narrow

molecular weight distribution.   In the event of slow initiation events relative to

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[60] Schulz, D. N., A. F. Halasa and A. E. Oberster "Anionic Polymerization Initiators Containing Protected Functional Groups and Functionally Terminated Diene Polymers." *J. Polym. Sci. Polymer Chemistry Edition* **1973***, 12*, 153-166.Schulz, D. N. and A. F. Halasa "Anionic Polymerization Initiators Containing Protected Functional Groups. II." *J. Polym. Sci. Polymer Chemistry Edition* **1977***, 15*, 2401-2410.
[61] Quirk, R. P., S. H. Jang, K. Han, H. Yang, B. Rix and Y. Lee "Anionic Synthesis of Hydroxyl-Functionalized Polymers Using Protected, Functionalized Alkyllithium and Isoprenyllithium Initiators". *Functional Polymers*, 1998; pp 71-84.
[62] Quirk, R. P., S. H. Jang and J. Kim "Recent Advances in Anionic Synthesis of Functionalized Elastomers using Functionalized Alkyllithium Initiators." *Rubber Rev., Rubber Chem. Tech.* **1996***, 69*, 444.Hudelson, C. L., K. Yamauchi and T. E. Long "Unique combinations of macromolecular topology and functionality." *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2002***, 43*, 485-486.Elkins, C. L., K. Yamauchi and T. E. Long "Synthesis and characterization of self-complementary multiple hydrogen bonding poly(isoprene) star polymers." *Polym. Prepr.* **2003***, 44*, 576-577.

propagation, a broadened molecular weight distribution will be observed, as was shown for the polymerization of styrene with tBDMSPrLi described above.

Criterion 4. *The protecting groups are stable during anionic polymerization.* The fourth criterion is that the protected functionality should be stable to the anionic polymerization conditions in order to obtain a well-defined polymer. Initial work with protected functional initiators based on mixed acetals showed loss of functionality during the polymerization.[63] More recent work has shown that the protected hydroxyl initiator tBDMSPrLi is stable during living anionic polymerization.[64]

Criterion 5. *The protecting group must be easily removed.* Use of protected functional initiators to introduce chain end functionality has no utility if the protecting group cannot be easily removed. Typically, deprotection is effected using mild acidic conditions, such as one molar hydrochloric acid at 65 °C. Tetrabutylammonium fluoride was also used to efficiently remove the tert-butyldimethylsilyl protecting group.[65]

If a protected functionalized initiator fulfills these requirements, it should be suitable for living anionic polymerization.[66] The use of functionalized initiators has several advantages over traditionally used electrophilic reagents in synthesizing end-functionalized polymers.[67] Each functionalized initiator molecule will produce a macromolecule with the desired functionality at the chain end regardless of the molar

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[63] Schulz, D. N., A. F. Halasa and A. E. Oberster "Anionic Polymerization Initiators Containing Protected Functional Groups and Functionally Terminated Diene Polymers." *J. Polym. Sci. Polymer Chemistry Edition* **1973**, *12*, 153-166.

[64] Handlin, D. L., R. C. Bening and C. L. Willis "Preparation of low viscosity terminally functionalized isoprene polymers." US, 1994.

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

[66] Quirk, R. P., S. H. Jang, K. Han, H. Yang, B. Rix and Y. Lee "Anionic Synthesis of Hydroxyl-Functionalized Polymers Using Protected, Functionalized Alkyllithium and Isoprenyllithium Initiators". *Functional Polymers*, 1998; pp 71-84.

[67] Quirk, R. P., S. H. Jang and J. Kim "Recent Advances in Anionic Synthesis of Functionalized Elastomers using Functionalized Alkyllithium Initiators." *Rubber Rev., Rubber Chem. Tech.* **1996**, *69*, 444.

mass of the polymer being synthesized. The use of functionalized initiators avoids the

problems associated with electrophilic addition reagents, such as efficient and rapid

mixing with viscous polymers, the stability of the anionic chain end, and selective

reactivity.[68] Functionalized initiators also provide the ability to synthesize telechelic and

heterotelechelic polymers, functionalized block polymers and star-branched polymers

with functional groups on each arm (Figure 2-1).[69]

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[68] Hsieh, H. L. and R. P. Quirk "*Anionic Polymerization: Principles and Practical Applications*"; Marcel Dekker: New York, 1996.

[69] Quirk, R. P., S. H. Jang, H. Yang and Y. Lee "Polymer Synthesis Using Functionalized Alkyllithium Initiators: Telechelic, heterotelechelic and functionalized star-branched polymers." *Macromol. Symp.* **1998**, *132*, 281-291.

$$I\!-\!P^1H$$

$$ROH \uparrow$$

$$I\!-\!P^1E$$

$$E\!-\!X$$

$$I\!-\!R^{\ominus}Li^{\oplus} + n\ \text{monomer(1)} \longrightarrow I\!-\!P^{1\ominus}Li^{\oplus}$$

$$m\ \text{monomer(2)}$$

$$I\!-\!P^1\text{-}b\text{-}P^{2\ominus}Li^{\oplus} \xrightarrow{ROH} I\!-\!P^1\text{-}b\text{-}P^2H$$
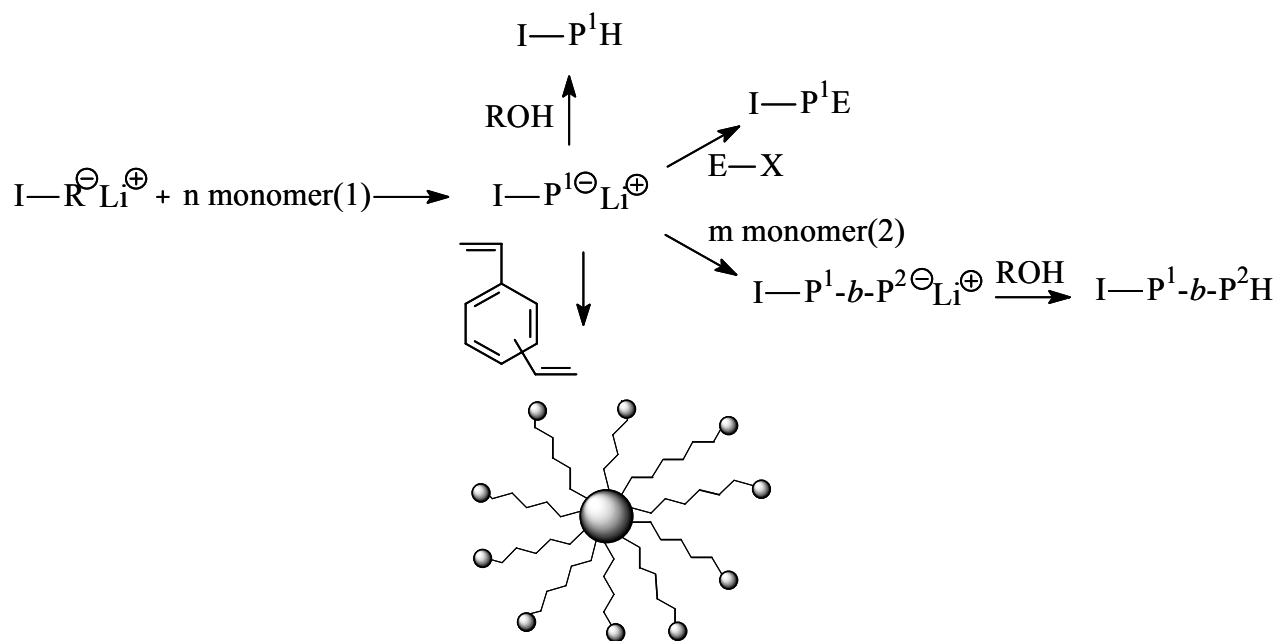
Figure 2-1. Series of reactions that the living anion of functionalized polymers may undergo (I = initiator functionality).[70] Where P indicates a polymer chain and E denotes an electrophilic terminating agent.

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[70] Ibid.

The first use of functionalized initiators in living anionic polymerization was reported by Schulz and Halasa in 1973.[71] In this study, the use of an acetal protecting group for the hydroxyl functionality was reported to be stable to both organolithium reagents and to the living chain ends. Using this initiator, they were able to prepare well-controlled polybutadiene with molecular weight distributions ranging from 1.05 to 1.08. In 1977, Schulz and Halasa reported the first use of a protected amine initiator, N,N-bis(trimethylsilyl) amine, in a living anionic polymerization.[72] Initiators containing this protected functionality demonstrated good molecular weight control, with molecular weight distributions ranging from 1.4 to 2.2. Removal of the protecting group for this system was simple and led to primary amine functionalities at the polymer chain ends.

In subsequent years, a variety of functionalities have been protected and used to initiate living anionic polymerizations of various monomers. Protected hydroxyl initiators have been used to initiate the polymerization of polyisoprene [73], polybutadiene [74], alkyl methacrylates [75], ethylene [76], and styrene [77], and poly(1,3-

[71] Schulz, D. N., A. F. Halasa and A. E. Oberster "Anionic Polymerization Initiators Containing Protected Functional Groups and Functionally Terminated Diene Polymers." *J. Polym. Sci. Polymer Chemistry Edition* **1973**, *12*, 153-166.

[72] Schulz, D. N. and A. F. Halasa "Anionic Polymerization Initiators Containing Protected Functional Groups. II." Ibid. **1977**, *15*, 2401-2410.

[73] Quirk, R. P., S. H. Jang and J. Kim "Recent Advances in Anionic Synthesis of Functionalized Elastomers using Functionalized Alkyllithium Initiators." *Rubber Rev., Rubber Chem. Tech.* **1996**, *69*, 444.Quirk, R. P., S. H. Jang, K. Han, H. Yang, B. Rix and Y. Lee "Anionic Synthesis of Hydroxyl-Functionalized Polymers Using Protected, Functionalized Alkyllithium and Isoprenyllithium Initiators". *Functional Polymers*, 1998; pp 71-84.Quirk, R. P. and R. T. Mathers "Surface-initiated living anionic polymerization of isoprene using a 1,1-diphenylethylene derivative and functionalization with ethylene oxide." *Polym. Bull.* **2001**, *45*, 471-477.Switek, K. A., F. S. Bates and M. A. Hillmyer "Star Polymer Synthesis Using Hexafluoropropylene Oxide as an Efficient Multifunctional Coupling Agent." *Macromolecules* **2004**, *37*, 6355-6361.Quirk, R. P., J. J. Ma, G. Lizarraga, Q. Ge, H. Hasegawa, Y. J. Kim, S. H. Jang and Y. Lee "Anionic synthesis of hydroxy-functionalized polymers using functionalized intiators and electrophilic termination." *Macromol. Symp.* **2000**, *161*, 37-44.Frick, E. M. and M. A. Hillmyer "Polylactide-b-polyisoprene-b-polylactide triblock copolymers: New thermoplastic elastomers containing biodegradable segments." *Abstr. Pap.-Am. Chem. Soc.* **2001**, *221st POLY*.

[74] Quirk, R. P., S. H. Jang, H. Yang and Y. Lee "Polymer Synthesis Using Functionalized Alkyllithium Initiators: Telechelic, heterotelechelic and functionalized star-branched polymers." *Macromol. Symp.* **1998**, *132*, 281-291.Quirk, R. P., S. H. Jang and J. Kim "Recent Advances in Anionic Synthesis of Functionalized

cyclohexadiene) [78] .   Protected amine initiators have been used to initiate the

polymerization of dienes[79], ethylene oxide[80], styrene[81], and poly(dimethylsiloxane).[82]

2.3.2 Propagation Reactions

As discussed previously, the aggregation state in hydrocarbon media of the

reactive alkyllithium species in living anionic polymerization plays an important role. In

order to evaluate propagation reactions in living anionic polymerizations, aggregation

state must be taken into account. Additionally, separating the initiation reaction from the

propagation reaction simplifies the kinetic analysis. However, in order to separate the

Elastomers using Functionalized Alkyllithium Initiators." *Rubber Rev., Rubber Chem. Tech.* **1996**, *69*, 444.Quirk, R. P. and S. H. Jang "Anionic Synthesis of Hydroxy-Functionalized Polybutadienes Using Protected, Functionalized Organolithium Initiators." *Polym. Mater. Sci. Eng.* **1997**, *76*, 8-9.Quirk, R. P., S. H. Jang, K. Han, H. Yang, B. Rix and Y. Lee "Anionic Synthesis of Hydroxyl-Functionalized Polymers Using Protected, Functionalized Alkyllithium and Isoprenyllithium Initiators". *Functional Polymers*, 1998; pp 71-84.Quirk, R. P., J. J. Ma, G. Lizarraga, Q. Ge, H. Hasegawa, Y. J. Kim, S. H. Jang and Y. Lee "Anionic synthesis of hydroxy-functionalized polymers using functionalized intiators and electrophilic termination." *Macromol. Symp.* **2000**, *161*, 37-44.Hwang, J., M. D. Foster and R. P. Quirk "Synthesis of 4-, 8-, 12-arm star-branched polybutadienes with three different chain-end functionalities using a functionalized initiator." *Polymer* **2004**, *45*, 873-880.

[75] Tong, J.-D., C. Zhou, S. Ni and M. A. Winnik "Synthesis of Meth(acrylate) Diblock Copolymers Bearing a Fluorescent Dye at the Junction Using A Hydroxyl-Protected Initiator and the Combination of Anionic Polymerization and Controlled Radical Polymerization." *Macromolecules* **2001**, *34*, 696-705.Quirk, R. P. and R. S. Porzio "The Anionic Synthesis of Functionalized Linear and Star-branced Poly(methyl methacrylates) Using Protected Hydroxy-Functionalized Alkyllithium Initiators." *Polym. Prepr.* **1997**, *38*, 463-464.Mizawa, T., K. Takenaka and T. Shiomi "Synthesis of alpha-Maleimide-omega-Dienyl Heterotelechelic Poly(methyl methacrylate) and Its Cyclization by the Intramolecular Diels-Alder Reaction." *J. Polym. Sci. Part A* **2000**, *38*, 237-246.

[76] Zhang, P. and J. S. Moore "Synthesis and characterization of PEE-PEO diblock copolymers with complementary end-groups for hydrogen-bond heteroassociation." *J. Polym. Sci. Part A* **2000**, *38*, 207-219.

[77] Quirk, R. P., S. H. Jang and J. Kim "Recent Advances in Anionic Synthesis of Functionalized Elastomers using Functionalized Alkyllithium Initiators." *Rubber Rev., Rubber Chem. Tech.* **1996**, *69*, 444.

[78] Quirk, R. P., F. You, C. Wesdemiotis and M. A. Arnould "Anionic Synthesis and Characterization of omega-Hydroxyl-Functionalized Poly(1,3-Cyclohexadiene)." *Macromolecules* **2004**, *37*, 1234-1242.

[79] Miura, Y., K. Hirota, H. Moto and B. Yamada "High-Yield Synthesis of Functionalized Alkoxyamine Initiators and Approach to Well-Controlled Block Copolymers Using Them." Ibid. **1999**, *32*, 8356-8362.Hadjichristidis, N., S. Pispas and M. Pitsikalis "End-Functionalized polymers with zwitterionic end-groups." *Prog. Polym. Sci.* **1999**, *24*, 875-915.Ishizu, K., H. Kitano, T. Ono and S. Uchida "Synthesis and characterization of polyfunctional star-shaped macromonomers." *Polymer* **1999**, *40*, 3229-3232.

[80] Ishizu, K. and T. Furukawa "Synthesis of functionalized poly(ethylene oxide) macromonomers." *Polymer* **2001**, *42*, 7233-7236.

[81] Hadjichristidis, N., S. Pispas and M. Pitsikalis "End-Functionalized polymers with zwitterionic end-groups." *Prog. Polym. Sci.* **1999**, *24*, 875-915.

[82] Elkins, C. L. and T. E. Long "Living Anionic Polymerization of Hexamethylcyclotrisiloxane (D3) Using Functionalized Initiation." *Macromolecules* **2004**, *37*, 6657-6659.

two stages, quantitative conversion from initiator to propagating anion must be achieved. As stated above, Worsfold and Bywater were among the first to study the living anionic polymerization of styrene in benzene using n-butyllithium.[83]   They showed in this study that initiator species were not entirely consumed at the beginning of the reaction when the monomer concentration was less than 1.08 M.   Later studies determined that when greater than millimolar concentrations of n-butyllithium were used, reactive initiator species were present throughout the polymerization.[84]   However, when sec-butyllithium was used in place of n-butyllithium to initiate styrene polymerization, rapid consumption of initiator was observed at the beginning of the polymerization.   Therefore, most studies examining the propagation steps of living anionic polymerizations have been conducted using s-butyllithium as initiator.   Even when using s-butyllithium to separate initiation from propagation, the kinetics of both diene and styrene polymerizations remain complicated due to the aggregate structure of the propagating chain end in solution.   The degree of association in styrene polymerizations has been probed using a variety of techniques, such as light scattering, UV-visible spectroscopy, and viscometry.   These studies have shown that the reactive poly(styryllithium) chain end exists as a dimmer in hydrocarbon solvents.[85]   It was later shown in similar studies that poly(butadienyllithium) exists as a tetramer in hydrocarbon solvents.[86]   While the

[83] Worsfold, D. J. and S. Bywater "Anionic polymerization of styrene." *Can. J. of Chem.* **1960**, *38*, 1891.
[84] Hsieh, H. L. "Molecular weight and molecular weight distribution of polymers prepared from butyllithiums." *J. Polym. Sci.* **1965**, *A3*, 163.
[85] Johnson, A. F. and D. J. Worsfold "Anionic polymerization of butadiene and styrene." *J. Polym. Sci. A* **1965**, *3*, 449.Morton, M., L. J. Fetters, R. A. Pett and J. F. Meijer "Association behavior of polystyryllithium, polyisoprenyllithium, and polybutadienyllithium in hydrocarbon solvents." *Macromolecules* **1970**, *3*, 327-332.
[86] Worsfold, D. J. and S. Bywater "Degree of association of polystyryl-, polyisoprenyl-, and polybutadienyllithium in hydrocarbon solvents." *Macromolecules* **1972**, *5*, 393-397.

reaction order for propagation is independent of polymerization solvent, the relative rate of polymerization is a function of both solvent and additives.[87]

2.3.2.1 Effect of Polar Additives

Polar additives are often used to tune aggregate structure and ion pair interactions in living anionic polymerizations.[88] The addition of a polar solvent changes the ion pair interactions and understanding the effect of polar solvents on an anionic polymerization is necessary to controlling the reaction rate and stereochemical selectivity.   When polymerizations are carried out in non-polar hydrocarbon media with a lithium counterion, a high degree of cis-1,4-microstructure is observed in the backbone of the polymer. Upon the addition of polar solvents, the polar solvent complexes with the lithium cation, weakening the ion pair between the lithium cation and the carbanionic polymer chain end. Typical polar additives in living anionic polymerizations include THF, diethyl ether, tetramethylethylenediamine (TMEDA), and dipieridinoethane (dipip).[89]   In the anionic polymerization of dienes, the addition of a polar solvent increases the amount of 1,2 addition with respect to 1,4 addition in the backbone of the polymer. The change in nature of the ion pair also results in different degrees of cis or trans stereochemistry of the poly(diene).[90]   The degree of interaction of the lithium

[87] Young, R. N., R. P. Quirk and L. J. Fetters "*Advances in Polymer Science"*; Springer-Verlag: Berlin, 1984.

[88] 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.Weiss, 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*, 79-81.Richards, D. H. "The polymerization and copolymerization of butadiene." *Chem. Soc. Rev.* **1977**, *6*, 235-260.

[89] West, P. and R. Waack "Colligative property measurements on oxygen- and moisture-sensitive compounds. I. Organolithium reagents in donor solvents at 25 °." *J. Am. Chem. Soc.* **1967**, *89*, 4395-4399.

[90] Weiss, 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

counterion with the polar solvent and the nature of the remaining interaction between the lithium cation and the polymer chain end determine the final architecture of the polymer backbone. The greater the interaction between the polar solvent and the lithium counterion, the more 1,2 enchainment is observed in the backbone of the polymer.[91] Polar solvents with more than one complexation site have larger associations with the lithium cation.[92]

As stated previously, it is believed that propagation of the polymer chain only occurs when the species is in its unaggregated, or free form. Therefore, it is important to understand the effect of the addition of polar solvents on the degree of aggregation. The size of the ion pair aggregate is a function of both solvent polarity and temperature. In a non-polar hydrocarbon solvent, the ion pair aggregate shows an increase in degree of aggregation as the temperature is decreased.[93] However, in polar solvents, this relationship is reversed. As the temperature is decreased, the degree of aggregation also decreases.[94] A decrease in the aggregation number causes an increase in the rate of

K." *Chem. Ber.* **1990**, *123*, 79-81.Richards, D. H. "The polymerization and copolymerization of butadiene." *Chem. Soc. Rev.* **1977**, *6*, 235-260.

[91] Milner, R., R. N. Young and A. R. Luxton "A viscometric study of the interaction of polybutadienyllithium with N, N, N', N'-tetramethylethylenediamine in benzene." *Polymer* **1983**, *24*, 543.Quirk, 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.: Polym. Chem. Ed.* **1981**, *19*, 1445.

[92] Quirk, R. P., D. E. Kester and R. D. Delaney "Solvation of Alkyllithium Compounds. Heats of Interaction of Lewis Bases with n-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 Trimethlsilylmethyllithium versus n-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.

[93] Kottke, T. and D. Stalke "Structures of Classical Reagents in Chemical Synthesis: (nBuLi)6, (tBuLi)4, and the Metastable (tBuLi-Et2O)2." *Angew. Chem. Int. Ed.* **1993**, *32*, 580.

[94] Bauer, W., W. R. Winchester and P. von Rague Schleyer "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, 1H, 13C, 6Li NMR." *J. Am.*

initiation of polymerization. Therefore solvent polarity also affects the rate of initiation of polymerization.

2.3.2.2 Effect of Alkoxides

Although alkoxides are not generally considered to be Lewis bases in anionic polymerizations, they also have the ability to alter the stereochemistry,[95] the rate,[96] and the degree of 1,2 versus 1,4 enchainment.[97] The effect of alkoxides on anionic polymerizations is commonly called salt effects. The interaction that governs these effects is the same as that for polar solvents or Lewis bases. The alkoxide is able to donate a pair of electrons to the aggregate. Lithium alkoxides have been shown to slow the rate of polymerization of styrene, butadiene, and isoprene. The lithium alkoxide complexes with the propagating chain aggregate resulting in a less active chain end and a slower rate of polymerization.[98] Although the use of a lithium counterion with the alkoxide results in a slower rate of polymerization, the use of other alkali cations, such as sodium, potassium, and rubidium has been shown to increase the rate of polymerization.[99] Along with the increase in the rate of the reaction, a higher degree of

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Chem. Soc. **1990**, *112*, 6190.Bauer, W. and D. Seebach "Determination of the degree of aggregation of organolithium compounds by cryoscopy in tetrahydrofuran." *Helv. Chim. Acta* **1984**, *67*, 1972.

[95] Hsieh, H. L. and R. P. Quirk "*Anionic Polymerization: Principles and Practical Applications*"; Marcel Dekker: New York, 1996.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*, 197-206.

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

[97] Hsieh, H. L. and C. F. Wofford "Alkyllithium and alkali metal tert-butoxide as polymerization initiator." *J. Polym. Sci., Polym. Chem. Ed.* **1969**, *7*, 449-460.

[98] 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.

[99] Hsieh, H. L. and C. F. Wofford "Alkyllithium and alkali metal tert-butoxide as polymerization initiator." *J. Polym. Sci., Polym. Chem. Ed.* **1969**, *7*, 449-460.

1,2 enchainment is also observed with these cations that is not observed using lithium counterions.[100]

The use of different counterions than lithium in the initiator has also been explored to alter the properties of the resulting macromolecules. It has been shown that the use of lithium as counterion results in good stereochemical control of diene polymerizations, with high degrees of 1,4-enchainment observed. While the use of sodium as a counterion has not been well-studied, due to generally poor yields from these reactions, the use of the soluble organosodium initiator 2-ethylhexyl sodium (2EHS) has been reported.[101] It was reported that 2EHS initiated the polymerization of isoprene and the rate of initiation exhibited a first order dependence on initiator concentration. Additionally, both isoprene and butadiene polymerizations initiated with 2EHS were found to exhibit extensive chain transfer, and addition of Lewis bases to the reaction inhibited this chain transfer. A higher degree of cis-enchainment was also observed when using 2EHS as an anionic initiator for diene polymerizations. The authors attributed these changes to a dimeric association of the reactive centers. In addition to sodium based initiators, both barium and magnesium based initiators have been reported. Aggarwal et al. reported the use of barium alkoxide-hydroxide or barium di alkoxide salts to initiate the polymerization of butadiene and this initiating system resulted in

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[100] Hsieh, H. L. and R. P. Quirk "*Anionic Polymerization: Principles and Practical Applications*"; Marcel Dekker: New York, 1996.

[101] 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." *Polym. Int.* **1995***, 37*, 165.Pakuro, N. I., A. A. Yakbovich-Arest and L. V. Shcheglova "Investigation of the initiation reaction of isoprene polymerization with 2-ethylhexyl sodium in heptane." *Macromol. Chem. Phys.* **1995***, 198*, 3855.

polybutadiene with a high percentage (79%) of trans 1,4-microstructure.[102]   These

polymers exhibited enough stereoregularity to undergo strain-induced crystallization.

Defieux et al. reported the use of mixed initiators of alkyllithiums and alkylmagnesiums

in an attempt to slow the polymerization of styrene at elevated temperatures.[103]

2.3.3   Termination and Introduction of Functionality

The living nature of anionic polymerizations and the persistence of the reactive

center throughout the polymerization render these macromolecules ideal for chain end

functionalization reactions, due to the ability to quantitatively endcap the living polymer

terminus.[104]   A variety of endcapping possibilities were outlined in Figure 2-1 and

include termination with a proton source, such as methanol, termination with an

electrophilic reagent to place a desired functional group at the terminus, addition of a

second monomer to yield a block copolymer, or coupling of the living anionic chain ends

with a divinyl compound to yield a star polymer. In recent years, the capping of the ω-

terminus with electrophilic reagents has received renewed interest and has been used to

tune polymer physical properties through the introduction of a small molecule

endcapper.[105]   Several variables are used to optimize electrophilic endcapping reactions,

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[102] 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". *Advances in Elastomers and Rubber Elasticity*; Plenum: New York, 1986.

[103] 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., Div. Polym. Chem.)* **2000**, *41*, 1386.

[104] Hsieh, H. L. and R. P. Quirk "*Anionic Polymerization: Principles and Practical Applications*"; Marcel Dekker: New York, 1996.

[105] Yamauchi, 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*, 8599-8604.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, X., K. Tanaka,

and include solvent, temperature, concentration, stoichiometry, and additives. One of the most well-studied electrophilic endcapping reagents is ethylene oxide, which incorporates a hydroxyl group at the polymer chain end. Quirk et al. reported the endcapping of poly(styryllithium) oligomers ranging in molecular weight from 1300-9900 g/mol with an excess of ethylene oxide.[106] The authors reported the reaction of a single ethylene oxide unit at the polymer chain end and did not observe ether linkages which would indicate oligomerization. Other researchers have used this method to introduce a well-defined hydroxyl group at the ω-chain end.[107] Other functionalities were introduced at the ω-chain end through various reactions with the living anionic terminus. Quirk et al. introduced an epoxide functionality at the chain end through reaction with epichlorohydrin. The authors were able to optimize reaction conditions to functionalize both polystyryllithium and polybutadienyllithium with an epoxide group in greater than 90% yield.[108] Cernohous et al. were able to functionalize several living polymer chain ends, including polystyryllithium, polyisoprenyllithium, poly(methyl methacryllithium),

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.
[106] Quirk, 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.
[107] Ji, H., S. Nobuyuki, W. K. Nonidez and J. W. Mays "Characterization of hydroxyl-end-capped polybutadiene and polystyrene produced by anionic polymerization technique via TLC/MALDI TOF mass spectrometry." *Polymer* **2002**, *43*, 7119-7123.Hudelson, C. L., K. Yamauchi and T. E. Long "Unique combinations of macromolecular topology and functionality." *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2002**, *43*, 485-486.Elkins, C. L., K. Yamauchi and T. E. Long "Synthesis and characterization of self-complementary multiple hydrogen bonding poly(isoprene) star polymers." *Polym. Prepr.* **2003**, *44*, 576-577.Yamauchi, 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*, 8599-8604.Yamauchi, K., J. R. Lizotte and T. E. Long "Synthesis and Characterization of Novel Complementary Multiple-Hydrogen Bonded (CMHB) Macromolecules via a Michael Addition." *Macromolecules* **2002**, *35*, 8745-8750.Yamauchi, K. and T. E. Long "Synthesis and characterization of telechelic multiple hydrogen-bonded polymers via living anionic polymerization." *Polym. Mater. Sci. Eng.* **2001**, *85*, 465-466.Yamauchi, K. and T. E. Long "Synthesis and characterization of telechelic multiple hydrogen bonded (MHB) macromolecules via living anionic polymerization." *Polym. Prepr.* **2002**, *43*, 698-699.Yamauchi, K. and T. E. Long "Synthesis and characterization of novel multiple-hydrogen bonded macromolecules via a Michael addition." *Polym. Prepr.* **2002**, *43*, 337-338.
[108] Quirk, R. P. and Q. Zhuo "Anionic Synthesis of Epoxide-Functionalized Macromonomers by Reaction of Epichlorohydrin with Polymeric Organolithium Compounds." *Macromolecules* **1997**, *30*, 1531-1539.

and poly(vinyl pyridinyllithium), with di-*tert*-butyl maleate. Subsequent pyrolysis yielded the succinic anhydride chain end functionality.[109] Hirao et al. described the introduction of chloromethylphenyl groups to polystyrene using transformation of a methoxymethyl phenyl protecting group to chloromethylphenyl using BCl_3. Well-defined polymers bearing a definite number, ranging from one to four, of chloromethylphenyl groups were synthesized.[110] Halogen end groups were introduced to living anionic polymers using reaction with α,ω-dihaloalkanes. The reaction with 1,3-dichloropropane provided monofunctional polymers, however, endcapping using diphenylethylene prior to termination was necessary to yield both bromo- and iodo-functional polymers in good yields.[111] Hirao et al. were also able to introduce monosaccharide residues to living polystyryllithium and polyisoprenyllithium using a diphenylethylene derivative. These polymers showed interesting reverse micelle properties in solution.[112] Terminal amine groups have been introduced using a variety of endcapping reagents, such as N-benzylidenemethylamine, [113] 1-chloro-3-(dimethylamino)propane, [114] 1-benzyl-4-(3-chloropropy)piperazine, [115] [N,N-

[109] Cernohous, J. J., C. W. Macosko and T. R. Hoye "Anionic Synthesis of Polymers Functionalized with a Terminal Anhydride Group." Ibid., 5213-5219.

[110] Hirao, A. and M. Hayashi "Synthesis of Well-Defined Functionalized Polystyrenes with a Definite Number of Chloromethylphenyl Groups at Chains Ends or in Chains by Means of Anionic Living Polymerization in Conjunction with Functional Group Transformation." Ibid. **1999**, *32*, 6450-6460.

[111] Hirao, A., M. Tohoyama and S. Nakahama "Synthesis of End-Functionalized Polymers by Means of Living Anionic Polymerization. 8. Reactions of Living Anionic Polymers with alpha,omega-Dihaloalkanes." Ibid. **1997**, *30*, 3484-3489.

[112] Hayashi, M., S. Loykulnant, 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." Ibid. **1998**, *31*, 2057-2063.

[113] Quirk, R. P., T.-H. Cheong and T. Yoo "Anionic Synthesis of Secondary Amine Functionalized Polymers by Reaction of Polymeric Organolithiums with N-Benzylidenemethylamine." *Macromol. Chem. Phys.* **2002**, *203*.

[114] Charlier, P., R. Jerome, P. Teyssie and L. A. Utracki "Viscoelastic Properteis of Telechelic Ionomers. 2. Complexes alpha,omega-Diamino Polydienes." *Macromolecules* **1990**, *23*, 3313-3321.Charlier, P., R. Jerome, P. Teyssie and L. A. Utracki "Viscoelastic Properties of Immiscible Telechelic Polymer Blends: Effect of Acid-Base Interactions." *Macromolecules* **1992**, *25*, 2651-2656.Charlier, P., R. Jerome and P. Teyssie "Solution Behavior of alpha,omega-(Dimethylamino)polyisoprene Coordinated to Transition Metal

bis(trimethylsilyl)amino]butylchlorodimethylsilane, [116] and protected α-halo-ω-aminoalkanes. [117] Terminal amino groups are then amenable to many further functionalization reactions.

2.4 Synthesis of Polymers Containing Conjugated Dienes

2.4.1 Introduction

In 1929, Ziegler described the polymerization of butadiene using n-butyllithium, in which initiation and propagation proceeded, but termination and transfer reactions were not observed.[118] This was the first anionic polymerization system, although it was not recognized at the time and this work was not pursued, with focus shifting to non-living polymerization of butadiene. Firestone also reported the use of an insoluble lithium metal in the polymerization of isoprene in 1955. This resulted in a material with properties similar to those found in natural rubber.[119] In 1956, Szwarc coined the term "living" for these types of polymerizations.[120] In this seminal work, Szwarc described the nature of the living anionic system, in addition to recognizing the usefulness of the living anionic chain end in the synthesis of more complex architectures. Because anionic

Salts." *Macromolecules* **1990**, *23*, 1831-1837.Quirk, R. P. and Y. Lee "Quantitative Amine Functionalization of Polymeric Organolithium Compounds with 3-Dimethylaminopropyl Chloride in the Presence of Lithium Chloride." *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 145-151.

[115] Quirk, R. P., T. Yoo, T.-H. Cheong, J. A. Schwindeman and T. W. Brockman "Anionic Synthesis of Amine-Functionalized Polybutadienes and Their Hydrogenated Analogs." *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2002**, *43*, 973-974.

[116] Peters, M. A., A. M. Belu, R. W. Linton, L. Dupray, T. J. Meyer and J. M. DeSimone "Termination of Living Anionic Polymerizations Using Chlorosilane Derivatives: A General Synthetic Methodology for the Synthesis of End-Functionalized Polymers." *J. Am. Chem. Soc.* **1995**, *117*, 3380-3388.

[117] Ueda, M., A. Hirao and S. Nakahama "Synthesis of Polymers with Amino End Groups. 3. Reactions of Anionc Living Polymers with alpha-Halo-omega-aminoalkanes with a Protected Amino Functionality." *Macromolecules* **1990**, *23*, 939-945.

[118] Hsieh, H. L. and R. P. Quirk "*Anionic Polymerization: Principles and Practical Applications"*; Marcel Dekker: New York, 1996.

[119] Foster, F. C. and J. L. Binder "*Advances in Chemistry Series No 19"*; American Chemical Society, 1957.

[120] 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.

polymerizations depend on the stability of the anion, much of the research on dienes since that time has focused on the polymerization of butadiene and isoprene monomers.

2.4.2 Synthesis of Isoprene

With the ability to synthesize isoprene stereoselectively to yield high cis-1,4-microstructures as a possible replacement for natural rubber, the synthesis of isoprene monomer has become increasingly important. Currently, most isoprene production results from refinement of crude oil fractions, and will continue to provide the majority of isoprene in the near future. Specifically, isoprene is isolated from cracking of naphtha, a hydrocarbon fraction in the C_5 to C_8 boiling range.[121] At elevated temperatures and pressures, this fraction produces several products, including conjugated dienes. The resulting unsaturated hydrocarbons are then purified using a variety of separation techniques to remove unwanted side products. Although oil and oil-based products are readily available in today's market, the need for alternative synthetic strategies exist. Two main methods have been reported in the synthesis of isoprene monomer. In the first synthetic method, the dehydration of 2-methyl butanal was effected using a variety of catalysts, including aluminum phosphate based catalysts and boron phosphate based catalysts.[122] In general, these reactions proceeded in good yields (>80%) with side reactions producing 3-methylbutan-2-one. The second method is based on the Prins

[121] Steiner, H. "Aromatics from petroleum." *J. Inst. Petr.* **1947**, *33*, 410-435.Shepardson, R. M. "Aromatic hydrocarbons of high purity." US, 1948.Co., E. R. a. E. "Diene formation from olefinic hydrocarbon fractions": GB, 1959.

[122] Hutchings, G. J., I. D. Hudson and D. G. Timms "Dehydration of 2-methylbutanal to isoprene using aluminium phosphate catalysts." *Catalysis Letters* **1999**, *61*, 219-224.Forster, D. and G. E. Barker "Synthesis of isoprene from linear butenes": EP, 1983.Hutchings, G. J., I. D. Hudson, D. Bethell and D. G. Timms "Dehydration of 2-methylbutanal and methyl Isopropyl Ketone to Isoprene Using Boron and Aluminium Phosphate Catalysts." *J. Catalysis* **1999**, *188*, 291-299.

reaction of formaldehyde and isobutylene.[123]   Various catalyst systems have been evaluated for this reaction, including iron based catalysts, titanium based catalysts, and acidic molecular sieves as catalysts. The yield of isoprene from the Prins reaction is very dependent upon the choice of catalyst and various hydrocarbon side products are generally obtained.

2.4.3   Polymerization of Isoprene Using Various Methodologies

Natural rubber and its products have long been used in a variety of applications, ranging from historical reports of rubber balls in 500 B. C. to reports from Spanish explorers in the 15th and 16th centuries of water-proof shoes in Mexico and Brazil.[124]   To date, over 400 rubber latex producing plants have been identified and are cultivated in various tropical and sub-tropical countries. Synthetic rubbers were developed as a replacement for naturally occurring rubber materials, and are characterized as rubbers using the same general characteristics of natural rubber, such as high deformability, rapid recovery from deformation, and good mechanical strength. There are two general classes of synthetic rubbers, namely general purpose synthetic rubbers, and specialty synthetic rubbers.   General purpose rubbers, such as polybutadiene, polyisoprene, and styrene/butadiene copolymers, are used as a direct replacement for natural rubber. Specialty rubbers, in general, have been developed to fulfill a specific need, such as heat

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[123] Hall, D. W., F. L. Dormish and E. J. Hurley "New Synthesis of Isoprene Based on Formaldehyde and Isobutylene." *Ind. Eng. Chem. Prod. Res. Develop.* **1970**, *9*, 234-242.Rosenthal, R., G. A. Bonetti and H. Shalit "Synthesis of Isoprene": US, 1972.Dumitriu, E., D. Trong On and S. Kaliaguine "Isoprene by Prins Condensation over Acidic Molecular Sieves." *J. Catalysis* **1997**, *170*, 150-160.Dumitriu, E., V. Hulea, I. Fechete, C. Catrinescu, A. Auroux, J.-F. Lacaze and C. Guimon "Prins condensation of isobutylene and formaldehyde over Fe-silicates of MFI structure." *Appl. Cat. A: Gen.* **1999**, *181*, 15-28.
[124] Hsieh, H. L. and R. P. Quirk "*Anionic Polymerization: Principles and Practical Applications"*; Marcel Dekker: New York, 1996.

resistance, chemical resistance, or weatherability. Examples of specialty rubbers are polychloroprenes, polyurethanes, nitrile/butadiene copolymers, among others.

Several studies have shown that polyisoprene microstructure greatly influences the final properties of the polymer, ranging from highly crystalline *trans*-1,4-polyisoprene to amorphous *cis*-1,4-polyisoprene.[125] It was therefore advantageous to control the polymerization of isoprene in order to obtain the desired microstructure and ultimately optimum properties. Polydienes were polymerized over the years using a variety of methodologies such as emulsion polymerization,[126] living anionic polymerization,[127] Ziegler-Natta catalyzed polymerization,[128] and more recently using

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[125] Bruzzone, M., G. Corradini and F. Amato "Technological characteristics comparison of polyisoprene with different 1,4-cis. contents." *Rubber Plast. Age* **1965**, *278*, 278-283.Bruzzone, M., G. Corradini and F. Amato *Rubber Chem. and Tech.* **1966**, *39*, 1593.Scott, K. W., G. S. Trick, R. H. Mayor, W. M. Saltman and R. M. Pierson "Effect of structural imperfection on certain properties of stero rubber." *Rubber Plast. Age* **1961**, *42*, 175-179.Kent, E. G. and F. B. Swinney "Properties and applications of trans-1,4-polyisoprene." *Ind. Eng. Chem. Prod. Res. Develop.* **1966**, *5*, 134-138.

[126] Browning, G. L., Jr. "Polymerization of 1,3-butadiene": US, 1945.Ronay, G. S. and W. M. Sawyer, Jr. "cis-1,4-Polyisoprene emulsions and latexes." US, 1966.

[127] Yamazaki, N., T. Suminoe and S. Kambara "Kinetic studies of isoprene polymerization with several Ziegler-type catalysts." *Makromol. Chem.* **1963**, *65*, 157-173.Boor, J., Jr. "Ziegler polymerization of olefins. V. Site removal and site activation by electron donors." *J. Polym. Sci., Part A: Gen. Papers* **1965**, *3*, 995-1012.Gippin, M. "Polymerization of isoprene with tralkylaluminum-titanium chloride catalyst." US, 1970.Monakov, Y. B., I. R. Mullagaliev, E. Y. Kharitonova and V. N. Yuzarbaev "1,4-trans-polydienes. Synthesis, properties and application." *Oxid. Commun.* **2004**, *27*, 741-769.Costabile, C., G. Milano, L. Cavallo, P. Longo, G. Guerra and A. Zambelli "Stereoselectivity and chemoselectivity in Ziegler-Natta polymerization of conjugated dienes. 2. Mechanism for 1,2 syndiotactic polymerization of diene monomers with high energy s-ci eta 4 coordination." *Polymer* **2004**, *45*, 467-485.Anderson, A. G., A. Gridnev, G. Moad, E. Rizzardo and S. H. Thang "Polymerization initiators for controlling polymer molecular weight and structure." US, 1998.MacLeod, P. J., G. K. Hamer, P. Lukose and M. K. Georges "Functional polymers: random copolymers by stable free radical polymerization." *ACS Symposium Series* **1998**, *704 Functional Polymers*, 28-37.Georges, M. K., G. K. Hamer and N. A. Listigovers "Block Copolymer Synthesis by a Nitroxide-Mediated Living Free Radical Polymerization Process." *Macromolecules* **1998**, *31*, 9087-9089.Benoit, D., E. Harth, P. Fox, R. M. Waymouth and C. J. Hawker "Accurate Structural Control and Block Formation in the Living Polymerization of 1,3-Dienes by Nitroxide Mediated Procedures." *Macromolecules* **2000**, *33*, 363-370.Harth, E., B. Van Horn and C. J. Hawker "Acceleration in nitroxide mediated "living" free radical polymerizations." *Chem. Commun.* **2001**, *9*, 823-824.Bowden, N. B., K. A. Willets, W. E. Moerner and R. M. Waymouth "Synthesis of Fluorescently Labeled Polymers and Their Use in Single Molecule Imaging." *Macromolecules* **2002**, *35*, 8122-8125.Matthews, F. E. and E. H. Strange "Caoutchouc-like substances." GB, 1910.Harris, C. H.: US, 1913.Harris, C. H. *Ann.* **1911**, *383*, 157.Schlenk, W., J. Appenrodt, A. Michael and A. Thal "Metal additions to multiple bonds." *Ber.* **1914**, *47*, 473-490.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.Szwarc, M., M. Levy and R. Milkovich "Polymerization Initiated by Electron Transfer to Monomer. A New Method of Formation of

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living free radical polymerization.[129] Emulsion polymerization was shown to yield polyisoprene with cis-1,4-contents ranging from 90-95%, however, in comparison to living anionic processes, emulsion polymerization lacks good control over the polymerization and is not favored for the production of polyisoprene rubbers.[130]

Anionic polymerization is used industrially to produce polydiene rubbers, solution styrene/butadiene rubbers, thermoplastic elastomers, and also in non-rubber applications such as clear impact-resistant polystyrene resins and binders for solid rocket fuel. Diene monomers were first polymerized in the early 20th century using sodium metal as an initiator.[131] While the nature of the polymerization was not understood at the time, rubberlike materials were produced. As discussed previously, the first alkyllithium

Block Polymers." *J. Am. Chem. Soc.* **1956***, 78*, 2656.Foster, F. C. and J. L. Binder "*Advances in Chemistry Series No 19"*; American Chemical Society, 1957.Hsieh, H. L. and A. V. Tobolsky "Polymerization of isoprene by n-butyl lithium." *J. Polym. Sci.* **1957***, 25*, 245-247.

[128] Yamazaki, N., T. Suminoe and S. Kambara "Kinetic studies of isoprene polymerization with several Ziegler-type catalysts." *Makromol. Chem.* **1963***, 65*, 157-173.Boor, J., Jr. "Ziegler polymerization of olefins. V. Site removal and site activation by electron donors." *J. Polym. Sci., Part A: Gen. Papers* **1965***, 3*, 995-1012.Gippin, M. "Polymerization of isoprene with tralkylaluminum-titanium chloride catalyst." US, 1970.Monakov, Y. B., I. R. Mullagaliev, E. Y. Kharitonova and V. N. Yuzarbaev "1,4-trans-polydienes. Synthesis, properties and application." *Oxid. Commun.* **2004***, 27*, 741-769.Costabile, C., G. Milano, L. Cavallo, P. Longo, G. Guerra and A. Zambelli "Stereoselectivity and chemoselectivity in Ziegler-Natta polymerization of conjugated dienes. 2. Mechanism for 1,2 syndiotactic polymerization of diene monomers with high energy s-ci eta 4 coordination." *Polymer* **2004***, 45*, 467-485.

[129] Anderson, A. G., A. Gridnev, G. Moad, E. Rizzardo and S. H. Thang "Polymerization initiators for controlling polymer molecular weight and structure." US, 1998.MacLeod, P. J., G. K. Hamer, P. Lukose and M. K. Georges "Functional polymers: random copolymers by stable free radical polymerization." *ACS Symposium Series* **1998***, 704 Functional Polymers*, 28-37.Georges, M. K., G. K. Hamer and N. A. Listigovers "Block Copolymer Synthesis by a Nitroxide-Mediated Living Free Radical Polymerization Process." *Macromolecules* **1998***, 31*, 9087-9089.Benoit, D., E. Harth, P. Fox, R. M. Waymouth and C. J. Hawker "Accurate Structural Control and Block Formation in the Living Polymerization of 1,3-Dienes by Nitroxide Mediated Procedures." *Macromolecules* **2000***, 33*, 363-370.Harth, E., B. Van Horn and C. J. Hawker "Acceleration in nitroxide mediated "living" free radical polymerizations." *Chem. Commun.* **2001***, 9*, 823-824.Bowden, N. B., K. A. Willets, W. E. Moerner and R. M. Waymouth "Synthesis of Fluorescently Labeled Polymers and Their Use in Single Molecule Imaging." *Macromolecules* **2002***, 35*, 8122-8125.

[130] Ronay, G. S. and W. M. Sawyer, Jr. "cis-1,4-Polyisoprene emulsions and latexes." US, 1966.

[131] Matthews, F. E. and E. H. Strange "Caoutchouc-like substances." GB, 1910.Harris, C. H.: US, 1913.Harris, C. H. *Ann.* **1911***, 383*, 157.Schlenk, W., J. Appenrodt, A. Michael and A. Thal "Metal additions to multiple bonds." *Ber.* **1914***, 47*, 473-490.

polymerizations of dienes were conducted in 1929, [132] but the nature of these polymerizations was not understood until 1956 and the seminal work by Szwarc and coworkers.[133] It was work performed at Firestone in the early 1950's that regenerated interest in a synthetic replacement for natural rubber. Using lithium metal in hydrocarbon solvents, they were able to generate polyisoprene with similar structural features to natural rubber.[134] Additionally, Hsieh and Tobolsky demonstrated that high *cis*-polyisoprene was synthesized using alkyllithium reagents in heptane or benzene.[135] While the stereospecificity of living anionic polymerizations initially led to renewed interest, it was ultimately the control that living methodologies imparted over the final polymer structure that led to several important commercial products, as described above.[136] Since that time, living anionic polymerization of diene monomers have been intensely studied and the effect of various additives on polymer microstructure was discussed previously. Through the combination of living anionic polymerization methodologies and polar additives, the microstructure of polyisoprenes was tuned, ranging in microstructure from ~97% cis-1,4[137] to ~88% vinyl,[138] and thus altering the final physical properties of the system. While living anionic polymerization yields very well-defined polydienes with a desirable combination of vulcanizate properties, there are several disadvantages as well, including high cold flow, high compounded viscosity, and

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[132] 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.

[133] 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.

[134] Foster, F. C. and J. L. Binder "*Advances in Chemistry Series No 19*"; American Chemical Society, 1957.

[135] Hsieh, H. L. and A. V. Tobolsky "Polymerization of isoprene by n-butyl lithium." *J. Polym. Sci.* **1957**, *25*, 245-247.

[136] Hsieh, H. L. and R. P. Quirk "*Anionic Polymerization: Principles and Practical Applications*"; Marcel Dekker: New York, 1996.

[137] Al-Jarrah, M. M. F., R. L. Apikian and E. Ahmed *Polym. Bull.* **1984**, *12*, 433.

[138] Bywater, S. and D. J. Worsfold "Alkyllithium Anionic Polymerization Initiators in Hydrocarbon Solvents." *J. Organomet. Chem.* **1967**, *10*, 1.

poor processability.[139]   Increasing the molecular weight improves the cold flow, but decreases the processibility, while lowering the molecular weight improves processability, but leads to undesirable cold flow properties.   In order to address these problems, modification of the molar mass distribution or introduction of branching is often utilized. The molar mass distribution was modified using several techniques.   Use of an alkyllithium initiator with a slow initiation rate results in a broadened molar mass distribution, however, this generally results in only minor broadening, with molar mass distributions > 1.2.   One can also utilize a less soluble organolithium initiator that will dissolve slowly throughout the lifetime of the polymerization, resulting in a broader molar mass distribution.   However, the most common method to broaden molar mass distributions in polydiene polymerizations is using a continuous initiator addition to a batch process.   The rate of initiator addition is programmed and polymer product is withdrawn at the same rate.   This method is much more controllable and practical and results in a much broader molar mass distribution.   Because this method yields both very high molar mass and very low molar mass species, the processability is much improved, but cold flow can still be unacceptably high.   In order to improve cold flow properties, branching is most often used.   Branching can be achieved using a variety of techniques, including use of a divinyl comonomer, such as divinylbenzene,[140] and use of additives to cause metallation of the polymer backbone, and subsequently create new growth sites.[141] These methods lead to random branching with little control over the final polymer structure, however, the products are often quite useful commercially.   As discussed

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

[140] Zelinski, R. P. and H. L. Hsieh "Conjugated diene polymers." US, 1964.

[141] Halasa, A. F. "Metalation and grafting by anionic techniques." *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1972**, *13*, 678-683.

previously, chain end functionalization of living polymers can lead to a variety of interesting structures. Use of a polyfunctional coupling agent yields branched polymers with a much more well-defined structure and has been used to prepare model compounds for rheological studies.[142] This technique will be discussed in detail in a later section.

While living anionic polymerization generally yields polydienes with *cis*-1,4 microstructures ranging from 85-92%, use of a Ziegler type catalyst generates a polyisoprene with a *cis*-1,4 structure of greater than 96%. Horne and coworkers discovered the ability to use Ziegler catalyst of the $TiCl_4/Et_3Al$ variety to synthesize these highly stereoregular polyisoprenes.[143] The differences between these two types of synthetic polyisoprenes are significant because the processing characteristic of crystallinity under stress and green strength depend on the stearic purity and on molar mass distribution.[144] While the Ziegler type polyisoprenes are used as total replacements for natural rubber, those generated from alkyllithiums are not. Since the original discovery of the application of Ziegler type catalysts for isoprene polymerization, many studies have been published detailing the effect of catalyst composition on polydiene microstructure.[145] Compositions ranging from high cis-1,4-polyisoprene[146] to 1,4-

[142] Zelinski, R. P. and C. F. Wofford "Synthesis of trichain and tetrachain radial polybutadienes." *J. Polym. Sci.* **1965**, *A3*, 93-103.

[143] Gibbs, C. F., V. L. Folt, E. J. Carson and S. E. Horne, Jr. "Polymerization of conjugated diolefins and catalysts therefor." GB, 1963.Kahn, H. and S. E. Horne, Jr. "Isoprene polymerization": US, 1965.

[144] Hsieh, H. L. and R. P. Quirk "*Anionic Polymerization: Principles and Practical Applications"*; Marcel Dekker: New York, 1996.

[145] Yamazaki, N., T. Suminoe and S. Kambara "Kinetic studies of isoprene polymerization with several Ziegler-type catalysts." *Makromol. Chem.* **1963**, *65*, 157-173.Monakov, Y. B., Z. M. Sabirov and G. E. Zaikov "The mechanism of stereoregulation in diene polymerization on lanthanide catalytic systems." *New Develop. Chem. Biochem.* **2003**, 53-74.Yang, J.-H., M. Tsutsui, Z. Chen and D. E. Bergbreiter "New Binary Lanthanide Catalysts for Stereospecific Diene Polymerization." *Macromolecules* **1982**, *15*, 230-233.

[146] Yang, J.-H., M. Tsutsui, Z. Chen and D. E. Bergbreiter "New Binary Lanthanide Catalysts for Stereospecific Diene Polymerization." *Macromolecules* **1982**, *15*, 230-233.Fischbach, A., F. Perdih, P. Sirsch, W. Scherer and R. Anwander "Rare-Earth Ziegler-Natta Catalysts: Carboxylate-Alkyl Interchange." *Organometallics* **2002**, *21*, 4569-4571.

transpolyisoprene[147] and 1,2-syndiotactic polyisoprene[148] have been synthesized using Ziegler-type catalysis. Polymers synthesized using Ziegler catalysts have a broader molar mass distribution than those synthesized using living anionic polymerization, leading to a less well-defined structure overall, but still exhibit commercial utility. The role of the catalyst in dictating the polymer microstructure is not well-understood and remains an active area of research.

Although well-defined polydienes are able to be prepared using both living anionic polymerization techniques and Ziegler-type catalysis, there are drawbacks to both systems. As discussed previously, living anionic polymerization is very sensitive to protic impurities and oxygen, and requires rigorous laboratory techniques in order to synthesize polymer. The monomer families are therefore limited to generally non-functional monomers that are able to be rigorously purified. In Ziegler-prepared polydienes, residual heavy metal residues are sometimes undesirable for certain applications, and removal of these impurities is often times arduous. It is therefore desirable to synthesize polydienes using a free radical polymerization technique. The recent advent of stable radical polymerization methodologies has improved the ability to control vinyl polymerizations in comparison to conventional radical methodologies.[149]

[147] Monakov, Y. B., I. R. Mullagaliev, E. Y. Kharitonova and V. N. Yuzarbaev "1,4-trans-polydienes. Synthesis, properties and application." *Oxid. Commun.* **2004**, *27*, 741-769.
[148] Costabile, C., G. Milano, L. Cavallo, P. Longo, G. Guerra and A. Zambelli "Stereoselectivity and chemoselectivity in Ziegler-Natta polymerization of conjugated dienes. 2. Mechanism for 1,2 syndiotactic polymerization of diene monomers with high energy s-ci eta 4 coordination." *Polymer* **2004**, *45*, 467-485.
[149] 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*, 2987-2988.Hawker, C. J. ""Living" Free Radical Polymerization: A Unique Technique for the Preparation of Controlled Macromolecular Architectures." *Acc. Chem. Res.* **1997**, *30*, 373-382.Hawker, C. J., A. W. Bosman and E. Harth "New Polymer Synthesis by Nitroxide Mediated Living Radical Polymerizations." *Chem. Rev.* **2001**, *101*, 3661.Harth, E., B. Van Horn and C. J. Hawker "Acceleration in nitroxide mediated "living" free radical polymerizations." *Chem. Commun.* **2001**, *9*, 823-824.Odell, P. G., R. P. N. Veregin, L. M. Michalak and M. K. Georges "Characteristics of the Stable Free Radical Polymerization of Styrene in the Presence of 2-Fluoro-1-methylpyridinium-p-Toluenesulfonate." *Macromolecules* **1997**, *30*, 2232-2237.

More recently, nitroxide mediated polymerization (NMP) has been applied to the polymerization of 1,3-dienes, including butadiene and isoprene. Polyisoprenes with controlled molar mass and narrow molar mass distribution have been reported using several types of nitroxides, including α-hydrogen-based nitroxides.[150] An example of this type of reaction with styrene is shown in Scheme 2-2.

[150] Benoit, D., E. Harth, P. Fox, R. M. Waymouth and C. J. Hawker "Accurate Structural Control and Block Formation in the Living Polymerization of 1,3-Dienes by Nitroxide Mediated Procedures." *Macromolecules* **2000***, 33*, 363-370.Georges, M. K., G. K. Hamer and N. A. Listigovers "Block Copolymer Synthesis by a Nitroxide-Mediated Living Free Radical Polymerization Process." *Macromolecules* **1998***, 31*, 9087-9089.Bowden, N. B., K. A. Willets, W. E. Moerner and R. M. Waymouth "Synthesis of Fluorescently Labeled Polymers and Their Use in Single Molecule Imaging." *Macromolecules* **2002***, 35*, 8122-8125.Harth, E., B. Van Horn and C. J. Hawker "Acceleration in nitroxide mediated "living" free radical polymerizations." *Chem. Commun.* **2001***, 9*, 823-824.

Scheme 2-2. Nitroxide-mediated polymerization of styrene.
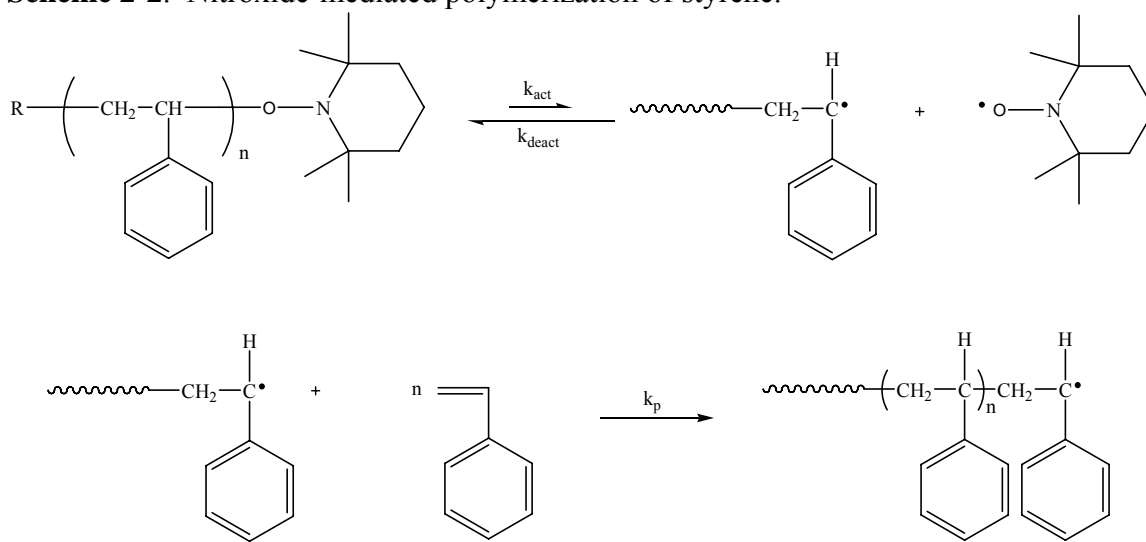
Although good control over the polymerization was maintained throughout the polymerization, control of stereochemistry using these techniques has not been achieved. Microstructures similar to those reported for conventional free radical polymerization methodologies are observed for nitroxide mediated polymerization of dienes, with a mixture of *cis*- and *trans*-1,4 triads.[151] This has been attributed to the ability of the propagating chain end, once dissociated from the nitroxide, to add monomer in a similar fashion to a conventional free radical process. Although control of microstructure is not yet possible, block copolymers have been synthesized using nitroxide mediated polymerization of isoprene with various monomers, including styrene, acrylates, and methacrylates.[152] Living free radical polymerization of dienes continues to be an active area of research.

2.4.4 Mechanism of Living Anionic Diene Polymerizations

In order to fully understand the kinetics of polymerizations, linear diene monomers have been intensely studied. In radical polymerizations of dienes, a high trans-1,4-polymer is observed.[153] This may be attributed to the preference of the monomer to be in the transoid or s-trans conformation, due to the decreased steric hindrance of this conformation over the cisoid or s-cis conformation. The trans-1,4-

[151] Georges, M. K., G. K. Hamer and N. A. Listigovers "Block Copolymer Synthesis by a Nitroxide-Mediated Living Free Radical Polymerization Process." *Macromolecules* **1998**, *31*, 9087-9089.Benoit, D., E. Harth, P. Fox, R. M. Waymouth and C. J. Hawker "Accurate Structural Control and Block Formation in the Living Polymerization of 1,3-Dienes by Nitroxide Mediated Procedures." *Macromolecules* **2000**, *33*, 363-370.

[152] Benoit, D., E. Harth, P. Fox, R. M. Waymouth and C. J. Hawker "Accurate Structural Control and Block Formation in the Living Polymerization of 1,3-Dienes by Nitroxide Mediated Procedures." *Macromolecules* **2000**, *33*, 363-370.Bowden, N. B., K. A. Willets, W. E. Moerner and R. M. Waymouth "Synthesis of Fluorescently Labeled Polymers and Their Use in Single Molecule Imaging." *Macromolecules* **2002**, *35*, 8122-8125.Georges, M. K., G. K. Hamer and N. A. Listigovers "Block Copolymer Synthesis by a Nitroxide-Mediated Living Free Radical Polymerization Process." *Macromolecules* **1998**, *31*, 9087-9089.

[153] Odian, G. "*Principles of Polymerization*"; 3rd ed.; John Wiley & Sons: New York, 1991.

polymer also exhibits greater stability than the cis-1,4-polymer.[154]   However, in living

anionic polymerization, a high degree of cis-1,4-polymer is observed when lithium is

used as the counterion.   It was originally believed that a six-membered transition state

was formed by the complexation of the carbanion-lithium counterion with the cisoid form

of the diene monomer, see Figure 2-2.[155]

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[154] Ibid.

[155] Bywater, S. "Polymerization intiated by lithium and its compounds." *Advances in Polymer Science* **1965**, *4*, 66-110.
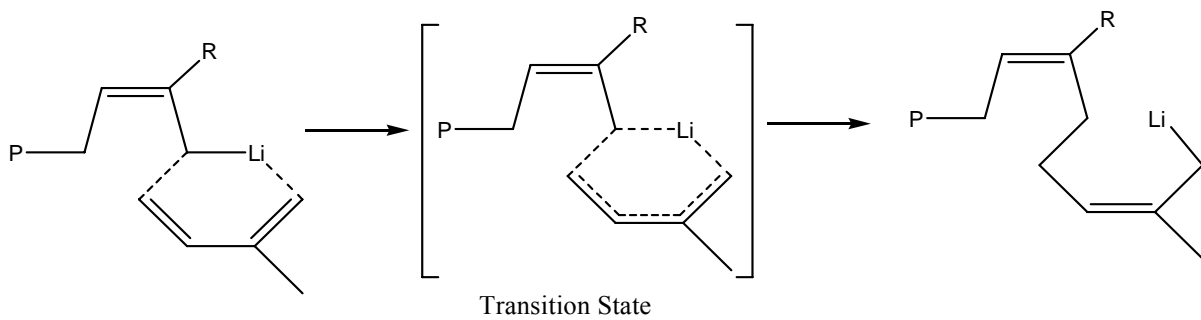
Figure 2-2. Poly(dienyllithium) complexes with the diene monomer in a six-membered transition state.

However, this theory was unable to explain the effect of monomer concentration on the stereochemistry of the polymer. This theory also did not take into account that the stereochemistry of the chain end is not fixed until the addition of the next monomer unit, which allows for isomerization of the chain end prior to monomer addition. The current theory is that the cis poly(dienyllithium) species that is originally formed may isomerize to the trans form.[156] A competition is set up between the cis/trans isomerization and the addition of the next monomer unit. At low monomer concentrations, the rate of isomerization is competitive with the rate of polymerization in the cis conformation, allowing for significant isomerization to the trans form. However, at high monomer concentrations, the rate of polymerization in the cis form is eight times higher than the rate of isomerization, with the polymer chain end rapidly reacting with monomer. High degrees of cis enchainment therefore results from high monomer concentrations. Although this model accounts for the dependency of polydiene microstructure on monomer concentration, it does not take into account the effect of aggregate structure on the polymerization. It has been shown that polydienyllithiums are aggregated into at least dimers and perhaps higher order aggregates in hydrocarbon solutions.[157] Additionally, the observed propagation rate constants are actually a composite of aggregate dissociation equilibrium and the kinetic step of monomer addition. Therefore, the actual kinetic situation is much more complex than current models describe. The role of

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[156] Worsfold, 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.

[157] Fetters, L. J., N. P. Balsara, J. S. Huang, H. S. Jeon, K. Almdal and M. Y. Lin "Aggregation in Living Polymer Solutions by Light and Neutron Scattering, A Study of Model Ionomers." Ibid. **1995**, *28*, 4996-5005.

aggregate structure on dimerization and propagation has not yet been addressed in a fundamental study.

2.5   Synthesis of Polymers Containing Siloxanes

2.5.1   Introduction

Poly(dimethylsiloxane) (PDMS) has a variety of properties that make it and PDMS-based materials attractive for a variety of industrial applications.[158] PDMS has excellent thermal and oxidative stability, as well as low absorption in the UV and good oxygen reactive ion etch resistance, which makes it useful for lithographic applications in microelectronics.[159]   PDMS also has high chain flexibility, low glass transition temperature, low surface energy, and a low solubility parameter. Polyorganosiloxanes also exhibit good thermal stability in air and have a wide temperature use range.[160] Industrially, PDMS is synthesized using the catalyzed ring opening reaction of octamethylcyclotetrasiloxane (D_4).[161] While this process remains important industrially for the production of organopolysiloxane, this polymerization is an equilibration process, in which both linear polymers and cyclic oligomers are formed, resulting in a broad molecular weight distribution. The synthesis of well-defined polysiloxanes remained elusive unti 1969, when Frye et al. proposed the use of the cyclic trimer

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[158] Bellas, V., H. Iatrou and N. Hadjichristidis "Controlled Anionic Polymerization of Hexamethylcyclotrisiloxane. Model Linear and Miktoarm Star Co- and Terpolymers of Dimethylsiloxane with Styrene and Isoprene." Ibid. **2000**, *33*, 6993-6997.Kiefer, L. A., T. H. Yoon, T. E. Glass, S. K. Jayaraman and J. E. McGrath "Synthesis and characterization of semicrystalline cycloaliphatic polyester/poly(dimethylsiloxane) segmented copolymers." *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 3495-3506.
[159] Gabor, A. H. and C. K. Ober "Silicon-containing block copolymer resist materials." *Microelectronics Technology. Polymers for Advanced Imaging and Packaging*: Washington, D. C., 1995; pp 281-298.
[160] Yilgor, I. and J. E. McGrath "Polysiloxane-containing copolymers: a survey of recent developments." *Adv. Polym. Sci.* **1988**, *86 (Polysiloxane Copolym./Anionic Polym.)*, 1-86.
[161] Eaborn, C. "*Organosilicon Compounds"*; Butterworth: London, 1960.

hexamethylcyclotrisiloxane (D₃) in the synthesis of well-defined anionic PDMS.[162] Due to the increased ring strain in the D₃ monomer, the rate of polymerization is greater and propagation occurs faster than ring-chain equilibrium reactions, resulting in polymers with narrow molecular weight distributions. These processes will be described below in detail.

2.5.2   Synthesis of Siloxane Monomers

Cyclic siloxane monomers are synthesized using the condensation of dichlorodialkyl-substituted silanes. The dichlorodialkyl-substituted silanes are synthesized using a Grignard reaction with the desired alkyl magnesium bromide and tetrachlorosilane in diethyl ether.[163] The substitution of the silicon tetrachloride with alkyl groups is dictated by the stoichiometry of the reaction and mono-, di-, and tri-alkyl substituted silanes were prepared, although a mixture of products is generally obtained.[164] Once the dichlorodialkylsilane has been isolated, it is generally added to an excess of water to yield cyclic monomer species.[165] The size of the cyclic species was controlled using temperature and acid catalysis, although a mixture of products is always obtained.

[162] Lee, C. L., C. L. Frye and O. K. Johansson "Selective polymerization of reactive cyclosiloxanes to give non-equilibrium molecular weight distributions. Monodisperse siloxane polymers." *Polym. Prepr.* **1969**, *10*, 1361-1367.Frye, C. L., R. M. Salinger, F. W. G. Fearon, J. M. Klosowski and D. Y. T. "Reactions of Organolithium Reagents with Siloxane Substrates." *J. Org. Chem.* **1970**, *35*, 1308.

[163] Gilliam, W. F., H. A. Liebhafsky and A. F. Winslow "Dimethyl Silicon Dichloride and Methyl Silicon Trichloride." *J. Am. Chem. Soc.* **1941**, *63*, 801-803.Rochow, E. G. and W. F. Gilliam "Polymeric methylsilicon oxides." *J. Am. Chem. Soc.* **1941**, *63*, 798-800.Hyde, J. F. and R. C. DeLong "Condensation products of the organosilanediols." *J. Am. Chem. Soc.* **1941**, *63*, 1194-1196.

[164] Hyde, J. F. and R. C. DeLong "Condensation products of the organosilanediols." *J. Am. Chem. Soc.* **1941**, *63*, 1194-1196.

[165] Ibid.Takiguchi, T. "Reactions of some organochlorosilanes in acetone." *J. Org. Chem.* **1958**, *23*, 1216-1217.Murata, H. "Raman spectra of hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane." *J. Chem. Phys.* **1951**, *19*, 659-660.Hunter, M. J., J. F. Hyde, E. L. Warrick and H. J. Fletcher "Organosilicon polymers. Cyclic dimethylsiloxanes." *J. Am. Chem. Soc.* **1946**, *68*, 667-672.

Fractional distillation was then used to isolate discrete cyclic siloxane species, which are then used for siloxane polymerizations.[166]

2.5.3 Polymerization of Siloxanes Using Non-Living Polymerization Methodologies

The ability to synthesize methylchlorosilanes, such as trimethylchlorosilane, dimethyldichlorosilane, and trimethylchlorosilane, in the early 1940's prompted research into the hydrolysis products of these types of compounds. Hyde and DeLong were the first to report the synthesis of a complex mixture of compounds from the hydrolysis of dimethyldichlorosilane, but only isolated and purified the cyclic trimer, hexamethylcyclotrisiloxane, from this mixture.[167] Rochow and Gilliam also reported the synthesis of "resinous products" from the hydrolysis of dimethyldichlorosilane and methyltrichlorosilane and described the formation of a siloxane network in which the methyl groups were directly bonded to silicon.[168] The first description of linear polysiloxanes developed from cyclic siloxanes was in 1946 by Patnode and Wilcock.[169] Linear polymers were achieved using mixtures of sulfuric acid with cyclic siloxane monomers and molar mass was controlled by the use of chain stoppers. This early work on linear polysiloxanes focused on the use of acid catalysis to yield high molecular weight polymers.[170] Since that time, research has focused mainly on the use of triflic

[166] Takiguchi, T. "Reactions of some organochlorosilanes in acetone." *J. Org. Chem.* **1958**, *23*, 1216-1217.Murata, H. "Raman spectra of hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane." *J. Chem. Phys.* **1951**, *19*, 659-660.Hunter, M. J., J. F. Hyde, E. L. Warrick and H. J. Fletcher "Organosilicon polymers. Cyclic dimethylsiloxanes." *J. Am. Chem. Soc.* **1946**, *68*, 667-672.

[167] Hyde, J. F. and R. C. DeLong "Condensation products of the organosilanediols." *J. Am. Chem. Soc.* **1941**, *63*, 1194-1196.

[168] Rochow, E. G. and W. F. Gilliam "Polymeric methylsilicon oxides." Ibid., 798-800.

[169] Patnode, W. and D. F. Wilcock "Methylpolysiloxanes." Ibid. **1946**, *68*, 358-363.

[170] Wilcock, D. F. "Vapor pressure-viscosity relations in methylpolysiloxanes." Ibid., 691-696.Sauer, R. O. "Organo-polysiloxanes": US, 1946.Sauer, R. O., W. J. Scheiber and S. D. Brewer "Derivatives of the methyldichlorosilanes. V. Polysiloxanes from methyldichlorosilane." *J. Am. Chem. Soc.* **1946**, *68*, 962-963.Wilcock, D. F. "Liquid methylpolysiloxane systems." *J. Am. Chem. Soc.* **1947**, *69*, 477-486.

acid for the cationic ring opening polymerization of cyclic siloxane monomers, generally D_3 and D_4.[171] While the mechanism of this polymerization remains unclear, it has been clearly demonstrated that propagation does not occur in the absence of excess triflic acid to catalyze the reaction.[172] In addition to triflic acid, several other initiation/catalyst systems have been studied for the cationic ring opening polymerization of cyclic siloxane monomers, including strong protic acids, such as sulfuric acid and perchloric acid,[173] bis(trifluromethane)-sulfonimide,[174] hydrochloric acid with antimony pentachloride,[175] and trisilyloxonium ions in the absence of protic acids.[176] Each of these initiators is able to produce polysiloxanes, however, yield of high molar mass polymer varies in each case, and a significant percentage of low molar mass cyclics is generally observed, due to the equilibrium nature of this process. In addition to cationic ring opening polymerization of cyclic siloxane monomers, anionic ring opening polymerization has also been extensively studied. The use of potassium hydroxide to initiate and catalyze anionic ring opening

[171] Chojnowski, J. and L. Wilczek "Mechanism of the polymerization of hexamethylcyclotrisiloxane (D3) in the presence of a strong protonic acid." *Makromol. Chem.* **1979**, *180*, 117-130.Steckle, W. P., Jr., E. Yilgor, J. S. Riffle, M. Spinu, I. Yilgor and R. S. Ward "Synthesis and characterization of thermally and chemically stable hydroxyl-terminated telechelic siloxane oligomers." *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*, 254-255.Cypryk, M. and J. Chojnowski "Monte Carlo simulation of the cyclization-chain extension kinetics for the cationic polymerization of hexmethylcyclotrisiloxane." *Macromolecules* **1991**, *24*, 2498-2505.Bischoff, R. and P. Sigwalt "Mechanism of Octamethylcyclotetrasiloxane Polymerization in the Presence of Siloxanediols." *Polym. Int.* **1996**, *40*, 99-109.

[172] Bischoff, R. and P. Sigwalt "Mechanism of Octamethylcyclotetrasiloxane Polymerization in the Presence of Siloxanediols." *Polym. Int.* **1996**, *40*, 99-109.Wilczek, L. and J. Chojnowski "Acidolytic Ring Opening of Cyclic Siloxane and Acetal Monomers. Role of Hydrogen Bonding in Cationic Polymerization Initiated with Protonic Acids." *Macromolecules* **1981**, *14*, 9-17.

[173] Cancouet, P., E. Daudet, G. Helary, M. Moreau and G. Sauvet "Functional Polysiloxanes. I. Microstructure of Poly(hydrogenmethylsiloxane-co-dimethylsiloxane)s Obtained by Cationic Copolymerization." *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 826-836.

[174] Desmurs, J.-R., L. Ghosez, J. Martins, T. Deforth and G. Mignani "Bis(trifluoromethane)sulfonimide initiated ring-opening polymerization of octamethylcyclotetrasiloxane." *J. Organomet. Chem.* **2002**, *646*, 171-178.

[175] Toskas, G., M. Moreau, M. Masure and P. Sigwalt "Controlled Cationic Polymerization of Hexamethycyclotrisiloxane." *Macromolecules* **2001**, *34*, 4730-4736.

[176] Wang, Q., H. Zhang, G. K. Suray Prakash, T. E. Hogen-Esch and G. A. Olah "Cationic Ring-Opening Polymerization of Cyclosiloxanes Initiated by Electron-Deficient Organosilicon Reagents." Ibid. **1996**, *29*, 6691-6694.

polymerization of octamethylcyclotetrasiloxane (D$_4$) was reported.[177] Several other basic

catalysts have been studied for the ring opening polymerization of cyclic siloxane

monomers, including ion exchangers of the ammonium chloride type,[178] phosphazene

bases,[179] and mixed alkali metal silanolates.[180] Although these more exotic systems have

shown improvement in various aspects of the polymerization, such as increased reaction

rate (phosphazene bases) and ease of catalyst removal (ion exchangers), alkali metal

hydroxides and silanolates represent the main class of initiators for anionic ring opening

polymerization of cyclic siloxanes.[181] The counter cation has been shown to be an

important factor in anionic ring opening polymerization, effecting the rate of

polymerization, the degree of polymerization, and the polydispersity of the final

polymer.[182] In these types of polymerizations, it is possible to control the molecular

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[177] Araki, T. and K. Ohsuga "Silicone rubber. III. Polymerization of cyclic dimethylsiloxane by ring opening." *Repts. Govt. Chem. Ind. Research Inst. Tokyo* **1955**, *50*, 161-171.Buechner, W., B. Degen, L. Fries, H. Judat, R. Mundil and K. H. Rudolph "Continuous manufacture of poly(diorganosiloxanes)." US, 1978.Sormani, P. M., R. J. Minton and J. E. McGrath "Anionic ring-opening polymerization of octamethylcyclotetrasiloxane in the presence of 1,3-bis(aminopropyl)-1,1,3,3-tetramethyldisiloxane." *ACS Symposium Series* **1985**, *286 (Ring-Opening Polymerization)*, 147-160.McGrath, J. E., P. M. Sormani, C. S. Elsbernd and S. Kilic "Kinetics, mechanisms, and synthesis studies of difuncitonal aminopropyl-terminated poly(dimethylsiloxane) oligomers." *Makromol. Chem., Macromol. Symp.* **1986**, *6*, 67-80.

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[180] Renkema, K. B., R. J. Matthews, T. L. Bush, S. K. Hendges, R. N. Redding, F. W. Vance, M. E. Silver, S. A. Snow and J. C. Huffman "The preparation of the mixed alkali metal silanolate K4Li4(OSiMe3)8-x and the effects of mixed alkali metals on the anion induced ring opening polymerization of octamethylcyclotetrasiloxane." *Inorg. Chim. Acta* **1996**, *244*, 185-190.

[181] McGrath, J. E., P. M. Sormani, C. S. Elsbernd and S. Kilic "Kinetics, mechanisms, and synthesis studies of difuncitonal aminopropyl-terminated poly(dimethylsiloxane) oligomers." *Makromol. Chem., Macromol. Symp.* **1986**, *6*, 67-80.Voorhoeve, R. J. H. "*Organohalosilanes: Precursors of Silicones"*; Elsevier: New York, 1967.Saam, J. C. "Formation of linear siloxane polymers." *Adv. Chem. Ser.* **1990**, *224 (Silicon-Based Polym. Sci.)*, 71-90.

[182] Saam, J. C. "Formation of linear siloxane polymers." *Adv. Chem. Ser.* **1990**, *224 (Silicon-Based Polym. Sci.)*, 71-90.

weight obtained by varying the amount of initiator to monomer, however broad molecular weight distributions are obtained due to the equilibrium nature of the polymerizations.

2.5.4   Living Anionic Polymerization of Siloxanes

In 1969, the living anionic polymerization of cyclic siloxane monomers was first achieved.[183]   While D_4 is not suitable for preparing well-defined polymers using living anionic polymerization, due to its unstrained character, it was found, in contrast, that the living anionic ring opening polymerization of D_3 was possible. This was attributed to the increased ring strain of the D_3 monomer in comparison with the larger cycles, which increased the reactivity. In general, the living anionic polymerization of D_3 is initiated using an alkyllithium reagent in a non-polar solvent such as cyclohexane at room temperature. This causes the formation of a monoadduct of initiator with D_3. DeSimone et al. confirmed the formation of this monoadduct using matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS).[184]   The reaction will not proceed further without the addition of a promoter to the solution.[185]   Upon addition of a promoter, the polymerization proceeds until all monomer has been consumed and is terminated.   Typical promoters for these polymerizations include tetrahydrofuran (THF),[186] diglyme,[187] triglyme, and dimethylsulfoxide (DMSO).[188]   All of the promotors

[183] Lee, C. L., C. L. Frye and O. K. Johansson "Selective polymerization of reactive cyclosiloxanes to give non-equilibrium molecular weight distributions. Monodisperse siloxane polymers." *Polym. Prepr.* **1969,** *10,* 1361-1367.

[184] Belu, A. M., J. M. DeSimone, R. W. Linton, G. W. Lange and R. M. Friedman "Evaluation of matrix-assisted laser desorption ionization mass spectrometry for polymer characterization." *J. Am. Soc. Mass Spectrom.* **1996,** *7,* 11-24.

[185] Frye, C. L., R. M. Salinger, F. W. G. Fearon, J. M. Klosowski and D. Y. T. "Reactions of Organolithium Reagents with Siloxane Substrates." *J. Org. Chem.* **1970,** *35,* 1308.

[186] Zilliox, J. G., J. E. L. Roovers and S. Bywater "Preparation and properties of polydimethylsiloxane and its block copolymers with styrene." *Macromolecules* **1975,** *8,* 573.

used for the anionic polymerization of D_3 are complexing agents for lithium cations. Their role is to reduce the amount of the originally formed silanolate aggregates to increase the rate of propagation to avoid side reactions.[189] However, it has been found that at conversions greater than 85% even D_3 polymerizations suffer from backbiting reactions.[190] Backbiting reactions consist of attack of the PDMS chains by their living ends and the formation of deactivated unstrained rings.[191] At high monomer concentrations, the reaction proceeds in a linear fashion, however, as the reactions approach high conversion, monomer starved conditions facilitate backbiting reactions.

Several methods have been developed to minimize or eliminate these deleterious side reactions. The simplest method employed is to terminate the reaction before side reactions can occur, typically at 80-85% conversion.[192] This is an effective method to deter these side reactions from occurring, however, this results in loss of yield. The use of cryptand [211] (Figure 2-3) as a ligating agent for the lithium cation also reduces the amount of equilibration reactions.[193] Addition of cryptand [211] causes the formation of

[187] Saam, J. C., D. Gordan and S. Lindsey "Block copolymers of polydimethylsiloxane and polystyrene." Ibid. **1970**, *3*, 1-4.
[188] Lee, C. L., C. L. Frye and O. K. Johansson "Selective polymerization of reactive cyclosiloxanes to give non-equilibrium molecular weight distributions. Monodisperse siloxane polymers." *Polym. Prepr.* **1969**, *10*, 1361-1367.
[189] Zundel, T., J. M. Yu, L. Lestel, D. Teyssie and S. Boileau "Trimethylsilylmethyllithium: a novel initiator for the anionic polymerization of cyclosiloxanes and vinyl monomers." *Macromol. Symp.* **1994**, *88*, 177-189.
[190] Juliano, P. C., W. A. Fessler and J. D. Cargioli "Proton magnetic resonance study of lithium silanolates. II. Effects of solvatin silanolates. II. Effects of solvating agent stoichiometry and temperature." *Polym. Prepr.* **1971**, *12*, 158-165.
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[192] Zilliox, J. G., J. E. L. Roovers and S. Bywater "Preparation and properties of polydimethylsiloxane and its block copolymers with styrene." *Macromolecules* **1975**, *8*, 573.Molenberg, A., H.-A. Klok, M. Moller, S. Boileau and D. Teyssie "Controlled Polymerization of Hexa-n-alkylcyclotrisiloxanes with long alkyl groups." *Macromolecules* **1997**, *30*, 792-794.
[193] Molenberg, A., H.-A. Klok, M. Moller, S. Boileau and D. Teyssie "Controlled Polymerization of Hexa-n-alkylcyclotrisiloxanes with long alkyl groups." *Macromolecules* **1997**, *30*, 792-794.Molenberg, A. and M. Moller "Polymerization of cyclotrisiloxanes by organolithium compounds and P2-Et base." *Macromol.*

cryptated lithium silanolate ion pairs, which suppresses aggregation of the chain ends and causes an increase in the interionic distance of the ion pairs.[194] This leads to a higher rate of polymerization than depolymerization and chain scrambling, thus avoiding the unwanted side reactions.[195] The propagation reaction is faster with the addition of cryptand [211] than with the addition of THF.[196] Therefore, with the use of the cryptand ligating agent reaction yields greater than 90% with less than 3% formation of cyclic oligomers were obtained.
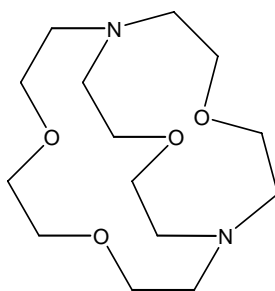
Figure 2-3. The structure of cryptand [211].

In a recent paper, Hadjichristidis has described a two-step protocol for the complete polymerization of D_3 without side reactions.[197] In the first step of the reaction, D_3 was initiated in benzene using *sec*-butyllithium at room temperature followed by the addition of an equal volume of THF to promote the polymerization. In this first step, the polymerization was allowed to proceed to 50% conversion at room temperature. For the

Chem. Phys. **1997**, *198*, 717-726.Boileau, S. "Anionic Polymerization of Cyclosiloxanes with Cryptates as Counterions". *Ring Opening Polymerization*; American Chemical Society: Washington, D. C., 1985.

[194] Boileau, S., P. Hemery, B. Kaempf, F. Schue and M. Viguier *J. Polym. Sci. Part B* **1974**, *12*, 217.Boileau, S., B. Kaempf, J. M. Lehn and F. Schue *J. Polym. Sci. Part B* **1974**, *12*, 203.Zundel, T., J. M. Yu, L. Lestel, D. Teyssie and S. Boileau "Trimethylsilylmethyllithium: a novel initiator for the anionic polymerization of cyclosiloxanes and vinyl monomers." *Macromol. Symp.* **1994**, *88*, 177-189.

[195] Boileau, S., P. Hemery, B. Kaempf, F. Schue and M. Viguier *J. Polym. Sci. Part B* **1974**, *12*, 217.Boileau, S., B. Kaempf, J. M. Lehn and F. Schue *J. Polym. Sci. Part B* **1974**, *12*, 203.

[196] Boileau, S. "Anionic Polymerization of Cyclosiloxanes with Cryptates as Counterions". *Ring Opening Polymerization*; American Chemical Society: Washington, D. C., 1985.

[197] Bellas, V., H. Iatrou and N. Hadjichristidis "Controlled Anionic Polymerization of Hexamethylcyclotrisiloxane. Model Linear and Miktoarm Star Co- and Terpolymers of Dimethylsiloxane with Styrene and Isoprene." *Macromolecules* **2000**, *33*, 6993-6997.

second step of the reaction, the temperature was lowered to –20 °C and the polymerization was allowed to proceed to completion before termination with an appropriate chlorosilane. THF was chosen as the promoter in this reaction due to its weak donor character that allows the reaction to proceed with few side reactions under the conditions stated.[198] These reaction conditions resulted in polymers with narrow polydispersities and conversions of ~100%.

Although siloxanes can be polymerized in a controlled fashion using living anionic techniques, PDMS homopolymer is a fluid at room temperature.[199] Therefore, in an effort to synthesize PDMS-polymers with dimensional stability, many investigators have targeted block, graft, and network polymers containing PDMS components. The use of living anionic polymerization facilitates the synthesis of well-defined block copolymer architectures. In 1988, Riffle described the synthesis of narrow distribution oxazoline/siloxane copolymers.[200] They were interested in these well-defined polymers because of the ability of the methyl groups on the backbone of the PDMS to provide a nonpolar sheath around the polymer. These model polymers were used to determine the parameters which control the surface structure, rate of attainment of that structure, and the dynamics of the structures as a function of environment of the orientation of PDMS toward an interface in a low energy air environment.

[198] Ibid.
[199] Miller, P. J. and K. Matyjaszewski "Atom Transfer Radical Polymerization of (Meth)acrylates from Poly(dimethylsiloxane) Macroinitiators." Ibid. **1999**, *32*, 8760-8767.
[200] Riffle, J. S., G. Sinai-Zingde, J. M. DeSimone, A. M. Hellstern, D. H. Chen and I. Yilgor "Narrow Distribution Oxazoline/Siloxane Copolymers." *Polym. Prepr.* **1988**, *29*, 93-96.

PDMS has also been copolymerized in both block and graft architectures with a variety of monomers, including ethylene,[201] styrene,[202] vinyl alcohol,[203] isobutylene,[204] and acrylates,[205], as well as others. Holohan et al. have described a variety of reactions that result in monofunctional poly(dimethylsiloxane) oligomers that may then be used for graft polymerizations.[206] PDMS has been used in several other synthetics routes including acting as a macroinitiator for the atom transfer radical polymerization of methacrylates,[207] as a macroinitiator for groups transfer polymerization of methacrylates,[208] in the synthesis of novel silicone magnetic materials,[209] in the synthesis

[201] Li, W. and B. Huang "Synthesis of polydimethylsiloxane macromonomer and its copolymerization with ethylene." *Makromol. Chem.* **1989**, *190*, 2373-2330.Hahn, S. F. and P. C. Vosejpka "Synthesis of Poly(ethylene-b-dimethylsiloxane-b-ethylene) by anionic polymerization and hydrogenation." *Polym. Prepr.* **1999**, *40*, 970.

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[203] Tezuka, Y., A. Fukushima and K. Imai "Synthesis of poly(vinyl alcohol)/poly(dimethylsiloxane) graft copolymer." *Makromol. Chem.* **1985**, *186*, 685-694.

[204] Wilczek, L., M. K. Mishra and J. P. Kennedy "The synthesis of poly(dimethylsiloxane-b-polyisobutylene-b-dimethylsiloxane) and poly(isobutylene-b-dimethylsiloxane) from alcohol-telechelic polysiobutylenes." *J. Macromol. Sci., Chem.* **1987**, *A24*, 1033-1049.

[205] Mason, J. P., T. Hattori and T. E. Hogen-Esch *ACS Div. Of Polym. Chem., Polym. Prepr.* **1989**, *30*, 259.Smith, S. D., J. M. DeSimone, H. Huang, G. York, D. W. Dwight, G. L. Wilkes and J. E. McGrath "Synthesis and characterization of poly(methyl methacrylate)-g-poly(dimethylsiloxane) copolymers. I. Bulk and surface characterization." *Macromolecules* **1992**, *25*, 2575.

[206] Holohan, A. T., M. H. George and J. A. Barrie "Monofunctional polydimethylsiloxane oligomers for graft copolymerization." *Macromol. Chem. Phys.* **1994**, *195*, 2965-2979.

[207] Miller, P. J. and K. Matyjaszewski "Atom Transfer Radical Polymerization of (Meth)acrylates from Poly(dimethylsiloxane) Macroinitiators." *Macromolecules* **1999**, *32*, 8760-8767.

[208] Hellstern, A. M., S. D. Smith and J. E. McGrath "Poly(methylmethacrylate)-poly(dimethylsiloxane) graft copolymers via sequential anionic and groups transfer copolymerization." *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*, 328-329.

[209] Riffle, J. S., M. Rutnakornpituk, M. Vadala, K. S. Wilson and J. Hoyt "Synthesis and Characterization of Novel Silicone Magnetic Materials." *Polym. Prepr.* **2000**, *41*, 1368.Stevenson, J. P., M. Rutnakornpituk, M. Vadala, A. R. Esker, S. W. Charles, S. Wells, J. P. Dailey and J. S. Riffle "Magnetic cobalt dispersions in poly(dimethylsiloxane) fluids." *J. Magn. Magn. Mater.* **2001**, *225*, 47-58.Rutnakornpituk, M., M. S. Thompson, L. A. Harris, K. E. Farmer, A. R. Esker and J. S. Riffle "Formation of cobalt nanoparticle dispersions in the presence of polysiloxane block copolymers." *Polymer* **2002**, *43*, 2337-2348.Vadala, M., M. S. Thompson, M. A. Zalich, T. G. St. Pierre and J. S. Riffle "Block copolysiloxanes and their complexation with cobalt nanoparticles." *Polymer* **2004**, *45*, 7449-7461.

of polyimide copolymers as potential aerospace materials,[210] and in the synthesis of model linear and miktoarm star co- and terpolymers.[211]

2.6   Synthesis of Star-Shaped Polymers

2.6.1   Introduction

Elucidation of structure-property relationships remains an ongoing field of study in polymer science. The introduction of long chain branching is known to affect polymer physical properties and processability as a result of changing the melt, solution, and solid-state properties of polymers.[212] It has been shown that branching results in a more compact structure in comparison to linear polymers of similar molecular weight, due to their high segment density, which alters the crystalline, mechanical, and viscoelastic properties of the polymer. While it is well-known that long chain branching greatly influences polymer physical properties, a fundamental understanding of structure-property relationships remains difficult due to the complexity of branched polymer structures. A branched polymer structure was described as a nonlinear polymer with multiple backbone chains radiating from junction points.[213] Star-shaped macromolecules constitute the simplest form of branched macromolecules, comprising only one branch point, and as such, have received significant attention in the elucidation of structure-

[210] Arnold, C. A., D. Chen, Y. P. Chen, J. D. Graybeal, R. H. Bott, T. Yoon, B. E. McGrath and J. E. McGrath "Polyimide-poly(dimethylsiloxane) segmented copolymers and polyblends as potential aerospace materials." *Polym. Mater. Sci. Eng.* **1988**, *59*, 934-940.

[211] Bellas, V., H. Iatrou and N. Hadjichristidis "Controlled Anionic Polymerization of Hexamethylcyclotrisiloxane. Model Linear and Miktoarm Star Co- and Terpolymers of Dimethylsiloxane with Styrene and Isoprene." *Macromolecules* **2000**, *33*, 6993-6997.Hadjichristidis, N. "Synthesis of Miktoarm Star Polymers." *J. Polym. Sci. Part A* **1999**, *37*, 857-871.

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[213] Roovers, J. E. L. "Branched polymers." *Encyclopedia of Polymer Science and Engineering*; Wiley: New York, 1985; pp 478.

property relationships.[214]   Although star polymers constitute the simplest branched structure, their synthesis remains challenging, and star polymers are often difficult to synthesize in a well-controlled manner.   Due to the complex nature of these macromolecules, controlled polymerization techniques, such as anionic,[215] cationic,[216] living free radical,[217] and group transfer (GTP) polymerization,[218] have typically been used to obtain well-defined star-shaped macromolecules.

Star polymers are typically synthesized using either a core-first approach, or an arm-first approach. In the core-first synthetic method, a multifunctional initiator is used and the number of arms is proportional to the number of functionalities on the initiator (Figure 2-4).[219]

[214] Hadjichristidis, N. "Synthesis of Miktoarm Star Polymers." *J. Polym. Sci. Part A* **1999**, *37*, 857-871.

[215] 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.

[216] 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, S. and J. P. Kennedy "Star Block Polymers of Multiple Polystyrene-b-Polyisobutylene Arms Radiating from a Polydivinylbenzene Core." *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2235-2243.

[217] 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*, 216-223.

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

[219] Zhang, X., J. Xia and K. Matyjaszewski "End-Functional Poly(t-butyl acrylate) Star Polymers by Controlled Radical Polymerization." *Macromolecules* **2000**, *33*, 2340-2345.
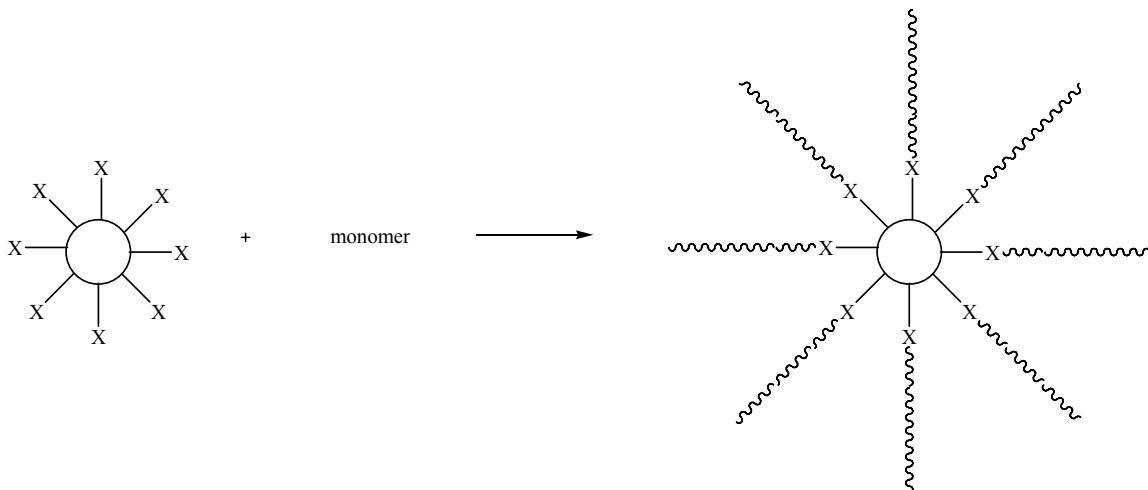
Figure 2-4. Synthesis of star-shaped polymers using the core-first method.

Using the core-first method, well-defined star-shaped macromolecules can be synthesized as long as initiation is rapid relative to propagation. While this approach was used in the first cationic synthesis of star-shaped polymers, containing three or four arms,[220] it tends to yield polymers with broadened molecular weight distributions.[221] In the arm-first synthetic method, linear arm polymers are synthesized and then coupled using a multifunctional linking agent or divinyl compound. In this case, the number of arms depends on the linking efficiency of the arm polymer to the multifunctional core and an alternative method is used to determine the number of arms (Figure 2-5). This approach is typically used in both living anionic and cationic syntheses of star-shaped polymers.[222]

[220] Mishra, M., B. Wang and J. P. Kennedy "Living carbocationic polymerization. IX. Three-arm star telechelic polyisobutylenes by C6H3(C(CH3)2OCH3)3/BCl3 complexes." *Polym. Bull.* **1987**, *17*, 307.
[221] Meneghetti, S. P., P. J. Lutz and D. Rein "Star-Shaped Polymers via Anionic Polymerization Methods." *Star and Hyperbranched Polymers*; Marcel Dekker: New York, 1999; pp 27.
[222] Ishizu, K. and K. 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.Storey, R. F., K. A. Shoemake and B. J. Crisholm "Synthesis and Characterization of Multi-Arm Star-Branched Polisobutylenes." *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 2003.

*= reactive chain end

DVB core
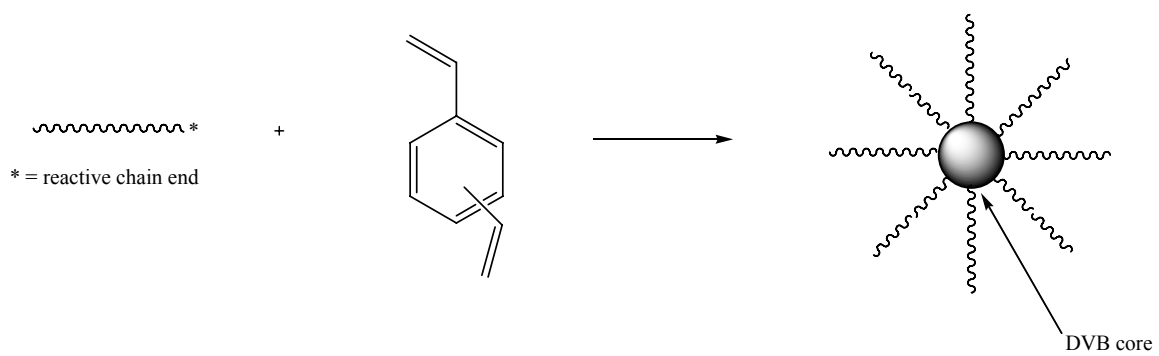
Figure 2-5. Synthesis of star-shaped polymers using the arm-first method.

As discussed previously, living anionic chain ends are very reactive and are used in a variety of chain end functionalization strategy. This characteristic of living chain ends makes living anionic polymerization ideal for the synthesis of complex architectures using chain end coupling reactions. The synthesis of star-shaped polymers using living anionic polymerization has been achieved using a variety of linking agents. Typical linking reagents for coupling of living anionic chain ends are chlorosilanes and their derivatives. However, these types of endcapping reagents are limited in their utility by the necessity for equal reactivity and accessibility of all reactives sites on the linking agent. Use of both silicon tetrachloride[223] and chloromethylated benzenes[224] have been hampered by these limiting factors. Other linking agents are dimethyl phthalate, trisallyloxytriazines, and divinylbenzene.[225] In some cases, the number of arms using the arm first approach is controlled by the number of functionalities on the linking agent, such as trichloromethylsilane or tetrachlorosilane. In other cases, such as divinylbenzene, the linking agent undergoes homopolymerization to form the core and the number of arms is greater than the functionality of the linker molecule.[226]

While the arm-first method is typically used in conjunction with living anionic polymerization to form well-defined star-shaped macromolecules, the core-first

[223] Morton, M., T. E. Helminiak, S. D. Gadkary and F. Bueche "Preparation and properties of monodisperse branched polystyrene." *J. Polym. Sci.* **1962**, *11*, 668.
[224] Wenger, F. and S. P. S. Yen "A simple process for controlled anionic polymerization. The preparation of monodisperse polystyrene." *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1961**, *2*, 295.
[225] 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.
[226] McGrath, J. E. "Anionic Polymerization: Kinetics, Mechanisms, and Synthesis". In *ACS Symposium Series*; American Chemical Society: Washington, D. C., 1981.

methodology has also been used. The core-first method requires the generation of a reactive core molecule prior to polymerization and this oftentimes leads to undesired coupling reactions between core molecules.[227] As the arms grow out from the core, the tendency to couple decreases. The main advantage to the core-first methodology is the ease of chain end functionalization at the star periphery. While star-shaped macromolecules synthesized using the arm-first method may be functionalized, the use of a protected functional initiator is generally required and will be discussed in detail in the next section. The advantages to a functionalized star-shaped macromolecule will also be discussed.

More recently, several of the techniques discussed above have been used in conjunction with one another to synthesize novel macromolecular architectures. For example, Muller et al. reported the use of both cationic and anionic polymerization to synthesize star-shaped block copolymers.[228] The polymerization of isobutylene was initiated using 1,3,5-tricumylchloride and terminated using diphenylethylene and methanol to yield a diphenylethylene methoxy group. This group was then transformed into an initiator for the anionic polymerization of methyl methacrylate using a K/Na alloy. Star-branched structures in which the arms are comprised of different polymer backbones were achieved using the arm-first approach and a difunctional diphenylethylene derivative. In this approach, the first monomer was polymerized using living anionic techniques and then terminated with the difunctional diphenylethylene derivative. The second monomer was then polymerized from the residual functionality on the

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

[228] Feldthusen, J., B. Ivan and A. 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.

diphenylethylene molecule to yield A_2B_2 type macromolecules. [229]   When macromolecules with less defined cores are synthesized, a variety of techniques have been employed, including the use of a bromomethylbenzene derivative in the synthesis of t-butyl methacrylate star-shaped macromolecules,[230] hyperbranched cores,[231] main chain functional graft sites, [232] and convergent coupling of arm polymers to synthesize dendritically branched polystyrene.[233]

2.6.2   Synthesis of Functional Star-Shaped Polymers

Chain-end functionalization is an additional challenge in the synthesis and characterization of complex polymer architectures.   As discussed previously, living anionic polymerization methodologies are typically used to synthesize star-shaped macromolecules due to the controlled nature of these reactions.   Functionalized alkyllithium initiators provide quantitative chain end functionalization and are an attractive alternative to electrophilic terminating reagents for the synthesis of chain-end functionalized polymers. Functionalized initiators facilitate the synthesis of telechelic and heterotelechelic polymers, functionalized block polymers, and star-shaped polymers

[229] Fernyhough, C. M., R. N. Young and R. D. Tack "Synthesis and Characterization of Polyisoprene-Poly(methylmethacrylate) AB Diblock and A2B2 Hteroarm Star Copolymers." Ibid. **1999**, *32*, 5760.

[230] Pitsikalis, M., S. Sioula, S. Pispas, 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 Polelectrolyte 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., Div. Polym. Chem.)* **1989**, *30*, 129.

[231] 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.

[232] Zhang, H. and E. Ruckenstein "Graft, Block-Graft, and Star Shaped Copolymers by an In Situ Coupling Reaction." Ibid. **1998**, *31*, 4753.

[233] Hsieh, H. L. and R. P. Quirk "*Anionic Polymerization: Principles and Practical Applications"*; Marcel Dekker: New York, 1996.

with functional groups on each arm terminus.[234] The use of the functional initiator 3-(t-butyldimethylsilyloxy)-1-propyllithium (tBDMSPrLi) was reported in the synthesis of a variety of polymers with various architectures, such as polyisoprene,[235] polybutadiene,[236] poly(methyl methacrylate),[237] and poly(1,3-cyclohexadiene)[238] to yield hydroxyl chain end functionalized polymers.

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[234] Quirk, R. P., S. H. Jang, H. Yang and Y. Lee "Polymer Synthesis Using Functionalized Alkyllithium Initiators: Telechelic, heterotelechelic and functionalized star-branched polymers." *Macromol. Symp.* **1998,** *132*, 281-291.

[235] Quirk, R. P., S. H. Jang and J. Kim "Recent Advances in Anionic Synthesis of Functionalized Elastomers using Functionalized Alkyllithium Initiators." *Rubber Rev., Rubber Chem. Tech.* **1996,** *69*, 444.Quirk, R. P., S. H. Jang, K. Han, H. Yang, B. Rix and Y. Lee "Anionic Synthesis of Hydroxyl-Functionalized Polymers Using Protected, Functionalized Alkyllithium and Isoprenyllithium Initiators". *Functional Polymers*, 1998; pp 71-84.Quirk, R. P. and R. T. Mathers "Surface-initiated living anionic polymerization of isoprene using a 1,1-diphenylethylene derivative and functionalization with ethylene oxide." *Polym. Bull.* **2001,** *45*, 471-477.Switek, K. A., F. S. Bates and M. A. Hillmyer "Star Polymer Synthesis Using Hexafluoropropylene Oxide as an Efficient Multifunctional Coupling Agent." *Macromolecules* **2004,** *37*, 6355-6361.Quirk, R. P., J. J. Ma, G. Lizarraga, Q. Ge, H. Hasegawa, Y. J. Kim, S. H. Jang and Y. Lee "Anionic synthesis of hydroxy-functionalized polymers using functionalized intiators and electrophilic termination." *Macromol. Symp.* **2000,** *161*, 37-44.Hudelson, C. L., K. Yamauchi and T. E. Long "Unique combinations of macromolecular topology and functionality." *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2002,** *43*, 485-486.Elkins, C. L., K. Yamauchi and T. E. Long "Synthesis and characterization of self-complementary multiple hydrogen bonding poly(isoprene) star polymers." *Polym. Prepr.* **2003,** *44*, 576-577.

[236] Quirk, R. P., S. H. Jang, H. Yang and Y. Lee "Polymer Synthesis Using Functionalized Alkyllithium Initiators: Telechelic, heterotelechelic and functionalized star-branched polymers." *Macromol. Symp.* **1998,** *132*, 281-291.Quirk, R. P., S. H. Jang and J. Kim "Recent Advances in Anionic Synthesis of Functionalized Elastomers using Functionalized Alkyllithium Initiators." *Rubber Rev., Rubber Chem. Tech.* **1996,** *69*, 444.Quirk, R. P. and S. H. Jang "Anionic Synthesis of Hydroxy-Functionalized Polybutadienes Using Protected, Functionalized Organolithium Initiators." *Polym. Mater. Sci. Eng.* **1997,** *76*, 8-9.Quirk, R. P., S. H. Jang, K. Han, H. Yang, B. Rix and Y. Lee "Anionic Synthesis of Hydroxyl-Functionalized Polymers Using Protected, Functionalized Alkyllithium and Isoprenyllithium Initiators". *Functional Polymers*, 1998; pp 71-84.Quirk, R. P., J. J. Ma, G. Lizarraga, Q. Ge, H. Hasegawa, Y. J. Kim, S. H. Jang and Y. Lee "Anionic synthesis of hydroxy-functionalized polymers using functionalized intiators and electrophilic termination." *Macromol. Symp.* **2000,** *161*, 37-44.Hwang, J., M. D. Foster and R. P. Quirk "Synthesis of 4-, 8-, 12-arm star-branched polybutadienes with three different chain-end functionalities using a functionalized initiator." *Polymer* **2004,** *45*, 873-880.

[237] Quirk, R. P. and R. S. Porzio "The Anionic Synthesis of Functionalized Linear and Star-branced Poly(methyl methacrylates) Using Protected Hydroxy-Functionalized Alkyllithium Initiators." *Polym. Prepr.* **1997,** *38*, 463-464.Mizawa, T., K. Takenaka and T. Shiomi "Synthesis of alpha-Maleimide-omega-Dienyl Heterotelechelic Poly(methyl methacrylate) and Its Cyclization by the Intramolecular Diels-Alder Reaction." *J. Polym. Sci. Part A* **2000,** *38*, 237-246.Tong, J.-D., C. Zhou, S. Ni and M. A. Winnik "Synthesis of Meth(acrylate) Diblock Copolymers Bearing a Fluorescent Dye at the Junction Using A Hydroxyl-Protected Initiator and the Combination of Anionic Polymerization and Controlled Radical Polymerization." *Macromolecules* **2001,** *34*, 696-705.

[238] Quirk, R. P., F. You, C. Wesdemiotis and M. A. Arnould "Anionic Synthesis and Characterization of omega-Hydroxyl-Functionalized Poly(1,3-Cyclohexadiene)." *Macromolecules* **2004,** *37*, 1234-1242.

While living anionic polymerization using functional initiation has proven an excellent pathway to chain-end functional polymers, other researchers have reported various methodologies for the preparation of star-shaped macromolecules with diverse chain-end functionalities. Hedrick et al. reported the core-first synthesis of star-shaped poly(ε-caprolactone) hydroxyl terminated macroinitators with six arms using ring opening polymerization and the subsequent transformation into atom transfer radical polymerization (ATRP) initiators.[239] The macroinitiators were then used to polymerize several monomers, including methyl methacrylate, hydroxyethyl methacrylate, or ethylene oxide. In a similar fashion, using living cationic polymerization, Gnanou and coworkers synthesized star-shaped polystyrenes and used functional group transformation to transform the chain-end functionality to either hydroxyl of amino at the periphery.[240] The hydroxyl terminated samples were also utilized as macroinitiators for ethylene oxide polymerization. In several cases, ATRP was used in acrylic polymerizations to yield polymers with hydroxyl[241], epoxy, amino, bromide, or cyano functionalized star polymers.[242] Utilizing a different approach, Hirao et al. have introduced functionality to star polymers using living anionic polymerization in conjunction with functionalized diphenylethylene (DPE) derivatives and organic functional group transformations.[243]

[239] Hedrick, J. L., M. Trollsas, C. J. Hawker, B. Atthoff, H. Claesson, A. Heise, R. D. Miller, D. Mecerreyes, R. Jerome and P. Dubois "Dendrimer-like Star Block and Amphiphilic Copolymers by Combination of Ring Opening and Atom Transfer Radical Polymerization." Ibid. **1998**, *31*, 8691-8705.
[240] Cloutet, E., J.-L. Fillaut, D. Astruc and Y. Gnanou "Star Block Copolymers and Hexafullerene Star via Derivatization of Star-Shaped Polystyrenes." Ibid. **1999**, *32*, 1043-1054.
[241] Coessens, V., J. Pyun, P. J. Miller, S. G. Gaynor and K. Matyjaszewski "Functionalization of polymers prepared by ATRP using radical addition reactions." *Macromol. Rapid Commun.* **2000**, *21*, 103-109.
[242] Zhang, X., J. Xia and K. Matyjaszewski "End-Functional Poly(t-butyl acrylate) Star Polymers by Controlled Radical Polymerization." *Macromolecules* **2000**, *33*, 2340-2345.
[243] Hayashi, M., K. Kojima and A. Hirao "Synthesis of Star-Branched Polymers by Means of Anionic Living Polymerization Coupled with Functional Group Transformation." Ibid. **1999**, *32*, 2425-2433.Hirao, A., M. Hayashi and N. Haraguchi "Synthesis of well-defined functionalized polymers and star branched polymers by means of living anionic polymerization using specially designed 1,1-diphenylethylene derivatives." *Macromol. Rapid Commun.* **2000**, *21*, 1171-1184.Hirao, A., M. Hayashi, S. Loykulnant, K.

Using this approach, functionality was introduced at the α-terminus, at block junctions, or at the core. Quirk et al. pioneered this work and Hirao et al. based their research on this work.[244] Fréchet and Hawker et al. have also recently reported the use of nitroxide mediated polymerization in the synthesis of functionalized star polymers.[245] They recently reported the synthesis of a series of compounds, ranging from simple to complex, and have focused on homo, block, and random copolymers with both apolar and polar vinylic repeat units and functional group integration in diverse positions. Ishizu et al. have also reported on the functionalization of polyisoprene star polymers with p-chloro styrene to yield a periphery of reactive styrene groups, capable of forming a crosslinked network.[246]

While both functional polymers and star-shaped polymers are prevalent in the literature, the combination of well-defined thermoreversible chain end interactions, such as multiple hydrogen bonding interactions, and star-shaped macromolecules is limited. Hadjichristidis et al. studied the synthesis and characterization of well-defined linear and star-shaped polystyrenes, polyisoprenes, and polybutadienes bearing both sulfo- and phosphoro-zwitterionic groups, which have a thermoreversible nature.[247] While these

Sugiyama, S. W. Ryu, N. Haraguchi, A. Matsuo and T. Higashihara "Precise syntheses of chain-multi-functionalized polymers, star-branched polymers, star-linear block polymers, densely branched polymers, and dendritic branched polymers based on iterative approach using functionalized 1,1-diphenylethylene derivatives." *Prog. Polym. Sci.* **2005**, *30*, 111-182.

[244] Quirk, R. P. "Scope and limitations of 1,1-diphenylethylene chemistry in anionic polymer synthesis." *Makromol. Chem., Macromol. Symp.* **1992**, *63*, 259-269.Quirk, R. P., T. Yoo and B. Lee "Anionic synthesis of heteroarm, star-branched polymers. Scope and limitations." *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 911-926.Hsieh, H. L. and R. P. Quirk "*Anionic Polymerization: Principles and Practical Applications"*; Marcel Dekker: New York, 1996.

[245] Bosman, A. W., R. Vestberg, A. Heumann, J. M. J. Frechet and C. J. Hawker "A Modular Approach toward Functionalized Three-Dimensional Macromolecules: From Synthetic Concepts to Practical Applications." *J. Am. Chem. Soc.* **2003**, *125*, 715-728.

[246] Ishizu, K., H. Kitano, T. Ono and S. Uchida "Synthesis and characterization of polyfunctional star-shaped macromonomers." *Polymer* **1999**, *40*, 3229-3232.

[247] Hadjichristidis, N., S. Pispas and M. Pitsikalis "End-Functionalized polymers with zwitterionic end-groups." *Prog. Polym. Sci.* **1999**, *24*, 875-915.Pispas, S., G. Floudas and N. Hadjichristidis "Microphase

studies have made great strides in delineating structure-property relationships for these materials, the reversible interaction is ionic and it is anticipated that their behavior will significantly differ from a multiple hydrogen bonding interaction. Meijer et al. have recently reported the synthesis of model low molar mass poly(ethylene oxide-*co*-propylene oxide) three arm star polymers bearing pendant quadruple hydrogen bonding functionalities.[248] These polymers were compared with three arm star polymers bearing urea chain ends, non-functional chain ends, and with a chemically crosslinked network and the influence of chain end functionality was studied. However, due to the hydrophilic nature of the parent polymer, the effect of atmospheric moisture on the polymer physical properties was not excluded. The introduction of thermally reversible interactions at the chain ends of star-shaped polymers is only one of the interesting families to which chain end functionalized polymers serve as a precursor. Organic functional groups, such as hydroxyl and amino, serve as stepping stones to diverse and rich functionalization strategies.

Separation in ABC Block Copolymers with a Short but Strongly Interacting Middle Block." *Macromolecules* **1999**, *32*, 9074-9077.Pispas, S. and N. Hadjichristidis "Synthesis and Dilute Solution Properties of Styrene-Isoprene Diblock Copolymers with Mesogenic-Zwitterionic End Groups." *Macromolecules* **2000**, *33*, 6396-6401.Pispas, S. and N. Hadjichristidis "Block copolymers with zwitterionic groups at specific sites: synthesis and aggregation behavior in dilute solutions." *J. Polym. Sci. Part A* **2000**, *38*, 3791-3801.Vlassopoulos, D., M. Pitsikalis and N. Hadjichristidis "Linear Dynamics of End-Functionalized Polymer Melts: Linear Chains, Stars, and Blends." *Macromolecules* **2000**, *33*, 9740-9746.Charalabidis, D., M. Pitsikalis and N. Hadjichristidis "Model linear and star-shaped polyisoprenes with phosphatidylcholine analogous end-groups, synthesis and association behavior in cyclohexane." *Macromol. Chem. Phys.* **2002**, *203*, 2132-2141.Sakellariou, G., S. Pispas and N. Hadjichristidis "Model omega-functionalized linear polystyrenes with one, two, and three sulfobetaine end grups: Synthesis, characterization, and association behavior." *Macromol. Chem. Phys.* **2003**, *204*, 146-154.
[248] Lange, R. F. M., M. van Gurp and E. W. Meijer "Hydrogen-Bonded Supramolecular Polymer Networks." *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 3657-3670.

2.7 Macromolecular Systems Involving Multiple Hydrogen Bonding

2.7.1 Introduction

The conventional synthesis of macromolecules involves either step-growth or chain polymerization to form repeat units joined by irreversible stable covalent bonds. High molecular weights of these irreversibly connected systems are desired to optimize physical properties and commercial utility. However, as molecular weight increases, the polymer melt viscosity increases as the 3.4 power of the weight average molecular weight.[249] Increased melt viscosity compromises potential solvent-free manufacturing, melt processability, thermal stability, and solubility of the final products. Although high molecular weight is necessary to obtain desired physical properties, the melt viscosity becomes increasingly prohibitive as molecular weight increases. Thermoreversible polymers present a possible solution to this dilemma. Ideally, at typical use temperatures, up to 150 °C, the reversible interaction would remain stable, but at melt processing temperatures, typically 275 °C for polyesters and polyamides, the interaction would become unstable, causing the polymer to dissociate into low molecular weight oligomers. This idealized macromolecule would have both the desired physical properties derived from high molecular weight polymers and low melt viscosity during processing and manufacturing. Several systems are currently under study as possible alternatives to the current irreversible synthetic routes, including hydrogen bonding, ionic interactions, as well as systems triggered by light and pH. The use of hydrogen bonding interactions in polymer synthesis will be detailed below.

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[249] Billmeyer, F. W. J. "*Textbook of Polymer Science"*; John Wiley & Sons: New York, 1984.

Lehn first introduced the idea of supramolecular chemistry in 1973 when he defined supramolecular chemistry as "chemistry beyond the molecule", and described molecules of higher complexity resulting from the association of two or more species by intermolecular forces.[250] Lehn's interest in supramolecular chemistry began with the complexation chemistry of alkali cations and has since expanded into a large number of related areas, such as anion coordination chemistry, coreceptor molecules with multiple recognition sites, supramolecular reactivity and catalysis, transport processes and carrier design, and others.[251] Lehn's work has provided the basis for a broad range of supramolecular investigations and the birth of a new type of molecule.

In recent years, hydrogen bonding interactions have received significant attention due to their reversible nature and the novel polymeric systems that are derived from these interactions.[252] These types of systems were shown to exhibit polymer-like properties both in solution and in the bulk from materials comprised of monomeric units reversibly bound by secondary hydrogen bonding interactions.[253] While hydrogen bonding

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[250] Lehn, J. M. "Supramolecular Chemistry-Scope and Perspectives Molecules, Supermolecules, and Molecular Devices (Nobel Lecture)." *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 89-112.Lehn, J. M. "Design to organic complexing agents. Strategies towards properties." *Structure and Bonding* **1973**, *16*, 1-69.

[251] Lehn, J. M. "Supramolecular Chemistry-Scope and Perspectives Molecules, Supermolecules, and Molecular Devices (Nobel Lecture)." *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 89-112.

[252] Brunsveld, L., B. J. B. Folmer, E. W. Meijer and R. P. Sijbesma "Supramolecular Polymers." *Chem. Rev.* **2001**, *101*, 4071-4097.Lehn, J. M., M. Mascal, A. DeCian and J. Fischer "Molecular recognition directed self-assembly of ordered supramolecular strands by cocrystallization of complementary molecular components." *Chem. Commun.* **1990**, *6*, 479-481.Lehn, J. M. "Perspectives in Supramolecular Chemistry-From Molecular Recognition towards Molecluar Informoation Processing and Self-Organization." *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1304-1319.Sherrington, D. C. and K. A. Taskinen "Self-assembly in synthetic macromolecular systems via multiple hydrogen bonding interactions." *Chem. Soc. Rev.* **2001**, *30*, 83-93.Ciferri, A. "Supramolecular Polymers"; Marcel Dekker: New York, 2000.Bong, D. T., T. D. Clark, J. R. Granje and M. R. Ghadiri "Self-assembling organic nanotubes." *Angew. Chem. Int. Ed.* **2001**, *40*, 988-1011.Rowan, A. E. and R. J. M. Nolte "Helical molecular programming." *Angew. Chem. Int. Ed.* **1998**, *37*, 63-68.

[253] Brunsveld, L., B. J. B. Folmer, E. W. Meijer and R. P. Sijbesma "Supramolecular Polymers." *Chem. Rev.* **2001**, *101*, 4071-4097.

interactions are known to affect polymer properties in such systems as polyurethanes[254] and polypeptides[255], more recent studies have focused on the use of elegant hydrogen bonding arrays in macromolecular design.[256] The use of these arrays in conjuction with irreversible, stable covalent bonding in polymer synthesis has yielded materials with novel thermally reversible properties. The strength and directionality of the interactions were tuned using the ability to design the desired geometry of the hydrogen bonding array.

Two main categories of multiple hydrogen bonding interactions exist in the literature. The first involves synthesis of small molecules with hydrogen bond functionality of two or greater. These small molecules self-assemble into a polymer-like structure based completely on hydrogen bonding interactions and are termed supramolecular polymers. [257] The second category couples hydrogen bonding interactions with conventional polymer chemistry, in which polymeric materials synthesized with covalent bonds are functionalized in some way with reversible hydrogen bonding interactions. The second category will be the focus of the majority of this review, although interesting examples from the first category will also be discussed. Polymers were functionalized with hydrogen bonding groups in a variety of ways, including terminal functionalization, both telechelic and monofunctional, as well as

[254] McKeirnan, R. L., A. M. Heintz, S. L. Hsu, E. D. T. Atkins, J. Pennelle and S. P. Gido "Influence of Hydrogen Bonding on the Crystallization Behavior of Semicrystalline Polyurethanes." *Macromolecules* **2002**, *35*, 6970-6974.

[255] Aggeli, A., M. Bell, N. Boden, J. N. Keen, P. F. Knowles, T. C. B. McLeish, M. Pitkeathly and S. E. Radford "Responsive gels formed by the spontaneous self-assembly of peptides into polymeric beta-sheet tapes." *Nature* **1997**, *386*, 259-262.

[256] Brunsveld, L., B. J. B. Folmer, E. W. Meijer and R. P. Sijbesma "Supramolecular Polymers." *Chem. Rev.* **2001**, *101*, 4071-4097.

[257] Lehn, J. M. "Perspectives in Supramolecular Chemistry-From Molecular Recognition towards Molecluar Informoation Processing and Self-Organization." *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1304-1319.

random functionalization of the polymer backbone. The incorporation of hydrogen bonding interactions with polymer chemistry yields a large class of interesting polymeric materials, which will be detailed below.

2.7.2 Nature of the Hydrogen Bonding Interaction

In general, hydrogen bonding interactions exist between a donor (A) and an acceptor (D). An acceptor is typically an electronegative atom possessing lone pair(s) of electrons, such as oxygen, nitrogen, or fluorine. A donor is typically a hydrogen atom bonded to an electrogenative atom, such as oxygen, nitrogen, or sulfur. The polarized nature of the bond between the hydrogen and the electronegative atom results in charge separation and an electropositive hydrogen. This electropositive hydrogen (D) is attracted to the electronegative atom (D) causing the formation of a hydrogen bond. The strength of this type of interaction is affected by a variety of factors, including acid/base strength, conformation, temperature, solvent, and humidity. It was shown that the acidity of the donor and the basicity/nucleophilicity of the acceptor play a significant role in the strength of the hydrogen bonding interaction.[258] Very weak acidic/basic interactions yield weaker overall hydrogen bonding interactions, while very strong acid/base interactions may result in a neutralization reaction and the formation of an ion pair. The nature of the electrostatic attractive and repulsive interactions of hydrogen bonds was explored by Coleman et al.[259]

[258] Beijer, F. H., R. P. Sijbesma, J. A. J. M. Vekemans, E. W. Meijer, H. Kooijman and A. L. Spek "Hydrogen-Bonded Complexes of Diaminopyridines and Diaminotriazines: Opposite Effect of Acylation on Complex Stabilities." *J. Org. Chem.* **1996**, *61*, 6371-6380.Kawakami, T. and T. Kato "Use of intermolecular hydrogen bonding between imidazolyl moieties and carboxylic acids for the supramolecular self-association of liquid-crystalline side-chain polymers and networks." *Macromolecules* **1998**, *31*, 4475-4479.
[259] Coleman, M. M., J. F. Graf and P. C. Painter "*Specific Interactions and the Miscibility of Polymer Blends*"; Technomic Pub. Co.: Lancaster, PA, 1991; 495.

The conformation of the hydrogen bonding array also plays a role in the strength of the hydrogen bonding interaction. Ideally, the hydrogen bond prefers to exist in a linear conformation between the heteroatoms, however, deviations from this preferred conformation are common due to constraints imparted by the larger molecular system. This preferred conformation for a hydrogen bond results in the ultimate directionality associated with hydrogen bonding interactions, in which associated donor-acceptor pairs prefer a specific orientation with respect to each other. The presence of hydrogen bonding sites on a polymeric backbone do not inherently fulfill the requirements for directional self-assembly. When no directionality is present, most hydrogen bonding materials will form microphases or gelation will occur.[260] However, when a unidirectional hydrogen bonding system is incorporated into the polymer backbone, the required self-assembly can be induced to form a thermally reversible polymer.

The strength of the hydrogen bonding interaction and the state of the equilibrium between associated and dissociated hydrogen bonds is also largely affected by environmental factors. Thermal energy is sufficient to dissociate single hydrogen bonds and create a thermodynamic equilibrium between associated and dissociated states. An increase in temperature shifts the equilibrium from associated to dissociated species. Solvent polarity also directly impacts the strength of the hydrogen bonding interaction. Deans et al. showed that solvent polarity has a large impact on hydrodynamic volume of polymers containing hydrogen bonding groups.[261] Water has also been shown to greatly influence hydrogen bonding interactions, and in general, shifts the equilibrium largely to

[260] Sijbesma, R. P., F. H. Beijer, B. J. B. Folmer, J. H. K. K. Hirschberg, R. F. M. Lange, J. K. L. Lowe and E. W. Meijer "Reversible Polymers Formed from Self-Complementary Monomers Using Quadruple Hydrogen Bonding." *Science* **1997**, *278*, 1601-1604.
[261] Deans, R., F. Ilhan and V. M. Rotello "Recognition-Mediated Unfolding of a Self-Assembled Polymeric Globule." *Macromolecules* **1999**, *32*, 4956-4960.

dissociated molecules and any properties derived from the hydrogen bonding interactions are generally lost.[262]

In general, hydrogen bonds have dissociation energies ranging from 1-10 kcal/mol, in contrast to covalent bonds which are typically on the order of 70-110 kcal/mol.[263] Due to this large difference in bond energies, distinct differences in the behaviors of hydrogen-bonded versus covalently bonded systems are observed. As discussed previously, hydrogen bonds are dissociated using thermal energy. Because of the large bond energies of covalent systems, the bonds are not generally dissociated using thermal energy. Due to the static nature of the covalent bond, kinetically favored structures are often obtained, rather than thermodynamic, as one would expect from thermally reversible, dynamic systems. While single hydrogen bonds are typically weak, the strength of hydrogen bonding interactions may be bolstered using multiple hydrogen bonding interactions. Supramolecular polymers resulting from multiple hydrogen bonding interactions were reported and have properties similar to covalent polymers, while materials from single hydrogen bonding interactions show little property enhancement.[264] The strength of hydrogen bonding interactions is often measured using the association constant (K_a), which is defined as the equilibrium between the associated and dissociated states. While single hydrogen bonds have a low association constant, increasing the number of hydrogen bonds in concert generally increases the association constant. Systems ranging from single to quadruple hydrogen bonds were well-studied

[262] Sontjens, S. H. M., R. P. Sijbesma, M. H. P. Genderen and E. W. Meijer "Stability and Lifetime of Quadruply Hydrogen Bonded 2-Ureido-4[1H]-pyrimidinone Dimers." *J. Am. Chem. Soc.* **2000**, *122*, 7487-7493.Lange, R. F. M., M. van Gurp and E. W. Meijer "Hydrogen-Bonded Supramolecular Polymer Networks." *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 3657-3670.

[263] Coleman, M. M., J. F. Graf and P. C. Painter "*Specific Interactions and the Miscibility of Polymer Blends*"; Technomic Pub. Co.: Lancaster, PA, 1991; 495.

[264] Brunsveld, L., B. J. B. Folmer, E. W. Meijer and R. P. Sijbesma "Supramolecular Polymers." *Chem. Rev.* **2001**, *101*, 4071-4097.

and will be discussed in this section and systems based on larger arrays containing both six[265] and eight[266] hydrogen bonds were also synthesized and characterized.

2.7.3 Systems Involving a Single Hydrogen Bond

2.7.3.1 Supramolecular Systems

Although single hydrogen bonds have a relatively weak interaction, several supramolecular systems were described in which liquid crystalline properties were observed from these types of hydrogen bonding interactions. Kato and Frechet reported the discovery of simple, single stranded, highly directional hydrogen bonds characterized by liquid crystallinity of the resulting materials.[267] In these early works, a variety of low molecular weight liquid crystalline complexes were prepared using these singly directional hydrogen bonds. This concept was then expanded to supramolecular systems.[268] They first proposed a mesogenic structure consisting of 2 components, 4-butoxybenzoic acid as the hydrogen bonding donor and trans-[(4-ethoxybenzoyl)oxy]-4'-stilbazole as the hydrogen bonding acceptor, as illustrated in Figure 2-6. Using this donor-acceptor pair, liquid crystalline systems were synthesized from non-liquid crystalline components.

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[265] Zeng, H., R. S. Miller, R. A. Flowers, II and B. Gong "A highly stable, six-hydrogen-bonded molecular duplex." *J. Am. Chem. Soc.* **2000***, 122*, 2635-2644.

[266] Folmer, B. J. B., R. P. Sijbesma, H. Kooijman, A. L. Spek and E. W. Meijer "Cooperative Dynamics in Duplexes of Stacked Hydrogen-Bonded Moieties." Ibid. **1999***, 121*, 9001-9007.

[267] Kato, T. and J. M. J. Frechet "A new approach to mesophase stabilization through hydrogen bonding molecular interactions in binary mixtures." Ibid. **1989***, 111*, 8533-8534.Kato, T. and J. M. J. Frechet "Stabilization of a liquid-crystalline phase through noncovalent interaction with a polymer side chain." *Macromolecules* **1989***, 22*, 3818-3819.Kato, T. and J. M. J. Frechet "Stabilization of a liquid-crystalline phase through noncovalent interaction with a polymer side chain." *Macromolecules* **1990***, 23*, 360.

[268] Kato, T. and J. M. J. Frechet "Hydrogen Bonding and the Self-Assembly of Supramolecular Liquid-Crystalline Materials." *Macromol. Symp.* **1995***, 98*, 311-326.Kato, T., N. Hirota, A. Fujishima and J. M. J. Frechet "Supramolecular hydrogen-bonded liquid-crystalline polymer complexes. Design of side-chain polymers and a host-guest system by noncovalent interaction." *J. Polym. Sci. A* **1996***, 34*, 57-62.Kihara, H., T. Kato, T. Uryu and J. M. J. Frechet "Supramolecular Liquid-Crystalline Networks Built by self-assembly of multifunctional hydrogen-bonding molecules." *Chem. Mater.* **1996***, 8*, 961-968.
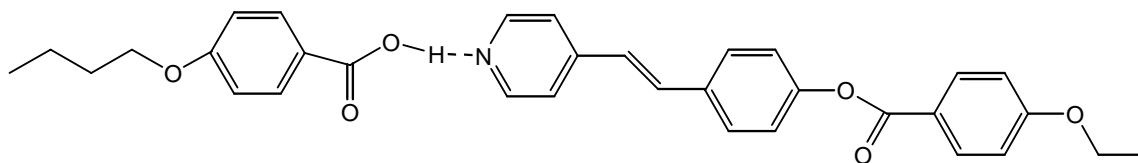
Figure 2-6. An example of directional single hydrogen bonding incorporated into a liquid crystalline polymer.

Using a similar type of interaction, Griffin et al. reported liquid crystalline behavior when a bis(pyridine) and a dicarboxylic acid were mixed together.[269] However, this system was described as highly dynamic due to the weakness of the single hydrogen bond and the subsequent material behavior was more similar to a small molecule system than a polymeric system. When this type of interaction was applied to a different system, distinctly different behavior was observed. In contrast to difunctional pyridine molecules interacting with difunctional carboxylic acid to theoretically form a high molecular weight linear supramolecular polymer, Griffin et al. instead utilized a tetrafunctional pyridyl compound with difunctional benzoic acid derivatives, Figure 2-7.[270] The formation of a network-like structure led to significant mechanical properties, including the ability to form fibers from the melt, presence of a T_g, and observance of broad crystallization and melting transitions in DSC characterization. The authors described the mixtures as similar to an A_2B_4 polycondensation reaction and investigation of the hydrogen bonding using infrared spectroscopy revealed significant coordination persisted above 100 °C. Extending this motif further, Jaunky et al. reported the incorporation of pyridyl groups into a calix[4]arene to yield a tetrafunctional molecule. This

[269] Bladon, P. and A. C. Griffin "Self-assembly in living nematics." *Macromolecules* **1993**, *26*, 6604-6610.Lee, C.-M., C. P. Jariwala and A. C. Griffin "Heteromeric liquid-crystalline association chain polymers: structure and properties." *Polymer* **1994**, *35*, 4550-4554.
[270] St. Pourcain, C. B. and A. C. Griffin "Thermoreversible Supramolecular Networks with Polymeric Properties." *Macromolecules* **1995**, *28*, 4116-4121.

functionalized calixarene molecule was found to complex with 4,4'-biphenol to yield infinite chains.[271] Using similar components, namely tartaric acid derivatives and bipyridine units, several groups have described the formation of hydrogen-bonded, chiral main-chain liquid crystalline polymers.[272]

[271] Jaunky, W., M. W. Hosseini, J. M. Plaeix, A. deCian, N. Kyritsakas and J. Fischer "Molecular braids: quintuple helical hydrogen bonded molecular network." *Chem. Commun.* **1999**, 2313-2314.
[272] Singh, A., Y. Lvov and S. B. Qadri "Formation of Supramolecular Assemblies by Complementary Assocation of Octadecyloxy Tartaric Acid and Bispyridyls." *Chem. Mater.* **1999**, *11*, 3196-3200.He, C., C.-M. Lee, A. C. Griffin, L. Bouteiller, N. Lacoudre, S. Boileau, C. Fouquey and J. M. Lehn "Chirality in some liquid crystalline association chain polymers." *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **1999**, *332*, 2761-2768.
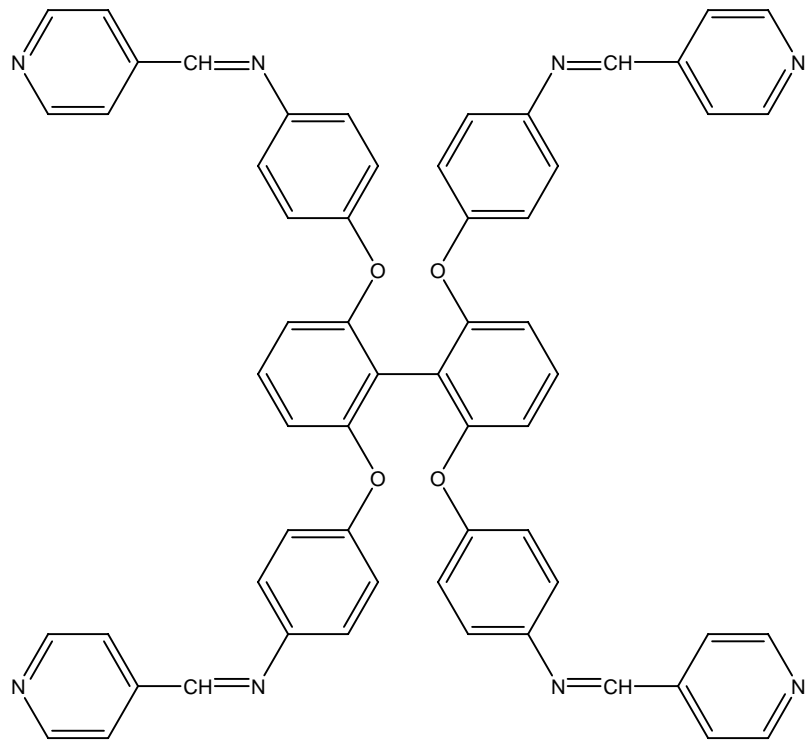
Figure 2-7. Tetrafunctional pyridyl compound involved in single hydrogen bonding with carboxylic acids.

2.7.3.2 Polymeric Systems

Based upon the pyridine/carboxylic acid motif described above, Fréchet and Kato et al. have described this type of interaction to synthesize a variety of linear and side-chain polymers and networks.[273] Specifically, polyacrylates and polysiloxanes were functionalized with pendant benzoic acid groups. When these polymers were mixed with stilbazoles, stable mesophases were observed due to the self-assembly of these molecules. Using a similar interaction, Lee et al. developed supramolecular rod-coil polymers based on the self-assembly of 4.4'-bipyridines with benzoic acid chain end functionalized polypropylene oxides.[274] These mixtures showed highly ordered liquid crystalline phases.

McKeirnan et al. studied the influence of hydrogen bonding on the crystallization behavior of polyurethanes using TEM, SAXS, and FTIR studies.[275] The polyurethanes were synthesized from long chain aliphatic diols with up to 32 methylene units and aliphatic diisocyantes with up to 12 methylene units. It was hypothesized that the long alkyl chains would dominate the crystallization behavior, however, it was found that hydrogen bonding played an important role, influencing the interchain spacing and the intersheet spacing. Investigation of the amide I region of the FTIR spectra showed that in

[273] Kawakami, T. and T. Kato "Use of intermolecular hydrogen bonding between imidazolyl moieties and carboxylic acids for the supramolecular self-association of liquid-crystalline side-chain polymers and networks." *Macromolecules* **1998**, *31*, 4475-4479.Kumar, U., T. Kato and J. M. J. Frechet "Use of Intermolecular Hydrogen Bonding for the Induction of Liquid Crystallinity in the Side Chain of Polysiloxanes." *J. Am. Chem. Soc.* **1992**, *114*, 6630-6639.Kato, T., H. Kihara, U. Kumar, T. Uryu and J. M. J. Frechet "Synthesis of a liquid-crystalline polymer network by self-organization via intermolecular hydrogen bridging bonds." *Angew. Chem. Int. Ed.* **1994**, *106*, 1728-1730.

[274] Lee, M., B.-K. Cho, Y.-S. Kang and W.-C. Zin "Hydrogen-Bonding-Mediated Formation of Supramolecular Rod-Coil Copolymers Exhibiting Hexagonal Columnar and Bicontinuous Cubic Liquid Crystalline Assemblies." *Macromolecules* **1999**, *32*, 8531-8537.

[275] McKeirnan, R. L., A. M. Heintz, S. L. Hsu, E. D. T. Atkins, J. Pennelle and S. P. Gido "Influence of Hydrogen Bonding on the Crystallization Behavior of Semicrystalline Polyurethanes." Ibid. **2002**, *35*, 6970-6974.

the melt approximately 75% of the urethane linkages were involved in hydrogen bonding, leading to the large effect on crystallization.

The effect of hydrogen bonding interactions was also investigated by Kuo et al. in the case of miscible polymer blends.[276] Three hydrogen bond donating polymers with different functional groups (phenolic, poly(vinyl phenol), and phenoxy) were blended with polycaprolactone (PCL) and the blends were investigated in terms of the rate of crystallization, the surface free energy of chain folding, crystalline lamaellar thickness, and the self-association versus cross-association of the polymer blends. Kuo et al. observed that the greater the interaction between the hydrogen bond donating polymer and the carbonyl group of the PCL, the slower the observed crystallization. However, the molecular weights of the hydrogen bond donating polymers were not similar, and crystallization remains a complex event and more intense study is necessary to deconvolute the influence of various factors on crystallization. Wang et al. also observed compatibilization based on single hydrogen bonding between poly(hydroxyl ether)s and poly(arylene oxide)s using FTIR and phosphorus NMR.[277] A control experiment involving polymers with no phosphine oxide group showed no miscibility and proved that the hydrogen bonding group enhanced miscibility.

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[276] Kuo, S. W., S. C. Chan and F. C. Chang "Effect of Hydrogen Bonding Strength on the Microstructure and Crystallization Behavior of Crystalline Polymer Blends." Ibid. **2003**, *36*, 6653-6661.Kuo, S. W. and F. C. Chang "Studies of Miscibility Behavior and Hydrogen Bonding in Blends of Poly(vinylphenol) and Poly(vinylpyrrolidone)." *Macromolecules* **2001**, *34*, 5224-5228.

[277] Wang, S., H. Zhuang, H. K. Shobha, T. E. Glass, M. Sankarapandian, Q. Ji, A. R. Schultz and J. E. McGrath "Miscibility of Poly(arylene phosphine oxide) Systems and Bisphenol A Poly(hydroxy ether)." *Macromolecules* **2001**, *34*, 8051-8063.

2.7.4 Systems Involving Double Hydrogen Bonding

2.7.4.1 Supramolecular Systems

When hydrogen bonding arrays have two or more hydrogen bonding interactions, two different classifications for these systems arise. Self-complementary hydrogen bonding arrays are characterized by their ability to hydrogen bond with themselves and each hydrogen bonding array is the same. In contrast, complementary hydrogen bonding arrays contain two distinctly different pieces which recognize each other, but do not self-dimerize.

In a similar fashion to the pyridine/carboxylic acid single hydrogen bonding arrays discussed above, Kato et al. extended the concept to double hydrogen bonding. It was observed that the induced liquid crystalline mesophase was enlarged when the double hydrogen bonding system involving 2-(acyl-amino)pyridine was used in complexation with benzoic acid.[278] Kanie et al. also observed liquid crystalline behavior imparted by the self-complementary double hydrogen bond association of folic acid derivatives. It was found that the length of the alkyl substituent controlled the type of liquid crystalline domain observed. It was also discovered using x-ray diffraction that changing the alkyl substituent resulted in conversion between ribbon-like arrangements to cyclic arrangements. Palacin et al. reported the synthesis of "molecular tapes", arising from a double hydrogen bonding interaction of diketopiperazines (DKPs), shown in Figure 2-8. These supramolecular polymers were surprisingly durable to changes in alkyl substitutions, suggesting a robust double hydrogen bonding interaction. However, it was

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[278] Kato, T. "Supramolecular liquid-crystalline materials: molecular self-assembly and self-organization through intermolecular hydrogen bonding." *Supramol. Sci.* **1996**, *3*, 53-59.Kato, T., M. Nakano, T. Moteki, T. Uryu and S. Ujiie "Supramolecular Liquid-Crystalline Side-Chain Polymers Built through a Molecular Recognition Process by Double Hydrogen Bonds." *Macromolecules* **1995**, *28*, 8875-8876.

found that the tapes exhibited different planarities depending on the alkyl substituents bound to the ring.[279]

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[279] Palacin, S., N. D. Chin, E. E. Simanek, C. J. MacDonald, G. M. Whitesides, T. M. McBridge and R. T. Palmore "Hydrogen-Bonded Tapes Based on Symmetrically Substituted Diketopiperazines: A Robust Structural Motif for the Engineering of Molecular Solids." *J. Am. Chem. Soc.* **1997**, *119*, 11807-11816.
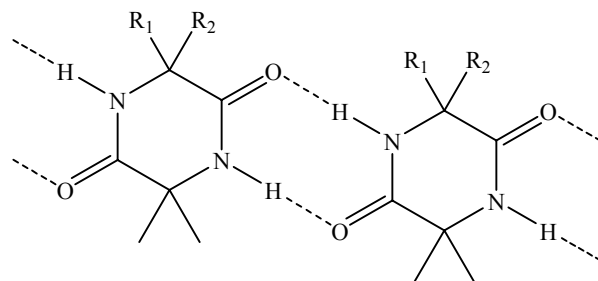
Figure 2-8. Supramolecular assembly of diketopiperazines.

2.7.4.2 Polymeric Systems

It is well-known that urea functionalities in polymer systems are capable of dimeric self-complementary multiple hydrogen bonding between the carbonyl oxygen and the two neighboring N-H hydrogens. It has been shown that these hydrogen bonding interactions increase the properties of both polyureas and poly(urethane urea)s.[280] The presence of physical crosslinks due to both microphase segregation and urea hydrogen bonding leads to a rubbery plateau in dynamic mechanical analysis and "pseudo-crosslinked" behavior. However, it was shown using SAXS that only a few urea groups participate in hydrogen bonding in each hard segment, and it was from these interactions that the differences in physical properties arose.[281]

A general method for increasing the strength of relatively weak hydrogen bonding interactions is the formation of crystalline domains and this phenomenon is often encountered in the chain extension of conventional polymers.[282] Lillya et al. synthesized poly(tetrahydrofuran) endcapped with benzoic acid functionalities and saw a dramatic improvement of the material properties, which they attributed to the formation of large crystalline domains of the hydrogen bonding groups.[283] The benzoic acid chain end functionalized poly(THF)s were waxy solids under ambient conditions while non-

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[280] Sung, C. S. P., T. W. Smith and N. H. Sung "Properties of segmented polyether poly(urethaneureas) based on 2,4-toluene diisocyanate. 2. Infrared and mechanical studies." *Macromolecules* **1980**, *13*, 117-121.Wang, C. B. and S. L. Cooper "Morphology and properties of segmented polyether polyurethane ureas." *Macromolecules* **1983**, *16*, 775-786.Allport, D. C. "Polyamides and polyureas from 2,2'- and 4,4'-bipiperidines." *Monograph* **1967**, *25*, 143-159.
[281] Tyagi, D., I. Yilgor, J. E. McGrath and G. L. Wilkes "Segmented organosiloxane copolymers. 2. Thermal and mechanical properties of siloxane-urea copolymers." *Polymer* **1984**, *25*, 1807-1816.
[282] Brunsveld, L., B. J. B. Folmer, E. W. Meijer and R. P. Sijbesma "Supramolecular Polymers." *Chem. Rev.* **2001**, *101*, 4071-4097.
[283] Lillya, C. P., R. J. Baker, S. Hutte, H. H. Winter, Y. G. Lin, J. Shi, L. C. Dickinson and J. C. W. Chien "Linear chain extension through associative termini." *Macromolecules* **1992**, *25*, 2076-2080.

functionalized analogs were viscous liquids. A distinct change in physical properties was observed above the melting point of the crystalline domains and was attributed to the loss of stabilization imparted by the phase separation. Additionally, when poly(dimethylsiloxane)s were functionalized with benzoic acid groups, the change in physical properties was much less than for poly(THF).[284]

Stadler et al. have also used a derivatized benzoic acid functionality to introduce hydrogen-bonding interactions into polymer systems.[285] Polybutadiene and polyisobutylene chain ends were functionalized using 4-(3,5-dioxo-1,2,4-triazolidin-4-yl)benzoic acid (urazoylbenzoic acid) groups as well as phenylurazole groups. Functionalization was readily achieved through reaction at residual polymeric double bonds. These functionalities allow for several different interactions between the chain ends, including acid:acid, urazole:urazole, and urazole:acid interactions.[286] This system remains one of the most well-studied double hydrogen bonding systems and a series of papers were published describing the hydrogen bonding interactions and their effect on polymer properties. In a similar fashion to the system described above, Stadler et al. found that urazole-functionalized polymers formed small crystalline domains, and that the functionalized polymers exhibited properties typical of thermoplastic elastomers. At low temperatures, the materials behaved similarly to a covalently bonded system, with

[284] Abed, S., S. Boileau, L. Bouteiller and N. Lacoudre "Supramolecular association of acid-terminated polydimethylsiloxanes. Part 1. Synthesis and characterization." *Polym. Bull.* **1997**, *39*, 317-324.Abed, S., S. Boileau and L. Bouteiller "Supramolecular Association of Acid-Terminated Poly(dimethylsiloxane)s. 2. Molecular Weight Distributions." *Macromolecules* **2000**, *33*, 8479-8487.

[285] Hilger, C., M. Drager and R. Stadler "Molecular Origin of Supramolecular Self-Assembling in Statistical Copolymers." *Macromolecules* **1992**, *25*, 2498-2501.Mueller, M., U. Seidel and R. Stadler "Influence of hydrogen bonding on the viscoelastic properties of thermoreversible networks: analysis of the local complex dynamics." *Polymer* **1995**, *36*, 3143-3150.Mueller, M., A. Dardin, U. Seidel, V. Balsamo, B. Ivan, H. W. Spiess and R. Stadler "Junction Dynamics in Telechelic Hydrogen Bonded Polyisobutylene Networks." *Macromolecules* **1996**, *29*, 2577-2583.

[286] Hilger, C., M. Drager and R. Stadler "Molecular Origin of Supramolecular Self-Assembling in Statistical Copolymers." *Macromolecules* **1992**, *25*, 2498-2501.

the hydrogen bonding interactions imparting mechanical properties, and at high temperatures, the materials behaved like low molecular weight polymers, because the hydrogen bonding interactions were dissociated. A variety of techniques were used to characterize these systems, including DSC,[287] light and x-ray scattering,[288] dynamical mechanical analysis, [289] dielectric spectroscopy, [290] deuterium NMR, [291] IR spectroscopy,[292] and melt rheology.[293]

[287] Stadler, R. and J. Burgert "Influence of hydrogen bonding on the properties of elastomers and elastomeric blends." *Makromol. Chem.* **1986***, 187*, 1681-1690.Hilger, C. and R. Stadler "Cooperative structure formation by combination of covalent and association chain polymers. 3. Control of association polymer chain length." *Makromol. Chem.* **1991***, 192*, 805-817.

[288] Schirle, M., I. Hoffman, T. Pieper, H.-G. Kilian and R. Stadler "Spherulite formation in a "noncrystalline" two-dimensional hydrogen-bond assembly." *Polym. Bull.* **1996***, 36*, 95-102.Bica, C. I. D., W. Burchard and R. Stadler "Dilute solution properties of polybutadiene modified by 4-phenyl-1,2,4-triazoline-3,5-dione." *Macromol. Chem. Phys.* **1996***, 197*, 3407-3426.

[289] Stadler, R. and L. D. L. Freitas "Thermoplastic elastomers by hydrogen bonding. 1. Rheological properties of modified polybutadiene." *Colloid Polym. Sci.* **1986***, 264*, 773-778.Freitas, L. D. L., J. Burgert and R. Stadler "Thermoplastic elastomers by hydrogen bonding. 5. Thermorheologically complex behavior by hydrogen bond clustering." *Polym. Bull.* **1987***, 17*, 431-438.Freitas, L. D. L. and R. Stadler "Thermoplastic elastomers by hydrogen bonding. 3. Interrelations between molecular parameters and rheological properties." *Macromolecules* **1987***, 20*, 2478-2485.Freitas, L. D. L. and R. Stadler "Thermoplastic elastomers by hydrogen bonding. 4. Influence of hydrogen bonding on the temperature dependence of the viscoelastic properties." *Colloid Polym. Sci.* **1988***, 266*, 1095-1101.Hilger, C. and R. Stadler "New multiphase architecture from statistical copolymers by cooperative hydrogen bond formation." *Macromolecules* **1990***, 23*, 2095-2097.Hilger, C., R. Stadler and L. D. L. Freitas "Multiphase thermoplastic elastomers by combination of covalent and association chain structures: 2. Small-strain dynamic mechanical properties." *Polymer* **1990***, 31*, 818-823.Hilger, C. and R. Stadler "Cooperative structure formation by combination of covalent and association chain polymers: 4. Designing functional groups for supramolecular structure formation." *Polymer* **1991***, 32*, 3244-3249.Mueller, M., U. Seidel and R. Stadler "Influence of hydrogen bonding on the viscoelastic properties of thermoreversible networks: analysis of the local complex dynamics." *Polymer* **1995***, 36*, 3143-3150.

[290] Mueller, M., R. Stadler, F. Kremer and G. Williams "On the Motional Coupling between Chain and Junction Dynamics in Thermoreversible Networks." *Macromolecules* **1995***, 28*, 6942-6949.Mueller, M., F. Kremer, R. Stadler, E. W. Fischer and U. Seidel "The molecular dynamics of thermoreversible networks as studied by broadband dielectric spectroscopy." *Colloid Polym. Sci.* **1995***, 273*, 38-46.

[291] Dardin, A., R. Stadler, C. Boeffel and H. W. Spiess "Molecular dynamics of new thermoplastic elastomers based on hydrogen bonding complexes: a deuteron nuclear magnetic resonance investigation." *Makromol. Chem.* **1993***, 194*, 3467-3477.

[292] Stadler, R. and L. D. L. Freitas "Thermoplastic elastomers by hydrogen bonding. 2. IR-spectroscopic characterization of the hydrogen bonding." *Polym. Bull.* **1986***, 15*, 173-179.Seidel, U., R. Stadler and G. G. Fuller "Relaxation Dynamics of Bidisperse Temporary Networks." *Macromolecules* **1994***, 27*, 2066-2072.

[293] Stadler, R. and L. D. L. Freitas "Thermoplastic elastomers by hydrogen bonding. 1. Rheological properties of modified polybutadiene." *Colloid Polym. Sci.* **1986***, 264*, 773-778.Freitas, L. D. L., J. Burgert and R. Stadler "Thermoplastic elastomers by hydrogen bonding. 5. Thermorheologically complex behavior by hydrogen bond clustering." *Polym. Bull.* **1987***, 17*, 431-438.Freitas, L. D. L. and R. Stadler "Thermoplastic elastomers by hydrogen bonding. 3. Interrelations between molecular parameters and rheological properties." *Macromolecules* **1987***, 20*, 2478-2485.Seidel, U., R. Stadler and G. G. Fuller

Nucleic acid base pairs, such as adenine, thymine, and uracil, were also incorporated into polymer structures and are an example of double hydrogen bonding moieties. A large body of literature has focused on the synthesis of polynucleotide analogs in an attempt to mimic nature's self-assembly.[294] These double hydrogen bonding units were also incorporated in more traditional polymer synthesis in various ways. Kahn et al. studied the template directed polymerization of acrylic monomers functionalized with both adenine and uridine.[295] Long et al. polymerized styrene anionically to yield well-defined hydroxyl terminated polymers. The hydroxyl group was subsequently transformed to an acrylic double bond, and nucleic acid base pair functionalization (adenine, thymine, 2,6-diaminopurine) was achieved through a Michael addition.[296] Nucleic acid base pairs were also introduced using post-polymerization modification of poly(ethylene imine).[297]

2.7.5 Systems Involving Triple Hydrogen Bonding

2.7.5.1 Supramolecular Systems

In higher order hydrogen bonding systems, the interactions between the arrays becomes much more complex, with secondary interactions playing an important role in

"Relaxation Dynamics of Bidisperse Temporary Networks." *Macromolecules* **1994**, *27*, 2066-2072.Seidel, U., R. Stadler and G. G. Fuller "Enhancement of Orientational Coupling in Bidisperse Polybutadiene Melts through the Implementation of Directed Interactions." *Macromolecules* **1995**, *28*, 3739-3740.

[294] Hoffmann, S. and W. Witkowski "Biomesogens and theirs models: possibilities of mesomorphic order in polynucleotide analogs." *ACS Symposium Series* **1978**, *74*, 178-236.Han, M. J. and J. Y. Chang "Polynucleotide analogues." *Adv. Polym. Sci.* **2000**, *153*, 1-36.Han, M. J., S. M. Park, J. Y. Park and S. H. Yoon "Polynucleotide analogs. 3. Synthesis, characterization, and physicochemical properties of poly(thymidylic acid) analogs." *Macromolecules* **1992**, *25*, 3534-3539.Inaki, Y. "Synthetic nucleic acid analogs." *Prog. Polym. Sci.* **1992**, *17*, 515-570.

[295] Khan, A., D. M. Haddelton, M. J. Hannon, D. Kukuji and A. Marsh "Hydrogen Bond Template-Directed Polymerization of Protected 5'-Acryloyl Nucleosides." *Macromolecules* **1999**, *32*.

[296] Yamauchi, K., J. R. Lizotte and T. E. Long "Synthesis and Characterization of Novel Complementary Multiple-Hydrogen Bonded (CMHB) Macromolecules via a Michael Addition." Ibid. **2002**, *35*, 8745-8750.

[297] Overberger, C. G. and Y. Inaki "Graft copolymers containing nucleic acid bases and L-alpha-amino acids." *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 1739-1758.

stabilization of the hydrogen bonding interaction. Repulsive secondary interactions between acceptors or donors results in destabilization of the overall hydrogen bonding array, while attractive secondary interactions increase the overall stability. The strongest multiple hydrogen bonding arrays are observed when donors and acceptors are alternated, minimizing deleterious secondary interactions. Jorgensen and Pranata used quantum mechanical calculations to support this observation.[298] Two main pairs of compounds were extensively studied in triple hydrogen bonding systems, namely the Janus wedge recognition pair comprised of cyanuric acid/barbituric acid derivatives and 2,6-diaminopyridine/thymine systems.

Lehn et al. have observed liquid crystallinity in complementary triple hydrogen bonding systems.[299] Mesogenic supramolecular assemblies were discovered when derivatives of the complementary heterocyclic groups 2,6-diaminopyridine and uracil were introduced together, see Figure 2-9. The pure compounds did not show liquid crystalline behavior, while a 1:1 mixture of the two gave a columnar hexagonal mesophase. When tartaric acid was functionalized with 2,6-diacylaminopyridine and uracil groups, triple helices were observed and the chirality of the helix was dictated by the original chirality of the tartaric acid.[300] Additionally, it was observed that the

[298] Jorgensen, W. L. and J. Pranata "Importance of secondary interactions in triply hydrogen bonded complexes: guanine-cytosine versus uracil-2,6-diaminopyridine." *J. Am. Chem. Soc.* **1990**, *112*, 2008-2010.Pranata, J., S. G. Wierschke and W. L. Jorgensen "OPLS potential functions for nucleotide bases. Relative association constants of hydrogen-bonded base pairs in chloroform." *J. Am. Chem. Soc.* **1991**, *113*, 2810-2819.

[299] Lehn, J. M. "Perspectives in Supramolecular Chemistry-From Molecular Recognition towards Molecluar Informoation Processing and Self-Organization." *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1304-1319.

[300] Fouquey, C., J.-M. Lehn and A.-M. Levelut "Molecular recognition directed self-assembly of supramolecular liquid crystalline polymers from complementary chiral components." *Adv. Material* **1990**, *2*, 254-257.Gulik-Krzywicki, T., C. Fouquey and J.-M. Lehn "Electron microscopic study of supramolecular liquid crystalline polymers formed by molecular-recognition-directed self-assembly from complementary chiral components." *Proc. Natl. Acad. Sci. U.S.A.* **1993**, *90*, 163-170.

morphology of precipitates formed from solution evaporation depended on initial concentration, indicating that the molecular recognition process occurs over a relatively long time scale.
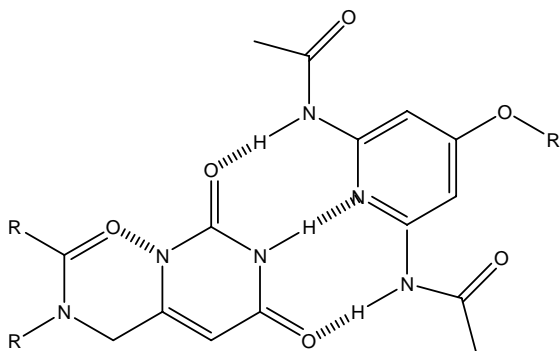
Figure 2-9. The complementary groups 2,6-diaminopyridine and uracil.

Lehn et al. have also described a supramolecular system comprised of 2,4,6-triaminopyridine (DAD) and barbituric acid derivatives (ADA), which are complementary through two arrays of three hydrogen bonds with each other as illustrated by Figure 2-10.[301] These two molecules in conjunction with one another were shown to self-assemble into molecular tapes.

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[301] Lehn, J. M. "Perspectives in Supramolecular Chemistry-From Molecular Recognition towards Molecluar Informoation Processing and Self-Organization." *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1304-1319.
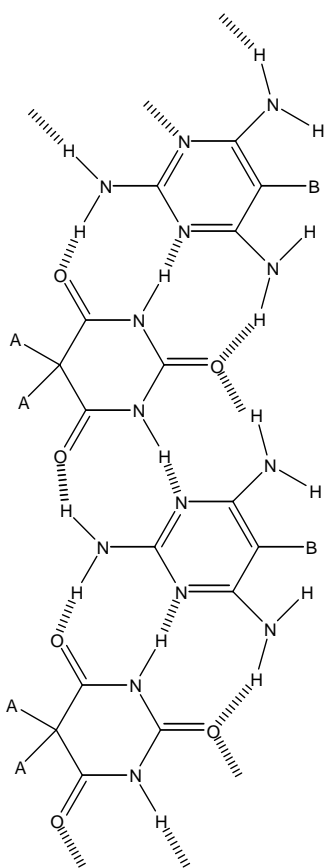
Figure 2-10. The 2,4,6-triaminopyrimidine and barbituric acid complementary interaction through two sets of 3 hydrogen bonds.

An interesting aspect of this system is that it allows for molecular sorting of like/unlike species and therefore introduces long range order to the polymer. This was shown to impart unique properties in the resulting polymer system. Systems such as this are under study to devise other patterns, such as ribbons, rings, etc., and ultimately molecular patterning. Lehn et al. also synthesized two Janus wedge type molecules with two faces, DDA and DAA, both of which were shown to form tapes through self-complementary interactions, but when mixed together resulted in a cyclic hexamer.[302]

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[302] Lehn, J. M., M. Mascal, A. DeCian and J. Fischer "Molecular ribbons from molecular recognition directed self-assembly of self-complementary molecular components." *J. Chem. Soc., Perkin Tran.* **1992**, *2*, 461-467.

Meijer has also synthesized a series of compounds with the ability to hydrogen bond at three sites simultaneously. [303]   Several 2,4-diamino-s-triazines, 2,6-diaminopyridines, and their acylated derivatives and their complexation behavior with uracil derivatives have been investigated using ^{1}H NMR and FTIR. In this study, it was shown that 2,4-diamino-s-triazine and uracil represented the most convenient couple for supramolecular chemistry because of their stable triple hydrogen bonding interaction. This couple minimizes the deleterious effect of secondary interactions, while optimizing the hydrogen bonding interactions. Whitesides et al. developed a series of disubstituted 2,4,6-triaminopyridines and studied their association with diethylbarbituric acid. [304] Varying the substituents controlled the formation of molecular tapes. Previous work from this group using melamine and cyanuric acid resulted in the formation of a two-dimensional infinite network.[305] Use of builky di-*tert*-butyl substituents on the melamine resulted in the formation of "crinkled" tapes.[306]

2.7.5.2 Polymeric Systems

The incorporation of triple hydrogen bonding arrays into polymer systems has focused mainly on the diaminopyridine/thymine couple. Rotello et al. reported the use of these hydrogen bonding interactions to reversibly attach small molecules, such as POSS

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[303] Beijer, F. H., R. P. Sijbesma, J. A. J. M. Vekemans, E. W. Meijer, H. Kooijman and A. L. Spek "Hydrogen-Bonded Complexes of Diaminopyridines and Diaminotriazines: Opposite Effect of Acylation on Complex Stabilities." *J. Org. Chem.* **1996**, *61*, 6371-6380.
[304] Zerkowski, J. A., J. C. MacDonald, C. T. Seto, D. A. Wierda and G. M. Whitesides "Design of Organic Structures in the Solid State: Molecular Tapes Based on the Network of Hydrogen Bonds Present in the Cyanuric Acid×Melamine Complex." *J. Am. Chem. Soc.* **1994**, *116*, 2382-2391.
[305] Seto, C. T. and G. M. Whitesides "Self-assembly based on the cyanuric acid-melamine lattice." Ibid. **1990**, *112*, 6409-6411.
[306] Zerkowski, J. A. and G. M. Whitesides "Steric Control of Secondary, Solid-State Architecture in 1:1 Complexes of Melamines and Barbiturates that Crystallize as Crinkled Tapes." Ibid. **1994**, *116*, 4298-4304.

structures and flavins, pendant to polymer backbones.[307] In some cases it was observed that polymer bound triple hydrogen bonding arrays interacted less efficiently with small molecules than small molecules interacted with each other.[308] This was attributed to conformational inaccessibility of polymer hydrogen bonding sites or to self-association between polymer-bound hydrogen bonding sites.

Rotello et al. also recently reported the synthesis of thermally reversible microspheres through non-covalent polymer cross-linking. Using a complementary multiple hydrogen bonding system consisting of bis-thymine units and diamidopyridine units on polystyrene, discrete micron-scale spherical aggregates were formed. The particle size was controlled through changes in the bis-thymine spacer, and more monodisperse particles were achieved through annealing.[309] Additionally, when thymine-functionalized polystyrene was mixed with diaminopyridine-functionalized polystyrene, vesicle formation was observed which were stable below 60 °C.[310]

[307] Norsten, T. B., E. Jeoung, R. J. Thibault and V. M. Rotello "Specific Hydrogen-Bond-Mediated Recognition and Modification of Surfaces Using Complementary Functionalized Polymers." *Langmuir* **2003***, 19*, 7089-7093.Ilhan, F., M. Gray and V. M. Rotello "Reversible Side Chain Modification through Noncovalent Interactions. "Plug and Play" Polymers." *Macromolecules* **2001***, 34*, 2597-2601.Carroll, J. B., A. J. Waddon, H. Nakade and V. M. Rotello ""Plug and Play" Polymers. Thermal and X-ray Characterizations of Noncovalently Grafted Polyhedral Oligomeric Silsesquioxane (POSS)-Polystyrene Nanocomposites." *Macromolecules* **2003***, 36*, 6289-6291.

[308] Duffy, D. J., K. Das, S. L. Hsu, J. Penelle, V. M. Rotello and H. D. Stidham "Binding Efficiency and Transport Properties of Molecularly Imprinted Polymer Thin Films." *J. Am. Chem. Soc.* **2002***, 124*, 8290-8296.Deans, R., F. Ilhan and V. M. Rotello "Recognition-Mediated Unfolding of a Self-Assembled Polymeric Globule." *Macromolecules* **1999***, 32*, 4956-4960.Ilhan, F., M. Gray and V. M. Rotello "Reversible Side Chain Modification through Noncovalent Interactions. "Plug and Play" Polymers." *Macromolecules* **2001***, 34*, 2597-2601.

[309] Thibault, R. J., P. J. Hotchkiss, M. Gray and V. M. Rotello "Thermally Reversible Formation of Microspheres through Non-Covalent Polymer Cross-Linking." *J. Am. Chem. Soc.* **2003***, 125*, 11249-11252.

[310] Ilhan, F., T. H. Galow, M. Gray, G. Clavier and V. M. Rotello "Giant Vesicle Formation through Self-Assembly of Complementary Random Copolymers." Ibid. **2000***, 122*, 5895-5896.

2.7.6   Systems Involving Quadruple and Higher Order Hydrogen Bonding

2.7.6.1   Supramolecular Systems

Supramolecular polymers derived from quadruple hydrogen bonding motifs begin to approach covalently bonded polymeric systems due to the strength of the hydrogen bonding interaction. However, as the number of hydrogen bonds is increased, so does the intricacy of the synthetic method. Meijer et al. overcame this shortcoming and developed a series of compounds based on commercially available materials through a facile synthetic process. They recently reported the synthesis of derivatives of 2-ureido-4-pyrimidone to produce a very stable quadruply hydrogen bonding complex which coordinates via a self-complementary donor-donor-acceptor-acceptor (DDAA) array of bonds, thus forming a strong unidirectional system in chloroform, with association constants of 6.0 x 10^7 M^{-1}.[311]   An example of this system is depicted in Figure 2-11.
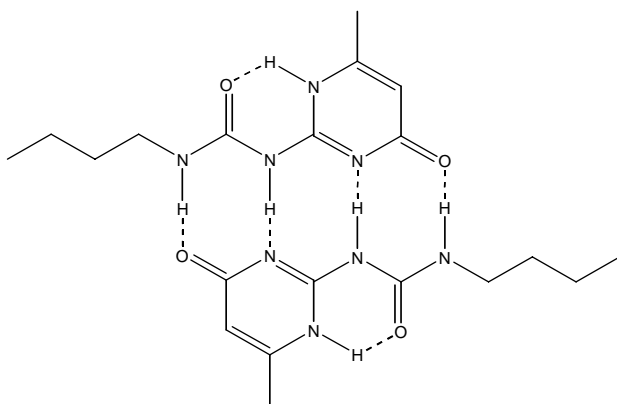
Figure 2-11. An example of the quadruple unidirectional hydrogen bonds found in 2-ureido-4-pyrimidone derivatives.

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[311] Sijbesma, R. P., F. H. Beijer, B. J. B. Folmer, J. H. K. K. Hirschberg, R. F. M. Lange, J. K. L. Lowe and E. W. Meijer "Reversible Polymers Formed from Self-Complementary Monomers Using Quadruple Hydrogen Bonding." *Science* **1997***, 278*, 1601-1604.

The dimer of 2-butylureido-6-methyl pyrimidone is representative of the directional quadruple hydrogen bonding found in derivatives of this type. The crystal structure obtained from this derivative distinctly showed the quadruple hydrogen bonding interaction, with the molecules aligned in a nearly planar fashion. Both bifunctional and monofunctional small molecules were prepared. Using the monofunctional compound, Meijer et al. were able to show that the hydrogen bonding was directional in a chloroform solution. The monofunctional compound acts as a chain stopper, wherein it caps the supramolecular polymeric chain end, making further complexation impossible. As it was added to the bifunctional solution, a dramatic drop in viscosity was observed upon small additions.[312] The chain stopper experiment is analogous to the way molar mass of a condensation polymer is limited by the addition of a monofunctional compound. The estimated molecular weight of the polymer formed from the bifunctional material was found to be 5×10^5 g/mol. From this, it was concluded that the low molar mass components combined to produce an effectively high molar mass linear polymer through unidirectional hydrogen bonding.

After the original work on this quadruple hydrogen bonded system, Meijer published a series of papers describing its application to many systems, including efforts to determine the effect of alkyl substitution on the stability of the quadruple hydrogen bonding interaction.[313] Several conformations are possible for the ureidopyrimidone system, the most stable form of which is the 6[1H]-pyrimidinone conformer, shown below in Figure 2-12-1. However, this form is unable to form the desired quadruple hydrogen bond. Both the 4[1H]-pyrimidinone (Figure 2-12-2) and the pyrimidin-4-ol

[312] Ibid.
[313] Beijer, F. H., R. P. Sijbesma, H. Kooijman, A. L. Spek and E. W. Meijer "Strong Dimerization of Ureidopyrimidones via Quadruple Hydrogen Bonding." *J. Am. Chem. Soc.* **1998**, *120*, 6761-6769.

(Figure 2-12-3) were capable of forming quadruple hydrogen bonds. Although the 6[1H]-pyrimidinone conformer is the most stable, both of these conformers were observed, possibly due to the stabilization arising from the formation of dimers. Corbin and Zimmerman showed similar results for a quadruple hydrogen bonding array, but developed an array that was not sensitive to tautomerization of the hydrogen bonding units, i.e., all tautomers were able to participate in hydrogen bonding.[314]

1   **2**   **3**
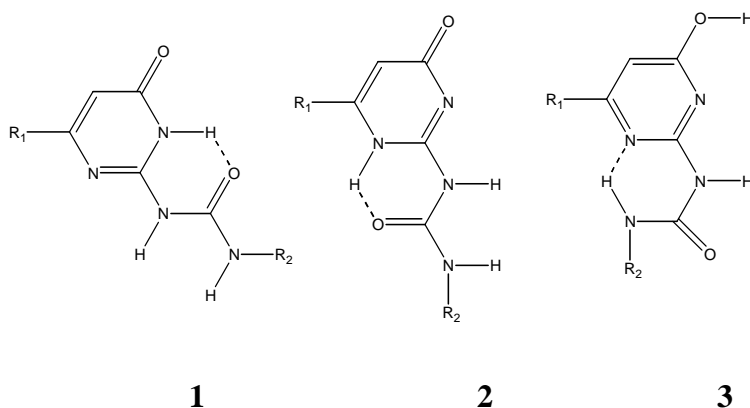
Figure 2-12. The three conformers of the ureidopyrimidone unit.

In addition, Meijer has shown that the most stable form of the quadruple hydrogen bonding unit may be achieved by adding alkyl substituents at the 6-position.[315] The 4[1H]-pyrimidinone conformer is further stabilized by an intermolecular hydrogen bond, which has been shown to greatly increase the dimidiation constants of multiple hydrogen bonded dimers.[316] They also showed that higher temperatures favored linear chain structures, whereas lower temperatures favored ring structures, and that increasing

[314] Corbin, P. S. and S. C. Zimmerman "Self-Association without regard to prototropy. A heterocycle that forms extremely stable quadruply hydrogen-bonded dimers." Ibid., 9710-9711.
[315] Beijer, F. H., R. P. Sijbesma, H. Kooijman, A. L. Spek and E. W. Meijer "Strong Dimerization of Ureidopyrimidones via Quadruple Hydrogen Bonding." Ibid., 6761-6769.
[316] Beijer, F. H., H. Kooijman, A. L. Spek, R. P. Sijbesma and E. W. Meijer "Self-Complementarity Achieved through Quadruple Hydrogen Bonding." *Angew. Chem. Int. Ed.* **1998**, *37*, 75-78.

temperature causes entropy-driven ring opening polymerization of the cyclic species.[317]

Luning and Kuhl reported the synthesis of complementary quadruple hydrogen bonding arrays with association constants on the order of 10^3 M^{-1}. More recently, Meijer et al. reported the complexation of a complementary multiple hydrogen bonding array with dimerization constants on the order of 10^6 M^{-1} (Figure 2-13).[318]

[317] Folmer, B. J. B., R. P. Sijbesma and E. W. Meijer "Unexpected Entropy-Driven Ring-Opening Polymerization in a Reversible Supramolecular System." *J. Am. Chem. Soc.* **2001**, *123*, 2093-2094.
[318] Ligthart, G. B. W. L., H. Ohkawa, R. P. Sijbesma and E. W. Meijer "Complementary Quadruple Hydrogen Bonding in Supramolecular Copolymers." Ibid. **2005**, *127*, 810-811.
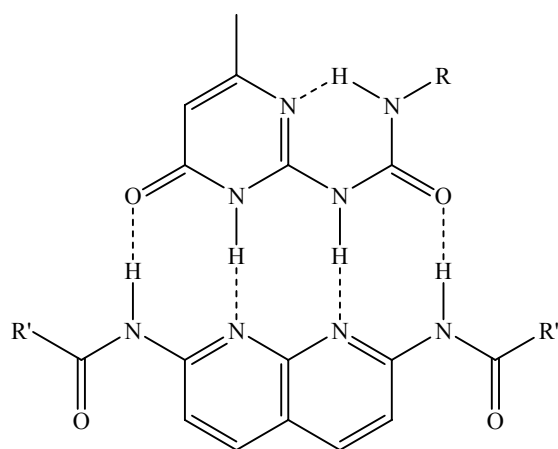
Figure 2-13. Quadruple hydrogen bonding interaction of UPy with Napy.

Li and coworkers first reported the complementary quadruple hydrogen bonding interaction of Meijer's ureidopyrimidinone unit (UPy) with 2,7-diamido-1,8-naphthyridines (Napy) and showed that one equivalent Napy disrupted UPy dimerization.[319] In order to synthesize supramolecular assemblies based on this motif, Meijer et al. synthesized a bifunctional Napy derivative. Subsequent studies involved the titration of bifunctional UPy molecules with bifunctional Napy molecules yielded and showed a sharp decrease in solution viscosity, attributed to the disruption of the UPy supramolecular polymer by the Napy heteroassociation. At concentrations above 10^{-5} M in solution, formation of the heterodimer between UPy and Napy was favored. High molar mass linear supramolecular polymers were formed at the appropriate concentrations.

Gong has recently described a six-hydrogen-bonded system that forms self-complementary duplexes and suggests that duplexes containing two different strands may also be designed.[320] This system is highly cooperative, which results in a very stable hydrogen bonding interaction through the six hydrogen bonds. Lehn et al. also reported the synthesis of a six-hydrogen bonded system based on the Janus wedge motif with association constants on the order to 10^4 M^{-1}.[321] Small molecules bearing one, two, or

[319] Wang, X.-Z., X.-Q. Li, X.-B. Shao, X. Zhao, P. Deng, X.-K. Jiang, Z.-T. Li and Y.-Q. Chen "Selective rearrangements of quadruply hydrogen-bonded dimer driven by donor-acceptor interaction." *Chem.--Eur. J.* **2003**, *9*, 2904-2913.Zhao, X., X.-Z. Wang, X.-K. Jiang, Y.-Q. Chen, Z.-T. Li and G.-J. Chen "Hydrazide-based quadruply hydrogen-bonded heterodimers. Structure, assembling selectivity, and supramolecular substitution." *J. Am. Chem. Soc.* **2003**, *125*, 15128-15139.Li, X.-Q., X.-K. Jiang, X.-Z. Wang and Z.-T. Li "Novel multiply hydrogen-bonded heterodimers based on heterocyclic ureas. Folding and stability." *Tetrahedron* **2004**, *60*, 2063-2069.Li, X.-Q., D.-J. Feng, X.-K. Jiang and Z.-T. Li "Donor-acceptor interaction-mediated arrangement of hydrogen bonded dimers." *Tetrahedron* **2004**, *60*, 8275-8284.
[320] Zeng, H., R. S. Miller, R. A. Flowers, II and B. Gong "A highly stable, six-hydrogen-bonded molecular duplex." *J. Am. Chem. Soc.* **2000**, *122*, 2635-2644.
[321] Berl, V., M. Schmutz, M. J. Krische, R. G. Khoury and J.-M. Lehn "Supramolecular polymers generated from heterocomplementary monomers linked through multiple hydrogen-bonding arrays-formation, characterization, and properties." *Chem. Eur. J.* **2002**, *8*, 1227-1244.

three arrays were synthesized and were used to construct linear and network structures with controlled degrees of branching and polymerization. Properties typically associating with high molar mass covalently bonded polymers systems, such as shear thinning in solution, fiber formation, and non-polar solvent induced gel formation were observed.

2.7.6.2 Polymeric Systems

Meijer et al. extended the self-complementary quadruple hydrogen bonding interaction to polymeric systems by synthesizing chain-end functionalized polymers. Poly(ethylene oxide-*co*-propylene oxide)s with the pyrimidone functionalized endgroups were prepared and compared to non-functionalized analogs. The lifetime of the hydrogen bonds to form dimers for this low molecular weight polymer at 30 °C was 0.1 seconds. This interaction resulted in significant mechanical properties. Comparison of the functionalized polymer to the non-functionalized cross-linked material showed that the hydrogen bonded polymer exhibited a higher plateau modulus. The hydrogen bonds act as entanglements and cause the formation of a dense thermodynamic network.[322] The crosslinks evident in the non-functionalized polymer were a function of kinetics and resulted in a much less dense network. Additionally, the quadruple hydrogen bonded polymer exhibited a rubbery plateau in storage modulus as well as viscoelastic and shear thinning melt rheological behaviors. The effect of water was also considered in this hygroscopic polymer system and it was determined that the materials properties severely decreased upon the addition of water.

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[322] Sijbesma, R. P., F. H. Beijer, B. J. B. Folmer, J. H. K. K. Hirschberg, R. F. M. Lange, J. K. L. Lowe and E. W. Meijer "Reversible Polymers Formed from Self-Complementary Monomers Using Quadruple Hydrogen Bonding." *Science* **1997**, *278*, 1601-1604.

After the hydrogen bonding stability of the quadruple hydrogen bonding unit had been optimized, Meijer then proceeded to incorporate the unit as chain ends for telechelic oligo- and poly(dimethylsiloxane). [323] Subsequent NMR, FTIR, and rheology measurements have illustrated that the ureidopyrimidinone groups associate via quadruple hydrogen bonds in a donor-donor-acceptor-acceptor (DDAA) array. DSC characterization showed a small, but distinct melting peak, attributed to formation of crystalline domains from multiple hydrogen bonding interactions. Due to this association, the polymers show many characteristics of entangled, high molecular weight polymers, including a plateau modulus of 10^5 Pa. Meijer has published several additional papers documenting the behavior of additional oligomeric systems incorporating the ureidopyrimidinone quadruple hydrogen bonding unit.[324]

Long et al. also described the synthesis and characterization of several chain-end self-complementary quadruple hydrogen bonding functionalized polymers, including polystyrene, polyisoprene, and block copolymers of styrene and isoprene.[325] It was observed that the glass transition temperature for the multiple hydrogen bond terminated

[323] Hirschberg, J. H. K. K., F. H. Beijer, H. A. van Aert, P. C. M. M. Magusin, R. P. Sijbesma and E. W. Meijer "Supramolecular Polymers from Linear Telechelic Siloxanes with Quadruple Hydrogen-Bonded Units." *Macromolecules* **1999**, *32*, 2696-2705.

[324] Lange, R. F. M., M. van Gurp and E. W. Meijer "Hydrogen-Bonded Supramolecular Polymer Networks." *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 3657-3670.Folmer, B. J. B., R. P. Sijbesma, H. Kooijman, A. L. Spek and E. W. Meijer "Cooperative Dynamics in Duplexes of Stacked Hydrogen-Bonded Moieties." *J. Am. Chem. Soc.* **1999**, *121*, 9001-9007.El-ghayoury, A., E. Peeters, A. P. H. J. Schenning and E. W. Meijer "Quadruple Hydrogen Bonded oligo(p-phenylene vinylene) Dimers." *Chem. Commun.* **2000**, 1969.

[325] Yamauchi, 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*, 8599-8604.Yamauchi, K. and T. E. Long "Synthesis and characterization of telechelic multiple hydrogen-bonded polymers via living anionic polymerization." *Polym. Mater. Sci. Eng.* **2001**, *85*, 465-466.Yamauchi, K. and T. E. Long "Synthesis and characterization of telechelic multiple hydrogen bonded (MHB) macromolecules via living anionic polymerization." *Polym. Prepr.* **2002**, *43*, 698-699.Elkins, C. L., K. Yamauchi and T. E. Long "Synthesis and characterization of self-complementary multiple hydrogen bonding poly(isoprene) star polymers." *Polym. Prepr.* **2003**, *44*, 576-577.Hudelson, C. L., K. Yamauchi and T. E. Long "Unique combinations of macromolecular topology and functionality." *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2002**, *43*, 485-486.

polymers was reproducibly higher than for the non-functionalized analogs. Additionally, melt rheological characterization showed that the melt viscosity at constant shear rate was 100 times higher for the multiple hydrogen bonding polymer than for the non-functionalize analog. Both DSC and melt rheological characterization suggested that the quadruple hydrogen bonding groups do not exist in discrete dimers in the melt, but as higher order aggregates. More recently, Long et al. reported the synthesis of telechelic multiple hydrogen bond functionalized poly(ethylene terephthalate) and poly(butylenes terephthalate).[326] These multiple hydrogen bond modified polyesters demonstrated acceptable mechanical performance and showed an order of magnitude decrease in the melt viscosity at 235 ºC over non-functional analogs, however, melt stability of the urethane linker limited melt processing.

Coates et al. reported the synthesis of non-polar poly(1-hexene) bearing pendant UPy groups, and these polymers exhibited elastomeric properties and reversibility in solution.[327] Specifically, a 2 mol percent incorporation of pendant UPy groups resulted in approximately 5 fold increases in both tensile elongation and stress at break. Long et al. also reported the synthesis of polymers bearing pendant UPy functionality.[328] A methacrylic monomer bearing the UPy functionality was synthesized in nearly quantitative yields and used to synthesize random copolymers with both n-butyl acrylate and methyl methacrylate. In the n-butyl acrylate system, melt rheological analysis and

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[326] Yamauchi, K., A. Kanomata, T. Inoue and T. E. Long "Thermoreversible Polyesters Consisting of Multiple Hydrogen Bonding (MHB)." *Macromolecules* **2004***, 37*, 3519-3522.
[327] Rieth, R. L., F. R. Eaton and G. E. Coates "Polymerization of ureidopyrimidinone-functionalized olefins by using late-transition metal Ziegler-Natta catalysts: synthesis of thermoplastic elastomeric polyolefins." *Angew. Chem. Int. Ed.* **2001***, 40*, 2153-2156.
[328] Yamauchi, K., J. R. Lizotte and T. E. Long "Thermoreversible Poly(alkyl acrylates) Consisting of Self-Complementary Multiple Hydrogen Bonding." *Macromolecules* **2003***, 36*, 1083-1088.McKee, M. G., C. L. Elkins and T. E. Long "Influence of self-complementary hydrogen bonding on solution rheology/electrospinning relationships." *Polymer* **2004***, 45*, 8705-8715.

proton NMR indicated that above 80 °C, the majority of the hydrogen bonds were dissociated. Additionally, a three fold increase in the 90 °C peel strength was observed with a 3 mol percent incorporation of UPy units.[329] In the methyl methacrylate system, the copolymers were used in an attempt to determine the effect of multiple hydrogen bonding associations on solution rheology and electrospinning performance. It was observed that with increasing multiple hydrogen bond incorporation, there were significant changes in both the solution rheology and electrospinning properties. Specifically, higher solution viscosity and lower entanglement concentrations were observed for copolymers with multiple hydrogen bonding groups. This resulted in significantly larger electrospun fibers compared to non-functionalized analogs at similar molar masses and concentrations.[330]

[329] Yamauchi, K., J. R. Lizotte and T. E. Long "Thermoreversible Poly(alkyl acrylates) Consisting of Self-Complementary Multiple Hydrogen Bonding." *Macromolecules* **2003**, *36*, 1083-1088.
[330] McKee, M. G., C. L. Elkins and T. E. Long "Influence of self-complementary hydrogen bonding on solution rheology/electrospinning relationships." *Polymer* **2004**, *45*, 8705-8715.

Chapter 3   Synthesis   and   Characterization   of   PDMS Homopolymers via Living Anionic Polymerization Using Functional Initiation

Taken from:
Elkins, Casey L.; Long, Timothy E. "Living Anionic Polymerization of Hexamethylcyclotrisiloxane (D3) Using Functionalized Initiation." *Macromolecules* **2004**, *37(17)*, 6657-6659.

3.1   Abstract

A series of poly(dimethylsiloxane) homopolymers were synthesized via living anionic polymerization using the protected functional initiator 3-[(N-benzyl-N-methyl)amino]-1-propyllithium.   Molecular weights were reproducibly controlled and narrow molecular weight distributions were obtained.   Well-defined tertiary amine functionality was observed at the polymer chain end using ^{1}H NMR spectroscopy.   The benzyl protecting group was easily removed to yield a secondary amine functionality without affecting the molecular weight or molecular weight distribution of the polymer. The secondary amine functionality is suitable for further modification reactions.

3.2   Introduction

Poly(dimethylsiloxane) (PDMS) possesses a variety of properties that are attractive for many industrial applications.[331]   PDMS exhibits excellent thermal and oxidative stability, as well as low absorption in the UV and good oxygen reactive ion etch resistance.   This latter attribute is important in microelectronics applications.[332]   PDMS

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[331]   Bellas, V., H. Iatrou and N. Hadjichristidis "Controlled Anionic Polymerization of Hexamethylcyclotrisiloxane.   Model Linear and Miktoarm Star Co- and Terpolymers of Dimethylsiloxane with Styrene and Isoprene." *Macromolecules* **2000**, *33*, 6993-6997.
[332] Gabor, A. H. and C. K. Ober "Silicon-containing block copolymer resist materials." *Microelectronics Technology. Polymers for Advanced Imaging and Packaging*: Washington, D. C., 1995; pp 281-298.

also has high chain flexibility, low glass transition temperature, low surface energy, and a low solubility parameter. Telechelic PDMS is readily synthesized via the catalyzed ring opening polymerization of octamethylcyclotetrasiloxane (D_4). [333] However, this equilibration process yields both linear polymers and cyclic oligomers, and a broad molar mass distribution is generally observed. In 1969, Frye et al. proposed the use of the cyclic trimer hexamethylcyclotrisiloxane (D_3) in the synthesis of narrow molar mass distribution PDMS. [334] Due to the increased ring strain in the D_3 monomer, the rate of polymerization is greater and living anionic polymerization occurs faster than D_4 ring-chain equilibrium reactions. Thus, well-defined polymers with narrow molar mass distributions are attainable. In general, the polymerization of D_3 is initiated using an alkyllithium reagent in a non-polar solvent such as cyclohexane at room temperature. These reaction conditions result in the formation of a monoadduct of initiator with D_3. The reaction will not proceed further without the addition of a polar promoter to the non-polar hydrocarbon solvent. [335] Upon addition of a polar additive, the polymerization proceeds until all monomer is consumed and the living siloxanolate is terminated. Typical promoters for these polymerizations include tetrahydrofuran (THF), [336] diglyme, [337] triglyme, [338] and dimethylsulfoxide (DMSO). [339] However, it was determined

[333] Eaborn, C. "*Organosilicon Compounds*"; Buttersworth: London, 1960.

[334] Lee, C. L., C. L. Frye and O. K. Johansson "Selective polymerization of reactive cyclosiloxanes to give non-equilibrium molecular weight distributions. Monodisperse siloxane polymers." *Polym. Prepr.* **1969**, *10*, 1361-1367.Frye, C. L., R. M. Salinger, F. W. G. Fearon, J. M. Klosowski and D. Y. T. "Reactions of Organolithium Reagents with Siloxane Substrates." *J. Org. Chem.* **1970**, *35*, 1308.

[335] Frye, C. L., R. M. Salinger, F. W. G. Fearon, J. M. Klosowski and D. Y. T. "Reactions of Organolithium Reagents with Siloxane Substrates." *J. Org. Chem.* **1970**, *35*, 1308.

[336] Lee, C. L., C. L. Frye and O. K. Johansson "Selective polymerization of reactive cyclosiloxanes to give non-equilibrium molecular weight distributions. Monodisperse siloxane polymers." *Polym. Prepr.* **1969**, *10*, 1361-1367.Zilliox, J. G., J. E. L. Roovers and S. Bywater "Preparation and properties of polydimethylsiloxane and its block copolymers with styrene." *Macromolecules* **1975**, *8*, 573.

[337] Saam, J. C., D. Gordan and S. Lindsey "Block copolymers of polydimethylsiloxane and polystyrene." *Macromolecules* **1970**, *3*, 1-4.

that at conversions greater than 85% D_3 polymerizations suffer from backbiting reactions. [340] Backbiting reactions consist of intramolecular attack of the living siloxanolate chain end and the subsequent formation of deactivated unstrained rings.[341] At high monomer concentrations, the molecular weight increased in a linear fashion with monomer conversion, however, as the reactions approached high conversion, monomer starved conditions facilitated backbiting reactions. Several methods were used to minimize or eliminate these deleterious side reactions. The simplest approach was intentional termination prior to side reactions, typically at 80-85% conversion.[342] This was an effective method to avoid these side reactions from occurring, however, this approach resulted in lower yields.

Living anionic polymerization provides many benefits over conventional free radical polymerization. Living anionic polymerization permits the synthesis of polymers with controlled molecular weight and a narrow molecular weight distribution. Stereochemical control, synthesis of block and graft copolymers, and functionalization reactions at the polymer chain ends are also possible. In general, polymers that are prepared using organolithium initiators are end-functionalized with a variety of post-

[338] Zilliox, J. G., J. E. L. Roovers and S. Bywater "Preparation and properties of polydimethylsiloxane and its block copolymers with styrene." Ibid. **1975**, *8*, 573.

[339] Lee, C. L., C. L. Frye and O. K. Johansson "Selective polymerization of reactive cyclosiloxanes to give non-equilibrium molecular weight distributions. Monodisperse siloxane polymers." *Polym. Prepr.* **1969**, *10*, 1361-1367.

[340] Juliano, P. C., W. A. Fessler and J. D. Cargioli "Proton magnetic resonance study of lithium silanolates. II. Effects of solvatin silanolates. II. Effects of solvating agent stoichiometry and temperature." Ibid. **1971**, *12*, 158-165.

[341] Maschke, U. and T. Wagner "Synthesis of high-molecular-weight poly(dimethylsiloxane) of uniform size by anionic polymerization, 1. Initiation by a monofunctional lithium siloxanolate." *Makromol. Chem.* **1992**, *193*, 2453-2466.

[342] Zilliox, J. G., J. E. L. Roovers and S. Bywater "Preparation and properties of polydimethylsiloxane and its block copolymers with styrene." *Macromolecules* **1975**, *8*, 573.Molenberg, A., H.-A. Klok, M. Moller, S. Boileau and D. Teyssie "Controlled Polymerization of Hexa-n-alkylcyclotrisiloxanes with long alkyl groups." *Macromolecules* **1997**, *30*, 792-794.

polymerization reactions involving electrophilic agents. [343]   However, many functionalization reactions are not quantitative and result in a mixture of chain end functionality. An alternative for the synthesis of end-functionalized polymers is the use of functionalized alkyllithium initiators and functionalized alkyllithium initiators ensure quantitative chain end functionalization. It is generally necessary to use a protecting group in the initiator because most functionalities of interest, such as hydroxyl, carboxyl, or amino, are not stable in the presence of organolithium reagents. [344]   A suitable protecting group is stable during anionic polymerization, but also readily removed after polymerization to generate the desired functional group. [345]

The use of functionalized initiators offers several advantages over conventional electrophilic termination reagents for the synthesis of end-functionalized polymers. [346] Each functionalized initiator molecule will produce a macromolecule with the desired functionality at the chain end regardless of the molar mass of the polymer. The use of functionalized initiators also avoids the problems associated with electrophilic addition reagents, such as efficient and rapid mixing with viscous polymers, the stability of the anionic chain end, and selective reactivity. [347] Functionalized initiators also facilitate the

[343] Hsieh, H. L. and R. P. Quirk "*Anionic Polymerization: Principles and Practical Applications"*; Marcel Dekker: New York, 1996.Goethals, E. J. "Telechelic Polymers: Synthesis and Applications"; CRC Press: Boca Raton, Fl, 1989.

[344] Schulz, D. N., S. Datta and R. M. Waymouth "Use of protecting groups in polymerization." *Polym. Mater. Sci. Eng.* **1997**, *76*, 3-5.Nakahama, S. and A. Hirao "Protection and polymerization of functional monomers: anionic living polymerization of protected monomers." *Prog. Polym. Sci.* **1990**, *15*, 299-335.Greene, T. W. and P. G. M. Wuts "*Protective Groups in Organic Synthsis"*; 3rd ed.; John Wiley & Sons: New York, 1999.

[345] Quirk, R. P., S. H. Jang, H. Yang and Y. Lee "Polymer Synthesis Using Functionalized Alkyllithium Initiators: Telechelic, heterotelechelic and functionalized star-branched polymers." *Macromol. Symp.* **1998**, *132*, 281-291.

[346] Quirk, R. P., S. H. Jang and J. Kim "Recent Advances in Anionic Synthesis of Functionalized Elastomers using Functionalized Alkyllithium Initiators." *Rubber Rev., Rubber Chem. Tech.* **1996**, *69*, 444.

[347] Hsieh, H. L. and R. P. Quirk "*Anionic Polymerization: Principles and Practical Applications"*; Marcel Dekker: New York, 1996.

synthesis of telechelic and heterotelechelic polymers, functionalized block polymers, and star-branched polymers with functional groups at each arm terminus.[348]

3.3   Experimental

3.3.1   Materials

Hexamethylcyclotrisiloxane (D_3) was stirred over calcium hydride at 80 °C for 48 hours, allowed to cool, degassed several times, and vacuum distilled (0.10 mm Hg, 23-25 °C).   3-[(N-benzyl-N-methyl)amino]-1-propyllithium (FMC Corporation Lithium Division, 0.95 M in cyclohexane), Pd/C (10 wt% Pd on activated carbon, Aldrich), and hydrogen (99.99%, Holox) were used without any further purification. Trimethylchlorosilane (Aldrich) was vacuum distilled from calcium hydride. Cyclohexane was stirred over sulfuric acid for 7 days, decanted, and distilled under nitrogen from sodium immediately prior to use.   Tetrahydrofuran (THF) was distilled under nitrogen from sodium and benzophenone immediately prior to use.   3-(t-butyldimethylsilyloxy)-1-propyllithium (tBDMSPrLi, FMC Corporation Lithium Division. 0.8 M in cyclohexane) was used as received.   Tetrabutylammonium fluoride (TBAF, Acros, 1 M solution in THF), dichloroacetic acid (DCAA, ????) were used as received.

3.3.2   Characterization

^{1}H NMR spectra were determined in CD_2Cl_2 and $CDCl_3$ at 400 MHz with a Varian Unity Spectrometer. Glass transition and melting temperatures were determined

[348] Quirk, R. P., S. H. Jang, H. Yang and Y. Lee "Polymer Synthesis Using Functionalized Alkyllithium Initiators: Telechelic, heterotelechelic and functionalized star-branched polymers." *Macromol. Symp.* **1998**, *132*, 281-291.

using a Perkin-Elmer Pyris 1 cryogenic DSC at a heating rate of 20 °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) using 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 tetrahydrofuran 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.

3.3.3 Anionic Polymerization of D_3 Using BMAPrLi

A 100 mL round-bottomed flask containing anhydrous cyclohexane (18.5 mL, 0.185 mol) and D_3 (10 g, 0.045 mol) was heated to 30 °C. 3-[(N-benzyl-N-methyl)amino]-1-propyllithium (1.05 mL, 1 mmol) was added to the solution to initiate the polymerization. The reaction was allowed to proceed for 4 h. After 4 h, THF (2 mL, 0.25 mol) was added to the reaction. The reaction was allowed to proceed for an additional 45 h. The reaction was terminated via the addition of trimethylchlorosilane (0.19 mL, 1.5 mmol).

3.3.4 Hydrogenolysis of Benzyl Protecting Group

A pressure vessel containing PDMS (5 g, 1.67×10^{-3} mol), THF (40 mL, 0.62 mol), and Pd/C (0.3 g) was pressured to 150 psi H_2 and placed in an oil bath at 100 °C. The reaction was allowed to proceed for 18 hours. The reaction mixture was allowed to

cool to room temperature and then filtered through a Celite bed to remove the catalyst. The solution was then concentrated and dried under vacuum.

3.3.5 Anionic Polymerization of D$_3$ Using tBDMSPrLi

A 100 mL round-bottomed flask containing anhydrous cyclohexane (18.5 mL, 0.185 mol) and D$_3$ (10 g, 0.045 mol) was heated to 30 °C. 3-(t-butyldimethylsilyloxy)-1-propyllithium (1.19 mL, 1 mmol) was added to the solution to initiate the polymerization. The reaction was allowed to proceed for 4 h. After 4 h, THF (2 mL, 0.25 mol) was added to the reaction. The reaction was allowed to proceed for an additional 45 h. The reaction was terminated via the addition of trimethylchlorosilane (0.19 mL, 1.5 mmol).

3.3.6 Acid-Catalyzed Deprotection of PDMS

A design of experiments (DOE) was used to determine appropriate reaction conditions for the acid-catalyzed deprotection of the silyl protecting group (Table 3-1). A representative reaction is described. PDMS (2.5 g, 25,300 g/mol, M_w/M_n = 1.39) was dissolved in 50 mL THF and placed in a 100 mL round-bottomed flask. Tetrabutylammonium fluoride (TBAF, 0.25 mL) was then added to the reaction flask. The reaction flask was placed in an oil bath at 60 °C for 4 hours. After the reaction was allowed to proceed, water and cyclohexane were added to the solution. The organic layer was collected and washed with water several times to remove residual acid catalyst. Three factors were varied in the DOE, as shown in Table 3-1, namely acid concentration, temperature, and time. Dichloroacetic acid was also used as an alternative to TBAF.

Table 3-1. Design of experiments (DOE) to determine viability of acid catalyzed deprotection using TBAF.

Sample	Conc. (mM)	Temp. (°C)	Time (hr)	M_n	PDI	Yield (%)
1	5	20	4	577	1.04	16
2	40	20	4	878	1.20	5
3	40	60	48	661	1.11	17
4	5	60	4	670	1.02	21
5	40	20	48	717	1.10	12
6	22.5	40	26	702	1.02	47
7	5	60	48	76500	1.01	0.5
8	5	20	48	14600	1.03	8
9	40	60	4	580	1.03	23

3.4　Results and Discussion

3.4.1　Suitability of BMAPrLi for D$_3$ Polymerization

A series of poly(dimethylsiloxane) (PDMS) homopolymers was synthesized using 3-[(N-benzyl-N-methyl)amino]-1-propyllithium as shown in Scheme 3-1.
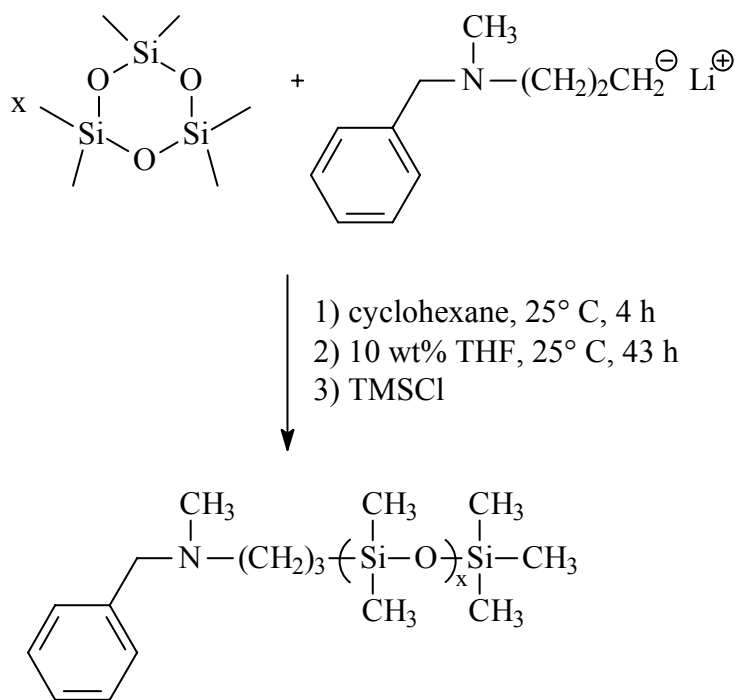
Scheme 3-1. Anionic polymerization of D$_3$ using 3-[(N-benzyl-N-methyl)amino]-1-propyllithium.

Upon the addition of the pink/red 3-[(N-benzyl-N-methyl)amino]-1-propyllithium to the reaction mixture, a pink/red color was immediately observed. Over the initial 4-hour reaction period, prior to the addition of the promoter, this color gradually faded to a yellow/orange color. It was postulated that this color shift was due to the formation of the monoadduct of initiator to D_3 monomer unit. Upon the addition of the promoter, THF, no further change in color was observed. Trimethylchlorosilane addition resulted in the immediate formation of lithium chloride salt and a colorless solution. The molecular weights and molecular weight distribution for a series of polymers are summarized in Table 3-2.

Table 3-2. Characterization of the poly(dimethylsiloxane) homopolymers prepared via anionic polymerization using BMAPrLi.

Sample	M_n (calc.)	$M_n{}^a$	$M_n{}^b$	$M_w/M_n{}^a$
PDMS-1	2400	2320	2380	1.13
PDMS-2	3750	2700	3260	1.13
PDMS-3	7500	5740	5400	1.13
PDMS-4	15000	17000	16500	1.03

[a] SEC conditions: THF, 40°C, DRI detector. [b] Determined via ^{1}H NMR spectroscopy using the endgroup resonances assigned to the benzene ring in the initiator fragment between 7.1 and 7.4 ppm in comparison to the methyl groups on the silicon of the repeating unit found at 0 ppm.

As described previously, D_3 polymerizations suffer from backbiting reactions, which are typical for many ring-opening polymerization processes, if monomer starved conditions occur, i.e., conversion is greater than 85 %. In order to avoid appreciable backbiting, our conversions were limited to 75 % and this was taken into consideration in the calculated molecular weights stated in Table 3-2. Yields were quantitative after considering the intentionally limited conversion (75 %). The molecular weights obtained from SEC agreed well with those calculated based on the grams of monomer to moles of initiator ratio. A factor that may contribute to discrepancies between calculated and SEC molecular weights is the reliance of the SEC refractive index detector on polystyrene standards. It is well known that it is not possible to obtain absolute molecular weights for PDMS via multiple angle laser light scattering due to the fact that PDMS is isorefractive with THF, which is the SEC solvent used. Thus, the SEC molecular weights for the PDMS homopolymers are in comparison to polystyrene standards. These polymers also exhibited monomodal SEC traces as illustrated in Figure 3-1. The thermal transitions observed for the functionalized PDMS samples agreed with those typically found in the literature, with a T_g of -126 °C and a T_m of -45 °C.[349]

[349] Nielsen, L. E. "*Mechanical Properties of Polymers"*; Reinhold: New York, 1962.
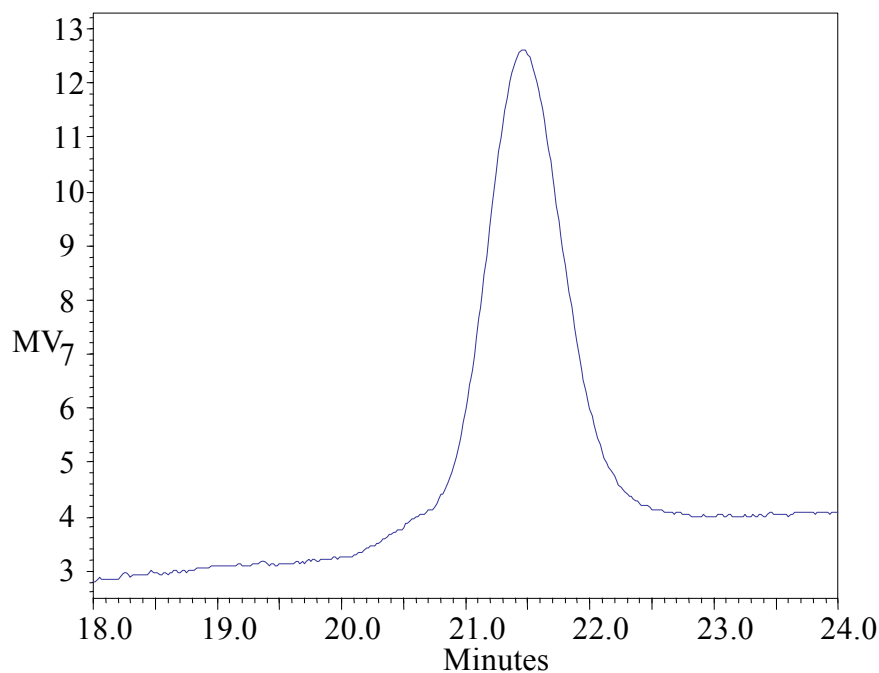
Figure 3-1. Monomodal SEC trace of 3.5K PDMS synthesized using 3-[(N-benzyl-N-methyl)amino]-1-propyllithium.

3.4.2 Confirmation of Polymer Structure

^{1}H NMR spectroscopic analysis was performed on the functionalized poly(dimethyl siloxanes). The number average molecular weights were determined via comparing the endgroup resonances assigned to the benzene ring in the initiator fragment between 7.1 and 7.7 ppm to the methyl groups on the silicon of the repeating unit found at 0 ppm. ^{1}H NMR number average molecular weights are particularly useful since PDMS is nearly isorefractive with THF, a typical SEC solvent. Thus, the PDMS peak in the SEC trace is relatively small, leading to a less accurate molecular weight determination.

3.4.3 Deprotection to Yield Secondary Amine Functionality

The protecting group on PDMS was quantitatively removed by hydrogenolysis to yield a secondary amine, as shown in Scheme 3-2. The polymer was dissolved in

cyclohexane or THF in the presence of a catalyst, such as Pd/C. The temperature was raised to 100 °C with a hydrogen pressure of 150 psi. The removal of the protecting group was confirmed using ^{1}H NMR spectroscopy and the reaction was quantitative for protecting group removal. The quantitative removal of the protecting group was observed in the ^{1}H NMR spectrum as shown in Figure 3-2. The upper ^{1}H NMR spectrum shows tertiary amine end-functionalized PDMS. After deprotection, the absence of resonances between 7.1 and 7.7 ppm indicated complete removal of the protecting group, as depicted in the lower ^{1}H NMR spectrum in Figure 3-2. The molecular weight and molecular weight distribution was unaffected by hydrogenolysis of the amine endgroup, as can be seen in the SEC trace shown in Figure 3-3. The secondary amine on the polymer chain end is amenable to many further functionalization reactions.
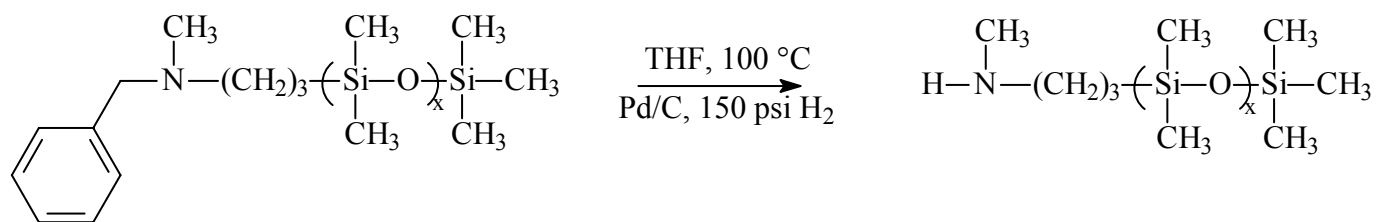
Scheme 3-2. Synthetic methodology for the deprotection of the amine functionality on PDMS.

Before deprotection

After deprotection

7.8   7.7   7.6   7.5   7.4   7.3   7.2   7.1   PPM
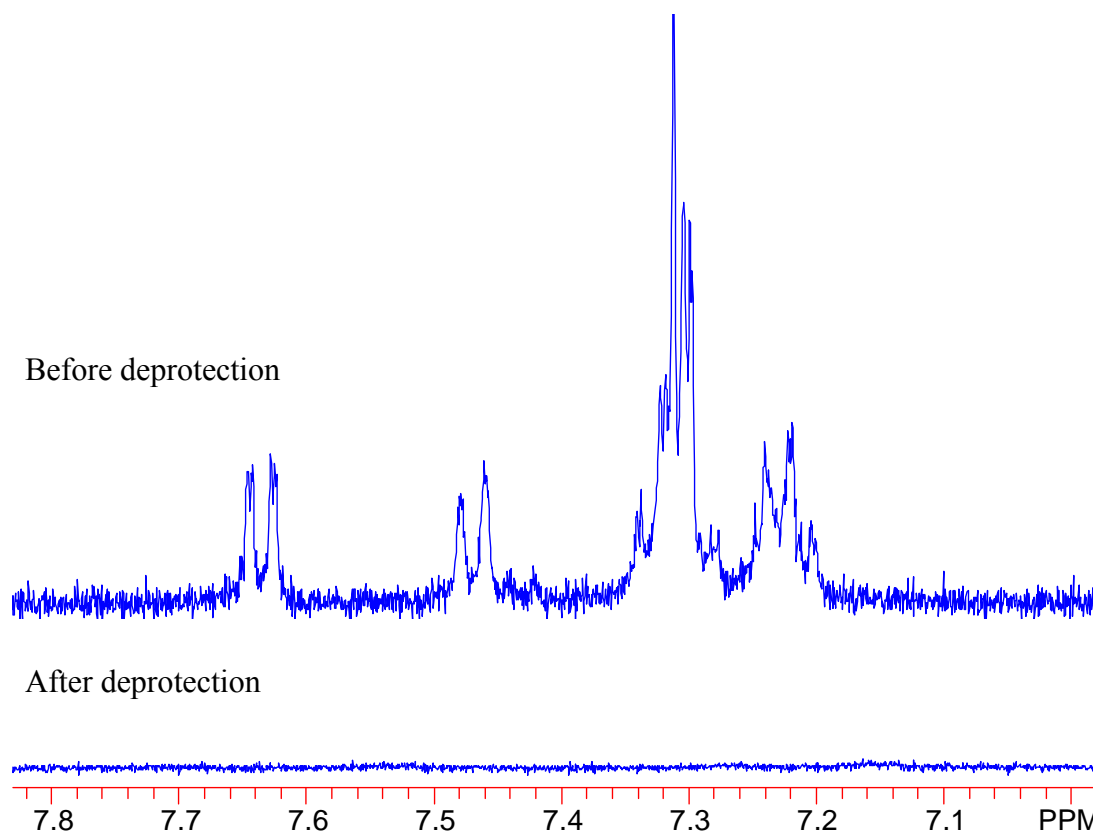
Figure 3-2. ^{1}H NMR spectra showing the quantitative removal of the benzyl protecting group to form a secondary amine terminal functionality. Polymer degradation was not observed.

Figure 3-3. Overlap of monomodal SEC traces of amine functionalized 3.5K PDMS before and after deprotection.
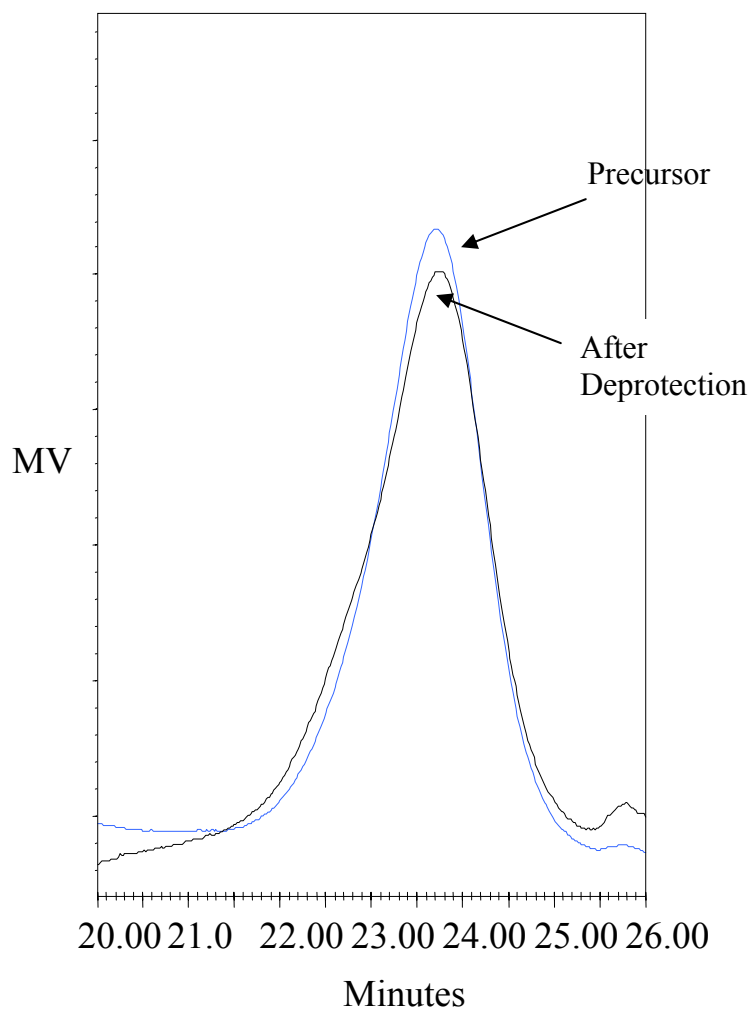
3.4.4 Suitability of tBDMSPrLi for D₃ Polymerization

A series of poly(dimethylsiloxane) (PDMS) homopolymers was synthesized using 3-(t-butyldimethylsilyloxy)-1-propyllithium as shown in Scheme 3-3. Upon the addition of the yellow 3-(t-butyldimethylsilyloxy)-1-propyllithium to the reaction mixture, a yellow color was immediately observed. The yellow color disappeared over the initial 4 hour reaction time and the solution remained colorless for the remainder of the reaction. Trimethylchlorosilane was added to terminate and endcap the living polymer chain end and resulted in the formation of lithium salts. The molecular weights and molecular weight distribution for a series of polymers are summarized in Table 3-3. As described above, conversion was limited to 75% in order to avoid backbiting reactions and this was taken into consideration in the calculated molar masses in Table 3-3. Quantitative yields were observed and molar masses, in general, agreed well with those calculated based on the moles of initiator/grams of monomer ratio, while maintaining a narrow molar mass distribution.

Scheme 3-3. Living anionic polymerization of D$_3$ using tBDMSPrLi.

Table 3-3. Characterization of protected hydroxyl functional PDMS.

M_n (target)	M_n (SEC)[a]	M_n (NMR)[b]	M_w/M_n[a]
8500	7200	6500	1.06
17000	12600	11500	1.07

[a]Determined using SEC at 40 °C in THF with MALLS detector. [b]Determined using ^{1}H NMR spectroscopy using a 400 MHz Varian NMR spectrometer in CDCl$_3$.

### 3.4.5 Confirmation of Polymer Structure

^{1}H NMR spectroscopic analysis was performed on the protected functionalized poly(dimethylsiloxanes) (Figure 3-4). All resonances were well-assigned and calculated molar masses agreed well with SEC molar masses. The number average molecular weights were determined via comparison of the endgroup resonances to the well-defined backbone resonances attributed to the methyl protons attached to the silicon of the repeating unit found at 0 ppm (Figure 3-4, peak a). Two distinct resonances were assigned to the functional endgroup and were used in the molar mass calculation, specifically those at 3.6 ppm assigned to the methylene adjacent to the silyl ether (Figure 3-4, peak b) and 0.9 ppm assigned to the t-butyl substituent on the protecting group (Figure 3-4, peak d). Methyl protons attached to the protecting group were indistinguishable from the polymer backbone (Figure 3-4, peak a).
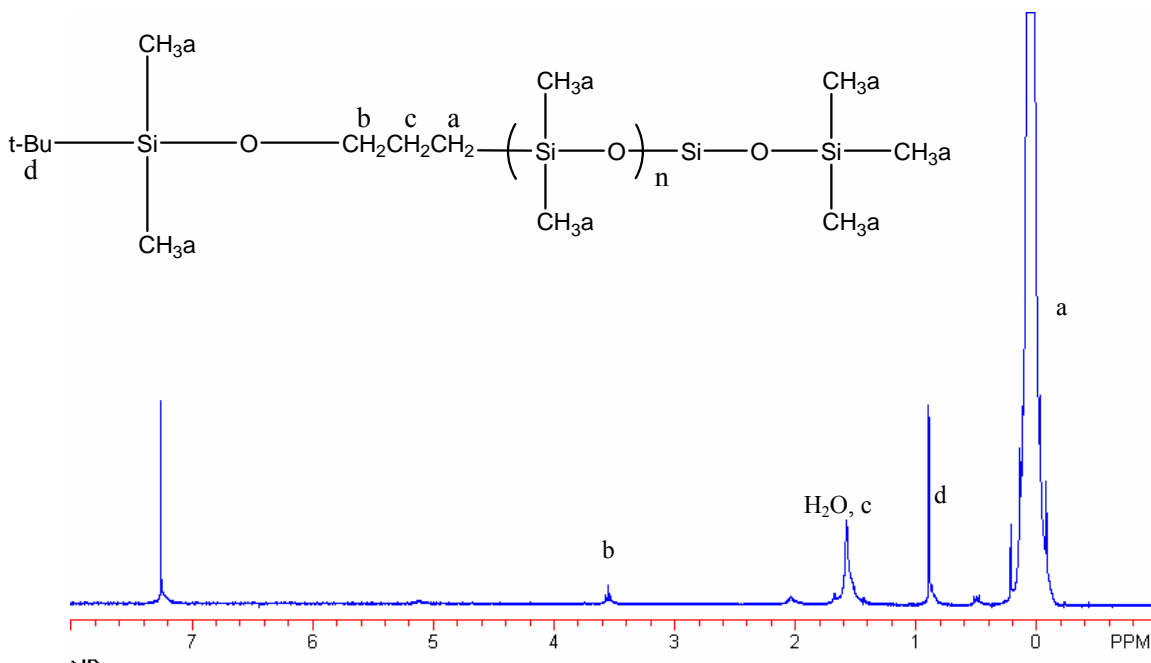
Figure 3-4. ^{1}H NMR spectrum of tBDMS-PDMS.

3.4.6 Degradation of Polymer Backbone due to Deprotection Conditions

Acid catalyzed deprotection of the silyl ether protecting group was attempted using a variety of conditions, as described in Table 3-1. Concentration of TBAF was varied from 5 mM to 40 mM, temperature from 20 °C to 60 °C, and time from 4 hours to 48 hours. Under most sets of reaction conditions, complete degradation of the siloxane polymer backbone was observed, yielding low molar mass oligomers. Overall yields were low, generally less than 20 percent, and this was attributed to the difficulty in isolating the low molar mass species. It was therefore concluded that TBAF was not an appropriate acid catalyst for the deprotection reaction due to the acid instability of the polymer backbone. Dichloroacetic acid was also used in an attempt to deprotect the polymer chain end to yield a hydroxyl functionality (Table 3-4). While dichloroacetic acid was not observed to degrade the polymer backbone, it was also not effective in removing the protecting group under a variety of conditions.

Table 3-4. Determination of viability of acid catalyzed deprotection using dichloroacetic acid.

Time (min.)	$M_n{}^a$	$M_w/M_n{}^a$
60	27429	1.41
120	28548	1.41
180	26284	1.52

[a]Determined using SEC at 40 °C in THF with MALLS detector.

3.5 Conclusions

PDMS homopolymers were synthesized via living anionic polymerization using protected functionalized initiators. Both a protected amine initiator and a protected hydroxyl initiator were used and controlled molar masses and narrow molar mass distributions were obtained from each system. The protected amine was successfully deprotected to quantitatively a secondary amine functionality at the polymer chain end. This secondary amine functionalized PDMS is suitable for diverse functionalization strategies. However, suitable deprotection conditions were not found for the protected hydroxyl group due to the acid sensitivity of the polymer backbone.

3.6 Acknowledgements

Chapter 4 Synthesis and Characterization of Amine and Hydroxyl Terminated Polyisoprene Homopolymers via Living Anionic Polymerization Using Functional Initiation

Taken in part from:
Elkins, C. L. and Long, T. E. *Macromolecules* **2005**, *submitted*.

4.1 Abstract

The polymerization of isoprene was controlled using both 3-(t-butyldimethylsilyloxy)-1-propyllithium and 3-[(N-benzyl-N-methyl)amino]-1-propyllithium functional initiators. Homopolymers with controlled molar mass and narrow molar mass distributions were synthesized and coupled efficiently with divinylbenzene to form star-shaped polymers. The star-shaped polymers were subsequently hydrogenated and deprotected quantitatively. Melt rheological characterization of a series of well-defined non-functional and hydroxyl functional poly(ethylene-*co*-propylene)s showed that high molar mass star-branched architectures (90,000 g/mol) behaved similarly to lower molar mass linear polymers (24,000 g/mol). Transitions in the same frequency range were observed in both storage modulus and complex viscosity measurements, with the star-branched macromolecules exhibiting broader transitions from the terminal-to-plateau regions. Moreover, the chain end hydroxyl groups on these poly(ethylene-*co*-propylene) star-shaped polymers are amenable to many further functionalization reactions.

4.2 Introduction

Star-shaped polymers encompass a unique architecture comprised of long chain branches radiating from a central core or branch point. Long chain branching is known to affect polymer physical properties and processability and the influence of polymer architecture on macromolecular properties is an ongoing field of study.[350] Star polymers are often difficult to synthesize in a well-controlled manner, complicating the elucidation of structure-property relationships. Chain-end functionalization is an additional challenge in the synthesis and characterization of these complex polymers. Living anionic polymerization methodologies are typically used to synthesize star-shaped macromolecules. Living anionic polymerization provides many benefits over conventional free radical polymerization. In living anionic polymerization, the molar mass of the polymer is reliably controlled, while maintaining a narrow molar mass distribution. It is also possible to control stereochemistry, synthesize block and graft copolymers, and functionalize polymer chain ends.

Polymers prepared using anionic initiators are generally end-functionalized with a variety of post-polymerization reactions involving electrophilic agents.[351] However, many of these functionalization reactions are not quantitative and result in undesirable side-products. Functionalized alkyllithium initiators provide quantitative chain end functionalization and are an attractive alternative for the synthesis of chain-end functionalized polymers. It is generally necessary to use a protecting group in the

[350] Long, V. C., G. C. Berry and L. M. Hobbs *Polymer* **1964**, *5*, 517-524.Burchard, W. *Adv. Polym. Sci.* **1999**, *143*, 111-194.Mandelkern, L. "*Crystallization of polymers. Volume 1 Equilibrium concepts."* Cambridge University Press, 2002.Janzen, J. and R. H. Colby "Diagnosing long-chain branching in polyethylenes." *J. Mol. Struct.* **1999**, *485-485*, 569-584.
[351] Hsieh, H. L. and R. P. Quirk "*Anionic Polymerization: Principles and Practical Applications"*; Marcel Dekker: New York, 1996.Goethals, E. J. "Telechelic Polymers: Synthesis and Applications"; CRC Press: Boca Raton, Fl, 1989.

initiator because most functionalities of interest, such as hydroxyl, carboxyl, and amino, are not stable in the presence of organolithium reagents.[352] A suitable protecting group is stable during anionic polymerization, but also readily removed after complete polymerization.[353] Functionalized initiators also facilitate the synthesis of telechelic and heterotelechelic polymers, functionalized block polymers, and star-shaped polymers with functional groups on each arm terminus. The use of the functional initiator 3-(t-butyldimethylsilyloxy)-1-propyllithium (tBDMSPrLi) was reported in the synthesis of a variety of polymers, such as polyisoprene,[354] polybutadiene,[355] poly(methyl methacrylate),[356] and poly(1,3-cyclohexadiene)[357] and tBDMSPrLi initiation provides a facile pathway to chain-end functionalized star-shaped polymers.

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[352] Schulz, D. N., S. Datta and R. M. Waymouth "Use of protecting groups in polymerization." *Polym. Mater. Sci. Eng.* **1997**, *76*, 3-5.Nakahama, S. and A. Hirao "Protection and polymerization of functional monomers: anionic living polymerization of protected monomers." *Prog. Polym. Sci.* **1990**, *15*, 299-335.Greene, T. W. and P. G. M. Wuts "*Protective Groups in Organic Synthesis*"; 3rd ed.; John Wiley & Sons: New York, 1999.

[353] Quirk, R. P., S. H. Jang, H. Yang and Y. Lee "Polymer Synthesis Using Functionalized Alkyllithium Initiators: Telechelic, heterotelechelic and functionalized star-branched polymers." *Macromol. Symp.* **1998**, *132*, 281-291.

[354] Quirk, R. P., S. H. Jang, K. Han, H. Yang, B. Rix and Y. Lee "Anionic Synthesis of Hydroxyl-Functionalized Polymers Using Protected, Functionalized Alkyllithium and Isoprenyllithium Initiators". *Functional Polymers*, 1998; pp 71-84.Quirk, R. P., S. H. Jang and J. Kim "Recent Advances in Anionic Synthesis of Functionalized Elastomers using Functionalized Alkyllithium Initiators." *Rubber Rev., Rubber Chem. Tech.* **1996**, *69*, 444.Quirk, R. P. and R. T. Mathers "Surface-initiated living anionic polymerization of isoprene using a 1,1-diphenylethylene derivative and functionalization with ethylene oxide." *Polym. Bull.* **2001**, *45*, 471-477.Switek, K. A., F. S. Bates and M. A. Hillmyer "Star Polymer Synthesis Using Hexafluoropropylene Oxide as an Efficient Multifunctional Coupling Agent." *Macromolecules* **2004**, *37*, 6355-6361.

[355] Quirk, R. P., S. H. Jang, H. Yang and Y. Lee "Polymer Synthesis Using Functionalized Alkyllithium Initiators: Telechelic, heterotelechelic and functionalized star-branched polymers." *Macromol. Symp.* **1998**, *132*, 281-291.Quirk, R. P., S. H. Jang and J. Kim "Recent Advances in Anionic Synthesis of Functionalized Elastomers using Functionalized Alkyllithium Initiators." *Rubber Rev., Rubber Chem. Tech.* **1996**, *69*, 444.Quirk, R. P. and S. H. Jang "Anionic Synthesis of Hydroxy-Functionalized Polybutadienes Using Protected, Functionalized Organolithium Initiators." *Polym. Mater. Sci. Eng.* **1997**, *76*, 8-9.Quirk, R. P., S. H. Jang, K. Han, H. Yang, B. Rix and Y. Lee "Anionic Synthesis of Hydroxyl-Functionalized Polymers Using Protected, Functionalized Alkyllithium and Isoprenyllithium Initiators". *Functional Polymers*, 1998; pp 71-84.Hwang, J., M. D. Foster and R. P. Quirk "Synthesis of 4-, 8-, 12-arm star-branched polybutadienes with three different chain-end functionalities using a functionalized initiator." *Polymer* **2004**, *45*, 873-880.

[356] Quirk, R. P. and R. S. Porzio "The Anionic Synthesis of Functionalized Linear and Star-branced Poly(methyl methacrylates) Using Protected Hydroxy-Functionalized Alkyllithium Initiators." *Polym. Prepr.* **1997**, *38*, 463-464.Tong, J.-D., C. Zhou, S. Ni and M. A. Winnik "Synthesis of Meth(acrylate)

Star polymers are typically synthesized using either a core-first approach, or an arm-first approach. In the core-first synthetic method, a multifunctional initiator is used. The number of arms is proportional to the number of functionalities on the initiator.[358] Using the core-first method, the exact number of arms is easily determined. In the arm-first synthetic method, linear arm polymers are synthesized and then coupled using a multifunctional linking agent or divinyl compound. In this case, the number of arms depends on the linking efficiency of the arm polymer to the multifunctional core and an alternative method was used to determine the number of arms. While both functional polymers and star-shaped polymers are prevalent in the literature, the combination of well-defined hydroxyl functionality and star-shaped macromolecules is limited. Hedrick et al. reported the core-first synthesis of star-shaped poly(ε-caprolactone) hydroxyl terminated macroinitiators with six arms and subsequent transformation into atom transfer radical polymerization (ATRP) initiators using ring opening polymerization.[359] Quirk et al. used the functional initiator tBDMSPrLi to synthesize star-shaped polymers

Diblock Copolymers Bearing a Fluorescent Dye at the Junction Using A Hydroxyl-Protected Initiator and the Combination of Anionic Polymerization and Controlled Radical Polymerization." *Macromolecules* **2001**, *34*, 696-705.Mizawa, T., K. Takenaka and T. Shiomi "Synthesis of alpha-Maleimide-omega-Dienyl Heterotelechelic Poly(methyl methacrylate) and Its Cyclization by the Intramolecular Diels-Alder Reaction." *J. Polym. Sci. Part A* **2000**, *38*, 237-246.

[357] Quirk, R. P., F. You, C. Wesdemiotis and M. A. Arnould "Anionic Synthesis and Characterization of omega-Hydroxyl-Functionalized Poly(1,3-Cyclohexadiene)." *Macromolecules* **2004**, *37*, 1234-1242.

[358] Zhang, X., J. Xia and K. Matyjaszewski "End-Functional Poly(t-butyl acrylate) Star Polymers by Controlled Radical Polymerization." Ibid. **2000**, *33*, 2340-2345.

[359] Hedrick, J. L., M. Trollsas, C. J. Hawker, B. Atthoff, H. Claesson, A. Heise, R. D. Miller, D. Mecerreyes, R. Jerome and P. Dubois "Dendrimer-like Star Block and Amphiphilic Copolymers by Combination of Ring Opening and Atom Transfer Radical Polymerization." Ibid. **1998**, *31*, 8691-8705.

from several monomer families including polybutadiene [360] and poly(methyl methacrylate).[361]

In this paper, the synthesis and characterization of a series of hydroxyl functionalized poly(ethylene-*co*-propylene) polymers of various architectures is described. Living anionic polymerization initiated with tBDMSPrLi proved a facile methodology for the preparation of chain-end functionalized polymers including star-shaped polymers with a functional periphery. Subsequent quantitative hydrogenation of the polyisoprene star polymers increased the thermal and oxidative stability of the polymer backbone.[362] The protecting group on the peripheral functionalities was removed using acid catalyzed hydrolysis rendering the peripheral groups suitable for diverse functionalization strategies.

4.3   Experimental

4.3.1   Materials

For tBDMSPrLi initiated polymerizations, isoprene (Aldrich, 99%) was passed through an alumina column, and subsequently through a molecular sieves column. For BMAPrLi initiated polymerizations, isoprene was vacuum distilled from dibutylmagnesium (0.10 mm Hg). 3-(t-butyldimethylsilyloxy)-1-propyllithium (tBDMSPrLi, FMC Corporation Lithium Division. 0.4 M in cyclohexane) and 3-[(N-

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[360] Quirk, R. P. and S. H. Jang "Anionic Synthesis of Hydroxy-Functionalized Polybutadienes Using Protected, Functionalized Organolithium Initiators." *Polym. Mater. Sci. Eng.* **1997**, *76*, 8-9.Hwang, J., M. D. Foster and R. P. Quirk "Synthesis of 4-, 8-, 12-arm star-branched polybutadienes with three different chain-end functionalities using a functionalized initiator." *Polymer* **2004***, 45*, 873-880.

[361] Quirk, R. P. and R. S. Porzio "The Anionic Synthesis of Functionalized Linear and Star-branced Poly(methyl methacrylates) Using Protected Hydroxy-Functionalized Alkyllithium Initiators." *Polym. Prepr.* **1997***, 38*, 463-464.

[362] Barrios, V. A. E., R. H. Najera, A. Petit and F. Pla "selective hydrogenation of butadiene-styrene copolymers using a Ziegler-Natta type catalyst, kinetic study." *Eur. Polym. J.* **2000***, 36*, 1817-1834.

benzyl-N-methyl)amino]-1-propyllithium (FMC Corporation Lithium Division, 0.95 M in cyclohexane) were used as received. Ethylene oxide (Aldrich) was used as received. Divinylbenzene (Aldrich, 80% divinylbenzene comprising a mixture of isomers, 20% ethylvinylbenzene) was stirred over calcium hydride for 24 hours, degassed several times, and vacuum distilled (0.10 mm Hg, 23-25 °C). Divinylbenzene was then vacuum distilled from dibutylmagnesium (0.10 mm Hg, 23-25 °C). Nickel octoate (Shepherd Chemicals, 8% (w/w) in mineral spirits) was used as received. Triethylaluminum (Aldrich, 1.4 M in hexane) was used as received. Palladium on activated carbon (Aldrich, 10 % (w/w)) was used as received. For tBDMSPrLi initiated polymerizations, cyclohexane (EM Science, ACS grade) was passed through an alumina column, and subsequently through a molecular sieves column immediately prior to use. For BMAPrLi initiated polymerizations, cyclohexane was stirred over sulfuric acid for 7 days, decanted, and distilled under nitrogen from sodium immediately prior to use.

4.3.2 Anionic Polymerization of Isoprene Using BMAPrLi

A 100 mL round-bottomed flask containing anhydrous cyclohexane (50 mL, 0.46 mol) and isoprene (5 g, 0.074 mol) was heated to 30 °C. 3-[(N-benzyl-N-methyl)amino]-1-propyllithium (0.35 mL, 0.33 mmol) was added to the solution to initiate polymerization. The reaction (Scheme 1) was allowed to proceed for 3.5 hr. The reaction was terminated via the addition of degassed methanol. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.0 – 7.6 ppm (m, benzyl-protons), 5.1 ppm (b, 1,4-polyisoprene), 4.75 ppm (b, 3,4-polyisoprene), 1.0 – 2.2 (b, –CH$_3$, –CH$_2$–, CH in polyisoprene units).
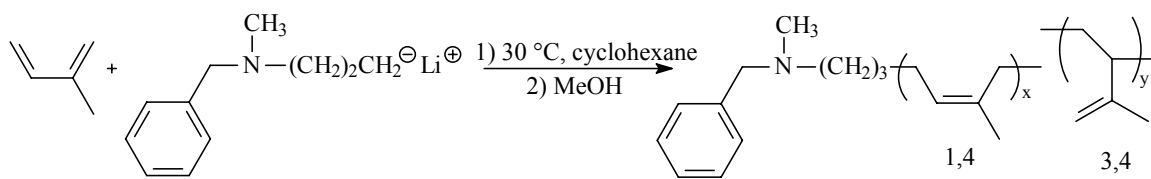
Scheme 4-1. Living anionic polymerization of isoprene using BMAPrLi.

4.3.3 Simultaneous Hydrogenation and Deprotection of Functionalized Polyisoprene

A polyisoprene star polymer (3.0 g, 0.02 mmol) and a preformed nickel catalyst (approximately 20 mL, 0.10 mmol) were dissolved in cyclohexane (500 mL) and added to a 600 mL reactor. The reactor was pressurized with hydrogen and vented three times. The vessel was pressurized with hydrogen (90 psi) and heated to 50 °C for 24 hours. The nickel catalyst was extracted with three citric acid (Aldrich, 98%, 500 mL, 50 mmol) washes. The cyclohexane solution was concentrated to 100 mL by removing solvent in vacuo. The polymer solution was then precipitated into isopropanol (600 mL) and dried in vacuo at 60 °C for 24 hours. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 1.0 – 2.0 (b, –CH$_3$, –CH$_2$–, CH in poly(ethylene-*co*-propylene) units).

4.3.4 Synthesis of linear telechelic polyisoprene

All polymerizations were conducted using a glass anionic reactor system, which contained stainless steel transfer lines for isoprene (monomer) and cyclohexane (solvent) as described previously.[363] In addition, the reactor was equipped with magnetic stirring and temperature control using steam/cold water passed through stainless steel coils within the 600 mL glass polymerization vessel. Additional reaction components were introduced through a septum sealed port. The system was maintained at constant nitrogen pressure (10-15 psi).

The 600 mL reaction vessel was charged with cyclohexane (500 mL, 4.64 mol) and isoprene (45 mL, 0.44 mol) and maintained at 50 ℃. 3-(t-butyldimethylsilyloxy)-1-

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[363] Hoover, J. M. and J. E. McGrath "A laboratory-scale, low-pressure for living polymerizations and polymer modification studies." *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1986**, *27*, 150-151.

propyllithium (4.47 mL, 2 mmol) was added to the solution to initiate polymerization, targeting a 15,000 g/mol polymer. The reaction was allowed to proceed for 2 h to ensure quantitative conversion. Degassed methanol was added to terminate the polymerization and generate monofunctional polyisoprenes. An excess of ethylene oxide was bubbled through the polymerization solution and allowed to react for 30 min to prepare telechelic polyisoprenes. The polymerization was terminated using degassed methanol as depicted in Scheme 4-2a. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 5.1 ppm (b, 1,4-polyisoprene), 4.75 ppm (b, 3,4-polyisoprene), 3.6 ppm (t, CH_2-O-Si(CH$_3$)$_2$(C(CH$_3$)$_3$), 1.0 – 2.2 (b, –CH$_3$, –CH$_2$–, CH in polyisoprene units), 0.9 ppm (s, CH$_2$-O-Si(CH$_3$)$_2$(C(CH_3)$_3$), 0.04 ppm (s, CH$_2$-O-Si(CH_3)$_2$(C(CH$_3$)$_3$).
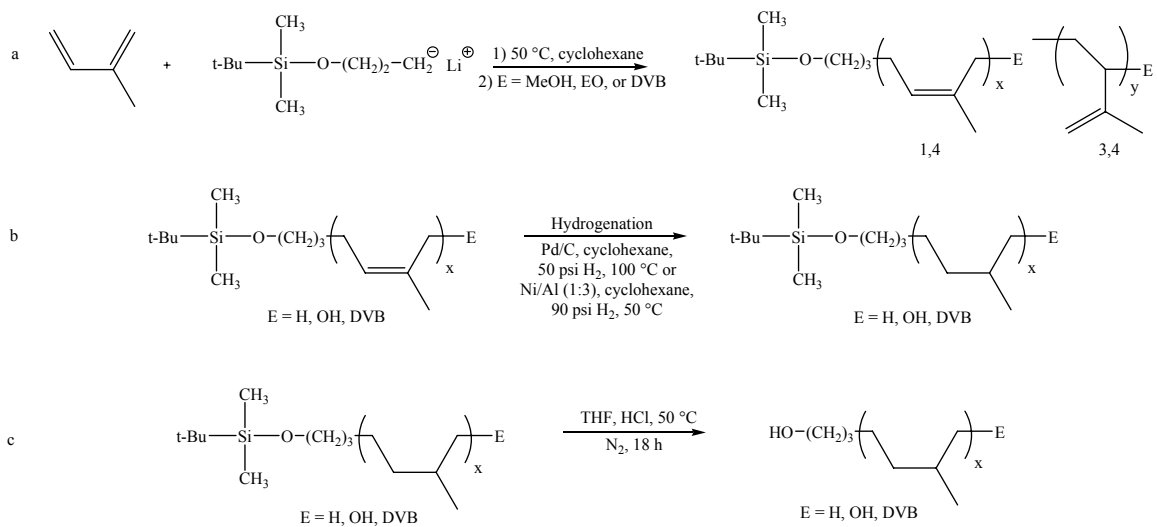
Scheme 4-2. Synthesis of chain-end functionalized polyisoprene homopolymers.

4.3.5   Synthesis of star-shaped telechelic polyisoprene

The 600 mL reaction vessel was charged with cyclohexane (500 mL, 4.64 mol) and isoprene (45 mL, 0.44 mol) and maintained at 50 ºC.   3-(t-butyldimethylsilyloxy)-1-propyllithium (4.47 mL, 2 mmol) was added to the solution to initiate polymerization, targeting a 15,000 g/mol polymer. The reaction was allowed to proceed for 2 h. After 2 h, an aliquot was removed and terminated with degassed methanol.   Divinylbenzene (1.89 mL, 10.7 mmol) was added to the solution to couple the polyisoprene arms.   The reaction was allowed to proceed overnight. The reaction was terminated via the addition of degassed methanol as depicted in Scheme 4-2a. ^{1}H NMR assignments corresponded to those from linear polyisoprene and resonances for divinylbenzene were not observed, presumably due to immobility in the star core.

4.3.6   Hydrogenation of linear polyisoprene polymers.

A linear polyisoprene (18 g) was dissolved in cyclohexane (110 mL) and added to a 500 mL pressure vessel. Pd/C (2.5 g) catalyst was added and the reactor was pressurized with hydrogen and vented three times. The vessel was pressurized with hydrogen (50 psi) and heated to 100 °C for 24 h.   The Pd/C catalyst was removed using filtration through Celite. The cyclohexane solution was concentrated to 100 mL in vacuo. The polymer solution was then precipitated into isopropanol (600 mL) and dried in vacuo at 60 °C for 24 h as depicted in Scheme 4-2b. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 3.6 ppm (t, CH_2-O-Si(CH$_3$)$_2$(C(CH$_3$)$_3$), 1.0 – 2.0 (b, –CH$_3$, –CH$_2$–, CH in poly(ethylene-*co*-propylene) units), 0.9 ppm (s, CH$_2$-O-Si(CH$_3$)$_2$(C(CH_3)$_3$), 0.04 ppm (s, CH$_2$-O-Si(CH_3)$_2$(C(CH$_3$)$_3$).

4.3.7 Synthesis of the preformed nickel hydrogenation catalyst.

The nickel hydrogenation catalyst was synthesized as previously described.[364] Cyclohexane (15 mL) and nickel octoate (0.228 g, 0.66 mmol) were added to a septum sealed 100 mL round-bottomed flask that was purged with nitrogen. Triethylaluminum (TEA, 1.36 mL) was added dropwise to the nickel solution. An opaque, black colloidal suspension formed immediately and was allowed to age for 15 minutes at room temperature under a nitrogen atmosphere.

4.3.8 Hydrogenation of polyisoprene star-shaped polymers.

A polyisoprene star polymer (3.0 g, 0.02 mmol) and a preformed nickel catalyst (approximately 20 mL, 0.10 mmol) were dissolved in cyclohexane (500 mL) and added to a 600 mL reactor. The reactor was pressurized with hydrogen and vented three times. The vessel was pressurized with hydrogen (90 psi) and heated to 50 °C for 24 h. The nickel catalyst was extracted from the polymer solution with three citric acid (Aldrich, 98%, 500 mL, 50 mmol) washes following quantitative hydrogenation. The cyclohexane solution was concentrated to 100 mL, precipitated into isopropanol (600 mL), and dried in vacuo at 60 °C for 24 h as summarized in Scheme 4-2b. ^{1}H NMR assignments corresponded to those of hydrogenated linear polyisoprene.

4.3.9 Removal of protecting group from poly(ethylene-*co*-propylene)

The quantitatively hydrogenated poly(ethylene-*co*-propylene) (1.0 g, 0.007 mmol) was dissolved in tetrahydrofuran (THF, 50 mL) and concentrated hydrochloric acid (10

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[364] Hoover, J. M., T. C. Ward and J. E. McGrath "The Influence of Hydrogenation on Star Block Copolymers based on Tertiary butyl styrene-isoprene-divinylbenzene." *Polym. Prepr.* **1985**, 252-254.Hoover, J. M., T. C. Ward and J. E. McGrath "*Advances in Polyolefins. The World's Most Widely Used Polymers.*" D. Reidel Publishing Co.: Dordrecht, Neth., 1987.

M, 5 mL) was added to the solution. The solution was allowed to stir for 18 h at 50 ºC and precipitated into isopropanol twice to remove residual hydrochloric acid. The polymer was then dried at 60 ºC under vacuum for 24 h as depicted in Scheme 4-2c. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 3.6 ppm (t, CH_2-OH), 1.0 – 2.0 (b, –CH$_3$, –CH$_2$–, CH in poly(ethylene-*co*-propylene) units).

4.3.10 Characterization.

^{1}H NMR spectra were determined in CDCl$_3$ at 400 MHz with a Varian Unity Spectrometer. Glass transition and melting temperatures were determined using a Perkin-Elmer Pyris 1 cryogenic DSC at a heating rate of 10 °C/min under nitrogen. Glass transition temperatures are reported as the transition mid point during the second heat. Molecular weights were determined using size exclusion chromatography (SEC) with a Waters Alliance SEC system equipped with a Wyatt miniDAWN multiple angle laser light scattering detector. Melt rheological analysis was carried out using a TA Instruments AR2000 rheometer with 25 mm parallel plate geometry and a 5 % strain amplitude. Master curves for a reference temperature of 50 °C were created based on the time-temperature superposition correspondence principle. Temperature sweeps were carried out at a frequency of 1 Hz.

4.4   Results and Discussion

4.4.1   Suitability of BMAPrLi for Isoprene Polymerization

A series of linear polyisoprene homopolymers ranging in molar mass from 5000 g/mol to 40,000 g/mol were synthesized using the functional initiator 3-[(N-benzyl-N-methyl)amino]-1-propyllithium (BMAPrLi). Excellent molar mass control was observed

using both SEC and ^{1}H NMR spectroscopy and narrow molar mass distributions were observed (Table 4-1). The benzyl protecting group at the polymer chain end was clearly observed using ^{1}H NMR spectroscopy. Figure 4-1a shows a representative ^{1}H NMR spectrum and the key resonances are those at 7.3 ppm associated with the benzyl protecting group and 5.1 and 4.75 ppm associated with the olefinic backbone (1,4- and 3,4-enchainment, respectively). The number average molar mass was calculated using comparison of the protecting group resonances with the olefinic backbone resonances. It was also observed that the use of the polar initiator fragment did not significantly change the 1,4- versus 3,4-enchainment of the polymer backbone, with 92% 1,4-enchainment and 8% 3,4-enchainment, typical of diene polymerizations carried out in non-polar media.

M_n (target)	M_n (SEC)[a]	M_n (NMR)[b]	M_w/M_n [a]
5000	7200	6500	1.08
10000	13000	12500	1.08
20000	17800	17000	1.11
40000	39100	43000	1.06

[a] Determined using SEC at 40 °C in THF with a MALLS detector. [b] Determined using a Varian 400 MHz NMR spectrometer at 25 °C in CDCl$_3$.

Table 4-1. Molar mass control for anionic polymerization of isoprene using BMAPrLi.
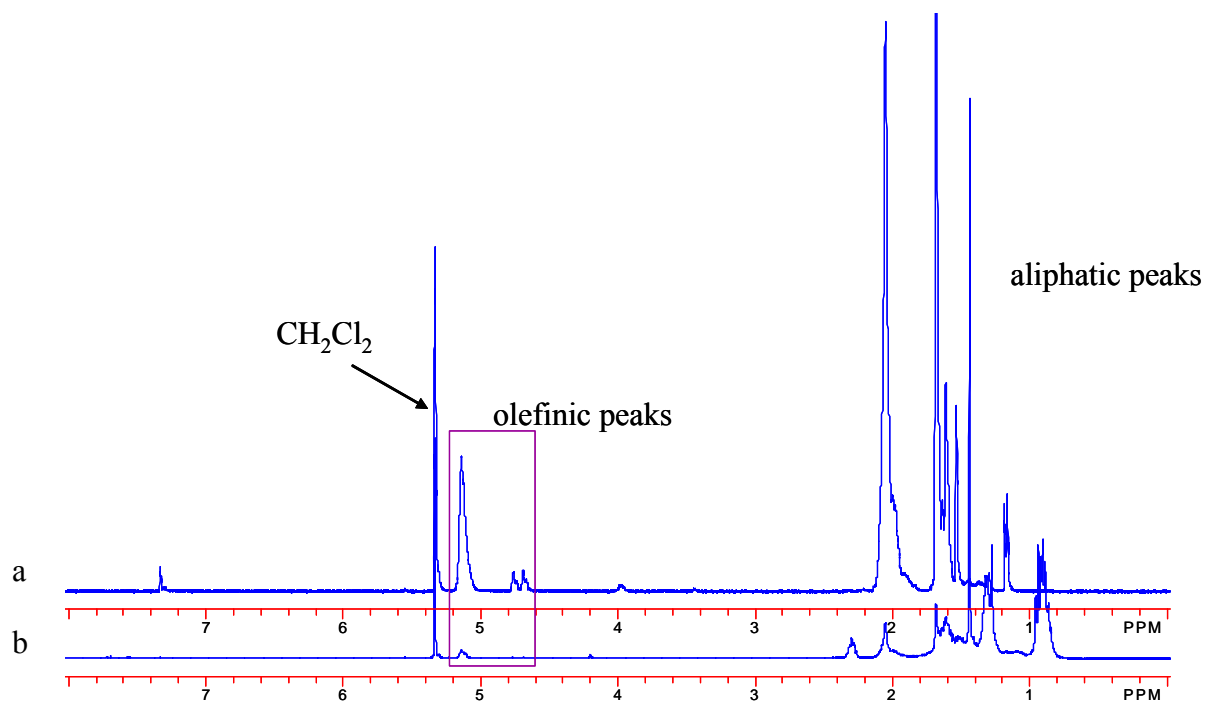
Figure 4-1. a) ^{1}H NMR spectrum of BMAPrLi initiated polyisoprene b) hydrogenated and deprotected BMAPrLi initiated polyisoprene.

4.4.2   Hydrogenation and Deprotection to Yield Secondary Amine Functionality

Hydrogenation of the BMAPrLi initiated polyisoprenes was carried out using the homogeneous catalyst system consisting of triethylaluminum and nickel octoate (3:1). Near quantitative hydrogenation was observed, as shown in Figure 4-1b. Interestingly, the hydrogenation conditions were sufficient to quantitatively remove the benzyl protecting group to yield a secondary chain end amine group, as was shown using the disappearance of the peak at 7.3 ppm.   Ultimately, however, the presence of the secondary amine on the polymer chain end precluded the ability to remove the homogeneous catalyst from the polymer solution.   Repeated citric acid washes proved ineffective in removing the catalyst from the polymer solution.   Column chromatography was also not able to separate the catalyst from the polymer solution.   It was suggested that the secondary amine was able to interact strongly with the nickel/aluminum catalyst system, making separation difficult.   Due to this difficulty, further study was not conducted on this system.

4.4.3   Suitability of tBDMSPrLi for Isoprene Polymerization

The polymerization of isoprene was controlled using the protected hydroxyl initiator tBDMSPrLi and homopolymers with narrow molar mass distributions were obtained (Table 4-2). It was assumed that impurities present in the initiator solution did not play a large role in the polymerization due to the controlled molar mass and narrow molar mass distributions. Subsequent endcapping with ethylene oxide and termination with methanol produced telechelic functional polymers. Polyisoprene star polymers were synthesized using the tBDMSPrLi initiator and subsequent coupling with divinyl benzene

(DVB).   Narrow molar mass distributions were observed for the polyisoprene homopolymer arms prior to coupling with DVB.   Relatively narrow molar mass distributions of 1.26 to 1.36 were observed for the DVB coupled polyisoprene star polymers (Table 4-3) and SEC analysis confirmed high conversion of arm precursors to star-shaped polymers (Figure 4-3). The presence of the protecting group in the initiator fragment was confirmed using ^{1}H NMR spectroscopy. Peaks at 0.04 ppm (a) and and 0.90 ppm (b) in Figure 4-2a correspond to the methyl groups and t-butyl group bonded to silicon, respectively. Resonances associated with the aliphatic carbons of the polymer backbone (c) were present between 1 and 2 ppm. Distinct olefinic peaks were observed at 5.1 and 4.75 ppm, assigned to 1,4- and 3,4- enchainment, respectively. Similar microstructures were observed for polyisoprenes synthesized using either the protected hydroxyl initiator tBDMSPrLi or the more traditional *s*-butyllithium anionic initiator, and approximately 92% 1,4-enchainment and 8% 3,4-enchainment were observed in both cases.

Table 4-2. Molar mass control using tBDMSPrLi as initiator for the anionic polymerization of isoprene.

M_n (target)	M_n (SEC)[a]	M_n (NMR)[b]	M_w/M_n[a]	T_g (°C)[c]
5000	4300	4300	1.04	-64
10000	10900	9100	1.03	-65
20000	18600	19100	1.04	-61
47000	49900	52100	1.06	-62

[a] Determined using SEC at 40 °C in THF with a MALLS detector. [b] Determined using a Varian 400 MHz NMR spectrometer at 25 °C in CDCl$_3$. [c] Determined using a Perkin-Elmer Pyris 1 cryogenic DSC at a heating rate of 20 °C/min under nitrogen.
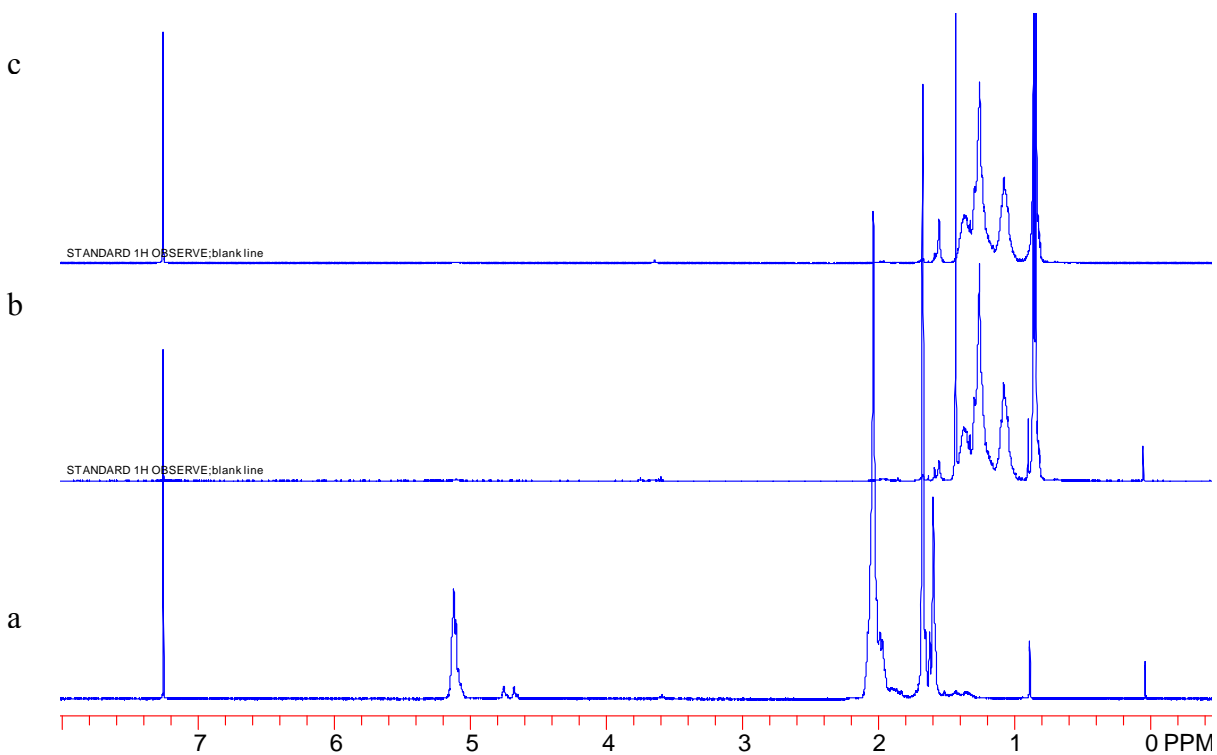
Figure 4-2. ^{1}H NMR showing a) tBDMS-polyisoprene, b) hydrogenated tBDMS-polyisoprene (poly(ethylene-*co*-propylene)), and c) hydroxyl terminated poly(ethylene-*co*-propylene).

Table 4-3. Synthesis of star-shaped polyisoprene via coupling with divinylbenzene.

Arm M_n (target)	Arm M_n (SEC)	Arm M_w/M_n	DVB: Initiator	Star M_n	Star M_w/M_n	Est. # Arms
5000	7400	1.04	4.0	88200	1.26	12
5000	8100	1.02	6.0	142000	1.25	17
10000	14000	1.05	4.0	108000	1.27	7
10000	10800	1.07	6.0	128000	1.37	12
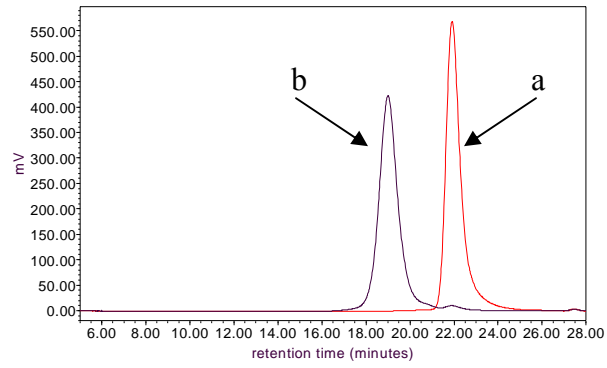
Figure 4-3. SEC traces showing the conversion of the a) polyisoprene arm polymers to b) star polymers.

4.4.4 Hydrogenation and Deprotection of tBDMSPrLi Initiated Polyisoprene

Quantitative hydrogenation of the polymer was necessary to avoid deleterious acid catalyzed coupling reactions and deprotect the hydroxyl functionality. The linear polyisoprenes were quantitatively hydrogenated generally in 12 h using heterogeneous palladium/carbon catalysis, while incomplete hydrogenation of the star-shaped polyisoprenes was observed after 7-10 days under identical hydrogenation conditions. Pendant olefins on the divinylbenzene core may have contributed to the difficulty in hydrogenation, due to the steric hindrance at the star polymer core. Previous literature reported hydrogenation of star-shaped polydienes at much higher temperatures (170 °C) and pressures (~800 psi), [365] and a homogeneous catalyst was required to quantitatively hydrogenate the star-shaped polyisoprenes under milder reaction conditions. A homogeneous nickel octoate/triethylaluminum catalyst system provided quantitative hydrogenation of the star-shaped polymers in 12 h at moderate pressures and temperatures. The ^{1}H NMR spectra indicated quantitative hydrogenation (Figure 4-2b). After hydrogenation, complete disappearance of the olefinic resonances at 4.7 and 5.1 ppm was observed, showing that complete saturation of the polymer backbone was accomplished. Quantitative deprotection was subsequently achieved under mild conditions using acid catalyzed hydrolysis and the peaks at 0.90 and 0.04 ppm associated with the protecting group disappeared (Figure 4-2c).

After hydrogenation, facile deprotection of the primary hydroxyl chain ends was achieved using acid catalysis. Subsequent modification of the hydroxyl groups yielded

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[365] 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.

well-defined non-functional, hydroxyl functional, and multiple hydrogen bond UPy functional poly(ethylene-co-propylene)s. Table 4-4 summarizes the monofunctional poly(ethylene-*co*-propylene)s, telechelic functional poly(ethylene-*co*-propylene)s, and star-shaped poly(ethylene-*co*-propylene)s with a periphery of functionality.

4.4.5 Physical properties characterization.

Linear and star-shaped poly(ethylene-*co*-propylene)s bearing chain-end hydroxyl groups were targeted as described in Table 4-4. Polymers containing hydroxyl groups in three different architectures (monofunctional, telechelic functional, and star periphery) were synthesized as described previously. The linear series consisted of two molecular weights, namely 12,000 g/mol and 24,000 g/mol, and two architectures, monofunctional, and telechelic functional. The sample nomenclature reflects these details, with a 12,000 g/mol polymer bearing no hydroxyl functionality (before deprotection of the tBDMS group) labeled as H-12K. A 12,000 g/mol polymer bearing a hydroxyl functionality (after acid-catalyzed deprotection) was labeled HO-12K. T is added to the nomenclature to delineate the samples with telechelic functionality. The star-shaped polymers were comprised of arms of number average molecular weights of 12,000 g/mol and had overall molecular weight ~90,000 g/mol, indicating an average number of arms per star macromolecule of 7.5. All of the poly(ethylene-*co*-propylene)s described in this paper exhibited T_g's between -60 and -65 ºC, independent of architecture or molecular weight, in agreement with literature values.[366]

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[366] Brandrup, J., E. H. Immergut and E. A. Grulke "Polymer Handbook"; 4th ed.; Wiley-Interscience: New York, NY, 1999.Gotro, J. T. and W. W. Graessley "Model Hydrocarbon Polymers: Rheological Properties of Linear Polyisoprenes and Hydrogenated Polyisoprenes." *Macromolecules* **1984**, *17*, 2767-2775.Mays, J., N. Hadjichristidis and L. J. Fetters "Characteristic Ratios of Model Polydienes and Polyolefins." *Macromolecules* **1984**, *17*, 2723-2728.

Table 4-4 Characterization of functionalized poly(ethylene-*co*-propylene)s.

Sample	M_n	M_w/M_n
H-12K	10700	1.32
HO-12K	16700	1.04
H-T-12K	11000	1.05
HO-T-12K	12600	1.06
H-24K	23000	1.05
HO-24K	22500	1.03
H-T-24K	24300	1.08
HO-T-24K	16300	1.19
H-Star	90700	1.37
HO-Star	87800	1.44

H : Non-functional
OH: Hydroxyl-functional
T : Telechelic functional

Melt rheology data for the non-functional and hydroxyl functional poly(ethylene-co-propylene)s obeyed time-temperature superposition (TTS) principles and master curves were constructed at a reference temperature of 50 °C. Storage modulus master curves for the linear non-functional and hydroxyl functional poly(ethylene-*co*-propylene)s showed characteristic linear chain responses for entangled polymers in the melt (Figure 4-4). As expected, the plateau modulus was observed at lower frequencies for the higher molar mass polymers. The non-functional star-branched macromolecules, although much higher in molar mass, transitioned to the plateau modulus in the same frequency range as the linear polymers. This was attributed to the highly compact structure of the star-branched macromolecules and an inability to entangle as effectively as the corresponding linear 90,000 g/mol poly(ethylene-*co*-propylene). In addition, the terminal-to-plateau transition was broader for the star macromolecules than for the linear polymers.
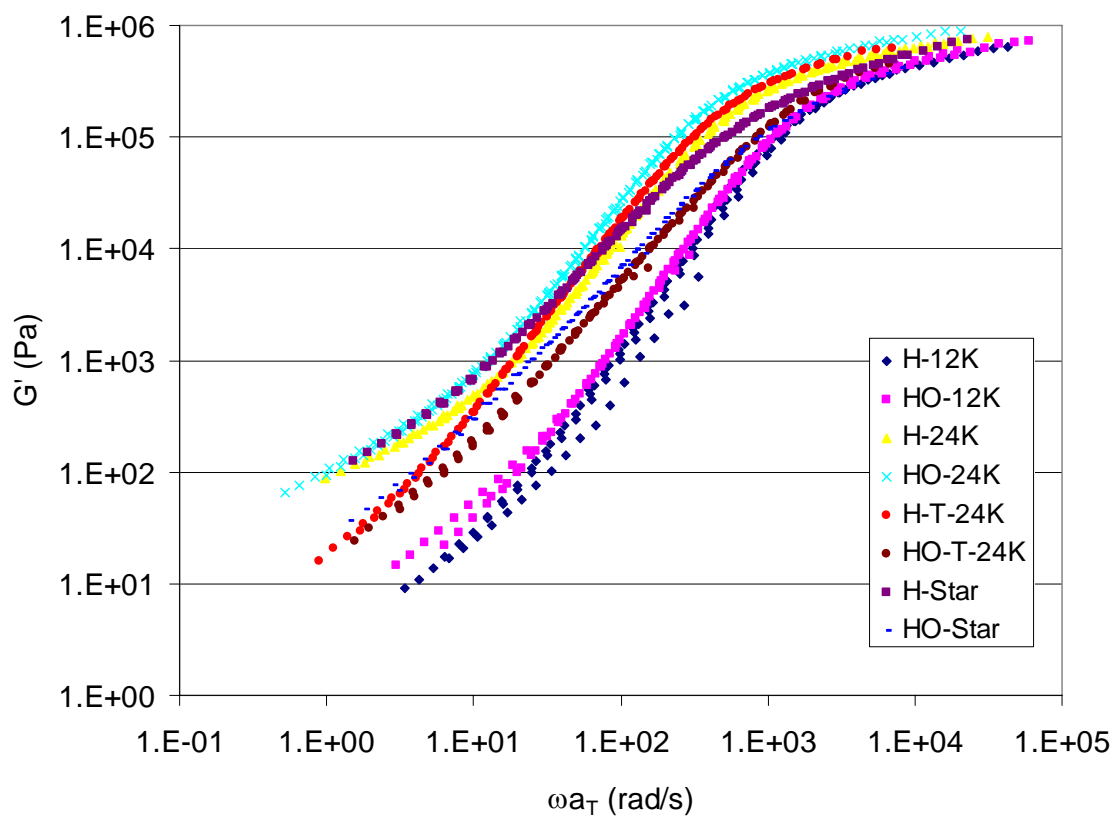
Figure 4-4. Storage modulus master curves for non-functional (H) and hydroxyl functional (OH) poly(ethylene-*co*-propylene)s of monofunctional, telechelic functional (T), and star periphery (star).

Figure 4-5 shows dynamic viscosity (η^*) master curves for the non-functional linear and star-shaped polymers at a reference temperature of 50 °C. The non-functionalized polymers displayed typical Newtonian flow behavior at low frequencies and transition to a shear-thinning region. The 12K polymers exhibited shear thinning behavior at a higher frequency than both the 24K polymers and the star-shaped polymers due to fewer entanglements of the lower molar mass polymers. The star-shaped polymers exhibited shear thinning in the same frequency range as the 24K g/mol non-functional polymers.

Figure 4-5. Complex viscosity master curves for non-functional (H) and hydroxyl functional (OH) poly(ethylene-*co*-propylene)s of monofunctional, telechelic functional (T), and star periphery (star).
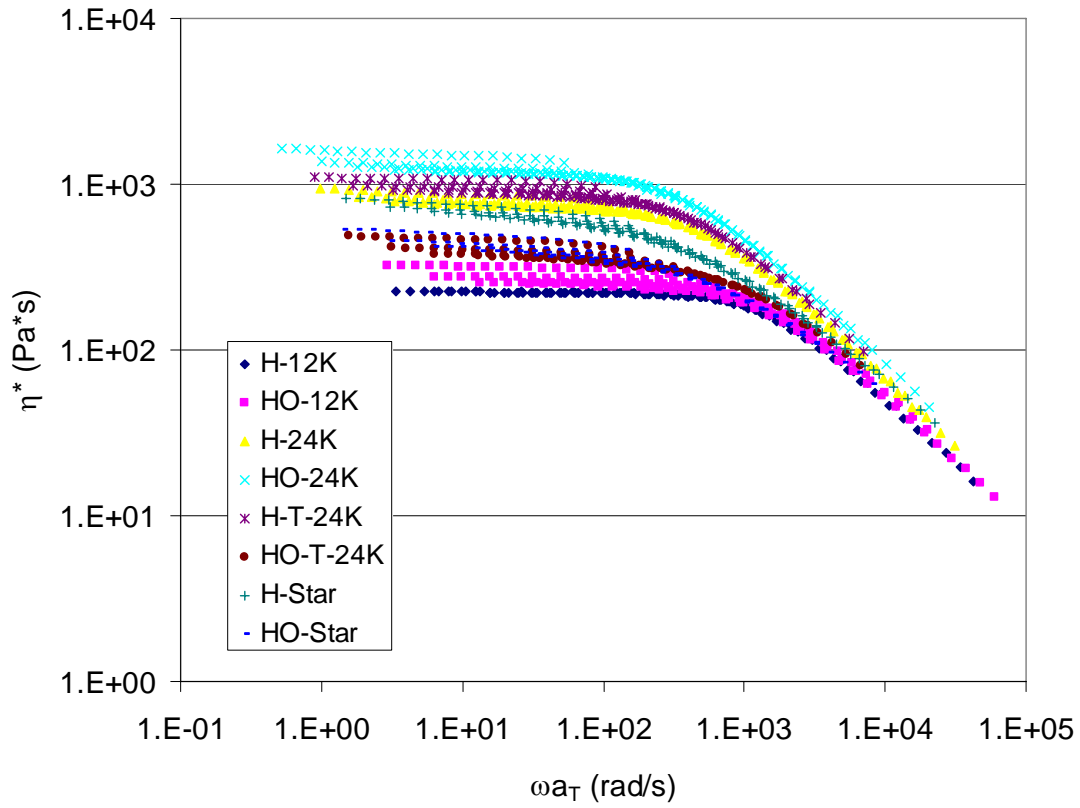
4.5 Conclusions

The polymerization of isoprene was controlled using both 3-(t-butyldimethylsilyloxy)-1-propyllithium and 3-[(N-benzyl-N-methyl)amino]-1-propyllithium functional initiators. Homopolymers with controlled molar masses and narrow molar mass distributions were synthesized and, in the case of tBDMSPrLi, coupled efficiently with divinylbenzene to form star-shaped polymers. Simultaneous hydrogenation and deprotection of BMAPrLi initiated polyisoprenes was achieved, however, the polymers were found to strongly associate with the catalyst and could not be separated. The tBDMSPrLi initiated polyisoprenes were subsequently hydrogenated and deprotected quantitatively. Melt rheological characterization of a series of well-defined non-functional and hydroxyl functional poly(ethylene-co-propylene)s showed that star-branched architectures of much higher molecular weight (90,000 g/mol) behaved similarly to 24,000 g/mol linear polymers. Transitions in the same frequency range were observed in both storage modulus and complex viscosity measurements and the star-branched macromolecules exhibited a broader transition from the terminal-to-plateau regions. The chain end hydroxyl functionalities of these poly(ethylene-*co*-propylene) polymers are then amenable to many further functionalization reactions.

4.6 Acknowledgements

Chapter 5 Self-Complementary Multiple Hydrogen Bond (*SCMHB*) Introduction to Hydroxyl Terminated Polyisoprene Homopolymers: Influence of Topology on Physical Properties of Hydrogen Bonded Polyisoprene Homopolymers

5.1 Abstract

High conversions of hydroxyl functionality to the 2-ureido-4[1*H*]-pyrimidone (UPy) quadruple hydrogen bonding group were achieved using isocyanate coupling and subsequent reaction with 6-methylisocytosine. Non-functional and UPy functional linear and star-shaped poly(ethylene-*co*-propylene)s were characterized using ^{1}H NMR spectroscopy, dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), tensile testing, and melt rheology. The observed glass transition temperatures were independent of molecular architecture for the UPy functionalized polymers and non-functionalized analogs using both DSC and DMA. Tensile testing revealed the UPy-star polymers exhibited a higher Young's modulus and lower percent elongation at failure compared to the UPy-T-24K analogs. Multiple hydrogen bonding of the UPy-star polymers creates a network-like structure as evidenced by the wider plateau region and longer terminal relaxation time observed in the UPy-star storage modulus master curves. In addition, complex viscosity master curves revealed network-like structure of the UPy-star polymers and non-Newtonian behavior in the low frequency range. Telechelic UPy

functional polymers exhibited a higher activation energy for stress relaxation than non-functional and mono-UPy functional polymers.

5.2 Introduction

The introduction of branching dramatically influences polymer physical properties and melt processability. [367] Long chain branching generally alters rheological and processing performance, while short chain branching influences thermal and mechanical solid-state behavior. Although it is well-known that long chain branching greatly influences polymer physical properties, fundamental understanding of structure-property relationships remains difficult due to the complexity of branched polymer architectures. Star-shaped macromolecules, which contain only one branch point, are a more simplified model of branched macromolecules and have received significant attention in the elucidation of structure-property relationships. [368] Although star polymers constitute the simplest branched structure, the synthesis of star-shaped polymers remains challenging, and well defined star polymers are often difficult to prepare in a controlled manner. Moreover, chain-end functionalization is an additional challenge in the synthesis and characterization of telechelic polymers.

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Controlled polymerization techniques, such as living anionic, [369] cationic, [370] free radical, [371] and group transfer (GTP) polymerization, [372] were reported earlier for the preparation of well-defined star-shaped macromolecules. Living anionic polymerization methodologies coupled with functionalized alkyllithium initiators were also used earlier to synthesize well-defined chain-end functionalized polymers in various architectures. The use of functionalized initiators has several advantages over more traditional electrophilic termination reagents for the synthesis of telechelic polymers. [373] Each functionalized initiator molecule ensures a macromolecule with the desired functionality at the chain end regardless of molar mass. The use of functionalized initiators avoids problems associated with electrophilic termination reagents, such as efficient and rapid mixing with viscous polymer solutions, stability of the anionic chain end, and selective reactivity. [374] Functionalized initiators also facilitate the synthesis of telechelic and heterotelechelic polymers, functionalized block polymers, and star-shaped polymers with

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[373] Quirk, R. P., S. H. Jang and J. Kim "Recent Advances in Anionic Synthesis of Functionalized Elastomers using Functionalized Alkyllithium Initiators." *Rubber Rev., Rubber Chem. Tech.* **1996**, *69*, 444.

[374] Hsieh, H. L. and R. P. Quirk "*Anionic Polymerization: Principles and Practical Applications"*; Marcel Dekker: New York, 1996.

functional groups on each arm terminus. [375] The use of the functional initiator 3-(t-butyldimethylsilyloxy)-1-propyllithium (tBDMSPrLi) was reported in the synthesis of a variety of polymers with various molecular architectures, including polyisoprene, [376] polybutadiene, [377] poly(methyl methacrylate), [378] and poly(1,3-cyclohexadiene) [379] to yield hydroxyl chain end functionalized polymers.

Although living anionic polymerization in combination with functional initiation has proven an excellent route to telechelic linear and star-shaped polymers, telechelic star-shaped macromolecules were also reported using various other methodologies. Hedrick

[375] Quirk, R. P., S. H. Jang, H. Yang and Y. Lee "Polymer Synthesis Using Functionalized Alkyllithium Initiators: Telechelic, heterotelechelic and functionalized star-branched polymers." *Macromol. Symp.* **1998**, *132*, 281-291.

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[378] Quirk, R. P. and R. S. Porzio "The Anionic Synthesis of Functionalized Linear and Star-branched Poly(methyl methacrylates) Using Protected Hydroxy-Functionalized Alkyllithium Initiators." *Polym. Prepr.* **1997**, *38*, 463-464.Mizawa, T., K. Takenaka and T. Shiomi "Synthesis of alpha-Maleimide-omega-Dienyl Heterotelechelic Poly(methyl methacrylate) and Its Cyclization by the Intramolecular Diels-Alder Reaction." *J. Polym. Sci. Part A* **2000**, *38*, 237-246.Tong, J.-D., C. Zhou, S. Ni and M. A. Winnik "Synthesis of Meth(acrylate) Diblock Copolymers Bearing a Fluorescent Dye at the Junction Using A Hydroxyl-Protected Initiator and the Combination of Anionic Polymerization and Controlled Radical Polymerization." *Macromolecules* **2001**, *34*, 696-705.

[379] Quirk, R. P., F. You, C. Wesdemiotis and M. A. Arnould "Anionic Synthesis and Characterization of omega-Hydroxyl-Functionalized Poly(1,3-Cyclohexadiene)." *Macromolecules* **2004**, *37*, 1234-1242.

et al. reported the core-first synthesis of star-shaped poly(ε-caprolactone) hydroxyl terminated macroinitators with six arms using ring opening polymerization and the subsequent transformation into atom transfer radical polymerization (ATRP) initiators. [380] The macroinitiators were then used to polymerize several monomers, including methyl methacrylate, hydroxyethyl methacrylate, and ethylene oxide. In a similar fashion, Gnanou and coworkers used living cationic polymerization to synthesize star-shaped polystyrenes and transformed the peripheral chain-end functionality into either a hydroxyl or amine group. [381] The hydroxyl terminated samples were used as macroinitiators for ethylene oxide polymerization.

In several cases, ATRP was used in acrylic polymerizations to yield hydroxyl, [382] epoxy, [383] amino, bromide, or cyano functionalized star polymers. [384] Quirk et al. also introduced functionality to star-shaped polymers using living anionic polymerization in conjunction with functionalized diphenylethylene (DPE) derivatives and organic functional group transformations, and Hirao et al. subsequently based their efforts on this methodology. [385,386] Quirk was able to introduce functionality at either the α-terminus, block junctions, or core.

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[380] Hedrick, J. L., M. Trollsas, C. J. Hawker, B. Atthoff, H. Claesson, A. Heise, R. D. Miller, D. Mecerreyes, R. Jerome and P. Dubois "Dendrimer-like Star Block and Amphiphilic Copolymers by Combination of Ring Opening and Atom Transfer Radical Polymerization." Ibid. **1998**, *31*, 8691-8705.

[381] Cloutet, E., J.-L. Fillaut, D. Astruc and Y. Gnanou "Star Block Copolymers and Hexafullerene Star via Derivatization of Star-Shaped Polystyrenes." Ibid. **1999**, *32*, 1043-1054.

[382] Coessens, V., J. Pyun, P. J. Miller, S. G. Gaynor and K. Matyjaszewski "Functionalization of polymers prepared by ATRP using radical addition reactions." *Macromol. Rapid Commun.* **2000**, *21*, 103-109.

[383] Ibid.

[384] Zhang, X., J. Xia and K. Matyjaszewski "End-Functional Poly(t-butyl acrylate) Star Polymers by Controlled Radical Polymerization." *Macromolecules* **2000**, *33*, 2340-2345.

[385] Quirk, R. P. "Scope and limitations of 1,1-diphenylethylene chemistry in anionic polymer synthesis." *Makromol. Chem., Macromol. Symp.* **1992**, *63*, 259-269.Quirk, R. P., T. Yoo and B. Lee "Anionic synthesis of heteroarm, star-branched polymers. Scope and limitations." *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 911-926.Hsieh, H. L. and R. P. Quirk "*Anionic Polymerization: Principles and Practical Applications*"; Marcel Dekker: New York, 1996.Hayashi, M., K. Kojima and A. Hirao "Synthesis of Star-Branched Polymers by Means of Anionic Living Polymerization Coupled with Functional Group

Fréchet and Hawker et al. recently reported the use of nitroxide mediated polymerization in the synthesis of functionalized star polymers. [387] Using a modular approach, a library of compounds was synthesized with various compositions, including homo, block, and random copolymers with both apolar and polar vinylic repeat units and functional groups. Ishizu et al. also reported the functionalization of polyisoprene star polymers with p-chloromethyl styrene to yield a periphery of reactive styrene groups capable of forming a crosslinked network. [388]

While both functional polymers and star-shaped polymers are prevalent in the literature, the combination of well-defined thermoreversible chain end interactions, such as multiple hydrogen bonding interactions, and star-shaped macromolecules is limited. Hadjichristidis et al. studied the synthesis and characterization of well-defined linear and star-shaped polystyrenes, polyisoprenes, and polybutadienes bearing sulfo- and phosphoro-zwitterionic groups capable of thermoreversible association. [389] Although

Transformation." *Macromolecules* **1999**, *32*, 2425-2433.Hirao, A., M. Hayashi and N. Haraguchi "Synthesis of well-defined functionalized polymers and star branched polymers by means of living anionic polymerization using specially designed 1,1-diphenylethylene derivatives." *Macromol. Rapid Commun.* **2000**, *21*, 1171-1184.Hirao, A., M. Hayashi, S. Loykulnant, K. Sugiyama, S. W. Ryu, N. Haraguchi, A. Matsuo and T. Higashihara "Precise syntheses of chain-multi-functionalized polymers, star-branched polymers, star-linear block polymers, densely branched polymers, and dendritic branched polymers based on iterative approach using functionalized 1,1-diphenylethylene derivatives." *Prog. Polym. Sci.* **2005**, *30*, 111-182.

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[388] Ishizu, K., H. Kitano, T. Ono and S. Uchida "Synthesis and characterization of polyfunctional star-shaped macromonomers." *Polymer* **1999**, *40*, 3229-3232.

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these studies contributed significantly to the understanding of structure-property relationships, the reversible interaction is electrostatic and the behavior of polymers that interact through multiple hydrogen bonding is expected to differ significantly.

Meijer et al. recently reported the synthesis of model low molar mass poly(ethylene oxide-*co*-propylene oxide) three arm star-shaped polymers with pendant 2-ureido-4[1*H*]-pyrimidone (UPy) quadruple hydrogen bonding functionalities. [390] These polymers were compared with three arm star-shaped polymers bearing urea chain ends, non-functional chain ends, and a chemically crosslinked network. However, due to the hydrophilic nature of the parent polymer, the effect of atmospheric moisture on polymer physical properties was not excluded.

Previous research in our laboratories involved the synthesis of linear polystyrenes, polyisoprenes, microphase separated polystyrene-*block*-polyisoprene copolymers, and polyesters with chain end multiple hydrogen bonding sites. The influence of multiple hydrogen bond incorporation on physical properties was investigated using glass transition temperature, melt viscosity, and morphology. [391] Our current work focused on

Macromolecules **2000**, *33*, 6396-6401.Pispas, S. and N. Hadjichristidis "Block copolymers with zwitterionic groups at specific sites: synthesis and aggregation behavior in dilute solutions." *J. Polym. Sci. Part A* **2000**, *38*, 3791-3801.Vlassopoulos, D., M. Pitsikalis and N. Hadjichristidis "Linear Dynamics of End-Functionalized Polymer Melts: Linear Chains, Stars, and Blends." *Macromolecules* **2000**, *33*, 9740-9746.Charalabidis, D., M. Pitsikalis and N. Hadjichristidis "Model linear and star-shaped polyisoprenes with phosphatidylcholine analogous end-groups, synthesis and association behavior in cyclohexane." *Macromol. Chem. Phys.* **2002**, *203*, 2132-2141.Sakellariou, G., S. Pispas and N. Hadjichristidis "Model omega-functionalized linear polystyrenes with one, two, and three sulfobetaine end grups: Synthesis, characterization, and association behavior." *Macromol. Chem. Phys.* **2003**, *204*, 146-154.

[390] Lange, R. F. M., M. van Gurp and E. W. Meijer "Hydrogen-Bonded Supramolecular Polymer Networks." *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 3657-3670.

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the effects of multiple hydrogen bonding and polymer topology on mechanical, thermal, and rheological properties. Living anionic polymerization initiated with tBDMSPrLi was a facile synthetic methodology for the preparation of well-defined polymers with three different chain ends (non-functional, hydroxyl functional, and UPy functional) in three architectures i.e., linear monofunctional, linear telechelic functional, and star-shaped with functionality at each arm terminus.

5.3 Experimental

5.3.1 Materials

Tetrahydrofuran (EM Science, HPLC grade) was distilled from sodium/benzophenone immediately prior to use. Isophoronediisocyanate (Aldrich, 98%) was used as received. Dibutyl tin dilaurate (Aldrich, 99%) was dissolved in THF as a 1 wt% solution. 6-methylisocytosine (Aldrich, 98%) was dried at 100 ºC under vacuum overnight to remove moisture impurity. Dimethyl sulfoxide (Aldrich, anhydrous grade) was used as received. Eicosanol (Aldrich) was dried under vacuum at 80 ºC overnight immediately prior to use.

5.3.2 Characterization

^{1}H NMR spectra were determined in CDCl$_3$ at 400 MHz with a Varian Unity Spectrometer. Glass transition and melting temperatures were determined using a Perkin-Elmer Pyris 1 cryogenic DSC at a heating rate of 10 °C/min under nitrogen. Glass

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8750.Yamauchi, K., A. Kanomata, T. Inoue and T. E. Long "Thermoreversible Polyesters Consisting of Multiple Hydrogen Bonding (MHB)." *Macromolecules* **2004**, *37*, 3519-3522.

transition temperatures are reported as the transition mid point during the second heat. Molecular weights were determined at 40 ºC in tetrahydrofuran (THF, HPLC grade) at 1 mL/min using polystyrene standards on a Waters 717+ Auto-sampler SEC equipped with 3 in-line PLgel 5 μm MIXED-C columns, a Waters 410 differential RI detector an in-line Wyatt Technologies miniDAWN multiple angle laser light scattering (MALLS). Melt rheological analysis was carried out using a TA Instruments AR2000 rheometer with 25 mm parallel plate geometry and a 5 % strain amplitude. Master curves for a reference temperature of 50 °C were created based on the time-temperature superposition correspondence principle. Temperature sweeps were carried out at a frequency of 1 Hz. In-situ FTIR monitoring was performed with an ASI Applied Systems ReactIR™ 1000 reaction analysis system with a stainless steel DiComp™ probe.[392] A comparison of peak height versus a common baseline point was performed to eliminate data scatter due to baseline drift. Stress-strain experiments were performed using dogbone-shaped film samples cut using a die as specified in ASTM D3368. The tensile tests were performed under ambient conditions on a 5500R Instron® universal testing machine at a crosshead displacement rate of 10 mm/min. Samples were tested in sets of 6 for each polymer. Stress vs. strain profiles were recorded using Merlin® software at an acquisition rate of 50 milliseconds per each data point. Pneumatic grips were used and no slippage was observed during the test. Dynamic light scattering data was collected using a Proterion (Protein Solutions) dynamic light scattering instrument DynaPro-E-50-830 with a 90 degree detector and a wavelength of 826.3 nm at 25 °C.

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[392] Pasquale, A. J. and T. E. Long *Macromolecules* **1999**, *32*, 7954-7957.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*, 216-223.

5.3.3 Model Compound Study: Introduction of Self-Complementary Multiple Hydrogen Bonding Groups to Long Chain Alcohols Monitored Using in situ FTIR Spectroscopy

A typical reaction setup is described. Eicosanol (10g, 33.6 mmol) and THF (11.4 mL) were added to a 100 mL, septum-sealed round-bottomed flask with a magnetic stir bar under a nitrogen flush. The ATR probe tip was completely immersed in the solution, and the reaction vessel was placed in an oil bath and allowed to equilibrate at 60 ºC. IPDI (8.5 mL, 40.3mmol) and DBTDL (0.01 mL, 1 x 10^{-2} mmol) were added to the reaction mixture using a syringe and one complete FTIR spectrum was collected every 5 min for 12 h. In the second step of the reaction, MIC (12.1g, 96.7 mmol) and DMSO (1.7 mL, 15 vol%) were added to the reaction flask under a nitrogen flush. Additional spectra were collected every 5 min for 72 h. (Scheme 5-1)

Scheme 5-1. UPy modification of the model compound eicosanol.
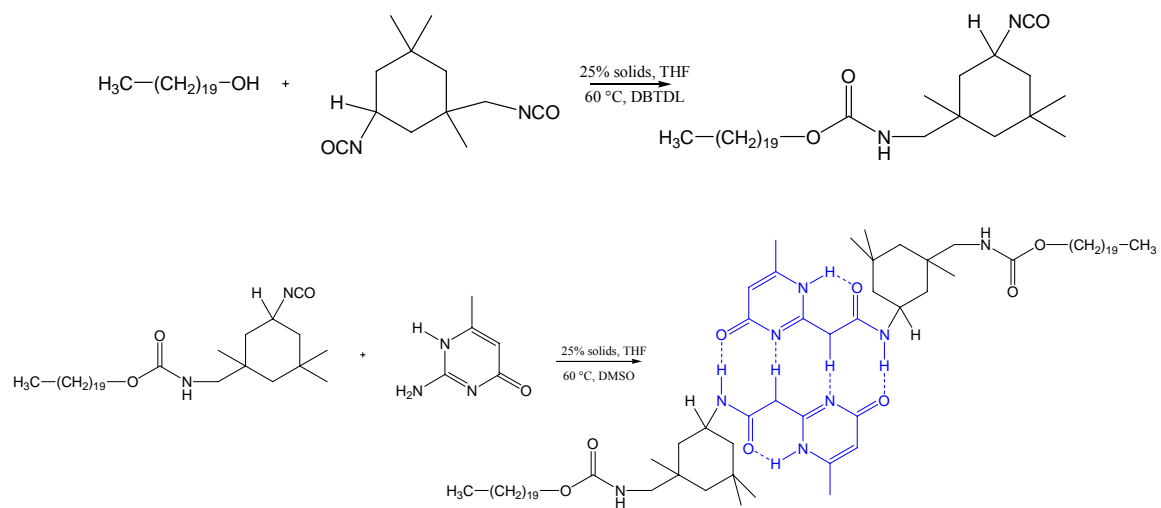
5.3.4 UPy Functionalization of Hydroxyl Terminated Poly(ethylene-*co*-propylene)s

The synthesis of hydroxyl terminated poly(ethylene-*co*-propylene)s was described in the previous chapter in detail.[393] After quantitative deprotection of poly(ethylene-*co*-propylene) was achieved, the UPy terminal group was attached in two steps. In the first step, the poly(ethylene-*co*-propylene) (1.0 g, 0.007 mmol) was dissolved in freshly distilled tetrahydrofuran (3.5 mL) and dibutyl tin dilaurate catalyst (0.01 mL) was added. Isophorone diisocyanate (0.29 mL, 1.36 mmol) was added to the solution and the reaction was allowed to proceed for 72 h at 60 °C to ensure complete conversion. In the second step, 6-methyl isocytosine (0.38 g/ 3 mmol) was added under a nitrogen flush and anhydrous DMSO (0.5 mL) was added as a cosolvent. The reaction proceeded under nitrogen at 60 °C for 72 h. The reaction solution was quenched using excess methanol and filtered in order to isolate the polymer. The product was dissolved in chloroform and filtered again in order to remove residual 6-methyl isocytosine. The polymer was precipitated into methanol, collected, and dried in vacuo. The complete series of polymers and non-functional analogs is summarized in Table 5-1. Residual 6-methyl isocytosine, isophorone diisocyanate, and coupled products were quantitatively removed through repeated filtration and selective solvent precipitation. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 12.9 – 13.2 (s, –N*H*–C(CH$_3$)= in UPy units), 11.8 – 12.1 (s, –N*H*–C=N–in UPy units), 10.4 – 10.7 (s, –CH$_2$N*H*–CO– in UPy units), 5.7 – 6.0 (s, NHC(CH$_3$)=C*H*O– in UPy units), 1.0 – 2.0 (b, –CH$_3$, –CH$_2$–, CH in poly(ethylene-*co*-propylene) units).

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[393] Elkins, C. L., K. Yamauchi and T. E. Long "Synthesis and characterization of self-complementary multiple hydrogen bonding poly(isoprene) star polymers." *Polym. Prepr.* **2003**, *44*, 576-577.

Table 5-1. Molar mass characterization and nomenclature.

M_n (M_w/M_n)	Polymer ID	Endgroup
12300 (1.04)	H-12K	Non-functional
	UPy-12K	Mono-UPy
	UPy-T-12K	Telechelic UPy
23400 (1.08)	H-24K	Non-functional
	UPy-24K	Mono-UPy
	UPy-T-24K	Telechelic UPy
Arm: 12000 Star: 90700 (1.37)	H-Star	Non-Functional Periphery
	UPy-Star	Star Periphery UPy

5.4   Results and Discussion

5.4.1   In situ FTIR Analysis of Eicosanol UPy Functionalization

Previously, UPy modification of poly(ethylene oxide-*co*-propylene oxide) copolymers was achieved in a two-step reaction sequence in which the precursor polymer was dissolved in chloroform and anhydrous pyridine at reflux was used to dissolve the subsequent reactants. [394]   Chain end modification of polystyrene and poly(styrene-*b*-polyisoprene) was also achieved using a similar methodology. [395]   However, when these reaction conditions were used with poly(ethylene-*co*-propylene), the relatively more non-polar polymer precursor was not soluble in pyridine.

A long chain (C_{20}) primary alcohol was used as a model compound to determine suitable reaction conditions for modification of the non-polar poly(ethylene-*co*-propylene) with the polar UPy quadruple hydrogen bonding group.   *In-situ* FTIR spectroscopy provided continuous data collection over the entire reaction process.   The long chain (C_{20}) primary alcohol was chosen as an appropriate model compound for the non-polar poly(ethylene-*co*-propylene) due to similar polarity and solubility.   THF was chosen as the reaction solvent due to facile solubility of poly(ethylene-co-propylene) in THF and the relative polarity of THF compared to chloroform.   The selective reaction of the IPDI primary isocyanate and the long chain alcohol in the first step was verified using

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[394] Lange, R. F. M., M. van Gurp and E. W. Meijer "Hydrogen-Bonded Supramolecular Polymer Networks." *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 3657-3670.
[395] Yamauchi, 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*, 8599-8604.

in-situ FTIR. Figure 5-1 depicts a representative FTIR spectrum obtained using *in-situ* monitoring. The disappearance of the HO- stretch (3500 cm^{-1}), decrease in the –NCO stretch (2250 cm^{-1}), and appearance of characteristic urethane stretches and bends (urethane carbonyl stretch (1720 cm^{-1}), urethane NH bend (1528 cm^{-1}), and urethane NH stretch (3325 cm^{-1})) indicated the reaction was complete in ~6 h. The secondary unreacted isocyanate remained due to the plateau of the isocyanate stretch after the initial reaction.

In the second step of the reaction, which involved the reaction of the remaining secondary isocyanate with MIC, identical reaction conditions were employed and freshly dried MIC powder was added under a nitrogen flush. Figure 5-2 shows a representative FTIR spectrum obtained during *in-situ* monitoring of the second step of the UPy modification. The MIC primary amine and the remaining secondary isocyanate did not react during the first 8 h under these reaction conditions (THF, 25% solids, 60 ºC). Upon addition of DMSO (15 vol% maximum) to avoid solution heterogeneity, infrared bends and stretches characteristic of urea (urea NH stretch (1673 cm^{-1}), urethane/urea bend (1560 cm^{-1})) and the MIC carbonyl stretch (1613 cm^{-1}) were observed. It was determined based on the isocyanate stretch (2250 cm^{-1}) (Figure 5-3) that the reaction was complete after ~48 h. *In-situ* FTIR spectroscopy of the oligomer functionalization reaction was not possible due to the low concentration of the functional end groups.

Figure 5-1. In-situ FTIR monitoring of the reaction of eicosanol with isophorone diisocyanate.
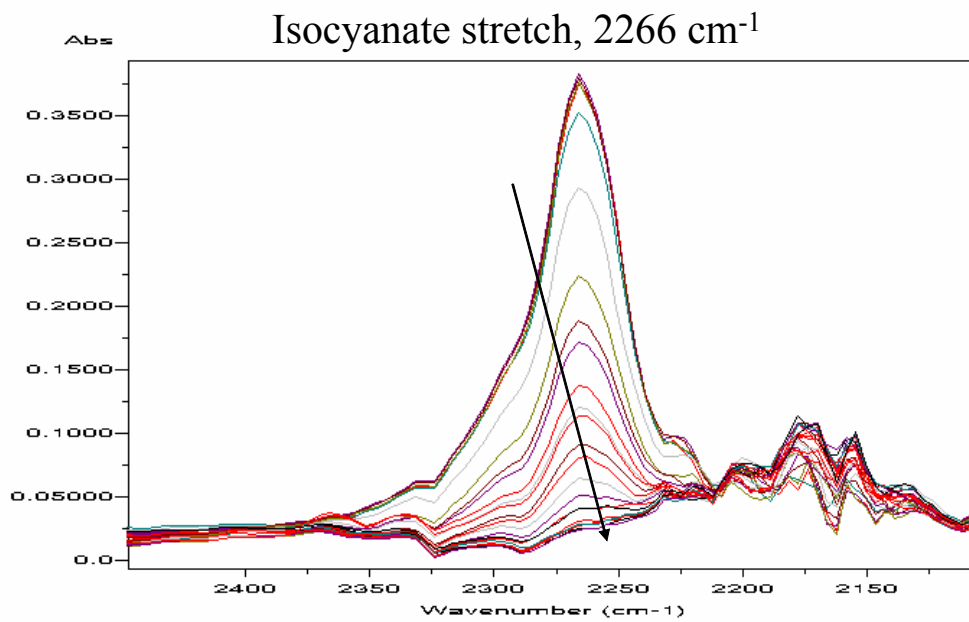

178
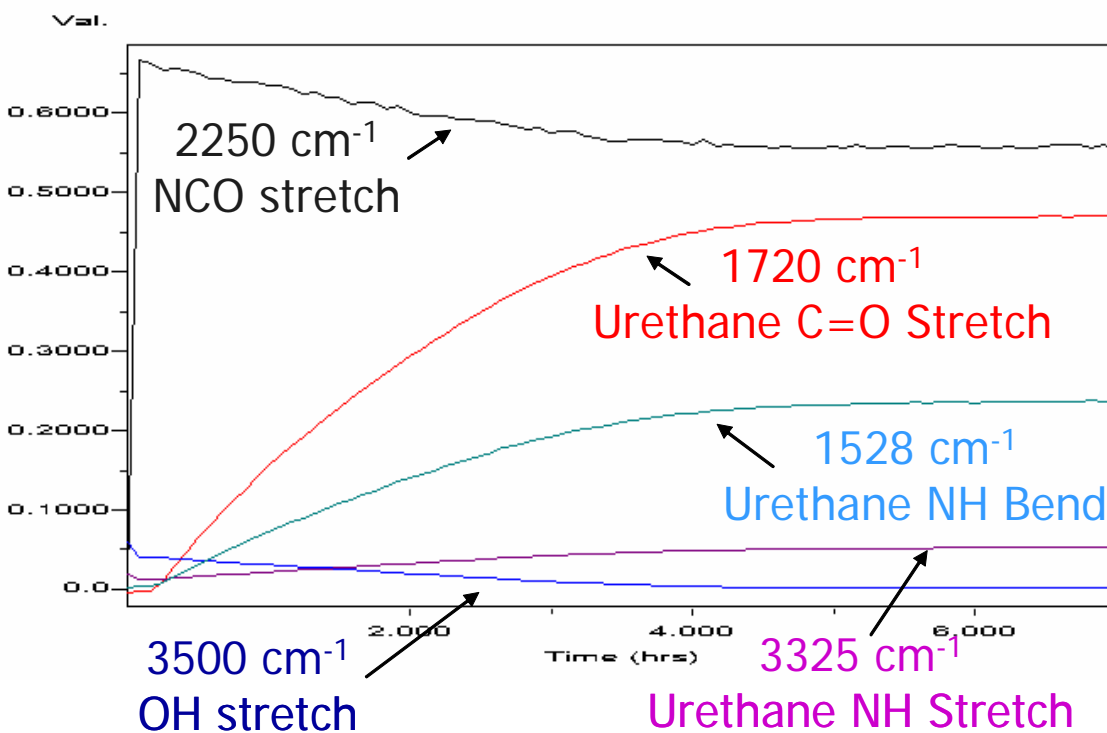
Figure 5-2. Reaction of IPDI-modified eicosanol with 6-methyl isocytosine.
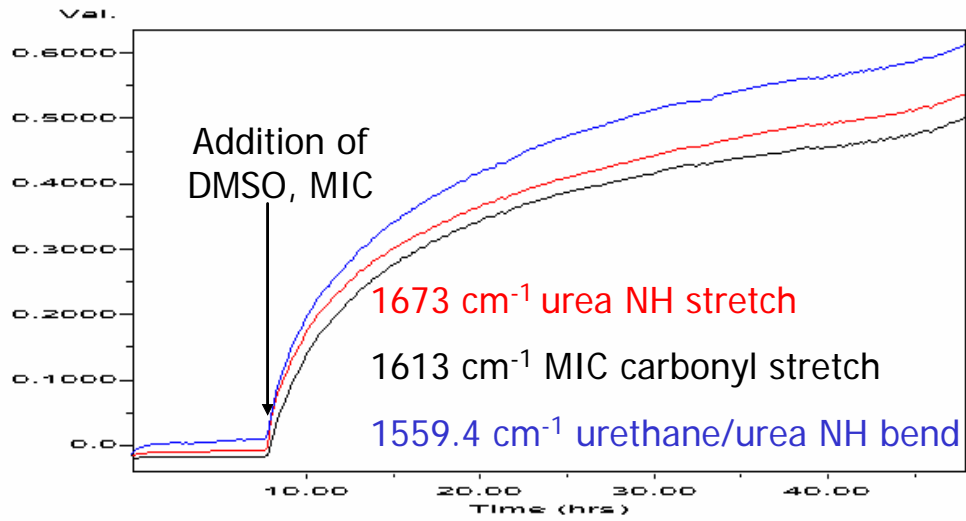
Figure 5-3. In-situ FTIR monitoring of isocyanate stretch during UPy functionalization of eicosanol.

Isocyanate stretch, 2266 cm^{-1}

5.4.2 UPy Modification of Poly(ethylene-*co*-propylene)s

The hydroxyl chain ends of the various poly(ethylene-*co*-propylene)s were derivatized using the reaction conditions identified in the *in-situ* FTIR model compound study and high conversions were achieved in all cases (Table 5-2). The characteristic UPy ^{1}H NMR resonances (3 NH hydrogens (10.5, 12, 13 ppm), methyne H on the pyrimidinone ring (5.8 ppm)) were compared with the aliphatic resonances of the polymer backbone (between 1 and 2 ppm) in order to determine the extent of chain end functionalization. Based on the ^{1}H NMR characterization, it was concluded that the reaction conditions were appropriate for polymeric systems as well as the model system studied. Conversions from hydroxyl to UPy endgroup ranged from 86-100 % for linear poly(ethylene-co-propylene)s and was 75% for star-shaped polymers. Although UPy functionalization of star-shaped poly(ethylene-co-propylene)s exhibited the lowest conversion of 75%, each star-shaped macromolecule contained on average six chain end UPy functional groups. While UPy functionalization was not quantitative, high conversions were achieved and the mole percent UPy content is summarized in Table 5-2. The molar incorporations are low, generally less than one mole percent, and no trend was observed between mole percent functionalization and physical properties and instead are dependent on molar mass and architecture of the parent polymer. UPy-12K, UPy-T-24K, and UPy-star polymers, for example, contained ~0.50 mole percent UPy functionality, however, significantly different properties were observed for each system. DSC analysis indicated the UPy functionality did not significantly change the -60 °C

181

glass transition temperature of the precursor poly(ethylene-*co*-propylene) (Table 5-2).[396] The glass transition was the only transition observed in the DSC scans.

Interestingly, the UPy-star and linear UPy-T-24K polymers formed ductile films when cast from solution, and DMA and tensile testing were used to study the mechanical performance of these films. (Figure 5-4) With DMA at 1 Hz, a distinct glass transition was observed for UPy-functionalized poly(ethylene-co-propylene)s at ~-40 °C. UPy-T-24K and UPy-star polymers exhibited a broad rubber plateau at 3×10^3 Pa, while UPy-T-12K and UPy-24K exhibited a narrower rubber plateau of the same magnitude. Comparison with the mechanical properties of non-functional counterparts was not possible because the non-functional analogs were viscous liquids at room temperature and did not form films. Stress-strain profiles for the UPy-star and linear UPy-T-24K films are shown in Figure 5-5. The UPy-T-24K sample ruptured at ~280% elongation and exhibited tensile properties typical of a viscous liquid under stress, with initial deformation due to uncoiling of the polymer chains and minimal subsequent increase in the stress required to continue elongation.[397]

The UPy-star samples, which contained similar molar content of UPy hydrogen bonding groups, displayed a distinctly different stress-strain profile.   The UPy-star samples exhibited initial elongation at low stress due to uncoiling of the polymer chains and subsequent increase in stress once the chains uncoiled. The UPy-star polymers are constrained in a network-like structure due to multiple hydrogen bonding interactions and

[396] Mays, J., N. Hadjichristidis and L. J. Fetters "Characteristic Ratios of Model Polydienes and Polyolefins." *Macromolecules* **1984***, 17*, 2723-2728.Gotro, J. T. and W. W. Graessley "Model Hydrocarbon Polymers: Rheological Properties of Linear Polyisoprenes and Hydrogenated Polyisoprenes." *Macromolecules* **1984***, 17*, 2767-2775.Brandrup, J., E. H. Immergut and E. A. Grulke "Polymer Handbook"; 4th ed.; Wiley-Interscience: New York, NY, 1999.
[397] Bikales, N. M. "*Mechanical Properties of Polymers"*; Wiley-Interscience: New York, NY, 1971.

cannot easily move past one another. The tensile strength of the UPy-star films (1.06 ± 0.11 MPa) was nearly twice that of the UPy-T-24K films (0.56 ± 0.02 MPa) and the ~140% elongation of the UPy-star film was lower than ~280% elongation of the UPy-T-24K film. A significant difference was observed in the Young's modulus of the UPy-T-24K (0.92 ± 0.05MPa) and UPy-star (1.65 ± 0.11 MPa) films. However, the UPy-T-24K polymer and UPy-star polymer exhibited similar toughness with values of 1.44 MJ/m^3 and 1.08 MJ/m^3 respectively, as was measured using the area under the curves. In general, the UPy-star poly(ethylene-co-propylene) exhibited increased tensile properties compared to the linear telechelic functionalized UPy-T-24K (Table 5-3).

Table 5-2. Functionalization of poly(ethylene-*co*-propylene)s and thermal characterization.

Sample	% Endcapping[a]	Mol% Endcapping	T_g (°C)[b]	T_g (°C)[c]
UPy-12K	90	0.54	Too fluid	ND
UPy-T-12K	95	1.14	-43	ND
UPy-24K	86	0.26	-41	ND
UPy-T-24K	100	0.60	-38	-62
UPy-Star	75	0.45	-39	-59

[a] NMR conditions: Varian Unity 400 MHz, CDCl$_3$, 1000 scans
[b] DMA conditions: 1 Hz, tension mode, 3 °C/min
[c] DSC conditions: Perkin Elmer Pyris, heating rate: 10 °C/min 2nd heat

Figure 5-4. Film forming ability of low T_g poly(ethylene-*co*-propylene) UPy-T-24K.
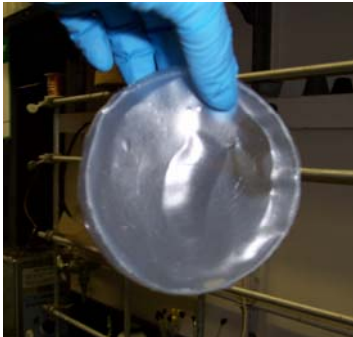
Figure 5-5. Stress-strain profiles for UPy functionalized poly(ethylene-*co*-propylene)s, UPy-T-24K and UPy-star.
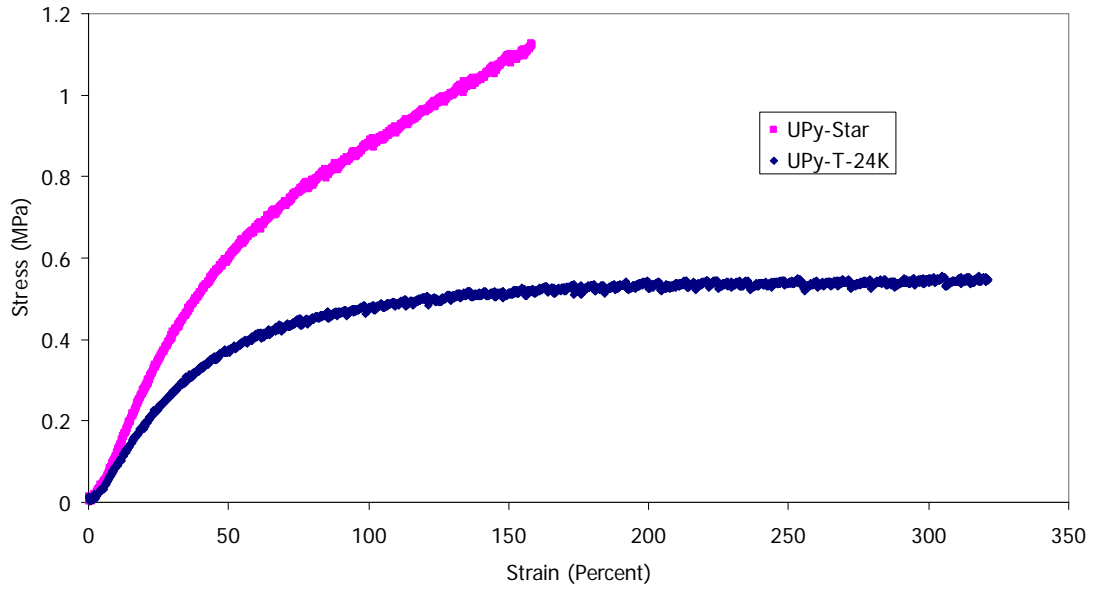
Table 5-3. Summary of tensile data for UPy-functionalized poly(ethylene-*co*-propylene)s, UPy-T-24K and UPy-star.

Sample	Modulus(MPa)	Tensile Strength (at Break) (MPa)	% Strain
UPy-T-24K	0.92 ± 0.05	0.56 ± 0.02	279 ± 59
UPy-Star	1.65 ± 0.11	1.06 ± 0.11	139 ± 37

It was also interesting to note that reliable SEC characterization of the UPy star polymers was not obtainable due to aggregation of the polyme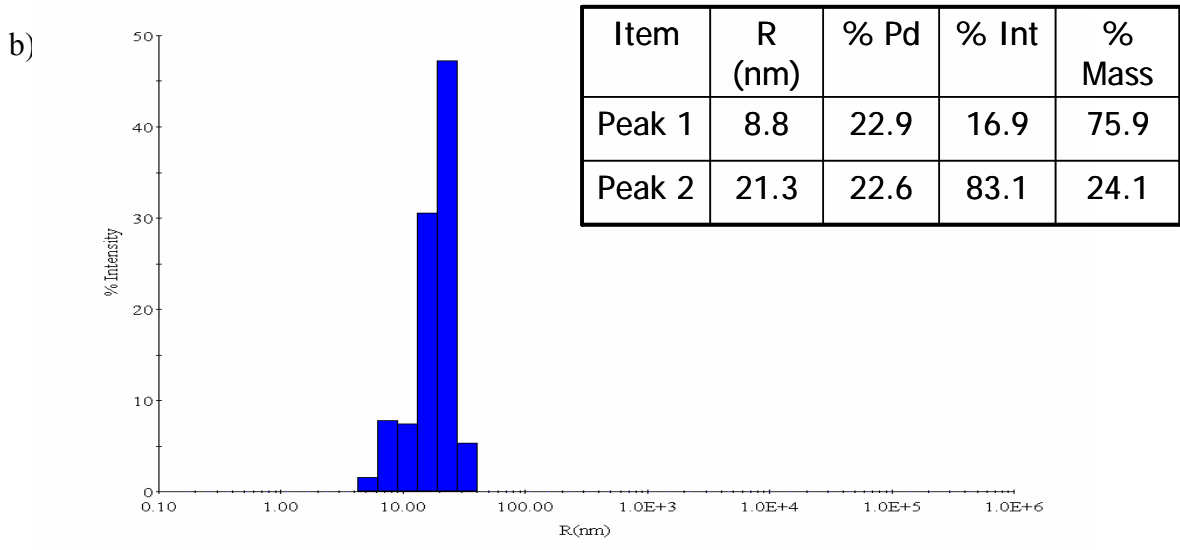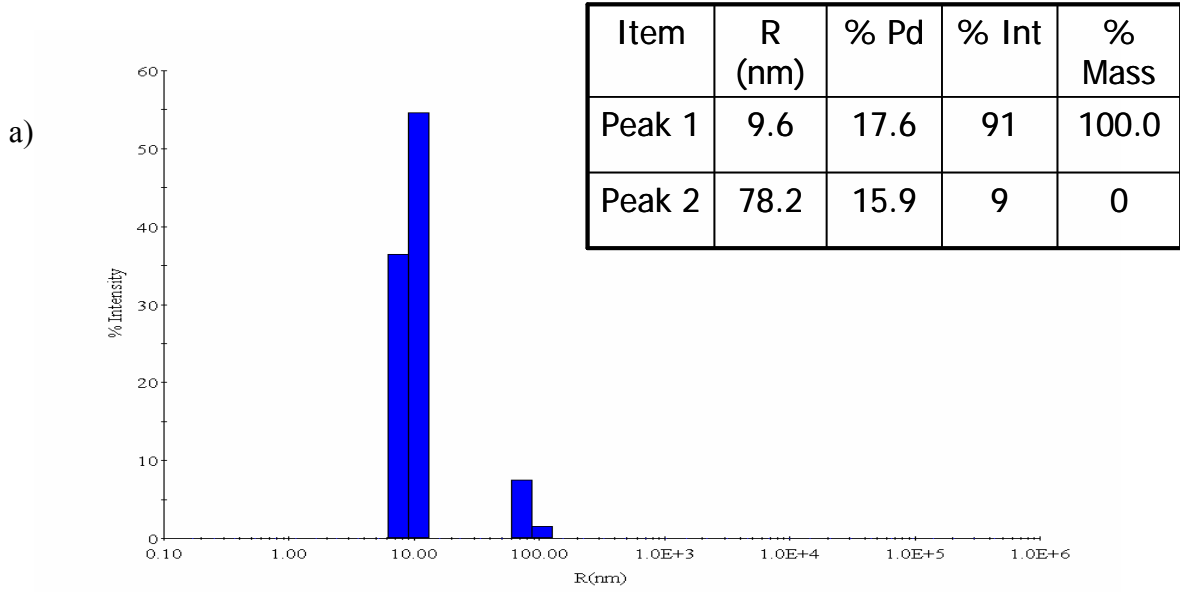rs at SEC concentrations. It was previously assumed that THF at 40 °C would dissociate these multiple hydrogen bonding interactions, and generally, linear polymers with UPy groups do not exhibit aggregation behavior under these conditions. However, UPy-star samples exhibited non-reproducible SEC curves when the same sample was submitted multiple times, with broadened molecular weight distributions ($M_w/M_n \geq 2.2$). Dynamic light scattering experiments were run on both a control, non-functional star polymer (H-star) and the UPy functional star polymer (UPy-star) in order to determine if the multiple hydrogen bonding groups were aggregating under SEC conditions (1 mg/mL in THF) (Figure 5-6). Figure 5-6a shows DLS results for H-star and only 1 primary peak is observed, with the peak at 100 nm attributed to dust, while Figure 5-6b shows DLS results for UPy-star, wherein 2 distinct peaks were observed. The first peak with a radius of gyration at ~9 nm for both samples was attributed to the non-associated star polymers, while the peak with a radius of gyration at ~20 nm was attributed to aggregated star polymers. Based on this data, it was determined that SEC characterization was unreliable for the UPy-star and it was assumed that no change in the molar mass or molar mass distribution occurred during functionalization, based upon characterization of the linear materials.

Figure 5-6. a) DLS of H-Star and b) DLS of UPy-star.

a)

Item	R (nm)	% Pd	% Int	% Mass
Peak 1	9.6	17.6	91	100.0
Peak 2	78.2	15.9	9	0

b)

| Item	R (nm)	% Pd	% Int	% Mass
Peak 1	8.8	22.9	16.9	75.9
Peak 2	21.3	22.6	83.1	24.1

5.4.3   Melt Rheological Characterization

Melt rheological characterization of well-defined non-functional and UPy functional poly(ethylene-*co*-propylene)s revealed that high molar mass star-branched architectures (90,000 g/mol) behaved very differently than lower molar mass linear copolymers (24,000 g/mol). The melt rheological behavior of the non-functional and hydroxyl functional samples was very similar and viscosity versus temperature profiles for the non-functional and hydroxyl terminated linear and star polymers were nearly superimposable.

Viscosity versus temperature profiles for various UPy modified poly(ethylene-*co*-propylene)s are shown in Figure 5-7. Monofunctional polymers of 12K and 24K molar mass exhibited higher viscosity at low temperature and reached a consistent viscosity at approximately 80 °C. The telechelic functional polymers exhibited higher viscosities than the monofunctional analogs and maintained significant viscosity at temperatures approaching 120 °C. The melt rheological properties of the UPy-star polymers were significantly different than the linear analogs.   The UPy-star polymers maintained significant viscosity to temperatures as high as 160 °C because the greater number of associations per star molecule (6 versus 2) requires driving the association/dissociation equilibrium much farther to the dissociated state to disrupt the network-like structure.

Figure 5-7. Complex viscosity versus T for UPy functional (UPy) poly(ethylene-*co*-propylene)s of monofunctional, and telechelic (T) functionality.
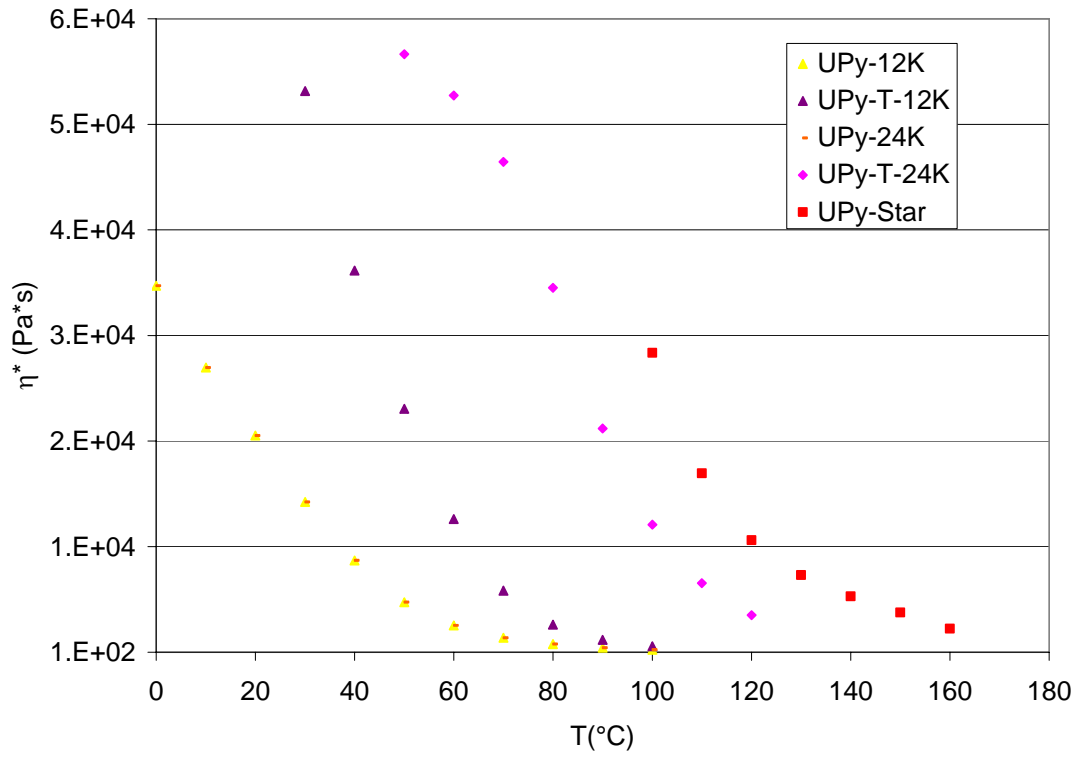
Melt rheology data for the non-functional and hydroxyl functional poly(ethylene-co-propylene)s obeyed time-temperature superposition (TTS) principles and master curves were constructed. Storage modulus master curves for the linear non-functional and hydroxyl functional poly(ethylene-*co*-propylene)s showed characteristic linear chain responses for entangled polymers in the melt. As expected, the plateau modulus was observed at lower frequencies for the higher molar mass polymers. The non-functional star-branched macromolecules, although much higher in molar mass, transitioned to the plateau modulus in the same frequency range as the linear polymers. This was attributed to the highly compact structure of the star-branched macromolecules and an inability to entangle as effectively as the corresponding linear 90,000 g/mol poly(ethylene-*co*-propylene). In addition, the terminal-to-plateau transition was broader for the star macromolecules than for the linear polymers.

Although rheology data for the non-functional polymers exhibited good time-temperature superposition, the data for the UPy-functionalized polymers did not permit TTS treatment. It was observed that the loss modulus (G'') isotherms were not superimposable in the rubbery plateau region for the UPy functionalized polymers. The TTS failure was attributed to the different temperature dependencies of the two mechanisms that governed the viscoelastic behavior, i.e., the polymer relaxation and the hydrogen bond association/dissociation equilibrium. Other researchers observed similar TTS failure for melt rheological studies of multiple hydrogen bond containing polymers. [398] Although TTS failed for the G'' data, relatively good superposition was observed for

[398] Mueller, M., U. Seidel and R. Stadler "Influence of hydrogen bonding on the viscoelastic properties of thermoreversible networks: analysis of the local complex dynamics." *Polymer* **1995**, *36*, 3143-3150.

both the storage modulus (G') and dynamic viscosity (η^*). This observation is consistent with earlier efforts by Fetters et al. who reported this phenomenon for polymers with strong ionic end groups. [399]

Figure 5-8 shows storage modulus master curves for the non-functional and UPy functional polymers at a reference temperature of 50 °C and their respective shift factor plots. The shift factor plots were smooth and showed a non-linear curvature, as was expected. While the non-functional linear poly(ethylene-*co*-propylene)s showed characteristic linear chain responses for entangled polymers in the melt, significant differences were observed between the non-functional and UPy functional macromolecules. The terminal region was shifted systematically to lower frequencies as the multiple hydrogen bonding interactions increased the apparent molar mass and disrupted chain reptation. The telechelic functional UPy-T-24K transitioned to the terminal region at the lowest frequency, which indicated the highest apparent molar mass. It was previously proposed that telechelic functional polymers of this type exhibit an end-to-end association in solution, with the resulting properties of a high molar mass polymer. [400]

[399] Fetters, L. J., W. W. Graessley, N. Hadjichristidis, A. D. Kiss, D. S. Pearson and L. B. Younghouse "Association Behavior of End-Functionalized Polymers. 2. Melt Rheology of Polyisoprenes with Carboxylate, Amine, and Zwitterion End Groups." *Macromolecules* **1988**, *21*, 1644-1653.
[400] Hirschberg, J. H. K. K., F. H. Beijer, H. A. van Aert, P. C. M. M. Magusin, R. P. Sijbesma and E. W. Meijer "Supramolecular Polymers from Linear Telechelic Siloxanes with Quadruple Hydrogen-Bonded Units." Ibid. **1999**, *32*, 2696-2705.

Figure 5-8. Storage modulus master curves for non-functional (H) and UPy functional (UPy) poly(ethylene-*co*-propylene)s of monofunctional, and telechelic (T) functionality. Labels in the legend from top to bottom correspond to curves from left to right.
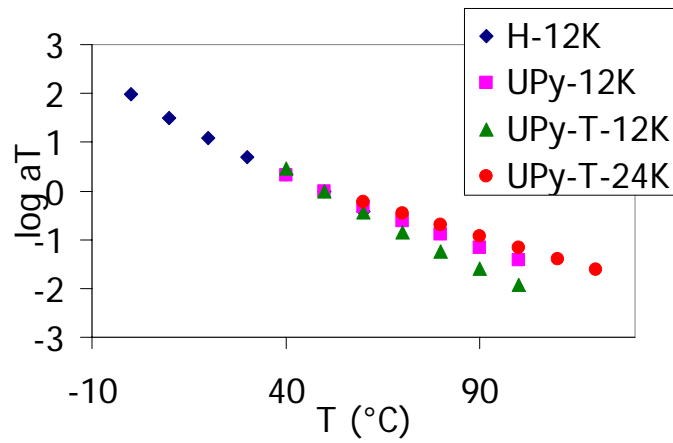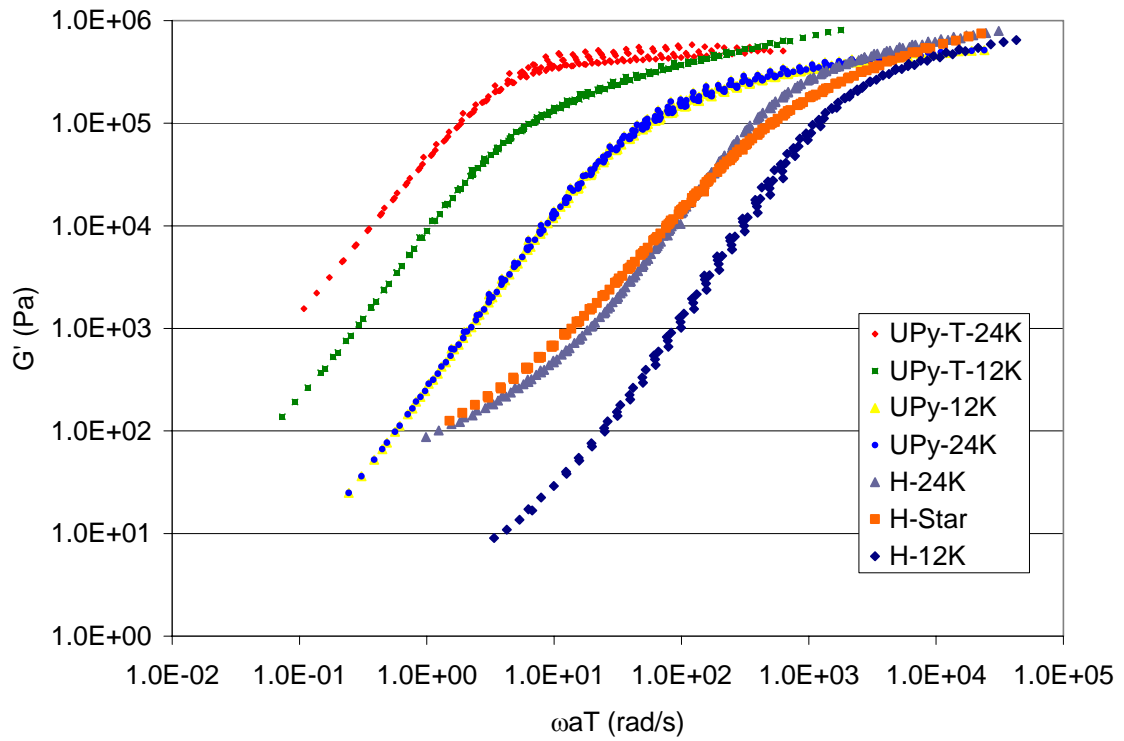
Since the UPy-T-24K polymer had a larger mass between UPy-functional groups, the resulting associated polymer had a higher apparent molar mass for a constant number of end-to-end associations. UPy-T-12K exhibited a terminal-to-plateau transition intermediate to UPy-T-24K and the monofunctional samples. The monofunctional samples UPy-12K and UPy-24K behaved in a similar fashion, and transitioned at a lower frequency than the non-functional polymers of similar molar mass. It was postulated that these polymers formed aggregates, but linear high molar mass aggregates were not formed due to only one functional end group. However, the presence of a terminal region indicated the physical crosslinks formed from the hydrogen bonding interactions were reversible in nature.

Figure 5-9 shows dynamic viscosity (η^*) master curves for the non-functional linear and star-shaped polymers at a reference temperature of 50 °C. The non-functionalized polymers displayed typical Newtonian flow behavior at low frequencies and transition to a shear-thinning region. The 12K polymers exhibited shear thinning behavior at a higher frequency than both the 24K polymers and the star-shaped polymers due to fewer entanglements of the lower molar mass polymers. The star-shaped polymers exhibited shear thinning in the same frequency range as the 24K g/mol non-functional polymers.

Figure 5-9. Complex viscosity master curves for non-functional (H) and UPy functional (UPy) poly(ethylene-*co*-propylene)s of monofunctional and telechelic (T) functionality. Labels in legend from top to bottom correspond to curves from top to bottom.
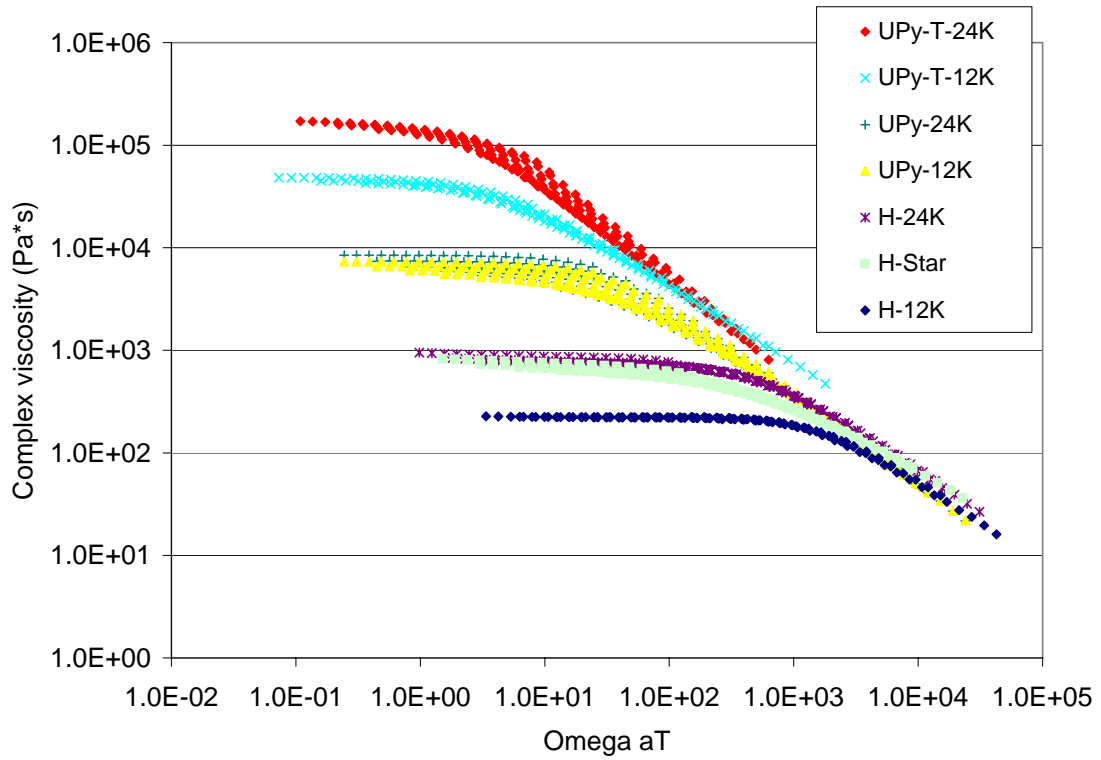
When UPy-functional polymers were compared with their non-functional counterparts, it was observed that the value of the zero shear viscosity was much higher due to the strong multiple hydrogen bonding interactions in the melt. The monofunctional samples (UPy-12K and UPy-24K) behaved similarly to one another and showed an order of magnitude increase in η_0 over non-functional equivalents, which was consistent with a higher apparent molar mass due to intermolecular associations. UPy-T-24K and UPy-T-12K exhibited an increase in η_0 of two orders of magnitude over corresponding non-functionalized analogs.

Shear thinning behavior occurred at lower frequencies for the telechelic UPy functional polymers than for the monofunctional UPy polymers due to the higher apparent degree of entanglement. A common reference temperature was not defined for the non-functional poly(ethylene-*co*-propylene)s and the UPy-star due to large differences in melt rheological behavior under these test conditions, and, as a result, the non-functional linear and star-shaped poly(ethylene-*co*-propylene)s were not directly compared to the UPy-star. Thus, the UPy-star was only compared to both mono- and telechelic functional UPy polymers.

Figure 5-10 shows the storage modulus master curves for the series of UPy-functional poly(ethylene-co-propylene)s. As discussed previously, the monofunctional samples UPy-12K and UPy-24K behaved similarly to one another and transitioned to the terminal region at higher frequencies than the telechelic samples UPy-T-12K and UPy-T-24K. The UPy-star polymers exhibited an initial loss of modulus due to relaxation of the linear arm segments of the star polymer, but showed a lengthening of the plateau region

197

due to physical crosslinks imparted through the network-like structure of the star multiple hydrogen bonding interactions. This behavior was significantly different than that observed for the linear UPy-functional polymers.

Similarly, in complex viscosity master curves (Figure 5-11), distinct differences were observed between the linear UPy-functional polymers and UPy-star. The complex viscosity increased compared to UPy-T-24K and shear thinning occurred at lower frequencies. Newtonian flow was not observed for UPy-star polymers and a zero shear viscosity was not determined. Similar behavior is observed in covalently crosslinked networks. The presence of UPy functionality at each arm terminus on the star polymer results in functionality greater than 2, which causes network-like properties through multiple hydrogen bonding interactions.

Figure 5-10. Storage modulus master curves for UPy functional (UPy) poly(ethylene-*co*-propylene)s of monofunctional, and telechelic (T) functionality. Labels in legend from bottom to top correspond to curves from top to bottom.
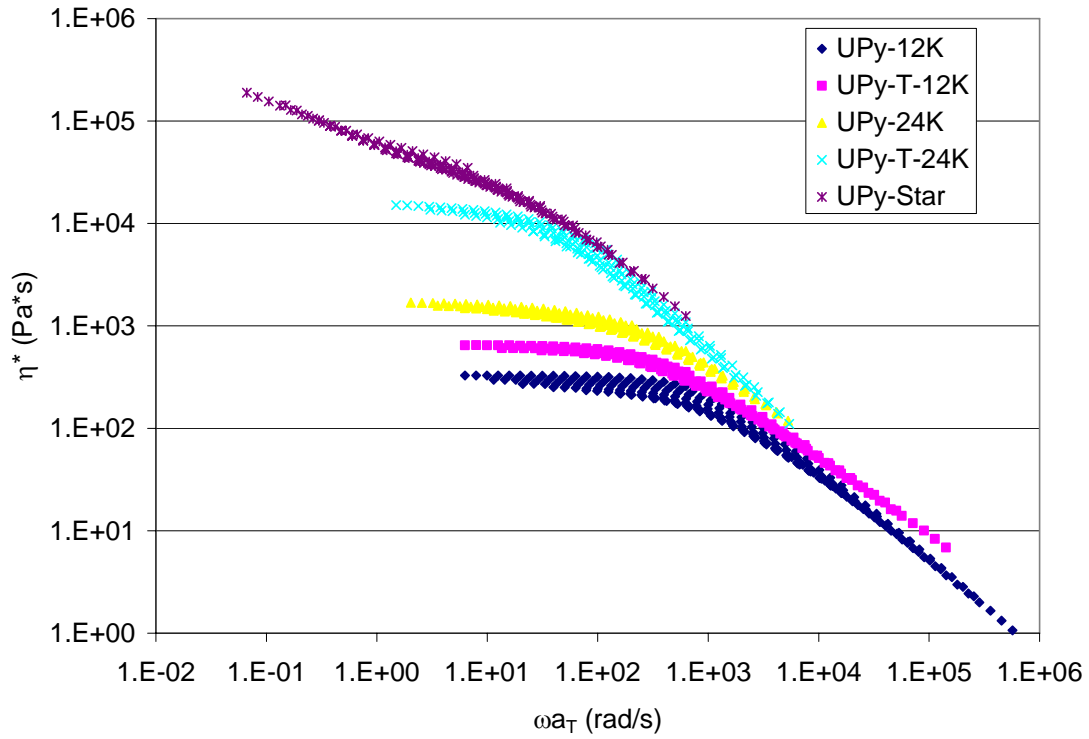
Figure 5-11. Complex viscosity master curves for UPy functional (UPy) poly(ethylene-*co*-propylene)s of monofunctional, and telechelic (T) functionality. Labels in legend from bottom to top correspond to curves from top to bottom.
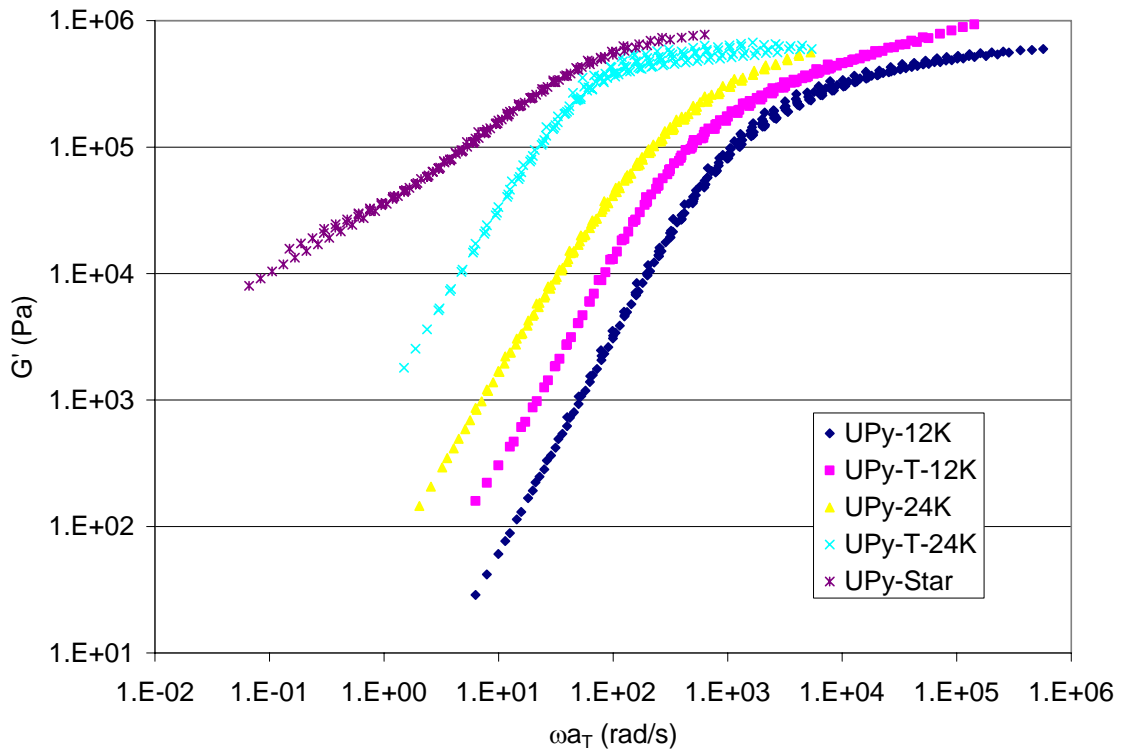
Activation parameters for stress relaxation of the poly(ethylene-*co*-propylene) series (non-functional and UPy-functional) were calculated from the temperature dependence of the zero-shear viscosity. Activation energies were calculated from the slope of a semilogarithmic plot of η_0 versus 1/T (Figure 5-12) using the following equation:

$$\eta = c e^{\Delta H/RT}$$

Excellent linear relationships were achieved for each polymer, and activation parameters for non-functional and mono-UPy functional poly(ethylene-*co*-propylene)s ranged from 55-60 kJ/mol. Telechelic UPy functional poly(ethylene-*co*-propylene)s exhibited an increased activation energy to stress relaxation of ~75 kJ/mol, which was considered a significant increase over the non-functional analogs. Telechelic association of UPy groups clearly influenced the barrier to relaxation, which increased the energy required for melt flow. Activation parameters for UPy-star were not calculated due to the absence of a zero-shear viscosity plateau for these polymers.

Figure 5-12. Semilogarithmic plot of the zero shear viscosity (η_0) of various poly(ethylene-*co*-propylene)s versus the reciprocal of the absolute temperature. Labels in legend from top to bottom correspond to curves from left to right.
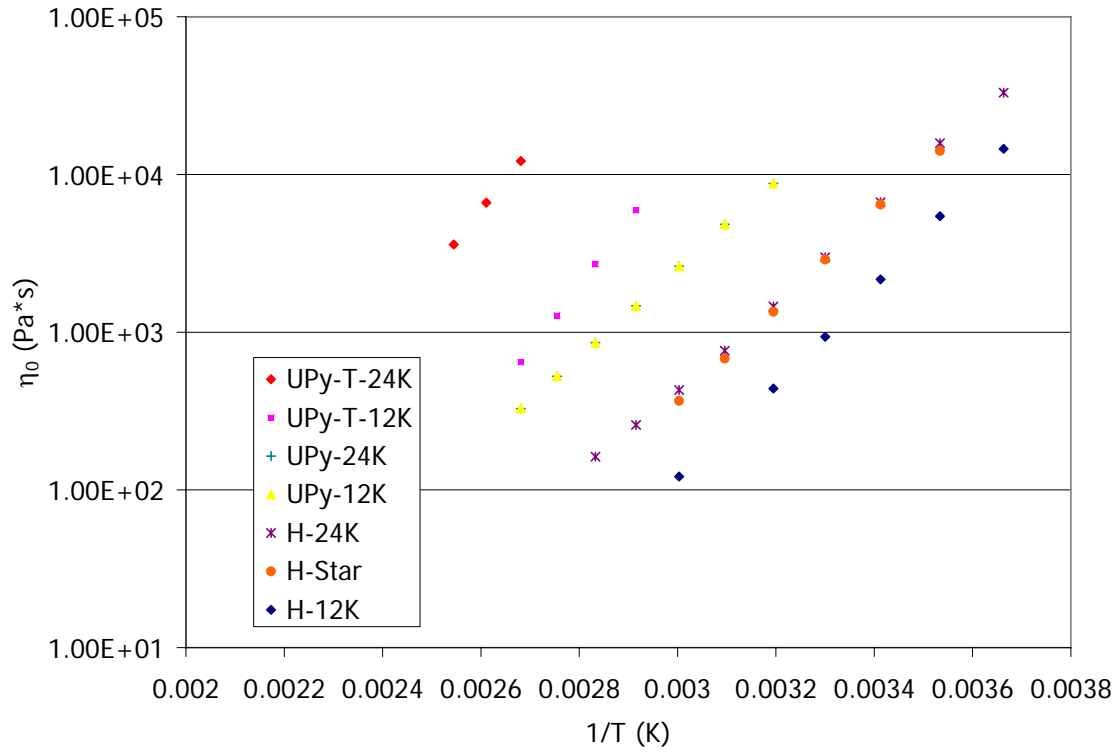
5.5 Conclusions

In-situ FTIR model compound studies were conducted to optimize reaction conditions for UPy modification of poly(ethylene-*co*-propylene). Subsequently, conversions ranging from 75-100% were achieved for linear and star-shaped poly(ethylene-*co*-propylene)s. DMA and DSC characterization revealed similar T_g's for non-functional and UPy functional polymers, in agreement with the expected value of -60 °C, for both linear and star-shaped polymers. In addition, UPy-stars exhibited an increased Young's modulus and decreased elongation at break compared to UPy-T-24K, indicating a higher entanglement density for the star-shaped polymers.

In general, UPy functionalized polymers exhibited significantly higher zero shear viscosities and lower frequency plateau-to-terminal transitions relative to non-functional analogs due to the higher apparent molar mass of the polymers with multiple hydrogen bonding interactions, and telechelic functional polymers exhibited enhanced changes over monofunctional counterparts. Storage modulus master curves showed a broadening in the plateau region for the star-shaped polymer, as well as an increase in the terminal relaxation time due to network-like behavior from the multiple hydrogen bonding interactions in comparison to linear UPy-functionalized counterparts. In addition, complex viscosity master curves further revealed the network-like structure of the star-shaped UPy functionalized polymer with non-Newtonian behavior in the low frequency range and the absence of a zero shear region. Activation energies for stress relaxation were calculated for the series of polymers and telechelic UPy functional polymers

showed a higher activation energy than non-functional and mono-UPy functional polymers.

5.6 Acknowledgements

Chapter 6   Synthesis and Characterization of Poly(2-ethylhexyl methacrylate) Copolymers Containing Pendant Self-Complementary Multiple Hydrogen Bonding Sites

6.1   Abstract

The synthesis and characterization of copolymers containing 2-ethylhexyl methacrylate (EHMA) and a quadruple hydrogen bonding site, 2-ureido-4[1*H*]-pyrimidone methacrylate (UPyMA), are described. An analogous dimeric hydrogen bond containing copolymer based on 2-ethylhexyl methacrylate and methacrylic acid (PEHMA-*co*-MAA) was also synthesized for comparative purposes. The glass transition temperatures of the PEHMA-*co*-UPyMA series increased linearly with increasing UPyMA content. Creep compliance measurements as a function of temperature indicated a decrease in the creep compliance with increasing UPyMA content over the range of 1 to 10 mol% UPyMA. Melt rheological analysis also showed an increase and lengthening of the plateau modulus as a function of frequency with increasing UPyMA content, as well as increasing complex viscosity as a function of temperature. The analogous PEHMA-*co*-MAA copolymer, which contained 11 mol% MAA, showed similar behavior in the melt rheological analysis to the PEHMA-*co*-UPyMA copolymer containing only 1 mol% UPyMA units. The multiple hydrogen bond containing copolymers were successfully analyzed using time-temperature superposition for the construction of master curves.

6.2 Introduction

Traditional syntheses of macromolecules have involved both step-growth and chain polymerization to form repeating units that are connected with irreversible, stable, covalent bonds. High molar masses of these irreversibly connected macromolecules are desired to optimize physical properties and commercial utility. However, increased melt viscosity of high molar mass polymers compromises potential solvent-free manufacturing, melt processability, thermal stability, and solubility of the final products. In recent years, supramolecular chemistry involving tailored non-covalent interactions, such as multiple hydrogen and tailored ionic bonding, has received renewed interest.[401] Thermoreversible

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polymers have emerged as a potential solution due to the unique combination of satisfactory mechanical properties at typical use temperatures and low melt viscosities during processing and manufacturing.   In order to achieve these families of supramolecular macromolecules, research efforts have focused on the incorporation of complementary multiple hydrogen bonding groups with high dimerization constants.[402]

Meijer et al. extended the self-complementary quadruple hydrogen bonding interaction to polymeric systems using chain-end functionalization of polymers.

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Poly(ethylene oxide-*co*-propylene oxide)s with the UPy endgroups were prepared and compared to non-functionalized analogs. Comparison of the functionalized polymer to the non-functionalized cross-linked material showed that the hydrogen bonded polymer exhibited a higher plateau modulus. The hydrogen bonds acted as entanglements and caused the formation of a dense thermodynamic network.[403] The crosslinks evident in the non-functionalized polymer were a function of kinetics and resulted in a much less dense network. Additionally, the quadruple hydrogen bonded polymer exhibited a rubbery plateau in storage modulus as well as viscoelastic and shear thinning melt rheological behaviors. Meijer et al. also incorporated UPy units as chain ends for telechelic oligo- and poly(dimethylsiloxane).[404] Subsequent NMR, FTIR, and rheology measurements have illustrated that the ureidopyrimidinone groups associate via quadruple hydrogen bonds in a donor-donor-acceptor-acceptor (DDAA) array. DSC characterization showed a small, but distinct melting peak, attributed to formation of crystalline domains from multiple hydrogen bonding interactions. Due to this association, the polymers show many characteristics of entangled, high molecular weight polymers, including a plateau modulus of 10^5 Pa. Meijer has published several additional papers documenting the behavior of additional oligomeric systems incorporating the ureidopyrimidinone quadruple hydrogen bonding unit.[405] Macromolecules that contain

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pendant multiple hydrogen bonds randomly dispersed in the polymer have also received significant attention in recent years due to their behavior as thermoplastic elastomers.[406] Stadler et al. demonstrated that non-polar polymers such as poly(1,3-butadiene) and polyisobutylene bearing pendant urazole derivatives had significantly different properties than the non-functionalized polymer due to the formation of a thermoreversible network.[407] Coates et al. more recently reported the synthesis of non-polar poly(1-hexane) bearing pendant UPy groups, and these polymers exhibited elastomeric properties and reversibility in solution.[408] Rotello et al. also recently reported the synthesis of thermally reversible microspheres through non-covalent polymer cross-linking. Using a complementary multiple hydrogen bonding system consisting of bis-thymine units and diamidopyridine units, discrete micron-scale spherical aggregates were formed. The particle size was controlled through changes in the bis-thymine spacer, and

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more monodisperse particles were achieved through annealing.[409] Tang et al. have also used amino acid residues as multiple hydrogen bonding moieties. Using L-valine and L-leucine, Tang and coworkers were able to tune the chain conformation of poly(phenylacetylenes), which ranged from helical to micellar spheres, and helical cables.[410]

Previous research in our laboratories has involved the synthesis of telechelic functionalized multiple hydrogen bonded polymers, such as polystyrene, polyisoprene, and microphase separated polystyrene-*block*-polyisoprene copolymers via living anionic polymerization to yield well-defined macromolecules. The influence of hydrogen bonding on glass transition temperature, melt viscosity, and morphology were reported.[411] More recently, the synthesis of telechelic multiple hydrogen bond functionalized polyesters and their properties were reported.[412] These multiple hydrogen bond modified polyesters demonstrated acceptable mechanical performance with an order of magnitude decrease in the melt viscosity at 235 ºC, although melt stability of the

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[412] Yamauchi, K., A. Kanomata, T. Inoue and T. E. Long "Thermoreversible Polyesters Consisting of Multiple Hydrogen Bonding (MHB)." *Macromolecules* **2004**, *37*, 3519-3522.

urethane functionality limited residence times for melt processing. In our earlier work, poly(n-butyl acrylate) copolymers containing pendant multiple hydrogen bonding units were synthesized and interesting rheological, thermal, and adhesive properties were reported.[413] Our current work has focused on the synthesis and characterization of poly(2-ethylhexyl methacrylate)s copolymers bearing pendant quadruple multiple hydrogen bonding sites over a broader range of compositions, and a comparison of their mechanical, rheological, and thermal properties with a carboxylic acid containing copolymer that is capable of only dimeric hydrogen bonding. Moreover, creep performance was not investigated previously, and it is hypothesized that multiple hydrogen bond containing, low glass transition temperature, poly(alkyl methacrylate)s will exhibit improved creep performance. In fact, the copolymers described herein have shown interesting elastomeric properties in both creep and tensile experiments. Creep properties reflect long term deformational behavior of viscoelastic materials under constant load, and are thus highly related to sagging of transverse sections in many engineered structures.[414] The fundamental cause of creep in a polymer is the tendency for flow under constant stress. Therefore, modification of the polymer with tailored non-covalent interactions is expected to influence the creep performance under proper test conditions. The mechanical properties of PEHMA-*co*-UPyMA copolymers was compared with copolymers containing the same PEHMA backbone and a pendant methacrylic acid group (PEHMA-*co*-MAA) in order to probe the advantages of multiple hydrogen bonding over a simpler dimeric hydrogen bonding site.

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[413] Yamauchi, K., J. R. Lizotte and T. E. Long "Thermoreversible Poly(alkyl acrylates) Consisting of Self-Complementary Multiple Hydrogen Bonding." Ibid. **2003**, *36*, 1083-1088.

[414] Findley, W. N., J. S. Lai and K. Onaran "*Creep and Relaxation of Nonlinear Viscoelastic Materials with an Introduction to Linear Viscoelasticity*"; Dover Publications, Inc.: New York, 1989.

6.3 Experimental

6.3.1 Materials

2-isocyanatoethyl methacrylate (Aldrich, 98%) was used as received. 2-Amino-4-hydroxy-6-methylpyrimidine (Aldrich, 98%) was dried under vacuum at 100 ºC overnight. Dimethyl sulfoxide (DMSO, Aldrich, anhydrous, 99.9+%) was used as received. 2-Ethylhexyl methacrylate (Aldrich, 98%) and *tert*-butyl methacrylate (Aldrich, 98%) were passed through a basic alumina column to remove inhibitor before use. Tetrahydrofuran (EM Science, HPLC grade), 2,2`-azobisisobutyronitrile (AIBN, Aldrich, 97%), *p*-dioxane (Alfa Aesar, 99% HPLC grade), and *p*-toluene sulfonic acid monohydrate (Aldrich, 98%) were used as received.

6.3.2 Characterization

^{1}H NMR spectra were determined in CDCl$_3$ at 400 MHz with a Varian Unity spectrometer. Glass transition temperatures were determined using a TA Instruments Q100 differential scanning calorimeter (DSC) at a heating rate of 10 °C/min under nitrogen. Glass transition temperatures are reported as the transition mid-point during the second heat. Molar masses were determined using size exclusion chromatography (SEC) with a Waters Alliance SEC system equipped with a Wyatt miniDAWN multiple angle laser light scattering detector. Creep experiments were performed with a TA Instruments DMA 2980® dynamic mechanical analyzer with tension clamp. A rectangular-shaped film sample (L x W x T = c.a. 20 mm x 6 mm x 0.2 mm) was subjected to tension stress (0.5 MPa) for 10 min. at each equilibrated temperature and the strain was monitored using a built-in optical encoder with a resolution of 10 nm. The temperature increment

between each isothermal experiment was 3 °C. Based on the time-temperature superposition correspondence principle, master curves for a reference temperature of 19 °C were created. Melt rheological analysis was conducted using a TA Instruments AR1000 rheometer with 25 mm parallel plate geometry and a 5 % strain amplitude. Based on the time-temperature superposition correspondence principle, master curves for a reference temperature of 65 °C were created. Temperature sweeps were carried out at a frequency of 1 Hz. Stress-strain experiments were performed using dogbone-shaped film samples cut using a die as specified in ASTM D3368. The tensile tests were performed under ambient conditions on a 5500R Instron® universal testing machine at a crosshead displacement rate of 25.4 mm/min. Duplicate samples were tested for each polymer. Stress vs. strain profiles were recorded using Merlin® software at an acquisition rate of 50 milliseconds per each data point. Pneumatic grips were used and no slippage was observed during the test.

6.3.3 UPyMA Monomer Synthesis

A 250-mL round-bottomed flask containing a magnetic stir bar was flame-dried under a nitrogen purge. 2-amino-4-hydroxy-6-methylpyrimidine (40.18g, 0.321 mol), 2-isocyanatoethyl methacrylate (54.8g, 0.353 mol), and DMSO (200 mL, 2.82 mol) were added to the flask under a nitrogen flush. The reaction flask was placed in an oil bath at 150 ºC and the reaction was allowed to proceed for 30 minutes. The reaction was subsequently cooled to room temperature and the product precipitated from solution. The product was vacuum filtered and washed copiously with methanol to remove both starting material and residual DMSO. The UPyMA monomer was then dried at room temperature under vacuum. The reaction scheme is depicted in Scheme 6-1.

Spectroscopic characterization was also detailed in our earlier publication.[415] ¹H NMR

(400 MHz, CDCl₃, δ): 13.0 (s, 1H, –N*H*–C(CH₃)=), 11.9 (s, 1H, –N*H*–C=N–), 10.5 (s,

1H, –CH₂N*H*–CO–), 6.2 (s, 1H, CH*H*cis=C(CH₃)), 5.8 (s, 1H, –NHC(CH₃)=C*H*CO–),

5.5 (s, 1H, CH*H*trans=C(CH₃)), 4.3 (s, 2H, –COOC*H₂*–), 3.6 (s, 2H, –COOCH₂C*H₂*NH–),

2.3 (s, 3H, –NHC(C*H₃*)=CH–CO–), 1.9 (s, 3H, CH₂=C(C*H₃*)). *m/z* = 280 (theoretical:

280.26).

Scheme 6-1. Synthetic strategy for UPyMA monomer.

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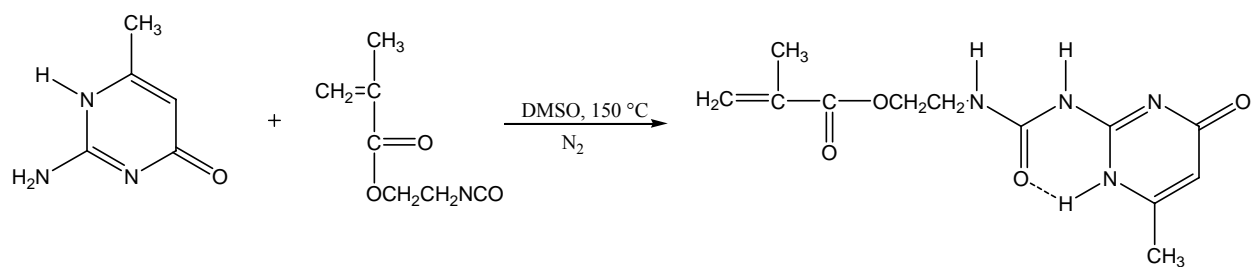
[415] Yamauchi, K., J. R. Lizotte and T. E. Long "Thermoreversible Poly(alkyl acrylates) Consisting of Self-Complementary Multiple Hydrogen Bonding." *Macromolecules* **2003***, 36*, 1083-1088.

6.3.4 PEHMA-co-UPyMA Copolymer Synthesis

A representative polymerization consisted of the following: a 500-mL round-bottomed flask equipped with a magnetic stir bar containing tetrahydrofuran (392 mL, 4.8 mol), 2-ethylhexyl methacrylate (32.5 mL, 0.14 mol), UPyMA monomer (1.26 g, 4.5 mmol), and AIBN (0.03 g, 0.18 mmol) was sparged with nitrogen and placed in an oil bath at 60 °C. The reaction was allowed to proceed for 24 hours. The reaction mixture was filtered and then precipitated into isopropanol and the polymer was collected and dried under vacuum. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 12.9 – 13.2 (s, –NH–C(CH$_3$)= in UPyMA units), 11.8 – 12.1 (s, –NH–C=N–in UPyMA units), 10.4 – 10.7 (s, –CH$_2$NH–CO– in UPyMA units), 5.7 – 6.0 (s, NHC(CH$_3$)=CHO– in UPyMA units), 3.7 – 4.4 (s, –OCH_2CH$_2$– in EHMA units), 3.1 – 3.7 (s, –OCH_2CH$_2$– in UPyMA units), 0.6 – 2.8 (b, –CH$_3$, –CH$_2$–, CH in UPyMA and EHMA units). Similarly, copolymers containing 2-ethylhexyl methacrylate and t-butyl methacrylate were synthesized for comparison. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 3.7 – 4.4 (s, –OCH_2CH$_2$– in EHMA and tBMA units), 0.6 – 2.8 (b, –CH$_3$, –CH$_2$–, CH in tBMA and EHMA units), 1.5 (s, (CH_3)$_3$–C–OC=O in tBMA units). The synthetic methodology is summarized in Scheme 6-2.

Scheme 6-2. Synthetic strategy for novel PEHMA-*co*-UPyMA copolymers.
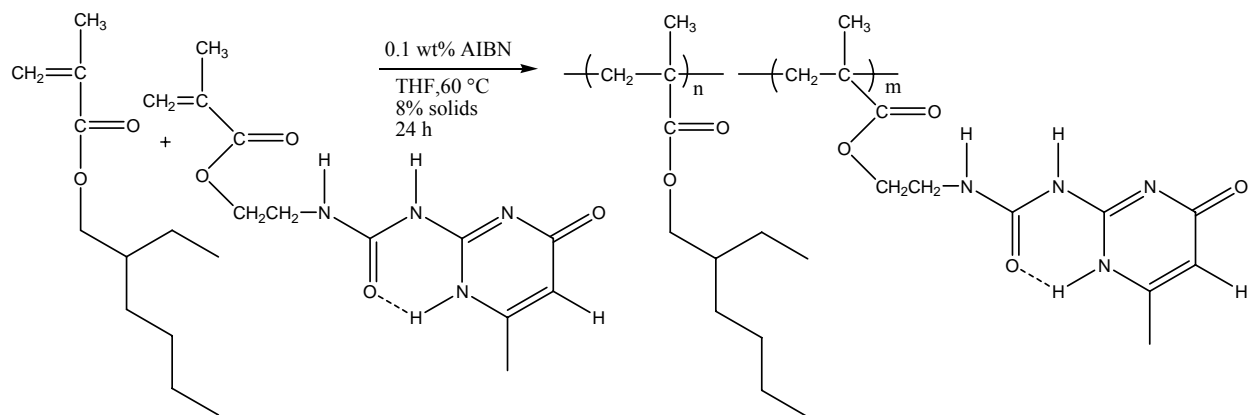
6.3.5 Deprotection of *t*-Butyl Methacrylate Containing Copolymers

The PEHMA-*co*-tBMA copolymer (4.3 g) was dissolved in p-dioxane (82 mL) with p-toluene sulfonic acid monohydrate (0.108g) in a 250-mL round-bottomed flask. The reaction mixture was placed in an oil bath at 100 ºC and allowed to proceed for 48 hours. The polymer was then precipitated into methanol/water (80/20 v/v) and collected and dried under vacuum. Isolated yields were generally 65-70%, which are typical for a conventional free radical polymerization at these reaction conditions. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 3.7 – 4.4 (s, –OC*H*$_2$CH$_2$– in EHMA and MAA units), 0.6 – 2.8 (b, –CH$_3$, –CH$_2$–, CH in MAA and EHMA units).

6.4 Results and Discussion

Our previous literature demonstrated the synthesis of PnBA-*co*-UPyMA random copolymers using DMSO as the polymerization solvent.[416] In order to investigate the effect of UPy quadruple hydrogen bonding interactions on mechanical properties, a system with a higher T$_g$ was chosen, namely 2-ethylhexyl methacrylate. Copolymers of n-butyl methacrylate and UPyMA proved too brittle to perform tensile and creep experiments, while PEHMA-co-UPyMA worked well.   However, when DMSO was utilized for the preparation of 2-ethylhexyl methacrylate based copolymers, several critical differences were observed and an alternative polymerization solvent was chosen. Several solvents were explored, including ethyl acetate, toluene, and THF, and only THF

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[416] Ibid.

provided solubility throughout the polymerization for copolymer products with sufficient molar mass and isolated yield.

In order to elucidate the role of multiple hydrogen bonding in the final copolymer products, a random copolymer containing a t-butyl ester protected carboxylic acid was synthesized. Identical polymerization conditions to the UPyMA containing copolymers were utilized in order to minimize differences in the polymer backbone and to ensure a random copolymerization process. It is widely recognized that acrylic monomers generally undergo polymerization in a random fashion in the presence of a good solvent for most monomers.[417] Solubility issues were not encountered using this strategy, and the copolymer was subsequently deprotected to yield a PEHMA-*co*-MAA copolymer. This copolymer contained a simple carboxylic acid, which is capable of hydrogen bonding in a dimeric fashion.[418] This copolymer contained an equivalent molar concentration of multiple hydrogen bonding groups as UPy-10 and provided an important comparison between a dimeric hydrogen bonding group and a quadruple hydrogen bonding group.

After appropriate reaction conditions were defined to reproducibly synthesize these copolymers, a series of PEHMA-*co*-UPyMA copolymers were synthesized using free radical polymerization techniques. Copolymer composition, molar mass, and molar mass distribution are summarized in Table 6-1. Several compositions were prepared wherein the amount of the multiple hydrogen bonding monomer was varied. The composition of the copolymers was confirmed using ^{1}H NMR spectroscopy, and

[417] Brandrup, J., E. H. Immergut and E. A. Grulke "Polymer Handbook"; 4th ed.; Wiley-Interscience: New York, NY, 1999.
[418] Cleveland, C. S., S. P. Fearnley, Y. Hu, M. E. Wagman, P. C. Painter and M. M. Coleman "Infrared characterization and determination of self-association equilibrium constants for methacrylic acid copolymers." *J. Macromol. Sci., Physics* **2000**, *B39*, 197-223.

characteristic resonances that were assigned to the multiple hydrogen bonding group were used to calculate the molar concentration of the UPyMA monomer. Specifically, five distinct resonances associated with the UPyMA were observed. The incorporation of UPyMA monomer was quantified using a comparison with a well-resolved resonance for PEHMA that was assigned to the methylene adjacent to the ester at 4.0 ppm (Figure 6-1, peak e). The comparison of this resonance with several resonances that are unique to the UPyMA unit, specifically those associated with the methylene adjacent to the ester (Figure 6-1 peak f), three NH hydrogens (Figure 6-1, peak a, b, and c), and the methyne hydrogen on the pyrimidinone ring (Figure 6-1, peak d) was performed. Vinylic resonances associated with the UPyMA monomer at 6.2, 5.8, and 5.5 ppm were not observed in the polymer ^{1}H NMR spectrum, which confirmed the absence of residual monomer. In general, copolymer compositions analyzed in this fashion corresponded well to the monomer feed. It was therefore determined that the UPyMA monomer was incorporated into the polymer in a predictable fashion and the incorporation was quantitative based on ^{1}H NMR spectroscopy. The solubility of the PEHMA-*co*-UPyMA copolymers exhibited similar solubility to PEHMA homopolymer and was soluble in THF, CHCl$_3$, and toluene and was insoluble in DMSO, DMF, CH$_3$OH, and water. The composition of the PEHMA-*co*-tBMA copolymer was also verified using ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of the copolymer only differed to the PEHMA homopolymer with one additional peak at 1.5 ppm that was attributed to the *tert*-butyl ester alkyl. The incorporation of tBMA into the polymer was calculated through comparison of this additional peak to the peak from the methylene adjacent to the ester on 2-ethylhexyl methacrylate. The PEHMA-*co*-tBMA copolymer was subsequently

219

deprotected using classical acid catalysis, and quantitative deprotection was confirmed using ^{1}H NMR spectroscopy with complete disappearance of the resonance at 1.5 ppm which was assigned to the t-butyl ester alkyl.

Table 6-1. Composition and molar mass characterization of PEHMA-*co*-UPyMA and PEHMA-*co*-MAA copolymers.

Sample ID	Hydrogen Bonding Group	Mol % Incorporation of H-Bonding Group[b]	M_w[c]	M_w/M_n[c]
PEHMA	N/A	N/A	146000	2.76
UPy-1	UPy	1	130000	1.99
UPy-3	UPy	3	125000	2.02
UPy-5	UPy	5	128000	1.68
UPy-7	UPy	7	105000	2.15
UPy-10	UPy	10	110000	1.84
MAA-11	MAA[a]	11	147000	1.72

[a]MAA represents methacrylic acid groups. [b]Determined using a Varian 400 MHz NMR spectrometer at 25 °C in CDCl$_3$. [c]Determined using SEC at 40 °C in THF with a MALLS absolute molar mass detector.
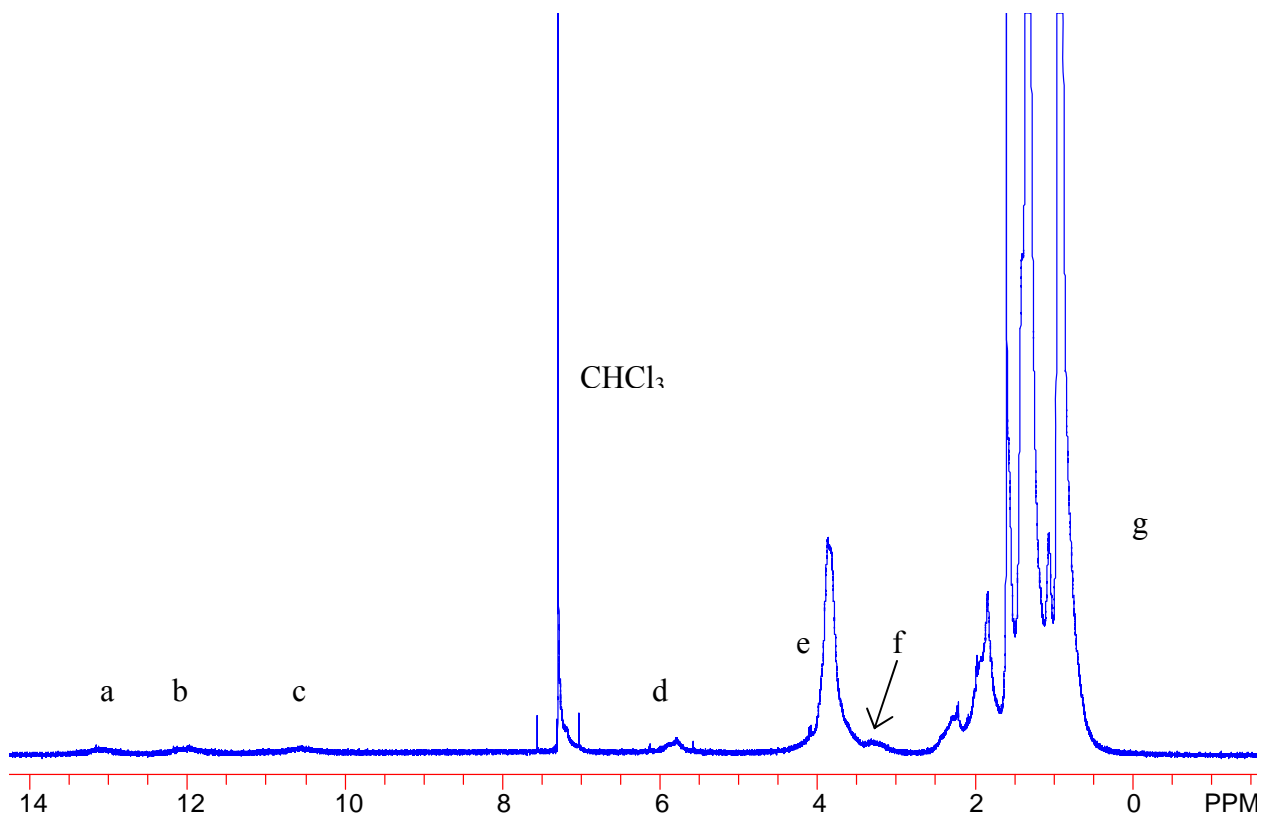
Figure 6-1. Representative ^{1}H NMR spectrum of PEHMA-co-UPyMA copolymer.

Figure 6-2 shows the relationship between UPyMA content in the copolymer and the T_g. As was shown previously in the literature for other random copolymer compositions[419], a linear increase in the T_g was observed with increase in UPyMA content. This expected trend was attributed to incorporation of the strongly interacting UPyMA units. The absence of two T_g's for the copolymers suggested a random copolymerization of the two monomers. Although the increase in T_g suggests a random copolymerization, the effect of hydrogen bonding interactions during the polymerization were not considered and may have influenced the randomness of the polymerization. Thermal characterization was also performed on the PEHMA-*co*-MAA copolymer. The T_g for MAA-11 was 12 ºC, which was distinctly less than the T_g for the UPy-10 copolymer (20 ºC) at a similar molar incorporation of hydrogen bonding sites. In a similar fashion to the UPyMA copolymers, only one T_g was observed for the methacrylic acid containing copolymer, which suggested a random copolymerization. In addition, the T_g value corresponded well with the value predicted using the Fox equation. However, the increase in T_g over the 2-EHMA homopolymer was significantly less for the MAA-11 copolymer than for the UPy-10 copolymer. Because the increase in T_g was attributed to strong hydrogen bonding interactions, we concluded that the hydrogen bonding interactions were weaker for the dimeric methacrylic acid containing copolymers than for the UPyMA containing copolymers at similar molar concentrations.

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[419] Yamauchi, K., J. R. Lizotte and T. E. Long "Thermoreversible Poly(alkyl acrylates) Consisting of Self-Complementary Multiple Hydrogen Bonding." *Macromolecules* **2003**, *36*, 1083-1088.
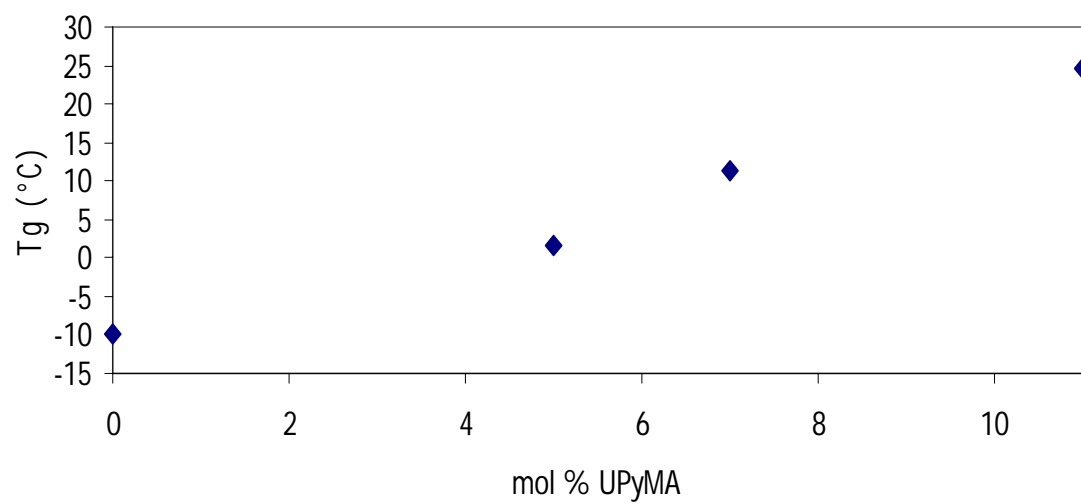
Figure 6-2. Linear relationship between T_g and UPy content.

Creep experiments were performed on two PEHMA-*co*-UPyMA copolymers (UPy-5 and UPy-11). It was found that UPy-5 and UPy-11 differed significantly in their deformation behavior over time and temperature. Creep compliance measurements after 10 min of tensional loading over a range of temperatures were obtained in triplicate for both samples. It was apparent from these measurements that the onset of significant deformation increased approximately 20 °C for UPy-11 compared to UPy-5. This was attributed to the increased level of multiple hydrogen bonding in the copolymer. When these copolymers containing multiple hydrogen bonding UPy groups were compared with a dimeric hydrogen bonding MAA site, significant differences were observed. The creep compliance measurement of MAA-11 after 10 min of tensional loading over a temperature range was significantly higher than both UPy-5 and UPy-11, which also indicated relatively weaker secondary bonding interactions. This data is summarized in Figure 6-3.
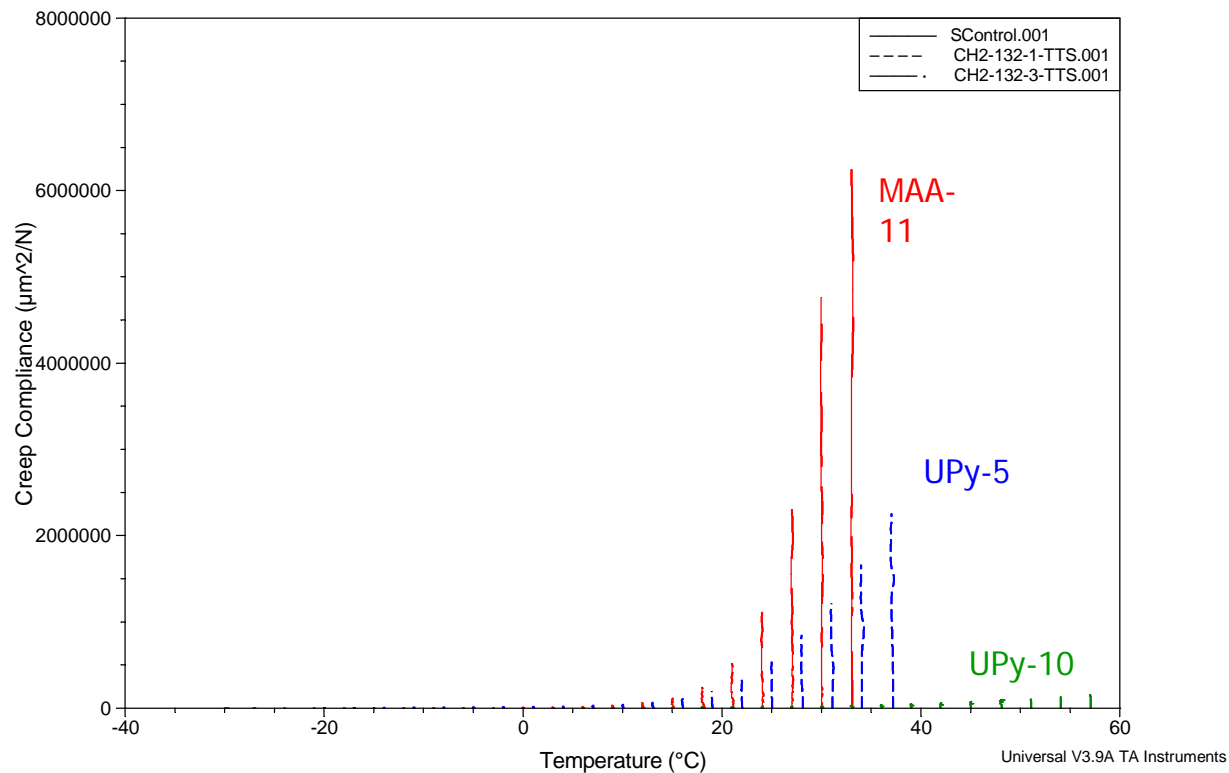
Figure 6-3. Comparison of creep compliance of UPy-5, UPy-10, and MAA-11 upon heating, 10 min residence time at each temperature. An increase in the creep compliance was observed with decrease in hydrogen bond content (UPy-5) and strength (MAA-11).

Long term creep behavior was also studied as a complementary approach for the comparison of creep behavior of these two samples at a similar reference temperature. Master curves over 10 decades of time scale were plotted on the same compliance scale. In the UPy-5 sample, the change in time for a change in compliance from 3.5 to 5.0 $\mu m^2/N$ was 4 decades, whereas the same change in compliance for the UPy-11 sample required 8 decades of change in time scale under a test stress of 0.5 MPa. Under these experimental conditions, the MAA-11 sample showed similar creep behavior to the UPy-5 sample, which also suggested that secondary bonding interactions were contributing to the creep behavior. However, the relative strength of the hydrogen bonding interactions was clearly observed between these two samples, with the MAA sample requiring twice the number of groups to achieve a similar creep compliance. These creep experiments illustrate the performance enhancement that is achieved using multiple non-covalent associations and the data is summarized in Figure 6-4.

Figure 6-4. Creep compliance master curves comparing a) UPy-5, b) UPy-10, and c) MAA-11.

a)

b)
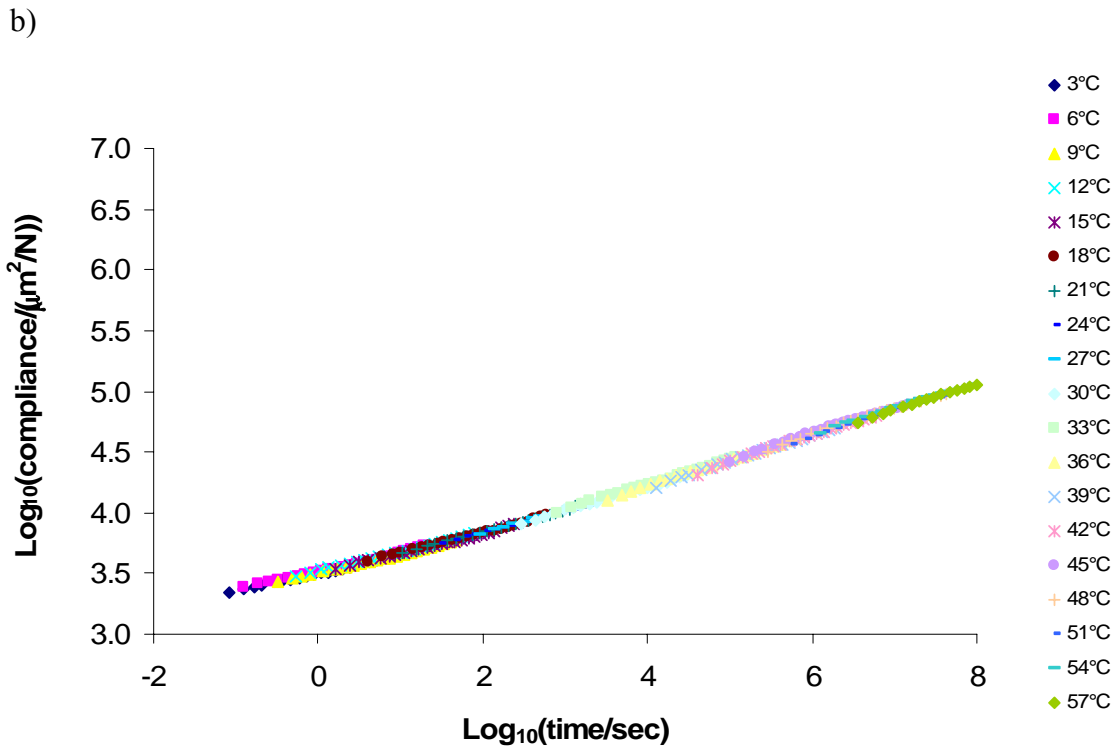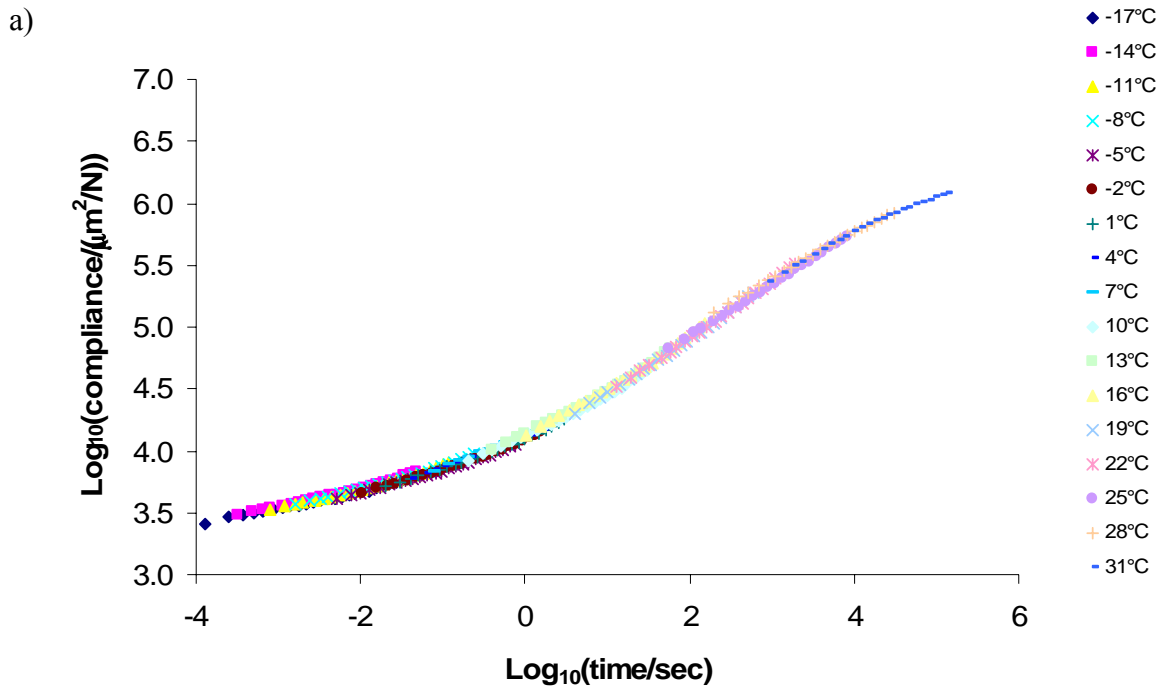
c)
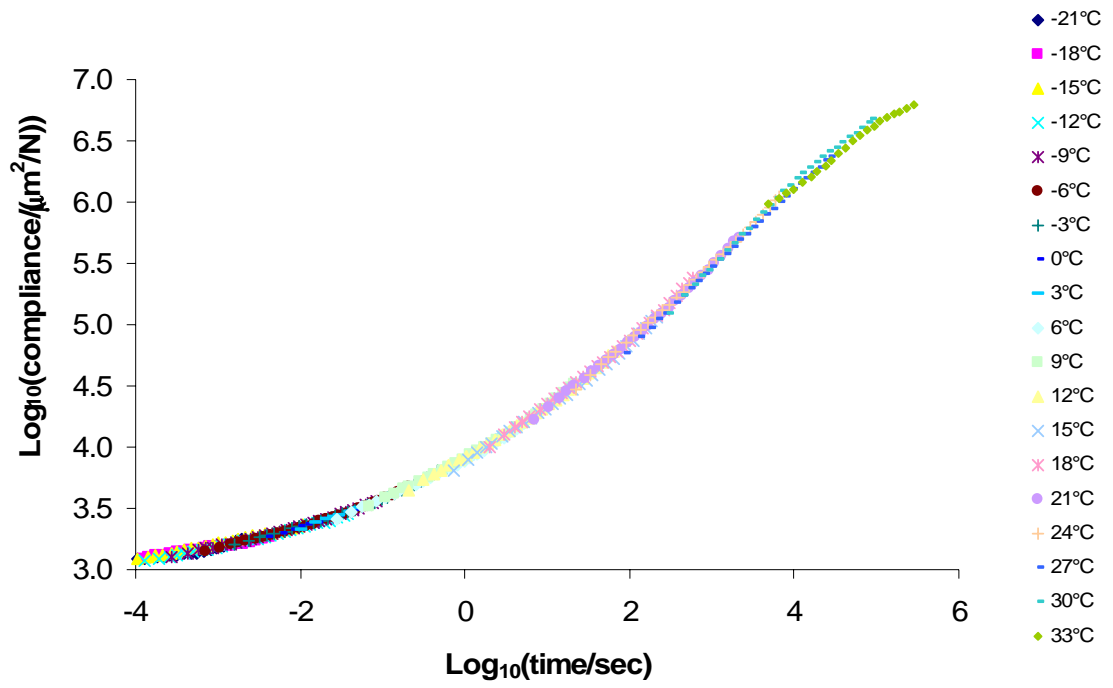
Previously in our laboratories, copolymers based on UPyMA and n-butyl acrylate were synthesized.[420]   These copolymers were investigated in terms of their adhesive properties, and it was determined that peel strength increased with increasing UPyMA content. In the work herein, copolymers that were *not* pressure sensitive adhesives were synthesized in order to investigate effect of UPy content on tensile properties. Tensile experiments were conducted on UPyMA containing copolymers and stress-strain behavior is shown in Figure 6-5. Coates et al. have described the stress-strain analysis on a similar series of 1-hexene-*co*-UPy copolymers.[421] In their earlier work, they described non-functional 1-hexene homopolymers in comparison to UPy-copolymers of different molar masses containing 2 mol% functionality. In general, it was found that non-functional polymers displayed tensile properties that were typical of a viscous liquid, while the functional polymers displayed distinct elastomeric behavior. In our series, we observed similar trends, while also investigating the effect of molar concentration of multiple hydrogen bonding sites. The PEHMA homopolymer and UPy-1 displayed tensile properties that are typical for a viscous liquid, with initial deformation due to uncoiling of the polymer chains and minimal subsequent increase in the stress required to continue elongation.[422] These polymers did not exhibit rupture under the test conditions, and each exhibited percent elongations of over 1100%, at which point the experiment was halted. With increasing UPyMA content in the copolymers with similar weight average molecular weight, distinct differences in the stress-strain profiles were observed. UPy-3 and UPy-5 exhibited initial elongation at low stresses, due to uncoiling of the polymer

[420] Ibid.

[421] Rieth, R. L., F. R. Eaton and G. E. Coates "Polymerization of ureidopyrimidinone-functionalized olefins by using late-transition metal Ziegler-Natta catalysts: synthesis of thermoplastic elastomeric polyolefins." *Angew. Chem. Int. Ed.* **2001**, *40*, 2153-2156.

[422] Bikales, N. M. "*Mechanical Properties of Polymers*"; Wiley-Interscience: New York, NY, 1971.

chains and subsequent increase in the stress once the chains uncoiled. This was attributed to the inability of the polymer chains to easily move past one another due to constraints introduced as a result of the multiple hydrogen bonding interactions. These polymers exhibited increased tensile strengths over PEHMA and UPy-1, with values of 4.84 and 4.36 MPa, respectively. As the UPyMA content increased, the polymer films became more brittle and the percent elongation at break was lower. While UPy-3 exhibited a percent elongation of 490 %, with increasing UPyMA content, this value decreased significantly, to 260 % for UPy-5 and to 14 % for UPy-7. Tensile strengths for UPy-3, UPy-5, and UPy-7 were relatively constant, with values of 4.80 MPa, 4.40 MPa, and 4.40 MPa respectively. UPy-11 was too brittle to obtain reliable data, due to fracture at the clamp sites. Modulus values were obtained for PEHMA-*co*-UPyMA copolymers, and a significant difference (10-fold) was observed between the PEHMA homopolymer (5 ± 1 MPa) and UPy-7 (49 ± 2 MPa). In general, the incorporation of UPy sites increased the stiffness of the polymer as was shown using both modulus values and stress-strain profiles.

**Figure 6-5.** Stress-strain profiles for PEHMA-*co*-UPyMA copolymers.
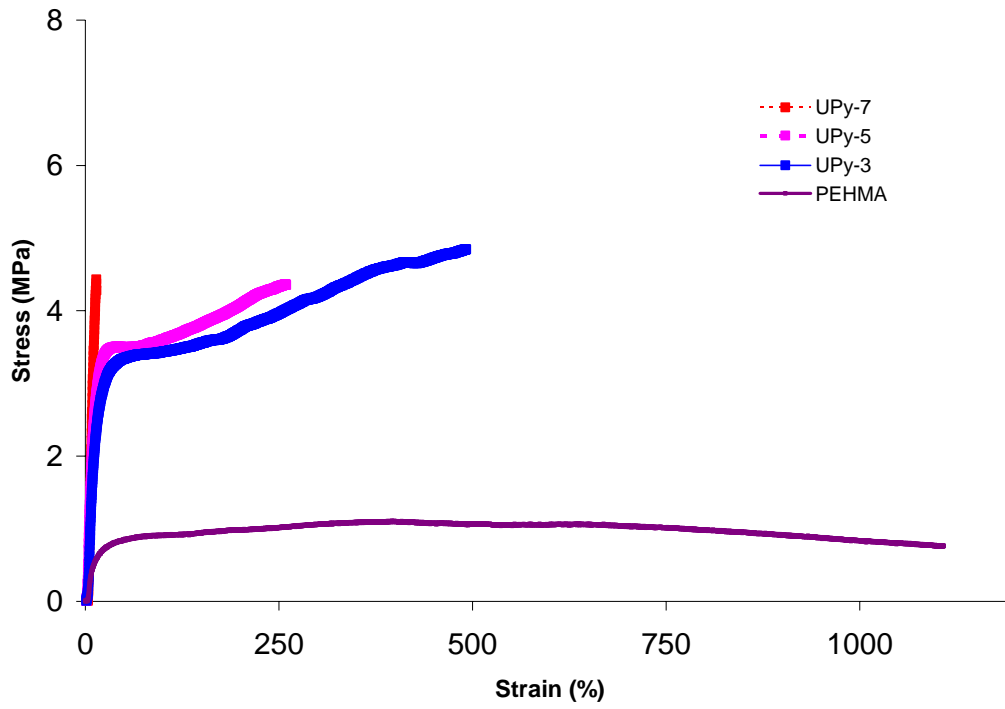
Melt rheological characterization was also conducted on UPyMA and MAA containing copolymers. Master curves of storage modulus versus frequency were constructed for all polymers described herein (Figure 6-6). It was observed that with increasing UPyMA incorporation, the plateau modulus was dramatically lengthened and increased. This change was attributed to the presence of physical cross-links due to increased intermolecular hydrogen bonding. The MAA-11 sample, which contained a simple carboxylic acid hydrogen bond, behaved similarly to UPy-1 and did not show a lengthened and increased plateau modulus, as was observed for the other UPy copolymers. This was attributed to the weaker association between two carboxylic acids (MAA) compared to the quadruple hydrogen bonding group (UPy). However, when the superposition was corrected for T_g effects, and the effects of multiple hydrogen bonding interactions could be studied, a less distinct effect was observed. The same trends were observed, but to a lesser extent (Figure 6-7). The shift factor plots are shown in Figure 6-8 and show behavior consistent with good superposition, with a smooth flow and curvature. It was also observed that the complex viscosity increased with an increase in hydrogen bond incorporation, which was attributed to physical cross-linking due to hydrogen bonding and the formation of higher apparent molar mass. The onset of shear thinning also occurred at lower frequency with an increase in hydrogen bonding and a zero shear viscosity was not determined for UPy content above 1 mol %. Moreover, MAA-11 behaved similarly to UPy-1, with a slightly higher zero shear rate viscosity, which further supported a relatively weaker secondary interaction. This data is summarized in Figure 6-9. Similarly, the superposition was corrected for T_g effects, and

233

while the same trends were observed, the effect of hydrogen bonding interactions was decreased in comparison to the non-corrected plots (Figure 6-10).
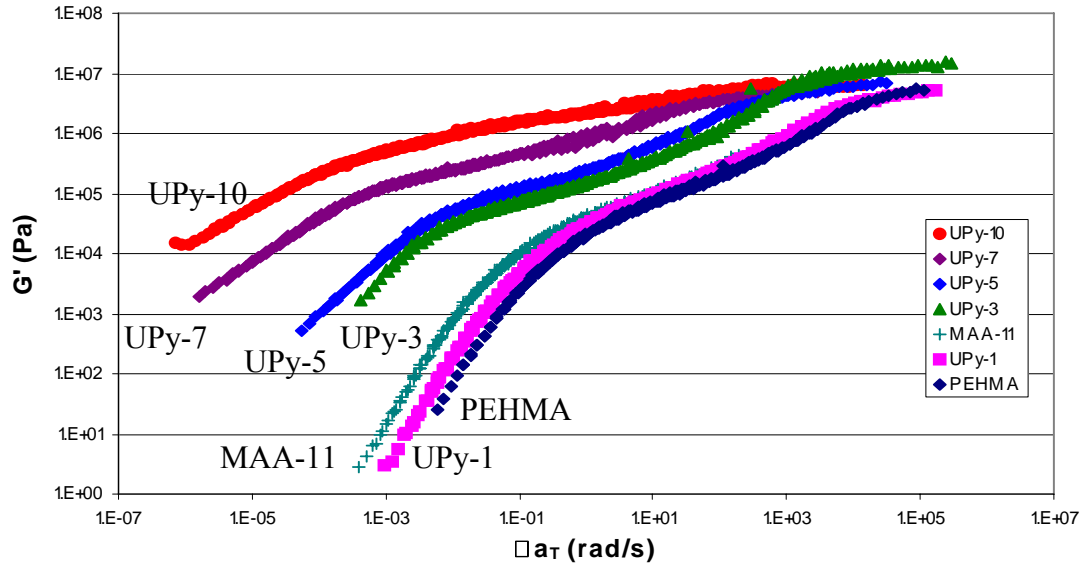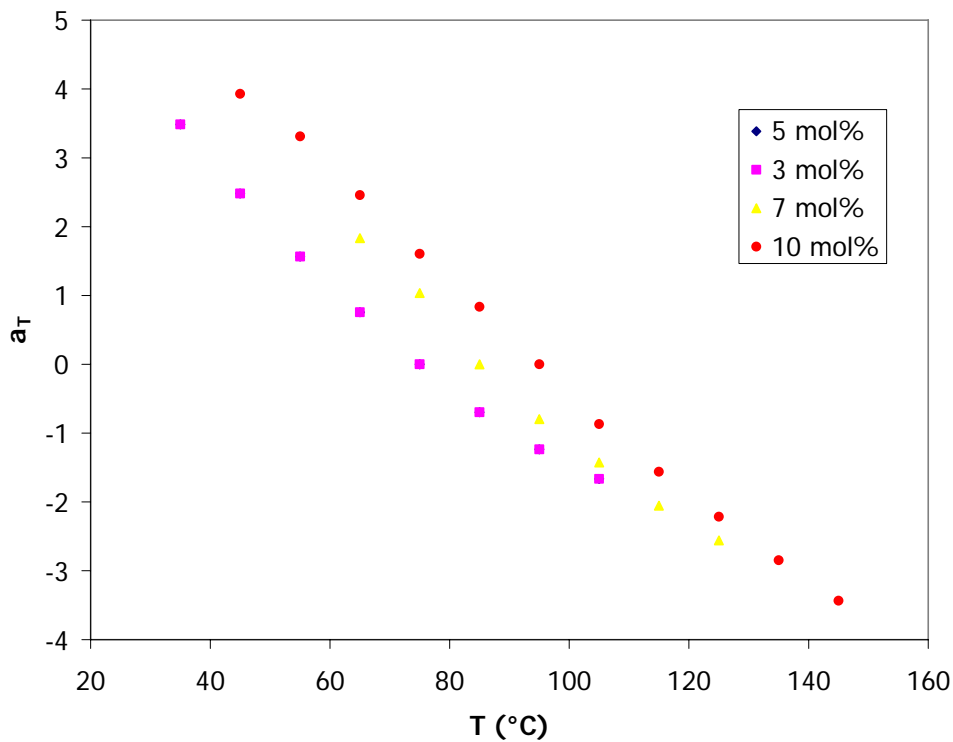
Figure 6-6. Comparison of storage modulus master curves for the series PEHMA-*co*-UPyMA copolymers and the PEHMA-*co*-MAA copolymer control**.**
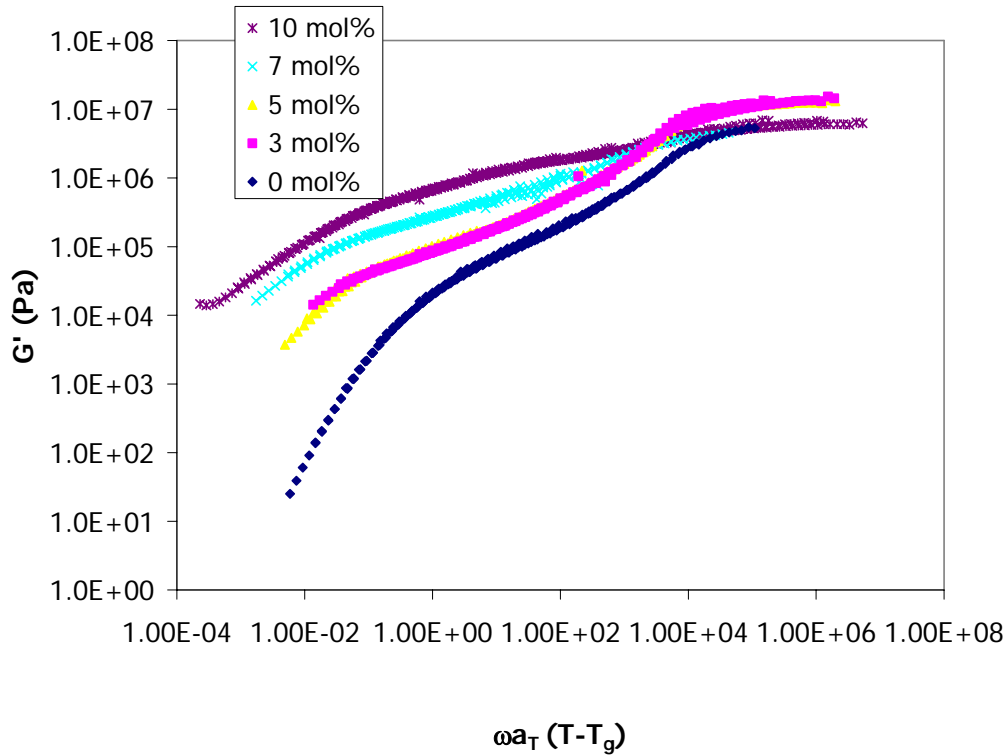
Figure 6-7. Comparison of storage modulus master curves for the series PEHMA-*co*-UPyMA copolymers shifted at a constant interval above T_g.

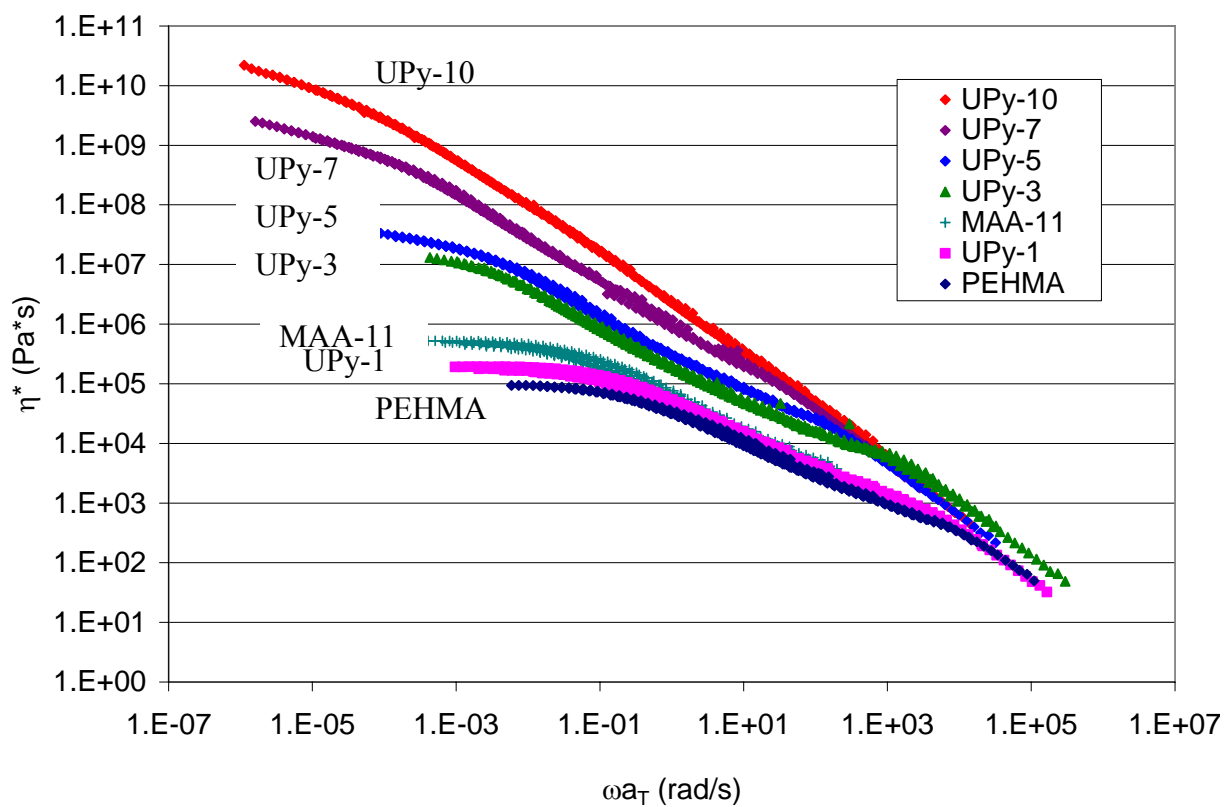**Figure 6-8.** Shift factor plots for the PEHMA-co-UPyMA copolymers.

Figure 6-9. Comparison of complex viscosity master curves for the series PEHMA-*co*-UPyMA copolymers and the PEHMA-*co*-MAA copolymer control.
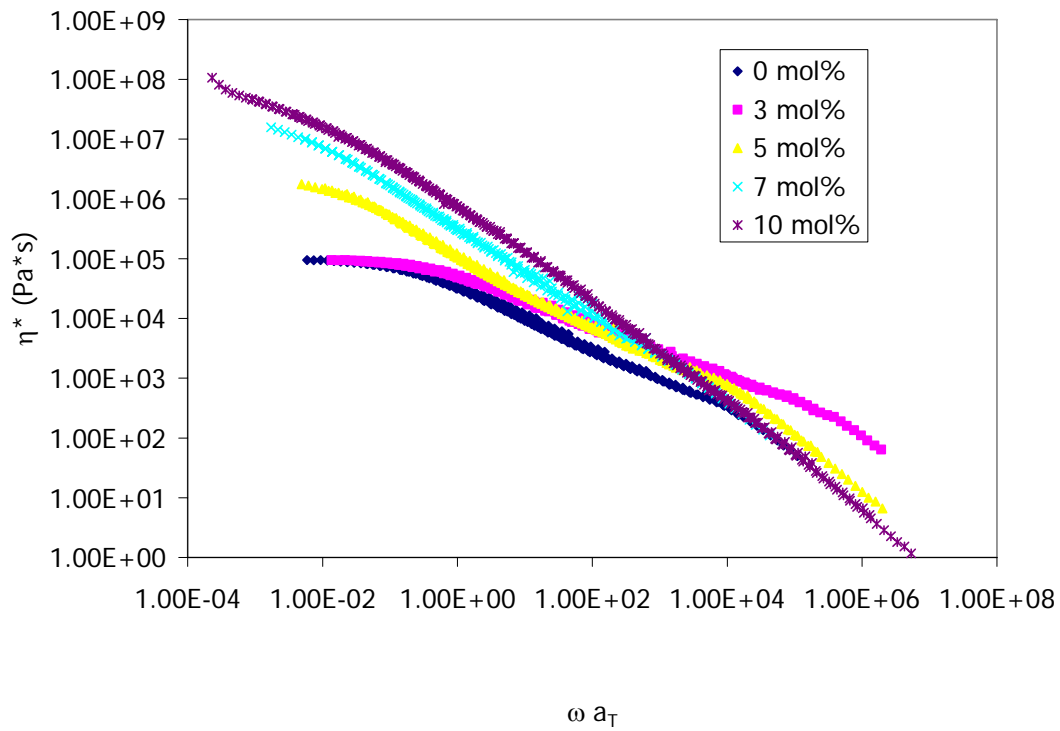
Figure 6-10. Comparison of complex viscosity master curves for the series PEHMA-*co*-UPyMA copolymers shifted at a constant interval above T_g.

Melt rheological analysis also provided complex viscosity versus temperature profiles for the copolymers as shown in Figure 6-11. In general, the complex melt viscosity of the copolymers increased for each temperature with an increase in UPy content. At the lowest temperature that was suitable for data collection (55 ºC), the complex melt viscosity of UPy-10 was 30 times higher than a PEHMA homopolymer at equivalent molar mass. Complex melt viscosities of copolymers that contain intermediate UPy levels are also intermediate in complex viscosity in a predictable fashion. As temperature was increased, the complex melt viscosity of the PEHMA homopolymer rapidly decreased to a relatively constant value between 75 and 85 ºC. UPy-1 exhibited similar behavior to the PEHMA homopolymer. However, at UPy concentrations above 1 mol%, a significant complex melt viscosity was maintained above 85 ºC, with higher incorporations maintaining complex melt viscosity to higher temperatures. While higher UPy content extended the thermomechanical stability of the copolymers to higher temperatures, the copolymers reached a baseline complex viscosity. Even at these higher temperatures between 115-125 ºC, the intermediate compositions (UPy-3, UPy-5, and UPy-7) exhibited complex melt viscosities 5 times higher than the PEHMA homopolymer. This indicated that a lower level of multiple hydrogen bonding sites remained associated even at high temperatures, which was expected due to the equilibrium nature of hydrogen bonding interactions. In general, UPy-10 exhibited a much different viscosity temperature profile than all other copolymers studied. When compared to copolymers with less UPy content, the viscosity decrease as a function of temperature was more gradual, and the slope was correspondingly less.   UPy-10 maintained significant complex melt viscosity to higher temperatures than all the other

copolymers. At 145 ºC, UPy-10 exhibited a complex viscosity that was 2 times higher than UPy-7 and 6 times higher than UPy-5, which suggested a higher level of multiple hydrogen bond associations. It was proposed that the difference between UPy-10 and the lower UPy molar content containing copolymers was attributed to a critical concentration of multiple hydrogen bonding groups, above which, significantly different properties and structure were observed. However, due to limited solubility during polymerization for higher than 10 mol% UPy containing copolymers, samples were not available for further characterization. Further experiments including the incorporation of alkyl modified pyrimidone derivatives are necessary to substantiate this presumption, as well as weaker hydrogen bonding arrays and non-functional analogs, and Meijer et al. have reported the preparation of alkyl substituted pyrimidones to impart better solubility.[423] Additionally, Rubinstein and Semenov postulated that the degree of intra- versus inter-molecular association is very important in determining the properties of "sticky" polymers in solution.[424] Further experiments are necessary to determine the degree of association in our "sticky" copolymers.

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[423] Beijer, F. H., R. P. Sijbesma, H. Kooijman, A. L. Spek and E. W. Meijer "Strong Dimerization of Ureidopyrimidones via Quadruple Hydrogen Bonding." *J. Am. Chem. Soc.* **1998**, *120*, 6761-6769.
[424] Rubinstein, M. and A. N. Semenov "Dynamics of Entangled Solutions of Associating Polymers." *Macromolecules* **2001**, *34*, 1058-1068.
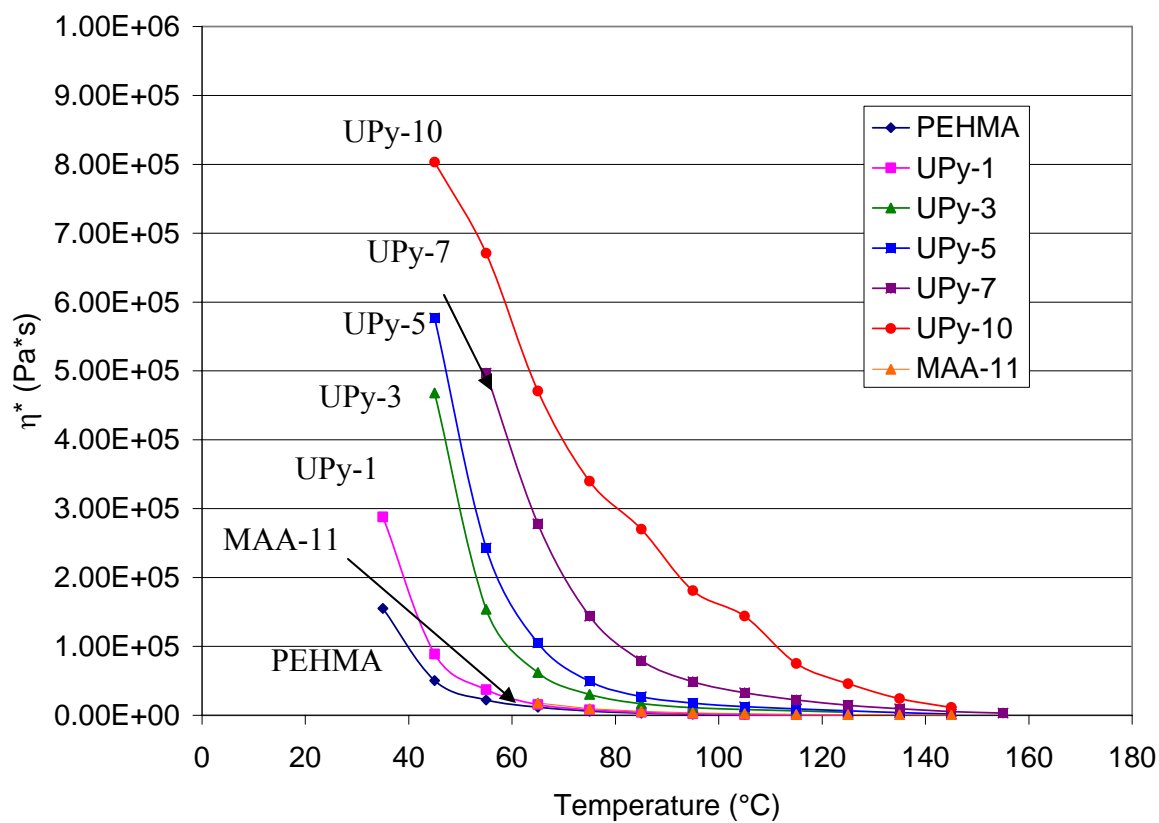
Figure 6-11. Comparison of complex viscosity versus T for the series of PEHMA-*co*-UPyMA copolymers and the PEHMA-*co*-MAA copolymer control.

It is interesting to note that the dimeric hydrogen bonding copolymer, MAA-11, exhibited similar complex melt viscosity versus temperature behavior to the UPy-1 copolymer. MAA-11 did not exhibit higher melt viscosity, as was observed with UPy samples, and this was attributed to the much weaker hydrogen bonding interaction of the methacrylic acid unit. MAA-11 reached a baseline level of complex melt viscosity at temperatures that were similar to the PEHMA homopolymer and UPy-1 (between 75 and 85 °C). In general, PEHMA-*co*-UPyMA copolymers exhibited much higher melt viscosities than the controls (PEHMA and MAA-11) even at temperatures well above their respective T_g values. This was attributed to the strong hydrogen bonding interaction of the UPy groups, and with an increase in UPy concentration, higher melt viscosities were observed.

6.5 Conclusions

Pendant multiple hydrogen bonding groups were successfully incorporated into non-polar 2-ethylhexyl methacrylate containing copolymers with judicious selection of the polymerization solvent. The effect of non-covalent associations (UPy) in the solid state was probed using several methods, including tensile testing, creep compliance experiments, and melt rheological testing. Tensile experiments revealed that at low levels of UPy incorporation, copolymers exhibited a high percent elongation and low tensile strengths. With increasing UPy incorporation, the percent elongation decreased and the tensile strength increased to a constant level above 3 mol%. Modulus increased 10-fold from non-functional PEHMA to UPy-10. In creep experiment, it was shown that as the level of incorporation of UPy groups in the copolymer doubled, the time scale that

was required to induce the same level of compliance also increased two-fold under the test conditions employed. Since the creep behavior in general is a function of applied stress and time scale, more extensive exploration in terms of creep test conditions and the level of hydrogen bond incorporation will provide more quantitative relationships between the enhancement of secondary bonding and the creep behavior. Melt rheological analysis also showed interesting properties and confirmed that the extent of intermolecular non-covalent bonding largely dictated the polymer physical properties. Storage modulus master curves indicated that with increasing UPy content, the plateau modulus was significantly broadened and increased. In complex viscosity master curves, it was observed that increasing UPy content increased the complex viscosity and shear thinning occurred at lower frequencies. These changes in physical properties were attributed to physical crosslinks induced as a result of the multiple hydrogen bonding sites pendant to the polymer backbone. In general, the dimeric carboxylic acid hydrogen bond containing copolymer (MAA-11) behaved similarly to UPy-1, which indicated a relatively weaker hydrogen bonding capability of the carboxylic acid.

6.6   Acknowledgements

Chapter 7   Synthesis and Characterization of Poly(methyl methacrylate) via Living Anionic Polymerization Using tBDMSPrLi

7.1   Abstract

Living anionic polymerization was used to synthesize a series of well-defined poly(methyl methacrylate)s bearing one, two, or three terminal hydroxyl groups at the same polymer chain end. The protected functionalized initiator tBDMSPrLi was used in conjunction with a functional diphenylethylene derivative to yield several different architectures. Good control over the reaction was observed and narrow molar mass distributions were obtained. Confirmation of the polymer structure was obtained using ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. The protecting groups were readily removed under mildly acidic conditions.

7.2   Introduction

Living anionic polymerization provides the unique opportunity for well-defined introduction of functionality at both chain ends through either the initiation or termination step. The persistence of the reactive center throughout the polymerization renders these macromolecules ideal for chain end functionalization reactions, due to the ability to quantitatively endcap the living polymer terminus. [425]   Functionality is generally introduced at the polymer chain end through electrophilic termination to place the desired functionality at the terminus. In recent years, the capping of the ω-terminus with electrophilic reagents has received renewed interest and has been used to tune polymer

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[425] Hsieh, H. L. and R. P. Quirk "*Anionic Polymerization: Principles and Practical Applications*"; Marcel Dekker: New York, 1996.

physical properties through the introduction of a small molecule endcapper.[426]   One of

the most well-studied electrophilic endcapping reagents is ethylene oxide, which

incorporates a hydroxyl group at the polymer chain end.   Quirk et al. reported the

endcapping of poly(styryllithium) oligomers with an excess of ethylene oxide.[427]   Other

researchers have used this method to introduce a well-defined hydroxyl group at the ω-

chain end.[428]   Other functionalities were introduced at the ω-chain end through various

reactions with the living anionic terminus, including epoxides,[429] succinic anhydride,[430]

chloromethylphenyl groups,[431] halogens,[432] saccharides,[433] and amines.[434]

[426] Yamauchi, 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,* 8599-8604.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, X., 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.

[427] Quirk, 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.

[428] Ji, H., S. Nobuyuki, W. K. Nonidez and J. W. Mays "Characterization of hydroxyl-end-capped polybutadiene and polystyrene produced by anionic polymerization technique via TLC/MALDI TOF mass spectrometry." *Polymer* **2002,** *43,* 7119-7123.Hudelson, C. L., K. Yamauchi and T. E. Long "Unique combinations of macromolecular topology and functionality." *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2002,** *43,* 485-486.Elkins, C. L., K. Yamauchi and T. E. Long "Synthesis and characterization of self-complementary multiple hydrogen bonding poly(isoprene) star polymers." *Polym. Prepr.* **2003,** *44,* 576-577.Yamauchi, 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,* 8599-8604.Yamauchi, K., J. R. Lizotte and T. E. Long "Synthesis and Characterization of Novel Complementary Multiple-Hydrogen Bonded (CMHB) Macromolecules via a Michael Addition." *Macromolecules* **2002,** *35,* 8745-8750.Yamauchi, K. and T. E. Long "Synthesis and characterization of telechelic multiple hydrogen-bonded polymers via living anionic polymerization." *Polym. Mater. Sci. Eng.* **2001,** *85,* 465-466.Yamauchi, K. and T. E. Long "Synthesis and characterization of telechelic multiple hydrogen bonded (MHB) macromolecules via living anionic polymerization." *Polym. Prepr.* **2002,** *43,* 698-699.Yamauchi, K. and T. E. Long "Synthesis and characterization of novel multiple-hydrogen bonded macromolecules via a Michael addition." *Polym. Prepr.* **2002,** *43,* 337-338.

[429] Quirk, R. P. and Q. Zhuo "Anionic Synthesis of Epoxide-Functionalized Macromonomers by Reaction of Epichlorohydrin with Polymeric Organolithium Compounds." *Macromolecules* **1997,** *30,* 1531-1539.

[430] Cernohous, J. J., C. W. Macosko and T. R. Hoye "Anionic Synthesis of Polymers Functionalized with a Terminal Anhydride Group." Ibid., 5213-5219.

[431] Hirao, A. and M. Hayashi "Synthesis of Well-Defined Functionalized Polystyrenes with a Definite Number of Chloromethylphenyl Groups at Chains Ends or in Chains by Means of Anionic Living Polymerization in Conjunction with Functional Group Transformation." Ibid. **1999,** *32,* 6450-6460.

An alternative method to synthesize end-functionalized polymer chains is through the use of protected functionalized alkyllithium initiators, which provide quantitative chain end functionalization, while electrophilic termination often does not. It is generally necessary to use a protecting group in the initiator because most functionalities of interest, such as hydroxyl, carboxyl, or amino, are not stable in the presence of organolithium reagents.[435] A variety of functionalities have been protected and used to initiate living anionic polymerizations of various monomers. Protected hydroxyl initiators have been used to initiate the polymerization of polyisoprene [436],

[432] Hirao, A., M. Tohoyama and S. Nakahama "Synthesis of End-Functionalized Polymers by Means of Living Anionic Polymerization. 8. Reactions of Living Anionic Polymers with alpha,omega-Dihaloalkanes." Ibid. **1997**, *30*, 3484-3489.

[433] Hayashi, M., S. Loykulnant, 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." Ibid. **1998**, *31*, 2057-2063.

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polybutadiene[437], alkyl methacrylates[438], ethylene[439], and styrene[440], and poly(1,3-cyclohexadiene)[441]. Protected amine initiators have been used to initiate the polymerization of dienes[442], ethylene oxide[443], styrene[444], and poly(dimethylsiloxane).[445]

Anionic polymerization of methacrylic monomers was not possible until 1,1-diphenylethylene was used to reduce the reactivity of the alkyllithium initiator.[446] Because DPE does not homopolymerize, it was frequently utilized as an endcapping

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reagent or as a co-initiator, as in the case of methacrylate polymerizations.[447]   Star-shaped polymers were synthesized using functionalized diphenylethylene derivatives. After deprotection of the functional groups, mikto-arm star polymers were synthesized using the functional groups.[448] The living anionic polymerization of alkyl methacrylates was controlled using a variety of different diphenylethylene derivatives including 1-[4-{4-methylene-5-hexenyl}   -phenyl]   -1-phenylethylene,[449]   glucose   functionalized derivatives,[450] and 1,1-bis(4-*tert*-butyldimethylsilyloxyphenyl)ethylene.[451]

In the current work, the use of functionalized initiation and protected functionalized diphenylethylene derivatives was explored in the polymerization of methyl methacrylate. The use of the functionalized initiator tBDMSPrLi with a novel aliphatic diol-containing diphenylethylene   derivative   (1,1-bis-4,4'-(2-(*tert*-butyldimethylsilyloxy)ethoxy)phenylethylene BTOPE) provides the opportunity to synthesize macromolecules containing one, two, or three hydroxyl groups at one chain terminus.   BTOPE has an advantage over the protected bisphenol derivative discussed

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above, in that it is more suitable as a comonomer for polycondensation reactions in polyester synthesis. Additionally, the increased nucleophilicity of the aliphatic diol renders the macromolecules suitable for lactide ring-opening polymerization and solution polymerization of polyesters.

7.3 Experimental

7.3.1 Materials

4,4'-dihydroxybenzophenone (TCI America, 98%), ethylene carbonate (Aldrich, 97%), potassium carbonate (EM Science, 99%), *tert*-butylsilyl chloride (Aldrich, 98%), potassium *tert*-butoxide (TCI America, 98%), methyltriphenylphosphonium bromide (TCI America, 99%), pyridine (Aldrich, anhydrous), *sec*-butyllithium (FMC Lithium Division, 1.78 M), and 3-(*t*-butyldimethylsilyloxy)-1-propyllithium (tBDMSPrLi, FMC Corporation Lithium Division. 0.8 M in cyclohexane) were used as received. Methyl methacrylate (MMA, Aldrich, 99%) was stirred over CaH_2 (Aldrich, 95%) overnight and vacuum distilled (0.10 mm Hg). MMA was then titrated with triethylaluminum (Aldrich, 1.6 M) and vacuum distilled (0.10 mm Hg).[452] Lithium chloride (Aldrich, 98%) was dried under vacuum at 100 °C to remove residual moisture. Tetrahydrofuran (THF, Burdick and Jackson, HPLC) was stirred over sodium and benzophenone (Aldrich, 99%) and distilled under nitrogen immediately prior to use.

Allen, R. D., T. E. Long and J. E. McGrath "Preparation of High Purity, Anionic Polymerization Grade Alkyl Methacrylate Monomers." *Polym. Bull.* **1986**, *15*, 127-134. Long, T. E., C. D. DePorter, N. Patel, D. W. Dwight, G. L. Wilkes and J. E. McGrath "Poly(Alkyl Methacrylate-Methacrylate Carboxylate) Ion-Containing Block Copolymers." *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*, 214-216.

7.3.2 Characterization

^{1}H NMR spectra were determined in CDCl$_3$ at 400 MHz with a Varian Unity Spectrometer. Glass transition and melting temperatures were determined using a Perkin-Elmer Pyris 1 cryogenic DSC at a heating rate of 10 °C/min under nitrogen. Glass transition temperatures are reported as the transition mid point during the second heat. Molar masses were determined using size exclusion chromatography (SEC) with a Waters Alliance SEC system equipped with a Wyatt miniDAWN multiple angle laser light scattering detector.

7.3.3 Synthesis of 4,4'-bis(2-hydroxyethoxy)benzophenone

4,4'-Dihydroxybenzophenone (30.0 g, 141 mmol) and ethylene carbonate (37.3 g, 424 mmol) were dissolved in dimethylsulfoxide (Aldrich, anhydrous) and added to a 500 mL round-bottomed flask fitted with a reflux condenser and a magnetic stir bar. After 1 hour, potassium carbonate (46.9 g, 339 mmol) was added and the temperature was increased to 120 °C. The reaction was allowed to proceed for 8 hours and was then quenched in 500 mL 3M NaOH solution. The product was filtered and washed with dilute hydrochloric acid and then dried under vacuum.

7.3.4 Synthesis of 4,4'-bis-(2-*tert*-butyldimethylsilyloxy)ethoxy)benzophenone

4,4'-bis(2-hydroxyethoxy)benzophenone (13.0 g, 43.4 mmol) was dissolved in 150 mL anhydrous pyridine and the mixture was cooled to 0 °C using an ice bath. *tert*-Butyldimethylsilyl chloride (15 g, 100 mmol) was dissolved in 80 mL anhydrous pyridine and added to the reaction using a cannula. The reaction was allowed to proceed for 3 hours while warming to room temperature. The reaction was precipitated into a

dilute acid water/ice mixture. The product was isolated using vacuum filtration and dissolved in dichloromethane. The dichloromethane solution was washed with copiously with water to remove residual acid. The product was then isolated by removing the solvent in vacuo and dried under vacuum overnight.

7.3.5 Synthesis of 1,1'-bis-4-(2-(*tert*-butyldimethylsilyloxy)ethoxy)phenylethylene (BTOPE)

The ylide was generated from the reaction of potassium tert-butoxide (4 g, 36 mmol) and methyltriphenylphosphonium bromide (10 g, 28 mmol) in 20 mL THF cooled to 0 °C. 4,4'-bis-(2-*tert*-butyldimethylsilyloxy)ethoxy)benzophenone (10 g, 19 mmol) was dissolved in 200 mL THF and cooled to 0 °C. The ylide was added using a cannula to the 4,4'-bis-(2-*tert*-butyldimethylsilyloxy)ethoxy)benzophenone solution. The reaction was allowed to proceed for 3 hours and was quenched into a dilute acid/ice mixture. BTOPE was purified using flash silica column chromatography with dichloromethane as the mobile phase.

7.3.6 Synthesis of Poly(methyl methacrylate) Using BTOPE and sBuLi

A 100 mL round-bottomed flask equipped with a magnetic stir bar was flame-dried under a nitrogen purge. 50 mL freshly distilled THF was added to the reaction flask. A solution of known concentration was made from BTOPE and freshly distilled THF. The BTOPE solution was added to the reaction flask using a syringe. The reaction flask was then cooled to -78 °C and titrated with s-butyllithium until a persistent deep red color was observed. The calculated amount of s-butyllithium (0.63 mL, 1.25 mmol) was then added to the reaction flask. Methyl methacrylate (MMA, 5 g, 5.34 mL) was then

added dropwise to the reaction flask. The polymerization was allowed to proceed for 10 minutes and was terminated via the addition of degassed methanol. The solution was then precipitated into 9:1 methanol: water followed by precipitation into cyclohexane to remove residual BTOPE and dried under vacuum overnight.

7.3.7 Synthesis of Poly(methyl methacrylate) Using BTOPE and tBDMSPrLi

A 100 mL round-bottomed flask equipped with a magnetic stir bar was flame-dried under a nitrogen purge. A solution of known concentration was made from lithium chloride and freshly distilled THF. A solution of known concentration was also made from BTOPE and freshly distilled THF. Lithium chloride solution (0.042 g, 1 mmol) and BTOPE solution (0.53 g, 1 mmol) were added to the reaction flask using a syringe. THF was then added using a cannula until a total reaction volume of 50 mL was reached. The reaction flask was then cooled to 0 °C using an ice bath. The solution was then titrated with tBDMSPrLi until a persistent deep red color was observed, followed by the addition of the calculated amount of initiator (0.625 mL, 0.5 mmol). The reaction flask was then cooled to -78 °C and methyl methacrylate (MMA, 5 g, 5.34 mL) was then added dropwise. The polymerization was allowed to proceed for 10 minutes and was terminated via the addition of degassed methanol. The solution was then precipitated into 9:1 methanol: water followed by precipitation into cyclohexane to remove residual BTOPE and dried under vacuum overnight. This procedure was also used to synthesize PMMA using DPE and tBDMSPrLi.

7.3.8 Deprotection of PMMA to Yield Hydroxyl Functionality

BTOPE PMMA (5 g) was dissolved in THF (50 mL) and placed in a 100 mL round-bottomed flask equipped with a stir bar. To this was added 2 mL concentrated HCl and the reaction temperature was raised to 50 °C. The reaction was allowed to proceed overnight. The hydrolyzed polymer was precipitated into 9:1 methanol:water and dried under vacuum.

7.4   Results and Discussion

7.4.1   Suitability of tBDMSPrLi for MMA polymerization

Initial attempts to synthesize PMMA using the protected functional initiator tDBMSPrLi were largely unsuccessful. Conventional living anionic polymerization methodologies for methyl methacrylate were employed, including cryogenic reaction temperature (-78 °C), alkyllithium/diphenyl ethylene hindered initiator, and dropwise monomer addition. However, polymers with broad molar mass distributions were obtained under these reaction conditions, as shown in Table 7-1.

Table 7-1. Synthesis of PMMA using tBDMSPrLi without LiCl.

M_n (target)	M_n (SEC)[a]	M_w/M_n[a]	Yield (%)
5000	47100	2.78	29
10000	51000	2.93	12
20000	83900	3.45	17
5000	55700	2.04	22
5000	50700	2.14	17
5000	60700	1.66	9

[a]SEC conditions: 40 °C in THF with MALLS detector

Quirk et al. reported the use of lithium chloride as an additive to control the polymerization of methyl methacrylate using tBDMSPrLi and was able to achieve narrow molar mass distributions.[453] When lithium chloride was utilized as an additive in the living anionic polymerization of methyl methacrylate, targeted molar masses agreed well with both SEC and NMR molar masses, and narrow molar mass distributions were observed, Table 7-2. Figure 7-1 shows a narrow molar mass distribution monomodal SEC trace for PMMA synthesized using tBDMSPrLi as initiator. The structure of the PMMA was confirmed using ^{1}H NMR spectroscopy, and a representative spectrum is shown in Figure 7-2. Resonances at 0 ppm (a) and 0.9 ppm (b) correspond to the methyl and *tert*-butyl groups on the silicon of the protecting group, respectively. Resonances between 0.9 ppm and 2 ppm (e and f) were assigned to the aliphatic backbone protons of the polymer main chain. The resonance at 3.6 ppm (c) was attributed to the methyl group attached to the ester, and it was from comparison of this peak with the endgroup resonance at 0 ppm (a) that the number average molar masses were calculated.

[453] Quirk, R. P. and R. S. Porzio "The Anionic Synthesis of Functionalized Linear and Star-branced Poly(methyl methacrylates) Using Protected Hydroxy-Functionalized Alkyllithium Initiators." *Polym. Prepr.* **1997**, *38*, 463-464.

Table 7-2. Synthesis of PMMA using tBDMSPrLi with LiCl.

M_n (target)	M_n (SEC)[a]	M_n (NMR)[b]	M_w/M_n[a]	Yield (%)
10000	10500	10100	1.06	97
10000	9000	10600	1.06	87
10000	9000	8100	1.07	89

[a]SEC conditions: 40 °C in THF with MALLS detector
[b]NMR conditions: Varian 400 MHz at 25 °C in CDCl$_3$

$$M_n = 25700$$
$$M_w/M_n = 1.04$$
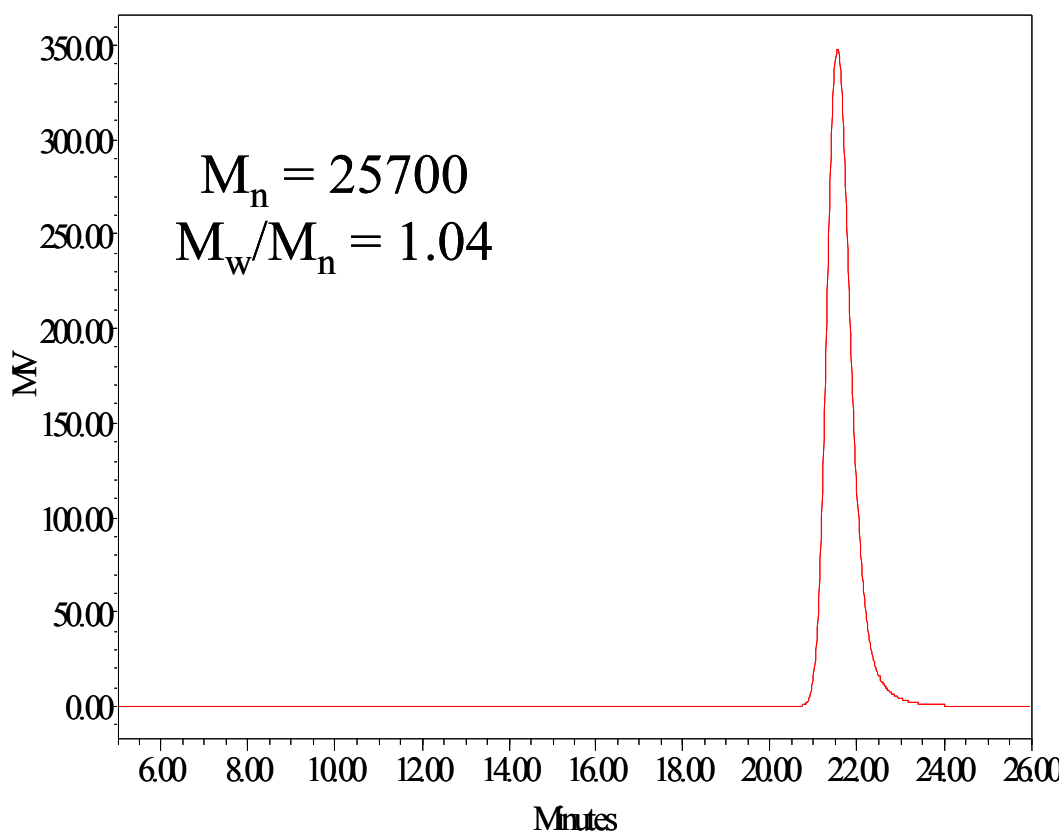
Figure 7-1. SEC trace showing narrow molar mass distribution monomodal tBDMS-PMMA.

Figure 7-2. ^{1}H NMR spectrum of representative tBDMS-PMMA.
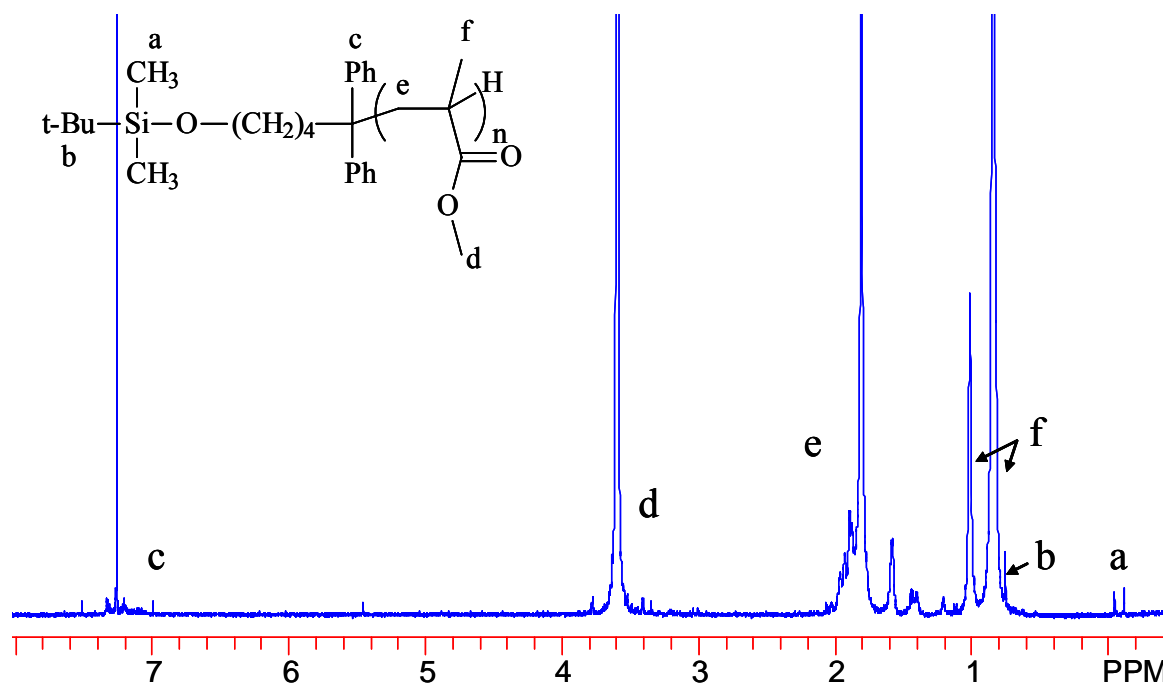
^{29}Si NMR spectroscopy was also used to characterize the tBDMS-PMMA and a representative spectrum is shown in Figure 7-3. Trialkyl substituted silicons were anticipated to have shifts between +10 and +25 ppm, however, the presence of two distinct silicon peaks was not anticipated for this polymer.[454] Because both silicon resonances were found in the trialkyl substituted region, loss of alkyl substituents on the silicon was eliminated as a possible side reaction. Ultimately, the presence of two resonances was attributed to the interaction of the silyl ether with the nearest carbonyl groups present on the polymer backbone, resulting in different chemical environments. ^{13}C NMR spectroscopy was also used to probe the possibility of a side reaction that would result in two silicon NMR resonances. While no evidence was found to explain the silicon NMR spectroscopy, evidence for a side reaction was found. This side reaction is shown in Scheme 7-1. A backbiting reaction is shown, in which the resonance form of the propagating anion attacks the silyl ether protecting group, forming an oxygen centered anion that is non-reactive toward polymerization of methyl methacrylate and a chain end double bond. ^{1}H NMR was not useful in detecting this double bond, due to the lack of hydrogens attached to the olefin. However, ^{13}C NMR spectroscopy was used to detect the presence of a small amount of olefin, as shown in Figure 7-5b. All resonances were well-assigned in the ^{13}C spectrum (Figure 7-5a) and the presence of a small amount (> 5%) of backbiting was confirmed. Although a small amount of backbiting was found to occur, the polymerization was well-controlled and well-defined polymers were obtained and no deleterious effects from this side reaction were found.

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[454] Derouet, D., S. Forgeard and J.-C. Brosse "Synthesis of alkoxysilyl-terminated polyisoprenes by means of "living" anionic polymerization. Part 2. Synthesis of trialkoxysilyl-terminated 1,4-polyisoprenes by reaction of polyisoprenyllithium with various functional trialkoxysilanes selcted as end-capping reagents." *Macromol. Chem. Phys.* **1999**, *200*, 10-24.
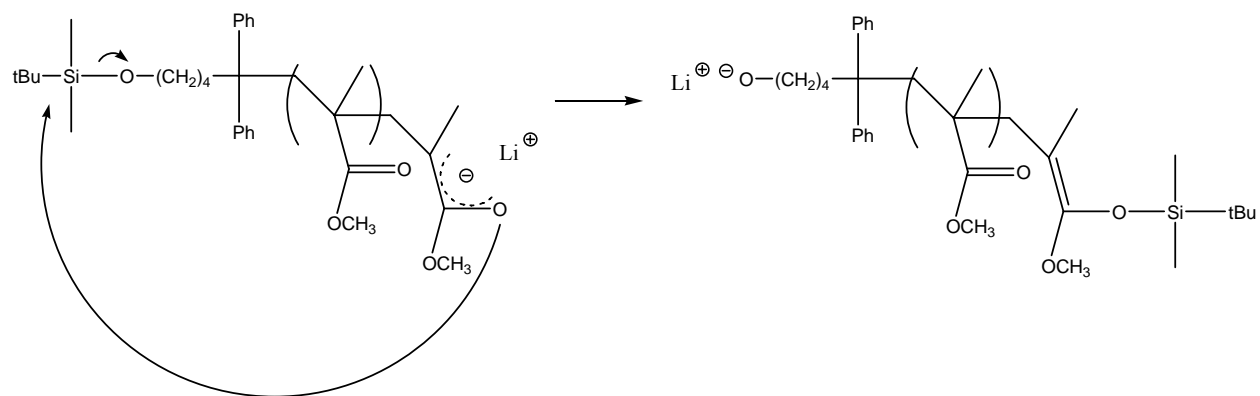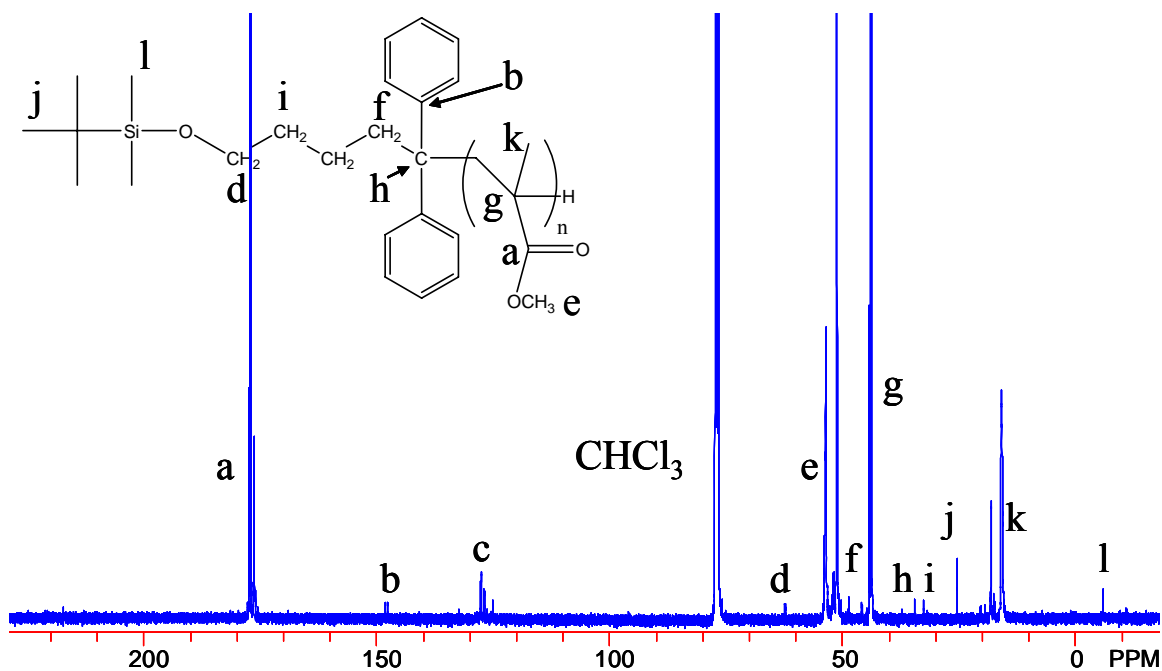
Figure 7-3. ^{29}Si NMR of tBDMS-PMMA.

R$_3$-*Si*-OR
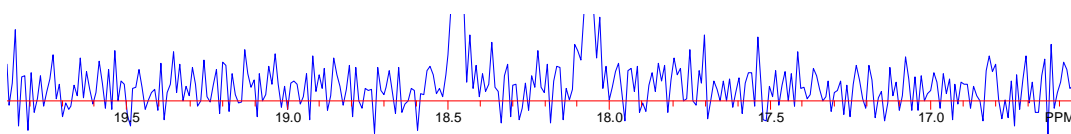
Scheme 7-1. Possible side reaction in PMMA synthesis usng tBDMSPrLi.
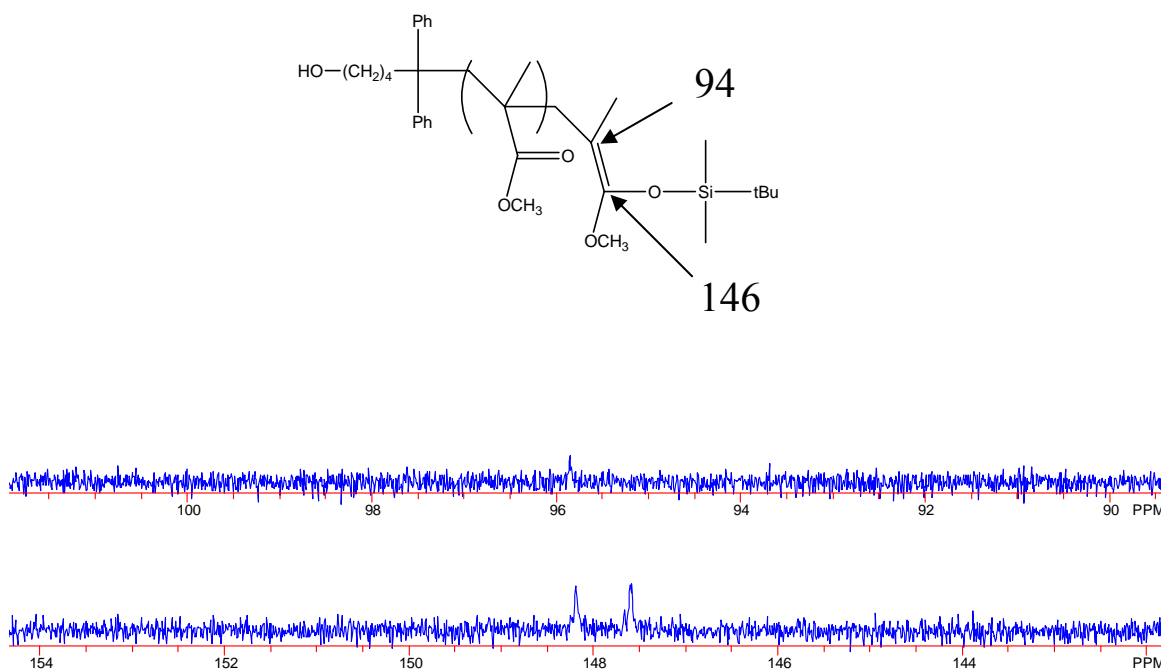
**Figure 7-4.** Quantitative ^{13}C NMR spectrum investigating presence of backbiting side reactions.

a)

b)

7.4.2 Synthesis of BTOPE

The use of tBDMSPrLi in the polymerization of methyl methacrylate yielded macromolecules with a single protected hydroxyl group at the polymer chain end. While this type of macromolecule has possible use as an endcapper in polycondensation reactions, it was desired to synthesize macromolecules with two or more functional groups at the same polymer chain end. To this end, a protected functionalized diphenylethylene derivative was synthesized bearing two protected aliphatic alcohols. 1,1'-bis-4-(2-(*tert*-butyldimethylsilyloxy)ethoxy)phenylethylene (BTOPE) was synthesized in a three step reaction process, summarized in Scheme 7-2. In the first step of the reaction, 4,4'-dihydroxybenzophenone was converted to the bisphenoxide using potassium carbonate and reaction with ethylene carbonate to yield 4,4'-bis)2-hydroxyethoxy)benzophenone. In the second step of the reaction, the aliphatic diol was protected using standard silyl chloride protection chemistry and reaction with *tert*-butyldimethylsilyl chloride proceeded in a quantitative fashion. The ^{1}H NMR spectrum of this product is shown in Figure 7-6. New resonances associated with the protecting group at 0.0 ppm and 0.9 ppm, corresponding to the methyl and tert-butyl groups on the silicon, respectively, confirmed the quantitative nature of the protecting reaction.

Scheme 7-2. Synthesis of BTOPE from 4,4'-dihydroxybenzophenone.
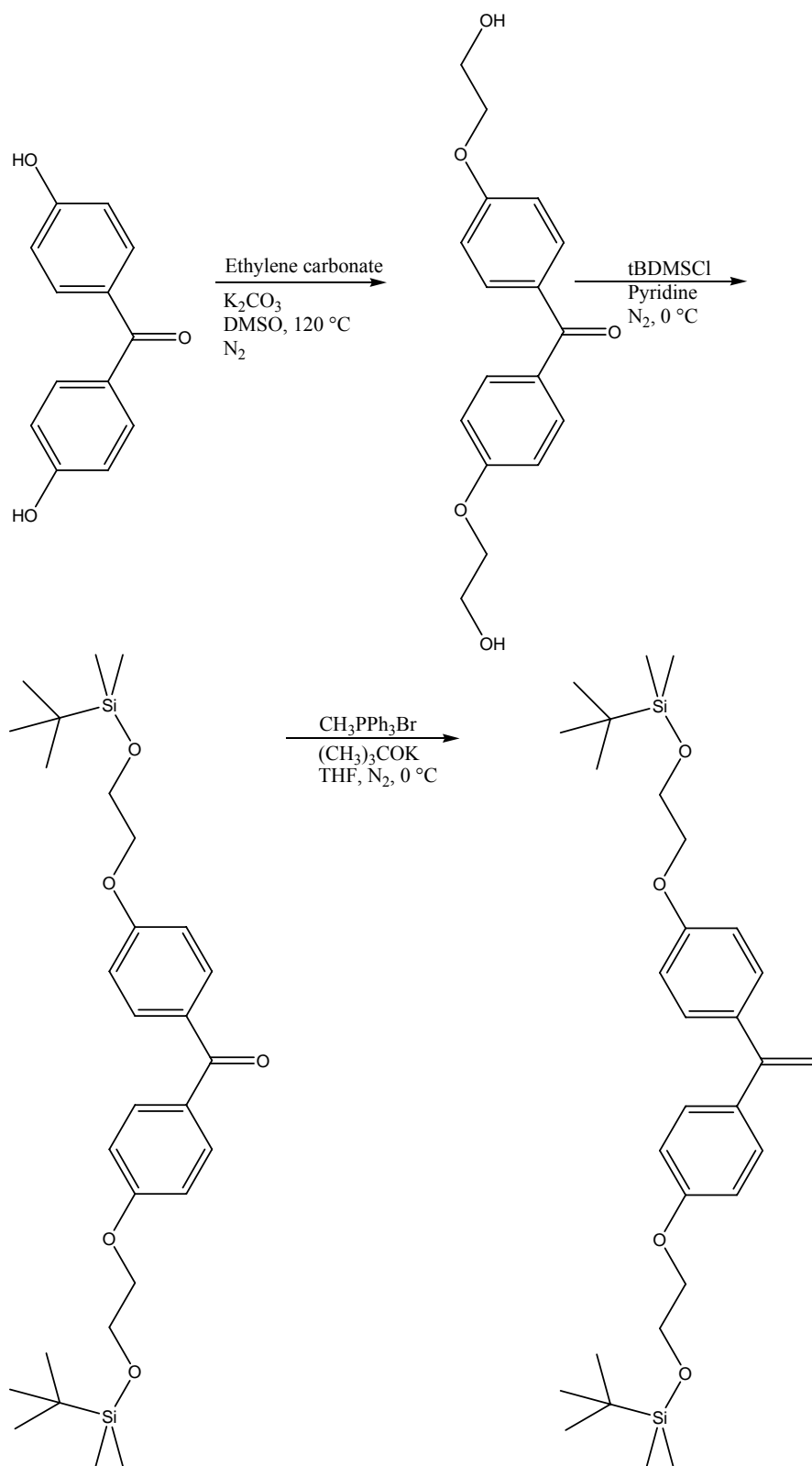
Figure 7-5. ^{1}H NMR spectrum of the tert-butyldimethylsilyl protected 4,4'-bis(2-hydroxyethoxy)benzophenone.
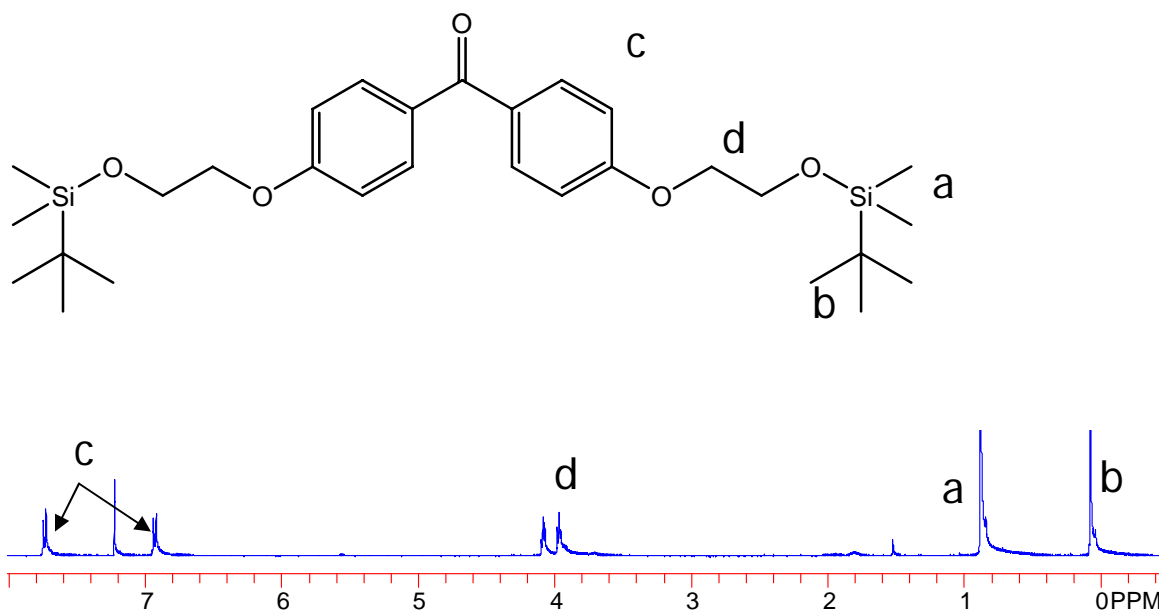
The final step of the reaction involved a Wittig reaction to convert the benzophenone group to a substituted diphenylethylene. The ylide was generated in situ from the reaction of methyl triphenylphosphonium bromide and potassium *t*-butoxide. The conversion of the benzophenone to the diphenylethylene was monitored using the characteristic benzylic olefin resonance at 5.2 ppm in the product, shown in Figure 7-7. The Wittig reaction was also monitored using ^{13}C NMR spectroscopy and the disappearance of the carbonyl carbon resonance at 194.6 associated with the benzophenone was observed upon completion of the reaction, Figure 7-8. The final reaction product was purified using flash column chromatography with dichloromethane as the mobile phase, followed by drying in the vacuum oven overnight immediately prior to use in living anionic polymerization. The use of BTOPE in conjunction with the conventional living anionic initiator *s*-butyllithium affords macromolecules with two protected hydroxyl functionalities, while the use of tBDMSPrLi affords macromolecules with three protected hydroxyl functionalities.

**Figure 7-6.** ^{1}H NMR spectra showing conversion from benzophenone to diphenylethylene.
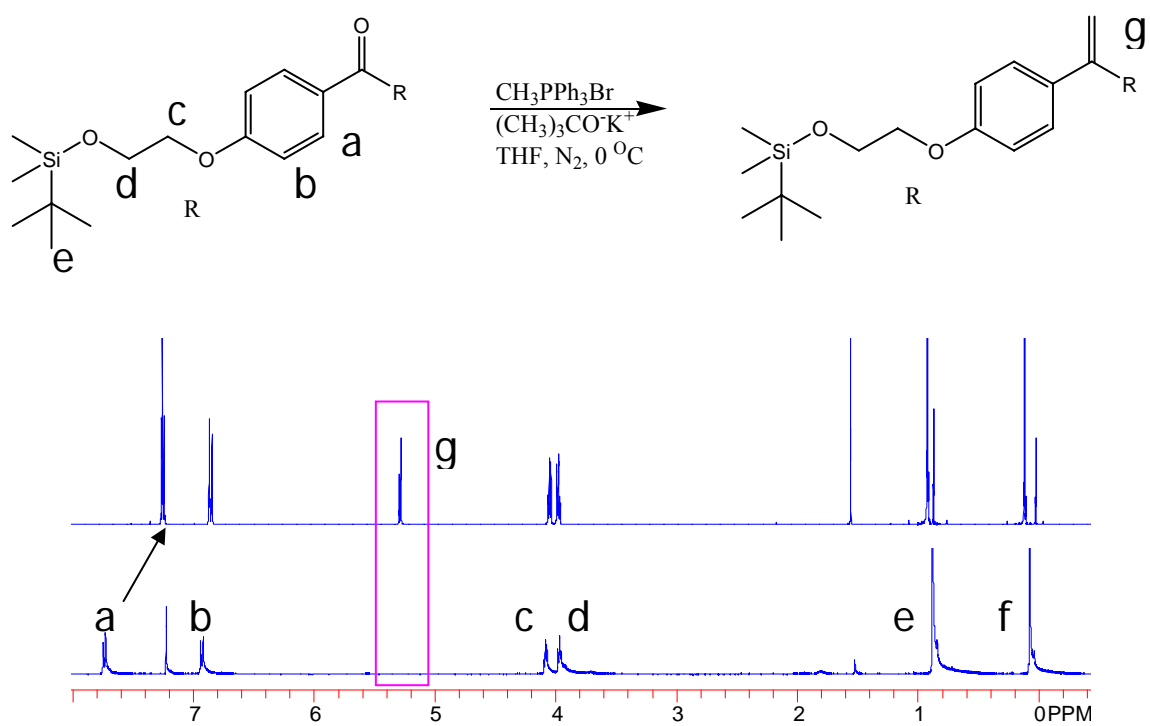
Figure 7-7. ^{13}C NMR spectrum following conversion of benzophenone to diphenylethylene via a Wittig reaction.
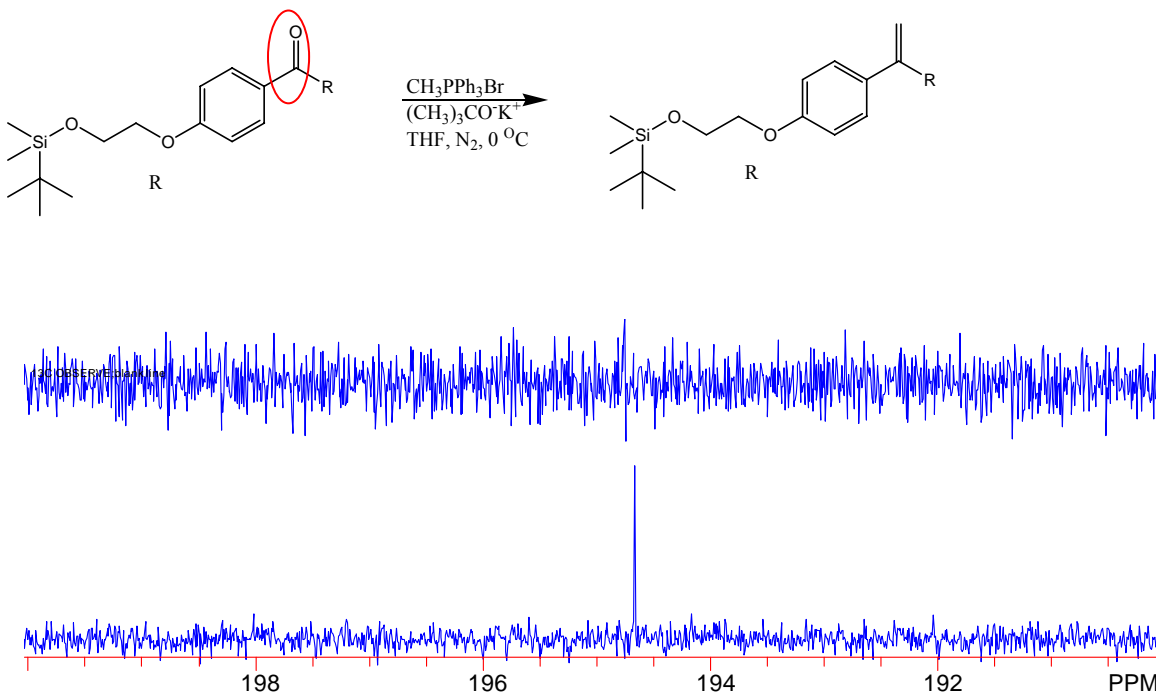
7.4.3 Polymer Synthesis Using BTOPE

Both s-butyllithium and tBDMSPrLi were used to initiate the living anionic polymerization of MMA using the functionalized diphenylethylene derivative BTOPE. When s-butyllithium was used, no lithium chloride was necessary to control the polymerization, while when tBDMSPrLi was used, lithium chloride was necessary. The reaction scheme for tBDMSPrLi initiated polymerization of MMA using BTOPE is depicted in Scheme 7-3. Well-defined polymers with narrow molar mass distributions were synthesized using both initiation systems, Table 7-3. Molar mass control remains elusive for these systems, with actual molar masses nearly triple targeted molar masses. However, the structure of the polymers was confirmed using ^{1}H NMR spectroscopy, as described above, with contributing resonances from both the initiator fragment and the BTOPE protecting groups. SEC molar masses agree well with those calculated using ^{1}H NMR spectroscopy based on the same resonaces as described above. Deprotection of the series of polymers was quantitatively achieved using mildly acidic conditions, and the series of well-defined mono-, di-, and tri-functional chain end hydroxyl functional PMMA's is useful in A_2/B_3 type polymerizations.

Scheme 7-3. Synthesis of PMMA using tBDMSPrLi and BTOPE.
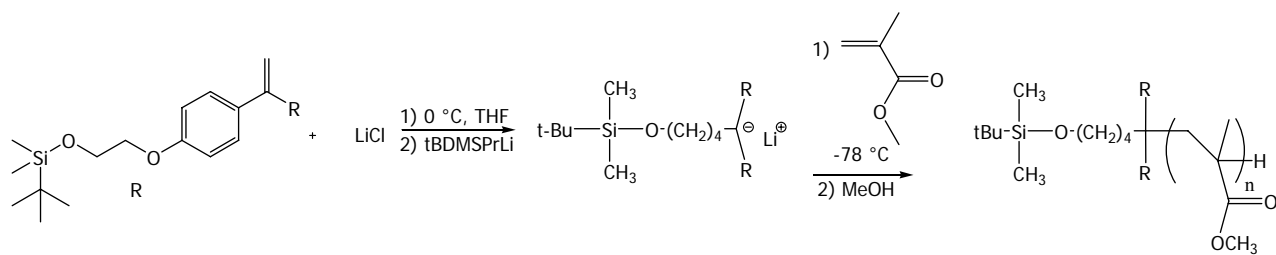
Table 7-3. Well-defined poly(methyl methacrylate) synthesized using BTOPE.

Initiator	M_n (Target)	M_n (NMR)[a]	Mn (SEC)[b]	M_w/M_n[b]
sBuLi	5000	15000	18800	1.01
sBuLi	10000	30000	34900	1.03
tBDMSPrLi	5000	13900	19400	1.22

[a]NMR conditions: Varian 400 MHz at 25 °C in CDCl$_3$

[b]SEC conditions: 40 °C in THF with MALLS detector

7.5 Conclusions

The polymerization of MMA was controlled using the protected functional initiator tBDMSPrLi with the addition of lithium chloride. Targeted molar masses were achieved and narrow molar mass distributions were observed. In an effort to synthesize well-defined A_2/B_3 type macromonomers, the functionalized diphenylethylene derivative BTOPE was synthesized through a three-step reaction process in good yields. Subsequently, the polymerization of MMA was controlled using both s-BuLi and tBDMSPrLi with BTOPE to yield di- and tri-functional macromonomers. Molar mass control remains elusive, however, narrow molar mass distributions were observed for the series. Acid catalyzed deprotection yielded a well-defined series of PMMA's with one, two, or three functional groups at the same polymer terminus, which are useful in A_2/B_3 polymerization strategies.

7.6 Acknowledgements

Chapter 8   Synthesis and Characterization of Hydroxyl Terminated Polyisobutylene

8.1   Abstract

Telechelic hydroxyl functionalized polyisobutylenes were synthesized using cationic polymerization and subsequent organic group transformation. Dicumyl chloride was synthesized as a difunctional cationic initiator and was utilized to synthesize both chloro- and allyl-terminated polyisobutylene. Well-controlled polmerizations were observed and narrow molar mass distributions were obtained. The allyl-terminated polyisobutylenes were subjected to hydroboration-oxidation chemistry to yield telechelic hydroxyl functionalized polyisobutylenes, and the primary hydroxyl functionality is effective in many further functionalization reactions.

8.2   Introduction

Living polymerizations are widely used to achieve well-defined macromolecular architectures, including block copolymers and chain end functionalized polymers. Since living anionic polymerization was discovered in the 1950's, it was extensively studied and a large body of literature exists detailing its development. However, the study of living cationic polymerization has lagged behind that of living anionic polymerization due to the inherent instability of propagating carbocations and their propensity to undergo chain transfer or termination reactions. Certain monomers, such as isobutylene, are only polymerizable using cationic polymerization. Polyisobutylene has several attractive properties, such as low T_g, thermal, oxidative, and hydrolytic stability, and high barrier

properties, that make it both an academically and industrially important polymer.[455] Higashimura et al. reported relatively long-lived carbocations in the late 1970's using I_2 as an initiator or coinitiator in the polymerization of p-methoxystyrene and isobutyl vinyl ether in non-polar solvents.[456] Kennedy et al. first reported the "quasi-living" polymerization of isobutylene and α-methylstyrene in 1980 under monomer starved conditions.[457] A linear increase in number average molar mass was observed with conversion and was attributed to the reversibility of chain transfer and termination events under the experimental conditions, which allowed for reiinitiation of growing polymer chains. However, the first truly living cationic polymerization was not reported until 1984, when Higashimura et al. described the cationic polymerization of vinyl ethers in non-polar solvents using hydrogen iodide/iodine.[458] The addition of hydrogen iodide facilitated fast initiation, and narrow molar mass distributions were observed. They later reported that vinyl ethers were polymerized under more conventional conditions, using an organoaluminum halide coinitiator, when a Lewis base or electron donor was added to the polymerization.[459]

[455] Kresge, E. N., R. H. Schatz and H.-C. Wang "Isobutylene polymers." *Encyclopedia of Polymer Science and Engineering*; 2nd ed.; Wiley-Interscience: New York, 1987; pp 423-448.Vairon, J.-P. and N. Spassky "Industrial cationic polymerizations: an overview". *Cationic Polymerization. Mechanism, Synthesis, and Applications*; Marcel Dekker: New York, 1996; pp 683-750.

[456] Higashimura, T. and O. Kishiro "Possible formation of living polymers of p-methoxystyrene by iodine." *Polym. J.* **1977**, *9*, 87-93.Ohtori, T., Y. Hirokawa and T. Higashimura "Studies on the nature of propagating species in cationic polymerization of isobutyl vinyl ether by iodine." *Polym. J.* **1979**, *11*, 471.

[457] Faust, R., A. Fehervari and J. P. Kennedy "Quasiliving carbocationic polymerization. II. The discovery: the alpha-methylstyrene system." *J. Macromol. Sci., Chem.* **1982**, *A18*, 1209-1228.

[458] Miyamoto, M., M. Sawamoto and T. Higashimura "Living polymerization of isobutyl vinyl ether with hydrogen iodide/iodine initiating system." *Macromolecules* **1984**, *17*, 265-268.

[459] Aoshima, S. and T. Higashimura "Living cationic polymerization of vinyl monomers by organoaluminum halides. 1. Ethylaluminum dichloride/ester initiating systems for living polymerization of vinyl ethers." *Polym. Bull.* **1986**, *15*, 417-423.

Kennedy et al. first discovered the living cationic polymerization of isobutylene initiated with tert-alkyl or tert-aryl esters and ethers in conjunction with BCl_3 or $TiCl_4$.[460] The living characteristics were attributed to rapid initiation, suppression of chain transfer to monomer, and reversible termination, as shown in Scheme 8-1. This equilibrium between dormant and active chains allowed for control and the living nature of carbocationic polymerization was attributed to this equilibrium.[461] The cationic polymerization of isobutylene was also controlled using electron donors, such as dimethyl sulfoxide and dimethylacetamide, with a variety of tert-alkyl (or aryl) chloride, ether, or alcohol/Lewis acid systems, with narrow molar mass distribution polymers.[462] Kennedy et al. also proposed a detailed mechanism for the living cationic polymerization of isobutylene initiated with tert-alkyl (or aryl) ester or ethers/BCl_3 or $TiCl_4$ complexes and proposed that the function of the electron donor was to stabilize the active carbocation.[463] The exact mechanism and kinetics of various carbocationic polymerizations remain under debate, but the utility of carbocation polymerizations in synthesizing well-defined macromolecules is well-understood.[464]

[460] Faust, R. and J. P. Kennedy "Living carbocationic polymerization. IV. Living polymerization of isobutylene." *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 1847-1869.Mishra, M. and J. P. Kennedy "Living carbocationic polymerization. VII. Living polymerization of isobutylene by tertiary alkyl (or aryl) methyl ether/boron trichloride complexes." *J. Macromol. Sci., Chem.* **1987**, *A24*, 933-948.

[461] Storey, R. F., B. J. Chisholm and L. B. Brister "Kinetic Study of the Living Cationic Polymerization of Isobutylene Using a Dicumyl Chloride/TiCl4/Pyridine Initiating System." *Macromolecules* **1995**, *28*, 4055-4061.

[462] Kaszas, G., J. E. Puskas, J. P. Kennedy and C. C. Chen "Electron-pair donors in carbocationic polymerization. III. Carbocation stabilization by external electron pair donors in isobutylene polymerization." *J. Macromol. Sci., Chem.* **1989**, *A26*, 1099-1014.

[463] Kaszas, G., J. E. Puskas, C. C. Chen and J. P. Kennedy "Electron pair donors in carbocationic polymerization. 2. Mechanism of living carbocationic polymerization and the role of in-situ or external electron pair donors." *Macromolecules* **1990**, *23*, 3909-3915.

[464] Puskas, J. E., P. Antony, Y. Kwon, C. Paulo, M. Kovar, P. R. Norton, G. Kaszas and V. Altstaedt "Macromolecular Engineering via Carbocationic Polymerization: Branched Structures, Block Copolymers and Nanostructures." *Macromol. Mater. Eng.* **2001**, *286*, 565-582.

Scheme 8-1. Equilibrium between active and dormant chain ends in cationic polymerization.
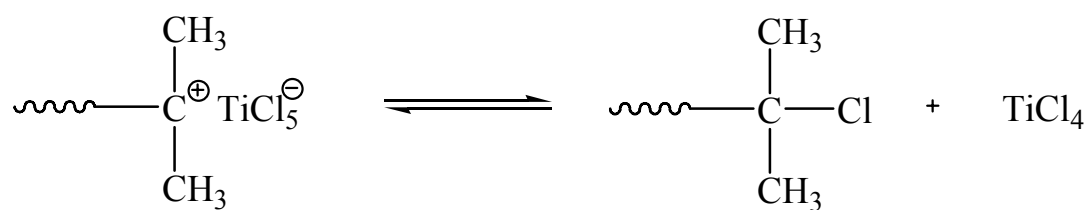
The synthesis of chain-end functionalized polyisobutylenes is of great interest due to the large number of quantitative derivatization possibilities they provide, and hydroxyl terminated polyisobutylenes are of particular interest. Carboxy- and hydroxyl-terminated polyisobutylenes were prepared using oxidative scission of isobutylene-diene copolymers.[465] However, the functionality was generally less than the desired functionality of 2.0. Hydroxyl terminated polyisobutylene was also synthesized using dehydrochlorination of dichloro-terminated polyisobutylene to yield terminal olefins, followed with quantitative hydroboration/oxidation to yield terminal hydroxyl functionality.[466] In our work, we synthesized a range of difunctional polyisobutylenes with chloro- or allyl endgroups.[467] Subsequently, the allyl-terminated polyisobutylenes were transformed into hydroxyl-terminated polymers using hydroboration/oxidation chemistry. The hydroxyl terminated polyisobutylenes are then useful in a variety of applications.

8.3 Experimental

8.3.1 Materials.

α,α,α',α'-tetramethyl-1,4-benzene-dimethanol (Aldrich, 99%), magnesium sulfate, hydrochloric acid, pyridine (Aldrich, anhydrous, 99.8%), TiCl$_4$ (Aldrich, 99.9%),

[465] Baldwin, F. P., G. W. Burton, K. Griesbaum and G. Hanington "Preparation of carboxy-terminated polyisobutylene." *Adv. Chem. Ser.* **1969**, *91*, 448-464.Jones, E. B. and C. S. Marvel "alpha,omega-glycols from isobutylenes and some derived block copolymers." *J. Polym. Sci. A-1* **1964**, *2*, 5313-5318.Stubbs, W. H., C. R. Gore and C. S. Marvel "alpha,omega-glycols from polyisobutylene." *J. Polym. Sci. A-1* **1966**, *4*, 447.Baldwin, F. P., J. V. Fusco and L. E. Gastwirt "Elastomeric prepolymers for adhesives and sealants provide improved strength and versatility." *Adhesives Age* **1967**, *10*, 22-29.Zapp, R. L., G. E. Serniuk and L. S. Minckler "Isocyanate reactions with difunctional polyisobutylenes." *Rubber Chem. and Tech.* **1970**, *43*, 1154-1187.
[466] Ivan, B., J. P. Kennedy and V. S. Chang "New Telechelic Polymers and Sequential Copolymers by Polyfunctional Initiator-Transfer Agents (Inifers). VII. Synthesis and Characterization of alpha, omega-Di(hydroxy)polyisobutylene." *J. Polym. Sci.: Polym. Chem. Ed.* **1980**, *18*, 3177-3191.
[467] Wilczek, L. and J. P. Kennedy "Electrophilic substitution of organosilicon compounds. I. Model studies of allylation tert-chlorine ended polyisobutylenes with allyltrimethylsilane." *Polym. Bull.* **1987**, *17*, 37-43.

allyltrimethylsilane (Aldrich, 99%), 9-BBN (Aldrich, 0.5M solution in THF), and 30% hydrogen peroxide (Aldrich) were used as received. Isobutylene was condensed over anhydrous $CaSO_4$ at -78 °C and distilled under reduced pressure. Dichloromethane was distilled from CaH_2 and stored over molecular sieves. Hexanes were stirred over concentrated H_2SO_4 for 7 days, followed by distillation from sodium immediately prior to use. Tetrahydrofuran was stirred over sodium/benzophenone and distilled immediately prior to use.

8.3.2 Synthesis of Dicumyl Chloride

200 ml of concentrated HCl was cooled to -10 °C using a salt/ice bath. Dicumyl alcohol, or $\alpha,\alpha,\alpha',\alpha'$-tetramethyl-1,4-benzene-dimethanol, (10g, 51.5 mmol) was added to the HCl. Immediately, 300 ml prechilled hexanes was added to the reaction mixture. The reaction was allowed to proceed for 2 hours. Upon completion, the organic layer was washed 3 times with distilled water, then dried using anhydrous magnesium sulfate. The solution was filtered to remove the drying agent and then chilled to -20 °C to crystallize the product. DCC was isolated using vacuum filtration and was vacuum stripped to remove residual solvents. The reaction is shown in Scheme 8-2. Note: This compound is not stable above room temperature.

Scheme 8-2. Synthetic scheme to synthesize dicumyl chloride from dicumyl alcohol.
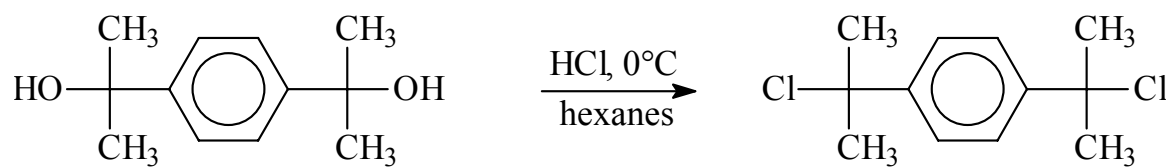
8.3.3 Polymerization of isobutylene

A typical polymerization is described. A 250 ml round-bottom flask containing a stir bar is septum sealed flame-dried under a nitrogen flush. To the reaction flask is added via syringe or cannula in the following order: dichloromethane (50 ml), hexanes (74 ml), DCC (3.5 ml of a 16 wt% solution in dichloromethane, 0.86g, 3.75 mmol), and pyridine (0.91 ml, 0.89g, 11.3 mmol). The reaction flask is then cooled to $-78\ °C$ using a dry ice/isopropanol bath. Positive nitrogen pressure is applied to the flask as it is cooled. Freshly distilled isobutylene (12.5 ml, 7.5g, 134 mmol) is transferred to a $-78\ °C$ graduated cylinder via a cannula and then from the graduated cylinder to the reaction flask via a cannula. $TiCl_4$ (8.22 ml, 14.2 g, 75 mmol) was then added to the reaction flask. Immediately, a yellow color was observed and the reaction became turbid. The polymerization was allowed to proceed for 15 minutes. Allyltrimethylsilane (2.4 ml, 1.71g, 15mmol) was then added to the reaction mixture. The polymerization is described in Scheme 8-3 and the endcapping reaction in Scheme 8-4. The color turned a deeper yellow/brown upon the addition. The reaction was allowed to proceed an additional 20 minutes. The reaction was then terminated using degassed methanol (40 ml). The reaction flask was allowed to warm to room temperature. The hexanes/dichloromethane phase was separated from the methanol phase and washed 2 times with methanol and 2 times with distilled water in order to remove residual catalyst. The solvent was then removed under reduced pressure and the polymer was dried under vacuum for 2 days.

Notes: The polymerization was carried out at 5 weight percent solids. The ratio of dichloromethane to hexane is 40:60 (v/v). The molar ratio of DCC:pyridine:TiCl$_4$ is 1:3:20. A 2-fold excess of allyltrimethylsilane to chlorine was used.
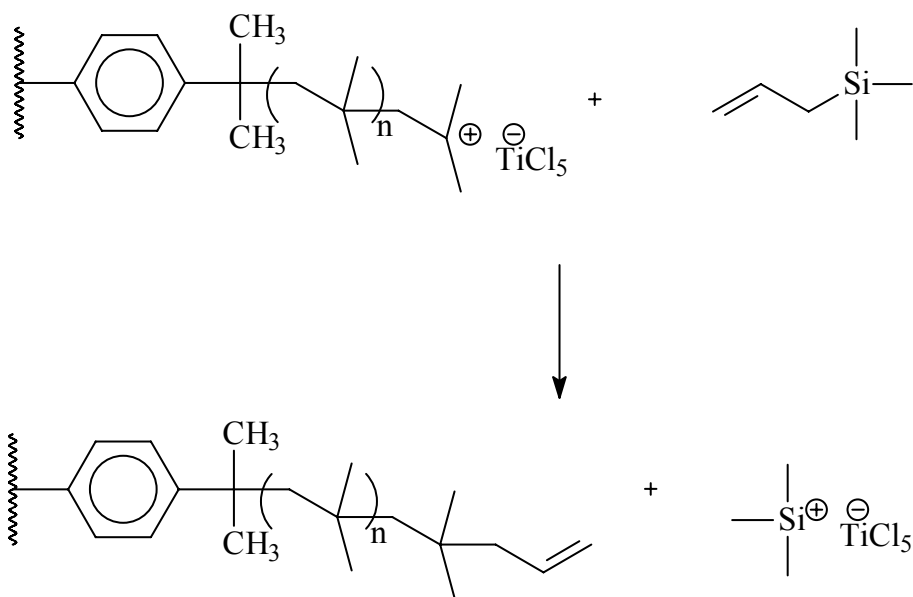
Scheme 8-3. Synthesis of difunctional polyisobutylene using dicumyl chloride as initiator.
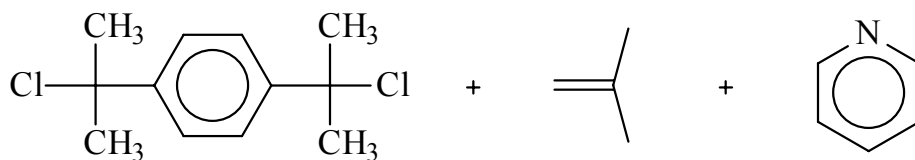
1) CH₂Cl₂/hexanes (40/60 v/v
   TiCl₄
   - 78 °C
2) MeOH
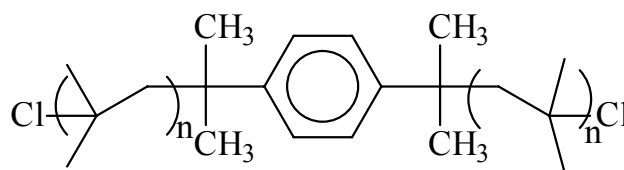
**Scheme 8-4.** Termination of polyisobutylene living chain end with allyltrimethylsilane to yield terminal olefins.

8.3.4 Hydroboration/oxidation of allyl-terminated PIB

PIB (0.5 g, 1.19 x 10^{-4} mol) was dissolved in 50 ml THF (freshly distilled from sodium/benzophenone). 9-BBN (Aldrich, 0.5M solution in THF, 5.95 x 10^{-5} mol, 0.12 ml) was added to the polymer solution. The reaction was allowed to proceed for 5 hours at room temperature. Stoichiometric amounts of 3N NaOH and subsequently 30% hydrogen peroxide were added dropwise. The mixture was allowed to react for 2 hours, then n-hexane was added, stirred, and the aqueous phase was saturated with potassium carbonate. The hexane layer was washed with 3 times with water and then dried using anhydrous magnesium sulfate. The product was isolated under reduced pressure and dried under vacuum. The reaction is shown in Scheme 8-5.

Scheme 8-5. Hydroboration/oxidation of olefin terminated polyisobutylene to yield telechelic hydroxyl functionalized polyisobutylene.
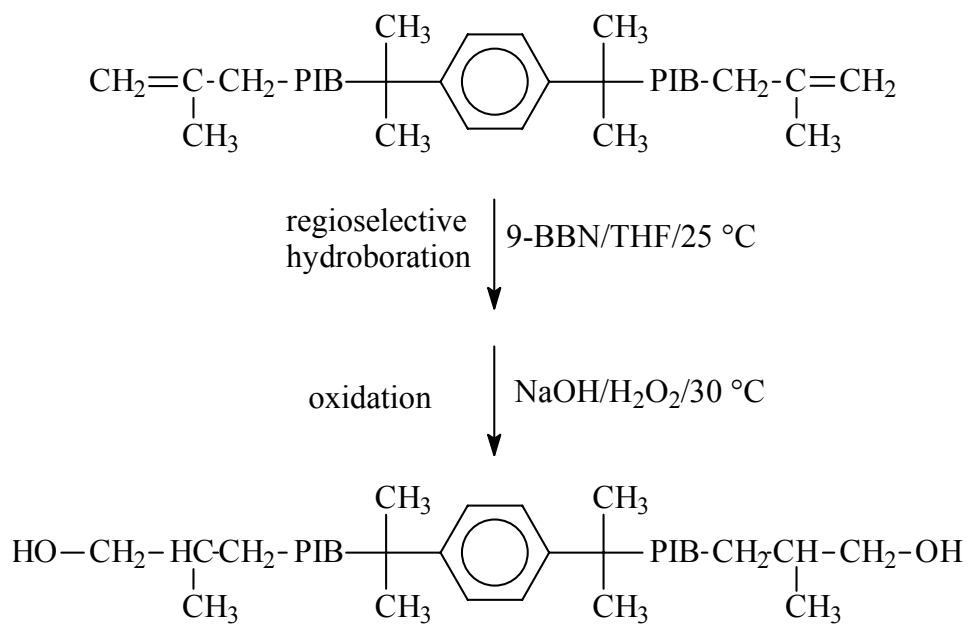
8.3.5 Characterization

^{1}H NMR spectra were determined in CDCl$_3$ at 400 MHz with a Varian Unity Spectrometer. Molar masses were determined at 40 ºC in tetrahydrofuran (THF, HPLC grade) at 1 mL/min using polystyrene standards on a Waters 717+ Auto-sampler SEC equipped with 3 in-line PLgel 5 μm MIXED-C columns, a Waters 410 differential RI detector an in-line Wyatt Technologies miniDAWN multiple angle laser light scattering (MALLS).

8.4 Results and Discussion

It was necessary to synthesize the difunctional initiator dicumyl chloride for the cationic polymerization of isobutylene because it is not commercially available. Dicumyl chloride was synthesized from dicumyl alcohol using hydrochlorination. Quantitative conversion was achieved and pure dicumyl chloride was easily isolated. Conversion was monitored using ^{1}H NMR spectroscopy, shown in Figure 8-1. The bottom spectrum represents the dicumyl alcohol starting material and three distinct resonances were observed at 7.5 ppm (protons associated with the benzene ring), 1.8 ppm (-O*H* resonances), and 1.6 ppm (protons on methyl substituents). All peaks were well-assigned and integrations corresponded to the anticipated structure. Upon hydrochlorination, a shift in the resonance associated with the benzene protons to 7.6 ppm was observed, as well as a shift in the resonance from methyl protons to 2.0 ppm and complete disappearance of the hydroxyl protons. Integrations supported the formation of the dichloro-substituted initiator species.

Figure 8-1. ^{1}H NMR spectra monitoring conversion from dicumyl alcohol to dicumyl chloride.
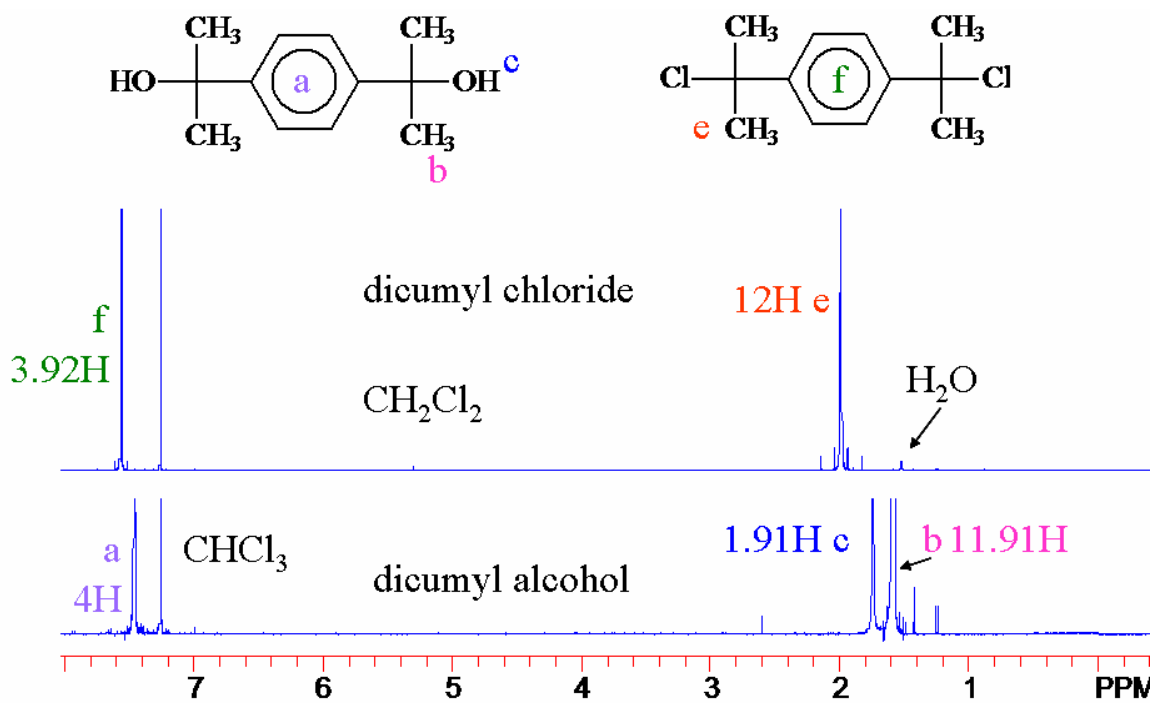
Using dicumyl chloride as a difunctional cationic initiator, well-defined polyisobutylenes were synthesized and endcapped with methanol or allyltrimethylsilane. The series of polymers is described in Table 8-1. While molar mass targeting remained challenging, narrow molar mass distribution polymers were synthesized and a representative SEC trace is shown in Figure 8-2. Methanol terminated polyisobutylenes yielded polymers with a terminal chlorine functionality and allyl-terminated polymers were obtained using allyltrimethylsilane as an endcapping reagent. Well-defined allyl terminated polyisobutylenes were not obtained and this was attributed to reagent purity and introduction of impurities due to the synthetic method. Well-defined allyl-terminated polyisobutylenes (Storey) were subsequently subjected to hydroboration-oxidation chemistry to transform the terminal allyl groups into hydroxyl groups.[468] Quantitative conversions were achieved and confirmed using ^{1}H NMR spectroscopy, as shown in Figure 8-3. Resonances associated with the allyl double bond at 4.6 and 4.9 ppm were quantitatively shifted to 3.2 and 3.4 ppm (-CH_2OH), while maintaining the DCC resonance at 7.2 ppm. Telechelic hydroxyl functional polyisobutylenes are then useful in a variety of organic modification reactions.

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[468] Ivan, B., J. P. Kennedy and V. S. Chang "New Telechelic Polymers and Sequential Copolymers by Polyfunctional Initiator-Transfer Agents (Inifers). VII. Synthesis and Characterization of alpha, omega-Di(hydroxy)polyisobutylene." *J. Polym. Sci.: Polym. Chem. Ed.* **1980**, *18*, 3177-3191.

Table 8-1. Characterization of chloro- and allyl-terminated polyisobutylenes synthesized using living cationic polymerization.

Sample	M_n (target)	M_n (SEC)[a]	M_n (NMR)[b]	M_w/M_n	Endgroup	% Functionality
CH3-14-1	10000	17600	14700	1.04	Cl	92
CH3-14-2	5000	8520	9100	1.07	Cl	85
CH3-22-1	2000	3350	ND	1.37	Allyl	ND
CH3-22-2	6000	12000	ND	1.07	Allyl	ND

Figure 8-2. Representative SEC trace for cationic polymerization of isobutylene.
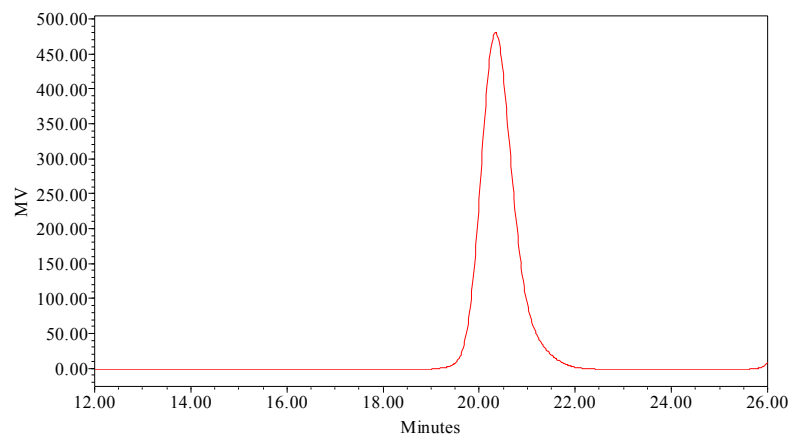
Figure 8-3. ^{1}H NMR spectra showing quantitative conversion from olefin endgroups to hydroxyl endgroups.
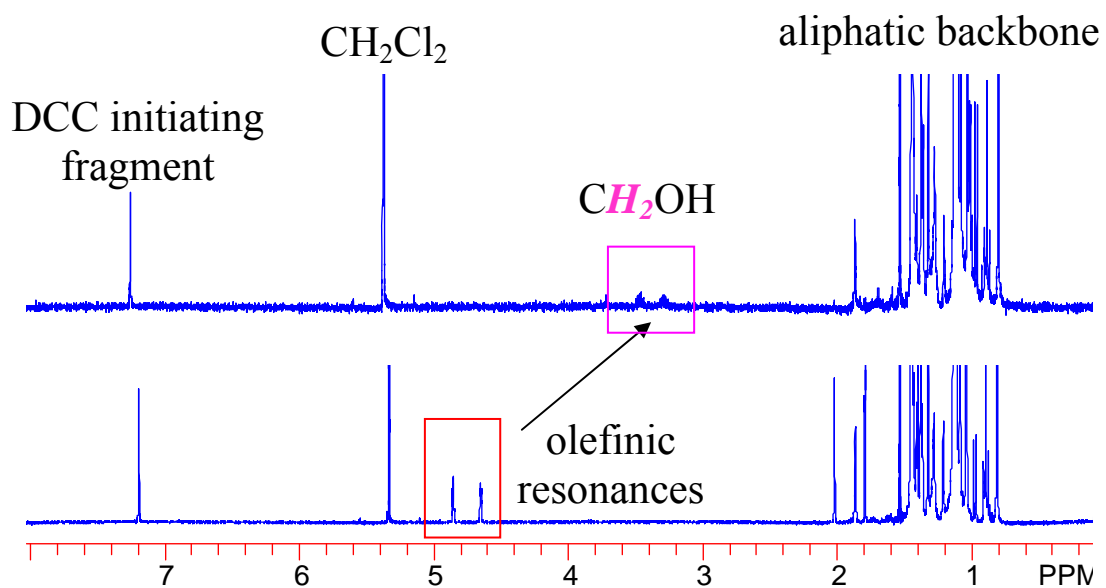
8.5 Conclusions

Dicumyl chloride was synthesized from dicumyl alcohol for use as a difunctional initiator for the cationic polymerization of isobutylene. Good yields and excellent purity were obtained. The living cationic polymerization of isobutylene was well-controlled using dicumyl chloride as initiator and pyridine as electron donor, and narrow molar mass distributions were obtained. Both chloro- and allyl-terminated polyisobutylenes were synthesized in good yields. Allyl-terminated polyisobutylenes were subsequently transformed to hydroxyl-terminated polymers using hydroboration oxidation chemistry. Quantitative conversions from the allyl-endgroup to hydroxyl-endgroup were observed. Hydroxyl terminated polyisobutylenes are then useful in a variety of applications.

8.6 Acknowledgements

Chapter 9 Overall Conclusions

Living anionic polymerization coupled with functional initiation was used to synthesize various monomers in an effort to yield well-defined chain end functional macromolecules. Nucleophilic dhain end functionality provides the ability to introduce myriad functionalities in a number of architectures. Specifically, D_3 was polymerized using both 3-[(N-benzyl-N-methyl)amino]-1-propyllithium and 3-(t-butyldimethylsilyloxy)-1-propyllithium to yield amine and hydroxyl end groups, respectively. Molar mass was controlled ranging from 5000-40000 g/mol with narrow molar mass distributions. Facile deprotection of the amine terminated polymer was achieved using mild hydrogenolysis conditions to yield well-defined amine terminated poly(dimethylsiloxane)s. However, acid catalyzed deprotection was not possible for the protected hydroxyl functionality due to the acid sensitivity of the poly(dimethylsiloxane) backbone and further work on this system should not be carried out. Overall, well-defined amine terminated polymers were synthesized with good molar mass control and yield.

In addition to polysiloxanes, the living polymerization of isoprene was controlled using 3-[(N-benzyl-N-methyl)amino]-1-propyllithium and 3-(t-butyldimethylsilyloxy)-1-propyllithium. Molar masses in the range from 5000-50000 were reproducibly controlled and narrow molar mass distributions were obtained. In contrast to the polysiloxanes, acid catalyzed deprotection was facile and yielded well-defined hydroxyl terminated polymers in several architectures, including linear and star-shaped. However, deprotection of the amine was not possible due to coordination of the amine functionality with the catalyst used in the deprotection step. Isolation proved challenging and further work in this area

is not advised. Using the terminal hydroxyl functionalities in the well-defined poly(ethylene-*co*-propylene)s, quadruple hydrogen bonding moieties (UPy) were introduced in a well-defined manner and with good yields (75-100%). Subsequent characterization was carried out on monofunctional, telechelic functional, and star-shaped UPy functional poly(ethylene-*co*-propylene)s using melt rheology and tensile testing. Melt rheological characterization revealed that telechelic linear polyisoprenes exhibited a a significant shift to lower frequencies (3 orders of magnitude) for the terminal-to-plateau transition in comparison to non-functional linear counterparts. A distinct increase in the complex viscosity was also observed, with a 3.5 order of magnitude increase over non-functional counterparts. Star-shaped UPy functional macromolecules exhibited network like behavior and did not show Newtonian behavior, even at low frequencies. An Arrhenius treatment of the melt viscosity data revealed an increase in activation energy to flow for the UPy functional polymers (~75 kJ/mol) in comparison with non-functional linear counterparts (55-60 kJ/mol). Tensile testing of the UPy functional polymers revealed that the star-shaped macromolecules exhibited increased tensile properties in comparison to the linear polymers, including an increased Young's modulus and tensile strength at break.

The final monomer polymerized using living polymerization coupled with functional iniation was methyl methacrylate. The protected hydroxyl initiator was used in conjunction with lithium chloride to control the polymerization and well-defined molar mass and molar mass distributions were observed. Deprotection yielded a well-defined monol macromonomer. In addition, diols and triols were synthesized using s-BuLi and tBDMSPrLi in conjunction with a protected diphenylethylene derivative (BTOPE),

containing two protected aliphatic diols. Acid catalyzed deprotected yielded well-defined di- and tri-ols, which are then useful in polyester synthesis or lactide ring-opening polymerization.

In contrast to the well-defined macromolecules synthesized using living anionic polymerization, another polymerization methodology was used to introduce pendant multiple hydrogen bonding interactions. A novel methacrylate monomer containing the pendant UPy group was synthesized in near quantitative yields (92%). Copolymers were synthesized using this monomer and 2-ethylhexyl methacrylate over a range of composition. Compositions ranging from 0 to 10 mol% UPy were synthesized, as well as a dimeric hydrogen bonding control containing 11 mol% methacrylic acid (MAA). Matched weight average molar mass was achieved and the series was ideal for melt rheological characterization. Melt rheological characterization revealed that increasing UPy content caused a significant shift to lower frequencies (2 orders of magnitude) for the terminal-to-plateau transition and a broadening of the rubbery plateau. The melt viscosity also increased dramatically (3 orders of magnitude) with UPy incorporation. The methacrylic acid control exhibited behavior similar to that of the PEHMA homopolymer. Through the synthesis and characterization of these macromolecules, the relationship between multiple hydrogen bonding and topology was probed, and distinct differences were observed with UPy incorporation, indicating a possible advantage for macromolecular design involving non-covalent bonding in processing applications. Further work to elucidate these relationships is necessary, and is described below.

Chapter 10   Suggested Future Work

10.1 Amine functional poly(dimethyl siloxane)s

1. Synthesize a series of difunctional linear poly(dimethylsiloxane)s with 3-[(N-benzyl-N-methyl)amino]-1-propyllithium and amine endcapping (1-chloro-3-(dimethylamino)propane).

    a. Utilize well-defined poly(dimethyl siloxane)s in polycondensation reactions as the soft block. Study the effect of molar mass on properties.

    b. Utilize monofunctional poly(dimethyl siloxane)s as chain stoppers and study the effect of molar mass on properties.

    c. Utilize amine functionalities for introduction of organic functionality, such as hydrogen bonding interactions or ionic groups.

2. Synthesize a series of star-shaped amine functionalized poly(dimethyl siloxanes) with 3-[(N-benzyl-N-methyl)amino]-1-propyllithium with different arm molar mass.

    a. Melt and solution rheology in comparison with non-functional and hydroxyl functional analogs.

    b. Examine the utility as multifunctional hyperbranching agents ($A_2 + B_n$ reactions) in polycondensation reactions.

10.2 Poly(ethylene-*co*-propylene) linear and star-shaped macromolecules with terminal functionality.

1. Use vertical shifting in time-temperature superposition treatments to optimize superposition.

2. Examine the effect of arm molar mass on melt and solution properties. Are similar properties attainable with lower molar mass arms, through network interactions, while enabling easier melt processing?

3. Compare melt and solution properties of star-shaped poly(ethylene-*co*-propylene)s with similar *total* molar mass linear poly(ethylene-*co*-propylene)s.

4. Perform creep and hysteresis experiments to study long-term behavior of polymers under typical use conditions.

5. Mix UPy-modified eicosanol with chain end functional UPy poly(ethylene-*co*-propylene)s and determine effect on properties.

6. Determine effect of moisture through controlled humidity experiments. Evaluate creep and tensile performance before and after specimen is subjected to humid environments.

7. Vary the microstructure of the parent polyisoprene using additives and study effect on properties.

8. Vary the multiple hydrogen bonding group; synthesize macromolecules with hydrogen bond groups with a range of association strengths and study the effects on melt and solution viscosities.

9. Synthesize polymers with a comparable incorporation of pendant multiple hydrogen bonding groups and compare to chain-end functional polymers.

10.3 Free radical copolymers with pendant multiple hydrogen bonding groups

1. Synthesize a series of polymers with incorporation of multiple hydrogen bonding monomer above 10 mol%

    a. Use LiCl to interrupt hydrogen bonding interactions during polymerization and determine effect on randomness.

    b. Use in-situ FTIR to determine reactivity ratios of copolymerization to determine randomness.

    c. Investigate melt and solution rheology to define hypothesized hydrogen bonding threshold.

    d. Determine effect of moisture through controlled humidity experiments. Evaluate creep and tensile performance before and after specimen is subjected to humid environments.

    e. Use AFM to probe possible microphase separation.