

Synthesis and Characterization of Tailored Macromolecules via Stable Free Radical Polymerization Methodologies

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Jeremy Lizotte

Abstract:

The stable free radical polymerization methodology for production of controlled macromolecules was investigated using a novel monomer, 2-vinylnaphthalene. Initial polymerizations resulted in molecular weight distributions typical of conventional free radical polymerization techniques (>2.0). Manipulation of the initiator concentration and the molar ratio of initiator to nitroxide demonstrated no significant control over the resulting polymer products. Analysis of the polymerization kinetics for a 2-vinylnaphthalene polymerization performed in the presence and absence of the free radical initiator revealed identical monomer consumption profiles as well as pseudo first order kinetics indicating a significant degree of the thermal polymerization was occurring at the polymerization temperature (130 °C). Comparison of the thermal polymerization propensity of 2-vinylnaphthalene and styrene revealed an increased tendency for 2-vinylnaphthalene to undergo thermal polymerization. Styrene is considered highly active in its propensity to thermally polymerize. However, an Arrhenius analysis using *in situ* FTIR was employed to determine the activation energy for the thermal polymerization of styrene and 2-vinylnaphthalene. The 2-vinylnaphthalene activation energy for thermal polymerization was determined for the first time to be almost 30 kJ/mol less than styrene. A novel modified Mayo mechanism was proposed for the 2-vinylnaphthalene thermal initiation mechanism. Moreover, this thermal initiation was employed to initiate nitroxide mediated polymerizations of styrene. This first use of a 2-vinylnaphthalene initiating system resulted in polystyrene with a large macrocyclic initiating fragment. The presence of the initiating moiety was studied using both UV-Vis spectroscopy and ^1H NMR spectroscopy.

The extension of stable free radical polymerization to the acrylate monomer family was examined using a novel nitroxide mediator, *N-tert-butyl-N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (DEPN). The synthesis of DEPN was

monitored using *in situ* FTIR spectroscopy to determine optimum reaction conditions. The purified nitroxide was subsequently employed in the synthesis of various block and random acrylate copolymers. The production of a unique amphiphilic block copolymer consisting of acrylic sequences was achieved. Poly(*t*-butyl acrylate-*b*-2ethylhexyl acrylate-*b*-*t*-butyl acrylate) was synthesized using the SFRP process. The *t*-butyl functionalities were subsequently removed in a post-polymerization acid catalyzed hydrolysis. The effect of steric bulk and electronic factors on the resulting SFRP process was also investigated and revealed similar polymerization kinetics for various alkyl acrylates. However, addition of a hydroxyl containing monomer, 2-hydroxyethyl acrylate, resulted in an increase in the polymerization rate up to 2 times. The rate enhancement was attributed to hydrogen bonding effects and this was confirmed using the unprecedented addition of dodecanol, which also demonstrated a significant rate enhancement.

Block copolymers were also achieved using a novel difunctional nitroxide synthesized from 4-hydroxy TEMPO and 1,6-hexamethylene diisocyanate. The identity of the nitroxide was confirmed using mass spectrometry and ¹H NMR. The dinitroxide was used in the polymerization of styrene and subsequently used to produce symmetric ABA triblock copolymers with *t*-butyl styrene using a unique two-step polymerization route. In addition, the dinitroxide demonstrated an increased tendency for decomposition due to the complex mediation equilibrium. The decomposition was studied using GPC to evaluate the decomposition effects on the polymerization.

Results of the research efforts presented herein are written as individual research reports with contributing authors and pertinent literature reviews presented at the beginning of each chapter.

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Chapter 1 : Introduction

1.1 Research Significance and Impact

With growing specificity of polymer applications, increased synthetic control is required in the preparation of materials for advanced technological purposes. Predictable molecular weights and molecular weight distributions in addition to controlled chemical composition are essential for the design of systems for future technologies. Furthermore, manipulation of polymer architecture is essential in the design of specific polymeric materials. Research objectives will address both fundamental issues and the utility of living polymerization techniques to produce new materials with tailored properties through control of the molecular weight, polydispersity, chemical composition, and architecture. Particular attention will be given to elucidation of the stable free radical polymerization (SFRP) methodology. Recently, SFRP and other controlled free radical polymerization techniques have been shown to produce well-defined polymerization reactions resulting in controlled molecular weights and narrow polydispersities. The controlled stable free radical polymerization process was initially employed in an investigation using a previously unexplored monomer, 2-vinylnaphthalene (2VN) (Figure 1.1).¹ Poly(2-vinylnaphthalene) has been previously used in luminescence studies and was primarily prepared via living anionic polymerization techniques or simple free radical polymerization. This monomer offers unique potential as a fluorescent label when attached to the end of a desired polymer chain. Functionalization of common polymers is often used to produce materials with new polymeric properties. For example, modification of the 2VN ring substituents can be employed to systematically vary the properties of resulting polymer product. SFRP of styrene has proven highly successful and controllable. Investigation of the 2VN monomer was expected to operate in a similar fashion to previously studied styrene. However, the styrene monomer is also well known as a thermally polymerizable monomer and the contribution of thermal polymerization in the 2VN system was also thoroughly examined utilizing novel real-time polymerization monitoring techniques. *In situ* FTIR spectroscopy was employed to follow the stable free

¹ Shirakawa, E.; Yamasaki, K.; Hiyama, T. "Nickel-Catalyzed Cross-Coupling Reactions of Aryl Halides with Organostannanes," *Journal of the Chemical Society, Perkin Transactions 1: Organic and Bio-Organic Chemistry* 17, (1997), 2449-2450.

radical polymerization and provide data on monomer conversion and polymerization kinetics. Previous efforts in our laboratories have demonstrated the utility of this apparatus.

Furthermore, living propagating intermediates are capable of additional growth with the sequential addition of monomer to the reaction system. The production of precise block copolymers consequently becomes feasible. It was anticipated that both graft and block copolymers via SFRP would be attainable with amphiphilic nature suitable for application in pressure sensitive adhesives. Conventional methods for production of triblock copolymers involved three sequential monomer additions to yield the symmetric ABA structure. A novel nitroxide mediator was studied that would allow the production of symmetric ABA type triblock copolymers via a new more facile two-step synthetic pathway.

Research objectives in the area of adhesion science also involved the production of amphiphilic type copolymers composed of alkyl acrylate monomers. Control of the acrylate polymerization using the stable free radical polymerization techniques required the investigation and production of a novel mediating agent. The nitroxide was used to study the steric and electronic effects derived from monomer structure on the stable free radical polymerization mechanism. In addition, the ability to control the polymerization rate via addition of hydrogen bonding additives was examined.

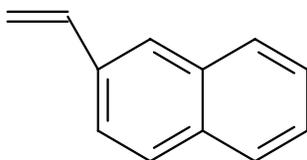


Figure 1.1: Unconventional monomer, 2-vinylnaphthalene, to be investigated using controlled radical polymerization methods.

Furthermore, with the capability of precise control over the polymerization, manipulation of the architecture would allow the synthesis and evaluation of novel macromolecular structures. Research efforts will probe the fundamental areas of star

polymer synthesis examining the reaction system and compositional effects on polymer performance. These highly branched structures exhibit a variety of unusual and advantageous properties. Initially, it is seen that the branching associated with stars lowers the hydrodynamic dimension. Also, star polymers display a lower melt and solution viscosity compared to their linear counterparts. Hence, it was possible to produce a polymer with an extremely high molecular weight, which does not exhibit the processing difficulties typical of many high molecular weight linear polymers. This low viscosity feature holds true for star systems only to a particular molecular weight where entanglements again become prominent and then the viscosity scales exponentially with the molecular weight of the star arms.² Furthermore, the many arms of the star were amenable to functionalization in SFRP due to the ester group that remains from initiation via benzoyl peroxide (BPO). This ester group could be hydrolyzed and subsequently derivatized to produce desired telechelic functionality.

The primary objectives involving fundamental mechanistic understanding of tailored architectures will impact the production of novel adhesive systems. In particular, polymeric materials were synthesized which exhibit thermal and mechanical properties designed for use in pressure sensitive adhesive applications. Specifically, the research endeavored to generate an amphiphilic type polymer, which incorporated a hydrophilic segment for adhesive enhancement and a hydrophobic aliphatic section to aid in developing a novel set of suitable mechanical characteristics. The hydrophilic segments were designed to preserve high temperature performance. Systematic variation of polymer compositions were designed to illuminate the capabilities of controlled free radical polymerization techniques to produce highly controlled polymeric materials. Moreover, the molecular composition of adhesive formulations was examined to provide insight into the effect of hydrogen bonding groups inclusion in the polymer backbone.

² Kraus, G.; Gruver, J. T. "Effect of Random Long-Chain Branching on the Melt Viscosity of Polybutadiene," *SCI Monograph* 26, (1967), 30-48.

Chapter 2 : Literature Review

2.1 Pressure Sensitive Adhesives

2.1.1 Introduction

Pressure sensitive adhesives (PSA) represent a major class of adhesive materials currently of interest commercially and scientifically. The appeal of PSAs arises primarily from their ease of use. They require no special care for storage and application, and the adhesive requires only short time with little force necessary. The existence of fluid-like properties in the polymer results in brief contact periods necessary to allow adequate wetting of the substrate. The ability to adhere to a substrate and oppose debonding results from the resistance to deformation that also exists.³ A precarious balance of the viscoelastic properties in the polymer is crucial to produce the desired PSA properties. To obtain the required properties, PSAs are typically prepared from the blending of a rubber-type polymer with a low molecular weight resin tackifier. Petroleum fractions are cationically polymerized to produce low molecular weight resin tackifiers, which are primarily responsible for the fluid-like properties while the elastomeric fraction accounts for the resistance to deformation.

The specificity of properties required for formulation of a functional PSA necessitates an adherence to explicit limits concerning parameters like T_g and modulus. The ability of a PSA to wet the surface is vital for proper performance. Consequently, the T_g associated with the material must be at a suitable temperature to allow a high degree of flow at the application temperature, which is usually room temperature for most general purpose PSA's. The wetting of the substrate by the PSA is then dependent on the chemical identity of the surface and the PSA material. The modulus also plays a critical role in PSA performance. Typically, PSA materials exhibit a rubbery plateau region above the glass transition temperature. It is crucial that the modulus corresponding to this region falls below a specified limit termed the Dahlquist criterion. The Dahlquist criterion for tack requires that the modulus of the material be below 3×10^6 dynes/cm² during an application time of one second in order to perform adequately in wetting

³ Wake, W. C. *Adhesion and the Formulation of Adhesives*, 2nd ed. (New York: Applied Science Publishers, 1982); Petrie, E. M. *Handbook of Adhesives and Sealants* (New York: McGraw-Hill, 2000).

processes.⁴ Though certain restrictions are placed on the formulation of PSA's, there is a degree of variation in properties that produce PSA suitable for various applications. Typically, researchers employ what are termed viscoelastic windows (VW) to describe various ranges of properties like T_g and modulus appropriate for a particular application.⁵ These VW's model the relationship between storage modulus (G') and loss modulus (G'') that can be determined by examining the rheological master curves of a PSA material. Properties present at the bonding and debonding frequencies are addressed as well as the dissipation and resistance to deformation characteristics of a material typical of a specified viscoelastic window.

2.1.2 Basic Principles of Adhesion

Adhesion is described as the linking of two materials by mechanical and/or chemical means on the atomic or molecular level.⁶ Mechanical adhesion involves the physical interlocking of materials with hooks or rings as is present in VelcroTM.⁷ Chemical adhesion results from the interaction of the molecular species present in the adhered materials. These chemical interactions occur primarily due to van der Waals forces, hydrogen bonding, and ionic interactions.⁸ Occasionally, covalent interactions are responsible for adhesion resulting from the reaction of chemical species within an adhesive system. However, short-range molecular interactions are the prominent mode of bonding in adhesives. Van der Waals forces are involved in the physical adsorption of the adhesive to the substrate. Hydrogen bonding relies on strong polar forces to provide adhesion. Chemisorption can also provide adhesive ability by ionic interactions of the adhesive with the substrate as is seen in coordination bonding. Due to the nature of these mechanisms of adhesion, intimate contact is necessary between the adhesive and the substrate. Hence, the wettability of an adhesive on a particular substrate is a major

⁴ Pocius, A. V. *Adhesion and Adhesives Technology* (New York: Hanser Publishers, 1997).

⁵ Chang, E. P. "Viscoelastic Windows of Pressure-Sensitive Adhesives," *Journal of Adhesion* 34, (1991), 189-200; Yang, H. W. H.; Chang, E. P. "The Role of Viscoelastic Properties in the Design of Pressure-Sensitive Adhesives," *Trends in Polymer Science* 5, (1997), 380-384.

⁶ *Handbook of Adhesion*, ed. D. E. Packham (Bath, Great Britain: Longman Scientific and Technical, 1992).

⁷ *Handbook of Adhesion*, ed. D. E. Packham (Bath, Great Britain: Longman Scientific and Technical, 1992).

⁸ *Handbook of Adhesion*, ed. D. E. Packham (Bath, Great Britain: Longman Scientific and Technical, 1992).

consideration. Wettability refers to the ability of an adhesive to form an extensive contact area allowing as much interaction as is possible. The extent of wetting is a function of the fluid nature of the adhesive. The wetting of a surface by a polymer adhesive is predictable using the surface energy relationship between the substrate and the adhesive. Contact angle measurements correlate with the degree of wetting of a liquid on a substrate, and high contact angles suggest a small degree of wetting indicating that cohesive forces of the materials are much stronger than adhesive forces. Wetting (W), also termed spreading (S), is described in equation 1, which relates the surface energies of the adhesive (γ_l), substrate (γ_s), and interface (γ_{sl}) of the substrate and adhesive. Spreading is favored when the difference between work of adhesive forces (W_A) and work of cohesive forces (W_C) is greater than or equal to zero, which indicates that W_A between the adhesive and substrate is greater than W_C within each of the components.⁹ This fluid nature must be precisely balanced with solid properties that resist debonding once the adhesive interaction has been formed.¹⁰

$$\text{Equation 1: } S = W_A - W_C = \gamma_s + \gamma_l - \gamma_{sl}$$

Various factors affect adhesive performance. These factors are considered in the prediction of adhesive capabilities described by the equation for the practical work of adhesion (Equation 2).¹¹ The work of adhesion is simply the sum of two factors, the first of which is a measure of the work of bonding (W_{th}), which is the energy required to form the adhesive system. The latter factor is a function of the thermodynamic work of adhesion [$g(W_{Th})$] and the viscoelastic properties of the adhesive [$\phi(T,Rate)$].

$$\text{Equation 2: } W_{adh} = W_{th} + g(W_{th})\phi(T,Rate)$$

⁹ Lollis, N. J. D. *Adhesives, Adherends, Adhesion*, 2nd ed. (Malabar, Florida: Robert E. Krieger Publishing Company, Inc, 1985).

¹⁰ *Handbook of Adhesion*, ed. D. E. Packham (Bath, Great Britain: Longman Scientific and Technical, 1992).

¹¹ Gent, A. V.; Hamed, G. R. *Journal of Adhesion* 7, (1975), 91.

Both the adhesive and the substrate play a vital role in the design of the adhesive system. The polymeric adhesive must be capable of some sort of short-range molecular interaction with the surface of the substrate. Hence, comprehension of the nature of the substrate is essential. Surface techniques such as electron spectroscopy for chemical analysis (ESCA) and atomic force microscopy (AFM) along with scanning electron microscopy (SEM) are used extensively to characterize the substrate surface.¹²

2.1.3 Amphiphilic Nature of Polymers in Adhesive Applications

A primary concern for most adhesive applications is an adequate interaction between the adhesive and the substrate. The strength of desired interactions are dependent upon the nature of the application. The ability to interact favorably with a great variety of substrates is a potential advantage. Amphiphilic type polymers contain chain sequences that exhibit favorable interaction with different types of systems. Polymer chains may contain both hydrophilic and hydrophobic sequences, which impart interesting dual properties. The dual nature of these polymer systems results in various applications including stabilizing emulsions, dispersions and polymer blends.¹³ In addition, amphiphiles have found use in surface modifications and other industrial applications.¹⁴ Great interest in these materials is found due to their performance in solvent systems, both aqueous and organic. The amphiphilic nature of the polymer allows some degree of interaction with any solvent regardless of its polarity. These

¹² Parker, A. A.; Kolek, P. L. "Characterization of Poly(Aminosiloxane) Surface Chemistry on Aluminum Oxide," *Journal of Adhesion* 73, (2000), 197-214; Oeberg, K.; Edland, U.; Eliasson, B.; Shchukarev, A.; Seshadri, K.; Allara, D. "Spectroscopic Characterization of the Bonding, Orientation, and Coverage of Copper Tetraazaphthalocyanine Monolayer Films on SiO₂ Surfaces," *Journal of Physical Chemistry B* 104, (2000), 10627-10634; Wistara, N.; Zhang, X.; Young, R. A. "Properties and Treatments of Pulp from Recycled Paper. Part II. Surface Properties and Crystallinity of Fibers and Fines," *Cellulose* 6, (1999), 325-348; Nanda, A. K.; Kishore, K. "Thermal-Initiating Potentialities of Poly(Methyl Methacrylate) Peroxide: Metamorphosis of Block-into-Block Copolymer and Comparative Studies on Surface Texture and Morphology," *Journal of Polymer Science, Part A: Polymer Chemistry* 39, (2001), 546-554.

¹³ *Amphoterics Surfactants*, ed. C. L. Hilton (New York: Marcel Dekker, 1982).

¹⁴ Zushun, X.; Changfeng, Y.; Shiyuan, C.; Linxian, F. "Study on the Micellization of Amphiphilic Graft Copolymer Ps-G-PeO in Toluene," *Polymer Bulletin* 44, (2000), 215-222; Janssen, H. M.; Peeters, E.; Zundert, M. F. v.; Genderen, H. M. v.; Meijer, E. W. "Unconventional, Amphiphilic Polymers Based on Chiral Poly(Ethylene Oxide) Derivatives. I. Synthesis and Characterization," *Macromolecules* 30, (1997), 8113-8128.

interactions are normally manifested in the form of micelles and aggregates, which find extensive use in emulsion and dispersion polymerizations.¹⁵

Many adhesive applications operate on hydrophilic interactions due to the polar nature of many substrates. Consequently, many polymers that possess the proper viscoelastic properties for adhesive applications must be augmented with a hydrophilic chain via blending or via copolymerization. Copolymerization and blending are employed extensively to introduce new properties to a polymeric material. For example, PET and PBT are blended with polycarbonate to improve chemical resistance and processability.¹⁶ As the application for adhesives become more specific and rigorous, researchers are forced to introduce new properties to satisfy the application's needs. Copolymerization and blending not only allows greater interaction with the substrate, but it also offers a method for establishing more appropriate mechanical and thermal properties in the polymers.¹⁷ In adhesive applications, tailored properties will allow the formulation of a system exhibiting desired interaction, in addition to specifically engineered mechanical properties. Special properties may also be introduced in the adhesive, such as biodegradative linkages, which may be used to subsequently release therapeutic agents from the adhesive in a controlled manner.

2.1.4 Biodegradation of Polymer Adhesive Systems

With the increasing concern for the environmental impact of chemistry, much consideration has been focused on environmentally benign polymer chemistry. These

¹⁵ Chen, X.; Smid, J. "Micellization of and Solute Binding to Amphiphilic Poly(Ethylene Oxide) Star Polymers in Aqueous Media," *Langmuir* 12, (1996), 2207-2213; Yu, Y.; Eisenberg, A. "Control of Morphology through Polymer-Solvent Interactions in Crew-Cut Aggregates of Amphiphilic Block Copolymers," *Journal of the American Chemical Society* 119, (1997), 8383-8384.

¹⁶ Odian, G. *Principles of Polymerization*, 3rd ed. (New York: John Wiley and Sons, Inc., 1991); John, J.; Bhattacharya, M. "Synthesis and Properties of Reactively Compatibilized Polyester and Polyamide Blends," *Polymer International* 49, (2000), 860-866.

¹⁷ Jha, A.; Bhowmick, A. K. "Thermoplastic Elastomeric Blends of Nylon-6/Acrylate Rubber: Influence of Interaction on Mechanical and Dynamic Mechanical Thermal Properties," *Rubber Chemistry and Technology* 70, (1997), 798-814; Oommen, Z.; Groeninckx, G.; Thomas, S. "Dynamic Mechanical and Thermal Properties of Physically Compatibilized Natural Rubber/Poly(Methyl Methacrylate) Blends by the Addition of Natural Rubber-Graft-Poly(Methyl Methacrylate)," *Journal of Polymer Science, Part B: Polymer Physics* 38, (2000), 525-536.

efforts have involved the use of alternative solvent systems,¹⁸ solid state polymerization methods¹⁹ and the production of materials that will not result in long term pollution after their use.²⁰ Biodegradable materials can be used to design products that have short application times and will degrade naturally over time. The primary means of degradation in biodegradable materials is hydrolysis or enzymatic degradation using various microbes. Originally, instability due to hydrolysis was thought to be an undesirable characteristic of some industrial polymers.²¹ However, with the onset of environmental awareness, comprehension and manipulation of this reactivity has become well studied. In order to take advantage of hydrolysis, most biodegradable materials contain ester linkages. A vast majority of the current research has concerned the synthesis of poly(lactide) shown in Figure 2.1 or similar compounds containing an aliphatic ester group in the backbone.²²

¹⁸ Guan, Z.; Combes, J. R.; Menciloglu, Y. Z.; DeSimone, J. M. "Homogeneous Free Radical Polymerizations in Supercritical Carbon Dioxide: 2. Thermal Decomposition of 2,2'-Azobis(Isobutyronitrile)," *Macromolecules* 26, (1993), 2663-2669.

¹⁹ Chaudhary, A. K.; Lopez, J.; Beckman, E. J.; Russell, A. J. "Biocatalytic Solvent-Free Polymerization to Produce High Molecular Weight Polyesters," *Biotechnology Progress* 13, (1997), 318-325.

²⁰ Petre, M.; Zarnea, G.; Adrian, P.; Gheorghiu, E. "Biodegradation and Bioconversion of Cellulose Wastes Using Bacterial and Fungal Cells Immobilized in Radiopolymerized Hydrogels," *Resources Conservation and Recycling* 27, (1999), 309-322.

²¹ *Biocompatibility of Clinical Implant Materials*, ed. D. F. Williams (Boca Raton, Florida: CRC Press, 1981).

²² Zhong, W.; Ge, J.; Gu, Z.; Li, W.; Chen, X.; Yi, Z.; Yang, Y. "Study on Biodegradable Polymer Materials Based on Poly(Lactic Acid). I. Chain Extending of Low Molecular Weight Poly(Lactic Acid) with Methylenediphenyl Diisocyanate," *Journal of Applied Polymer Science* 74, (1999), 2546-2551; Kurcok, P.; Dubois, P.; Sikorska, W.; Jedlinski, Z.; Jerome, R. "Macromolecular Engineering of Lactones and Lactides. 24. Controlled Synthesis of (R,S)-B-Butyrolactone-B-E-Caprolactone Block Copolymers by Anionic and Coordination Polymerization," *Macromolecules* 30, (1997), 5591-5595; Liu, S.-J.; Tsai, C.-H.; Lin, S.-S.; Ueng, S. W.-N. "Processing of Biodegradable Polymer Composites as a Drug Delivery System in Vitro," *International Polymer Processing* 14, (1999), 322-325; Schmack, G.; Tandler, B.; Vogel, R.; Beyreuther, R.; Jacobsen, S.; Fritz, H.-G. "Biodegradable Fibers of Poly(L-Lactide) Produced by High-Speed Melt Spinning and Spin Drawing," *Journal of Applied Polymer Science* 73, (1999), 2785-2797; Miyajima, M.; Koshika, A.; Okada, J.; Ikeda, M. "Effect of Polymer/Basic Drug Interactions on the Two-Stage Diffusion-Controlled Release from a Poly(L-Lactic Acid) Matrix," *Journal of Controlled Release* 61, (1999), 295-304; Miyajima, M.; Koshika, A.; Okada, J. i.; Ikeda, M. "Mechanism of Drug Release from Poly(L-Lactic Acid) Matrix Containing Acidic or Neutral Drugs," *Journal of Controlled Release* 60, (1999), 199-209; Meredith, J. C.; Amis, E. J. "Lest Phase Separation in Biodegradable Polymer Blends: Poly(D,L-Lactide) and Poly(E-Caprolactone)," *Macromolecular Chemistry and Physics* 201, (2000), 733-739.

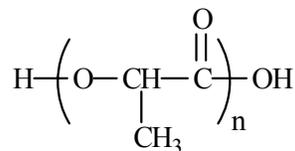


Figure 2.1: Structure of poly(lactic acid) containing ester linkages.

As water contacts the polymer, the reactive carbonyl groups will hydrolyze and cleave the macromolecule into much shorter units. Control of the degradation and other mechanical properties associated with these biodegradable polymers can be manipulated to an extent via copolymerization and blending.²³ In order to improve the mechanical properties of poly(D,L-lactide), Schmidt and Hillmyer copolymerized D,L-lactide with isoprene to toughen the polymer in a fashion similar to that of high impact polystyrene (HIPS), which resulted in a material exhibiting many characteristics of a microphase-separated lamellar morphology.²⁴ Other polymer systems have also been investigated as viable biodegradative materials. Poly(vinyl alcohol) (Figure 2.2) has been shown to be

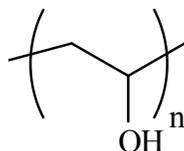


Figure 2.2: Structure of biodegradable poly(vinyl alcohol).

capable of biodegradation via enzymatic degradation.²⁵ Additionally, starch polymers have been used as biodegradable materials due to its ability to hydrolyze in the presence

²³ Zheng, J.; Manuel, W. S.; Hornsby, P. J. "Transfection of Cells Mediated by Biodegradable Polymer Materials with Surface-Bound Polyethylenimine," *Biotechnology Progress* 16, (2000), 254-257; Cordewener, F. W.; Dijkgraaf, L. C.; Ong, J. L.; Agrawal, C. M.; Zardeneta, G.; Milam, S. B.; Schmitz, J. P. "Particulate Retrieval of Hydrolytically Degraded Poly(Lactide-Co-Glycolide) Polymers," *Journal of Biomedical Materials Research* 50, (2000), 59-66; Schmidt, S. C.; Hillmyer, M. A. "Synthesis and Characterization of Model Polyisoprene-Poly(lactide) Diblock Copolymers," *Macromolecules* 32, (1999), 4794-4801; Lu, L.; Stamatias, G. N.; Mikos, A. G. "Controlled Release of Transforming Growth Factor B1 from Biodegradable Polymer Microparticles," *Journal of Biomedical Materials Research* 50, (2000), 440-451.

²⁴ Schmidt, S. C.; Hillmyer, M. A. "Synthesis and Characterization of Model Polyisoprene-Poly(lactide) Diblock Copolymers," *Macromolecules* 32, (1999), 4794-4801.

²⁵ Tschech, A.; Zeyer, J.; Kastien, H.; Sutter, H. P. "Microbial-Degradation of Synthetic-Polymers - a Literature- Review," *Material Und Organismen* 27, (1992), 203-233.

of water.²⁶ Starch has been employed as both a packaging material and as a hot melt adhesive.²⁷ The use of starch as a loose fill packing material has not shown significance in the U.S. market, but Korea has widespread production of starch based polymer products. The utility of starches in industry previously required a plasticizer for the starch adhesive to be processed. The most common plasticizer for starch is water. However, recent advances have seen the formulation of modified starch systems that involve no additional chemicals or moisture for processing.²⁸ Another possibility is the modification of a polymer to produce a material capable of biodegradation. Kurane et al. synthesized a sugar branched polymer originating from poly(vinyl alcohol) (PVOH) that displayed ideal degradative characteristics in that it degrades more readily than PVOH and does not require the assistance of the specific decomposition microbes that PVOH degradation necessitates.²⁹ Rather, the modified PVOH macromolecule easily degrades by more abundant and common microbial species. This ease of degradation is attributed to the low molecular weight of the main chain PVOH in material. This low molecular weight sample is easily degraded without the use of PVOH assimilating microbes. Modified PVOH polymers with molecular weights above a specified limit also displayed the inability to degrade because the main chain PVOH content had reached levels requiring special assimilating microbes.

Poly(vinyl alcohol) is used as the premodified polymer and degrades readily with microbes, which are not abundant in many waste areas. Degradation mechanisms are proposed to include both random attack and a terminal unzipping depolymerization process.³⁰ Hence, the sugar pendant groups were used to create polymer material that

²⁶ Ohtani, N.; Ishidao, T.; Iwai, Y.; Arai, Y. "Hydrolysis of Starch or Pullulan by Glucoamylase or Pullulanase Immobilized on Poly(N-Isopropylacrylamide) Gel," *Colloid and Polymer Science* 277, (1999), 197-202.

²⁷ Kim, S. H.; Kim, Y. H. "R&D Status of Biodegradable Polymers in Korea," *Macromolecular Symposia* 144, (1999), 85-99; Blumenthal, M.; Paul, C. W. "Starch-Based Hot Melts for Adhesive Applications," *Tappi Journal* 77, (1994), 193-195.

²⁸ Blumenthal, M.; Paul, C. W. "Starch-Based Hot Melts for Adhesive Applications," *Tappi Journal* 77, (1994), 193-195.

²⁹ Tokiwa, Y.; Fan, H.; Hiraguri, Y.; Kurane, R.; Kitagawa, M.; Shibatani, S.; Maekawa, Y. "Biodegradation of a Sugar Branched Polymer Consisting of Sugar, Fatty Acid, and Poly(Vinyl Alcohol)," *Macromolecules* 33, (2000), 1636-1639.

³⁰ Solaro, R.; Corti, A.; Chiellini, E. "Biodegradation of Poly(Vinyl Alcohol) with Different Molecular Weights and Degree of Hydrolysis," *Polymers for Advanced Technologies* 11, (2000), 873-878.

was degradable by a larger variety of more abundant microbes. Figure 2.3 details the degradation rate of PVOH and the sugar branched polymer along with the constituents of that modified PVOH. The experiment utilizes a biochemical demand tester using the oxygen consumption method in soil at 25 °C. The lack of degradation of the PVOH is indicative of the absence of the necessary microbes for degrading PVOH. Inclusion of the sugar on the side chain results in the desired degradation and increases the material's susceptibility to degradation.

2.1.5 Photocrosslinking in Pressure Sensitive Adhesives

Continuing economic and environmental concerns have prompted studies to investigate alternative crosslinking processes for adhesive system. Photo-induced crosslinking has emerged as a viable option to replace thermal and chemical curing methodologies for hot melt and pressure sensitive adhesives (PSA's). Several studies have reported the effects of crosslinking on the resulting PSA properties. Kraton D (poly(styrene-*b*-butadiene-*b*-styrene)) has been crosslinked using a conventional chemical crosslinker, Irgacure 651 (2,2-dimethoxy-1,2-diphenylethan-1-one) to affect the adhesive properties of the polymer.³¹ Crosslinking of the poly(butadiene) blocks in the triblock copolymer significantly reduced peel strength and tack while having little effect on the surface energy of the system. This observed reduction in peel strength can be exploited in situations such as medical grade PSA where it is desirable to turn the adhesive properties "on and off" for application and removal, respectively. Webster and coworkers have detailed the attached of a crosslinkable functionality within a poly(alkyl methacrylate) adhesive material.³² A copolymer of itaconic anhydride, 2-ethylhexyl acrylate and *n*-butyl acrylate were polymerized using conventional free radical

³¹ Staeger, M.; Finot, E.; Brachais, C. H.; Auguste, S.; Durand, H. "Surface Investigation of Adhesive Formulation Consisting of Uv Sensitive Triblock Poly(Styrene-B-Butadiene-B-Styrene) Copolymer," *Applied Surface Science* 185, (2002), 231-242.

³² Boyne, J. M.; Millan, E. J.; Webster, I. "Peeling Performance of a Novel Light Switchable Pressure-Sensitive Adhesive," *International Journal of Adhesion and Adhesives* 21, (2001), 49-53; Webster, I. "The Development of a Pressure-Sensitive Adhesive for Trauma-Free Removal," *International Journal of Adhesion and Adhesives* 19, (1999), 29-34; Chivers, R. A.; Webster, I., "Investigations into the Mechanism of Adhesion of a Novel Light-Deactivatable Pressure-Sensitive-Adhesive" (paper presented at the Adhesion '99, Cambridge, UK, 1999); Webster, I. "Adhesives," (World Patent #WO 96/29374: 1996); Webster, I. "Adhesives," (World Patent #WO 99/18136: 1999); Webster, I. "Adhesives," (US Patent # 6,184,264 B1: Smith & Nephew, 2001).

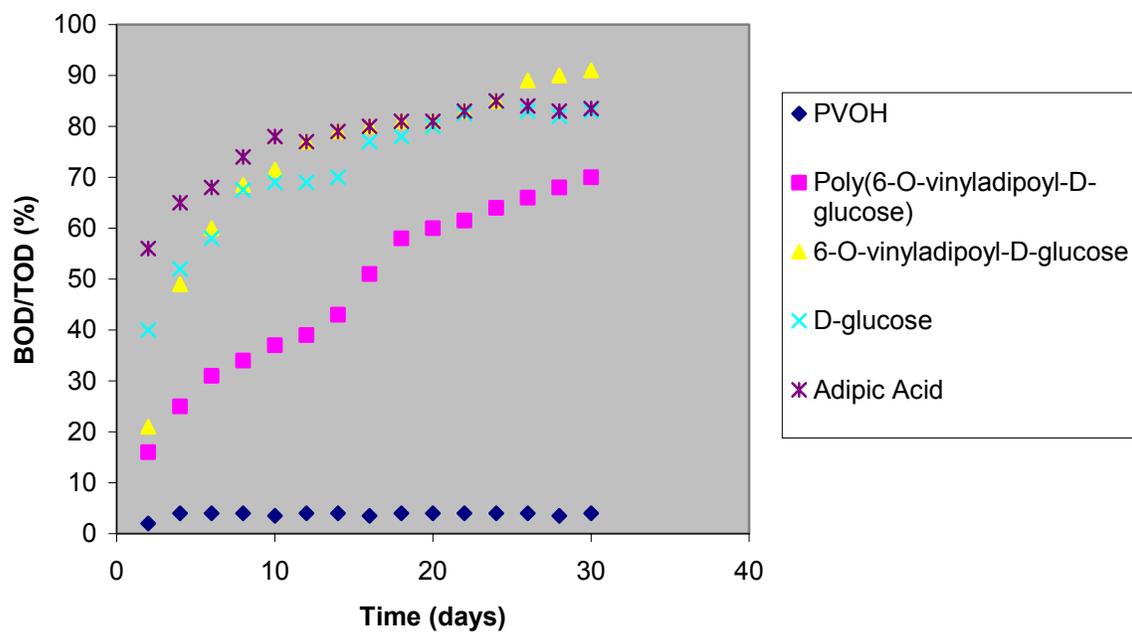


Figure 2.3: Oxygen uptake of poly(6-O-vinyladipoyl-D-glucose) and its constituents compared to PVOH performed with a BOD tester using 100 mg/L of polymer concentration in soil at 25 °C.³³

³³ Tokiwa, Y.; Fan, H.; Hiraguri, Y.; Kurane, R.; Kitagawa, M.; Shibatani, S.; Maekawa, Y. "Biodegradation of a Sugar Branched Polymer Consisting of Sugar, Fatty Acid, and Poly(Vinyl Alcohol)," *Macromolecules* 33, (2000), 1636-1639.

polymerization methodologies. The anhydride functionality of the resulting terpolymer was reacted with 2-hydroxyethyl methacrylate to open the anhydride linkage and attach polymerizable unsaturated site. The functionalized copolymer was mixed with the photoinitiator, Irgacure 784, and irradiated with a halogen lamp or ambient sunlight. A significant decrease in the peel strength of the material was observed (up to 79%) due to free radical polymerization of the pendant methacrylate functionalities. In addition, the degree of peel strength reduction corresponded to the dosage of light introduced to the adhesive.

Photocrosslinking has been achieved via a variety of photoactive functional groups.³⁴ In contrast to conventional methodologies that employ photoinitiators functionalities such as coumarins and cinnamates crosslink via a [2+2] cycloaddition that is not a radical driven process.³⁵ The dimerization process associated with these photoactive functionalities involves the cycloaddition of two ethylene groups and is heavily dependant on the dosage of light available and does not exhibit a cascading effect

³⁴ L. M. Minsk, W. P. V. D., & E. M. Robertson "Photosensitization of Polymeric Cinnamic Esters," (U.S. Patent # 2,670,286: 1954): Krauch, C.; Farid, S.; Schenck, G. "Photo-C₄-Cyclodimerisation Von Coumarin," *Chem. Ber.* 99, (1966), 625-633: Schonberg, A.; Latif, N.; Moubasher, R.; Awad, W. "Photochemical Reactions. Part Xv. (a) Photopolymerization of Coumarins and Related Substances. (B) Photo-Addition and -Reduction Processes of Aromatic Ketones," *Journal of the Chemical Society*, (1950), 374-379: Saigo, K.; Yonezawa, N.; Sekimoto, K.; Hasegawa, M.; Ueno, K.; Nakanishi, H. "Optically Active *Anti* Head-to-Head Coumarin Dimer. Resolution, Absolute Configuration, and Molecular Structure," *Bulletin of the Chemical Society of Japan* 58, (1985), 1000-1005: Kuckling, D.; Adler, H. J. P.; Arndt, K. F.; Hoffmann, J.; Plotner, M.; Wolff, T. "Photocrosslinking of Thin Films of Temperature-Sensitive Polymers," *Polymers for Advanced Technologies* 10, (1999), 345-352: Coursan, M.; Desvergne, J. P.; Deffieux, A. "Reversible Photodimerisation of Omega-Anthrylpolystyrenes," *Macromolecular Chemistry and Physics* 197, (1996), 1599-1608: Reiser, A. *Photoreactive Polymers: The Science and Technology of Resists* (Wiley-Interscience, 1989): Zahir, S. "Studies in the Photodimerization of the Diglycidyl Ether of 4,4'-Dihydroxychalcone," *Journal of Applied Polymer Science* 23, (1979), 1355-1372: Oh, D. H. C. a. S. J. "Photochemical Reactions of a Dimethacrylate Compound Containing a Chalcone Moiety in the Main Chain," *European Polymer Journal* 38, (2002), 1559-1564: L. M. Minsk, W. P. V. D., & E. M. Robertson "Photosensitization of Polymers," (U.S. Patent # 2,670,285: 1954): L. M. Minsk, W. P. V. D., & E. M. Robertson "Photosensitization of Cinnamate Acid Esters," (U.S. Patent # 2,670,287: 1954): E. Robertson, W. D., L. Minsk "Photosensitive Polymers. Ii. Sensitization of Poly(Vinyl Cinnamate)," *Journal of Applied Polymer Science* 2, (1959), 308-311: L. M. Minsk, J. G. S., W. P. Van Deusen, & J. F. Wright "Photosensitive Polymers. I. Cinnamate Esters of Poly(Vinyl Alcohol) and Cellulose," *Journal of Applied Polymer Science* 2, (1959), 302-307.

³⁵ Reiser, A. *Photoreactive Polymers: The Science and Technology of Resists* (Wiley-Interscience, 1989): Yujun Zheng, M. M., Sarita V. Mello, Mustapha Mabrouki, Fotios M. Andreopoulos, Veeranjanyulu Konka, Si M. Pham, and Roger M. Leblanc "Peg-Based Hydrogel Synthesis Via the Photodimerization of Anthracene Groups," *Macromolecules* 35, (2002), 5228 -5234.

typical of photoinduced free radical curing mechanisms. Andreopoulos and coworkers recently examined the photocrosslinking of poly(ethylene glycol) (PEG) based hydrogels functionalized with cinnamates.³⁶ 4-Armed PEG (MW=20,000) star-shaped polymers were reacted with cinnamylidene acetyl chloride to yield star polymers with a photoactive periphery. Swelling experiments showed that the polymers were no longer soluble in water. In addition, the photoreversible nature of the [2+2] cycloaddition process was exploited to control the degree of swelling observed in the hydrogels. Photocleavage was induced using lower wavelength light and was utilized to control the degree of swelling of the hydrogel caused by the reversible dimerization or cleavage of crosslinking sites.

In a similar investigation, Andreopoulos used nitrocinnamate groups attached to an eight-arm PEG star in order to increase the sensitivity of the reversible photoreaction via introduction of more crosslinking sites. The surfaces of the hydrogels were studied using environmental scanning electron microscopy (ESEM) and changes in surface topology were observed upon irradiation.³⁷ Photodimerization of the cinnamate groups caused the rough surfaces of the hydrogels to become smooth. Moreover, irradiation with the lower wavelength light caused the hydrogels to revert to their original surface roughness. UV-Vis spectroscopy showed that the nitrocinnamate materials exhibited greater photosensitivity than the cinnamate modified PEG hydrogel.³⁸

³⁶ Andreopoulos, F. M.; Beckman, E. J.; Russell, A. J. "Photoswitchable Peg-Ca Hydrogels and Factors That Affect Their Photosensitivity," *Journal of Polymer Science Part a-Polymer Chemistry* 38, (2000), 1466-1476: Andreopoulos, F. M.; Deible, C. R.; Stauffer, M. T.; Weber, S. G.; Wagner, W. R.; Beckman, E. J.; Russell, A. J. "Photocissable Hydrogel Synthesis Via Rapid Photopolymerization of Novel Peg-Based Polymers in the Absence of Photoinitiators," *Journal of the American Chemical Society* 118, (1996), 6235-6240: Andreopoulos, F. M.; Roberts, M. J.; Bentley, M. D.; Harris, J. M.; Beckman, E. J.; Russell, A. J. "Photoimmobilization of Organophosphorus Hydrolase within a Peg-Based Hydrogel," *Biotechnology and Bioengineering* 65, (1999), 579-588: Economy, J.; Andreopoulos, A. G. "A New Concept for Recycling of Thermosetting Resins .1. The Case of Crosslinkable Copolyesters," *Polymers for Advanced Technologies* 7, (1996), 561-570: Fischer, J.; Henry, R.; Hoover, J.; Lindsay, G.; Stenger-Smith, J.; Chafin, A. P. "Main Chain Chromophoric Polymers with Second Order Nonlinear Optical Properties," (USA: 1993): Zheng, Y. J.; Andreopoulos, F. M.; Micic, M.; Huo, Q.; Pham, S. M.; Leblanc, R. M. "A Novel Photocissile Poly(Ethylene Glycol)-Based Hydrogel," *Advanced Functional Materials* 11, (2001), 37-40.

³⁷ Zheng, Y. J.; Andreopoulos, F. M.; Micic, M.; Huo, Q.; Pham, S. M.; Leblanc, R. M. "A Novel Photocissile Poly(Ethylene Glycol)-Based Hydrogel," *Advanced Functional Materials* 11, (2001), 37-40.

³⁸ Yujun Zheng, M. M., Sarita V. Mello, Mustapha Mabrouki, Fotios M. Andreopoulos, Veeranjanyulu Konka, Si M. Pham, and Roger M. Leblanc "Peg-Based Hydrogel Synthesis Via the Photodimerization of Anthracene Groups," *Macromolecules* 35, (2002), 5228 -5234: Zheng, Y. J.; Andreopoulos, F. M.; Micic,

The coumarin group has also been used extensively since the mid 1960's and has recently been studied as feasible photoreversible functionalities.³⁹ Early efforts by Saegusa and coworkers investigated the photoreversible gelation of polyoxazolines with coumarin functionalities attached to the polymer endgroup. Polymers with various degrees of coumarin modification (1.2-30.4%) were irradiated using a 450 W high-pressure Hg lamp. The researchers utilized UV-Vis to monitor the coumarin λ_{max} changes corresponding to the conversion of coumarin dimerization. The UV-Vis analysis showed 95% of the coumarin groups had dimerized with 350 min. of irradiation at $\lambda > 300$ nm. In addition, UV-Vis data monitoring the photocleavage indicated that 55-60% of the dimers reverted back to the starting material. Furthermore, solubility experiments were performed and the resulting polymer films were soluble in methanol prior to irradiation. The crosslinked polymer was no longer soluble; however, irradiation at 253 nm returned the polymer to its original state and made it fully soluble again.

Chen and coworkers have also extensively studied the reversible photodimerization of coumarin derivatives in poly(vinyl acetate) (PVAc).⁴⁰ 7-Hydroxycoumarin and 7-hydroxy-4-methylcoumarin were synthesized with different alkyl ester chain lengths. These photoactive molecules were dispersed in PVAc and irradiated with > 300 nm light. The photoreversibility of the system was analyzed using UV-Vis spectroscopy to monitor the change in absorbance associated with the photodimerization and cleavage processes. Increasing the length of the alkyl ester chain length resulted in greater rates of dimerization and attachment of a methyl group at the 4 position enhanced the rate of dimerization 200 times. Other efforts have examined the incorporation of groups containing coumarin derivatives into polyacrylates, polyamides,

M.; Huo, Q.; Pham, S. M.; Leblanc, R. M. "A Novel Photocleavable Poly(Ethylene Glycol)-Based Hydrogel," *Advanced Functional Materials* 11, (2001), 37-40.

³⁹ Delzenne, G. A.; Laridon, U. "Photosensitive Polymers I. Synthesis and Properties of Coumarin-Modified Polymers," *36th Congress International De Chimie Industrielle* 3, (1967), 373-378; Chujo, Y.; Sada, K.; Saegusa, T. "Reversible Gelation of Polyoxazoline by Means of Diels-Alder Reaction," *Macromolecules* 23, (1990), 2636-2641; Chujo, Y.; Sada, K.; Saegusa, T. "Polyoxazoline Having a Coumarin Moiety as a Pendant Group. Synthesis and Photogelation," *Macromolecules* 23, (1990), 2693-2697.

⁴⁰ Chen, Y.; Chou, C. F. "Reversible Photodimerization of Coumarin Derivatives Dispersed in Poly(Vinyl Acetate)," *Journal of Polymer Science Part A-Polymer Chemistry* 33, (1995), 2705-2714.

polyurethanes, polyethers, and polyesters.⁴¹ In particular, 7-acryloyloxy-4-methylcoumarin was copolymerized with various alkyl acrylate monomers. The acrylate copolymer was irradiated in chloroform solution at 300 nm for the dimerization process and at 254 nm, for the photocleavage process. Formation of the cyclobutane crosslinks resulted in a decrease in the double bond absorbance at 310 nm. Subsequently, an increase in the 310 nm absorbance was observed upon irradiation at 254 nm as expected. However, it was also determined that irradiation at 254 nm resulted in an equilibrium process between dimerization and cleavage.

2.2 Controlled Free Radical Polymerization

2.2.1 Introduction

Living polymerization routes permit the synthesis of well-defined macromolecules possessing predictable molecular weights, narrow molecular weight distribution, and controlled chemical composition.⁴² Emerging technologies have increasingly required the ability to control macromolecular architecture. Traditionally, control of chain growth polymer architecture has been accomplished using living anionic,⁴³ cationic,⁴⁴ or group-transfer polymerization⁴⁵ methods. However, recent

⁴¹ Chen, Y.; Geh, J. L. "Copolymers Derived from 7-Acryloyloxy-4-Methylcoumarin and Acrylates .1. Copolymerizability and Photocrosslinking Behaviours," *Polymer* 37, (1996), 4473-4480; Chen, Y.; Geh, J. L. "Copolymers Derived from 7-Acryloyloxy-4-Methylcoumarin and Acrylates .2. Reversible Photocrosslinking and Photocleavage," *Polymer* 37, (1996), 4481-4486; Chen, Y.; Wu, J. D. "Preparation and Photoreaction of Copolymers Derived from N-(1-Phenylethyl)Acrylamide and 7-Acryloyloxy-4-Methyl Coumarin," *Journal of Polymer Science Part a-Polymer Chemistry* 32, (1994), 1867-1875; Chen, Y.; Hong, R. T. "Photopolymerization of 7,7'-Coumarinyl Polymethylene Dicarboxylates: Fluorescence and Kinetic Study," *Journal of Polymer Science Part a-Polymer Chemistry* 35, (1997), 2999-3008; Chen, Y.; Jean, C. S. "Polyethers Containing Coumarin Dimer Components in the Main Chain .1. Synthesis by Photopolymerization of 7,7'-(Polymethylenedioxy)Dicoumarins," *Journal of Applied Polymer Science* 64, (1997), 1749-1758; Chen, Y.; Jean, C. S. "Polyethers Containing Coumarin Dimer Components in the Main Chain .2. Reversible Photocleavage and Photopolymerization," *Journal of Applied Polymer Science* 64, (1997), 1759-1768; Chen, Y.; Chen, K. H. "Synthesis and Reversible Photocleavage of Novel Polyurethanes Containing Coumarin Dimer Components," *Journal of Polymer Science Part a-Polymer Chemistry* 35, (1997), 613-624.

⁴² Webster, O. W. "Living Polymerization Methods," *Science* 251, (1991), 887-893.

⁴³ Frontini, G. L.; Elicabe, G. E.; Meira, G. R. "Optimal Periodic Control of a Continuous Living Anionic-Polymerization .2. New Theoretical Results," *Journal of Applied Polymer Science* 33, (1987), 2165-2177; Szwarc, M. "Living" Polymers," *Nature* 178, (1956), 1168-1169.

⁴⁴ Sawamoto, M.; Enoki, T.; Higashimura, T. "End-Functionalized Polymers by Living Cationic Polymerization .1. Mono Functional and Bifunctional Poly(vinyl Ethers) with Terminal Malonate or Carboxyl Groups," *Macromolecules* 20, (1987), 1-6.

developments have demonstrated the extension of controlled polymerizations to stable free radical polymerization (SFRP),⁴⁶ reversible addition-fragmentation transfer polymerization (RAFT),⁴⁷ and atom transfer radical polymerization (ATRP).⁴⁸ For both processes, the living nature of the polymerization arises from the absence of appreciable transfer reactions and the facile reversibility of the termination reactions. The termination steps involve the formation of a weak covalent bond that can be thermally homolytically cleaved to produce a stable radical and a radical capable of propagation.

2.2.2 Synthesis and Characterization of Polymers by Stable Free Radical Polymerization (SFRP) and Reversible Addition-Fragmentation Transfer Polymerization (RAFT)

Initial investigation in the area of living free radical chemistry undertaken by Otsu et al. involved investigation of the use of iniferters in radical polymerizations to control termination and transfer reactions.⁴⁹ The iniferters reversibly react with the growing radical to interchange between a capped dormant state and uncapped propagation state (Figure 2.4). Unfortunately, the iniferter compounds yielded polymers with unsatisfactory polydispersities as compared to other living systems.

⁴⁵ Sogah, D. Y.; Hertler, W. R.; Webster, O. W.; Cohen, G. M. "Group Transfer Polymerization - Polymerization of Acrylic- Monomers," *Macromolecules* 20, (1987), 1473-1488.

⁴⁶ Hawker, C. J. "Molecular-Weight Control by a Living Free-Radical Polymerization Process," *Journal of the American Chemical Society* 116, (1994), 11185-11186.

⁴⁷ Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Moad, G.; Thang, S. H. "Living Radical Polymerization with Reversible Addition- Fragmentation Chain Transfer (Raft Polymerization) Using Dithiocarbamates as Chain Transfer Agents," *Macromolecules* 32, (1999), 6977-6980.

⁴⁸ Wang, J. S.; Matyjaszewski, K. "Controlled Living Radical Polymerization - Halogen Atom- Transfer Radical Polymerization Promoted by a Cu(I)Cu(II) Redox Process," *Macromolecules* 28, (1995), 7901-7910.

⁴⁹ Otsu, T.; Ohya, T. "Head-to-Head Vinyl Polymers. 8. Preparation and Characterization of New Polymers Composed of Head-to-Head and Head-to-Tail Methoxycarbonylethylene Units," *Makromolekulare Chemie, Rapid Communications* 3, (1982), 193-197; Otsu, T.; Yoshida, M. "Role of Initiator-Transfer Agent-Terminator (Iniferter) in Radical Polymerizations: Polymer Design by Organic Disulfides as Iniferters," *Makromolekulare Chemie, Rapid Communications* 3, (1982), 127-132.

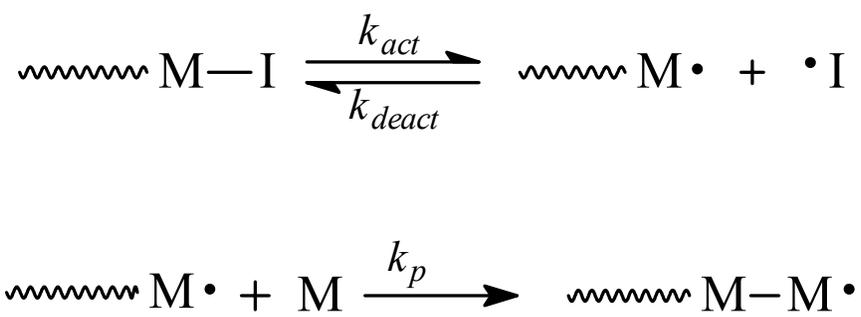


Figure 2.4: Mechanism of living character by use of iniferters (I).

Development of the iniferter technology is most evident in the stable free radical and reversible addition fragmentation chain transfer polymerization techniques, which utilize a stable free radical mediator. In the case of SFRP, the stable free radical species was a nitroxide, such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). The TEMPO nitroxide and other similar analogues were first used in applications as hindered amine light stabilizers or HALS. Research efforts have investigated the use of HALS as radical scavengers and this radical trapping phenomena was extended to the SFRP technique.⁵⁰ Rizzardo, Solomon and Moad were the first to demonstrate that TEMPO reacted with carbon-centered radicals at diffusion-controlled rates generated during free radical polymerization.⁵¹ At temperatures typically associated with the process (40-60 °C), the TEMPO capped molecules were stable and did not participate further in the reaction. Further work investigated the same concept at slightly elevated temperatures (80-100 °C), which yielded low molecular weight oligomers, but generated a basis for future efforts in controlled free radical polymerization.⁵² Following the seminal work of Georges with styrene,⁵³ preliminary experiments with TEMPO and styrene have demonstrated the capability of the system to produce controlled molecular weight polymers with narrow include, acrylates, methacrylates, dienes and acrylamides although the polymerizations of these monomers mediated with TEMPO required complicated reaction conditions and yielded only slightly well-defined polymer products.⁵⁴ On the contrary, monomers with

⁵⁰ Bortolus, P.; Dellonte, S.; Faucitano, A.; Gratani, F. "Photostabilizing Mechanisms of Hindered-Amines Light Stabilizers: Interaction with Electronically Excited Aliphatic Carbonyls," *Macromolecules* 19, (1986), 2916-2922: Sedlar, J.; Marchal, J. "The Determination of Small Amounts of Organic Hydroperoxides in the Presence of Hindered Amine Light Stabilizers and Their Nitroxyls," *Polymer Degradation and Stability* 19, (1987), 251-262: Lucki, J.; Rabek, J. F.; Raanby, B.; Watanabe, Y. "The Role of Hindered Piperidine (Hals) Compounds for the Stabilization of Polypropylene against Oxidation Reactions Caused by Ozone and Oxidative Products Formed During Photolysis of Ozone," *Journal of Applied Polymer Science* 36, (1988), 1067-1085: Moad, G.; Rizzardo, E.; Solomon, D. H.; Beckwith, A. L. J. "Absolute Rate Constants for Radical-Monomer Reactions: The Nitroxide Method," *Polymer Bulletin* 29, (1992), 647-652.

⁵¹ Moad, G.; Rizzardo, E.; Solomon, D. H. "A Product Study of the Nitroxide Inhibited Thermal Polymerization of Styrene," *Polymer Bulletin* 6, (1982), 589-593: Moad, G.; Rizzardo, E.; Solomon, D. H. "Selectivity of the Reaction of Free Radicals with Styrene," *Macromolecules* 15, (1982), 909-914: Rizzardo, E.; Solomon, D. H. "A New Method for Investigating the Mechanism of Initiation of Radical Polymerization," *Polymer Bulletin* 1, (1979), 529-534.

⁵² Solomon, D. H.; Rizzardo, E.; Caciolo, P. "4,581,429," (U.S. Patent: 1986).

⁵³ Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. "Narrow Molecular-Weight Resins by a Free-Radical Polymerization Process," *Macromolecules* 26, (1993), 2987-2988.

⁵⁴ Keoshkerian, B.; Georges, M.; Quinlan, M.; Veregin, R.; Goodbrand, B. "Polyacrylates and Polydienes to High Conversion by a Stable Free Radical Polymerization Process: Use of Reducing Agents,"

molecular weight distributions.⁵⁵ Recent advances have extended the utility of SFRP to chemical structures similar to styrene have shown efficiently controlled polymerizations. One study highlights the polymerization of 4-vinylpyridine for use as a modifier of a silicon substrate.⁵⁶ The polymerization, which resulted in molecular weight distributions of 1.13-1.25, was mediated with 4-hydroxy TEMPO to give a hydroxyl functionalized polymer. Another report detailed the polymerization of a *para*-substituted styrene derivative, dimethyl vinylbenzylphosphonate, mediated with TEMPO.⁵⁷ Again, the polymerization yielded well-defined macromolecules and the characteristics of a controlled polymerization system were observed.

SFRP offers several advantages as an alternative to anionic type living polymerizations. Both techniques have been shown to yield controlled molecular weights and narrow molecular weight distributions. However, anionic polymerizations require precise laboratory techniques in addition to rigorous preparation of the reagents and

Macromolecules 31, (1998), 7559-7561: Li, D. W.; Brittain, W. J. "Synthesis of Poly(N,N-Dimethylacrylamide) Via Nitroxide-Mediated Radical Polymerization," *Macromolecules* 31, (1998), 3852-3855: Listigovers, N. A.; Georges, M. K.; Odell, P. G.; Keoshkerian, B. "Narrow-Polydispersity Diblock and Triblock Copolymers of Alkyl Acrylates by a "Living" Stable Free Radical Polymerization," *Macromolecules* 29, (1996), 8992-8993.

⁵⁵ Zaremski, M. Y.; Plutalova, A. V.; Garina, E. S.; Lachinov, M. B.; Golubev, V. B. "On the Mechanism and Kinetics of Tempo-Mediated Radical Copolymerization," *Macromolecules* 32, (1999), 6359-6362: Hawker, C. J. "'Living" Free Radical Polymerization: A Unique Technique for the Preparation of Controlled Macromolecular Architectures," *Accounts of Chemical Research* 30, (1997), 373-382: MacLeod, P. J.; Veregin, R. P. N.; Odell, P. G.; Georges, M. K. "Stable Free Radical Polymerization of Styrene: Controlling the Process with Low Levels of Nitroxide," *Macromolecules* 30, (1997), 2207-2208: Veregin, R. P. N.; Odell, P. G.; Michalak, L. M.; Georges, M. K. "The Pivotal Role of Excess Nitroxide Radical in Living Free Radical Polymerizations with Narrow Polydispersity," *Macromolecules* 29, (1996), 2746-2754: Hawker, C. J.; Barclay, G. G.; Orellana, A.; Dao, J.; Devonport, W. "Initiating Systems for Nitroxide-Mediated "Living" Free Radical Polymerizations: Synthesis and Evaluation," *Macromolecules* 29, (1996), 5245-5254: Devonport, W.; Michalak, L.; Malmstrom, E.; Mate, M.; Kurdi, B.; Hawker, C. J.; Barclay, G. G.; Sinta, R. "'Living" Free-Radical Polymerizations in the Absence of Initiators: Controlled Autopolymerization," *Macromolecules* 30, (1997), 1929-1934: Wan, X. H.; Tu, H. L.; Tu, Y. F.; Zhang, D.; Sun, L.; Zhou, Q. F.; Dong, Y. P.; Tang, M. "Nitroxide-Mediated Free Radical Synthesis of Mesogen-Jacketed Liquid Crystal Polymers," *Chinese Journal of Polymer Science* 17, (1999), 189-192: Greszta, D.; Matyjaszewski, K. "Mechanism of Controlled/"Living" Radical Polymerization of Styrene in the Presence of Nitroxyl Radicals. Kinetics and Simulations," *Macromolecules* 29, (1996), 7661-7670: Greszta, D.; Matyjaszewski, K. "Living Radical Polymerization: Kinetic Results - Comments," *Macromolecules* 29, (1996), 5239-5240.

⁵⁶ Chen, Z. J.; Cai, J.; Jiang, X. Q.; Yang, C. Z. "Nitroxide-Mediated Radical Polymerization of 4-Vinylpyridine and Its Application on Modification of Silicon Substrate," *Journal of Applied Polymer Science* 86, (2002), 2687-2692.

⁵⁷ Boutevin, B.; Hervaud, Y.; Boulahna, A.; El Asri, M. "Free-Radical Polymerization of Dimethyl Vinylbenzylphosphonate Controlled by Tempo," *Macromolecules* 35, (2002), 6511-6516.

solvents used in the reaction. On the other hand, SFRP necessitates less rigorous lab procedures and purification of the reagents is minimal although the presence of oxygen in the reaction continues to be a concern for the radical process.⁵⁸ Further, SFRP has proven tolerant to the existence of various substituents in common monomers like styrene, which has been successfully polymerized with acetoxy or chloromethyl substituents.⁵⁹ These polymerizations proceeded to a range of adequate molecular weights ($M_n \sim 2500-30000$ g/mol) and moderate polydispersities ($M_w/M_n \sim 1.2-1.3$) below the theoretical limit for radical reactions.

The TEMPO species is superior to the original iniferters due to its ability to remain as a stable radical and not initiate another polymer chain. Furthermore, the reversible homolysis of the carbon oxygen bond only requires heating to ~ 115 °C where the equilibrium becomes essentially a diffusion controlled process. Although this polymerization has proven successful with styrene, extension of the technique to other monomer families requires further manipulation of the reaction conditions to provide greater control.

The polymerization mechanism is key to the successful establishment of a living type system. The basis for the livingness of the SFRP process is the equilibrium that

⁵⁸ Hawker, C. J.; Barclay, G. G.; Dao, J. L. "Radical Crossover in Nitroxide Mediated "Living" Free Radical Polymerizations," *Journal of the American Chemical Society* 118, (1996), 11467-11471; Veregin, R. P. N.; Georges, M. K.; Kazmaier, P. M.; Hamer, G. K. "Free-Radical Polymerizations for Narrow Polydispersity Resins - Electron-Spin-Resonance Studies of the Kinetics and Mechanism," *Macromolecules* 26, (1993), 5316-5320; Skene, W. G.; Scaiano, J. C.; Listigovers, N. A.; Kazmaier, P. M.; Georges, M. K. "Rate Constants for the Trapping of Various Carbon-Centered Radicals by Nitroxides: Unimolecular Initiators for Living Free Radical Polymerization," *Macromolecules* 33, (2000), 5065-5072; Veregin, R. P. N.; Georges, M. K.; Hamer, G. K.; Kazmaier, P. M. "Mechanism of Living Free-Radical Polymerizations with Narrow Polydispersity - Electron-Spin-Resonance and Kinetic-Studies," *Macromolecules* 28, (1995), 4391-4398.

⁵⁹ Barclay, G. G.; Hawker, C. J.; Ito, H.; Orellana, A.; Malenfant, P. R. L.; Sinta, R. F. "The "Living" Free Radical Synthesis of Poly(4-Hydroxystyrene): Physical Properties and Dissolution Behavior," *Macromolecules* 31, (1998), 1024-1031; Kazmaier, P. M.; Daimon, K.; Georges, M. K.; Hamer, G. K.; Veregin, R. P. N. "Nitroxide-Mediated "Living" Free Radical Polymerization: A Rapid Polymerization of (Chloromethyl)Styrene for the Preparation of Random, Block, and Segmental Arborescent Polymers," *Macromolecules* 30, (1997), 2228-2231.

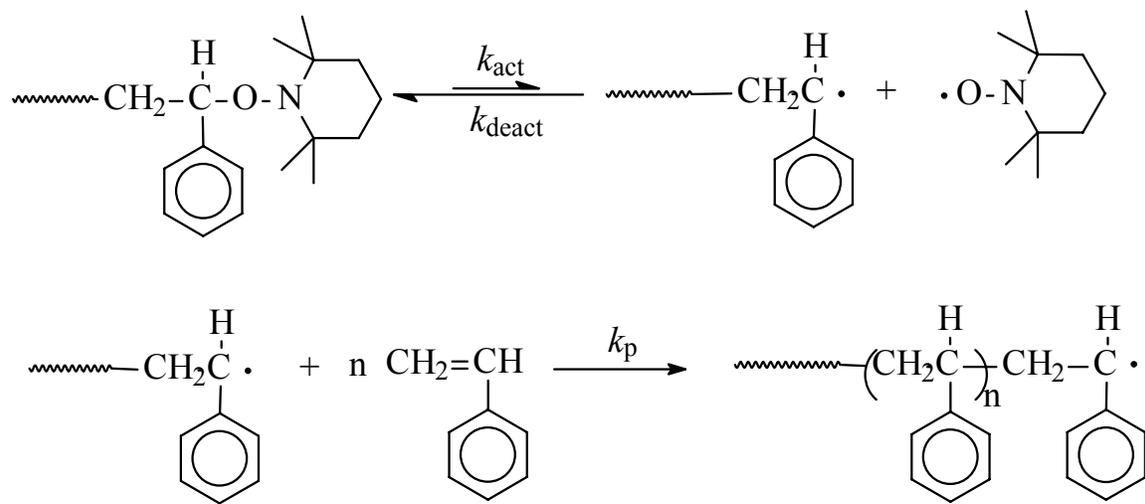
exists between the activated and deactivated species.⁶⁰ The nitroxide radical either caps the carbon-centered radical or exists independently (Scheme 2.1). Recent efforts in the various laboratories have extensively examined the basis of SFRP processes. Fischer has undertaken an examination of the “persistent radical effect” that is responsible for control in any controlled free radical polymerization methodology.⁶¹ The study detailed various rate expressions describing the kinetics associated with the SFRP process. In addition, the concentration profiles for the different reaction species were plotted. The concentration of dormant species remained constant over the course of the polymerization while the persistent radical concentration increased and the transient radical concentration decreased. While this report was based on some experimental data, it was primarily a summation of other research efforts. Consequently, Boutevin and coworkers endeavored to verify the application of the kinetic expressions with actual experimental evidence.⁶² The polymerization of styrene mediated with DEPN was examined and the resulting kinetic data was examined using rate expressions from Fischer’s seminal report. The previously described “persistent radical effect” was distinctly observed in the limit of low viscosity or monomer conversion in a bulk system. Higher viscosities resulted in termination rates that were not negligible. Moreover, the researchers were able to calculate the equilibrium constant for the styrene/DEPN system. Fukuda has performed a similar study in which the polymerization of styrene was studied.⁶³ The polymerization was initiated using a PS-DEPN oligomer and the effects of added BPO were analyzed according to the “persistent radical effect” theory. Experimental evidence again supported the theory described in Fischer’s report showing

⁶⁰ Fukuda, T.; Terauchi, T. "Mechanism of "Living" Radical Polymerization Mediated by Stable Nitroxyl Radicals," *Chemistry Letters*, (1996), 293-294; Fukuda, T.; Terauchi, T.; Goto, A.; Ohno, K.; Tsujii, Y.; Miyamoto, T.; Kobatake, S.; Yamada, B. "Mechanisms and Kinetics of Nitroxide-Controlled Free Radical Polymerization," *Macromolecules* 29, (1996), 6393-6398; Georges, M. K.; Quinlan, M.; Keoshkerian, B.; Odell, P. G. "Stable Free Radical Polymerization (Sfrp) - Limitations?," *Abstracts of Papers of the American Chemical Society* 212, (1996), 161-POLY; Zhu, S.; Wang, W. J. "Analytical Function for Molecular Weight Development in Living Polymerization," *Journal of Polymer Science Part B-Polymer Physics* 37, (1999), 961-964.

⁶¹ Fischer, H. "The Persistent Radical Effect in Controlled Radical Polymerizations," *Journal of Polymer Science Part a-Polymer Chemistry* 37, (1999), 1885-1901.

⁶² Lutz, J. F.; Lacroix-Desmazes, P.; Boutevin, B. "The Persistent Radical Effect in Nitroxide Mediated Polymerization: Experimental Validity," *Macromolecular Rapid Communications* 22, (2001), 189-193.

⁶³ Yoshikawa, C.; Goto, A.; Fukuda, T. "Quantitative Comparison of Theory and Experiment on Living Radical Polymerization Kinetics. 1. Nitroxide-Mediated Polymerization," *Macromolecules* 35, (2002), 5801-5807.



Scheme 2.1: Mechanistic view of TEMPO mediated SFRP.

monomer conversion exhibiting a 2/3-order dependence on time as expected. In addition, they were able to calculate the equilibrium constant of the styrene/DEPN system at 80 °C. Their calculated value agreed well with previously determined values as well as the value predicted using theoretical calculations.

Other research efforts have focused on the different stages of SFRP and the nature of the reaction process during those stages. Zetterlund and coworkers explored the early stages of the stable free radical polymerization of styrene using 1,1,3,3-tetraethylisoindoline-2-oxyl (TEISO) nitroxide to mediate the polymerization.⁶⁴ The styrene polymerization mediated with the TEISO nitroxide proceeded in a living fashion. An alkoxyamine based on TEISO and cumene was synthesized. The bulky nature of the alkyl group allowed homolysis at low temperatures (60 °C). However, addition of styrene and the subsequent capping reaction resulted in inactive polystyrene oligomers. High pressure liquid chromatography of the oligomers showed the presence of nine different species corresponding to unimers, dimers and so on up to octamers. The concentration of these oligomers remains constant over the course of a 6 h reaction indicating that the formation of the oligomers occurred in a single activation cycle. A similar study investigated the trends in various polymer characteristics during the course of a stable free radical polymerization of n-butyl acrylate mediated using DEPN.⁶⁵ The researchers determined that SFRP possessed characteristics of both living anionic polymerization and conventional free radical polymerization, but the living character was dominant. Moreover, they ascertained that the SFRP system shows a non-zero initial mass of polymer which correlates well with the previous data from Zetterlund. Also, they demonstrated that the monomer conversion kinetics were independent of the concentration of the initiator. This was a result of the small equilibrium rate constant

⁶⁴ Cresidio, S. P.; Aldabbagh, F.; Busfield, W. K.; Jenkins, I. D.; Thang, S. H.; Zayas-Holdsworth, C.; Zetterlund, P. B. "Alkoxyamine-Mediated "Living" Radical Polymerization: Ms Investigation of the Early Stages of Styrene Polymerization Initiated by Cumyl-Teiso," *Journal of Polymer Science Part a-Polymer Chemistry* 39, (2001), 1232-1241.

⁶⁵ Chauvin, F.; Alb, A. M.; Bertin, D.; Tordo, P.; Reed, W. F. "Kinetics and Molecular Weight Evolution During Controlled Radical Polymerization," *Macromolecular Chemistry and Physics* 203, (2002), 2029-2041.

associated with the polymerization ($K_{eq}=1.53 \times 10^{-10}$ M), which also lead to living character of the system.

Early investigations also involved the study of more controlled initiating systems. The first SFRP systems used a bimolecular system where benzoyl peroxide (BPO) was employed as a radical source and TEMPO was included as the mediating agent. The original initiating approach possessed the possibility of decomposition products, which led to unfavorable effects on the molecular weight control, architecture, and any control of the polymer chain ends. In order to remedy the situation, Hawker devised a unimolecular initiation system that eliminated many of the issues associated with the bimolecular systems.⁶⁶ The decomposition products such as phenyl radicals and carbon dioxide were eliminated facilitating a lower molecular weight distribution because various types of radicals were no longer being produced simultaneously. The relative reactivities of various radicals produced during the initiator decomposition (Figure 2.5) resulted in different initiation rates.⁶⁷

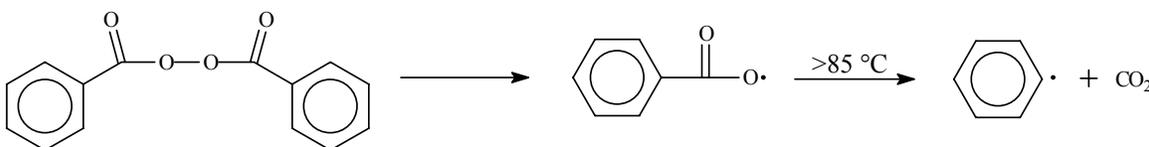


Figure 2.5: Reactions leading to decomposition products of benzoyl peroxide.

Consequently, growth of the polymer chains does not all start simultaneously at the same time, as is the case for many living systems. Unfortunately, the original efforts to produce a unimolecular initiator proved tedious and distracted from the facile nature of the SFRP process. Further investigations have resulted in the synthesis of unimolecular initiating systems requiring fewer steps and simpler isolation techniques.⁶⁸ Chain end

⁶⁶ Hawker, C. J. "Molecular-Weight Control by a Living Free-Radical Polymerization Process," *Journal of the American Chemical Society* 116, (1994), 11185-11186.

⁶⁷ Odian, G. *Principles of Polymerization*, 3rd ed. (New York: John Wiley and Sons, Inc., 1991).

⁶⁸ Wang, D.; Wu, Z. "Facile Synthesis of New Unimolecular Initiators for Living Radical Polymerizations," *Macromolecules* 31, (1998), 6727-6729; Wang, D. K.; Bi, X. D.; Wu, Z. "Convenient Synthesis and Application of a New Unimolecular Initiator," *Macromolecules* 33, (2000), 2293-2295.

control is also addressed with these new initiating systems. This control arose from the fact that the ester bond of the BPO can be reacted before the polymerization to produce a desired end group.⁶⁹ Additionally, the phenyl ring of the BPO possesses the potential of being fluorescently labeled prior to use as an initiator.⁷⁰ In addition to decomposition of the initiating species, SFRP also suffers from possible decomposition of the nitroxide mediator. Early efforts detailed the decomposition mechanism associated with TEMPO, which leads to permanent deactivation of the nitroxide radical.⁷¹ The deactivation occurred via a hydrogen abstraction step. The TEMPO radical typically removed an hydrogen radical from a carbon on the polymer backbone that was usually adjacent to the propagating radical resulting in the formation of a terminal site of unsaturation. The mechanism was investigated using an alkoxyamine model compound. Heating the alkoxyamine at conventional SFRP reaction temperatures resulted in the formation of a TEMPO hydroxylamine and styrene as evidence in the NMR and HPLC analysis. Other research groups have studied similar effects and evaluated the effects on the resulting level of control in the SFRP systems and the side products.⁷² These efforts elucidated an upper limit of monomer conversion that was attainable in a controlled fashion. In addition, appreciable broadening of the molecular weight distributions was observed at these limits supporting the loss of polymerization control.

Another limitation of the TEMPO mediated systems is the long reaction times needed for completion of the reaction. This characteristic is a result of the equilibrium that exists between the dormant and active radical species. The rate of deactivation of the propagating radical is orders of magnitude greater than that of the activating rate. Hence,

⁶⁹ Hawker, C. J.; Hedrick, J. L. "Accurate Control of Chain-Ends by a Novel Living Free-Radical Polymerization Process," *Macromolecules* 28, (1995), 2993-2995.

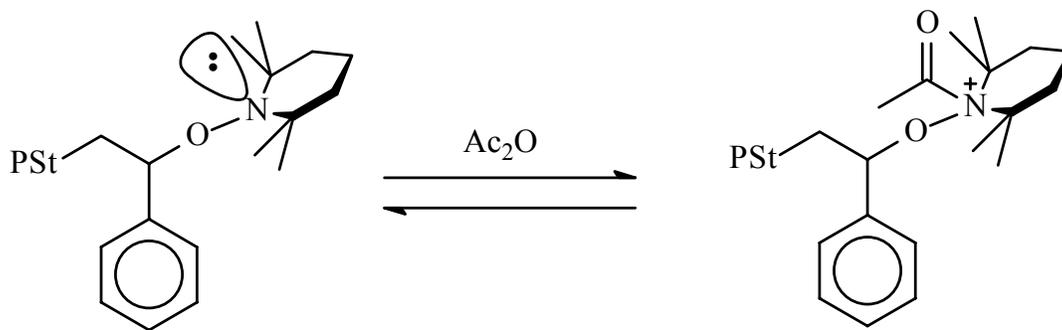
⁷⁰ Frank, B.; Gast, A. P.; Russell, T. P.; Brown, H. R.; Hawker, C. "Polymer Mobility in Thin Films," *Macromolecules* 29, (1996), 6531-6534.

⁷¹ Li, I.; Howell, B. A.; Matyjaszewski, K.; Shigemoto, T.; Smith, P. B.; Priddy, D. B. "Kinetics of Decomposition of 2,2,6,6-Tetramethyl-1-(1-Phenylethoxy)Piperidine and Its Implications on Nitroxyl-Mediated Styrene Polymerization," *Macromolecules* 28, (1995), 6692-6693.

⁷² Souaille, M.; Fischer, H. "Living Free Radical Polymerizations Mediated by the Reversible Combination of Transient Propagating and Persistent Nitroxide Radicals. The Role of Hydroxylamine and Alkene Formation," *Macromolecules* 34, (2001), 2830-2838; Moffat, K. A.; Hamer, G. K.; Georges, M. K. "Stable Free Radical Polymerization Process: Kinetic and Mechanistic Study of the Thermal Decomposition of Mb-Tmp Monitored by Nmr and ESR Spectroscopy," *Macromolecules* 32, (1999), 1004-1012.

the equilibrium lies far to the left in the dormant state. This equilibrium limits the concentration of active radicals slowing the rate of the reaction. In order to enhance the reaction rate, the concentration of the propagating radicals at any moment had to be increased. Additives were employed to reduce the levels of excess TEMPO or activate the TEMPO radical toward homolytic cleavage.⁷³ Georges and coworkers have successfully utilized reducing agents and other polar compounds, such as camphor sulfonic acid (CSA), to control the concentration of excess TEMPO in the reaction mixture that slows the rate. The reducing agents serve to eliminate oxygen, which leads to early termination reactions. In addition, the additives were proposed to react with the excess nitroxide and subsequently reduce its concentration. Initially, CSA was investigated to increase the rate as well as control the degree of autopolymerization occurring in the reaction. This methodology was also employed in the application of 2-fluoro-1-methylpyridinium *p*-toluenesulfonate to the SFRP process. Reducing agents were employed in another case to reduce the amount of oxygen present in the system, which is thought to generate excess nitroxide leading to premature termination of the polymer chains. Hawker and researchers have also attempted to create an environment, which favors the existence of the activated radical species. They proposed the acetylation of the tertiary nitrogen with anhydrides leading to greater propensity of cleavage of the C—ON bond (Scheme 2.2). The electron-withdrawing acyl group on nitrogen renders it more electron deficient causing the nitroxide radical to be more favored than in the absence of acylation. Acylation produces no deleterious effects on control of polymerization.

⁷³ Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K.; Saban, M. "Narrow Polydispersity Polystyrene by a Free-Radical Polymerization Process - Rate Enhancement," *Macromolecules* 27, (1994), 7228-7229; Malmstrom, E.; Miller, R. D.; Hawker, C. J. "Development of a New Class of Rate-Accelerating Additives for Nitroxide-Mediated 'Living' Free Radical Polymerization," *Tetrahedron* 53, (1997), 15225-15236; Odell, P. G.; Veregin, R. P. N.; Michalak, L. M.; Georges, M. K. "Characteristics of the Stable Free Radical Polymerization of Styrene in the Presence of 2-Fluoro-1-Methylpyridinium *P*-Toluenesulfonate," *Macromolecules* 30, (1997), 2232-2237.



Scheme 2.2: Acylation of TEMPO nitrogen.

Manipulation of the stable free radical polymerization rate has been achieved through a variety of other techniques. The mediation equilibrium dictates the rate of SFRP polymerizations. Consequently, changing the direction of that equilibrium can facilitate increases or decreases in the corresponding rate. An investigation by Fukuda explored the effect of introducing radical species into the stable free radical polymerization of styrene.⁷⁴ A free radical initiator, *t*-butyl hydroperoxide (tBHP), was added to a styrene polymerization using an oligomeric alkoxyamine macroinitiator. Systematically increasing the concentration of tBHP resulted in a steady increase in the rate of the polymerization. The observed polymerization rate of styrene was enhanced 3 times without any appreciable broadening of the molecular weight distribution. Unfortunately, no clear mechanistic explanation was provided as to the source of rate enhancement due to tBHP inclusion. In another study, an excess of the nitroxide radical was investigated as a possible method to reduction of polymerization rates.⁷⁵ As expected based on the mediation equilibrium that governs the SFRP kinetics, the introduction of more nitroxide mediator served to retard the rate of the polymerizations of *n*-butyl acrylate. However, no significant effects on the molecular weight distribution and molecular weight were observed. Fischer's seminal work details the various methods

⁷⁴ Goto, A.; Fukuda, T. "Effects of Radical Initiator on Polymerization Rate and Polydispersity in Nitroxide-Controlled Free Radical Polymerization," *Macromolecules* 30, (1997), 4272-4277.

⁷⁵ Lacroix-Desmazes, P.; Lutz, J. F.; Chauvin, F.; Severac, R.; Boutevin, B. "Living Radical Polymerization: Use of an Excess of Nitroxide as a Rate Moderator," *Macromolecules* 34, (2001), 8866-8871.

to manipulate the rate of polymerization in SFRP systems.⁷⁶ Three primary methods of rate manipulation were discussed and included the previously described use of extra conventional initiator or autoinitiation. However, this method was deemed effective only when the polymerization system exhibits high degrees of livingness without the inclusion of the extra initiator. In addition, the generation rate of extra initiating species was required to be slower than the activation step in the mediation equilibrium. Another method for alterations in the rate was via natural or additive induced decay of the persistent free radical nitroxide concentration. The lower nitroxide concentration shifted the equilibrium in favor of the active intermediate and resulted in faster polymerization. A final method was important for systems that do not exhibit high degrees of control due to extremely rapid polymerization rates. This method employed excess mediator to control the concentration and lifetime of the active intermediate. Recent work in Hawker's laboratory has explored chemical methods of enhancing SFRP rates. A set of novel α -hydrogen nitroxide mediators was synthesized and possessed a one, two or three hydroxyl groups. The tendency of nitroxides to hydrogen bond has been previously examined.⁷⁷ Therefore, it was conjectured that the close proximity of the hydrogen bonding hydroxyl functionality would serve to lock in the nitroxide in its inactive form. The polymerization of styrene using these novel mediators was examined and the presence of the hydroxyl group served to increase the rate of the polymerization supporting the hypothesis. Moreover, the nature of the monomer being polymerized affected the degree of the rate enhancement.

A final augmentation to the original scheme for SFRP is the development of an improved mediating species. The mediator is the key component degree of control attainable utilizing the stable free radical methodology and can also significantly affect the rate of polymerization. The original mediator, TEMPO, was limited in the versatility

⁷⁶ Souaille, M.; Fischer, H. "Rate Enhancement and Retardation Strategies in Living Free Radical Polymerizations Mediated by Nitroxides and Other Persistent Species: A Theoretical Assessment," *Macromolecules* 35, (2002), 248-261.

⁷⁷ Beckwith, A. L. J.; Bowry, V. W.; Ingold, K. U. "Kinetics of Nitroxide Radical Trapping .1. Solvent Effects," *Journal of the American Chemical Society* 114, (1992), 4983-4992; Studer, A. "Tin-Free Radical Cyclization Reactions Using the Persistent Radical Effect," *Angewandte Chemie-International Edition* 39, (2000), 1108-1111.

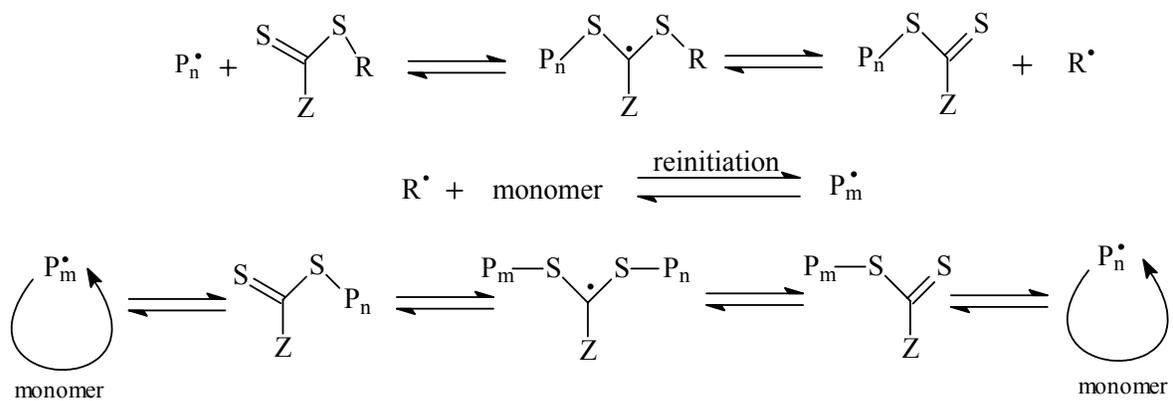
of monomers which it could successfully control the polymerization. Augmentation of the range of nitroxides available for the SFRP process will be discussed further in the following section.

In addition to SFRP and atom transfer radical polymerization (ATRP),⁷⁸ RAFT techniques have been investigated as a supplemental controlled radical method for the synthesis of defined macromolecules. Though comprehension of the RAFT process remains in its infancy, recent studies have elucidated a great deal of information concerning the mechanism and factors affecting this process. The RAFT polymerization mechanism (Scheme 2.3) operates on the reversible addition and fragmentation of the propagating radical to dithioesters, dithiocarbamates, or trithiocarbonates, a stable radical species (Figure 2.6).⁷⁹

The RAFT process offers a significant advantage over other controlled free radical processes in its ability to polymerize a variety of monomers. Further, the process is successful with these monomers in a range of reaction conditions producing narrow molecular weight distributions around 1.2 and as low as 1.04 while still allowing high molecular weights ($M_n \sim 90000$). The original work on investigation of the RAFT process examined the ability of dithioester "RAFT" agents. Thang and coworkers demonstrated the utility of these thioesters, performing polymerizations in bulk, solution, emulsion, and suspension type systems. They were able to produce an array of molecular weights utilizing both peroxide and azo-based initiators. The living nature of the polymerization process was confirmed by the linear correlation between time and conversion. Additionally, the reactions yielded narrow polydispersity polymers with predictable

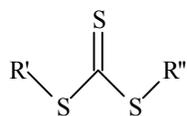
⁷⁸ Patten, T. E.; Matyjaszewski, K. "Atom Transfer Radical Polymerization and the Synthesis of Polymeric Materials," *Advanced Materials* 10, (1998), 901-915.

⁷⁹ Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. "Living Free-Radical Polymerization by Reversible Addition- Fragmentation Chain Transfer: The Raft Process," *Macromolecules* 31, (1998), 5559-5562.



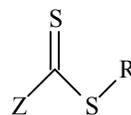
Scheme 2.3: Mechanistic view of living nature of the RAFT process.

Trithiocarbonates



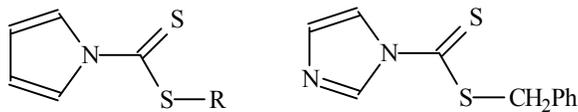
R'=CH₃, CH₂Ph, CH(CH₃)Ph
R''=C(CH₃)₂CN, CH(Ph)CO₂H, CH₂Ph, CH(CH₃)Ph

Dithioesters



Z=Ph
R=C(CH₃)₂Ph, CH(CH₃)Ph, CH₂Ph, C(CH₃)₂CN

Dithiocarbamates



R=CH₂Ph or C(CH₃)₂CN

Figure 2.6: Possible RAFT mediating agents.

molecular weights based on the ratio of monomer to transfer agent. Finally, the ability to form block copolymers and chain extension upon the addition of more monomer verifies the living capability of the macromolecule. Also, in an effort to absolutely verify the existence of the mediating radical species, electron spin resonance spectroscopy (ESR) observation was used in situ to probe the identity of the radical formed during a RAFT polymerization. ESR results exhibited a resonance attributable to the intermediate RAFT agent radical. Additionally, the ESR data proved useful in elucidating the speed of the reversible addition fragmentation mechanism on a relative basis between monomers.⁸⁰ In a similar fashion to the SFRP process, the transfer agent like the mediating compound is key to the controlled capabilities of the polymerization process. The transfer agents, $S=C(Z)SR$, are exchanged between active and dormant chains to generate the living character associated with the RAFT process. The rate of interchange must be fast in relation to the rate of propagation of the active chains to produce a living system. Successful controlled polymerizations have been carried out with the RAFT process using dithioesters,⁸¹ dithiocarbamates,⁸² and trithiocarbonates.⁸³ Dithioesters were used as the original transfer agents and resemble the compound seen in Figure 8. Choice of the R and Z are implicitly linked to the performance of the transfer agent in the RAFT process. A high transfer constant is necessary for the transfer agent to be adequate in establishing a living system. Hence, the Z group must be employed to facilitate the activation of the C=S double bond toward radical addition. Aryl and alkyl substituents are typically found to yield "RAFT" agents with high transfer constants. The R group should be capable of easily leaving the thiocarbonyl moiety and initiating a free radical polymerization. After further investigation, certain dithiocarbamate species demonstrated

⁸⁰ Hawthorne, D. G.; Moad, G.; Rizzardo, E.; Thang, S. H. "Living Radical Polymerization with Reversible Addition- Fragmentation Chain Transfer (Raft): Direct ESR Observation of Intermediate Radicals," *Macromolecules* 32, (1999), 5457-5459.

⁸¹ Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. "Living Free-Radical Polymerization by Reversible Addition- Fragmentation Chain Transfer: The Raft Process," *Macromolecules* 31, (1998), 5559-5562.

⁸² Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Moad, G.; Thang, S. H. "Living Radical Polymerization with Reversible Addition- Fragmentation Chain Transfer (Raft Polymerization) Using Dithiocarbamates as Chain Transfer Agents," *Macromolecules* 32, (1999), 6977-6980.

⁸³ Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Krstina, J.; Moad, G.; Postma, A.; Thang, S. H. "Living Polymers by the Use of Trithiocarbonates as Reversible Addition-Fragmentation Chain Transfer (Raft) Agents: Atriblock Copolymers by Radical Polymerization in Two Steps," *Macromolecules* 33, (2000), 243-245.

the ability to perform controlled free radical polymerization via the RAFT technique. Previously, some dithiocarbamates proved ineffective as RAFT agents. However, it was found that their low transfer constants are primarily the result of the delocalization of the lone pair electrons of the nitrogen onto the C=S double bond. The delocalization of the electron leads to a resonance structure where there is a double bond between the nitrogen and carbon and a single bond between the sulfur and carbon. This decreases the double bond character of the C=S double bond and results in lower reactivity decreasing the transfer constant. Therefore, structures **1** and **2** in Figure 2.7 represent thiocarbamates incapable of acting as RAFT agents. To remedy the issue of delocalized electrons, a ring was introduced that required the lone pair nitrogen electrons to participate in its system to produce an aromatic ring. Compounds **3** and **4** demonstrate the inclusion of a ring in the structure to ensure that the nitrogen lone pair does not serve to deactivate the C=S double bond. Thang and coworkers established the viability of RAFT agents derived from imidazoles and pyrroles exhibiting their ability in the polymerization of styrenic and acrylic type monomers.⁸⁴

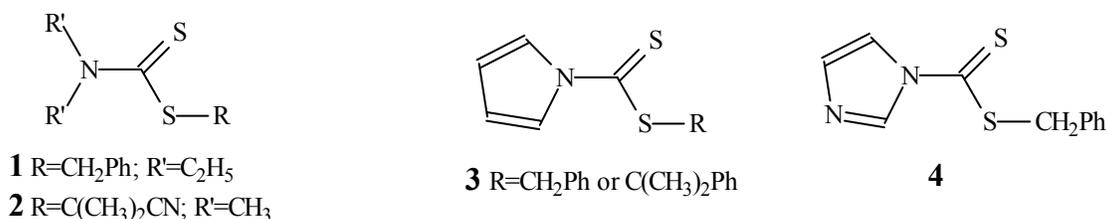


Figure 2.7: Carbamates investigated for use as RAFT agents.

A final manipulation of the transfer agent has been examined in the study of the use of trithiocarbonates (Figure 2.6) in the RAFT process.⁸⁵ These transfer agents have proven effective in the preparation of narrow molecular weight distribution

⁸⁴ Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Moad, G.; Thang, S. H. "Living Radical Polymerization with Reversible Addition- Fragmentation Chain Transfer (Raft Polymerization) Using Dithiocarbamates as Chain Transfer Agents," *Macromolecules* 32, (1999), 6977-6980.

⁸⁵ Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Krstina, J.; Moad, G.; Postma, A.; Thang, S. H. "Living Polymers by the Use of Trithiocarbonates as Reversible Addition-Fragmentation Chain Transfer (Raft) Agents: Atriblock Copolymers by Radical Polymerization in Two Steps," *Macromolecules* 33, (2000), 243-245.

macromolecules. A primary advantage of trithiocarbonates is the ability to perform a two-step polymerization to form an ABA triblock copolymer. The active functional group in the polymerization is located in the center of the polymer. Therefore, the A groups are polymerized first and subsequently the B group is polymerized directly into the middle of the A block. It is important to consider the nature of the solvent being used to ensure that both blocks being synthesized will be sufficiently extended in conformation to allow monomer transport to the reactive center. Verification of the functionality location was accomplished by comparing the molecular weight before and after a polymer with a trithiocarbonate functional group in the center is treated with a nucleophile. The resulting polymer will possess a molecular weight equal to approximately half the molecular weight of the parent polymer. Poly(methyl methacrylate) synthesized via the RAFT process using trithiocarbonate transfer agents exhibited a number average molecular weight of 66,900 g/mol. Following treatment of this polymer with ethylene diamine in THF, the resulting polymer displayed an M_n of 37,900 g/mol. Additionally, it is noted that the polydispersity experiences minimal effects changing from 1.09 in the parent polymer to 1.16 after treatment by the nucleophile. The wide range of available transfer agents for the RAFT process and the tolerance to a variety of monomers illustrates the significance of the RAFT. In addition, the predictable molecular weights produced in the polymerizations augment the value of this process.

In an effort to understand the basis behind the controlled polymerizations, two unconventional monomers will be investigated as candidates for polymerization via SFRP. 2-Vinylnaphthalene and 4-cyanostyrene are unusual monomers not previously examined in the context of the SFRP. Naphthalene derivatives have been used widely in various chromophoric and energy transfer studies.⁸⁶ Vinylnaphthalene is typically seen in two forms with the vinyl group attached at the one or two position (Figure 2.8).

⁸⁶ Geuskens, G.; Soukrati, A. "Investigation of Polyacrylamide Hydrogels Using 1- Anilinonaphthalene-8-Sulfonate as Fluorescent Probe," *European Polymer Journal* 36, (2000), 1537-1546.

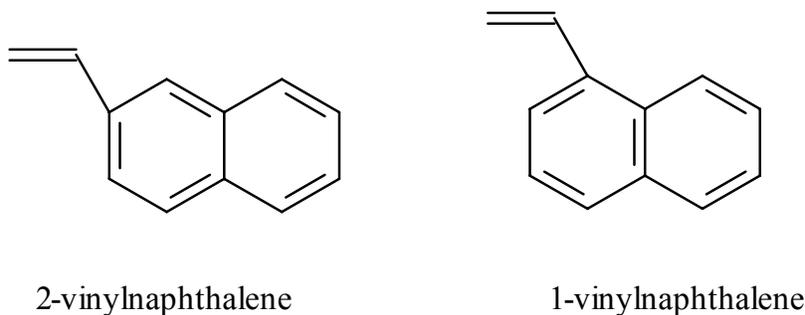


Figure 2.8: Isomers of vinylnaphthalene.

The luminescence studies conducted on the polymer resulting from this monomer indicate its possibility for use as a fluorescent label on the end of a polymer chain. Primary methods of synthesis for the polymers utilized in these studies are simple free radical techniques; however, more recently, it has been shown that poly(2-vinylnaphthalene) can be produced in a living anionic polymerization process.⁸⁷ By producing a “living” chain of poly(2-vinylnaphthalene), it is plausible to subsequently add a supplemental monomer to be polymerized into the chain. This produces a labeled polymer chain that can be tracked by simple fluorescence analysis.⁸⁸

A large range of properties are available with simple modifications of a known monomer or polymer. 4-Cyanostyrene simply requires the attachment of a nitrile group in the para position of a styrene molecule.⁸⁹ Though styrene has been shown to polymerize well with the known controlled free radical processes, introduction of the nitrile substituent complicates the synthesis and results in loss of control in the polymerization. Hence, controlled synthesis of poly(4-cyanostyrene) has primarily been performed using living anionic polymerization techniques.⁹⁰ The potential applications

⁸⁷ Nossarev, G. G.; Hogen-Esch, T. E. "Anionic Polymerization of 2-Vinylnaphthalene," *Polymer Preprints (American Chemical Society, Division of Polymer Chemistry)* 41, (2000), 135-136.

⁸⁸ Kobayashi, T.; Fukaya, T.; Fujii, N. "Fluorescence Probing of Ph Responsive Properties of Polymeric Membranes Having Covalently Bound Naphthalene and Carboxylic Acid Moieties," *Journal of Membrane Science* 164, (2000), 157-166.

⁸⁹ Shirakawa, E.; Yamasaki, K.; Hiyama, T. "Cross-Coupling Reaction of Organostannanes with Aryl Halides Catalyzed by Nickel-Triphenylphosphine or Nickel-Lithium Halide Complex," *Synthesis-Stuttgart*, (1998), 1544-1549.

⁹⁰ Ishizone, T.; Hirao, A.; Nakahama, S. "Anionic-Polymerization of Monomers Containing Functional-Groups .6. Anionic Block Copolymerization of Styrene Derivatives Parasubstituted with Electron-

for the cyano derivative of the styrene are for enhancement of styrenic properties and metal coordination through the nitrile group in collaboration with Hoyt et al.⁹¹

2.2.3 Novel Nitroxide Mediators for SFRP

Although initial efforts in SFRP using TEMPO as the mediating agent proved effective in controlling the polymerization of styrene, extension of the polymerization process to other monomer families including dienes and acrylates was difficult and often resulted in polymer products with broad molecular weight distributions.⁹² Polymerizations involving monomers, such as acrylates, were influenced significantly by the buildup of a large excess of the nitroxide species and lead to slowing of the reaction. This effect is due to the dormant and active chain equilibrium lying heavily in favor of dormant species and termination due to oxygen ingress. Eventually, the excess mediating agent reached levels where the propagation reaction essentially stopped due to those high levels of nitroxide species. The excess effectively halted all propagation because only the dormant state of the radical was present. Georges and coworkers utilized in-situ ESR to monitor the effect of TEMPO concentration on the progress of an SFRP type process.⁹³ Additionally, they were able to examine the effects of the TEMPO concentration on the

Withdrawing Groups," *Macromolecules* 26, (1993), 6964-6975: Ishizone, T.; Sugiyama, K.; Hirao, A.; Nakahama, S. "Anionic-Polymerization of Monomers Containing Functional-Groups .5. Anionic Polymerizations of 2-Cyanostyrene, 3-Cyanostyrene, and 4-Cyanostyrene," *Macromolecules* 26, (1993), 3009-3018: Ishizone, T.; Utaka, T.; Ishino, Y.; Hirao, A.; Nakahama, S. "Anionic Polymerization of Monomers Containing Functional Groups .10. Anionic Polymerizations of N-Aryl-N-(4-Vinylbenzylidene)Amines," *Macromolecules* 30, (1997), 6458-6466.

⁹¹ Hoyt, J. K.; Phillips, J. P.; Riffle, J. S. "Nitrile Containing Polysiloxane Adhesives and Sealants," *Polymeric Materials Science and Engineering* 83, (2000), 23-24.

⁹² Listigovers, N. A.; Georges, M. K.; Odell, P. G.; Keoshkerian, B. "Narrow-Polydispersity Diblock and Triblock Copolymers of Alkyl Acrylates by a "Living" Stable Free Radical Polymerization," *Macromolecules* 29, (1996), 8992-8993: Georges, M. K.; Hamer, G. K.; Listigovers, N. A. "Block Copolymer Synthesis by a Nitroxide-Mediated Living Free Radical Polymerization Process," *Macromolecules* 31, (1998), 9087-9089: Keoshkerian, B.; Georges, M.; Quinlan, M.; Veregin, R.; Goodbrand, B. "Polyacrylates and Polydienes to High Conversion by a Stable Free Radical Polymerization Process: Use of Reducing Agents," *Macromolecules* 31, (1998), 7559-7561: Georges, M. K.; Listigovers, N. A.; Odell, P. G.; Hamer, G. K.; Quinlan, M.; Veregin, R. P. N. "The "Living" Stable Free Radical Polymerization - the Acrylate Conundrum," *Abstracts of Papers of the American Chemical Society* 213, (1997), 50-POLY: Odell, P. G.; Rabien, A.; Michalak, L. M.; Veregin, R. P. N.; Quinlan, M. H.; Moffat, K. A.; MacLeod, P. J.; Listigovers, N. A.; Honeyman, C. H.; Georges, M. K. "The Pivotal Role of Nitroxide Concentration in Stable Free Radical Polymerization of Acrylates," *Abstracts of Papers of the American Chemical Society* 214, (1997), 183-POLY.

⁹³ Moffat, K. A.; Hamer, G. K.; Georges, M. K. "Stable Free Radical Polymerization Process: Kinetic and Mechanistic Study of the Thermal Decomposition of Mb-Tmp Monitored by Nmr and ESR Spectroscopy," *Macromolecules* 32, (1999), 1004-1012.

kinetics of SFRP and showed that the kinetics respond to the gradual decline in TEMPO concentration as the reaction proceeds. Several researchers have investigated alternative nitroxide mediators in order to extend the range of controllable monomers to include acrylates, dienes and acrylamides.⁹⁴ The presence of an α -hydrogen seemed to be structurally significant in enhancing the capability to maintain low levels of excess mediator. Gnanou was the first to show this significance, demonstrating that the α -hydrogen enabled extensive control over the polymerization process of n-butyl acrylate.⁹⁵ This *N-tert-butyl-N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (DEPN) molecule included an open chain structure and a phosphonate ester functionality and exhibited results superior to those obtained with the simple TEMPO mediator. The source of the improved control resulting from utilization of the α -hydrogen nitroxide stemmed from a combination of factors. Both steric and electronic factors influenced the nature of the SFRP equilibrium that exists in a nitroxide mediated polymerization.⁹⁶ Fukuda measured and studied the rate constants of activation in order to examine the effect of the nitroxide structure on resulting equilibrium.⁹⁷ In this report, the conventional TEMPO mediator was investigated in addition to di-*tert*-butyl nitroxide (DBN) and the novel DEPN mediator (Figure 2.9).

Comparison of the TEMPO and DBN mediators allowed the elucidation of the steric effects involved in the mediation process. The rate constant for activation (k_{act})

⁹⁴ Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. "Development of a Universal Alkoxyamine for "Living" Free Radical Polymerizations," *Journal of the American Chemical Society* 121, (1999), 3904-3920; Li, D. W.; Brittain, W. J. "Synthesis of Poly(N,N-Dimethylacrylamide) Via Nitroxide-Mediated Radical Polymerization," *Macromolecules* 31, (1998), 3852-3855; Grimaldi, S.; Finet, J. P.; Le Moigne, F.; Zeghdaoui, A.; Tordo, P.; Benoit, D.; Fontanille, M.; Gnanou, Y. "Acyclic Beta-Phosphonylated Nitroxides: A New Series of Counter-Radicals for "Living"/Controlled Free Radical Polymerization," *Macromolecules* 33, (2000), 1141-1147.

⁹⁵ Benoit, D.; Grimaldi, S.; Robin, S.; Finet, J. P.; Tordo, P.; Gnanou, Y. "Kinetics and Mechanism of Controlled Free-Radical Polymerization of Styrene and N-Butyl Acrylate in the Presence of an Acyclic Beta-Phosphonylated Nitroxide," *Journal of the American Chemical Society* 122, (2000), 5929-5939; Benoit, D.; Grimaldi, S.; Finet, J. P.; Tordo, P.; Fontanille, M.; Gnanou, Y. "Controlled Free-Radical Polymerization in the Presence of a Novel Asymmetric Nitroxyl Radical," *Abstracts of Papers of the American Chemical Society* 213, (1997), 465-POLY.

⁹⁶ Sobek, J.; Martschke, R.; Fischer, H. "Entropy Control of the Cross-Reaction between Carbon-Centered and Nitroxide Radicals," *Journal of the American Chemical Society* 123, (2001), 2849-2857.

⁹⁷ Goto, A.; Fukuda, T. "Comparative Study on Activation Rate Constants for Some Styrene/Nitroxide Systems," *Macromolecular Chemistry and Physics* 201, (2000), 2138-2142.

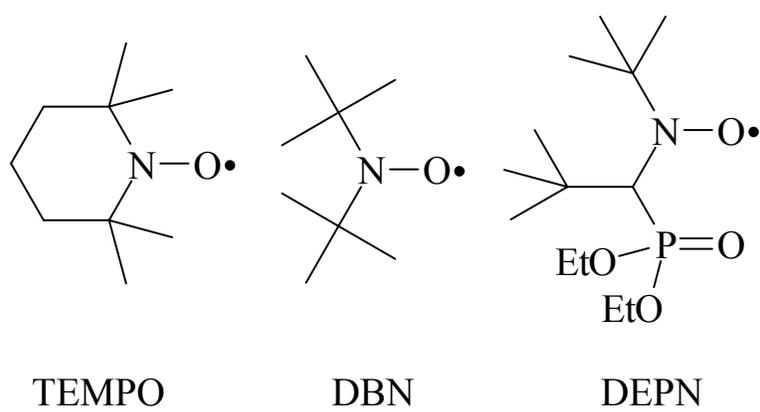


Figure 2.9: Nitroxide mediators studied to examine nitroxide structure effects on SFRP equilibrium.

associated with the open chain DBN was higher than that observed using the TEMPO mediator indicating a greater propensity to exist in the active intermediate state under DBN mediation. The Arrhenius enthalpic and entropic parameters were also determined (Table 2.1) to examine the electronic and steric contributions. Steric effects resulting from bulky groups attached to the nitroxide nitrogen were reflected in the entropic frequency factor (A_{act}). An enthalpic factor (E_{act}) was also determined and reflects both the electronic and steric effects of the system.

Table 2.1: Arrhenius parameters and rate constant of activation for several nitroxides.⁹⁸

Alkoxyamine	A_{act}/s^{-1}	$E_{act}/(kJ/mol)$	$10^3 k_{act}/s^{-1}$
PS-TEMPO	3.0×10^{13}	124	1.0
PS-DBN	3.8×10^{14}	120	42
PS-DEPN	2.0×10^{15}	130	11

As expected, the steric effects of the DBN open chain structure resulted in a order of magnitude higher A_{act} compared to TEMPO. The E_{act} for DBN was only slightly higher than that observed for the DBN reflecting the similar electronic nature of the two mediators. Comparison of DBN and DEPN demonstrated an extension of the previously observed trend with DEPN possessing a higher A_{act} due to bulkier side groups. However, the higher E_{act} parameter observed for DEPN compared to DBN indicated that the electronic withdrawing effects attributed to the presence of the phosphonate functionality were more significant in dictating the enthalpic parameter of the activation rate constant than the steric factors. This work by Fukuda involved the study of the dissociation of polystyryl-nitroxide adducts. Other studies by Hans Fischer, examined identical reaction parameters using low molecular weight alkoxyamine adducts for 27 different nitroxide

⁹⁸ Goto, A.; Fukuda, T. "Comparative Study on Activation Rate Constants for Some Styrene/Nitroxide Systems," *Macromolecular Chemistry and Physics* 201, (2000), 2138-2142.

mediating agents.⁹⁹ The results of this study demonstrated similar trends associated with the different nitroxide mediators. The effects of the alkyl group structure of the alkoxyamine on the resulting studies will be discussed later. In addition to the phosphonylated nitroxides introduced by Gnanou, Hawker simultaneously demonstrated the utilization of a series of phenyl containing nitroxides that also possess an α -hydrogen.¹⁰⁰ Using these novel mediating agents, the researchers were able to polymerize a series of monomers in homopolymerizations and copolymerizations with styrene and butyl acrylate. Homopolymerizations of functional monomers such as acrylonitrile and *N,N*-dimethylacrylamide proceeded to high conversions and the resulting polymer products exhibited molecular weight distributions from 1.12-1.21 and high molecular weights approaching 50,000 g/mol. In addition, copolymerizations of styrene and butyl acrylate with comonomers possessing functionalities such as a basic amine, a carboxylic acid, a perfluorinated alkyl chain, or a glycidyl group. Only in the case of the carboxylic acid and glycidyl functionality was percentage of comonomer limited to 50% or less. In addition to the two seminal works by Gnanou and Hawker, several other efforts have examined the effects of nitroxide structure manipulations on the control of the SFRP process. Georges utilized a 4-oxo-TEMPO nitroxide to control the polymerization of acrylates. However, molecular weight distributions of the resulting polymers were still relatively broad (1.4-1.67) and the integrity of the polymer end group was questionable.¹⁰¹

Another investigation performed in the Matyjaszewski laboratories, employed a TEMPO derivative with a phosphonic acid group in the 4-position.¹⁰² The hydrogen bonding associated with the phosphonic acid group altered the nature of the mediation

⁹⁹ Marque, S.; Le Mercier, C.; Tordo, P.; Fischer, H. "Factors Influencing the C-O-Bond Homolysis of Trialkylhydroxylamines," *Macromolecules* 33, (2000), 4403-4410.

¹⁰⁰ Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. "Development of a Universal Alkoxyamine for "Living" Free Radical Polymerizations," *Journal of the American Chemical Society* 121, (1999), 3904-3920.

¹⁰¹ Keoshkerian, B.; Georges, M.; Quinlan, M.; Veregin, R.; Goodbrand, B. "Polyacrylates and Polydienes to High Conversion by a Stable Free Radical Polymerization Process: Use of Reducing Agents," *Macromolecules* 31, (1998), 7559-7561.

¹⁰² Matyjaszewski, K.; Gaynor, S. G.; Greszta, D.; Mardare, D.; Shigemoto, T.; Wang, J. S. "Unimolecular and Bimolecular Exchange-Reactions in Controlled Radical Polymerization," *Macromolecular Symposia* 95, (1995), 217-231.

equilibrium for that nitroxide. This early work led to further investigations into intramolecular and intermolecular hydrogen bonding effects¹⁰³ on other nitroxides. In particular, a group in Europe examined H-bonding effects on the C—O bond homolysis of low molecular weight alkoxyamines.¹⁰⁴ The proposed mechanism of hydrogen bonding is an interaction of the hydrogen bonding donor functionality with the oxygen atom of the nitroxide molecule (Figure 2.10). Homolysis of a nonpolar alkoxyamine in polar and nonpolar solvents showed a distinct difference in the rate of the reaction. Introduction of the polar solvent led to faster dissociation of the C—O bond. Moreover, covalent attachment of a hydrogen bonding donor to the nitroxide significantly

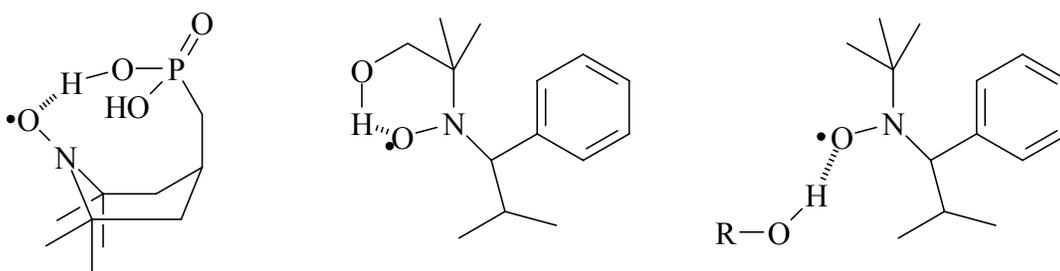


Figure 2.10: Nitroxide intramolecular and intermolecular hydrogen bonding.¹⁰⁵

accelerated the rate of C—O bond homolysis. In order to eliminate differences in the polarity caused by attachment of the hydroxyl functionality, the hydrogen bonding studies were performed on hydroxy and methoxy functional analogues that possess approximately similar polar character. The alkoxyamine derivative possessing a hydroxyl group on the β -carbon of the nitroxide (Figure 2.10) exhibited a faster rate of dissociation ($k_d=2.9 \times 10^{-3} \text{ s}^{-1}$) compared to the same molecule possessing a methoxy functionality at the same β -carbon location ($k_d=1.3 \times 10^{-3} \text{ s}^{-1}$). Further evidence for the presence of intramolecular hydrogen bonding was established using electron spin

¹⁰³ Beckwith, A. L. J.; Bowry, V. W.; Ingold, K. U. "Kinetics of Nitroxide Radical Trapping .1. Solvent Effects," *Journal of the American Chemical Society* 114, (1992), 4983-4992.

¹⁰⁴ Marque, S.; Fischer, H.; Baier, E.; Studer, A. "Factors Influencing the C-O Bond Homolysis of Alkoxyamines: Effects of H-Bonding and Polar Substituents," *Journal of Organic Chemistry* 66, (2001), 1146-1156.

¹⁰⁵ Beckwith, A. L. J.; Bowry, V. W.; Ingold, K. U. "Kinetics of Nitroxide Radical Trapping .1. Solvent Effects," *Journal of the American Chemical Society* 114, (1992), 4983-4992.

resonance (ESR) measurements. Nitroxides can exist in one of two resonance states (Figure 2.11).¹⁰⁶ The ESR hyperfine coupling constant (a_N) associated with a triol alkoxyamine and a protected triol alkoxyamine were studied to examine hydrogen bonding interactions. The presence of hydrogen bonding donor groups stabilized structure **B** in Figure 2.11 and lead to an increase in the hyperfine coupling constant. On the other hand, the alkoxyamine that possessed no hydrogen bonding groups exhibited a coupling constant consistent with a nitroxide radical.

Hawker extended the investigation of the hydrogen bonding nitroxide to the polymerization of butyl acrylate.¹⁰⁷ Attachment of a single hydroxyl functionality to the nitroxide yielded a slight increase in the rate of polymerization of styrene.¹⁰⁸ Subsequently, three hydroxyl groups were added to the nitroxide structure and the resulting nitroxide was again employed in the controlled polymerization of styrene. The researcher observed a ~50% increase in the rate of the polymerization allowing high monomer conversion in 3-4 hours. Interestingly, the application of this tris-hydroxy nitroxide to the controlled polymerization of acrylates resulted in a dramatic order of magnitude increase in the rate of polymerization. Dienes and acrylamides were also examined and differing degrees of rate enhancement were observed for each monomer family. In addition to acceleration of the polymerization, the novel mediator also allowed for a reduction in the polymerization temperatures without sacrificing control or conversion.

Other researchers have examined nitroxide derivatives that more closely resembled the original TEMPO mediator introduced by Georges.¹⁰⁹ Some work examined the use of TEMPO functionalized at the 4-position with oxo- and acetamido-

¹⁰⁶ Janzen, E. G. *Topics in Stereochemistry*, ed. E. L. Eliel, vol. 6 (New York: Wiley Interscience, 1971).

¹⁰⁷ Harth, E.; Van Horn, B.; Hawker, C. J. "Acceleration in Nitroxide Mediated 'Living' Free Radical Polymerizations," *Chemical Communications*, (2001), 823-824.

¹⁰⁸ Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. "Development of a Universal Alkoxyamine for "Living" Free Radical Polymerizations," *Journal of the American Chemical Society* 121, (1999), 3904-3920.

¹⁰⁹ Veregin, R. P. N.; Georges, M. K.; Hamer, G. K.; Kazmaier, P. M. "Mechanism of Living Free-Radical Polymerizations with Narrow Polydispersity - Electron-Spin-Resonance and Kinetic-Studies," *Macromolecules* 28, (1995), 4391-4398.

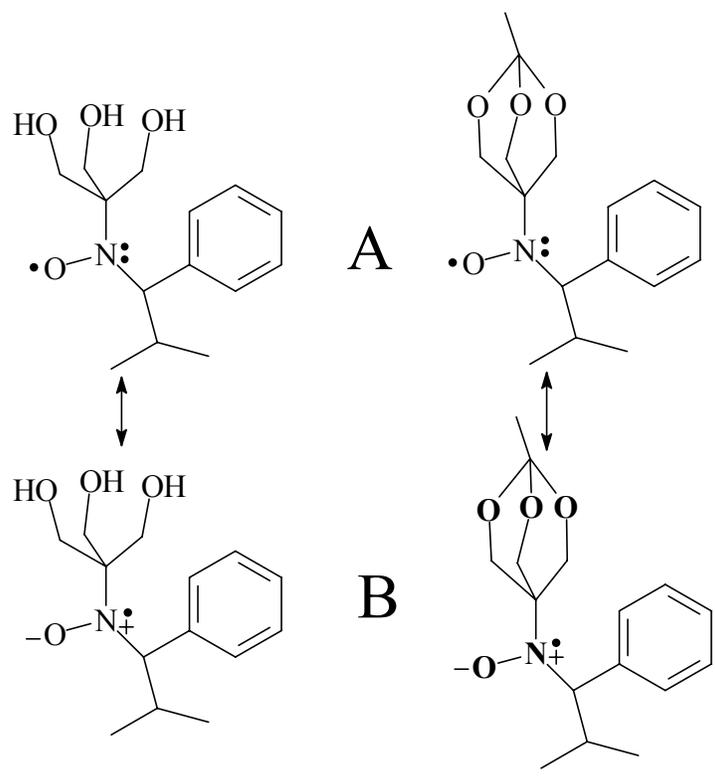


Figure 2.11: Resonance structures for triol alkoxyamine and protected triol alkoxyamine.

functionalities.¹¹⁰ Addition of these substituents to the nitroxide mediator resulted in an accelerated polymerization of styrene compared to TEMPO mediation. The size of the group in the α -position of the nitroxide also significantly affected the mediation performance.¹¹¹ Nitroxides possessing spiro structures (Figure 2.12) were employed in the polymerization of styrene. Conventional SFRP of styrene using TEMPO requires polymerization temperatures above 110 °C to yield well-defined macromolecules. Introduction of the spiro structures allowed efficiently controlled styrene stable free radical polymerization to proceed at temperatures as low as 70 °C. Polymerizations temperatures from 70-100 °C yielded products with molecular weight distributions below 1.3 and predicted molecular weights agreed well with the experimentally determined values. Calculated mediation equilibrium constants for the spiro nitroxides were two orders of magnitude higher than the equilibrium constant associated with a TEMPO mediated process.

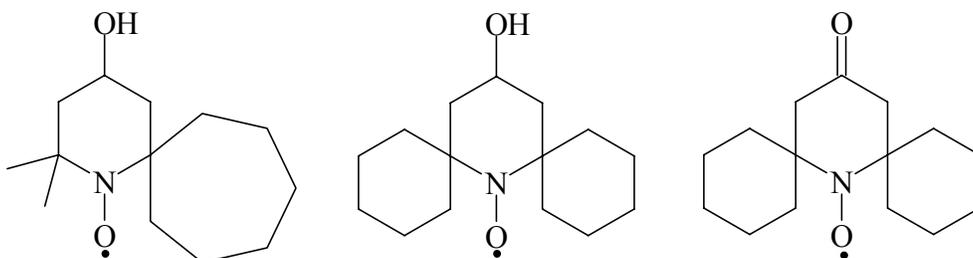


Figure 2.12: Nitroxides possessing spiro type structures.

Other efforts by Georges investigated the use of five member 2,2',5,5'-tetramethylpyrrolidine-*N*-oxyl (PROXYL) nitroxide to mediate the polymerization of styrene. The strength of the C—O bond determined using ESR was approximately 25 kJ/mol less than the bond strength associated with a TEMPO C—O bond. Moreover,

¹¹⁰ Han, C. H.; Drache, M.; Baethge, H.; Schmidt-Naake, G. "3-Oxo-2,2,6,6-Tetramethylpiperidine-*N*-Oxyl (4-Oxo-Tempo)- and 4-Acetamido-2,2,6,6-Tetramethylpiperidine-*N*-Oxyl (4-Acetamido-Tempo)-Controlled Free Radical Polymerization of Styrene," *Macromolecular Chemistry and Physics* 200, (1999), 1779-1783.

¹¹¹ Miura, Y.; Nakamura, N.; Taniguchi, I. "Low-Temperature "Living" Radical Polymerization of Styrene in the Presence of Nitroxides with Spiro Structures," *Macromolecules* 34, (2001), 447-455.

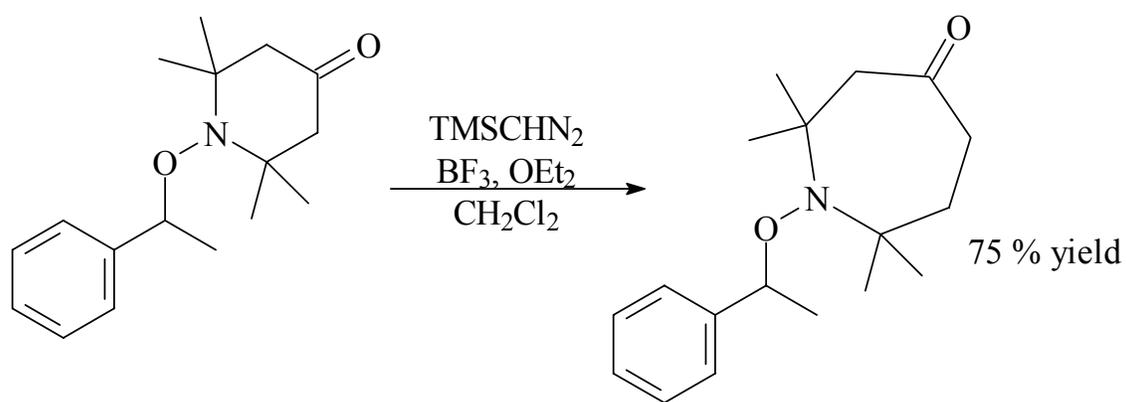
efforts focused on substitution on the ring to further weaken the C—O bond and enhance the rate of these controlled free radical polymerizations.¹¹² Polymerization control using the substituted PROXYL nitroxides was similar to that observed using the TEMPO mediated process. The polymerization products exhibited a linear relationship between molecular weight and conversion and the resulting molecular weight distributions were narrow (<1.48).¹¹³ Investigations of the unsubstituted PROXYL nitroxide styrene polymerization kinetics revealed similar polymerization rates compared to styrene mediated with TEMPO. However, addition of a phenyl group to the α -position significantly accelerated the rate of styrene monomer conversion. The researchers attributed this enhancement to a shift in the mediation equilibrium towards the reactive radical intermediate. The shift was a result of increased steric bulk around the C—O bond from the phenyl substituent. Although some success was achieved via reduction in the nitroxide ring size and addition of substituents, some workers have also examined the effect of enlarging the nitroxide ring size.¹¹⁴ The report details the synthesis of seven and eight membered cyclic nitroxides via ring enlargement of smaller alkoxyamines derived from ketone containing nitroxides such as 4-oxo-TEMPO. The ring enlargement was achieved using the TMS-diazomethane method (Scheme 2.4).

In addition to keto-alkoxyamines, the hydroxyl containing nitroxide moieties were obtained via sodium borohydride reduction in methanol of the keto-precursors. These alkoxyamines were subsequently utilized in the controlled polymerization of both styrene and butyl acrylate. In general, the novel mediators yielded relatively controlled polymerizations of styrene up to 40,000 g/mol with molecular weight distributions typically ranging from 1.2-1.5; however, linear correlations between molecular weight

¹¹² Puts, R. D.; Sogah, D. Y. "Control of Living Free-Radical Polymerization by a New Chiral Nitroxide and Implications for the Polymerization Mechanism," *Macromolecules* 29, (1996), 3323-3325; Yamada, B.; Miura, Y.; Nobukane, Y.; Aota, M., "Controlled Radical Polymerizations" (paper presented at the American Chemical Society National Meeting, Washington, D.C., 1998); Yamada, B.; Miura, Y.; Nobukane, Y.; Aota, M. "Styrene Polymerization Mediated by Five-Membered Cyclic Nitroxides," *Abstracts of Papers of the American Chemical Society* 213, (1997), 463-POLY.

¹¹³ Cameron, N. R.; Reid, A. J.; Span, P.; Bon, S. A. F.; van Es, J.; German, A. L. "Studies on Controlled Radical Polymerisation Using 5-Membered Cyclic Proxyl Nitroxides and Corresponding Alkoxyamines," *Macromolecular Chemistry and Physics* 201, (2000), 2510-2518.

¹¹⁴ Schulte, T.; Studer, A. "New Seven- and Eight-Membered Cyclic Alkoxyamines for the Living Free Radical Polymerization," *Macromolecules* 36, (2003), 3078 -3084.



Scheme 2.4: Ring enlargement reaction to produce seven and eight-membered cyclic nitroxide moieties.

and conversion were observed. These mediating system were then tested in the polymerization of butyl acrylate. Polymer products generally exhibited broadened molecular weight distributions indicating only modest control of the polymerization of the acrylate monomer. ESR was further employed to investigate the C—O bond dissociation energy (BDE) and resulted indicated that increasing the ring size systematically lowers the BDE as expected.

In addition to enhancing the control of the polymerization, manipulation of the structure of the nitroxide mediator was utilized to enable dual functionality of the mediating agent. In one report, commercially available 4-hydroxy TEMPO was used a nucleophile to synthesize a nitroxide radical with a polymerizable group attached through the 4-position.¹¹⁵ A methacrylate and styrenic derivative of the polymerizable nitroxide was accomplished by reaction with methacryloyl chloride and 4-chloromethylstyrene, respectively (Figure 2.13).

The vinyl group attached to the nitroxide was randomly incorporated into the polymer and subsequently the mobility of the nitroxide mediator was significantly reduced. The reduction in mobility resulted in a shift in the mediation in favor of the active intermediate. This shift was directly reflected in the rate of the styrene polymerization mediated with the vinyl-functionalized nitroxide, which was accelerated compared to a similar polymerization mediated with 4-hydroxy TEMPO. Another distinct difference in the polymerization using the polymerizable nitroxide was the resulting macromolecular structure. A branched structure resulted from the random attachment of propagating chains to the nitroxide functionalities positioned along the polymer backbone upon cooling. A characteristic multimodal SEC chromatogram was observed as a result of the branched structure and consequently the corresponding molecular weight distributions were large. The branched macromolecule was treated

¹¹⁵ Li, C. M.; He, J. P.; Li, L.; Cao, J. Z.; Yang, Y. L. "Controlled Radical Polymerization of Styrene in the Presence of a Polymerizable Nitroxide Compound," *Macromolecules* 32, (1999), 7012-7014; Tao, Y. F.; He, J. P.; Wang, Z. M.; Pan, J. Y.; Jiang, H. J.; Chen, S. M.; Yang, Y. L. "Synthesis of Branched Polystyrene and Poly(Styrene-B-4-Methoxystyrene) by Nitroxyl Stable Radical Controlled Polymerization," *Macromolecules* 34, (2001), 4742-4748.

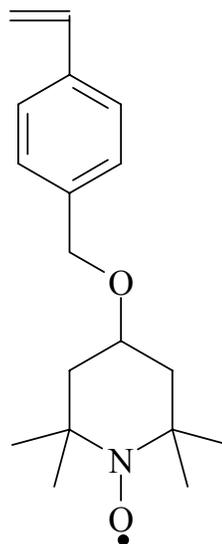
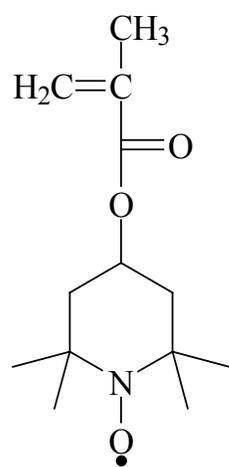
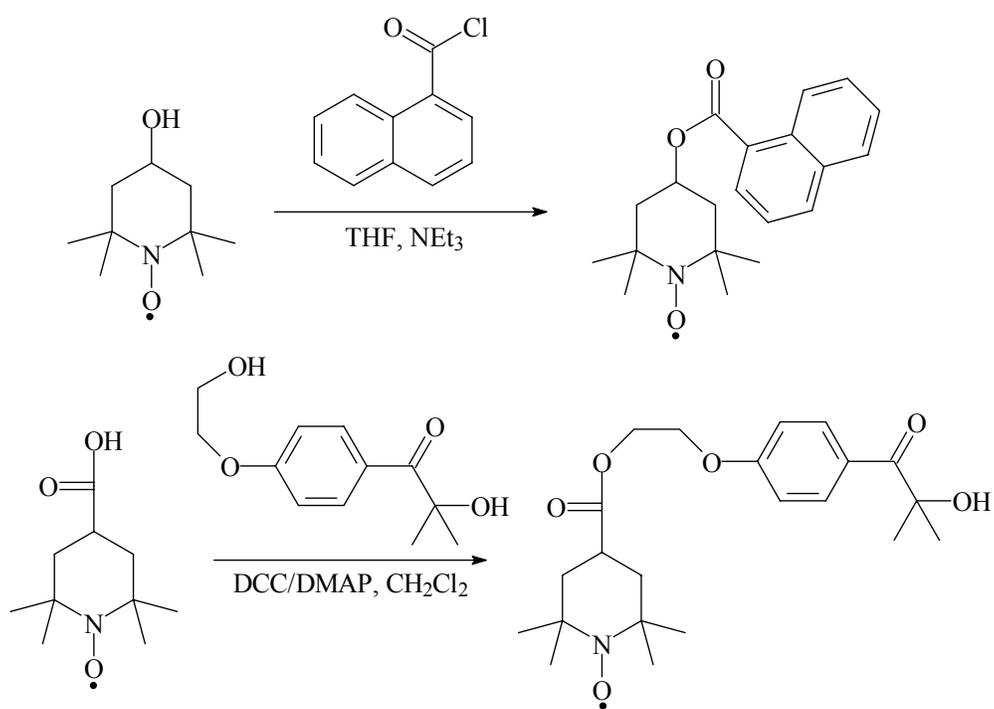


Figure 2.13: Nitroxide free radicals possessing a polymerizable vinyl group.

with heat and ascorbic acid or phenylhydrazine to cleave the branch points and irreversibly cap the nitroxide functionalities. Upon post-polymerization treatment, the SEC chromatograms returned to the conventional SFRP shape exhibiting narrow, monomodal distribution that overlapped with the low molecular weight shoulder of the branched SEC chromatograms. This result indicated that the polymer products were a mixture of both branched and linear polystyrene. The branched polymer products were further utilized as macroinitiators for the polymerization of 4-methoxystyrene. The solution polymerizations in toluene displayed an increase in viscosity with reaction time and proton NMR of the resulting polymer product exhibited a distinct resonance at 3.8 ppm characteristic of methoxy hydrogens.

Turro et al and Ballesteros et al. performed another manipulation of the nitroxide structure was wherein they attached a photoactive group to the end of a polymer chain.¹¹⁶ In Turro's report, the functionalized nitroxide derivatives were obtained using nitroxide substituted with a hydroxyl or carboxylic acid functionality at the 4-position (Scheme 2.5). In the case of the hydroxyl containing nitroxide, the precursor was reacted with an acid chloride attached to a photoactive species. On the other hand, a photoactive group possessing an aliphatic hydroxyl functionality was employed to react with the carboxylic acid group of the nitroxide precursor. Both photoactive nitroxides were synthesized in greater than 60 % yields. The resulting nitroxide free radicals were subsequently employed in the controlled polymerization of the styrene. The researchers indicated that the polymer products contained the nitroxides used in the polymerization based on NMR and fluorescence spectroscopy. However, no data was presented to describe the nature of the products such as molecular weight and polydispersity. In the nitroxide labeled with a naphthyl group, fluorescence of the naphthyl group was significantly reduced due to the presence of the radical. Upon capping of the polymer chain, the radical was no longer present and the resulting fluorescence increased. This phenomena was employed to study

¹¹⁶ Turro, N. J.; Lem, G.; Zavarine, I. S. "A Living Free Radical Exchange Reaction for the Preparation of Photoactive End-Labeled Monodisperse Polymers," *Macromolecules* 33, (2000), 9782-9785; Ballesteros, O. G.; Maretti, L.; Sastre, R.; Scaiano, J. C. "Kinetics of Cap Separation in Nitroxide-Regulated "Living" Free Radical Polymerization: Application of a Novel Methodology Involving a Prefluorescent Nitroxide Switch," *Macromolecules* 34, (2001), 6184-6187.



Scheme 2.5: Functional nitroxide radicals possessing photoactive groups.

the length of time that passed before the nitroxide concentration reached a steady state. Fluorescence spectra increased over the course of the polymerization due to nitroxide capping of the propagating polymer radicals until 45 min indicating that the free nitroxide concentration had reached a steady state. Mediation of a styrene polymerization using the nitroxide derived from the dihydroxy ketone yielded a polymer with a photoactive initiating group attached to the end of the polymer chain. The resulting polymer could act as a macroinitiator for a subsequent polymerization.

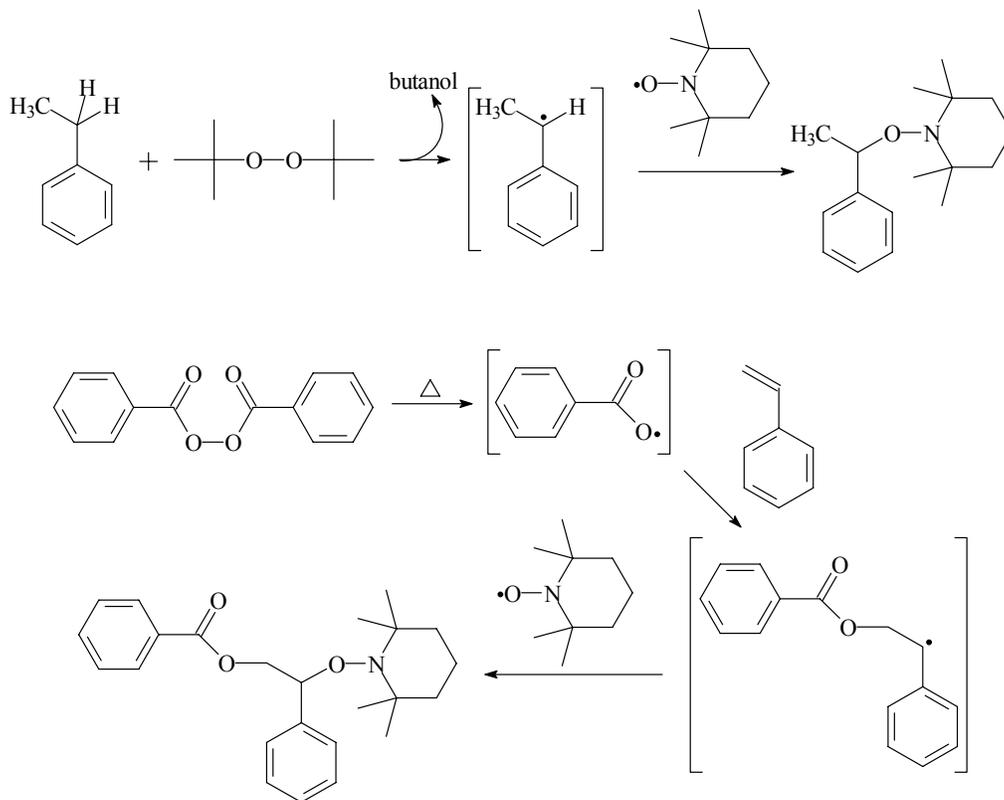
2.2.4 Unimolecular Alkoxyamine Initiators for SFRP

Initial efforts in the stable free radical polymerization investigation focused on the use of a bimolecular initiating system consisting of benzoyl peroxide and a stable nitroxide, typically TEMPO. Unfortunately, the actual initiator concentration was not consistent or completely controlled resulting in an less well-defined system.¹¹⁷ Development a more well-defined initiation process prompted an investigation into unimolecular alkoxyamine initiators. Alkoxyamine initiators mimic the polymer chain end consisting of an alkyl group coupled to a stable nitroxide mediator. These small molecules will decompose at the homolytically unstable C—O bond generating an initiating radical and a nitroxide radical in the proper stoichiometric ratio. Hawker has pioneered the examination of various synthetic pathways for obtaining viable initiating species for SFRP.¹¹⁸ In this report, two general methods for the generation of an alkoxyamine initiator were reported (Scheme 2.6).

One method employed a nitroxide radical trap in which a nitroxide coupled with a secondary benzylic radical generated from a hydrogen abstraction with an active oxygen centered radical such as a *t*-butoxy radical. Priddy et al. simultaneously reported the use of di-*t*-butyl peroxide to generate benzylic radicals that were subsequently trapped with

¹¹⁷ Hawker, C. J.; Bosman, A. W.; Harth, E. "New Polymer Synthesis by Nitroxide Mediated Living Radical Polymerizations," *Chemical Reviews* 101, (2001), 3661-3688.

¹¹⁸ Hawker, C. J.; Barclay, G. G.; Orellana, A.; Dao, J.; Devonport, W. "Initiating Systems for Nitroxide-Mediated "Living" Free Radical Polymerizations: Synthesis and Evaluation," *Macromolecules* 29, (1996), 5245-5254.

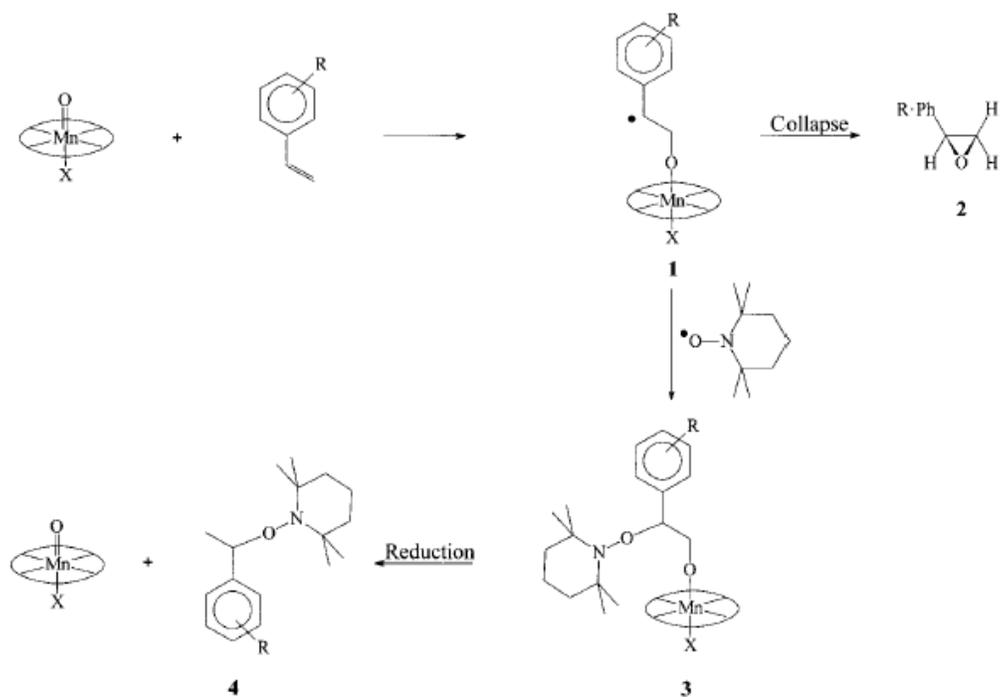


Scheme 2.6: Methodologies for the synthesis of alkoxyamine unimolecular initiators using a nitroxide trapping pathway.

TEMPO.¹¹⁹ In addition, examination styrene polymerizations initiated using these alkoxyamine revealed a significant correlation between the structure of the initiator and the efficiency of the initiation process. Alkoxyamines possessing an α -methyl group instead of an α -hydrogen adjacent to the C—O bond exhibited higher initiation efficiencies. In addition to hydrogen abstraction, low temperatures nitroxide trapping was also utilized to synthesize unimolecular initiating species. This method involved a reaction mixture consisting of a radical generator such as benzoyl peroxide (BPO), a stable free radical nitroxide such as TEMPO, and a monomer such as styrene. The mixture was heated to 80 °C for 20 h. The BPO decomposed into two benzyloxy radicals, which do not react with the TEMPO radical. The benzyloxy radicals added across the styrene double bond resulting in a styryl centered radical. TEMPO radicals present in the reaction mixture quickly trapped the styryl radical. The low reaction temperature prevented homolysis of the C—O bond resulting in the low molecular weight alkoxyamine product. While this product was produced in moderate yields (~50%), the nature of the reaction resulted in the production of various styrene oligomers including unimers, dimers, trimers, etc. requiring extensive column chromatography. Both methods resulted in alkoxyamine initiators that efficiently initiated styrene stable free radical polymerization. Well-defined alkoxyamines possessing various functional groups were obtained in a reaction of functionalized styrene monomers with Jacobsen's catalyst to yield a radical intermediate (Scheme 2.7).¹²⁰ The radical intermediate was trapped with added nitroxide and the resulting product was reduced to the corresponding alkoxyamine. This synthetic pathway was found to be extremely robust with moderate reaction conditions and tolerated functionalities such a ester, ether, hydroxyl, choro, and vinyl groups.

¹¹⁹ Li, I.; Howell, B. A.; Ellaboudy, A.; Kastl, P. E.; Priddy, D. B. "Synthesis, Characterization, and Evaluation of Initiators for Living Free Radical Polymerization: Synthesis of Polystyrene with Controlled Structure," *Polymer Preprints (American Chemical Society, Division of Polymer Chemistry)* 36, (1995), 469-470.

¹²⁰ Dao, J.; Benoit, D.; Hawker, C. J. "A Versatile and Efficient Synthesis of Alkoxyamine Lfr Initiators Via Manganese Based Asymmetric Epoxidation Catalysts," *Journal of Polymer Science Part a-Polymer Chemistry* 36, (1998), 2161-2167.



Scheme 2.7: Synthesis of the functionalized alkoxyamines using the Jacobsen's catalyst for asymmetric epoxidation.¹²¹

¹²¹ Dao, J.; Benoit, D.; Hawker, C. J. "A Versatile and Efficient Synthesis of Alkoxyamine Lfr Initiators Via Manganese Based Asymmetric Epoxidation Catalysts," *Journal of Polymer Science Part a-Polymer Chemistry* 36, (1998), 2161-2167.

In an additional report, Braslau examined the use of nucleophilic substitution reactions for the synthesis of alkoxyamine initiators.¹²² 1-Bromoethyl benzene was converted to benzylic hydrazine creating a substrate with a good leaving group. The corresponding nitroxide was converted to an oxygen centered anion using reduction with lead oxide. Introduction of the benzylic hydrazine solution to the nitroxide solution resulted in a displacement of the hydrazine to give the desired alkoxyamine. Utilization of these methodologies allowed the synthesis of a library of alkoxyamines that were examined on the basis of their ability to mediate acrylate, acrylamide, and acrylonitrile polymerizations. The structures seen in Figure 2.14 represent the most successful alkoxyamine derivatives.

In all cases, the polymerization of styrene initiated and mediated using the alkoxyamines depicted above from the Hawker report proceeded in a controlled fashion exhibiting narrow molecular weight distributions. In particular, alkoxyamines **3** and **4** were studied extensively and compared to the performance of TEMPO. Molecular weight and polydispersity control was observed in bulk polymerization with molecular weight of up to 70,000 g/mol being achieved. Moreover, addition of accelerating agents previously used with TEMPO such as acetic anhydride (AA) and camphor sulfonic acid (CSA) resulted in increased observed rate constants. However, the effect of these additives was reduced compared to TEMPO mediated polymerization of styrene due to instability of the α -hydrogen nitroxide. Lower polymerization temperature were also feasible using these novel alkoxyamines with efficient polymerization control being demonstrated at temperatures as low as 85 °C. Extension of the alkoxyamines to the controlled polymerization of acrylates was also examined. Experimental observations revealed only slightly controlled polymerization when using alkoxyamines **3** and **4** (MWD=1.44). Polymerizations of the acrylates proceeded at much higher rates

¹²² Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. "Development of a Universal Alkoxyamine for "Living" Free Radical Polymerizations," *Journal of the American Chemical Society* 121, (1999), 3904-3920; Braslau, R.; Burrill, L. C.; Siano, M.; Naik, N.; Howden, R. K.; Mahal, L. K. "Low-Temperature Preparations of Unimolecular Nitroxide Initiators for "Living" Free Radical Polymerizations," *Macromolecules* 30, (1997), 6445-6450.

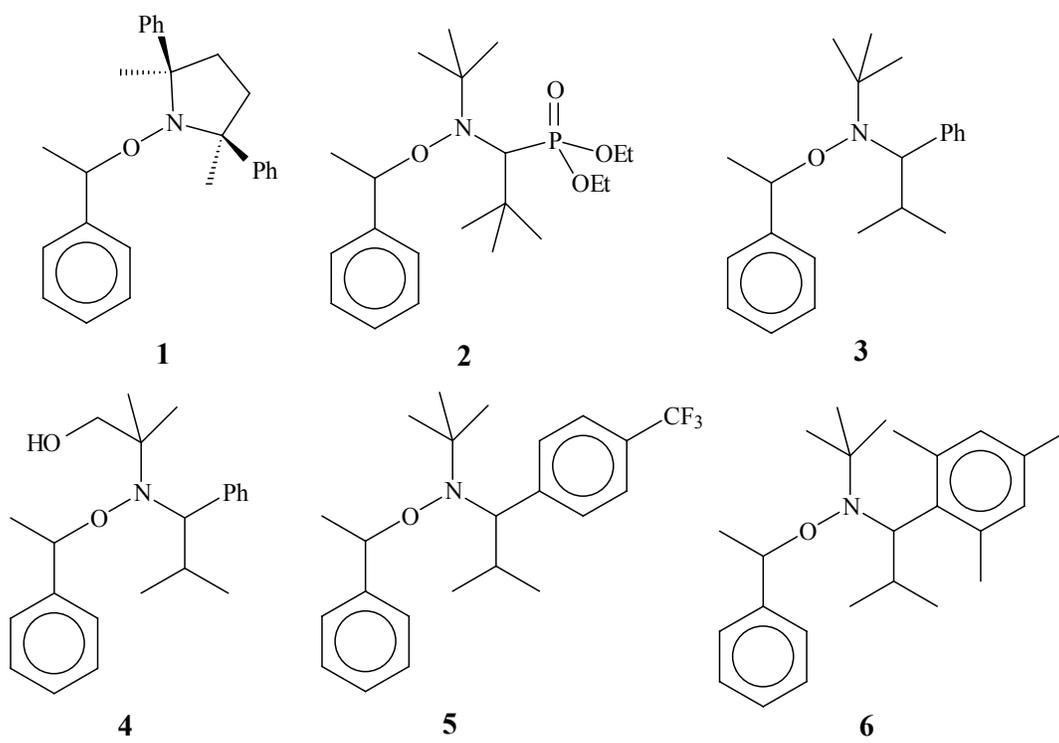
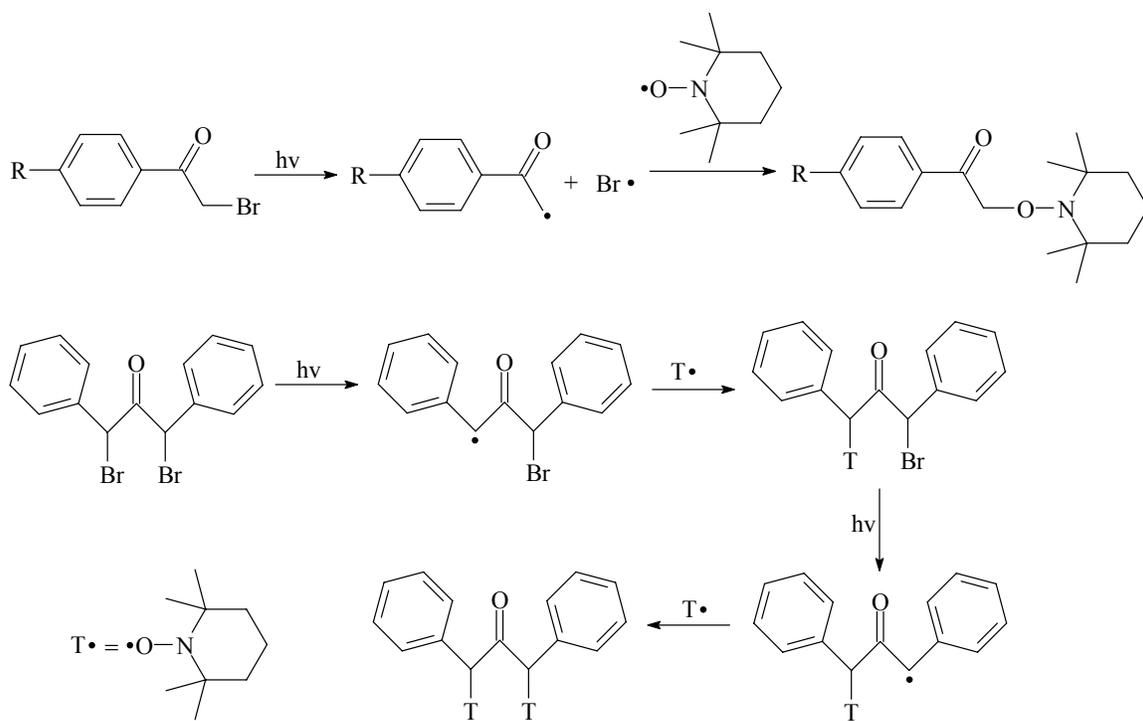


Figure 2.14: Alkoxyamine unimolecular initiators for stable free radical polymerization.

compared to styrene. The addition of additives such as CSA and AA resulted in increased polymerization; however, broadened molecular weight distributions were also observed (MWD>2.0). Additional nitroxide mediator was added to the polymerization mixture to slow the polymerization and enhance control. The addition of 0.01 equivalents of free nitroxide compared to alkoxyamine significantly altered the resulting polymerization rate and polymer molecular weight distribution (MWD=1.25). Increasing the ratio of nitroxide to alkoxyamine continued to reduce the polydispersity (1.06-1.13), but also lengthened the polymerization times. The alkoxyamines were further employed in the initiation and mediation of other functional monomers such as acrylamides and acrylonitriles.

Several researchers have examined more closely some of the synthetic pathways described by Hawker. In a similar investigation, researchers elaborated on the use of hydrogen abstraction to generate a radical that was subsequently capped with a nitroxide species. A *t*-butoxy radical was generated using irradiation of di-*t*-butyl peroxide.¹²³ Subsequently, this active radical was generated in the presence of various functionalized benzene derivatives. The *t*-butoxy radical abstracted the hydrogen from the benzylic position generating a relatively stable radical intermediate. Capping with TEMPO yielded the desired alkoxyamine initiators. Photodebromination was further employed to create a variety of alkoxyamines. Photo-induced cleavage of the carbon bromine bond resulted in stabilized benzyl or phenacyl radicals (Scheme 2.8). The photodebromination pathway also proved a viable route to difunctional alkoxyamines. 1,3-Dibromo-1,3-diphenylacetone was irradiated with light at 350 nm resulting in a step-wise process to yield a difunctional alkoxyamine that generates two adjacent benzylic radicals upon heating separated with a ketone functionality. In all cases, the mechanism of the light induced synthetic pathways was monitored using laser flash photolysis to observe the corresponding radicals generated in the debromination step. Moreover, preliminary polymerizations of styrene were also performed and yielded white powdery products in

¹²³ Connolly, T. J.; Baldovi, M. V.; Mohtat, N.; Scaiano, J. C. "Photochemical Synthesis of Tempo-Capped Initiators for "Living" Free Radical Polymerization," *Tetrahedron Letters* 37, (1996), 4919-4922.



Scheme 2.8: Photodebromination pathways for unimolecular alkoxyamine synthesis.

greater than 85 % yield. However, no molecular weight data was offered to confirm the controlled nature of the polymerizations.

Further studies have sought to elucidate a high yield route to functional alkoxyamines. Yamada and coworkers again employed hydrogen abstraction using the *t*-butoxy radical; however, the radical was generated using thermal decomposition of di-*t*-butyl peroxalate.¹²⁴ This peroxalate decomposed at 35 °C to yield two butoxy radicals and two molecules of carbon dioxide. Decomposition in the presence of functional ethyl benzene derivatives such as 4-bromoethyl benzene resulted in an alkoxyamine possessing an aromatic bromine functionality that was subsequently converted to other functional derivatives. The advantage of this process to achieve alkoxyamines was the high yield of the reactions typically greater than 80 %. In addition, isolation of the products was achieved using evaporation of the unreacted ethyl benzene and simple column chromatography to obtain the pure alkoxyamine product. Utilization of the alkoxyamines in the controlled polymerization of styrene yielded narrow molecular weight distributions and controlled molecular weights. Researchers have extended the use of the *t*-butoxy radical hydrogen abstraction derived from di-*t*-butyl peroxalate thermal decomposition to other nitroxides including α -hydrogen containing nitroxides.¹²⁵ The resulting alkoxyamines were used in the controlled polymerization of styrene studied using ESR analysis to elucidate the corresponding polymerization kinetics.

A report by Matyjaszewski and coworkers has explored versatile and simple synthetic pathway for alkoxyamine formation.¹²⁶ They employed the halogen transfer method associated with ATRP polymerization technique to produce radicals that were

¹²⁴ Miura, Y.; Hirota, K.; Moto, H.; Yamada, B. "High-Yield Synthesis of Alkoxyamine Initiators Carrying a Functional Group by Reaction of Ethylbenzenes with Di-Tert- Butyl Diperoxalate in the Presence of Nitroxides," *Macromolecules* 31, (1998), 4659-4661: Miura, Y.; Hirota, K.; Moto, H.; Yamada, B. "High-Yield Synthesis of Functionalized Alkoxyamine Initiators and Approach to Well-Controlled Block Copolymers Using Them," *Macromolecules* 32, (1999), 8356-8362.

¹²⁵ Drockenmuller, E.; Catala, J. M. "Synthesis of a New Stable Beta-Sulfinyl Nitroxide and the Corresponding Alkoxyamine for Living/Controlled Radical Polymerization of Styrene: Kinetic and ESR Studies," *Macromolecules* 35, (2002), 2461-2466.

¹²⁶ Matyjaszewski, K.; Woodworth, B. E.; Zhang, X.; Gaynor, S. G.; Metzner, Z. "Simple and Efficient Synthesis of Various Alkoxyamines for Stable Free Radical Polymerization," *Macromolecules* 31, (1998), 5955-5957.

subsequently trap with free nitroxide present in the reaction mixture. This technique enable the synthesis of unimolecular initiators from any organic halide precursor molecule (Figure 2.15). Typically bromo or chloro substituted molecules were utilized and transfer of the halide resulted in a resonance stabilized radical. TEMPO and 4-hydroxy-TEMPO were used to trap the radicals and yielded the corresponding alkoxyamines at greater than 70% in all cases. Bulk polymerizations of styrene in the presence of these unimolecular initiators resulted in varied control over the polymerization. The ethyl benzene derivative exhibited adequate control; however, the methyl benzene derived initiator exhibited broadened molecular weight distributions that were attributed to slow initiation. While the tertiary ester containing initiator demonstrated good polymerization control, the secondary analogue did not. Although this report only details the use of TEMPO and closely associated derivatives, other researchers have investigated the use of the ATRP nitroxide trap synthetic pathway. Tordo and his coworkers investigated a variety of alkoxyamines trapping the ATRP generated radicals with TEMPO, DEPN and 2,2,5,5-tetramethyl-4-phenyl-3-azahexane-3-oxyl (TIPNO), a nitroxide Hawker designed.¹²⁷ This report demonstrated the extension of the ATRP nitroxide trap to include the more versatile α -hydrogen containing nitroxides. Moreover, the researchers employed the method previously discussed in which the oxy radical was converted to an anion and subsequently used to attack the appropriate electrophile in a S_N2 type reaction. The resulting alkoxyamine library was studied utilizing ESR to ascertain the BDE associated with each unimolecular initiator. In addition, the enthalpic and entropic parameter contribution were also determined for each molecule. The initiation and mediation of styrene polymerization was also examined and it was found that the alkoxyamines were able to produce controlled polymer products

¹²⁷ Le Mercier, C.; Acerbis, S. B.; Bertin, D.; Chauvin, F.; Gimes, D.; Guerret, O.; Lansalot, M.; Marque, S.; Le Moigne, F.; Fischer, H.; Tordo, P. "Design and Use of Beta-Phosphorus Nitroxides and Alkoxyamines in Controlled/"Living" Free Radical Polymerizations," *Macromolecular Symposia* 182, (2002), 225-247.

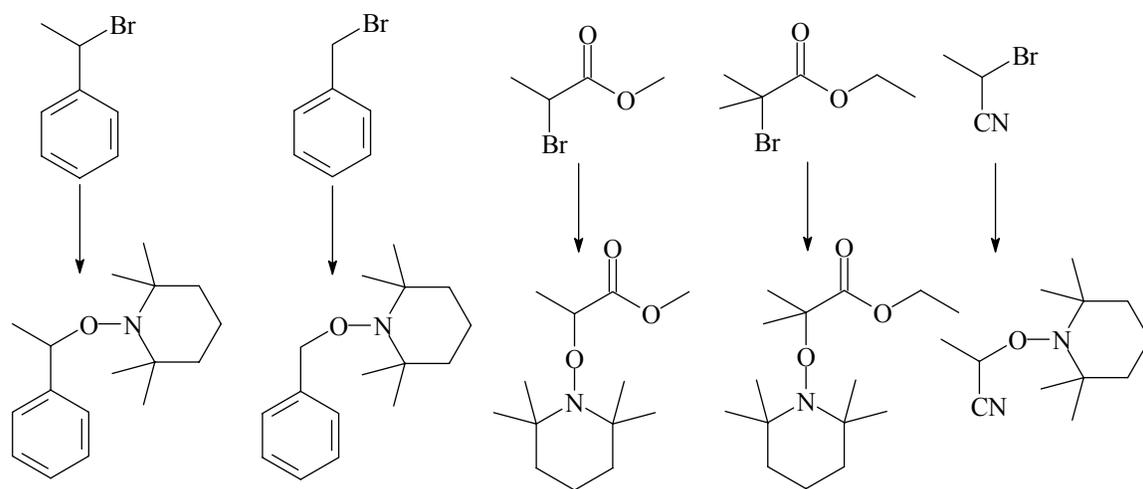


Figure 2.15: Alkoxyamines synthesized from the conventional ATRP halogen transfer synthetic route.

consistent with other studies.¹²⁸ However, depending on the initiating fragment and the mediating fragment, certain limitations in conversion and achievable molecular weight were observed. Other researchers have also utilized the DEPN based alkoxyamine derived from the ATRP nitroxide trap to polymerize functional monomers and complex block copolymers.¹²⁹

The design of alkoxyamine initiator enables researchers to tailor the mediation equilibrium during the initial stages of the SFRP process. Both steric and electronic factors may contribute to bond dissociation energy and the equilibrium constant of the system.¹³⁰ Several groups have examined specifically the sterics effects and their role in the dissociation of the C—O alkoxyamine bond in the SFRP process. Fukuda reported an investigation on TEMPO, DBN, and DEPN decomposition.¹³¹ He was able to correlate the decomposition of the nitroxide mediator, which resulted in the formation of a hydroxylamine and terminal site of unsaturation in the polymer, to the activation rate constant (k_{act}) corresponding to the rate constant for homolytic cleavage of the C—O bond in an alkoxyamine. DBN based alkoxyamines showed higher k_{act} values than the TEMPO analogue and this difference was attributed to bulkier open ring structure of DBN. The cyclic structure associated with TEMPO resulted in reduced steric strain at the C—O bond. In another report, Marque introduced bulky groups to the ring of a

¹²⁸ Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. "Development of a Universal Alkoxyamine for "Living" Free Radical Polymerizations," *Journal of the American Chemical Society* 121, (1999), 3904-3920; Gnanou, Y.; Robin, S.; Guerret, O.; Couturier, J. L. "Macromolecular Engineering Using Novel Alkoxyamines," *Abstracts of Papers of the American Chemical Society* 220, (2000), 264-POLY; Le Mercier, C.; Lutz, J. F.; Marque, S.; Le Moigne, F.; Tordo, P.; Lacroix-Desmazes, P.; Boutevin, B.; Couturier, J. L.; Guerret, O.; Martschke, R.; Sobek, J.; Fischer, H. "Use of Phosphonylated Nitroxides and Alkoxyamines in Controlled/"Living" Radical Polymerization," *ACS Symp. Ser.* 768, (2000), 108-122.

¹²⁹ Diaz, T.; Fischer, A.; Jonquieres, A.; Brembilla, A.; Lochon, P. "Controlled Polymerization of Functional Monomers and Synthesis of Block Copolymers Using Beta-Phosphonylated Nitroxide," *Macromolecules* 36, (2003), 2235-2241.

¹³⁰ Lutz, J. F.; Lacroix-Desmazes, P.; Boutevin, B.; Le Mercier, C.; Gimes, D.; Bertin, D.; Tordo, P. "Comparative Study of a Series of Nitroxides and Alkoxyamines in Controlled/"Living" Radical Polymerization," *Abstracts of Papers of the American Chemical Society* 224, (2002), 508-POLY; Bowry, V. W.; Ingold, K. U. "Kinetics of Nitroxide Radical Trapping .2. Structural Effects," *Journal of the American Chemical Society* 114, (1992), 4992-4996.

¹³¹ Goto, A.; Kwak, Y.; Yoshikawa, C.; Tsujii, Y.; Sugiura, Y.; Fukuda, T. "Comparative Study on Decomposition Rate Constants for Some Alkoxyamines," *Macromolecules* 35, (2002), 3520-3525.

piperazinone derived alkoxyamine.¹³² Using ESR the energy of activation necessary to dissociate the C—O bond was examined. The four methyl groups attached to the two α -carbons were systematically changed to ethyl groups. Increasing the number of ethyl groups resulted in a decrease in the corresponding activation energy, which was rationalized as a steric effect from introducing bulkier groups in close proximity to the C—O bond.

Although previous work has demonstrated a distinct steric effect resulting from bulky groups attached to the nitroxide moiety of an alkoxyamine, examination of the alkyl group has shown no such similar effect.¹³³ This report examined a series of alkoxyamines derived from the DEPN mediator and a polystyrene alkyl chain. The length of the alkyl chain was varied from 1 to 495 styrene monomer units. The rate constant of dissociation corresponding to k_{act} was determined using ESR measurements of the nitroxide concentration in the reaction mixture. The calculated rate constant demonstrated no significant correlation between dissociation and alkyl chain length ranging in value from 4.0 to 7.8 (10^{-3} s^{-1}). Although increasing the length of the alkyl group resulted in no difference in dissociation propensity, altering the steric bulk directly adjacent to the C—O bond exhibited a distinct effect when going from one alkyl group to a bulkier one.¹³⁴ For instance, using a cumene based alkyl group versus an ethyl benzene based alkyl group resulted a reduced activation energy due to greater steric bulk around the C—O bond derived from the presence of the extra methyl group.

Electronic differences between alkoxyamines have also displayed marked effects on the resulting C—O bond homolysis. Comparison of DBN and DEPN based alkoxyamines revealed a difference in the activation rate attributed to the presence of an

¹³² Marque, S.; Sobek, J.; Fischer, H.; Kramer, A.; Nesvadba, P.; Wunderlich, W. "Steric Effects of Ring Substituents on the Decay and Reformation Kinetics of Piperazinone-Based Alkoxyamines," *Macromolecules* 36, (2003), 3440-3442.

¹³³ Bertin, D.; Chauvin, F.; Marque, S.; Tordo, P. "Lack of Chain Length Effect on the Rate of Homolysis of Polystyryl-Sg1 Alkoxyamines," *Macromolecules* 35, (2002), 3790-3791.

¹³⁴ Marque, S.; Le Mercier, C.; Tordo, P.; Fischer, H. "Factors Influencing the C-O-Bond Homolysis of Trialkylhydroxylamines," *Macromolecules* 33, (2000), 4403-4410.

electron withdrawing group.¹³⁵ DBN and DEPN were expected to exhibit similar steric effects on C—O bond homolysis. Therefore, the three fold increase in rate constant going from DEPN to DBN resulted from an increased bond dissociation energy due to electron withdrawing from the phosphonate ester. The lower electron density in the bond made it more difficult to homolytically cleave. In addition, it was observed the more polar reaction solvents induced bond homolysis and increased the k_{act} .

It has further been demonstrated that hydrogen bonding may play a significant role in the ability to cleave the C—O alkoxyamine bond. Beckwith and Ingold initially reported the presence of hydrogen bonding effects in the trapping of nitroxide free radicals.¹³⁶ The interaction was result of the stabilization of one of the resonances structures associated with nitroxides.¹³⁷ Marque has demonstrated the extension of this concept to the alkoxyamines employed in the SFRP process.¹³⁸ The activation rate constant for an alkoxyamine with a hydroxyl containing nitroxide was significantly greater than the one without the hydroxyl functionality. The researchers synthesized two alkoxyamines of similar structure with one possessing three hydroxyl functionalities and one possessing three protected hydroxyl groups incapable of participating in hydrogen bonding. Analysis of the resulting k_{act} 's revealed that the alkoxyamine possessing the three hydroxyl groups homolytically dissociated more than an order of magnitude faster than the corresponding alkoxyamine containing protected hydroxyl groups. In addition to elucidating hydrogen bonding effects, the researchers determined that the C—O dissociation rate constant of TEMPO-based alkoxyamines scales in a linear fashion with C—H bond dissociation energy of the corresponding hydrocarbon (Figure 2.16). This discovery will allow the determination and design of appropriate alkyl groups for SFRP techniques.

¹³⁵ Goto, A.; Fukuda, T. "Comparative Study on Activation Rate Constants for Some Styrene/Nitroxide Systems," *Macromolecular Chemistry and Physics* 201, (2000), 2138-2142.

¹³⁶ Beckwith, A. L. J.; Bowry, V. W.; Ingold, K. U. "Kinetics of Nitroxide Radical Trapping .1. Solvent Effects," *Journal of the American Chemical Society* 114, (1992), 4983-4992.

¹³⁷ Janzen, E. G. *Topics in Stereochemistry*, ed. E. L. Eliel, vol. 6 (New York: Wiley Interscience, 1971).

¹³⁸ Marque, S.; Fischer, H.; Baier, E.; Studer, A. "Factors Influencing the C-O Bond Homolysis of Alkoxyamines: Effects of H-Bonding and Polar Substituents," *Journal of Organic Chemistry* 66, (2001), 1146-1156.

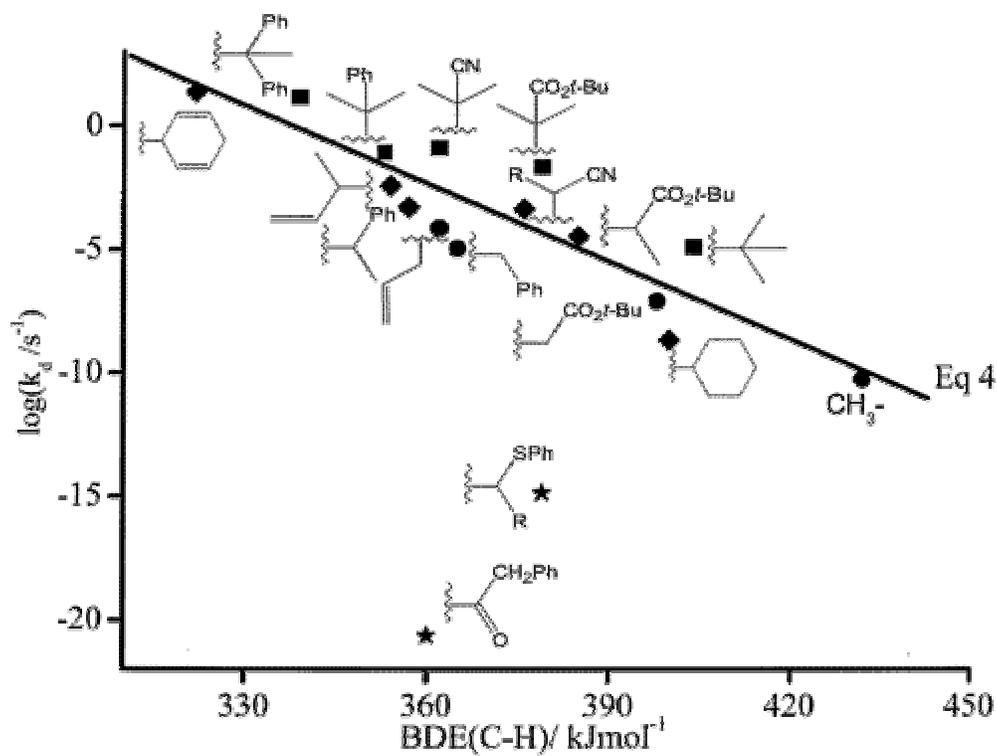


Figure 2.16: Correlation between k_{act} of TEMPO-based alkoxyamines and the C—H bond dissociation energy of the corresponding hydrocarbons.¹³⁹

¹³⁹ Marque, S.; Fischer, H.; Baier, E.; Studer, A. "Factors Influencing the C-O Bond Homolysis of Alkoxyamines: Effects of H-Bonding and Polar Substituents," *Journal of Organic Chemistry* 66, (2001), 1146-1156.

In addition to research focusing on improvement of initiation and mediation in the SFRP system, efforts have also examined the design of alkoxyamine initiators to produce complex polymer architectures. Several studies have investigated the use of difunctional and trifunctional alkoxyamine initiators (Figure 2.17) to produce interesting block and star-shaped polystyrene and poly(n-butyl acrylate).¹⁴⁰ The alkoxyamines possessing two or three functionalities possessed the DEPN mediator moiety enabling the researchers to investigate a variety of monomers. However, the multifunctional unimolecular initiators required the addition of a slight excess of free DEPN mediator due the decomposition of some nitroxide during the polymerization. This synthetic method was consistent with results obtained earlier.¹⁴¹

The difunctional initiator was used to homopolymerize both styrene and n-butyl acrylate and the resulting polymer product exhibited narrow molecular weight distributions characteristic of a controlled process. However, limiting the monomer conversion (<70%) in the n-butyl acrylate polymerization was essential to achieve MWD's below 1.3 during initial investigations. The initiation efficiency was studied to determine the reactivity of each initiator end. Styrene was polymerized and the resulting polystyrene was hydrolyzed to obtain two polymers, one from each side of the difunctional initiator. Analysis of the molecular weights and distribution showed that both ends of the alkoxyamine initiate with almost 100% efficiency with the functionality calculated as $f=1.97$. The difunctional initiator also enabled the facile two step synthesis of a ABA

¹⁴⁰ Charleux, B.; Farcet, C.; Pirri, R.; Guerret, O. "Use of a Difunctional Alkoxyamine Initiator in the Miniemulsion Polymerization of N-Butyl Acrylate," *Abstracts of Papers of the American Chemical Society* 224, (2002), 663-POLY: Malmstrom, E. E.; Hawker, C. J. "Macromolecular Engineering Via 'Living' Free Radical Polymerizations," *Macromolecular Chemistry and Physics* 199, (1998), 923-935: Priddy, D. B.; Howell, B. A. "Utility/Limitations of Nitroxide Mediated Polymerization for Low Cost Manufacture of Improved Styrenic Polymers," *Abstracts of Papers of the American Chemical Society* 224, (2002), 665-POLY: Gnanou, Y.; Robin, S.; Guerret, O.; Couturier, J. L. "Macromolecular Engineering Using Novel Alkoxyamines," *Abstracts of Papers of the American Chemical Society* 220, (2000), 264-POLY: Robin, S.; Guerret, O.; Couturier, J. L.; Gnanou, Y. "Synthesis of Stars and Starlike Block Copolymers from a Trialkoxyamine Used as Initiator," *Macromolecules* 35, (2002), 2481-2486: Robin, S.; Guerret, O.; Couturier, J. L.; Pirri, R.; Gnanou, Y. "Synthesis and Characterization of Poly(Styrene-B-N-Butyl Acrylate-B-Styrene) Triblock Copolymers Using a Dialkoxyamine as Initiator," *Macromolecules* 35, (2002), 3844-3848.

¹⁴¹ Fischer, H. "The Persistent Radical Effect in Controlled Radical Polymerizations," *Journal of Polymer Science Part a-Polymer Chemistry* 37, (1999), 1885-1901.

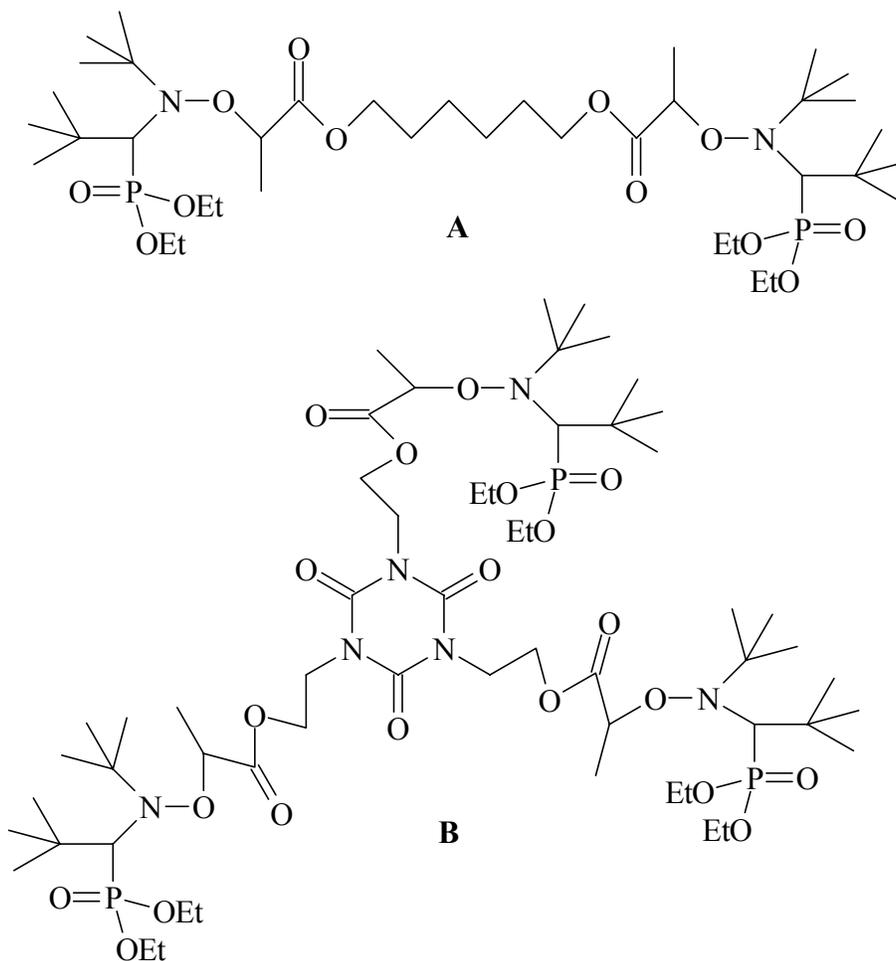


Figure 2.17: Difunctional and trifunctional alkoxyamine initiators for the synthesis of block copolymers and star polymers, respectively.

type triblock copolymer composed of two outer polystyrene blocks and a central poly(*n*-butyl acrylate) block. The polymerization conditions were optimized with excess nitroxide and limited monomer conversion to produce triblocks with relatively narrow molecular weight distributions (1.35-145). SEC analysis demonstrated that no poly(*n*-butyl acrylate) macroinitiator remained after the second polymerization step. Another group has also detailed the synthesis of a difunctional alkoxyamine possessing terminal TEMPO moieties for mediation.¹⁴² The synthetic route described employs coupling of two monofunctional alkoxyamines using phosgene and a reactive hydroxyl group. Polystyrene molecules resulting from the use of the difunctional alkoxyamine possessed a central carbonate linkage that was cleaved after the polymerization. Again, the polymer molecular weights before hydrolysis were equal to twice the polymer molecular weights after hydrolysis indicating that both functionalities were initiating with equal efficiency.

More complex polymeric architectures such as stars are often achieved using a divinyl molecule such as divinyl benzene to create a crosslinked microgel core with polymeric arms extending from the core.¹⁴³ Another feasible route to well-defined star shaped polymers is through the use of a multifunctional initiator. Robin et al. utilized the trifunctional alkoxyamine initiator (Figure 2.17b) to synthesize high molecular weight three-armed star polymers. The use of excess nitroxide reduced the observed molecular weight distributions and reducing the polymerization temperature yielded the same effect. Limiting conversion allowed the production of well-defined stars and reduced the degree of star-star coupling observed in the reactions. In addition to star-shaped homopolymers, star-shaped block copolymer were achieved using a poly(*n*-butyl acrylate) star-shaped homopolymer as a macroinitiator for a subsequent styrene polymerization.

¹⁴² Li, I. Q.; Knauss, D. M.; Priddy, D. B.; Howell, B. A. "Synthesis and Reactivity of Functionalized Alkoxyamine Initiators for Nitroxide-Mediated Radical Polymerization of Styrene," *Polymer International* 52, (2003), 805-812.

¹⁴³ Pasquale, A. J.; Long, T. E. "Synthesis of Star-Shaped Polystyrenes Via Nitroxide-Mediated Stable Free-Radical Polymerization," *Abstracts of Papers of the American Chemical Society* 219, (2000), 611-POLY.

2.3 Star-Shaped Polymer Systems

2.3.1 Introduction

The increased specialization required in many of today's polymer applications requires the production of polymer systems of with property specificity. A great deal of control over polymeric materials properties like molecular weight and polydispersity has been gained with the implementation of living or controlled polymerization techniques. These techniques can be further extended to synthesize macromolecules with controlled architectures. Star-shaped polymers represent a class of controlled architecture polymers that have garnered a substantial degree of attention for synthesis using living or controlled processes. Star polymers have been successfully produced via living methodologies including anionic,¹⁴⁴ cationic,¹⁴⁵ and group transfer radical¹⁴⁶ propagating chains. Branched polymers offer a variety of novel properties to polymer systems and star polymers represent the most basic form possessing a single branching site. Synthesis of star polymers can be achieved via three basic methodologies. Initially, the "arm first" method can be used, which involves the linking of living polymerization chains with a coupling agent of plural functionality. Also, the "core first" method can be employed where a multifunctional initiator is used to produce living polymerization arms. The final method is a derivatization of the "arm first" method and entails the use of a divinyl species to produce a linking reaction of living polymerization arms.¹⁴⁷

Interest in the area of star polymers stems from their unique characteristics, which are derived from the unusual spatial arrangement of the polymer chains and the extensive peripheral functionality.¹⁴⁸ Particularly, the rheological properties associated with star

¹⁴⁴ Knauss, D. M.; Al-Muallem, H. A.; Huang, T. Z.; Wu, D. T. "Polystyrene with Dendritic Branching by Convergent Living Anionic Polymerization," *Macromolecules* 33, (2000), 3557-3568.

¹⁴⁵ Storey, R. F.; Shoemaker, K. A. "Poly(Styrene-B-Isobutylene) Multiarm Star-Block Copolymers," *Journal of Polymer Science Part a-Polymer Chemistry* 37, (1999), 1629-1641; Kadokawa, J.; Kobayashi, S. "Synthesis of Linear and Star-Shaped Phosphorus-Containing Telechelic Polymers Via Living Cationic Ring-Opening Polymerization Using a Halobenzene/Nickel(II) Bromide Catalyst," *Macromolecular Symposia* 95, (1995), 121-136.

¹⁴⁶ Webster, O. W. "The Use of Group Transfer Polymerization for the Control of Polymethacrylate Molecular Structure," *Makromolekulare Chemie, Macromolecular Symposia* 33, (1990), 133-143.

¹⁴⁷ Abrol, S.; Kambouris, P. A.; Looney, M. G.; Solomon, D. H. "Studies on Microgels .3. Synthesis Using Living Free Radical Polymerization," *Macromolecular Rapid Communications* 18, (1997), 755-760.

¹⁴⁸

polymer systems are of distinct significance. The rheological nature of these systems is a result of their compact structure, which leads to smaller hydrodynamic volumes. Hence, it is possible to synthesize a star polymer with a similar molecular weight to a linear counterpart and maintain a smaller hydrodynamic dimension. Additionally, due to the fact that these systems are produced using living or controlled processes, there is no sacrifice of molecular weight or polydispersity control.¹⁴⁹ The smaller hydrodynamic volumes for these polymer systems allow them to be utilized as rheology modifiers for processing improvement.¹⁵⁰ Further, the plural functionality also allows control over solubility by chain end alteration and offers the possibility for post polymerization cross-linking.¹⁵¹

2.3.2 Star Polymers Synthesized by SFRP and RAFT

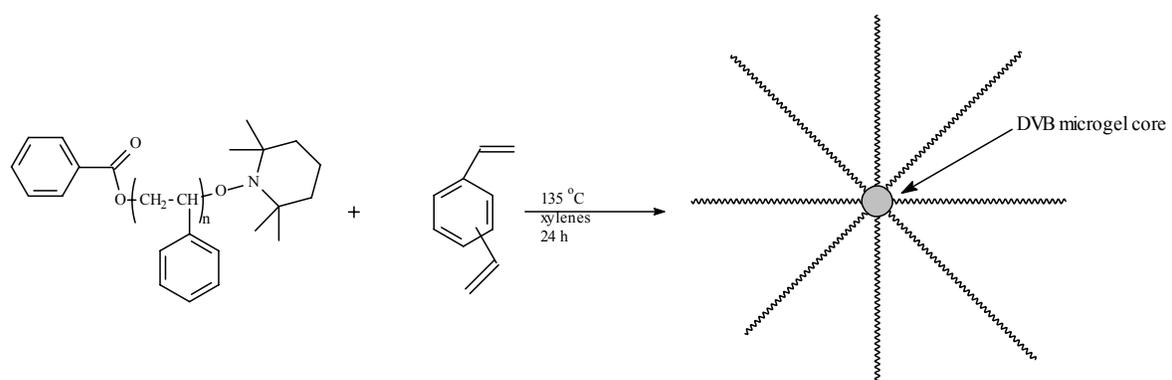
Various living techniques have been applied to the production of star-shaped polymers. The controlled radical processes seem to offer the most ideal situation for synthesis of stars with variable compositions due to their ability to function with a diverse range of monomers. The use of SFRP as an avenue to the synthesis of star-shaped polymers has proven successful. The SFRP process utilizes the variation of the “arm first” method, which employs a divinyl compound that undergoes a linking reaction (Scheme 2.9).

Fukuda and Ide have undertaken the primary investigation of star synthesis by SFRP in their studies of the pendant vinyl reactivity and gelation. They successfully produced star polymers by addition of a small amount of a divinyl agent, 4,4'-

¹⁴⁹ Xia, J. H.; Zhang, X.; Matyjaszewski, K. "Synthesis of Star-Shaped Polystyrene by Atom Transfer Radical Polymerization Using an "Arm First" Approach," *Macromolecules* 32, (1999), 4482-4484; Long, T. E.; Kelts, L. W.; Turner, S. R.; Wesson, J. A.; Mourey, T. H. "Synthesis and Characterization of Well-Defined Star Polymers Via a Controlled Sol-Gel Process," *Macromolecules* 24, (1991), 1431-1434.

¹⁵⁰ Angot, S.; Murthy, K. S.; Taton, D.; Gnanou, Y. "Atom Transfer Radical Polymerization of Styrene Using a Novel Octafunctional Initiator: Synthesis of Well-Defined Polystyrene Stars," *Macromolecules* 31, (1998), 7218-7225.

¹⁵¹ Knischka, R.; Lutz, P. J.; Sunder, A.; Mulhaupt, R.; Frey, H. "Functional Poly(Ethylene Oxide) Multiarm Star Polymers: Core- First Synthesis Using Hyperbranched Polyglycerol Initiators," *Macromolecules* 33, (2000), 315-320; Zhang, X.; Xia, J. H.; Matyjaszewski, K. "End-Functional Poly(Tert-Butyl Acrylate) Star Polymers by Controlled Radical Polymerization," *Macromolecules* 33, (2000), 2340-2345.



Scheme 2.9: Synthetic approach for the formation of star-shaped polymers.

divinylbiphenyl at the end of the polymerization.¹⁵² Initially, these workers investigated the experimental results of a number of studies that indicate that the covalent network formation associated with the divinyl systems formed by conventional free radical techniques proceeds in an unorthodox non-ideal fashion. The proposed source of the deviation from ideality as described in the Flory and Stockmayer (FS) theories is the result of intramolecular crosslinks by the pendant vinyl groups.¹⁵³ In order for the system to obey the FS theories, it is necessary to randomly distribute the pendant vinyls. In conventional systems, the polymerization is fast leading to heterogeneity of the pendant vinyl groups around the growing radical resulting in cyclics from intramolecular reactions. The slower living polymerization initiates simultaneously and proceeds in a controlled fashion leading to homogeneity and random distribution of the pendant vinyl groups. The living nature of this type of synthesis permits well-defined studies and production of materials without cross-linking associated with the intramolecular reactions. Additionally, Fukuda et al. have considered some aspects of the gels produced by the controlled radical process.¹⁵⁴ Crosslink number (density) and swelling ratio represent characteristics of particular importance in these star systems, and can be readily examined by application of the mean-field FS theory. Using the equations set up in the FS theory, the researchers were able to calculate the value of the critical cross-link number for this system to experience gelation. The predicted number and calculated number differ by a factor of two; however, this is a significant improvement from the conventional systems, which typically vary from the FS prediction by one or two orders of magnitude. Again, the correlation between the experimental values and those of the FS theory is attributed to the ability of the living system to give a homogeneous pendant vinyl environment. This random distribution of the pendant vinyls leads to a more homogeneous gel formation. It is seen that the swelling ratio in the living systems decreases over the course of the reaction indicating increase in the cross-linking, which occurs with a homogeneous environment. On the other hand, conventional systems show

¹⁵² Ide, N.; Fukuda, T. "Nitroxide-Controlled Free-Radical Copolymerization of Vinyl and Divinyl Monomers. Evaluation of Pendant-Vinyl Reactivity," *Macromolecules* 30, (1997), 4268-4271.

¹⁵³ Stockmayer, W. H. "Theory of Molecular Size Distribution and Gel Formation in Branched Polymers. I. General Cross Linking," *J. Chem. Phys.* 12, (1944), 125-131.

¹⁵⁴ Ide, N.; Fukuda, T. "Nitroxide-Controlled Free-Radical Copolymerization of Vinyl and Divinyl Monomers. 2. Gelation," *Macromolecules* 32, (1999), 95-99.

a constant swelling ratio, indicative of postgel behavior, over the course of the entire reaction due to the fact that the heterogeneous environment leads to unwanted intramolecular cyclizations, which form a series of premature microgels.

In an additional report, Pasquale and Long detail the synthesis of high molecular weight star-shaped styrene polymers via TEMPO terminated oligomers coupled by incorporation of divinylbenzene (DVB). They were able to produce star-shaped polymers with molecular weights of 320 kg/mol with polydispersities around 3.0. The production of the star polymers required an intricate study of the concentration ratio of the divinyl species to solvent. Without the proper ratio between the DVB and xylenes, the reaction would either gel or produce no stars. Further, the relationship between the intrinsic viscosities of the stars and linear polymers of equal molecular weight were investigated, and the intrinsic viscosities for the stars were approximately half the value predicted by the Mark-Houwink-Sakurada relation. These lower viscosities were consistent with expectation that the high degree of branching would lead to different rheological properties than expected from the linear counterparts.¹⁵⁵

The discovery of facile alkoxyamine synthesis resulted in the generation of unimolecular initiators capable of producing star-shaped polymer products. Hawker and Gnanou have investigated the use of trifunctional alkoxyamines to yield well-defined three arm star polymers.¹⁵⁶ Gnanou's initiator possessed three alkoxyamine functionalities composed of a labile C—O bond and a DEPN mediating group. Star-shaped polymers of styrene and n-butyl acrylate were readily synthesized with relatively narrow molecular weight distributions ranging from 1.09 to 1.40. The addition of supplemental free nitroxide was critical to produce well-defined polymers. Moreover, the monomer conversion associated with the polymerization significantly effected the

¹⁵⁵ Pasquale, A. J.; Long, T. E. "Real-Time Monitoring of the Stable Free Radical Polymerization of Styrene Via in-Situ Mid-Infrared Spectroscopy," *Macromolecules* 32, (1999), 7954-7957; Pasquale, A. J.; Long, T. E. "Synthesis of Star-Shaped Polystyrenes Via Nitroxide-Mediated Stable Free-Radical Polymerization," *Abstracts of Papers of the American Chemical Society* 219, (2000), 611-POLY.

¹⁵⁶ Robin, S.; Guerret, O.; Couturier, J. L.; Gnanou, Y. "Synthesis of Stars and Starlike Block Copolymers from a Trialkoxyamine Used as Initiator," *Macromolecules* 35, (2002), 2481-2486; Hawker, C. J.; Bosman, A. W.; Harth, E. "New Polymer Synthesis by Nitroxide Mediated Living Radical Polymerizations," *Chemical Reviews* 101, (2001), 3661-3688.

resulting polydispersities. The higher the conversion lead to broadened molecular weight distributions. In addition to star homopolymers, block were also constructed and consisted of an n-butyl acrylate inner shell with a styrene outer shell. The resulting star-shaped block copolymers exhibited slightly greater distribution; however, polydispersities as low as 1.18 were achieved. It was also notable that star-star coupling was not observed up to 86% monomer conversion.

The SFRP methodology has also been used in more unconventional routes to star-shaped polymers. A group in Japan has employed an alkoxyamine functionalized with a β -cyclodextrin group to produce polymer that self-associate into a star-shaped structure.¹⁵⁷ The hydroxyl functionalities of the glucose rings of cyclodextrin were acetylated prior to the polymerization of styrene to inhibit association during the polymerization. The resulting polystyrene macromolecules were deacetylated and dissolved in toluene, a good solvent for polystyrene. The hydrophilic character of the cyclodextrin resulted in aggregation in the nonpolar toluene and the authors reported star-shaped polymer architectures with 6-13 arms based on static laser light scattering measurements.

In an additional report, Hawker used a scaffold to create star-like polymers.¹⁵⁸ Surface initiated stable free radical polymerization was performed from the surface of silica nanoparticles. The nanoparticles were functionalized with alkoxyamine unimolecular initiator groups via a reaction with the silanol functionality on the particle's surface. The functionalized nanoparticles were then stirred in styrene monomer and a comonomer at 120 °C and dimethyl formamide with some free alkoxyamine. The polymerizations proceeded for 24 h and the resulting product was isolated using dilution with THF and subsequent centrifugation to collect the silica particles covered with

¹⁵⁷ Narumi, A.; Kawasaki, K.; Kaga, H.; Satoh, T.; Sugimoto, N.; Kakuchi, T. "Glycoconjugated Polymer 6. Synthesis of Poly Styrene-Block- (Styrene-Graft-Amylose) Via Potato Phosphorylase-Catalyzed Polymerization," *Polymer Bulletin* 49, (2003), 405-410: Narumi, A.; Miura, Y.; Satoh, T.; Kaga, H.; Kakuchi, T. "Synthesis of End-Functionalized Polymer with Cyclodextrin Based on Tempo-Mediated Radical Polymerization," *Abstracts of Papers of the American Chemical Society* 224, (2002), 504-POLY.

¹⁵⁸ Blomberg, S.; Ostberg, S.; Harth, E.; Bosman, A. W.; Van Horn, B.; Hawker, C. J. "Production of Crosslinked, Hollow Nanoparticles by Surface- Initiated Living Free-Radical Polymerization," *Journal of Polymer Science Part a-Polymer Chemistry* 40, (2002), 1309-1320.

polymer brushes emanating from silica core. The brushes were composed of a block of random copolymer of styrene and the selected comonomer, malice anhydride or vinyl benzocyclobutene, and block of pure styrene homopolymer. The presence of the comonomer enabled post-polymerization crosslinking of the brush arms. Moreover, the silica particles were subsequently decomposed via treatment with a 26% aqueous solution of HF. This reaction yielded hollow nanoparticles with a crosslinked polystyrene shell. However, SEM analysis of the resulting particles showed that the particle shell integrity was weak and the spheres had collapsed.

In addition to the SFRP methods, RAFT polymerization techniques in concert with the core first methods for production of star polymers were investigated.¹⁵⁹ With this method, a precise number of arms were formed that radiate from a preformed central core molecule. For the star formed by the RAFT process, the core molecule, benzene, is functionalized by substituents acting as RAFT agents (Figure 2.18). The core molecules examined by Thang and coworkers possessed a varied number of functional groups and produced stars with four or six arms.

Molecular weights for the star polymers synthesized by RAFT methods proved to be substantially lower than those produced by the SFRP method. Also, the conversions for the RAFT stars required longer reaction times to achieve levels comparable to those reported by Pasquale and Long. SFRP star polymers were produced with conversions of 77 % with 24 h reaction times. On the other hand, the RAFT star-shaped polymers required approximately 64 hours to reach comparable levels of conversion, 73 % for the four-armed star and 72 % for the six-armed star. The core first method possesses a more favorable aspect to the arm first method in the fact that the star polymers are not polluted with oligomers arms as seen in the SFRP methods. Furthermore, the RAFT stars are suitable for facile production of block copolymer stars since the mediating agent is

¹⁵⁹ Chong, B. Y. K.; Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H. "A More Versatile Route to Block Copolymers and Other Polymers of Complex Architecture by Living Radical Polymerization: The Raft Process," *Macromolecules* 32, (1999), 2071-2074; *Acs Symposium Series*, ed. K. Matyjaszewski, vol. 768, *Controlled/Living Radical Polymerization: Progress in Atrp, Nmp, and Raft* (Oxford University Press, 2000).

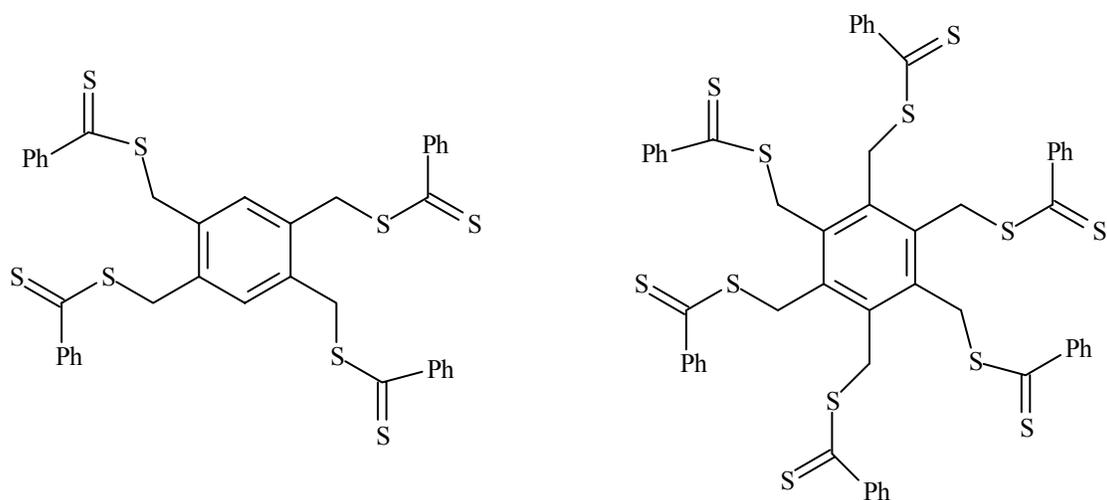


Figure 2.18: RAFT agents for production of star-shaped polymers.

located on the end of the growing arms in contrast to the TEMPO method, which produces stars with the TEMPO mediating moiety located within the divinyl core.

2.4 Block, Random and Graft Copolymerization Systems

2.4.1 Introduction

The increasing complexity of polymer applications has required the production of materials with varied properties. Often homopolymers do not afford the scope of attributes necessary to many applications. Copolymerization allows the formulation of polymer materials with properties characteristic of two homopolymers contained in a single copolymer material. The monomers within a copolymer can be distributed in various fashions; random, statistical, alternating, segmented, block, or graft (Figure 2.19).¹⁶⁰

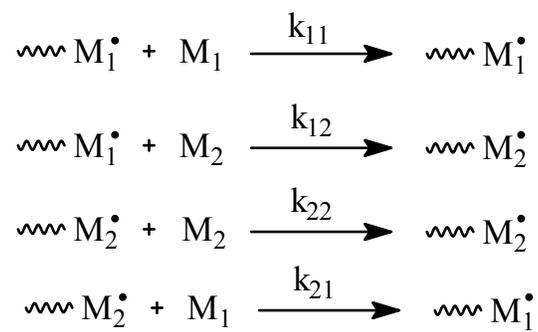
Random and statistical copolymers vary only slightly from each other in that the random system follows no statistical pattern. Alternating copolymerization is governed by a ratio of the propensity of the monomers to homopropagate or crosspropagate. This ratio is termed the reactivity ratio and relies heavily on the assumption that the reactivity of the growing chain is affected solely by the nature of the monomer unit located at the propagating carbon centered radical, termed the terminal method (Figure 2.20). The reactivity ratios determined for a particular copolymerization will dictate the nature of the repeating structure. A high reactivity ratio indicates a tendency to homopropagate and a lower ratio signifies a preference for crosspropagation between monomers.¹⁶¹ In addition to the terminal method for calculation of reactivity ratios, the nonlinear least squares method proposed by Tidwell and Mortimer allows the computation of these values

¹⁶⁰ Tidwell, P. W.; Mortimer, G. A. "An Improved Method of Calculating Copolymerization Reactivity Ratios," *J. Polymer Sci., Pt. A* 3, (1965), 369-387.

¹⁶¹ Noshay, A.; McGrath, J. E. *Block Copolymers* (New York: Academic Press, 1977).

Statistical	ABBABABBAAABABBABAAB
Alternating	ABABABABABABABABABAB
Block	AAAAAAAAA-BBBBBBBBBBB
Segmented	-(AAAAAAAAA-BBBBBBBBBBB) _m -
Graft	<pre> AAAAAAAAAAAAAAAAAAAAAAAA B B B B B B B B B B B B B B B B B </pre>

Figure 2.19: Possible arrangements of monomers in a copolymer.



$$r_1 = k_{11}/k_{12} \qquad r_2 = k_{22}/k_{21}$$

Figure 2.20: Rate constants and reactivity ratios used in the terminal method distribution determination.

without objective examination of the data, with quantitative error, and with examination of their accuracy in the copolymer equation.¹⁶²

Polymerizing with monomers possessing extremely low reactivity ratios can produce a perfectly alternating copolymer. Segmented copolymerization refers to a situation where short sequences of different monomers are produced in a copolymer. Block and graft copolymers involve long sequences of a specific monomer covalently linked to a sequence of a comonomer. Block copolymers have found application as dispersants, compatibilizers, and viscosity modifiers.¹⁶³ In contrast to segmented copolymers, block copolymers contain long sequences and rarely repeat the sequences more than twice in one chain. Synthesis of the block systems is possible by living polymerization, sequential growth from oligomer end groups, and interaction of functionalities on oligomer ends. The most successful synthesis of block copolymers proceeds via living or controlled polymerization processes, which until recently primarily concerned anionic methods.¹⁶⁴ Another important characteristic of block copolymers is their interesting phase behavior. When the blocks of a copolymer become substantially long, the sequences can microphase separate due to the incompatibility of the sequences in each other.¹⁶⁵ Hence, the copolymer will exhibit distinct properties of both homopolymers whereas when the sequences are adequately short, no phase separation occurs. In this situation, analysis of the polymer shows an averaging of the properties of the two homopolymers. For example, one could observe two distinct T_g 's with phase separation, but without the phase separation, an weighted average of the T_g 's would be observed.¹⁶⁶ Though anionic polymerization has provided satisfactory results, the need to

¹⁶² Tidwell, P. W.; Mortimer, G. A. "An Improved Method of Calculating Copolymerization Reactivity Ratios," *J. Polymer Sci., Pt. A* 3, (1965), 369-387.

¹⁶³ Georges, M. K.; Hamer, G. K.; Listigovers, N. A. "Block Copolymer Synthesis by a Nitroxide-Mediated Living Free Radical Polymerization Process," *Macromolecules* 31, (1998), 9087-9089; Tuzar, Z.; Pospisil, H.; Plestil, J.; Lowe, A. B.; Baines, F. L.; Billingham, N. C.; Armes, S. P. "Micelles of Hydrophilic-Hydrophobic Poly(Sulfobetaine)-Based Block Copolymers," *Macromolecules* 30, (1997), 2509-2512.

¹⁶⁴ Morton, M. *Anionic Polymerization: Principles and Practice* (New York: Academic Press, 1983); Morton, M.; Fetters, L. J. *Polymerization Processes in Anionic Polymerizations and Block Copolymers*, ed. I. Skiest (New York: Wiley Interscience, 1977); Rempp, P.; Franta, E.; Herz, J. E. "Macromolecular Engineering by Anionic Methods," *Advances in Polymer Science* 86, (1988), 145-173.

¹⁶⁵ *Block Copolymers Science and Technology*, ed. D.J. Meier (Chur: Harwood Academic Publishers, 1983).

¹⁶⁶ Aggarwal, S. L., ed., *Block Copolymers* (New York: Plenum Press, 1970).

incorporate a variety of monomers into a copolymer has required a synthesis method that is more tolerant to different monomer types. Furthermore, with anionic polymerization it is necessary to perform the block sequence in a precise order due to the reactivity of the propagating anions.¹⁶⁷ The introduction of controlled free radical processes has allowed researchers to perform copolymerization with monomers deemed incompatible for living anionic methods. However, anionic methods of polymerization have also been employed in conjunction with controlled free radical techniques to produce well-defined block and graft copolymer systems. Hedrick and researchers have demonstrated this capability by altering the polymer chain end to allow multiple methods of polymerization for a single polymer chain.¹⁶⁸

Graft copolymers are similar to block copolymers in that they possess long sequences of monomer units. However, graft copolymer architecture differs substantially from typical block copolymers. In graft copolymers, monomer sequences are grafted or attached to points along a main polymer chain. Grafted chains generally possess molecular weights less than that of the main chain. Typical syntheses of the grafts occur by polymerization initiated at some reactive point along the backbone or by copolymerization of a macromonomer. Polymerization from the polymer backbone is possible via anionic, cationic, and radical techniques, but all require some functional unit capable of further reaction.¹⁶⁹ Graft copolymers perform similar functions to block copolymers in that they contain moieties with varying properties. Compatibilization represents a major area of application for grafts because the grafted chains can be used to solubilize a polymer blend system containing two immiscible polymers. Additionally, graft copolymers offer unique solution, mechanical and morphological properties that

¹⁶⁷ Listigovers, N. A.; Georges, M. K.; Odell, P. G.; Keoshkerian, B. "Narrow-Polydispersity Diblock and Triblock Copolymers of Alkyl Acrylates by a "Living" Stable Free Radical Polymerization," *Macromolecules* 29, (1996), 8992-8993.

¹⁶⁸ Hawker, C. J.; Hedrick, J. L.; Malmstrom, E. E.; Trollsas, M.; Mecerreyes, D.; Moineau, G.; Dubois, P.; Jerome, R. "Dual Living Free Radical and Ring Opening Polymerizations from a Double-Headed Initiator," *Macromolecules* 31, (1998), 213-219.

¹⁶⁹ Odian, G. *Principles of Polymerization*, 3rd ed. (New York: John Wiley and Sons, Inc., 1991).

make them ideal for utilization as viscosity modifiers and thermoplastic elastomers.¹⁷⁰ The unique molecular architecture of graft copolymers leads to peculiar morphological properties. The chain lengths of the grafted arms and backbone block dictate the morphology that arises in the polymer. Changes in the composition of the graft copolymer alter the resulting polymer morphology. A variety of morphologies is possible ranging from lamellar to cylindrical to spherical.¹⁷¹

2.4.2 Synthesis of Block, Random and Graft Copolymers via SFRP and RAFT

The production of copolymers often requires the incorporation of different types of monomers in the same polymer chain. Anionic methods are highly sensitive to the monomer types as well as the order in which the monomers are polymerized. The advent of living radical polymerization techniques has enabled the fabrication of block copolymers with traditionally incompatible monomers. The reversible termination that occurs at the growing radical center of controlled free radical polymerization allows the sequential addition of monomer sequences. SFRP type polymerizations have proven highly successful in production of block copolymers containing monomer sequences not previously allowed by anionic type polymerization methods. Lansun and coworkers performed an extensive study to examine the capability of SFRP methods to produce block copolymers from dissimilar vinyl monomers.¹⁷² Their investigation explored the copolymerization of a macroinitiator polystyrene oligomer with acrylates, methacrylates, acetates, and acrylamides. The researchers successfully produced well-defined block copolymers when initiating the methacrylates and the acrylamide examined in the study. However, the vinyl acetate and acrylate monomer were not successfully copolymerized with the polystyrene macroinitiator. The GPC chromatograms revealed that the polymerizations were primarily block forming and resulted in forming only a small

¹⁷⁰ Gido, S. P.; Lee, C.; Pochan, D. J.; Pispas, S.; Mays, J. W.; Hadjichristidis, N. "Synthesis, Characterization, and Morphology of Model Graft Copolymers with Trifunctional Branch Points," *Macromolecules* 29, (1996), 7022-7028.

¹⁷¹ Ruokolainen, J.; Saariaho, M.; Ikkala, O.; ten Brinke, G.; Thomas, E. L.; Torkkeli, M.; Serimaa, R. "Supramolecular Routes to Hierarchical Structures: Comb-Coil Diblock Copolymers Organized with Two Length Scales," *Macromolecules* 32, (1999), 1152-1158.

¹⁷² Yousi, Z.; Jian, L.; Rongchuan, Z.; Jianliang, Y.; Lizong, D.; Lansun, Z. "Synthesis of Block Copolymer from Dissimilar Vinyl Monomer by Stable Free Radical Polymerization," *Macromolecules* 33, (2000), 4745 - 4749.

amount of homopolymer from chain transfer. Georges initially illustrated the capability of TEMPO mediated polymerization of dienes.¹⁷³ He demonstrated the ability to produce block copolymers of isoprene with a polystyrene prepolymer and maintain relatively narrow molecular weight distributions of approximately 1.3.

A key to demonstrating the success of the block formation for SFRP systems is verification of the transfer of the nitroxide moiety during propagation. ¹H NMR has become essential by showing a change in the shift of the methyl protons of the nitroxide species when attached to different monomer units. Along with Lansun and coworkers, Georges group has confirmed the transfer of the nitroxide utilizing NMR.¹⁷⁴ Due to the nature of the nitroxide species, a complicated NMR pattern arises representing the protons of the four nitroxide methyls. Georges and coworkers illustrated the shift in the proton spectrum from four distinct peaks at 0.2, 0.4, 0.9, and 1.1 ppm associated with attachment to a styrene unit in the macroinitiating homopolymer to a set of two peaks at 1.1 and 1.2 ppm when the second monomer unit, butadiene, has been sequentially added to the polystyrene homopolymer. The shift of the nitroxide resonances downfield is consistent with shielding abilities of the styrene unit and the butadiene unit. The upfield shifts at 0.2 and 0.4 are a result of the electron shielding from the adjacent phenyl ring. Consequently, the addition of the butadiene to the end of the chain removes these shielding effects and the proton shifts move farther downfield. In order to accurately monitor the chain ends, the molecular weights associated with these polymers were low. Researchers also demonstrated that high molecular weight copolymers could be formed with the polystyrene initiators yielding PS-*b*-PMMA and PS-*b*-PEMA with molecular weights of 165 kg/mol and 118 kg/mol, respectively. Additionally, these reactions

¹⁷³ Tuzar, Z.; Pospisil, H.; Plestil, J.; Lowe, A. B.; Baines, F. L.; Billingham, N. C.; Armes, S. P. "Micelles of Hydrophilic-Hydrophobic Poly(Sulfobetaine)-Based Block Copolymers," *Macromolecules* 30, (1997), 2509-2512.

¹⁷⁴ Benoit, D.; Harth, E.; Fox, P.; Waymouth, R. M.; Hawker, C. J. "Accurate Structural Control and Block Formation in the Living Polymerization of 1,3-Dienes by Nitroxide-Mediated Procedures," *Macromolecules* 33, (2000), 363-370; Georges, M. K.; Hamer, G. K.; Listigovers, N. A. "Block Copolymer Synthesis by a Nitroxide-Mediated Living Free Radical Polymerization Process," *Macromolecules* 31, (1998), 9087-9089.

produced polymers with relatively narrow molecular weight distributions ranging from 1.2-1.5.¹⁷⁵

While these early efforts demonstrated some success in the synthesis of well-defined block copolymers, the advent of α -hydrogen containing nitroxides has enabled access to more controlled structures. Using the α -hydrido type alkoxyamine for initiation, successful extension of the SFRP technique to diene homopolymerizations was achieved. Hawker employed the novel alkoxyamine to examine the ability to form diene homopolymers and random copolymers with various monomers.¹⁷⁶ The researchers successfully synthesized a variety of molecular weight poly(isoprene) homopolymers with molecular weight distributions from 1.08 to 1.14. These prepolymers were later employed as macroinitiators in the production of block copolymers with styrene and *t*-butyl acrylate. It was observed that transfer of the propagating radical from isoprene to styrene proceeded in a controlled fashion and vice versa. However, upon addition of the acrylate monomer, efficient initiation using the polyisoprene macroinitiator was not observed as evidenced in the broadened molecular weight distributions and the presence of residual polyisoprene homopolymer. The inability to convert the propagating isoprene radical into a *t*-butyl acrylate radical was attributed to the corresponding radical reactivities. The acrylate radical was more reactive and consequently the more stable isoprene radical was not converted. The use of an acrylate macroinitiator was employed to construct the same block copolymer in the reverse direction. The acrylic macroinitiator efficiently initiated the isoprene homopolymerization yielding diblock copolymers with narrow molecular weight distributions (1.09-1.22).

¹⁷⁵ Ruokolainen, J.; Saariaho, M.; Ikkala, O.; ten Brinke, G.; Thomas, E. L.; Torkkeli, M.; Serimaa, R. "Supramolecular Routes to Hierarchical Structures: Comb-Coil Diblock Copolymers Organized with Two Length Scales," *Macromolecules* 32, (1999), 1152-1158.

¹⁷⁶ Benoit, D.; Harth, E.; Fox, P.; Waymouth, R. M.; Hawker, C. J. "Accurate Structural Control and Block Formation in the Living Polymerization of 1,3-Dienes by Nitroxide-Mediated Procedures," *Macromolecules* 33, (2000), 363-370.

A similar phenomena was observed in a later study involving attempted block copolymerization of n-butyl acrylate and styrene.¹⁷⁷ The stability of the styryl radical prohibited the efficient crossover to the acrylate radical. In addition to the reactivity issue, it was found that the incompatibility of the styrene macroinitiator with the growing acrylate block impeded the crossover process. Analysis revealed that the blocking efficiency, or crossover, was approximately 0.7 using the styrenic macroinitiator. An improvement in the blocking efficiency was facilitated upon introduction of a small percentage of styrene with the n-butyl acrylate. The result of this addition was a tapered sequence between the pure styrene and pure acrylate blocks. The styrene monomer was consumed preferentially during the initial stages of the polymerization. The result was a retardation of the polymerization rate, which allowed a more complete crossover of all the polymer chains from styrene to n-butyl acrylate. While this method does allow the synthesis of more controlled block copolymers, the presence of the tapered sequence may lead to a deterioration of the mechanical properties typically associated with microphase separated morphologies. Another route to these well-defined styrene and n-butyl acrylate block copolymers was reported.¹⁷⁸ The researchers synthesized a difunctional alkoxyamine initiator to be used for a triblock copolymer. The initial step was the homopolymerization of n-butyl acrylate resulting in a difunctional macroinitiator. The next step was the polymerization of styrene. The crossover from n-butyl acrylate to styrene was a highly efficient process and enabled the production of the well-defined blocks that yield highly microphase separated morphologies.

Various other research groups have investigated the use of SFRP for the synthesis of well-defined block copolymers. Diaz and coworkers utilized the DEPN mediator to construct block copolymers consisting of 4-vinyl pyridine and dimethylacrylamide. The resulting investigation showed controlled polymerizations of both monomers up to relatively high monomer conversion (~60%). Use of the DEPN mediator allowed the

¹⁷⁷ Robin, S.; Gnanou, Y. "Triblock Copolymers Based on Styrene and N-Butyl Acrylate by Nitroxide-Mediated Radical Polymerization: Problems and Solutions," *Macromolecular Symposia* 165, (2001), 43-53.

¹⁷⁸ Robin, S.; Guerret, O.; Couturier, J. L.; Pirri, R.; Gnanou, Y. "Synthesis and Characterization of Poly(Styrene-B-N-Butyl Acrylate-B-Styrene) Triblock Copolymers Using a Dialkoxyamine as Initiator," *Macromolecules* 35, (2002), 3844-3848.

researchers to obtain significantly long blocks of both monomers unlike previous efforts.¹⁷⁹ Desimone and coworkers have also demonstrated the utility of the SFRP process for synthesizing block copolymers using both the conventional TEMPO mediator and the novel α -hydrido nitroxides.¹⁸⁰ A block copolymer of styrene and a styrenic derivative possessing a perfluorinated chain in the 4-position was constructed and exhibited well-defined properties. In addition, DEPN was utilized to synthesize a poly(styrene-*b*-tetrahydroperfluorodecyl acrylate) macromolecule with a molecular weight distribution of 1.10-1.14.

Random copolymers have also proven successful when employing the SFRP system to copolymerization. Copolymerization of monomers with styrene has enabled the production of high molecular weight macromolecules with monomer units that do not adequately homopolymerize under ideal SFRP conditions. Hawker and coworkers investigated the random copolymerization of methyl methacrylates and butyl acrylate with styrene using SFRP techniques.¹⁸¹ They demonstrated the ability to form narrow polydispersity random copolymers. In addition, they elucidated the effects of the monomer feed ratio on the ability of the polymerization to proceed in a controlled manner and produce prescribed molecular weights and narrow distributions. It was determined that as the percentage of styrene decreased in the monomer feed the molecular weight dropped and the polydispersity broadened, which is consistent with the inability of SFRP to control the methacrylate and acrylate. Other researchers have investigated copolymerization of *n*-butyl methacrylate with styrene and closely examined the kinetics of the polymerization.¹⁸² The kinetic analysis confirmed the earlier reports of Hawker

¹⁷⁹ Fischer, A.; Brembilla, A.; Lochon, P. "Influence of Initiator in Controlled Radical Polymerization Using Nitroxide Capping: The Case of N,N-Dimethylacrylamide. Synthesis of Block Copolymers of 4-Vinylpyridine and N,N-Dimethylacrylamide," *European Polymer Journal* 37, (2001), 33-37.

¹⁸⁰ Lacroix-Desmazes, P.; Boutevin, B.; Taylor, D. K.; DeSimone, J. M. "Synthesis of Fluorinated Block Copolymers by Nitroxide-Mediated Radical Polymerization for Supercritical Carbon Dioxide Applications," *Abstracts of Papers of the American Chemical Society* 224, (2002), 507-POLY.

¹⁸¹ Hawker, C. J.; Elce, E.; Dao, J. L.; Volksen, W.; Russell, T. P.; Barclay, G. G. "Well-Defined Random Copolymers by a "Living" Free-Radical Polymerization Process," *Macromolecules* 29, (1996), 2686-2688.

¹⁸² Cuervo-Rodriguez, R.; Fernandez-Monreal, C.; Madruga, E. L. "Sequence Distribution and Stereoregularity in Styrene/Butyl Methacrylate Copolymers Obtained at High Conversion by Stable Free-Radical Polymerization," *Macromolecular Rapid Communications* 23, (2002), 834-838; Cuervo-Rodriguez, R.; Fernandez-Monreal, C.; Madruga, E. L. "Kinetic Study of the Stable Free-Radical

showing that increasing the n-butyl methacrylate content decreased the control of the polymerization. Hawker has also examined the random copolymerization of functional monomers. He was able to demonstrate the formation of a random copolymer consisting of di(octadecyl) acrylamide and a acrylate monomer possessing a protected sugar functionality. In a another study, Miyamoto was able to synthesize a block copolymer containing a block of randomized styrene-acrylonitrile.¹⁸³ Although acrylonitrile was not successfully homopolymerized via SFRP, the copolymerization generated a narrow polydispersity polymer containing a block of randomly copolymerized styrene and acrylonitrile initiated with polystyrene oligomers. Styrene has also been utilized as a comonomer to produce polymers with other functionalities such as acrylates or vinyl pyridines.¹⁸⁴ In both studies, increasing the styrene feed ratio resulted in more controlled polymerizations as evidenced in the molecular weight distribution values.

In a similar fashion to SFRP, RAFT techniques have been employed in the manufacturing of well-defined block copolymers. RAFT agents proposed by Thang and coworkers are able to mediate the formation of controlled architectures. They have reported the controlled use of thiocarbonylthio species along with trithiocarbonates (Scheme 2.10) in fabrication of macromolecules with highly controlled molecular weights and compositions.¹⁸⁵ The RAFT agents provide a simple route to both di- and tri- block copolymers in a minimal number of synthetic steps. The diblock copolymer requires an initiating species with the attachment of a single RAFT agent attached and the

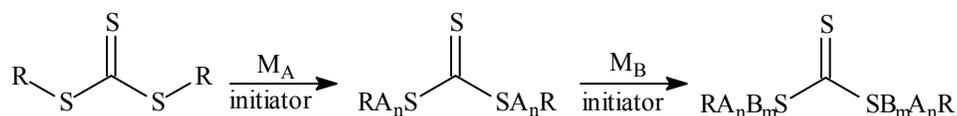
Copolymerization of Styrene with Butyl Methacrylate," *Journal of Polymer Science Part a-Polymer Chemistry* 40, (2002), 2750-2758.

¹⁸³ Fukuda, T.; Terauchi, T.; Goto, A.; Tsujii, Y.; Miyamoto, T. "Well-Defined Block Copolymers Comprising Styrene Acrylonitrile Random Copolymer Sequences Synthesized by "Living" Radical Polymerization," *Macromolecules* 29, (1996), 3050-3052.

¹⁸⁴ Bisht, H. S.; Ray, S. S.; Pandey, D.; Sharma, C. D.; Chatterjee, A. K. "Copolymerization of Dodecyl-4-Vinyl Benzoate and Dodecyl Acrylate by Conventional, Atom Transfer, and Nitroxide-Mediated Free-Radical Polymerization," *Journal of Polymer Science Part a-Polymer Chemistry* 40, (2002), 1818-1830; Lokaj, J.; Holler, P. "Nitroxide-Mediated Homopolymerization and Copolymerization of 2-Vinylpyridine with Styrene," *Journal of Applied Polymer Science* 80, (2001), 2024-2030.

¹⁸⁵ Mayadunne, R. T. A.; Rizzardo, E.; Chieffari, J.; Krstina, J.; Moad, G.; Postma, A.; Thang, S. H. "Living Polymers by the Use of Trithiocarbonates as Reversible Addition-Fragmentation Chain Transfer (RAFT) Agents: A Triblock Copolymers by Radical Polymerization in Two Steps," *Macromolecules* 33, (2000), 243-245; Chong, B. Y. K.; Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H. "A More Versatile Route to Block Copolymers and Other Polymers of Complex Architecture by Living Radical Polymerization: The RAFT Process," *Macromolecules* 32, (1999), 2071-2074.

living nature of the RAFT agent, which becomes located at the end of the growing chain, allows the further addition of monomer. Simple modification of the initiating species to contain two RAFT agents allows a two-step production of an ABA type triblock copolymer. In this case, the block initially polymerized remains in the middle while subsequent polymerization takes place on both ends of this initial species.



Scheme 2.10: Facile two-step synthesis of ABA triblock copolymer by RAFT.

Molecular weights for the diblocks synthesized by RAFT techniques using thiocarbonylthio compounds were as high as 52 kg/mol and polydispersities ranged from 1.06-1.24. Correspondingly, ABA triblocks were well defined with a range of molecular weight distribution from 1.08-1.18 for molecular weights up to 112 kg/mol. The trithiocarbonates agents performed in a likewise manner producing controlled and predictable high molecular weight materials. Another interesting feature of block copolymers formed by the RAFT process is the post polymerization reactions that can be performed. Specifically, attack with a nucleophile at the RAFT agent site cleaves off the mediating species leaving an S—H end group. In the triblocks synthesized with the trithiocarbonates, the nucleophilic attack at the thiocarbonyl produces two diblock copolymers with essentially identical molecular weights equal to half that of the original triblock.

Graft copolymers have also seen attention in controlled radical studies, which use the methods to form graft systems with highly controlled architectures. Initially, studies have primarily devoted attention to the use of both the ATRP techniques as well as SFRP. Matyjaszewski and researchers showed the successful production of a graft polymer via ATRP polymerization of the both the polymer backbone and the grafted chains (Scheme

2.11).¹⁸⁶ These polymers required the synthesis of a monomer unit, which can be polymerized by ATRP techniques and subsequently undergo another ATRP process on the side chain.

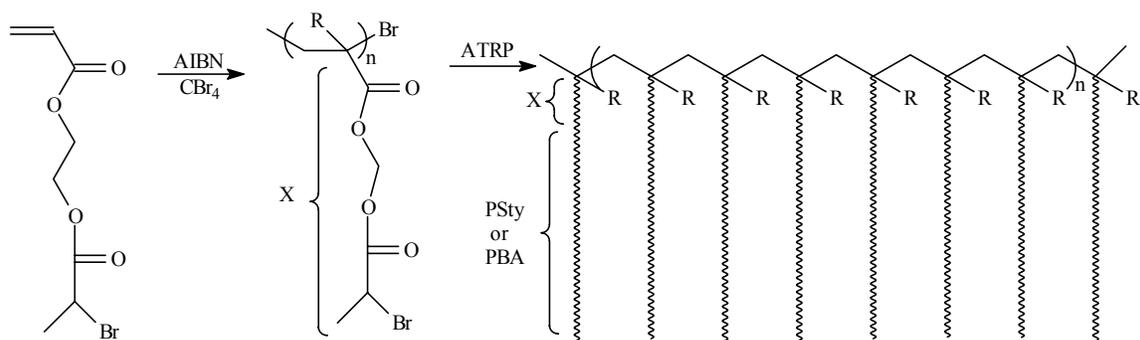
In a similar report, Fukuda and coworkers performed an ATRP type polymerization on initiating systems that were covalently grafted to a silica substrate.¹⁸⁷ The initiating systems were attached to the silica substrate via Langmuir-Blodgett techniques to produce a monolayer of ATRP initiating system (Figure 2.21). The next step performed was the ATRP polymerization of methyl methacrylate to produce a polymer grafted directly to the silica surface. Hawker and coworkers additionally investigated the polymerization of initiating systems covalently linked to a substrate.¹⁸⁸ However, in addition to ATRP, they examined the use of SFRP as a polymerization technique for producing well-defined graft arms. They verified the success of the polymerization on the substrate by cleaving the grafted chains and demonstrating comparable molecular weights to polymers synthesized in the bulk. The molecular weights proved almost identical with M_n of 51 kg/mol for the surface grafted system and 48 kg/mol for the bulk system. Also, the polydispersity for the grafted system proved to be slightly superior at 1.14 than that of the bulk polymerization. The greater control of the polymerization process in the graft systems was ascribed to the absence of chains resulting from autopolymerization. Shimada further explored the use of SFRP to form graft copolymer materials.¹⁸⁹ In their study, a poly(propylene) polymer is treated with gamma radiation in air to induce the formation of peroxide groups along the chain. These groups are successively reacted with styrene and TEMPO to produce pendant groups capable of SFRP polymerizations. The peroxide pendant groups were verified by infrared

¹⁸⁶ Beers, K. L.; Gaynor, S. G.; Matyjaszewski, K.; Sheiko, S. S.; Moller, M. "The Synthesis of Densely Grafted Copolymers by Atom Transfer Radical Polymerization," *Macromolecules* 31, (1998), 9413-9415.

¹⁸⁷ Ejaz, M.; Yamamoto, S.; Ohno, K.; Tsujii, Y.; Fukuda, T. "Controlled Graft Polymerization of Methyl Methacrylate on Silicon Substrate by the Combined Use of the Langmuir-Blodgett and Atom Transfer Radical Polymerization Techniques," *Macromolecules* 31, (1998), 5934-5936.

¹⁸⁸ Husseman, M.; Malmstrom, E. E.; McNamara, M.; Mate, M.; Mecerreyes, D.; Benoit, D. G.; Hedrick, J. L.; Mansky, P.; Huang, E.; Russell, T. P.; Hawker, C. J. "Controlled Synthesis of Polymer Brushes by "Living" Free Radical Polymerization Techniques," *Macromolecules* 32, (1999), 1424-1431.

¹⁸⁹ Miwa, Y.; Yamamoto, K.; Sakaguchi, M.; Shimada, S. "'Living" Radical Graft Polymerization of Styrene to Polypropylene with 2,2,6,6-Tetramethylpiperidiny-1-Oxy," *Macromolecules* 32, (1999), 8234-8236.



Scheme 2.11: Synthesis of graft copolymer via ATRP of both the arms and backbone.

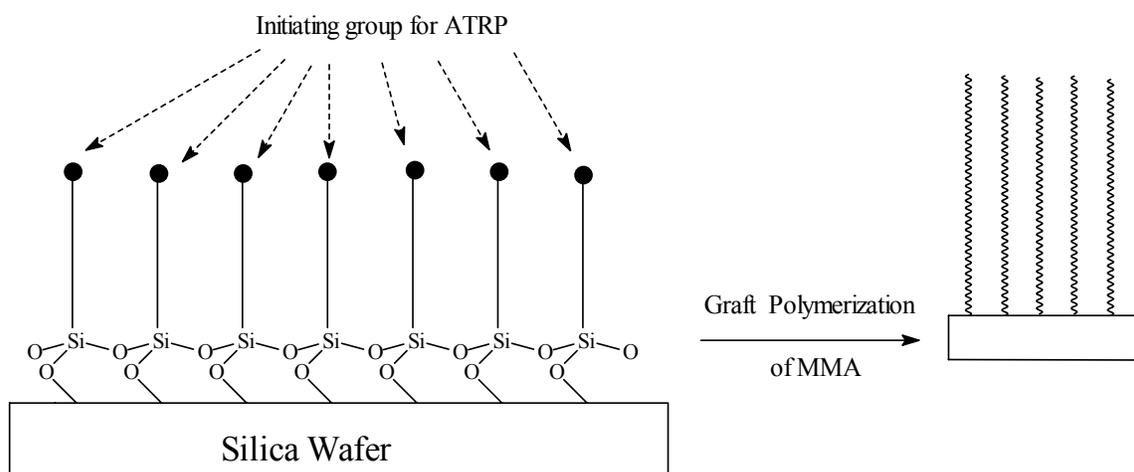


Figure 2.21: Formation of graft copolymer via ATRP of initiating groups covalently linked to silica substrate.

spectroscopy. Some non-grafted impurity did result and consequently lead to the production of non-grafted polymer chains in the final product. Molecular weights of the non-grafted impurities slightly exceeded those of the grafted chains. The TEMPO proved successful in controlling both the molecular weights of the free polymer as well as that of the grafted chains. This work is similar to that reported by Tobolsky who added a peroxide initiation site to the end of a polymer through a isocyanate linkage.¹⁹⁰ A final instance for the utilization of SFRP in the formation of graft copolymers is reported by Hawker and coworkers.¹⁹¹ They were able to employ SFRP in conjunction with a metallocene catalyzed polymerization to produce a graft type copolymer. Initially, an olefin possessing an alkoxyamine substituent was copolymerized with propene using a zirconium metallocene catalyst. Following the initial polymerization, the pendant groups containing the nitroxide moiety were subjected to SFRP polymerization conditions to produce polystyrene grafts. Again, cleavage of the grafted arms was used to examine the ability of the SFRP system to produce controlled polymer chains. Though the final graft copolymers possessed molecular weight distributions as high as 2.90, this dispersity is accredited to the disperse nature of metallocene catalyzed process. The broad nature was attributed to statistical variation in the number of initiating sites on the poly(olefin) backbone and the more disperse nature of the pregrafted poly(olefin). Cleavage of the graft arms produced polymer chains with polydispersities typical of SFRP techniques. SFRP proved advantageous for producing the desired controlled graft copolymer in addition to offering the possibility for further polymerization through the reactive alkoxyamine that remains on the graft chain ends.

2.5 Heterogeneous Stable Free Radical Polymerization Processes

While bulk or solution type polymerizations represent systems that are well defined in the stable free radical polymerization field, heterogeneous polymerization processes are often preferred in industry as environmentally benign alternatives to the

¹⁹⁰ Tobolsky, A. V. "Block Copolymers Formed by Reaction of an Isocyanate-Terminated Polymer with a Dual-Function Free-Radical Initiator and an Ethylenically Unsaturated Monomer," (U.S.: 1966).

¹⁹¹ Stehling, U. M.; Malmstrom, E. E.; Waymouth, R. M.; Hawker, C. J. "Synthesis of Poly(Olefin) Graft Copolymers by a Combination of Metallocene and "Living" Free Radical Polymerization Techniques," *Macromolecules* 31, (1998), 4396-4398.

solution and bulk methods.¹⁹² The importance of this technique has prompted an investigation into the utilization of SFRP in various heterogeneous polymerization schemes including suspension, dispersion, and various forms of emulsion polymerizations.¹⁹³ The elevated temperatures associated with the SFRP process required the use of high pressure systems because water was used as the dispersive phase and will boil at 100 °C. These early investigation revealed a distinct effect upon addition of TEMPO to the heterogeneous polymerization of styrene. Initial experiments without added nitroxide mediator resulted in high molecular weight polymer products and near complete monomer conversion. The addition of small amounts of TEMPO significantly reduced the degree of monomer conversion and resulted in lower molecular weight distributions. The molecular weights of the polymer latexes increased linearly with conversion. Unfortunately, high monomer conversion resulted in broadened polydispersities. One possible contributor to the broad distributions was the enhanced propensity for styrene thermal initiation via the Mayo mechanism, which led to alternative initiating radicals for polymerization.

Research efforts to optimize the heterogeneous SFRP process have focused on the polymerization of styrene due to its highly controlled polymerization under SFRP conditions. The loss of living character for styrene emulsion polymerization prompted an investigation into miniemulsion systems that possess a costabilizer causing the production of smaller colloidal droplets (~0.05-0.20 µm) compared to emulsion systems (~5-50 µm). The use of the miniemulsion pathway eliminates the particle nucleation step characteristic of emulsion polymerizations and has lead to greater success in controlling the polymerization process.¹⁹⁴ Georges continued previous work when he studied the

¹⁹² Matyjaszewski, K., ed., *Controlled Radical Polymerization*, vol. 685, *Acs Symposium Series* (1998).

¹⁹³ Bon, S. A. F.; Bosveld, M.; Klumperman, B.; German, A. L. "Controlled Radical Polymerization in Emulsion," *Macromolecules* 30, (1997), 324-326: Gabaston, L. I.; Jackson, R. A.; Armes, S. P. "Living Free-Radical Dispersion Polymerization of Styrene," *Macromolecules* 31, (1998), 2883-2888: Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. "Narrow Molecular-Weight Resins by a Free-Radical Polymerization Process," *Macromolecules* 26, (1993), 2987-2988: Marestin, C.; Noel, C.; Guyot, A.; Claverie, J. "Nitroxide Mediated Living Radical Polymerization of Styrene in Emulsion," *Macromolecules* 31, (1998), 4041-4044.

¹⁹⁴ Farcet, C.; Lansalot, M.; Charleux, B.; Pirri, R.; Vairon, J. P. "Mechanistic Aspects of Nitroxide-Mediated Controlled Radical Polymerization of Styrene in Miniemulsion, Using a Water- Soluble Radical Initiator," *Macromolecules* 33, (2000), 8559-8570: Pan, G. F.; Sudol, E. D.; Dimonie, V. L.; El-Aasser, M.

effects of CSA addition to the polymerization process. Although partitioning was expected to play a role in the effectiveness of CSA in rate acceleration, a distinct enhancement of rate was observed in the systems with the additive.¹⁹⁵ In addition to converting to a miniemulsion system, the chemical character of the nitroxide can be investigated as a means for improving polymerization control.¹⁹⁶ The researchers compared TEMPO derivatives with substitution in the 4-position to examine solubility effects. TEMPO was functionalized with a hydrogen, a hydroxyl, an acetate, and a benzoate group and the derivatives were subsequently utilized to mediate the emulsion polymerization of styrene. The acetate functionalized derivative yielded the most controlled polymers (MWD=1.29) up to 81% conversion. The effects of initiator solubility were also investigated. Model studies have also been performed that investigated manipulation of the polymerization recipe using a water soluble initiator.¹⁹⁷ The researchers found that the optimum conditions required a perfect stoichiometric ratio of nitroxide to propagating radicals. This balance yielded high conversion low molecular weight distribution polymer products. In addition, increasing the aqueous volume to organic volume ratio improved the polymerization "livingness".

The introduction of alternative nitroxides discovered in the laboratories of Gnanou¹⁹⁸ and Hawker¹⁹⁹ have enabled extension of the heterogeneous SFRP to

S. "Nitroxide-Mediated Living Free Radical Miniemulsion Polymerization of Styrene," *Macromolecules* 34, (2001), 481-488; Prodpran, T.; Dimonie, V. L.; Sudol, E. D.; El-Aasser, M. S. "Nitroxide-Mediated Living Free Radical Miniemulsion Polymerization of Styrene (Vol 155, Pg 1, 2000)," *Macromolecular Symposia* 163, (2001), A1-A1; Prodpran, T.; Dimonie, V. L.; Sudol, E. D.; El-Aasser, M. S. "Nitroxide-Mediated Living Free Radical Miniemulsion Polymerization of Styrene," *Macromolecular Symposia* 155, (2000), 1-14.

¹⁹⁵ Cunningham, M. F.; Tortosa, K.; Lin, M.; Keoshkerian, B.; Georges, M. K. "Influence of Camphorsulfonic Acid in Nitroxide-Mediated Styrene Miniemulsion Polymerization," *Journal of Polymer Science Part A-Polymer Chemistry* 40, (2002), 2828-2841.

¹⁹⁶ Cao, J. Z.; He, J. P.; Li, C. M.; Yang, Y. L. "Nitroxide-Mediated Radical Polymerization of Styrene in Emulsion," *Polymer Journal* 33, (2001), 75-80.

¹⁹⁷ Ma, J. W.; Cunningham, M. F.; McAuley, K. B.; Keoshkerian, B.; Georges, M. K. "Model Studies of Nitroxide-Mediated Styrene Miniemulsion Polymerization - Opportunities for Process Improvement," *Macromolecular Theory and Simulations* 12, (2003), 72-85.

¹⁹⁸ Grimaldi, S.; Finet, J. P.; Le Moigne, F.; Zeghdaoui, A.; Tordo, P.; Benoit, D.; Fontanille, M.; Gnanou, Y. "Acyclic Beta-Phosphonylated Nitroxides: A New Series of Counter-Radicals for "Living"/Controlled Free Radical Polymerization," *Macromolecules* 33, (2000), 1141-1147.

¹⁹⁹ Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. "Development of a Universal Alkoxyamine for "Living" Free Radical Polymerizations," *Journal of the American Chemical Society* 121, (1999), 3904-3920.

monomers such as n-butyl acrylate. Georges investigated the use of a hydroxyl α -hydrogen containing nitroxide in the miniemulsion polymerization of n-butyl acrylate.²⁰⁰ The resulting polymer latexes exhibited low MWD's and high monomer conversion (86%) for 3 h polymerization times. Other researchers in France employed a difunctional alkoxyamine possessing two DEPN mediator moieties for the miniemulsion polymerization of n-butyl acrylate.²⁰¹ The resulting molecular weight distributions were relatively narrow, but required limiting the monomer conversion. Above 70 % monomer conversion, molecular weight distributions began to broaden and polymerization proceeded in a uncontrolled fashion. This result was consistent with earlier results utilizing a difunctional alkoxyamine.²⁰² The kinetic and structural characteristics of the n-butyl acrylate SFRP miniemulsion system has also been investigated.²⁰³ The results of this study were consistent with the results obtained from bulk polymerization pathways. Initiator efficiency was improved upon use of a alkoxyamine initiator rather than a conventional free radical initiator and the resulting polymerization kinetics were similar to those of a bulk system. The structural properties of the product polymers were also similar to those obtained in bulk polymerization systems. Branched polymers were formed and the structure was confirmed using ¹³C NMR. The mechanism of branching was proposed as chain backbiting based on MALDI-TOF mass spectrometry analysis, which showed a single mediator fragment for each corresponding initiating fragment.

A significant advantage of the stable free radical polymerization is the ability to synthesis complex architectures such as block copolymers. Consequently, several investigations have explored the possibility of producing block copolymers in a

²⁰⁰ Keoshkerian, B.; Szkurhan, A. R.; Georges, M. K. "Nitroxide-Mediated Miniemulsion Acrylate Polymerization," *Macromolecules* 34, (2001), 6531-6532.

²⁰¹ Charleux, B.; Farcet, C.; Pirri, R.; Guerret, O. "Use of a Difunctional Alkoxyamine Initiator in the Miniemulsion Polymerization of N-Butyl Acrylate," *Abstracts of Papers of the American Chemical Society* 224, (2002), 663-POLY.

²⁰² Robin, S.; Guerret, O.; Couturier, J. L.; Pirri, R.; Gnanou, Y. "Synthesis and Characterization of Poly(Styrene-B-N-Butyl Acrylate-B-Styrene) Triblock Copolymers Using a Dialkoxyamine as Initiator," *Macromolecules* 35, (2002), 3844-3848.

²⁰³ Farcet, C.; Belleney, J.; Charleux, B.; Pirri, R. "Structural Characterization of Nitroxide-Terminated Poly(N- Butyl Acrylate) Prepared in Bulk and Miniemulsion Polymerizations," *Macromolecules* 35, (2002), 4912-4918; Farcet, C.; Nicolas, J.; Charleux, B. "Kinetic Study of the Nitroxide-Mediated Controlled Free-Radical Polymerization of N-Butyl Acrylate in Aqueous Miniemulsions," *Journal of Polymer Science Part a-Polymer Chemistry* 40, (2002), 4410-4420.

heterogeneous polymerization process. Researchers explored the use of TEMPO terminated polystyrene formed from a miniemulsion polymerization.²⁰⁴ A polystyrene oligomers was reacted for different times and the resulting molecular weights and molecular weight distributions were determined. All reactions showed no broadening of MWD's indicating the absence of chain termination. The polystyrene oligomers were then heated in the presence of n-butyl acrylate. The GPC peak of the resulting polymer was shifted completely from the original peak position. This indicated a complete transfer of the TEMPO mediator to the acrylate monomer. In addition, the resulting molecular weight distribution was narrow (MWD=1.18) indicating a controlled process. The ability of TEMPO to control acrylate polymerizations is contrary to previously observed results but raises the possibility of mediating alternative monomers with commercially available TEMPO. A similar report by Tortosa has shown results contrary to those reported in Georges study.²⁰⁵ A TEMPO capped polystyrene was used as a macroinitiator in the polymerization of n-butyl acrylate. Addition of the n-butyl acrylate resulted in a significant broadening of the molecular weight distribution. Moreover, greater acrylate monomer conversion yielded more broadened molecular weight distributions.

A further study provided more substantial results using a more suitable mediator, DEPN.²⁰⁶ First a n-butyl acrylate homopolymer was synthesized in a miniemulsion system. The resulting latexes exhibited molecular weight distributions typically between 1.2 and 1.4 for monomer conversions up to 80%, which were achieved within 6.5 h. For the block copolymer synthesis, the initial n-butyl acrylate polymerization was stopped before full monomer conversion and the latex was swollen with styrene monomer. The swollen latex particles were then heated to the appropriate reaction temperature and the polymerization began. A linear increase in molecular weight compared to monomer

²⁰⁴ Keoshkerian, B.; MacLeod, P. J.; Georges, M. K. "Block Copolymer Synthesis by a Miniemulsion Stable Free Radical Polymerization Process," *Macromolecules* 34, (2001), 3594-3599.

²⁰⁵ Tortosa, K.; Smith, J. A.; Cunningham, M. F. "Synthesis of Polystyrene-Block-Poly (Butyl Acrylate) Copolymers Using Nitroxide-Mediated Living Radical Polymerization in Miniemulsion," *Macromolecular Rapid Communications* 22, (2001), 957-961.

²⁰⁶ Farcet, C.; Charleux, B.; Pirri, R. "Poly(N-Butyl Acrylate) Homopolymer and Poly N-Butyl Acrylate-B-(N-Butyl Acrylate-Co-Styrene) Block Copolymer Prepared Via Nitroxide-Mediated Living/Controlled Radical Polymerization in Miniemulsion," *Macromolecules* 34, (2001), 3823-3826.

conversion was observed indicating a controlled system. Moreover, the complete shift of the GPC peak and the narrowed molecular weight distribution indicated the chain extension occurred in a well-defined manner. However, polymerizations that proceeded to greater than 95% conversion exhibited broadened MWD's. DSC analyses of the resulting block copolymers exhibited a single glass transition temperature that indicated incomplete phase separation of the polymer blocks.

2.6 Summary

The capabilities associated with the living polymerization systems will allow the production of highly defined materials necessary for many current applications. Architecture and molecular weight control are significantly enhanced with the controlled radical techniques as well as tolerance to a variety of functional groups. These methods of polymerization offer a facile procedure relative to the stringent laboratory techniques necessary for anionic type polymerizations and make available a degree of control similar to that of anionic methods. The utility of these schemes will be employed in the synthesis of multiphase block and graft copolymer systems, which will serve in pressure sensitive adhesive applications.

Chapter 3 Investigations of Thermal Polymerization in the Stable Free Radical Polymerization of 2-Vinylnaphthalene

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3.1 Abstract

The feasibility of utilizing stable free radical polymerization (SFRP) in the synthesis of well-defined poly(2-vinylnaphthalene) homopolymers was investigated. Efforts to control molecular weight by manipulating initiator concentration while maintaining a 2,2,6,6-tetramethylpiperidiny-1-oxy (TEMPO):benzoyl peroxide (BPO) molar ratio of 1.2:1 proved unsuccessful. In addition, systematic variations of the TEMPO: BPO molar ratio did not result in narrow molecular weight distributions (MWD). *In situ* FTIR indicated that the rate of monomer disappearance under SFRP and thermal conditions were identical. This observation indicated a lack of control in the presence of the stable free radical, TEMPO. The similarities in chemical structure between styrene and 2-vinylnaphthalene suggested thermally initiated polymerization occurred via the Mayo mechanism. A kinetic analysis of the thermal polymerization of styrene and 2-vinylnaphthalene suggested that the additional fused ring in 2-vinylnaphthalene increased the propensity for thermal polymerization. The observed rate constant for thermal polymerization of 2-vinylnaphthalene was determined using *in situ*

FTIR spectroscopy and was found to be one order of magnitude greater than styrene assuming pseudo first order kinetics. Also, an Arrhenius analysis indicated that the activation energy for the thermal polymerization of 2-vinylnaphthalene to be 30 kJ/mol less than styrene.

3.2 Introduction

A primary attribute of controlled and living polymerizations is the ability to tailor macromolecular structure to satisfy performance criteria for advanced technologies. Moreover, living polymerization methodologies allow the synthesis of block copolymers with uniform block size and well-defined morphologies.²⁰⁷ The synthesis of star, block, and graft copolymers via living polymerization processes has received significant attention.²⁰⁸ Living methodologies have traditionally involved anionic initiators;

²⁰⁷ Lacroix-Desmazes, P.; Delair, T.; Pichot, C.; Boutevin, B. "Synthesis of Poly(Chloromethylstyrene-B-Styrene) Block Copolymers by Controlled Free-Radical Polymerization," *Journal of Polymer Science Part a-Polymer Chemistry* 38, (2000), 3845-3854: Monteiro, M. J.; Sjoberg, M.; van der Vlist, J.; Gottgens, C. M. "Synthesis of Butyl Acrylate-Styrene Block Copolymers in Emulsion by Reversible Addition-Fragmentation Chain Transfer: Effect of Surfactant Migration Upon Film Formation," *Journal of Polymer Science Part a-Polymer Chemistry* 38, (2000), 4206-4217: Listigovers, N. A.; Georges, M. K.; Odell, P. G.; Keoshkerian, B. "Narrow-Polydispersity Diblock and Triblock Copolymers of Alkyl Acrylates by a "Living" Stable Free Radical Polymerization," *Macromolecules* 29, (1996), 8992-8993: Georges, M. K.; Hamer, G. K.; Listigovers, N. A. "Block Copolymer Synthesis by a Nitroxide-Mediated Living Free Radical Polymerization Process," *Macromolecules* 31, (1998), 9087-9089: Wang, J. S.; Matyjaszewski, K. "Controlled Living Radical Polymerization - Halogen Atom- Transfer Radical Polymerization Promoted by a Cu(I)Cu(II) Redox Process," *Macromolecules* 28, (1995), 7901-7910: Tuzar, Z.; Pospisil, H.; Plestil, J.; Lowe, A. B.; Baines, F. L.; Billingham, N. C.; Armes, S. P. "Micelles of Hydrophilic-Hydrophobic Poly(Sulfobetaine)-Based Block Copolymers," *Macromolecules* 30, (1997), 2509-2512: Chen, W. L.; Shull, K. R. "Hydrophilic Surface Coatings from Acrylic Block Copolymers," *Macromolecules* 32, (1999), 6298-6306.

²⁰⁸ Stenzel-Rosenbaum, M.; Davis, T. P.; Chen, V.; Fane, A. G. "Star-Polymer Synthesis Via Radical Reversible Addition- Fragmentation Chain-Transfer Polymerization," *Journal of Polymer Science Part a-Polymer Chemistry* 39, (2001), 2777-2783: Tsoukatos, T.; Pispas, S.; Hadjichristidis, N. "Star-Branched Polystyrenes by Nitroxide Living Free-Radical Polymerization," *Journal of Polymer Science Part a-Polymer Chemistry* 39, (2001), 320-325: Pasquale, A. J.; Long, T. E. "Synthesis of Star-Shaped Polystyrenes Via Nitroxide-Mediated Stable Free-Radical Polymerization," *Journal of Polymer Science Part a-Polymer Chemistry* 39, (2001), 216-223: Angot, S.; Murthy, K. S.; Taton, D.; Gnanou, Y. "Atom Transfer Radical Polymerization of Styrene Using a Novel Octafunctional Initiator: Synthesis of Well-Defined Polystyrene Stars," *Macromolecules* 31, (1998), 7218-7225: Mourey, T. H.; Miller, S. M.; Wesson, J. A.; Long, T. E.; Kelts, L. W. "Hydrolysis and Condensation Coupling of (Trimethoxysilyl)Phenyl-Terminated Polystyrene Macromonomers," *Macromolecules* 25, (1992), 45-52: Stehling, U. M.; Malmstrom, E. E.; Waymouth, R. M.; Hawker, C. J. "Synthesis of Poly(Olefin) Graft Copolymers by a Combination of Metallocene and "Living" Free Radical Polymerization Techniques," *Macromolecules* 31, (1998), 4396-4398: Beers, K. L.; Gaynor, S. G.; Matyjaszewski, K.; Sheiko, S. S.; Moller, M. "The Synthesis of Densely Grafted Copolymers by Atom Transfer Radical Polymerization," *Macromolecules* 31, (1998), 9413-9415.

however, monomer intolerance has led to the rapid development of controlled radical processes that are capable of producing well-defined polymers from monomers possessing diverse functional groups. Stable free (SFRP), atom transfer (ATRP), and reversible addition-fragmentation transfer (RAFT) radical polymerizations have emerged as three complimentary methodologies.²⁰⁹

Styrene was initially shown to polymerize with controlled molecular weights and narrow molecular weight distributions (MWD) via stable free radical polymerization processes.²¹⁰ Since these initial investigations, advancements in the use of controlled free radical polymerization methodologies have enabled the extension of SFRP techniques to a variety of monomers.²¹¹ In addition, unimolecular alkoxyamine initiators have resulted

²⁰⁹ Wang, J. S.; Matyjaszewski, K. "Living Controlled Radical Polymerization - Transition-Metal-Catalyzed Atom-Transfer Radical Polymerization in the Presence of a Conventional Radical Initiator," *Macromolecules* 28, (1995), 7572-7573: Rodlert, M.; Harth, E.; Rees, I.; Hawker, C. J. "End-Group Fidelity in Nitroxide-Mediated Living Free-Radical Polymerizations," *Journal of Polymer Science Part a-Polymer Chemistry* 38, (2000), 4749-4763: Gaynor, S. G.; Matyjaszewski, K., "Controlled/Living Radical Polymerization" (paper presented at the ACS, 2000): Ma, Q. G.; Wooley, K. L. "The Preparation of T-Butyl Acrylate, Methyl Acrylate, and Styrene Block Copolymers by Atom Transfer Radical Polymerization: Precursors to Amphiphilic and Hydrophilic Block Copolymers and Conversion to Complex Nanostructured Materials," *Journal of Polymer Science Part a-Polymer Chemistry* 38, (2000), 4805-4820: Matyjaszewski, K.; Qiu, J.; Tsarevsky, N. V.; Charleux, B. "Atom Transfer Radical Polymerization of N-Butyl Methacrylate in an Aqueous Dispersed System: A Miniemulsion Approach," *Journal of Polymer Science Part a-Polymer Chemistry* 38, (2000), 4724-4734: Georges, M. K. "An Overview of the Nitroxide-Mediated Living-Radical Polymerization Process," *Polymeric Materials Science and Engineering* 80, (1999), 283-284: Malmstrom, E. E.; Hawker, C. J. "Macromolecular Engineering Via 'Living' Free Radical Polymerizations," *Macromolecular Chemistry and Physics* 199, (1998), 923-935: Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. "Living Free-Radical Polymerization by Reversible Addition- Fragmentation Chain Transfer: The Raft Process," *Macromolecules* 31, (1998), 5559-5562: Monteiro, M. J.; Hodgson, M.; De Brouwer, H. "The Influence of Raft on the Rates and Molecular Weight Distributions of Styrene in Seeded Emulsion Polymerizations," *Journal of Polymer Science Part a-Polymer Chemistry* 38, (2000), 3864-3874: De Brouwer, H.; Schellekens, M. A. J.; Klumperman, B.; Monteiro, M. J.; German, A. L. "Controlled Radical Copolymerization of Styrene and Maleic Anhydride and the Synthesis of Novel Polyolefin-Based Block Copolymers by Reversible Addition-Fragmentation Chain-Transfer (Raft) Polymerization," *Journal of Polymer Science Part a-Polymer Chemistry* 38, (2000), 3596-3603.

²¹⁰ Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. "Narrow Molecular-Weight Resins by a Free-Radical Polymerization Process," *Macromolecules* 26, (1993), 2987-2988.

²¹¹ Keoshkerian, B.; Georges, M.; Quinlan, M.; Veregin, R.; Goodbrand, B. "Polyacrylates and Polydienes to High Conversion by a Stable Free Radical Polymerization Process: Use of Reducing Agents," *Macromolecules* 31, (1998), 7559-7561: Fukuda, T.; Terauchi, T.; Goto, A.; Tsujii, Y.; Miyamoto, T. "Well-Defined Block Copolymers Comprising Styrene Acrylonitrile Random Copolymer Sequences Synthesized by "Living" Radical Polymerization," *Macromolecules* 29, (1996), 3050-3052: Benoit, D.; Harth, E.; Fox, P.; Waymouth, R. M.; Hawker, C. J. "Accurate Structural Control and Block Formation in

in a more controlled SFRP process and have enabled more well-defined end group functionality and molecular weight.²¹² Styrenic derivatives have received significant attention to evaluate the substituent effects on the SFRP process.²¹³ These styrenic monomers typically possessed a functional group in the para position of the aromatic ring. The results for stable free radical polymerization of the styrenic derivatives were consistent with styrene exhibiting controlled molecular weights with narrow MWDs. In addition, SFRP methodologies for the styrenic derivatives included camphor sulfonic acid (CSA) to suppress thermal polymerization associated with styrene and its derivatives.²¹⁴ Only limited investigations have addressed the effect of an additional fused ring such as 2-vinylnaphthalene (2VN) (Figure 3.1).²¹⁵ The appeal of 2VN stems from both a higher glass transition temperature (123 °C) and its fluorescent properties that would enable the synthesis of fluorescently labeled macromolecules. Earlier investigations that involved 2VN polymerizations in the presence of nitroxides displayed poor control. This was attributed to solubility effects of the resulting polymer, which exhibited micellar behavior and a correspondingly more compact conformation. In

the Living Polymerization of 1,3-Dienes by Nitroxide-Mediated Procedures," *Macromolecules* 33, (2000), 363-370.

²¹² Hawker, C. J.; Barclay, G. G.; Orellana, A.; Dao, J.; Devonport, W. "Initiating Systems for Nitroxide-Mediated "Living" Free Radical Polymerizations: Synthesis and Evaluation," *Macromolecules* 29, (1996), 5245-5254; Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. "Development of a Universal Alkoxyamine for "Living" Free Radical Polymerizations," *Journal of the American Chemical Society* 121, (1999), 3904-3920.

²¹³ Keoshkerian, B.; Georges, M. K.; Boilsboissier, D. "Living Free-Radical Aqueous Polymerization," *Macromolecules* 28, (1995), 6381-6382; Ma, J. W.; Cunningham, M. F.; McAuley, K. B.; Keoshkerian, B.; Georges, M. K. "Nitroxide Partitioning between Styrene and Water," *Journal of Polymer Science Part a-Polymer Chemistry* 39, (2001), 1081-1089; Kazmaier, P. M.; Daimon, K.; Georges, M. K.; Hamer, G. K.; Veregin, R. P. N. "Nitroxide-Mediated "Living" Free Radical Polymerization: A Rapid Polymerization of (Chloromethyl)Styrene for the Preparation of Random, Block, and Segmental Arborescent Polymers," *Macromolecules* 30, (1997), 2228-2231; Barclay, G. G.; Hawker, C. J.; Ito, H.; Orellana, A.; Malenfant, P. R. L.; Sinta, R. F. "The "Living" Free Radical Synthesis of Poly(4-Hydroxystyrene): Physical Properties and Dissolution Behavior," *Macromolecules* 31, (1998), 1024-1031.

²¹⁴ Keoshkerian, B.; Georges, M. K.; Boilsboissier, D. "Living Free-Radical Aqueous Polymerization," *Macromolecules* 28, (1995), 6381-6382; Devonport, W.; Michalak, L.; Malmstrom, E.; Mate, M.; Kurdi, B.; Hawker, C. J.; Barclay, G. G.; Sinta, R. "Living" Free-Radical Polymerizations in the Absence of Initiators: Controlled Autopolymerization," *Macromolecules* 30, (1997), 1929-1934.

²¹⁵ Nowakowska, M.; Zapotoczny, S.; Krewicz, A. "Synthesis of Poly(Sodium Styrenesulfonate-Block-Vinylnaphthalene) by Nitroxide-Mediated Free Radical Polymerization," *Macromolecules* 33, (2000), 7345-7348; Long, T. E.; Lizotte, J. R.; Colby, R. H.; Erwin, B. "Investigation of the Suitability of the Stable Free Radical Polymerization of 2-Vinylnaphthalene," *Polym. Mater. Sci. Eng.* 84, (2001), 64-65; Marsitzky, D.; Blainey, P.; Carter, K. R. "Controlled Radical Polymerization of Electroluminescent Vinyl Derivatives," *Polymer Preprints (American Chemical Society, Division of Polymer Chemistry)* 42, (2001), 468-469.

particular, Nowakowska et al. recently examined the utility of 2-vinylnaphthalene as the second monomer in the formation of a water-soluble diblock copolymer with sodium styrenesulfonate.²¹⁶

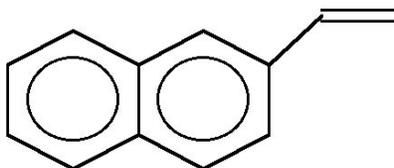


Figure 3.1: 2-Vinylnaphthalene monomer.

A significant complication in the stable free radical polymerization of styrene is the contribution of thermally initiated polymerization due to elevated reaction temperatures that are required for the SFRP propagation step. Styrene is well-known to undergo thermal initiation at typical reaction temperatures for SFRP.²¹⁷ Initiation occurs via the Mayo mechanism (Scheme 3.1) where two free radicals capable of initiation are produced when a monomer unit reacts with a Diels Alder adduct initially formed from two monomer units.²¹⁸ The adjacent aromatic ring provides resonance stabilization to both resulting radicals. Strong acids, such as CSA, have been employed to reduce the propensity for thermal polymerization.²¹⁹ It is proposed that strong acids protonate the Diels Alder adduct resulting in aromatization prior to radical formation. In addition to reducing thermal polymerization, CSA has also been employed in a reductive fashion to reduce the concentration of the free nitroxide.²²⁰

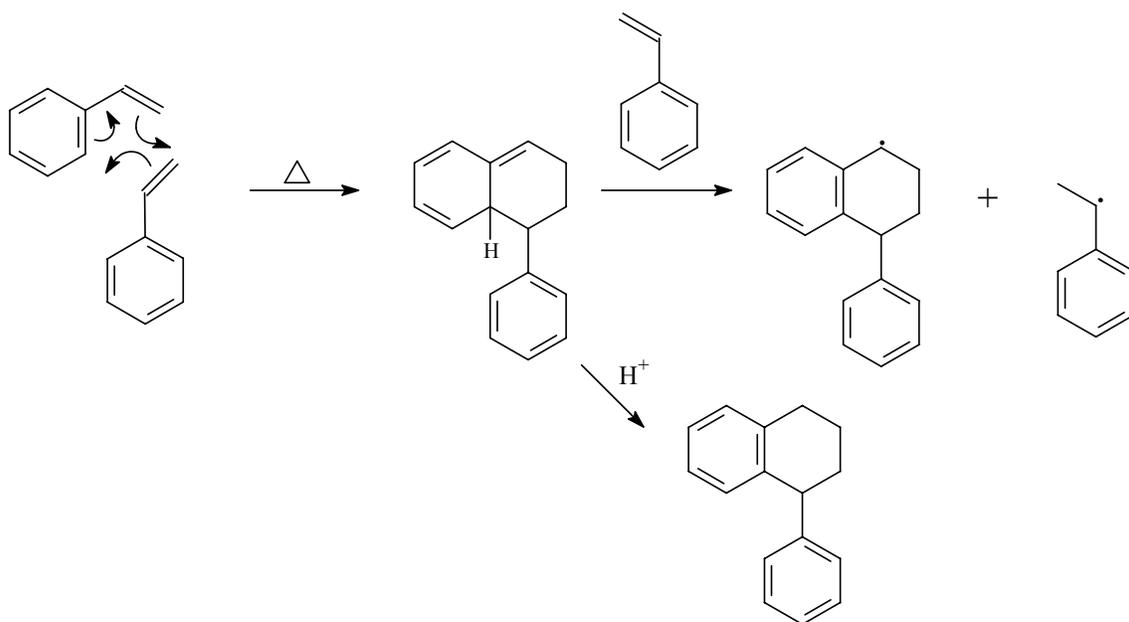
²¹⁶ Keoshkerian, B.; Georges, M.; Quinlan, M.; Veregin, R.; Goodbrand, B. "Polyacrylates and Polydienes to High Conversion by a Stable Free Radical Polymerization Process: Use of Reducing Agents," *Macromolecules* 31, (1998), 7559-7561.

²¹⁷ Priddy, D. B.; Howell, B. A. "Utility/Limitations of Nitroxide Mediated Polymerization for Low Cost Manufacture of Improved Styrenic Polymers," *Abstracts of Papers of the American Chemical Society* 224, (2002), 665-POLY; Priddy, D. B. "Recent Advances in Styrene Polymerization," *Advances in Polymer Science* 111, (1994), 67-114.

²¹⁸ Michalak, L.; Malmstroem, E.; Hawker, C.; Barclay, G.; Sinta, R. "Living Free Radical Polymerizations: Role of Autopolymerization and Nitroxide Mobility.," *Polymer Preprints (American Chemical Society, Division of Polymer Chemistry)* 38, (1997), 727-728.

²¹⁹ Buzanowski, W. C.; Graham, J. D.; Priddy, D. B.; Shero, E. "Spontaneous Polymerization of Styrene in the Presence of Acid - Further Confirmation of the Mayo Mechanism," *Polymer* 33, (1992), 3055-3059.

²²⁰ Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K.; Saban, M. "Narrow Polydispersity Polystyrene by a Free-Radical Polymerization Process - Rate Enhancement," *Macromolecules* 27, (1994), 7228-7229.



Scheme 3.1: Mayo thermal initiation mechanism for styrene and with intervention of strong acids.

It is hypothesized that the propensity for thermal initiation will significantly depend on the stability of the resulting radicals. The resonance stabilization effects of a second aromatic ring on the initiating radicals will be examined. The altered radical stability is hypothesized to affect the concentration of initiating radicals and the thermal initiation temperature. A ReactIR 1000 *in situ* FTIR spectrometer was utilized to monitor the thermal polymerization of 2VN and styrene. The capabilities of *in situ* spectroscopy for the analysis of polymerization processes have been previously described.²²¹ The polymerization of 2VN in the presence of 2,2,6,6-tetramethylpiperidiny-1-oxy (TEMPO) and benzoyl peroxide (BPO) was monitored via *in situ* FTIR spectroscopy and compared to the thermal polymerization of 2VN in the absence of TEMPO and free radical initiators. The observed rate constants for the pseudo first order thermal polymerization kinetics for 2VN and styrene were also determined. Thermal polymerization activation energies were calculated to quantitatively ascertain the relative rates of 2VN and styrene thermal polymerization.

3.3 Experimental

3.3.1 Materials.

Benzoyl peroxide, 97% (BPO) (FW 242.23, mp 104-106 °C), 2,2,6,6-tetramethyl-1-piperidinyloxy, 98% (TEMPO) (FW 156.25, mp 36-40 °C), 2-vinylnaphthalene, 95% (2VN) (FW 154.21, mp 62-65 °C, contains up to 5% methanol), styrene (FW 104.15, bp 145-146 °C), and camphor sulfonic acid, 98% (CSA) (FW 232.3, mp 203-206 °C) were purchased from Aldrich and employed as received unless otherwise noted. Styrene, inhibited by 10-15 ppm of *t*-butyl catechol, was passed through a neutral alumina column to remove the inhibitor. Solvents, *m*-xylenes (FW 106.17, bp 137-144 °C, 98.5%) and chlorobenzene (FW 112.56, bp 132 °C, >99%), were used as received and purged with nitrogen prior to polymerization to remove oxygen.

²²¹ Storey, R. F.; Shoemaker, K. A. "Poly(Styrene-*B*-Isobutylene) Multiarm Star-Block Copolymers," *Journal of Polymer Science Part a-Polymer Chemistry* 37, (1999), 1629-1641; Pasquale, A. J.; Long, T. E. "Real-Time Monitoring of the Stable Free Radical Polymerization of Styrene Via *in-Situ* Mid-Infrared Spectroscopy," *Macromolecules* 32, (1999), 7954-7957.

3.3.2 Characterization.

Molecular weights were determined at 40 °C in THF (ACS grade) using polystyrene standards on a Waters SEC equipped with an autosampler and a 410 RI detector. *In situ* FTIR analysis was performed using an ASI Applied Systems ReactIR 1000 attenuated total reflectance (ATR) reaction apparatus equipped with a light conduit and DiComp (diamond composite) insertion probe.

3.3.3 In situ FTIR Monitoring and Stable free Radical Polymerization of 2-Vinylnaphthalene.

Stable free radical solution polymerization of 2-vinylnaphthalene monitored by *in situ* FTIR spectroscopy is described. Initially, all dry reagents, TEMPO (6.2 mg, 0.040 mmol), BPO (8.0 mg, 0.033 mmol), and 2VN (8.0 g, 51.95 mmol) were added to a three-necked 250 mL round-bottomed flask with a small magnetic stir bar. Two necks of the reaction vessel were wire sealed with rubber septa. The DiComp probe was inserted into the third fitted neck of the flask and sealed tight. The solvent, chlorobenzene (11.0 mL), was added using a syringe and the flask was purged with nitrogen for 10-15 minutes. The probe tip was positioned below the surface of the solvent to collect spectra of the reaction mixture. In all cases, monomer was added to the flask before the TEMPO and BPO to avoid an exothermic reaction associated with the mixing of TEMPO and BPO.²²² The reaction vessel was then placed in an oil bath heated at 130 °C and FTIR data collection was commenced. The ReactIR analysis system was programmed to collect a spectrum every 5 minutes for 24 hours. After 24 h, the reaction mixture was diluted at 25 °C with THF (~40 mL) to reduce the viscosity and then precipitated into methanol (~600 mL). The final polymer product was dried at reduced pressure overnight at room temperature.

3.3.4 Thermal Polymerization of 2-Vinylnaphthalene and Styrene.

Typical thermal solution polymerization of 2VN is described. The monomer (2.0 g) was added to a 50 mL round-bottomed flask with a small magnetic stir bar.

²²² Wang, D.; Wu, Z. "Facile Synthesis of New Unimolecular Initiators for Living Radical Polymerizations," *Macromolecules* 31, (1998), 6727-6729.

Chlorobenzene (2.7 mL) was then added to the reaction flask. The reaction vessel was wire sealed with a rubber septum and subsequently purged with nitrogen for 10-15 minutes. For the styrene systems, the monomer was syringed into the flask after sealing and purging. The reaction vessel was placed in an oil bath heated at 130 °C for 24 h. The reaction mixture was diluted with THF (~20 mL) and precipitated into methanol (~400 mL). The product polymer was dried at reduced pressure overnight at room temperature.

3.4 Results and Discussion

3.4.1 Suitability of 2-Vinylnaphthalene for Stable free Radical Polymerization.

2-Vinylnaphthalene was polymerized using typical SFRP conditions (0.1 wt% BPO, 24 h, 20 wt% solids in *m*-xylenes, 130 °C, 1.2:1 molar ratio of TEMPO to BPO). These conditions afforded little control over the polymer molecular weight distribution (MWD). Also, number average molecular weights (M_n) were limited to below 17000. The initial polymerization temperature was selected for direct comparison to styrene SFRP processes; however, the ideal temperature will be dependent on the specific dissociation energy of the 2VN TEMPO bond. It was also determined that temperatures ranging from 100-130 °C using SFRP conditions did not result in narrow molecular weight distributions. Various SFRP experimental factors were varied in an attempt to control the polymer MWD. Variations in the percent solids in the reaction mixture revealed that bulk reactions were preferred for limiting the molecular weight distribution and increasing the M_n to 30000-35000. However, molecular weight distributions for the bulk were higher than typical values for SFRP processes, i.e. ~1.55 versus ~1.10. 2VN was polymerized in chlorobenzene and exhibited similar results to those obtained in *m*-xylenes to ensure that chain transfer was not responsible for the broad molecular weight distributions or the loss of control of polymer molecular weight.

The initiator concentration and the molar ratio of nitroxide to the initiator, which are often varied to control the molecular weight and molecular weight distribution of the resulting polymers, did not display significant control over the resulting polymer structure. The initiator concentration was varied from 0.10 to 0.01 weight percent

relative to monomer (Table 3.1). Number average molecular weights ranged from 27100 to 31200, which were within the typical error for SEC. Also, the optimum molar ratio of TEMPO:BPO for styrene polymerization was established as 1.2:1 to provide a 1:1 ratio of TEMPO to initiating radical based on a 60% initiator efficiency.²²³ Attempts to control the molecular weight distribution by varying this molar ratio also proved unsuccessful. The molecular weight distribution and molecular weight remained constant over the range from 1.2:1 to 2:1. However, with a large excess of TEMPO (4.8:1), the molecular weight was significantly reduced (M_n 11200) while the opposite effect was seen with a molar ratio of 0.60:1.0 (M_n 43100). The observed changes in molecular weight are consistent with a similar study for stable free radical styrene polymerization.²²⁴ Although previous investigations have not examined molar ratios as high as 4.8:1, the molecular weight trend also is expected to be consistent for higher molar ratios. Unfortunately, the MWD remained high at all molar ratios. The decomposition of benzoyl peroxide will lead to a variety of initiating radicals in the reaction mixture.²²⁵

A unimolecular initiator was synthesized according to Hawker et al. to eliminate the possibility of multiple initiating species due to initiator decomposition (Scheme 3.2).²²⁶ The initiator was initially evaluated for styrene, since styrenic monomers are well suited for controlled polymerization via SFRP processes. As expected, the unimolecular initiator afforded excellent control of polystyrene molecular weight and molecular weight distribution (1.08). However, the classic unimolecular initiator did not result in well-defined poly(2-vinylnaphthalene) homopolymers and molecular weight distributions (1.60-1.80) exceeded typical SFRP values.

²²³ MacLeod, P. J.; Veregin, R. P. N.; Odell, P. G.; Georges, M. K. "Stable Free Radical Polymerization of Styrene: Controlling the Process with Low Levels of Nitroxide," *Macromolecules* 30, (1997), 2207-2208.

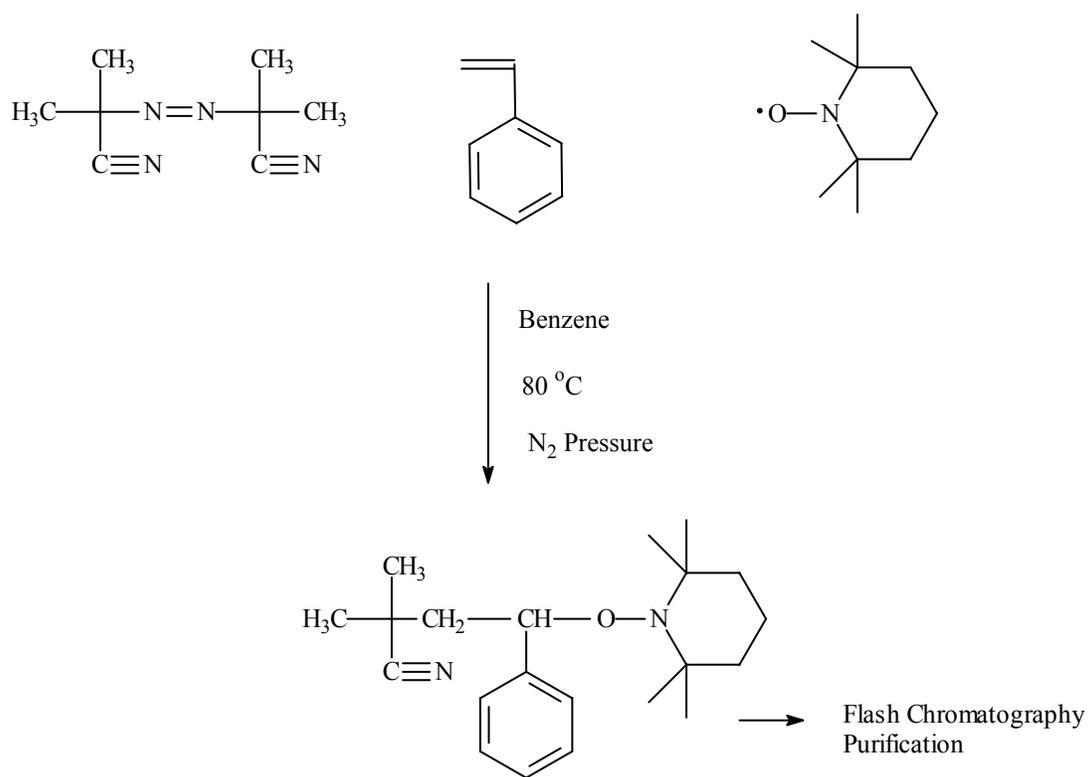
²²⁴ Barclay, G. G.; Hawker, C. J.; Ito, H.; Orellana, A.; Malenfant, P. R. L.; Sinta, R. F. "The "Living" Free Radical Synthesis of Poly(4-Hydroxystyrene): Physical Properties and Dissolution Behavior," *Macromolecules* 31, (1998), 1024-1031.

²²⁵ Odian, G. *Principles of Polymerization*, 3rd ed. (New York: John Wiley and Sons, Inc., 1991).

²²⁶ Hawker, C. J.; Barclay, G. G.; Orellana, A.; Dao, J.; Devonport, W. "Initiating Systems for Nitroxide-Mediated "Living" Free Radical Polymerizations: Synthesis and Evaluation," *Macromolecules* 29, (1996), 5245-5254.

Table 3.1: Effect of initiator concentration on polymer molecular weight and molecular weight distribution.

wt% BPO ^a	M_n^b	M_w/M_n^b	% isolated
0.10	27100	1.56	85
0.05	27300	1.63	78
0.01	31200	1.78	84
0.01	34900	1.74	85



Scheme 3.2: Reaction scheme for synthesis of unimolecular initiator.

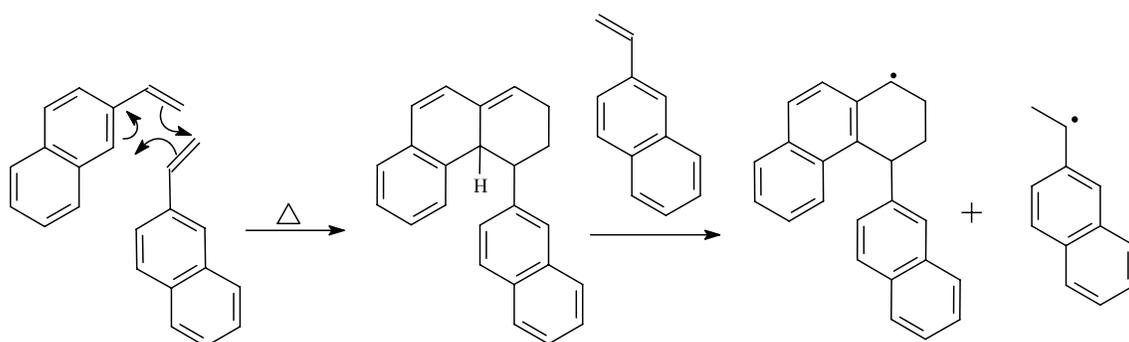
3.4.2 Thermal Initiation Contribution to the Polymerization of 2VN under SFRP Conditions.

The lack of molecular weight control over a broad range of initiator concentrations suggested that an alternative initiation process was occurring. The thermal polymerization of styrene is a well-documented process.²²⁷ Similarities in the chemical structure of styrene and 2VN suggested that thermal polymerization may occur via an identical mechanism. Polymerization of 2VN in the absence of added free radical initiator was quite facile. At typical SFRP temperatures, the thermal bulk polymerization of 2VN resulted in a polymer product with a number average molecular weight of 45300 and molecular weight distribution of 2.02. The reaction temperature was systematically varied to examine the propensity for 2VN to undergo thermal polymerization. At temperatures as low as 80 °C, 2VN was capable of producing a polymer product at ~65% conversion in 24 h with a molecular weight distribution of 1.93. A number of additives have been employed in earlier studies to prohibit and capture the species associated with the thermal initiation of styrene (Scheme 3.1).²²⁸ A similar mechanism is proposed for 2VN thermal initiation where the generated radicals are stabilized by two fused aromatic rings compared to one ring in styrene (Scheme 3.3). The reducing agent, camphor sulfonic acid (CSA), was utilized in an attempt to limit the proposed thermal initiating mechanism for 2VN. However, unlike in the styrene polymerization where CSA was successful in reducing thermal polymerization, an appreciable reduction in the thermal contribution was not observed for the thermal polymerization of 2VN.

In situ FTIR monitoring of 2VN polymerization under thermal and SFRP conditions (130 °C) revealed nearly identical reaction rates (within the error associated with *in situ* FTIR spectroscopy). All monitored polymerizations were performed in chlorobenzene to reduce exothermic effects associated with bulk thermal polymerization. The monomer consumption rates in the thermal and SFRP process were nearly identical

²²⁷ Bengough, W. I.; Park, G. B. "The Thermal Polymerization of Styrene at Temperatures up to 250°," *European Polymer Journal* 14, (1978), 889-894.

²²⁸ Mayo, F. R. "The Dimerization of Styrene," *Journal of the American Chemical Society* 90, (1968), 1289-1295; Chong, Y. K.; Rizzardo, E.; Solomon, D. H. "Confirmation of the Mayo Mechanism for the Initiation of the Thermal Polymerization of Styrene," *Journal of the American Chemical Society* 105, (1983), 7761-7762.



Scheme 3.3: Proposed thermal initiation mechanism for 2-vinylnaphthalene.

(Figure 3.2). Conversion of the monomer disappearance curves to kinetic plots of $\ln[M]$ versus time exhibited a linear relationship consistent with pseudo first order kinetics associated with SFRP and thermal polymerizations. Determination of the observed rate constants (k_{obs}) confirmed the identical rates of the two processes indicating that the thermal mechanism dominates initiation under SFRP conditions (Figure 3.3). The k_{obs} values for the polymerization of 2VN in thermal and SFRP conditions were $9.16 \times 10^{-2} \text{ h}^{-1}$ and $9.42 \times 10^{-2} \text{ h}^{-1}$, respectively. The small difference in observed rate constants is easily attributed to slight variance in experimental procedures and possibly to minimal participation of TEMPO in capping the propagating radical.

3.4.3 Comparison of the Thermal Polymerization of Styrene and 2-Vinylnaphthalene.

The propensity of styrene to thermally polymerize at reaction temperatures above $100 \text{ }^{\circ}\text{C}$ is well documented. Consequently, *in situ* FTIR was employed to monitor the solution thermal polymerization of both styrene and 2-vinylnaphthalene. 2VN displayed a marked increase in its tendency to undergo polymerization initiated via a thermal mechanism compared to styrene. The thermal polymerization of both monomers was monitored at 80 , 100 and $130 \text{ }^{\circ}\text{C}$ to elucidate the thermal initiation over a range of temperatures (Figure 3.4 & Figure 3.5). The rate of styrene consumption exhibited a steady decrease over the temperature range; monomer disappearance at $80 \text{ }^{\circ}\text{C}$ was almost negligible. On the contrary, 2VN displayed a substantial degree of thermal initiation and polymerization at all reaction temperatures, although decreasing the reaction temperature resulted in lower monomer conversion.

Examination of the observed rate constants determined using a pseudo first kinetics analysis illustrated a large variance in the thermal polymerization of styrene with the rate constants covering two orders of magnitude over the chosen temperature range. On the other hand, 2VN observed rate constants varied by a single order of magnitude over the range of examined temperatures. An Arrhenius plot of $\ln k_{\text{obs}}$ versus $1/T$ was constructed using the observed rate constants to determine the energy of activation for each process. Styrene exhibited an activation of 97.7 kJ/mol that agreed well with earlier

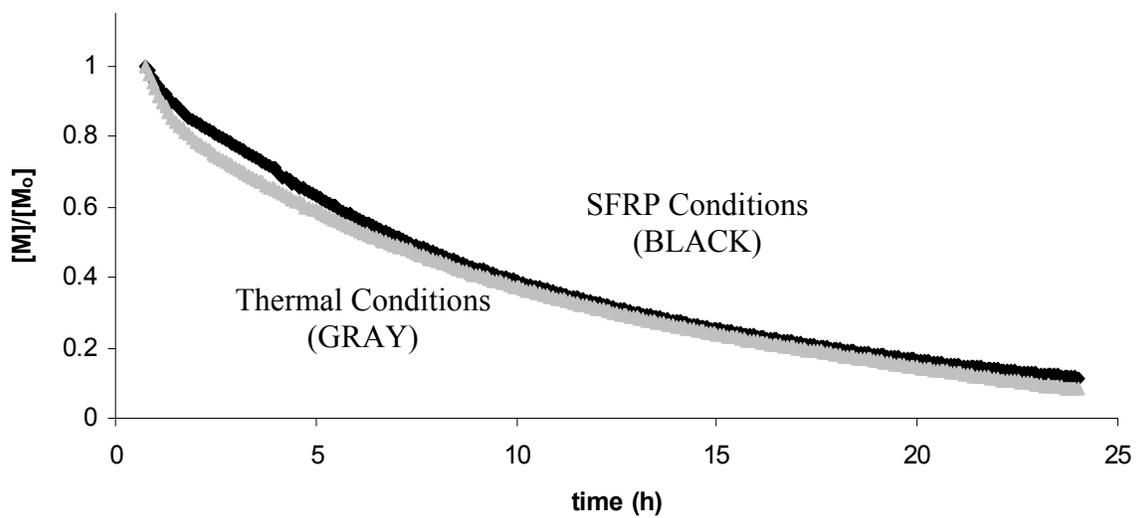


Figure 3.2: Plot of monomer disappearance versus time for SFRP and thermal conditions (the CH bending mode at 988 cm^{-1} was utilized for analysis).

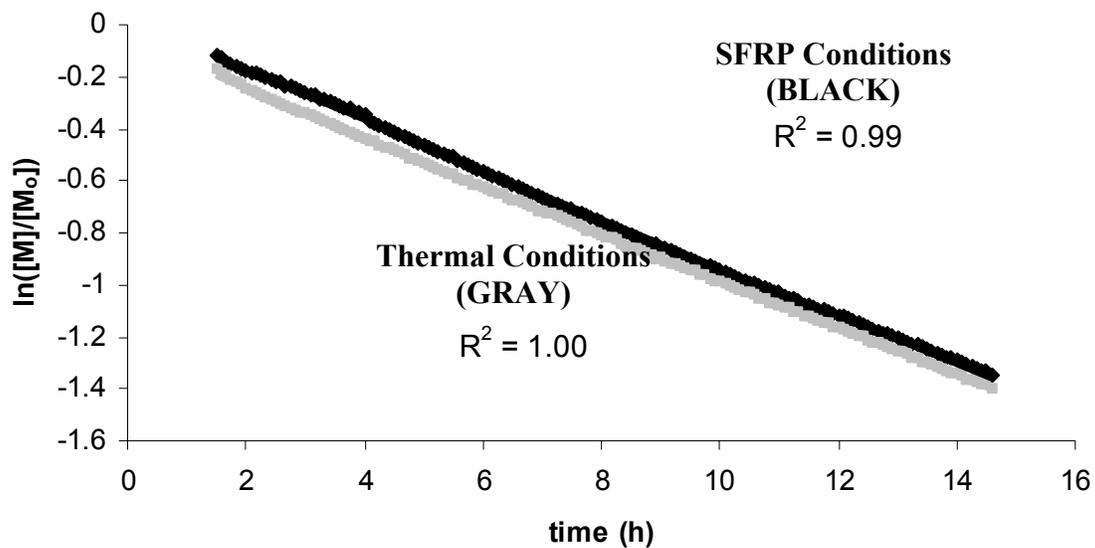


Figure 3.3: Pseudo first order kinetic plot for 2-vinylnaphthalene polymerized under SFRP and thermal conditions (assumes a steady state concentration of radicals).

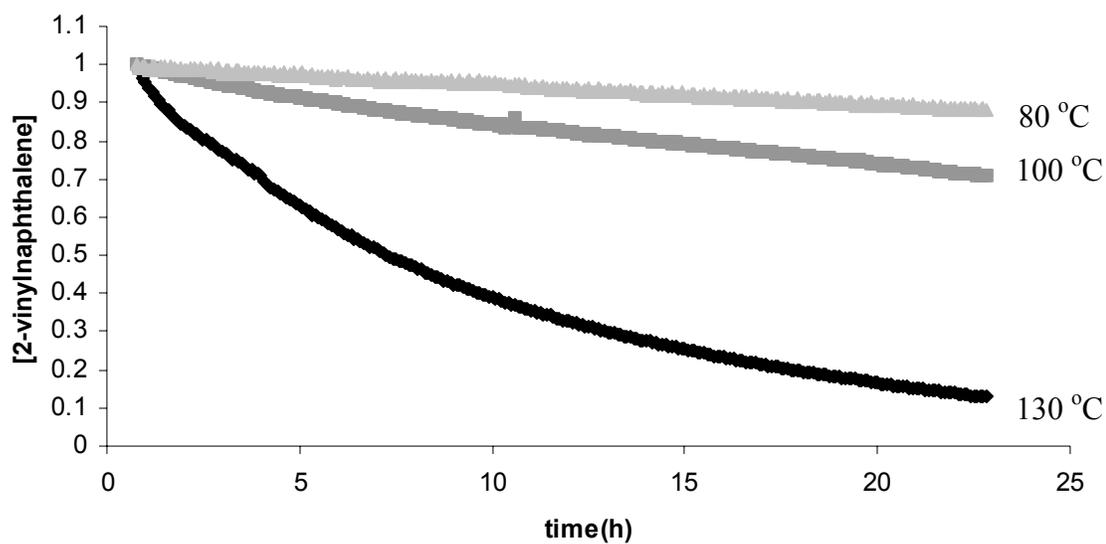


Figure 3.4: Disappearance of 2-vinylnaphthalene monomer at different temperatures in solution polymerization under thermal conditions (monitoring the CH bending mode at 988 cm^{-1}).

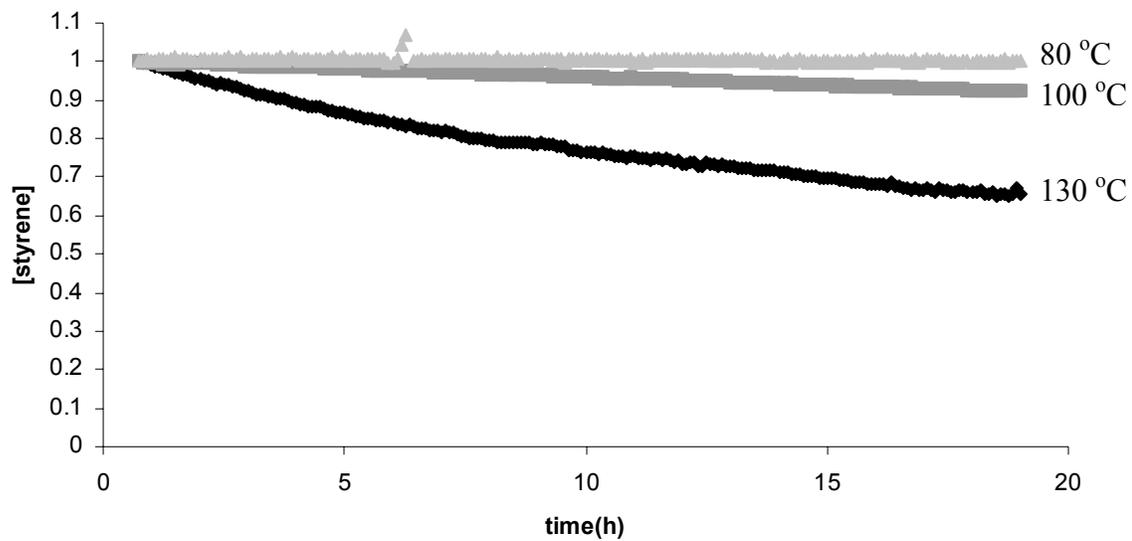


Figure 3.5: Disappearance of styrene monomer at different temperatures in solution polymerization under thermal conditions (monitoring the CH bending mode at 988 cm^{-1}).

literature (89.6 kJ/mol) (Figure 3.6).²²⁹ The 2-vinylnaphthalene monomer exhibited an expectedly lower energy of activation at 67.1 kJ/mol demonstrating the greater ease of thermal polymerization for this monomer compared to styrene (Figure 3.7). While the activation energy for thermal polymerization was lower in the 2VN system, the intercept in the Arrhenius analysis, which was related to the frequency factor (A), indicated that the styrene thermal polymerization process resulted in more collisions with proper orientation to react. The A value determined for the styrene thermal polymerization process was three orders of magnitude greater than observed in the case of 2VN thermal polymerization. The dominance of thermal polymerization in the 2VN system can be attributed to the lower activation energy for thermal polymerization compared to the energy (82 kJ/mol) associated with the dissociation of TEMPO from the end of the polymer chain.²³⁰ On the other hand, the thermal polymerization activation energy for styrene is higher than the TEMPO dissociation energy allowing nitroxide mediation to control molecular weight and MWDs. The greater ease of thermal polymerization was attributed to the enhanced stability of radicals formed according to the Mayo mechanism for thermal initiation. The two fused rings increase the stability of the radicals formed from the thermal initiation process lowering the energy necessary to produce the initiating radicals.

3.5 Conclusions

The polymerization of 2-vinylnaphthalene at elevated temperatures is severely complicated by facile thermal initiation. Additives that are designed to reduce the contribution of thermal polymerization were ineffective. Furthermore, *in situ* FTIR data confirmed the identical nature of the polymerization process under SFRP and thermal polymerization conditions showing observed rate constants of $9.42 \times 10^{-2} \text{ h}^{-1}$ and $9.16 \times 10^{-2} \text{ h}^{-1}$, respectively. Comparison of 2VN to styrene showed a greater susceptibility to thermal polymerization. Determination of the activation energies for styrene and 2VN

²²⁹ Hoyer, H. W.; Santoro, A. V.; Barrett, E. J. "Activation Energies for Styrene Polymerization by Differential Thermal Analysis," *Journal of Polymer Science, Polymer Chemistry Edition* 6, (1968), 1033-1034.

²³⁰ Veregin, R. P. N.; Odell, P. G.; Michalak, L. M.; Georges, M. K. "The Pivotal Role of Excess Nitroxide Radical in Living Free Radical Polymerizations with Narrow Polydispersity," *Macromolecules* 29, (1996), 2746-2754.

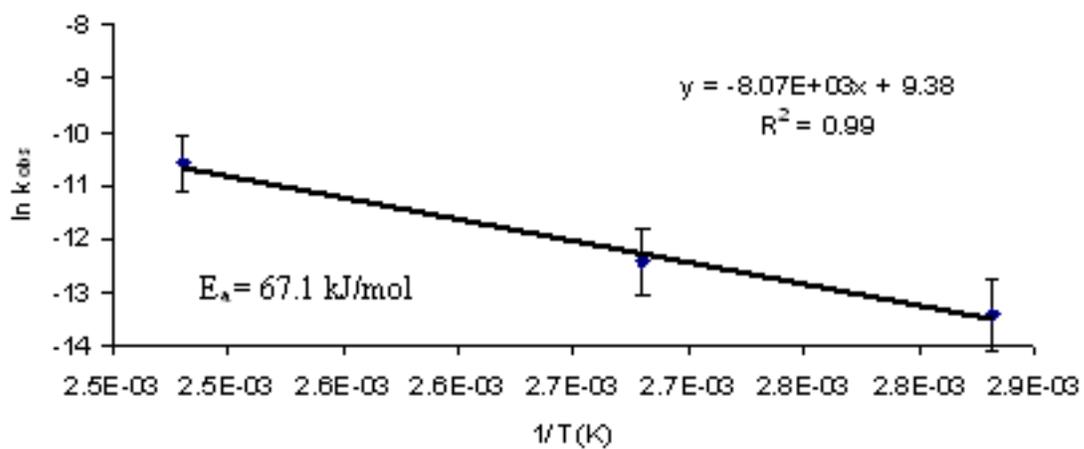


Figure 3.6: Arrhenius plot for the thermal polymerization of 2-vinylnaphthalene in chlorobenzene at 80, 100 and 130 °C

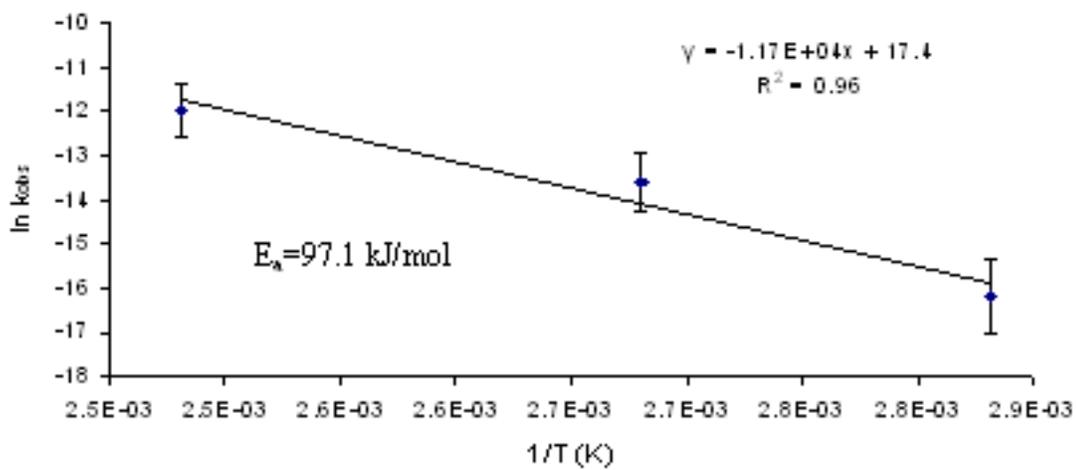


Figure 3.7: Arrhenius plot for the thermal polymerization of styrene in chlorobenzene at 80, 100 and 130 °C.

thermal polymerization confirmed that a significantly lower energy was required to produce significant thermal contributions. The E_a for thermal polymerization of 2-vinylnaphthalene was approximately 30 kJ/mol less than styrene. Although SFRP was unsuccessful for 2-vinylnaphthalene at typical reaction temperatures, lower reaction temperatures resulted in reduced thermal initiation. Consequently, future efforts will focus on the synergistic combination of additives and TEMPO derivatives that are suitable at lower reaction temperatures.

3.6 Acknowledgements

The authors would like to acknowledge the National Science Foundation (NSF CRIF 9974632) for *in situ* FTIR instrumentation support, the Petroleum Research Fund (35190-AC7), the 3M company, and the Center for Adhesive and Sealant Science (CASS) at Virginia Tech and the Adhesive and Sealant Council for financial support of this project.

Chapter 4 : Stable Free Radical Polymerization of Styrene in Combination with 2-Vinylnaphthalene Initiation

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4.1 Abstract

The elevated temperatures required for the SFRP process lead to thermal initiation of styrene via the classic Mayo mechanism. Studies have examined the utility of styrene thermal initiation in controlled autopolymerization processes. In addition, the thermal polymerization of 2-vinylnaphthalene (2VN), a styrenic derivative with an additional fused ring, was examined. An Arrhenius analysis of the 2VN thermal polymerization process using *in situ* FTIR spectroscopy demonstrated a greater propensity for 2VN thermal polymerization compared to styrene. A modified Mayo mechanism was proposed based on additional resonance stabilization in 2VN derived radicals compared to a single ring of resonance stabilization for styrene. The utility of 2-vinylnaphthalene as an initiator in the SFRP of styrene was investigated. 2-Vinylnaphthalene initiation resulted in polymers that are end-functionalized with a single 2VN unit or a polycyclic unit that results from the Diels-Alder reaction in the initiation mechanism. Variation of the styrene/2VN molar ratio in the presence of TEMPO enabled molecular weight control and narrow molecular weight distributions (~1.1-1.2). The integrity of the polymer end-groups were confirmed using ^1H NMR and UV-Vis spectroscopy. In addition, the UV-Vis absorbance of the 2VN initiating unit was used for construction of a calibration curve

for molecular weight prediction based on the intensity of the absorbance at 312 nm associated with 2VN initiation. The polymerization process was monitored using *in situ* FTIR and the observed rate constant of the system initiated with 2VN ($1.73 \times 10^{-5} \text{ s}^{-1}$) was comparable to BPO ($k_{\text{obs}} = 1.99 \times 10^{-5} \text{ s}^{-1}$) initiation.

Keywords: initiators, UV-vis and infrared spectroscopy, polystyrene, stable free radical polymerization

4.2 Introduction

The rigorous experimental requirements of anionic polymerization methodologies and electrophilic functional group intolerance have limited the potential impact of living polymerization.²³¹ Controlled radical polymerization is potentially more facile and offers a complementary approach to well-defined architecture and composition in addition to functional group tolerance.²³² Living anionic polymerization processes also permit the introduction of well-defined polymer end groups, which are introduced via a nucleophilic substitution of the living anionic chain end.²³³ However, recent efforts in stable free radical polymerization (SFRP) techniques have also demonstrated the ability to functionalize the polymer chain ends. Functionalized polymers were derived from both the SFRP initiator fragment and the nitroxide end group.²³⁴ For example, the synthesis of

²³¹ Hawker, C. J.; Hedrick, J. L.; Malmstrom, E.; Trollsas, M.; Stehling, U. M.; Waymouth, R. M. "Solvent-Free Polymerization and Processes," *ACS Symp. Ser.* 713, (1998), 127-139.

²³² Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. "Narrow Molecular-Weight Resins by a Free-Radical Polymerization Process," *Macromolecules* 26, (1993), 2987-2988; Wang, J. S.; Matyjaszewski, K. "Controlled Living Radical Polymerization - Atom-Transfer Radical Polymerization in the Presence of Transition-Metal Complexes," *Journal of the American Chemical Society* 117, (1995), 5614-5615; Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. "Living Free-Radical Polymerization by Reversible Addition- Fragmentation Chain Transfer: The Raft Process," *Macromolecules* 31, (1998), 5559-5562.

²³³ Quirk, R. P.; Kinning, D. J.; Fetters, L. J. *Comprehensive Polymer Science*, ed. S. L. Aggarwal, vol. 7 (London: Pergamon Press, 1989).

²³⁴ Malmstrom, E. E.; Hawker, C. J. "Macromolecular Engineering Via 'Living' Free Radical Polymerizations," *Macromolecular Chemistry and Physics* 199, (1998), 923-935; Turro, N. J.; Lem, G.; Zavarine, I. S. "A Living Free Radical Exchange Reaction for the Preparation of Photoactive End-Labeled Monodisperse Polymers," *Macromolecules* 33, (2000), 9782-9785; Ballesteros, O. G.; Maretta, L.; Sastre, R.; Scaiano, J. C. "Kinetics of Cap Separation in Nitroxide-Regulated "Living" Free Radical Polymerization: Application of a Novel Methodology Involving a Prefluorescent Nitroxide Switch," *Macromolecules* 34, (2001), 6184-6187; Beyou, E.; Jarroux, N.; Zydowicz, N.; Chaumont, P. "Functional End-Group Exchange of Nitroxide- or Bromo-Terminated Polystyrene," *Macromolecular Chemistry and Physics* 202, (2001), 974-979.

a unimolecular initiator comprising a protecting group and subsequent post-polymerization modification resulted in displacement of the protecting group and attachment of a fluorescent tag.²³⁵ On the other hand, the propagating chain end that contains a terminal nitroxide was also functionalized, and the single addition of maleic anhydride or other maleimide derivatives to the chain end was readily accomplished.²³⁶ In addition, functionalization at the propagating chain end was achieved using a functionalized nitroxide mediator, such as 4-hydroxy-TEMPO, and the resulting terminal hydroxyl group was suitable for further reactions.²³⁷

Although the utility of SFRP was broadly investigated for styrenics, acrylates, and acrylamides, most attention has focused on styrenic monomers.²³⁸ A prominent concern in the stable free radical polymerization of styrene is the propensity for thermal polymerization, and elevated temperatures required for the SFRP process result in the thermal initiation of styrene via the classic Mayo mechanism.²³⁹ Thermal initiation increases the radical concentration during polymerization and alters the nitroxide to radical molar ratio resulting in a loss of polymerization control. Strong acids such as camphor sulfonic acid (CSA) were employed to reduce the extent of thermal initiation in the stable free radical polymerization of styrenic derivatives.²⁴⁰ Further investigations

²³⁵ Frank, B.; Gast, A. P.; Russell, T. P.; Brown, H. R.; Hawker, C. "Polymer Mobility in Thin Films," *Macromolecules* 29, (1996), 6531-6534.

²³⁶ Harth, E.; Hawker, C. J.; Fan, W.; Waymouth, R. M. "Chain End Functionalization in Nitroxide-Mediated "Living" Free Radical Polymerizations," *Macromolecules* 34, (2001), 3856-3862.

²³⁷ Hawker, C. J.; Hedrick, J. L.; Malmstrom, E. E.; Trollsas, M.; Mecerreyes, D.; Moineau, G.; Dubois, P.; Jerome, R. "Dual Living Free Radical and Ring Opening Polymerizations from a Double-Headed Initiator," *Macromolecules* 31, (1998), 213-219.

²³⁸ Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. "Development of a Universal Alkoxyamine for "Living" Free Radical Polymerizations," *Journal of the American Chemical Society* 121, (1999), 3904-3920.

²³⁹ Georges, M. K.; Kee, R. A.; Veregin, R. P. N.; Hamer, G. K.; Kazmaier, P. M. "Nitroxide Mediated Free-Radical Polymerization Process - Autopolymerization," *Journal of Physical Organic Chemistry* 8, (1995), 301-305; Greszta, D.; Matyjaszewski, K. "Mechanism of Controlled/"Living" Radical Polymerization of Styrene in the Presence of Nitroxyl Radicals. Kinetics and Simulations," *Macromolecules* 29, (1996), 7661-7670; Mayo, F. R. "The Dimerization of Styrene," *Journal of the American Chemical Society* 90, (1968), 1289-1295.

²⁴⁰ Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K.; Saban, M. "Narrow Polydispersity Polystyrene by a Free-Radical Polymerization Process - Rate Enhancement," *Macromolecules* 27, (1994), 7228-7229; Buzanowski, W. C.; Graham, J. D.; Priddy, D. B.; Shero, E. "Spontaneous Polymerization of Styrene in the Presence of Acid - Further Confirmation of the Mayo Mechanism," *Polymer* 33, (1992), 3055-3059.

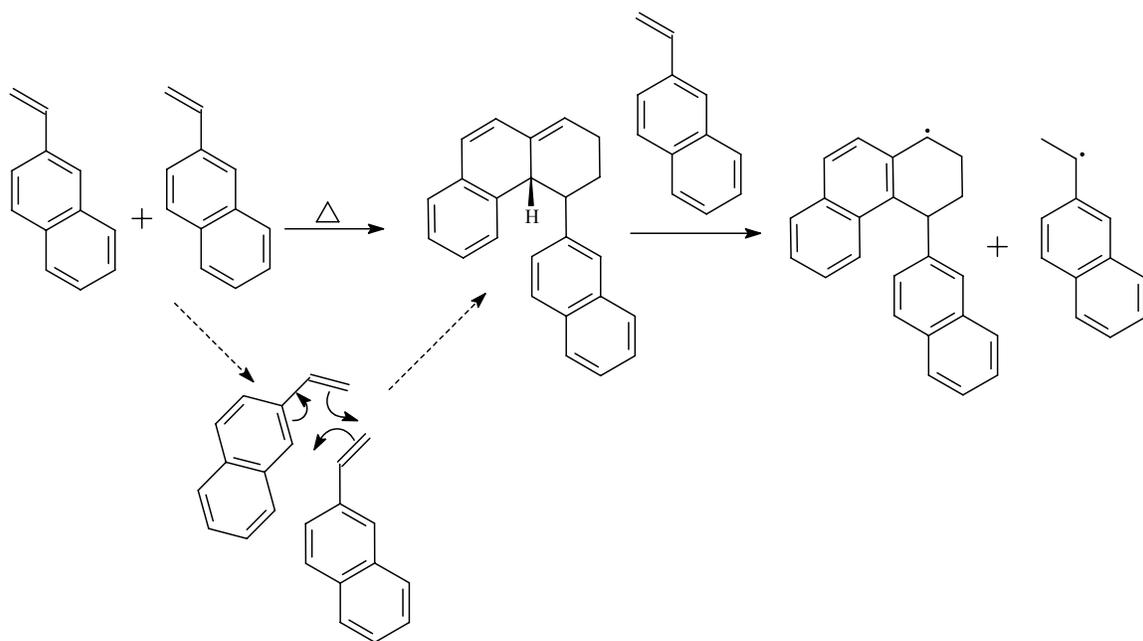
have explored the use of styrene thermal initiation in controlled autopolymerization processes. Various styrenic derivatives were employed in thermally initiated homopolymerizations and copolymerizations mediated with 2,2,6,6-tetramethylpiperidiny-1-oxy (TEMPO).²⁴¹ Polymerizations proceeded in a relatively controlled fashion with molecular weight distributions ranging from 1.15-1.49 depending on the molar ratio of TEMPO to monomer. Furthermore, number average molecular weights depended on the molar ratio of styrene to TEMPO.

In addition to various styrenic derivatives that possess functional groups in the *para* position,^[15] the thermal polymerization of 2-vinylnaphthalene (2VN), a styrenic derivative with an additional fused ring, was recently examined.²⁴² This study demonstrated a greater propensity for 2VN thermal polymerization compared to styrene. *In situ* FTIR spectroscopy was utilized in an Arrhenius analysis of the 2VN thermal polymerization process and the activation energy for styrene thermal polymerization was determined to be 30 kJ/mol greater than for 2VN thermal polymerization. A modified Mayo mechanism was proposed (Scheme 4.1), based on additional resonance stabilization in 2VN derived radicals compared to a single ring of resonance stabilization for styrene.

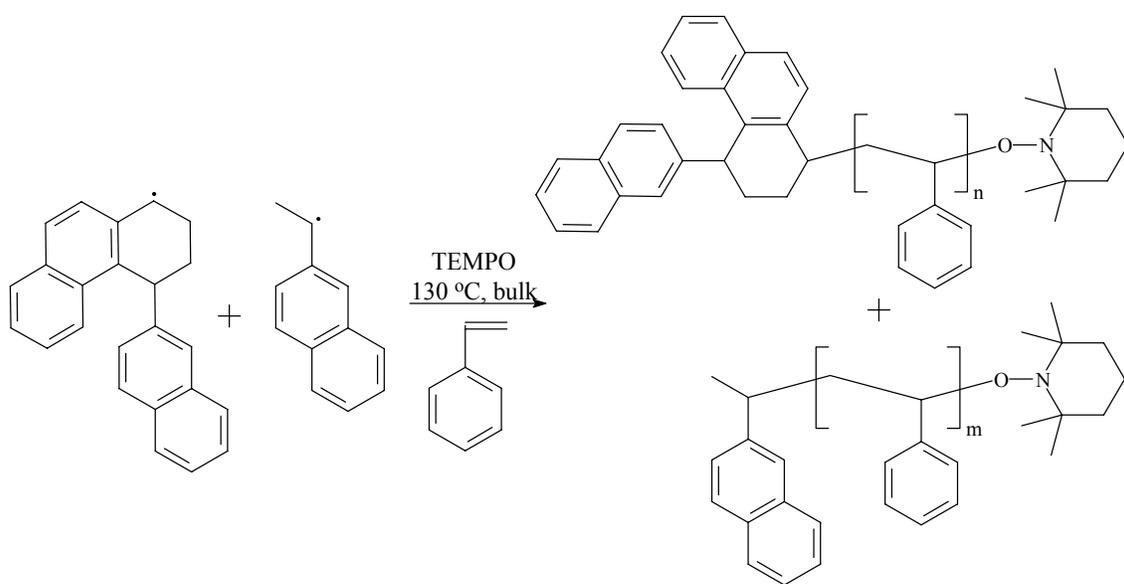
This manuscript describes the utility of 2-vinylnaphthalene as an initiator in the SFRP of styrene (Scheme 4.2). The discovery of free radical initiators that do not contain peroxide or azo linkages is particularly interesting for many commercial applications. 2-Vinylnaphthalene initiation will result in polymers that are end-functionalized with a single 2VN unit or a polycyclic unit that results from the Diels-Alder reaction in the initiation mechanism. The large difference in activation energies for 2VN versus styrene thermal initiation will result in consumption of 2VN in the early stages of polymerization.

²⁴¹ Devonport, W.; Michalak, L.; Malmstrom, E.; Mate, M.; Kurdi, B.; Hawker, C. J.; Barclay, G. G.; Sinta, R. "Living" Free-Radical Polymerizations in the Absence of Initiators: Controlled Autopolymerization," *Macromolecules* 30, (1997), 1929-1934.

²⁴² Lizotte, J. R.; Erwin, B. M.; Colby, R. H.; Long, T. E. "Investigations of Thermal Polymerization in the Stable Free-Radical Polymerization of 2-Vinyl Naphthalene," *Journal of Polymer Science Part a-Polymer Chemistry* 40, (2002), 583-590.



Scheme 4.1: Proposed Mayo mechanism for thermal initiation of 2-vinylnaphthalene.



Scheme 4.2: Stable free radical polymerization of styrene initiated via 2VN thermal initiation.

Although the Diels-Alder adduct of 2VN is the resonance favored product, it is possible that a Diels Alder adduct derived from styrene and 2VN will also form. Thus, the variation of the styrene/2VN molar ratio in the presence of TEMPO will enable control of the molecular weight and molecular weight distribution.

4.3 Experimental

4.3.1 Materials

Styrene, 2-vinylnaphthalene (2VN), benzoyl peroxide (BPO) and 2,2,6,6-tetramethylpiperdiny-1-oxy (TEMPO) were obtained from Aldrich. Styrene was purified via vacuum distillation (25 °C, 0.1 mm Hg) from calcium hydride using three freeze-thaw cycles, and 2VN was sublimed (25 °C, 0.1 mm Hg) immediately prior to use. BPO and TEMPO were used as received.

4.3.2 Characterization

¹H NMR spectra were collected on a Varian Unity-400 spectrometer in CDCl₃ at ambient temperature. Molecular weights were determined at 40 °C in THF (ACS grade) at 1 mL/min using polystyrene standards on a Waters SEC equipped with 3 in-line PLgel 5 μm MIXED-C columns with an autosampler and a 410 RI detector. UV-Vis measurements were performed on an Ocean Optics USB2000 miniature fiber optic spectrometer equipped with an *in situ* T300 RT transmission dip probe. *In situ* FTIR monitoring was performed with an ASI Mettler-Toledo ReactIR 1000 apparatus with a stainless steel dicomp insertion probe.²⁴³ A comparison of peak height versus a common baseline point was performed to eliminate data scatter due to baseline drift.

4.3.3 *In situ* FTIR Monitoring of the Stable Free Radical Polymerization of Styrene with 2VN Thermal Initiation

A typical polymerization of styrene including *in situ* FTIR spectroscopy is described. 2VN (215.6 mg, 1.4 mmole) and TEMPO (45.2 mg, 0.29 mmole) were added

²⁴³ Pasquale, A. J.; Long, T. E. "Real-Time Monitoring of the Stable Free Radical Polymerization of Styrene Via *in-Situ* Mid-Infrared Spectroscopy," *Macromolecules* 32, (1999), 7954-7957; Pasquale, A. J.; Long, T. E. "Synthesis of Star-Shaped Polystyrenes Via Nitroxide-Mediated Stable Free-Radical Polymerization," *Journal of Polymer Science Part a-Polymer Chemistry* 39, (2001), 216-223.

with a magnetic stir bar to a three-necked 100 mL round-bottomed flask fitted with the FTIR insertion probe. The reaction system was sealed and purged with nitrogen for 10 min. Styrene monomer (15 g, 144 mmole) was added to the reaction flask using a syringe. The reaction vessel was placed in an oil bath heated at 130 °C. Data collection was immediately commenced and FTIR spectra were collected every 5 min for 24 h. The reaction contents typically vitrified prior to 24 h, and the final polymer product was readily dissolved in THF (~50 mL) and subsequently precipitated into excess methanol.

4.4 Results and Discussion

4.4.1 2VN Thermal Initiation in Styrene SFRP

The stable free radical polymerization of styrene in the presence of TEMPO was thermally initiated using 2VN. Various polymerization parameters were systematically altered to evaluate their effects on the control of the styrene polymerization process and the resulting polymer composition. Autopolymerization of styrene for 24 h in the presence of a 30:1 molar ratio of styrene to TEMPO yielded a polymer with low conversion (<10%). However, the addition of initiator quantities of 2VN (20:1 molar ratio of styrene:2VN) at constant TEMPO concentration (2VN:TEMPO, 3.0:1.0), significantly increased the monomer conversion to 50% for identical polymerization times and temperatures. It should be noted that in addition to providing initiating radicals for the polymerization, it is possible that 2VN functions as a comonomer at early stages of the polymerizations. In addition to a higher monomer conversion, the resulting product exhibited a narrow molecular weight distribution (1.11). Variation of the styrene:2VN molar ratio (Table 4.1) at a constant 3.0:1.0 2VN:TEMPO molar ratio permitted empirical control of the molecular weights of the resulting polystyrene homopolymers. Although the molecular weight distributions were narrow, the relatively low monomer conversion after 24 h indicated a slow polymerization process. However, optimization of polymerization conditions (48 h) provided higher molecular weights ($M_n=25200$, $M_w/M_n=1.15$) and monomer conversions (80%). It was proposed that the presence of excess nitroxide in the polymerization process resulted in slow monomer conversion. Consequently, the molar ratio of 2VN to TEMPO was also systematically studied in order to determine the optimal molar ratio that maintained polymerization

Table 4.1: Polystyrene homopolymers initiated with various amounts of 2VN.

2VN (mol %) ^b	M_n^a	M_w/M_n^a	% Yield
1.0	6050	1.22	28
3.0	3130	1.12	31
5.0	2680	1.11	47
7.0	1170	1.09	12

^a Molecular weight determined using polystyrene standards

^b 1.5:1.0 2VN:TEMPO molar ratio

control and maximized monomer conversion at the shorter times. Molar ratios of 1.5 to 12.0 for 2VN:TEMPO were examined at a constant 2VN:styrene ratio and the polymerization results are shown in Table 4.2. The results indicated that polymerization control was maintained for molar ratios from 1.0 to 5.0. However, a broadening of the molecular weight distribution was observed at ratios greater than 5.0. In addition, an increase in the 2VN:TEMPO molar ratio resulted in an increase in the molecular weight of the polymer products. This result was expected because the lower TEMPO concentration was expected to shift the activation-deactivation equilibrium in favor of the active chain end and allowed for higher monomer conversions and molecular weights. The solvent effect on the polymerization process was also explored, and solution polymerizations in chlorobenzene at 130 °C resulted in similar molecular weights and conversions to bulk processes. Polymer products of similar molecular weight were isolated using both precipitation into methanol and solvent removal *in vacuo* and subsequently analyzed using GPC to investigate possible fractionation during polymer recovery. Polymer products isolated via both methods exhibited similar molecular weights and molecular weight distributions.

4.4.2 Polymer End-Group Analysis

Both ¹H NMR and UV-Vis spectroscopy were utilized to determine the nature of the polymer end groups. The presence of the TEMPO end group was verified using ¹H NMR, and the methyne proton that is adjacent to the terminal TEMPO unit was observed. Figure 4.1 depicts the ¹H NMR spectrum for a polystyrene homopolymer that was initiated using 2VN. Georges has also observed the methyne and methylene end groups of polystyrene derived from TEMPO mediation and BPO initiation, respectively.²⁴⁴ However, 2VN initiation resulted in a methylene unit that was not resolved from other aliphatic protons in the polymer main chain. Consequently, only the methyne of the TEMPO-capped terminal end was clearly observed in the ¹H NMR spectrum. The splitting pattern in the methyne proton signal was similar to the methyne ¹H NMR signal

²⁴⁴ Georges, M. K.; Hamer, G. K.; Listigovers, N. A. "Block Copolymer Synthesis by a Nitroxide-Mediated Living Free Radical Polymerization Process," *Macromolecules* 31, (1998), 9087-9089.

Table 4.2: Effect of 2VN:TEMPO molar ratio on polystyrene homopolymers.

2VN:TEMPO^b	M_n^a	M_w/M_n^a	% Yield
1.5	2680	1.11	47
2.0	2660	1.14	27
3.0	4750	1.15	60
4.0	4780	1.19	40
5.0	5340	1.11	35
6.0	6390	1.32	39
12.0	17300	1.52	68

^a Molecular weight determined using polystyrene standards

^b 5.0 mol% 2VN compared to styrene

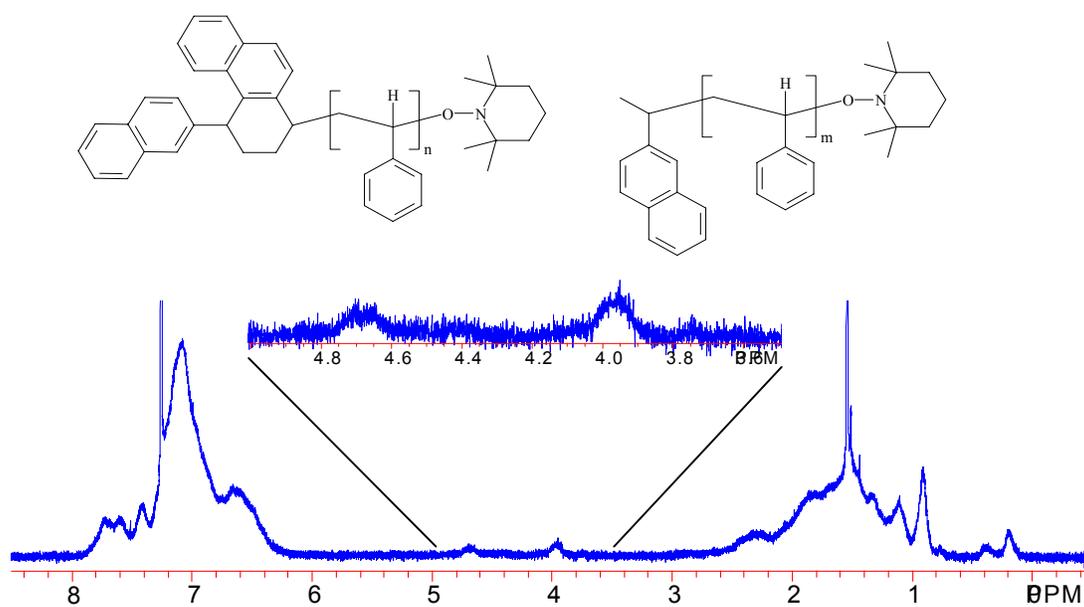


Figure 4.1: ^1H NMR spectrum for polystyrene initiated via 2VN thermal initiation.

observed earlier.²⁴⁵ Number average molecular weight estimation based on NMR integration values agreed well with molecular weight values determined using GPC (Table 4.3). This analysis includes only low molecular weight oligomers due to the low concentration of the single benzylic hydrogen that is adjacent the nitroxide end group used in ¹H NMR molecular weight determination. The methylene adjacent to the 2VN initiator fragment did not exhibit a well resolved NMR signal compared to the other backbone protons. In order to confirm the presence of the naphthalene containing end group, UV-Vis spectroscopy was utilized to observe an absorbance due to the presence of 2VN and a 2VN derived polycyclic unit that resulted from initiation. Figure 4.2a illustrates a comparison of the UV-Vis spectra for polystyrene homopolymers of similar molecular weight that were initiated using BPO and 2VN thermal initiation. Both spectra exhibited identical absorbances at 254 nm that were attributed to the characteristic phenyl absorbance of the styrene repeating unit. As expected, the presence of the 2VN resulted in significantly more absorbance at higher wavelengths (>290 nm), and a distinct shoulder was observed at 312 nm and was attributed to the absorbance of the 2VN initiator fragment. The absorbance intensity at 312 nm was used to create a linear calibration curve that related the absorbance intensity with the number average molecular weight as determined using GPC. Figure 4.2b depicts the UV-Vis spectra for various controlled molecular weight polystyrene homopolymers initiated with 2VN. A plot of the number average molecular weight versus the absorbance intensity at 312 nm (Figure 4.3) exhibited a linear relationship. If each polymer chain contains 2VN based fragments, then the molecular weight should be predictable based on UV-Vis absorbance. The calibration curve was subsequently employed for the prediction of the molecular weight of polymers that were initiated with 2VN (Table 4.3). While UV-Vis spectroscopy does not confirm the existence of either a 2VN single or polycyclic unit on the polymer chain end, earlier Arrhenius analysis of thermal polymerization activation energies for 2VN and styrene indicated that at the given polymerization temperatures,

²⁴⁵ Georges, M. K.; Hamer, G. K.; Listigovers, N. A. "Block Copolymer Synthesis by a Nitroxide-Mediated Living Free Radical Polymerization Process," *Macromolecules* 31, (1998), 9087-9089.

Table 4.3: Polymer molecular weight determined with ^1H NMR, SEC and UV-Vis spectroscopy calibration

M_n (SEC)	M_n (NMR) ^a	M_n (UV-Vis) ^b
4780	4640	6750
6390	6490	5100

^abased on methyne proton adjacent to TEMPO end group

^bbased on UV-Vis absorbance at 312 nm

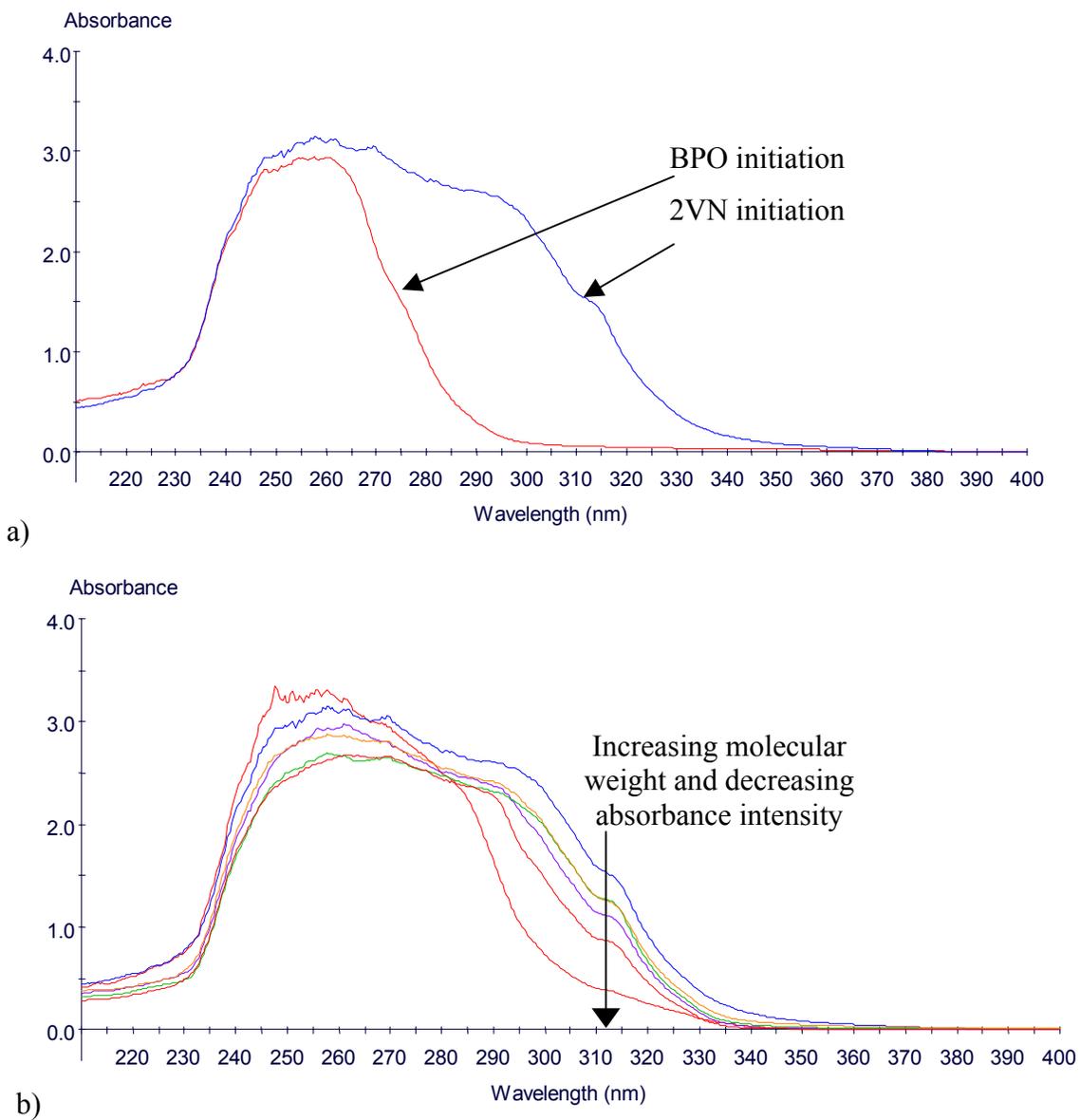


Figure 4.2: (a) UV-Vis spectra for polystyrene initiated by BPO and 2VN (b) UV-Vis spectra for various molecular weight polystyrenes initiated with 2VN.

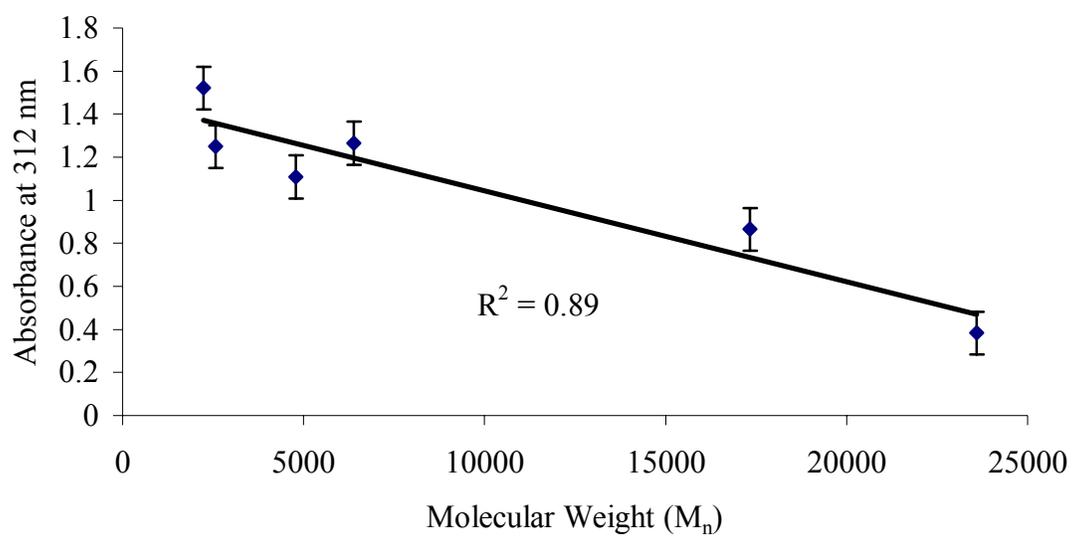


Figure 4.3: Molecular weight calibration curve for polystyrene based on 2VN initiating moiety absorbance.

2VN was consumed more readily than styrene via autopolymerization processes.²⁴⁶ Therefore, the initiator fragment was attributed to 2VN. Furthermore, it is unlikely that molecular weight control based on 2VN concentration was achievable without rapid consumption of 2VN as an initiator. Although molecular weights determined utilizing the UV-Vis calibration curve vary significantly from values determined with NMR and GPC, the experimental error associated with the UV-Vis analysis accounts for the observed differences.

4.4.3 *In situ* FTIR Analysis of Styrene SFRP Initiated with 2VN

The stable free radical polymerization of styrene that was initiated via 2VN thermal initiation was monitored using *in situ* FTIR spectroscopy. The disappearance of the vinyl CH stretch (988 cm^{-1}) associated with styrene monomer and the appearance of the aliphatic CH₂ stretch (3026 cm^{-1}) of polystyrene were monitored using an ASI ReactIR 1000 ATR FTIR spectrometer as described earlier.²⁴⁷ FTIR analysis of monomer conversion is depicted in Figure 4.4 for different times during the polymerization process. The presence of residual vinyl absorbances after 24 h indicated incomplete monomer conversion. Monomer conversion as determined using FTIR agreed well with gravimetric analysis and were approximately 60% at $130\text{ }^{\circ}\text{C}$ for 24 h in bulk.

The monomer disappearance and polymer appearance profiles resulted in a symmetrical X-shaped plot which is characteristic of a controlled polymerization process

²⁴⁶ Lizotte, J. R.; Erwin, B. M.; Colby, R. H.; Long, T. E. "Investigations of Thermal Polymerization in the Stable Free-Radical Polymerization of 2-Vinyl Naphthalene," *Journal of Polymer Science Part A-Polymer Chemistry* 40, (2002), 583-590.

²⁴⁷ Pasquale, A. J.; Long, T. E. "Real-Time Monitoring of the Stable Free Radical Polymerization of Styrene Via *in-Situ* Mid-Infrared Spectroscopy," *Macromolecules* 32, (1999), 7954-7957; Yoo, Y.; Johnson, L. K.; Falling, S. N.; Lizotte, J. R.; Long, T. E. "Maleation of Poly(3,4-Epoxy-1-Butene) for Accelerated Crosslinking in the Presence of a Redox Catalyst," *Journal of Polymer Science Part A-Polymer Chemistry* 40, (2002), 2789-2798; Williamson, D. T.; Elman, J. F.; Madison, P. H.; Pasquale, A. J.; Long, T. E. "Synthesis and Characterization of Poly(1,3-Cyclohexadiene) Homopolymers and Star-Shaped Polymers," *Macromolecules* 34, (2001), 2108-2114.

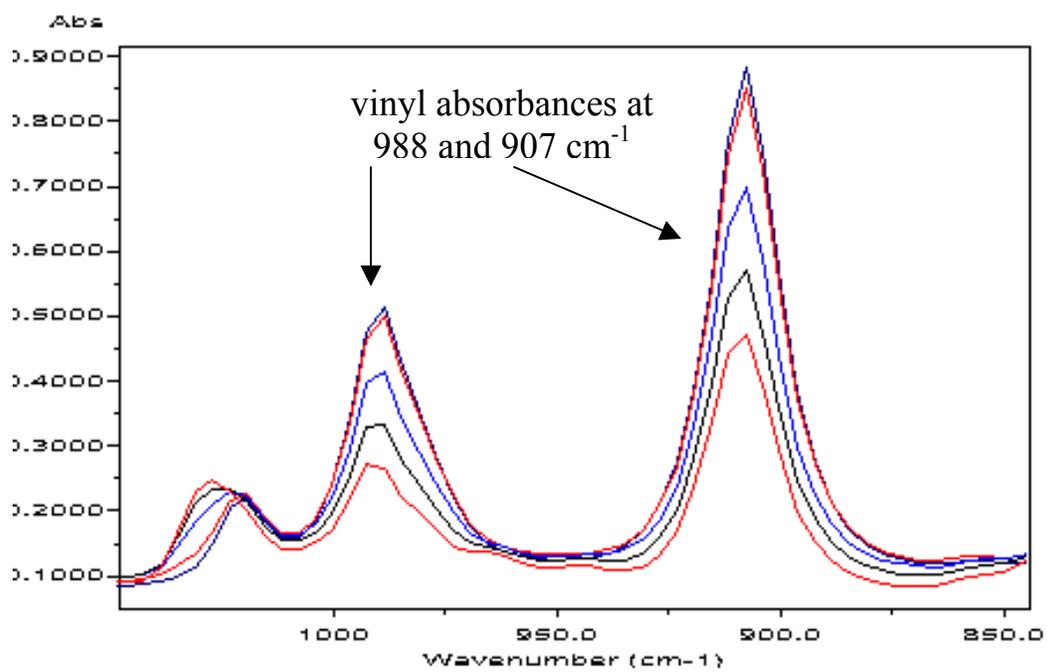


Figure 4.4: *In situ* FTIR spectra showing the decrease in vinyl absorbances during the polymerization of styrene.

such as SFRP.²⁴⁸ Also, an examination of the monomer disappearance profile revealed the existence of an induction period (~4 h) and the absence of appreciable styrene monomer consumption. This period was proposed to involve 2VN thermal initiation with formation of the Diels-Alder adduct and subsequent initiating radicals. The monomer disappearance profile was further utilized to analyze the polymerization kinetics (Figure 4.5). Pseudo first order reaction kinetics were used to analyze the monomer conversion data and the observed rate constant (k_{obs}) was $1.73 \times 10^{-5} \text{ s}^{-1}$, which agreed well with polystyrene SFRP initiated via BPO at $132 \text{ }^{\circ}\text{C}$ ($k_{\text{obs}}=1.99 \times 10^{-5} \text{ s}^{-1}$).^[21] This result was expected due to the formation of an identical propagating polystyrene radical derived from both conventional BPO and 2VN thermal initiators.

4.5 Conclusion

Stable free radical polymerization of styrene was successfully initiated using a novel 2VN thermal initiation method to yield polymer products with narrow molecular weight distributions (~1.1-1.2). The integrity of the mediating and initiating end-groups were confirmed using ^1H NMR and UV-Vis, respectively. In addition, the UV-Vis absorbance of the 2VN initiating unit was suitable for constructing a calibration curve for prediction of the molecular weight based on the intensity of the absorbance at 312 nm associated with 2VN initiation. The polymerization process was monitored using *in situ* FTIR and the observed rate constant of the system initiated with 2VN ($1.73 \times 10^{-5} \text{ s}^{-1}$) was comparable to BPO ($k_{\text{obs}}=1.99 \times 10^{-5} \text{ s}^{-1}$) initiation. Future efforts will explore the extension of the 2VN initiating system to other monomer systems using both controlled and conventional free radical polymerization methodologies.

4.6 Acknowledgements

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²⁴⁸ Pasquale, A. J.; Long, T. E. "Real-Time Monitoring of the Stable Free Radical Polymerization of Styrene Via in-Situ Mid-Infrared Spectroscopy," *Macromolecules* 32, (1999), 7954-7957.

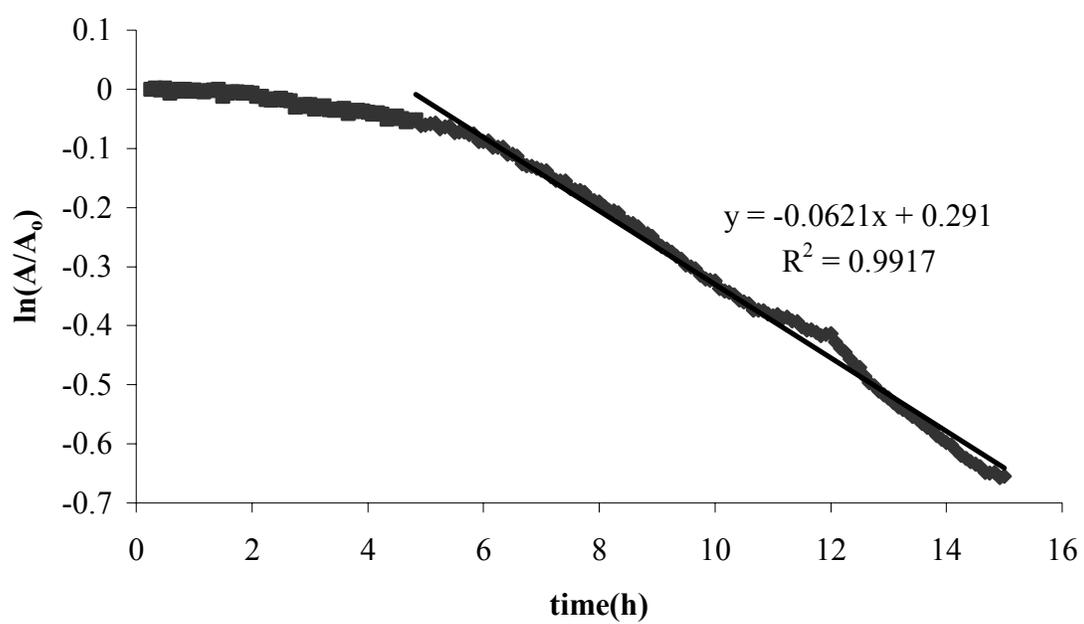


Figure 4.5 Pseudo first order kinetic plot of monomer disappearance in the SFRP of styrene initiated via 2VN thermal initiation.

Chapter 5 : A Novel Dinitroxide Mediating Agent for Stable Free Radical Polymerization

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5.1 Abstract

A novel dinitroxide mediating agent that was suitable for stable free radical polymerization was synthesized and utilized in the block copolymerization of styrene and *t*-butyl styrene. Quantitative yields of a novel dinitroxide based on 1,6-hexamethylene diisocyanate and 4-hydroxy-TEMPO were obtained. Various experimental parameters including nitroxide to initiator molar ratio were examined, and it was determined that the polymerization was most controlled under conditions similar to conventional TEMPO-mediated SFRP. Moreover, the dinitroxide mediator proved to be a viable route for the facile two-step synthesis of triblock copolymers of styrene and *t*-butyl styrene. However, the dinitroxide mediation process resulted in a higher than expected level of nitroxide decomposition resulting in polymers possessing a terminal alkoxyamine with an adjacent hydroxylamine rather than a preferred internal bisalkoxyamine. This decomposition resulted in the formation of diblock copolymer species during the triblock copolymer synthesis. GPC was employed to monitor the chain end decomposition kinetics and the determined rate constant ($5.89 \times 10^{-5} \text{ s}^{-1}$) for decomposition agreed well with previous studies for other dinitroxide mediating agents.

keywords: block copolymer, stable free radical polymerization, gel permeation chromatography

5.2 Introduction

Tailored macromolecules with well-defined physical properties are required for advanced technological applications. Traditionally, living anionic methodologies were employed in the synthesis of macromolecules with controlled composition and architecture.²⁴⁹ However, functional group intolerance, highly reactive organolithium initiators, and the necessity for stringent laboratory practices including use of high purity reagents and anhydrous solvents has limited the application of living anionic techniques. During the last decade, more robust controlled free radical polymerization techniques have received increased attention as potential alternatives for the synthesis of tailored macromolecules.²⁵⁰ Stable free radical polymerization (SFRP),²⁵¹ atom transfer radical

²⁴⁹ Quirk, R. P.; Kinning, D. J.; Fetters, L. J. *Comprehensive Polymer Science*, ed. S. L. Aggarwal, vol. 7 (London: Pergamon Press, 1989).

²⁵⁰ Malmstrom, E. E.; Hawker, C. J. "Macromolecular Engineering Via 'Living' Free Radical Polymerizations," *Macromolecular Chemistry and Physics* 199, (1998), 923-935; Patten, T. E.; Matyjaszewski, K. "Copper(I)-Catalyzed Atom Transfer Radical Polymerization," *Accounts of Chemical Research* 32, (1999), 895-903; Hawker, C. J.; Bosman, A. W.; Harth, E. "New Polymer Synthesis by Nitroxide Mediated Living Radical Polymerizations," *Chemical Reviews* 101, (2001), 3661-3688; *Acs Symposium Series*, ed. K. Matyjaszewski, vol. 768, *Controlled/Living Radical Polymerization: Progress in Atrp, Nmp, and Raft* (Oxford University Press, 2000); Matyjaszewski, K., "Controlled/Living Radical Polymerization: State of the Art in 2002," in *Advances in Controlled/Living Radical Polymerization, Acs Symposium Series* (Washington: AMER CHEMICAL SOC, 2003).

²⁵¹ Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. "Narrow Molecular-Weight Resins by a Free-Radical Polymerization Process," *Macromolecules* 26, (1993), 2987-2988; Li, I. Q.; Knauss, D. M.; Priddy, D. B.; Howell, B. A. "Synthesis and Reactivity of Functionalized Alkoxyamine Initiators for Nitroxide-Mediated Radical Polymerization of Styrene," *Polymer International* 52, (2003), 805-812; Diaz, T.; Fischer, A.; Jonquieres, A.; Brembilla, A.; Lochon, P. "Controlled Polymerization of Functional Monomers and Synthesis of Block Copolymers Using Beta-Phosphonylated Nitroxide," *Macromolecules* 36, (2003), 2235-2241; von Werne, T.; Patten, T. E. "Preparation of Structurally Well-Defined Polymer-Nanoparticle Hybrids with Controlled/Living Radical Polymerizations," *Journal of the American Chemical Society* 121, (1999), 7409-7410; von Werne, T. A.; Germack, D. S.; Hagberg, E. C.; Sheares, V. V.; Hawker, C. J.; Carter, K. R. "A Versatile Method for Tuning the Chemistry and Size of Nanoscopic Features by Living Free Radical Polymerization," *Journal of the American Chemical Society* 125, (2003), 3831-3838.

polymerization (ATRP),²⁵² and reversible addition fragmentation chain transfer polymerization (RAFT)²⁵³ have emerged as potential synthetic methodologies that yield well defined polymeric structures and compositions.

In controlled free radical polymerizations, a desirable equilibrium is achieved between a reactive radical intermediate and a dormant trapped radical.²⁵⁴ Stable free radical polymerization proceeds via free radical propagation in the presence of a stable nitroxide free radical. A nitroxide stable free radical couples with the propagating polymer radical and retards propagation, chain transfer, or termination. In effect, the stable nitroxide free radical reduces the propensity for termination or chain transfer and permits efficient simultaneous initiation. Previous SFRP studies have examined a variety of mononitroxides to mediate the polymerization of various monomers including

²⁵² Wang, J. S.; Matyjaszewski, K. "Controlled Living Radical Polymerization - Halogen Atom- Transfer Radical Polymerization Promoted by a Cu(I)Cu(II) Redox Process," *Macromolecules* 28, (1995), 7901-7910: Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. "Polymerization of Methyl-Methacrylate with the Carbon- Tetrachloride Dichlorotris(Triphenylphosphine)Ruthenium(II) Methylaluminum Bis(2,6-Di-Tert-Butylphenoxide) Initiating System - Possibility of Living Radical Polymerization," *Macromolecules* 28, (1995), 1721-1723: Matyjaszewski, K.; Xia, J. H. "Atom Transfer Radical Polymerization," *Chemical Reviews* 101, (2001), 2921-2990: Pintauer, T.; McKenzie, B.; Matyjaszewski, K., "Toward Structural and Mechanistic Understanding of Transition Metal-Catalyzed Atom Transfer Radical Processes," in *Advances in Controlled/Living Radical Polymerization, Acs Symposium Series* (Washington: AMER CHEMICAL SOC, 2003).

²⁵³ Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. "Living Free-Radical Polymerization by Reversible Addition- Fragmentation Chain Transfer: The Raft Process," *Macromolecules* 31, (1998), 5559-5562: Saricilar, S.; Knott, R.; Barner-Kowollik, C.; Davis, T. P.; Heuts, J. P. A. "Reversible Addition Fragmentation Chain Transfer Polymerization of 3-[Tris(trimethylsilyloxy) Silyl] Propyl Methacrylate," *Polymer* 44, (2003), 5169-5176: Lutz, J.-F.; Pakula, T.; Matyjaszewski, K., "Synthesis and Properties of Copolymers with Tailored Sequence Distribution by Controlled/Living Radical Polymerization," in *Acs Symposium Series: Advances in Controlled/Living Radical Polymerization* (2003): Chernikova, E.; Terpugova, P.; Bui, C. O.; Charleux, B. "Effect of Comonomer Composition on the Controlled Free-Radical Copolymerization of Styrene and Maleic Anhydride by Reversible Addition-Fragmentation Chain Transfer (Raft)," *Polymer* 44, (2003), 4101-4107: Wang, A. R.; Zhu, S. P. "Modeling the Reversible Addition-Fragmentation Transfer Polymerization Process," *Journal of Polymer Science Part a-Polymer Chemistry* 41, (2003), 1553-1566.

²⁵⁴ Veregin, R. P. N.; Georges, M. K.; Hamer, G. K.; Kazmaier, P. M. "Mechanism of Living Free-Radical Polymerizations with Narrow Polydispersity - Electron-Spin-Resonance and Kinetic-Studies," *Macromolecules* 28, (1995), 4391-4398: Veregin, R. P. N.; Odell, P. G.; Michalak, L. M.; Georges, M. K. "Molecular Weight Distributions in Nitroxide-Mediated Living Free Radical Polymerization: Kinetics of the Slow Equilibria between Growing and Dormant Chains," *Macromolecules* 29, (1996), 3346-3352: Fukuda, T.; Terauchi, T.; Goto, A.; Ohno, K.; Tsujii, Y.; Miyamoto, T.; Kobatake, S.; Yamada, B. "Mechanisms and Kinetics of Nitroxide-Controlled Free Radical Polymerization," *Macromolecules* 29, (1996), 6393-6398: Yoshikawa, C.; Goto, A.; Fukuda, T. "Quantitative Comparison of Theory and Experiment on Living Radical Polymerization Kinetics. 1. Nitroxide-Mediated Polymerization," *Macromolecules* 35, (2002), 5801-5807.

acrylates, dienes, and styrenic derivatives.²⁵⁵ In addition, Gnanou and coworkers have examined the synthesis and application of di- and trifunctional alkoxyamine unimolecular initiators for SFRP.²⁵⁶ A variety of polymer compositions and structures including star and graft copolymers have been investigated using SFRP methodologies.²⁵⁷

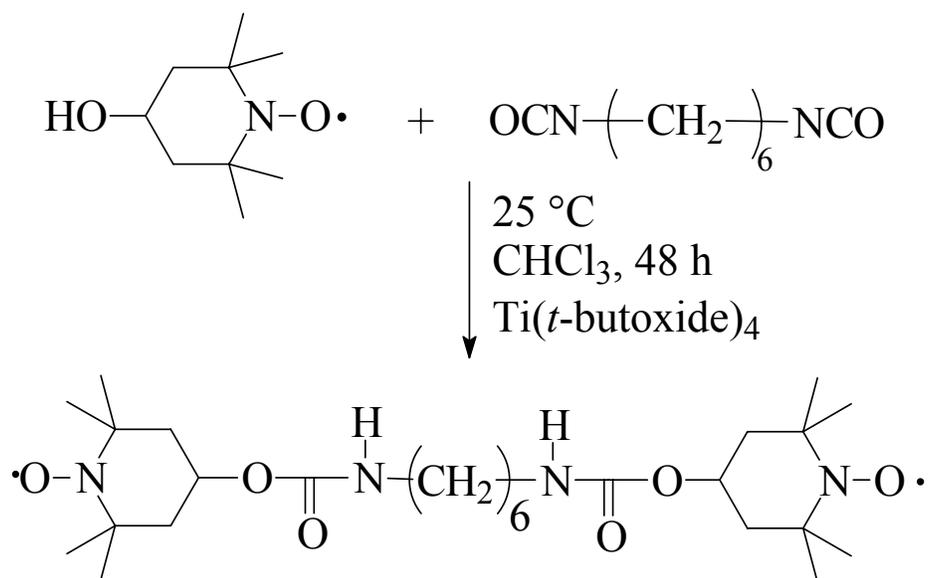
Use of a dinitroxide mediator shown in Scheme 5.1 for SFRP has only recently received sparse attention²⁵⁸, however, the presence of an internal bisalkoxyamine linker in a macromolecule may potentially lead to interesting reversible rheological and thermal properties such as a thermally induced reduction of molecular weight for improved melt

²⁵⁵ Georges, M. K.; Hamer, G. K.; Listigovers, N. A. "Block Copolymer Synthesis by a Nitroxide-Mediated Living Free Radical Polymerization Process," *Macromolecules* 31, (1998), 9087-9089; Keoshkerian, B.; Georges, M.; Quinlan, M.; Veregin, R.; Goodbrand, B. "Polyacrylates and Polydienes to High Conversion by a Stable Free Radical Polymerization Process: Use of Reducing Agents," *Macromolecules* 31, (1998), 7559-7561; Benoit, D.; Grimaldi, S.; Robin, S.; Finet, J. P.; Tordo, P.; Gnanou, Y. "Kinetics and Mechanism of Controlled Free-Radical Polymerization of Styrene and N-Butyl Acrylate in the Presence of an Acyclic Beta-Phosphonylated Nitroxide," *Journal of the American Chemical Society* 122, (2000), 5929-5939; Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. "Development of a Universal Alkoxyamine for "Living" Free Radical Polymerizations," *Journal of the American Chemical Society* 121, (1999), 3904-3920.

²⁵⁶ Robin, S.; Guerret, O.; Couturier, J. L.; Pirri, R.; Gnanou, Y. "Synthesis and Characterization of Poly(Styrene-B-N-Butyl Acrylate-B-Styrene) Triblock Copolymers Using a Dialkoxyamine as Initiator," *Macromolecules* 35, (2002), 3844-3848; Robin, S.; Guerret, O.; Couturier, J. L.; Gnanou, Y. "Synthesis of Stars and Starlike Block Copolymers from a Trialkoxyamine Used as Initiator," *Macromolecules* 35, (2002), 2481-2486.

²⁵⁷ Pasquale, A. J.; Long, T. E. "Synthesis of Star-Shaped Polystyrenes Via Nitroxide-Mediated Stable Free-Radical Polymerization," *Journal of Polymer Science Part a-Polymer Chemistry* 39, (2001), 216-223; Tsoukatos, T.; Pispas, S.; Hadjichristidis, N. "Star-Branched Polystyrenes by Nitroxide Living Free-Radical Polymerization," *Journal of Polymer Science Part a-Polymer Chemistry* 39, (2001), 320-325; Zhang, H. T.; Guo, Z. R.; Huang, J. L. "Preparation of a Copolymer of Methyl Methacrylate with a New Monomer, 2,2,6,6-Tetramethyl-4-Benzyloxy-Piperidinyl Methacrylate, and Its Initiation of the Graft Copolymerization of Styrene with a Controlled Radical Mechanism," *Journal of Polymer Science Part a-Polymer Chemistry* 40, (2002), 4398-4403; Li, C. M.; He, J. P.; Li, L.; Cao, J. Z.; Yang, Y. L. "Controlled Radical Polymerization of Styrene in the Presence of a Polymerizable Nitroxide Compound," *Macromolecules* 32, (1999), 7012-7014; Tao, Y. F.; He, J. P.; Wang, Z. M.; Pan, J. Y.; Jiang, H. J.; Chen, S. M.; Yang, Y. L. "Synthesis of Branched Polystyrene and Poly(Styrene-B-4-Methoxystyrene) by Nitroxyl Stable Radical Controlled Polymerization," *Macromolecules* 34, (2001), 4742-4748; Blomberg, S.; Ostberg, S.; Harth, E.; Bosman, A. W.; Van Horn, B.; Hawker, C. J. "Production of Crosslinked, Hollow Nanoparticles by Surface- Initiated Living Free-Radical Polymerization," *Journal of Polymer Science Part a-Polymer Chemistry* 40, (2002), 1309-1320; Gotz, H.; Harth, E.; Schiller, S. M.; Frank, C. W.; Knoll, W.; Hawker, C. J. "Synthesis of Lipo-Glycopolymer Amphiphiles by Nitroxide-Mediated Living Free-Radical Polymerization," *Journal of Polymer Science Part a-Polymer Chemistry* 40, (2002), 3379-3391.

²⁵⁸ Huang, W. L.; Chiarelli, R.; Charleux, B.; Rassat, A.; Vairon, J. P. "Unique Behavior of Nitroxide Biradicals in the Controlled Radical Polymerization of Styrene," *Macromolecules* 35, (2002), 2305-2317; Anderson, S. C.; Lizotte, J. R.; Long, T. E. "A Novel Dinitroxide Mediating Agent for Stable Free Radical Polymerization," *Polymer Preprints (American Chemical Society, Division of Polymer Chemistry)* 43, (2002), 277-278.



Scheme 5.1: Synthesis of difunctional nitroxide from hydroxy-TEMPO and 1,6-hexamethylene diisocyanate.

processability or polymer mixing.²⁵⁹ In addition, triblock copolymers are potentially formed in a more facile two-step synthetic process as opposed to conventional three-step processes. This report describes the dinitroxide-mediated polymerization of styrenic monomers and provides evidence for the formation of triblock copolymers (Scheme 5.2). Also, the thermal cleavage of the alkoxyamine bond and decomposition of the dinitroxide mediating agent in the presence of the propagating polymer radical was investigated. Decomposition of the dinitroxide results from the deactivation of a nitroxide functionality when the stable nitroxide radical abstracts a β -hydrogen from the propagating radical chain end to yield a hydroxylamine and a terminal site of unsaturation at the polymer chain end.

5.3 Experimental

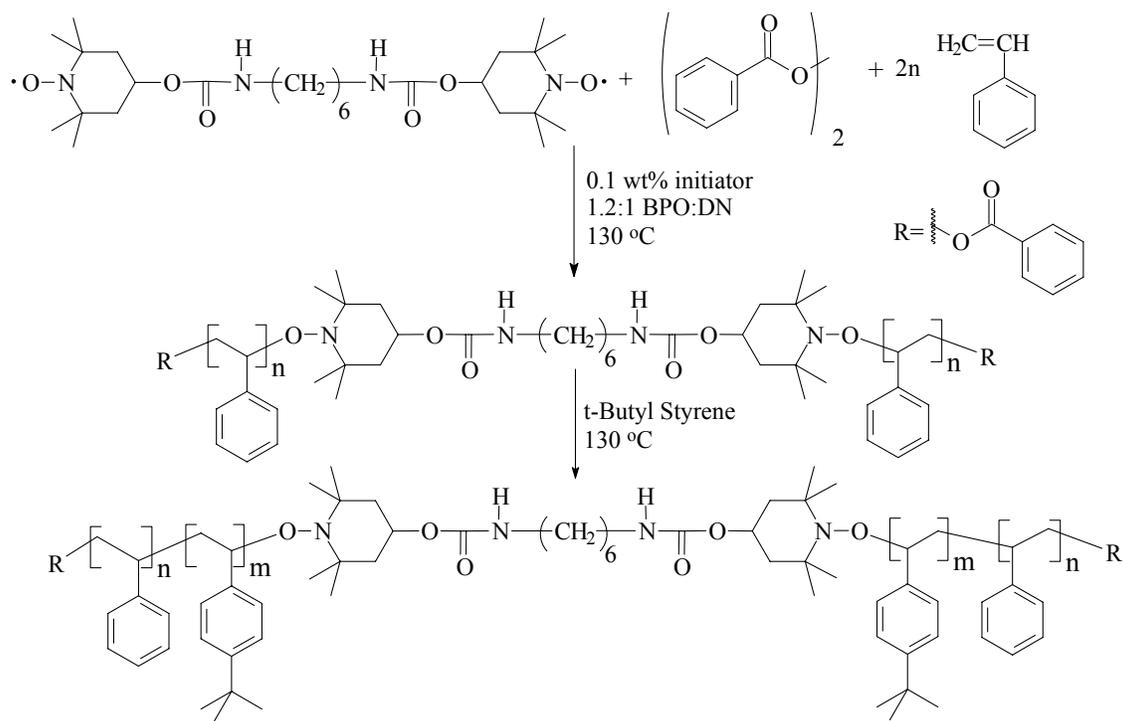
5.3.1 Materials

4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy (HO-TEMPO), benzoyl peroxide (BPO), 1,6-hexamethylene diisocyanate, titanium (IV) *t*-butoxide 97% (TBT), *t*-butyl styrene and styrene were purchased from Aldrich. Styrene and *t*-butyl styrene were deinhibited using column chromatography with neutral alumina and stored under nitrogen. All other reagents were used as received unless otherwise noted.

5.3.2 Instrumentation

¹H NMR spectra were collected on a Varian Unity-400 spectrometer in CDCl₃ at ambient temperature. Molecular weight determination was performed on a Waters SEC apparatus equipped with a 410 RI detector and an in-line miniDawn multiangle laser light scattering (MALLS) detector with a 690 nm laser. Matrix-Assisted Laser Desorption Ionization-Time of Flight mass spectrometry was collected using a VG Quattro Micromass with the analyte dispersed in a 3-nitrobenzyl alcohol matrix.

²⁵⁹ Otsuka, H.; Aotani, K.; Higaki, Y.; Takahara, A. "Polymer Scrambling: Macromolecular Radical Crossover Reaction between the Main Chains of Alkoxyamine-Based Dynamic Covalent Polymers," *Journal of the American Chemical Society* 125, (2003), 4064-4065.



Scheme 5.2: Polymerization of styrene and *t*-butyl styrene using the dinitroxide mediator in the production of a triblock copolymer.

5.3.3 Synthesis of 1,6-Hexanedicarbamic acid di(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl) ester (DN)

1,6-Hexamethylene diisocyanate (0.0056 mol, 942 mg) was added to a 50 mL flask equipped with a magnetic stir bar. 4-Hydroxy-TEMPO (0.0123 mol, 2.12 g) was also added to the flask in a 2.2:1.0 molar ratio of 4-hydroxy TEMPO to 1,6-hexamethylene diisocyanate. The reaction mixture was diluted with chloroform (~2 mL) and subsequently sealed with a rubber septum. Oxygen was removed from the reaction vessel using a nitrogen purge for 10 min. TBT catalyst (1-2 drops) was then added to the sealed system and the reaction was stirred at room temperature for 48 h. The reaction mixture was then diluted with methanol (30 mL) and then precipitated into water (~90 mL). The water/methanol solution was decanted, and the dinitroxide was collected as a thick red oil in 94% yield and dried in a vacuum oven overnight at 45 °C. ¹H NMR δ 4.6 (N—H, 2H), 4.2 (O—C—H, 2H), 3.3 (N—CH₂—CH₂, 4H), 1.2-1.8 (N—CH₂—CH₂, 8H) HRMS (MALDI-TOF): calcd for C₂₆H₄₈N₄O₆ (M⁺), 512.7; found, 512.3.

5.3.4 Dinitroxide-Mediated Polymerization of Styrene

BPO (0.012 mmol, 3.0 mg) and dinitroxide (0.0074 mmol, 3.8 mg) were added to a 50 mL round-bottomed flask in a 1.2:1.0 molar ratio of nitroxide:BPO. The flask was sealed with a rubber septum and purged with nitrogen for 20 minutes. Styrene (0.039, -4.0 g) was added to the reaction vessel using a syringe under nitrogen pressure. The reactor was then heated at 130 °C with magnetic stirring. After 24 h, the flask was removed and allowed to cool to room temperature. The vitrified polymer was dissolved in THF (~25 mL) and precipitated into methanol (~250 mL). The polymer product was collected using vacuum filtration and dried in a vacuum oven overnight at 65 °C. (isolated yield=57 %)

The poly(styrene-*b*-*t*-butyl styrene-*b*-styrene) triblock copolymer was formed using a low conversion (~33%) polystyrene macroinitiator. The macroinitiator (0.015mmol, 50 mg) was added to a 50 mL round-bottomed flask equipped with a magnetic stir bar. The flask was sealed with a rubber septum and sparged with nitrogen for 15 minutes. *t*-Butyl styrene (TBS) (0.094 mol, 15 g) was added to the flask via

syringe. The reaction mixture was stirred until the polymeric precursor was completely dissolved. The reaction vessel was then heated at 130 °C for 0.5 h. The reaction mixture became noticeably thicker and was subsequently diluted with THF (~30 mL). The polymer product was precipitated into methanol (~ 350 mL), collected using vacuum filtration, and dried in a vacuum oven overnight at 65 °C. (isolated polymer yield=15 %)

5.4 Results and Discussion

5.4.1 Synthesis of 1,6-Hexanedicarbamic acid di(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl) ester (DN)

The diisocyanate was reacted with 4-hydroxy-TEMPO to form a novel dinitroxide. The conventional isocyanate TBT catalyst was employed, and the reaction mixture remained dark red throughout the reaction indicating the TEMPO radical was present and unaffected by the reaction conditions. ¹H NMR analysis confirmed the dinitroxide composition showing the characteristic resonances associated with the methylene protons of the 1,6-hexamethylene diisocyanate linker at 1.2-1.8 ppm. (Figure 5.1) Also, the methylene protons adjacent to the urethane bond were observed at 3.3 ppm and the urethane N—H protons, absent in the diisocyanate, were observed at 4.2-4.8 ppm. Furthermore, the *m/z* (512.3 amu) determined experimentally using MALDI-TOF mass spectrometry was consistent with the theoretical *m/z* of 512.7 amu. In addition, the resulting dinitroxide was readily soluble in most organic solvents including acetone, methanol, and tetrahydrofuran.

5.4.2 Dinitroxide-Mediated Polymerizations of Styrene

The polymerization of styrene in the presence of the novel difunctional nitroxide mediator was conducted under conditions similar to those of conventional TEMPO mediated SFRP. The dinitroxide:initiator ratio was optimized at 0.6 moles of dinitroxide per mole of BPO initiator, which corresponded to the conventional 1.2:1.0 molar ratio of nitroxide:BPO. The styrene polymerizations were performed in the bulk at 130 °C. Initially, relatively low molecular weights were targeted in order to investigate the end groups of the resulting polymer products using ¹H NMR spectroscopy (Figure 5.2). The methylene and methyne protons associated with the styrene units in the polymer directly

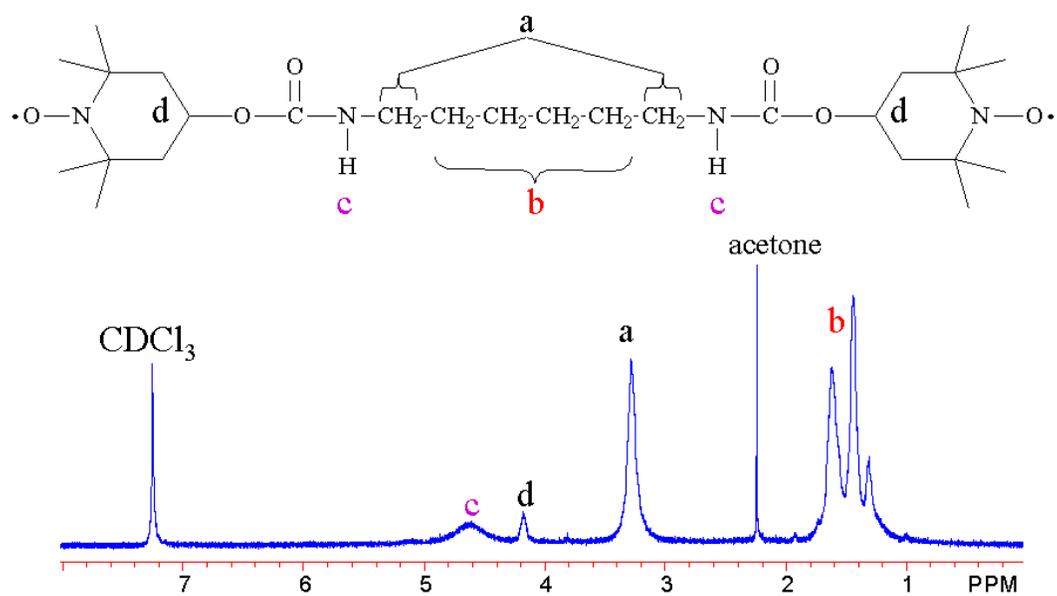


Figure 5.1: ^1H NMR spectrum of dinitroxide mediating agent.

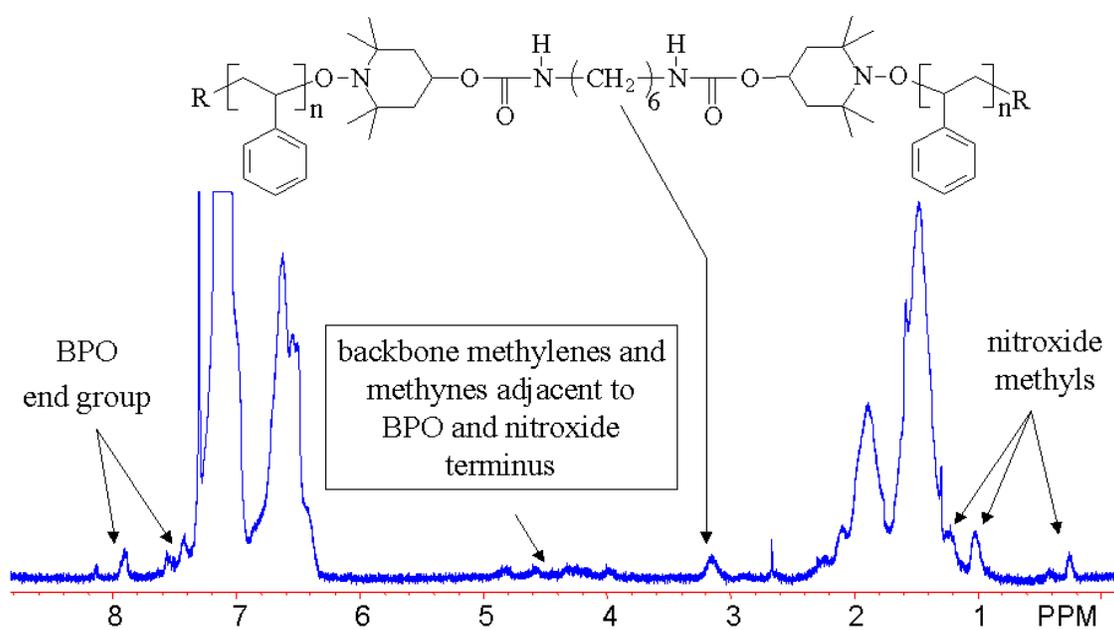


Figure 5.2: 1H NMR spectrum of low molecular weight polystyrene mediated with bisalkoxyamine linkage.

adjacent to the initiator fragment and the mediator fragment were observed at 4.0-4.8 ppm in a complex splitting pattern that was attributed to the polymer tacticity.²⁶⁰ The protons associated with the BPO initiator were observed in the aromatic region downfield from the aromatic styrene resonances. The TEMPO protons were observed in the range of 0.6-1.2 ppm as expected.²⁶¹ The methylene units attributed to the dinitroxide mediator were observed at 3.1 ppm. The molecular weights of the polystyrene samples based on integration of the dinitroxide methylene peaks are shown in Table 5.1 and agree well with the molecular weights determined using GPC analysis.

The various alkoxyamines that were investigated in the past demonstrated effective polymerization control as a function of temperature.²⁶² The strength of the C-O bond governs the temperature at which the equilibrium of the SFRP process exhibits desirable polymerization control while still allowing significant monomer conversion. At equilibrium, the dinitroxide mediator may exist in three forms: a symmetric molecule with two free nitroxide radicals, a symmetric molecule with two nitroxides each coupled to a propagating polymer chain forming alkoxyamine linkages, or an asymmetric dinitroxide molecule with one free nitroxide radical and a nitroxide coupled to a propagating polymer chain. The complex nature of this equilibrium prompted an examination of the polymerization temperature. The polymerization temperature was varied from 100 to 160 °C in the bulk and a constant dinitroxide:BPO molar ratio was maintained. An increase in the polymerization temperature resulted in an increased rate of monomer conversion and a broadened molecular weight distribution, which indicated

²⁶⁰ Georges, M. K.; Hamer, G. K.; Listigovers, N. A. "Block Copolymer Synthesis by a Nitroxide-Mediated Living Free Radical Polymerization Process," *Macromolecules* 31, (1998), 9087-9089.

²⁶¹ Georges, M. K.; Hamer, G. K.; Listigovers, N. A. "Block Copolymer Synthesis by a Nitroxide-Mediated Living Free Radical Polymerization Process," *Macromolecules* 31, (1998), 9087-9089.

²⁶² Le Mercier, C.; Acerbis, S. B.; Bertin, D.; Chauvin, F.; Gimes, D.; Guerret, O.; Lansalot, M.; Marque, S.; Le Moigne, F.; Fischer, H.; Tordo, P. "Design and Use of Beta-Phosphorus Nitroxides and Alkoxyamines in Controlled/"Living" Free Radical Polymerizations," *Macromolecular Symposia* 182, (2002), 225-247; Goto, A.; Fukuda, T. "Kinetic Study on Nitroxide-Mediated Free Radical Polymerization of Tert-Butyl Acrylate," *Macromolecules* 32, (1999), 618-623; Grimaldi, S.; Finet, J. P.; Le Moigne, F.; Zeghdaoui, A.; Tordo, P.; Benoit, D.; Fontanille, M.; Gnanou, Y. "Acyclic Beta-Phosphonylated Nitroxides: A New Series of Counter-Radicals for "Living"/Controlled Free Radical Polymerization," *Macromolecules* 33, (2000), 1141-1147.

Table 5.1: Polystyrene molecular weights based on GPC and ^1H NMR spectroscopy.

$M_n(\text{GPC})^a$ (g/mol)	M_w/M_n^a	$M_n(\text{NMR})^b$ (g/mol)
6560	1.32	5800
15700	1.34	16600

a) THF, 40 °C, 1 mL/min, polystyrene calibration, DRI detector

b) CHCl_3 , 25 °C, 400 MHz

inefficient control at the higher temperatures. Also, as the polymerization temperature was increased, the resulting molecular weight decreased due to more thermal initiation and increased initiator decomposition rates.²⁶³ The increased thermal initiation may also account for the observed increase in monomer as more initiating radicals would be expected to convert more monomer. Moreover, increased temperatures may have resulted in enhanced decomposition of the nitroxide mediating groups, which will be discussed in a later section. The decomposition of nitroxide mediating group may have lead to an uncontrolled polymerization and faster monomer conversion rates. As expected, the polymerization of styrene at ~115-130 °C yielded polymers with the narrowest molecular weight distributions and moderate monomer conversion (~50 %).

Initiator concentration also affected the molecular weight of the resulting polymer products. Table 5.2 summarizes the molecular weights for polymers that were produced using concentrations of BPO from 0.10 to 3.0 wt %. The molecular weight distributions ranged from 1.30 to 1.59 and are typical of polymerizations that are mediated with dinitroxides.²⁶⁴ It was presumed that the relatively broad molecular weight distributions were the result of the lower rate constant of recombination associated with the coupling reaction of a polymeric nitroxide and a propagating polymer radical as reported by Vairon et al.²⁶⁵ The broadest molecular weight distribution was observed using 0.10 wt% initiator. This was attributed to an increased relative contribution of initiating radical species resulting from styrene thermal autopolymerization. Typical GPC chromatograms for polystyrene synthesized with the dinitroxide mediator exhibited a small low molecular weight shoulder (Figure 5.3). This shoulder was attributed to decomposition of the nitroxide functionality resulting in two polymer populations; one group with an internal bisalkoxyamine (~40 mol%), and one group with either a terminal alkoxyamine

²⁶³ Lizotte, J. R.; Erwin, B. M.; Colby, R. H.; Long, T. E. "Investigations of Thermal Polymerization in the Stable Free- Radical Polymerization of 2-Vinyl Naphthalene," *Journal of Polymer Science Part a-Polymer Chemistry* 40, (2002), 583-590.

²⁶⁴ Huang, W. L.; Chiarelli, R.; Charleux, B.; Rassat, A.; Vairon, J. P. "Unique Behavior of Nitroxide Biradicals in the Controlled Radical Polymerization of Styrene," *Macromolecules* 35, (2002), 2305-2317.

²⁶⁵ Huang, W. L.; Chiarelli, R.; Charleux, B.; Rassat, A.; Vairon, J. P. "Unique Behavior of Nitroxide Biradicals in the Controlled Radical Polymerization of Styrene," *Macromolecules* 35, (2002), 2305-2317.

Table 5.2: GPC Analysis of Polystyrene from Bulk SFRP at 130 °C

[initiator] (wt% ^a)	M _n ^b (g/mol)	M _w /M _n ^b
0.10	94900	1.59
0.50	41100	1.31
1.0	19400	1.37
2.0	13600	1.30
3.0	6560	1.32

a)Based on total monomer weight

b)THF, 40 °C, 1 mL/min, polystyrene calibration, DRI detector

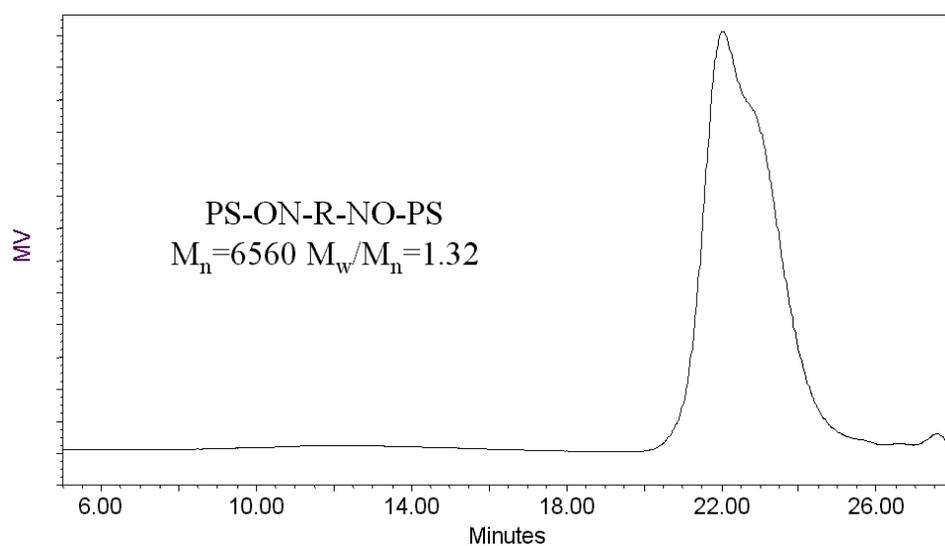


Figure 5.3. A typical GPC curve for polystyrene synthesized via dinitroxide-mediated SFRP.

with an adjacent hydroxylamine or a terminal site of unsaturation (~60 mol%). The mole percentages were approximated using OriginPro 7.0 peak fitting software.

5.4.3 Synthesis and Characterization of Triblock Copolymers via Dinitroxide-Mediated SFRP

A major advantage of controlled radical polymerization techniques is the ability to produce block copolymers.²⁶⁶ It is possible to synthesize both diblock and triblock copolymers via two and three step processes.²⁶⁷ Three sequential additions of monomer are required in SFRP processes that are mediated via conventional mononitroxides such as DEPN. The presence of an internal dinitroxide mediator in the polymer backbone may serve to simplify triblock copolymer formation. A facile two-step synthesis was demonstrated in which the sequential addition of styrene and *t*-butyl styrene resulted in the formation of a triblock copolymer (Scheme 5.2). This synthetic pathway can also be achieved with a difunctional alkoxyamine initiator.²⁶⁸ The initial styrene polymerization step produced a macromolecule with an internal bisalkoxyamine between two 3K polystyrene blocks (PS-ON-R-NO-PS). In the second step, *t*-butyl styrene was added to a solution of the polystyrene prepolymer at 130 °C resulting in the insertion of monomer units at the homolytically unstable alkoxyamine bond to create a triblock copolymer with a polystyrene outer blocks and a poly(*t*-butyl styrene) central block. In the second step, the molecular weight of the resulting polymer was increased from 6.5K to 99K. GPC analysis (Figure 5.4) indicated a monomodal distribution for the resulting triblock copolymer although the MWD was broadened relative to the polystyrene precursor indicating the polymer product likely consisted of both di- and triblock copolymers due nitroxide decomposition. A small peak at 23 min in the GPC chromatogram indicated the presence of some unreacted precursor polymer resulting from nitroxide decomposition.

²⁶⁶ Hawker, C. J. "Living" Free Radical Polymerization: A Unique Technique for the Preparation of Controlled Macromolecular Architectures," *Accounts of Chemical Research* 30, (1997), 373-382.

²⁶⁷ Robin, S.; Gnanou, Y. "Triblock Copolymers Based on Styrene and N-Butyl Acrylate by Nitroxide-Mediated Radical Polymerization: Problems and Solutions," *Macromolecular Symposia* 165, (2001), 43-53; Robin, S.; Guerret, O.; Couturier, J. L.; Pirri, R.; Gnanou, Y. "Synthesis and Characterization of Poly(Styrene-B-N-Butyl Acrylate-B-Styrene) Triblock Copolymers Using a Dialkoxyamine as Initiator," *Macromolecules* 35, (2002), 3844-3848.

²⁶⁸ Robin, S.; Guerret, O.; Couturier, J. L.; Pirri, R.; Gnanou, Y. "Synthesis and Characterization of Poly(Styrene-B-N-Butyl Acrylate-B-Styrene) Triblock Copolymers Using a Dialkoxyamine as Initiator," *Macromolecules* 35, (2002), 3844-3848.

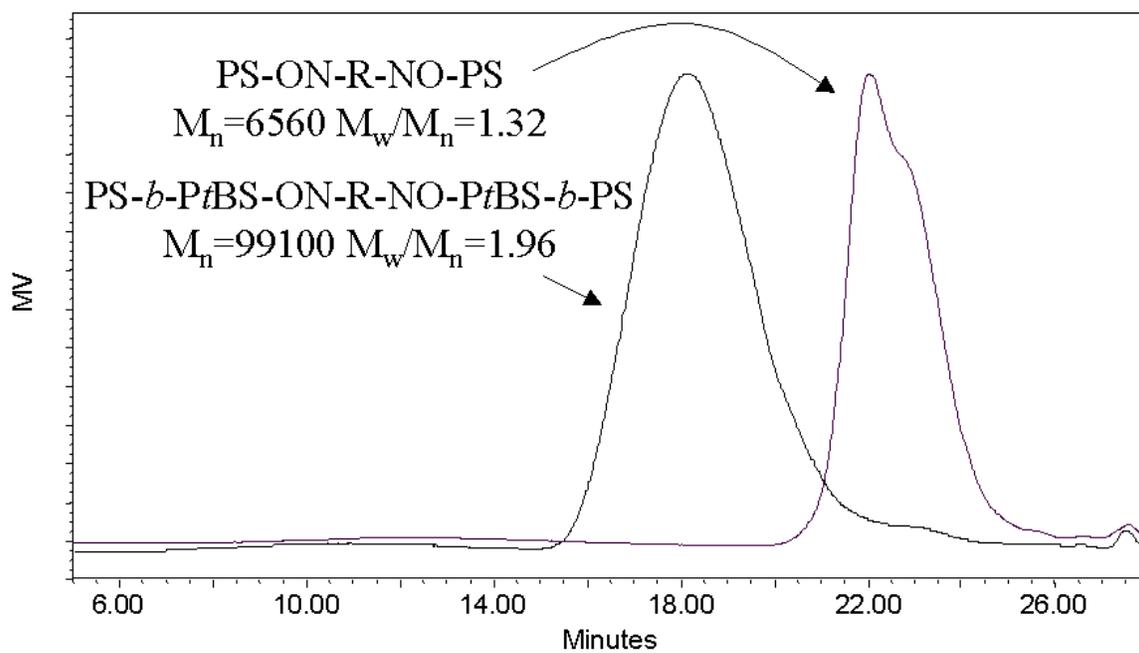


Figure 5.4: *t*-Butyl styrene chain extension of a polystyrene precursor synthesized with dinitroxide mediator.

indicating the polymer product likely consisted of both di- and triblock copolymers. ¹H NMR analysis confirmed the presence of *t*-butyl styrene with a resonance at ~1.15 ppm which was assigned to the *t*-butyl group (Figure 5.5). All solution cast films were optically clear indicating the absence of an appreciable amount of homopolystyrene contamination. DSC analysis also confirmed the incorporation of the *t*-butyl styrene with a T_g observed at 150 °C.

5.4.4 Thermally Induced Decomposition of Dinitroxide Mediator

Due to the structure of the dinitroxide mediator and the nature of the mediation process, thermal decomposition occurred more extensively compared to mononitroxide polymerization systems.²⁶⁹ The proposed mechanism of the decomposition reaction that may occur during polymerization is outlined in Figure 5.6.²⁷⁰ The decomposition occurred when the stable nitroxide radical abstracted a β-hydrogen from the propagating radical chain end. Thus, the formation of a hydroxylamine and a corresponding polymer possessing a terminal unsaturated site was confirmed using ¹H NMR spectroscopy.²⁷¹ The enhancement of the nitroxide decomposition process was attributed to the activation-deactivation equilibrium for a dinitroxide, which was shifted in favor of the uncapped radical intermediate.²⁷² The ability to activate and deactivate the propagating radical chain end is typically a rapid process. However, attachment of a polymer chain to the nitroxide functionality may limit the coupling reaction resulting in a higher concentration of the propagating radical and stable nitroxide.

²⁶⁹ Huang, W. L.; Chiarelli, R.; Charleux, B.; Rassat, A.; Vairon, J. P. "Unique Behavior of Nitroxide Biradicals in the Controlled Radical Polymerization of Styrene," *Macromolecules* 35, (2002), 2305-2317.

²⁷⁰ Moffat, K. A.; Hamer, G. K.; Georges, M. K. "Stable Free Radical Polymerization Process: Kinetic and Mechanistic Study of the Thermal Decomposition of Mb-Tmp Monitored by Nmr and Esr Spectroscopy," *Macromolecules* 32, (1999), 1004-1012.

²⁷¹ Moffat, K. A.; Hamer, G. K.; Georges, M. K. "Stable Free Radical Polymerization Process: Kinetic and Mechanistic Study of the Thermal Decomposition of Mb-Tmp Monitored by Nmr and Esr Spectroscopy," *Macromolecules* 32, (1999), 1004-1012; Huang, W. L.; Chiarelli, R.; Charleux, B.; Rassat, A.; Vairon, J. P. "Unique Behavior of Nitroxide Biradicals in the Controlled Radical Polymerization of Styrene," *Macromolecules* 35, (2002), 2305-2317.

²⁷² Huang, W. L.; Chiarelli, R.; Charleux, B.; Rassat, A.; Vairon, J. P. "Unique Behavior of Nitroxide Biradicals in the Controlled Radical Polymerization of Styrene," *Macromolecules* 35, (2002), 2305-2317.

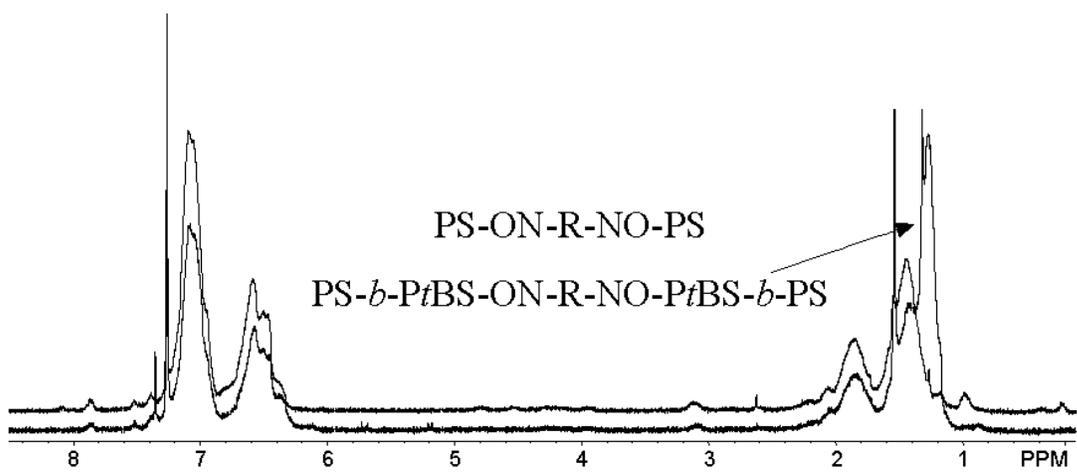


Figure 5.5: ^1H NMR spectrum of precursor polystyrene and poly(styrene-*b*-*t*-butyl styrene-*b*-styrene) with expected *t*-butyl resonances observed at 1.15 ppm.

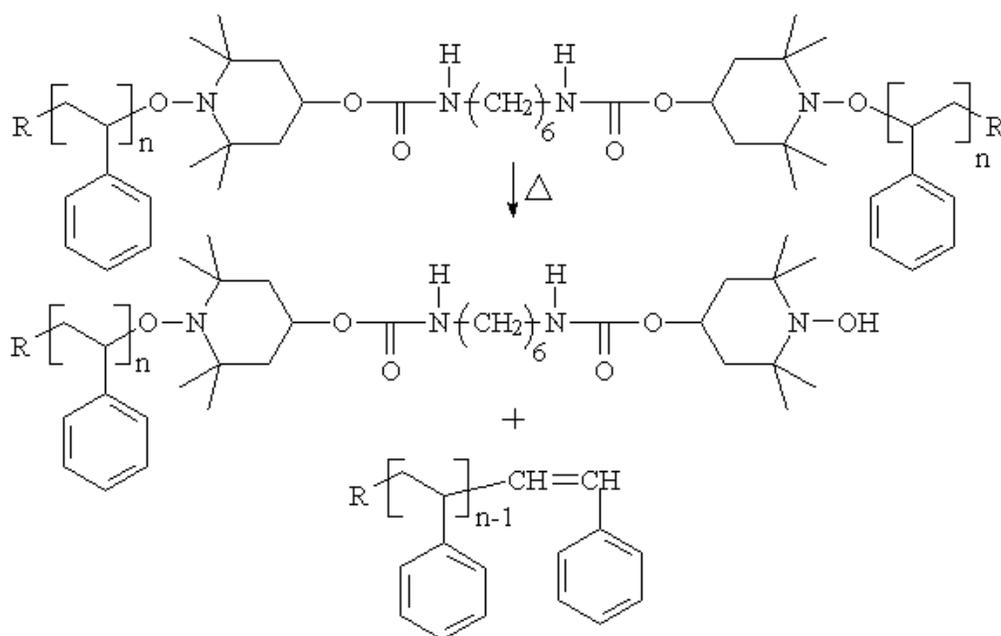


Figure 5.6: Thermal decomposition of dinitroxide mediating agent in the presence of a propagating polymer radical.

Previous studies by Vairon and coworkers extensively examined the rate of dinitroxide decomposition using NMR and molecular weight measurements.²⁷³ In our laboratories, the dinitroxide decomposition rate was determined by monitoring the polymer concentration with a internal bisalkoxyamine linker relative to polymer with a terminal alkoxyamine linkage utilizing GPC chromatograms. Polymers possessing a single, terminal nitroxide are the result of decomposition of one nitroxide functionality on the dinitroxide and exhibit a molecular weight equal to approximately one half the molecular weight of polymers possessing an internal bisalkoxyamine linkage. Using GPC with light scattering, a peak was observed at 22 minutes retention time that represented the polymer possessing an internal bis alkoxyamine and at 23 minutes, which was attributed to the lower molecular weight polymer containing only a terminal alkoxyamine. The relative intensities of the two peaks in the GPC chromatogram were used to create a decomposition profile.

Heating the polystyrene samples containing the internal bisalkoxyamine linker induced decomposition of the dinitroxide mediator. The solid polymer was heated under nitrogen at 130 °C for different time periods from 0.25 h up to 16 h. The GPC chromatograms demonstrated a reduction in the concentration of the higher molecular weight population and a corresponding increase in the concentration of polymers with a terminal alkoxyamine functionality from dinitroxide decomposition (Figure 5.7). The ratio of peak heights was used to determine the degree of decomposition and a decomposition profile was generated. The concentrations were normalized to the initial ratio since the initial sample contained some decomposed dinitroxide from the polymerization. A kinetic analysis of the bimolecular process was utilized to determine an apparent decomposition rate. The kinetic data demonstrated a good correlation ($R^2=0.97$) and the resulting apparent rate constant was $5.89 \times 10^{-5} \text{ s}^{-1}$ (Figure 5.8). This observed rate constant agreed well with the earlier efforts by Vairon et al. ($3.8 \times 10^{-5} \text{ s}^{-1}$) for other dinitroxide mediators.²⁷⁴

²⁷³ Huang, W. L.; Chiarelli, R.; Charleux, B.; Rassat, A.; Vairon, J. P. "Unique Behavior of Nitroxide Biradicals in the Controlled Radical Polymerization of Styrene," *Macromolecules* 35, (2002), 2305-2317.

²⁷⁴ Huang, W. L.; Chiarelli, R.; Charleux, B.; Rassat, A.; Vairon, J. P. "Unique Behavior of Nitroxide Biradicals in the Controlled Radical Polymerization of Styrene," *Macromolecules* 35, (2002), 2305-2317.

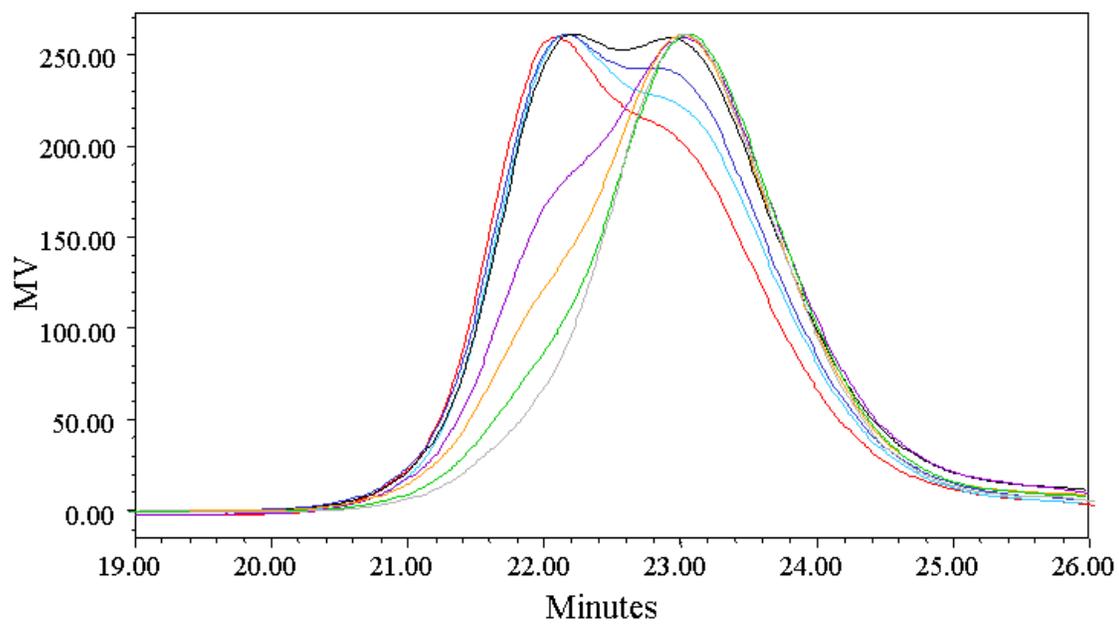


Figure 5.7: GPC chromatograms for polystyrenes consisting of an internal bisalkoxyamine linkage thermally treated for different periods of time.

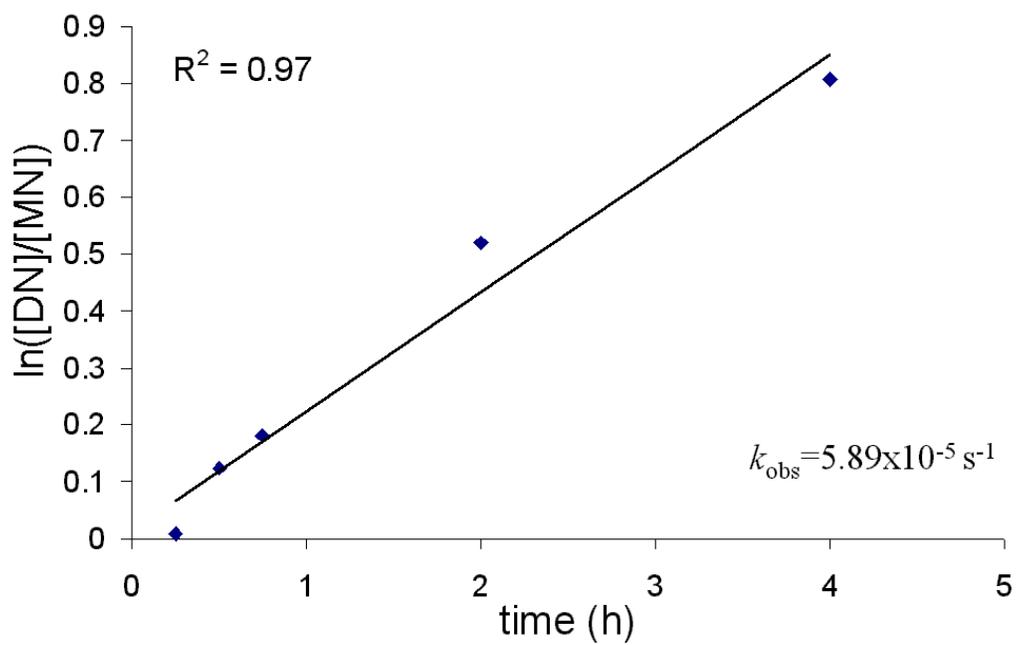


Figure 5.8: Apparent 1st order kinetic analysis of dinitroxide decomposition.

5.5 Conclusions

A novel dinitroxide mediating agent for stable free radical polymerization methodologies was synthesized and utilized in the polymerization of styrene and *t*-butyl styrene. Various experimental parameters were examined, and it was determined that the system operates most effectively under conditions similar to conventional TEMPO-mediated SFRP. Also, the dinitroxide mediator proved to be a viable route for the facile two-step synthesis of triblock copolymers. However, the nature of the dinitroxide mediation resulted in a high level of nitroxide decomposition resulting in polymers possessing a terminal alkoxyamine adjacent to a hydroxylamine rather than a bisalkoxyamine linkage. This decomposition resulted in the formation of diblock copolymers in addition to the targeted triblock copolymer species. GPC was employed to monitor the decomposition and the determined rate constant agreed well with previous studies on dinitroxide mediating agent decomposition.

5.6 Acknowledgements

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Chapter 6 : Stable Free Radical Polymerization Kinetics of Alkyl Acrylate Monomer Monitored Using *in situ* FTIR Spectroscopy

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6.1 Abstract

The polymerization of various alkyl acrylate homopolymerizations and copolymerizations were studied under SFRP conditions using *in situ* FTIR spectroscopy to monitor polymerization kinetics. The IR absorbance corresponding to the C—H deformation of the monomer (968 cm^{-1}) was measured to determine monomer conversion in real-time fashion and the monomer disappearance profiles were subsequently converted to pseudo first order kinetic plots. Altering the alkyl ester chain length and configuration did not significantly affect the resulting polymerization kinetics. However, addition of 2-hydroxyethyl acrylate (HEA) to a polymerization of n-butyl acrylate (nBA) substantially accelerated the rate of total monomer conversion increasing the observed rate constant almost two times. ^1H NMR spectroscopy also showed that the resulting HEA/nBA copolymers were enriched with HEA. Moreover, a similar but enhanced effect was also observed upon the addition of small amounts of dodecanol to an n-butyl acrylate homopolymerization increasing the observed rate constant more than two times.

Key words: stable free radical polymerization, *in situ* FTIR, polymerization kinetics, hydrogen bonding

6.2 Introduction

The advent of controlled free radical polymerization technologies such as stable free radical polymerization (SFRP) has enabled access to a myriad of polymer compositions and architectures.²⁷⁵ Previously, monomer families such as acrylates were difficult to polymerize using anionic methods due to functional group intolerance.²⁷⁶ While SFRP has allowed researchers to include these monomers in complex polymeric systems, several limitations still exist within the SFRP methodology. In particular, the nature of the SFRP process gives rise to longer polymerization times than conventional free radical or anionic polymerization processes.²⁷⁷

Many researchers have studied the SFRP process and the parameters that control the rate of the polymerization. Initial investigations involved examination of the stable free radical polymerization of styrene with polymerization rates enhanced using organic acid additives such as camphor sulfonic acid.²⁷⁸ The addition of these acids reduced the extent of autopolymerization and enhanced the polymerization rate; however, deleterious

²⁷⁵ Benoit, D.; Harth, E.; Fox, P.; Waymouth, R. M.; Hawker, C. J. "Accurate Structural Control and Block Formation in the Living Polymerization of 1,3-Dienes by Nitroxide-Mediated Procedures," *Macromolecules* 33, (2000), 363-370: Robin, S.; Guerret, O.; Couturier, J. L.; Gnanou, Y. "Synthesis of Stars and Starlike Block Copolymers from a Trialkoxyamine Used as Initiator," *Macromolecules* 35, (2002), 2481-2486: Robin, S.; Guerret, O.; Couturier, J. L.; Pirri, R.; Gnanou, Y. "Synthesis and Characterization of Poly(Styrene-B-N-Butyl Acrylate-B-Styrene) Triblock Copolymers Using a Dialkoxyamine as Initiator," *Macromolecules* 35, (2002), 3844-3848: Robin, S.; Gnanou, Y. "Triblock Copolymers Based on Styrene and N-Butyl Acrylate by Nitroxide-Mediated Radical Polymerization: Problems and Solutions," *Macromolecular Symposia* 165, (2001), 43-53.

²⁷⁶ Benoit, D.; Grimaldi, S.; Finet, J. P.; Tordo, P.; Fontanille, M.; Gnanou, Y. "Controlled Free-Radical Polymerization in the Presence of a Novel Asymmetric Nitroxyl Radical," *Abstracts of Papers of the American Chemical Society* 213, (1997), 465-POLY: Grimaldi, S.; Finet, J. P.; Le Moigne, F.; Zeghdoui, A.; Tordo, P.; Benoit, D.; Fontanille, M.; Gnanou, Y. "Acyclic Beta-Phosphonylated Nitroxides: A New Series of Counter-Radicals for "Living"/Controlled Free Radical Polymerization," *Macromolecules* 33, (2000), 1141-1147: Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. "Development of a Universal Alkoxyamine for "Living" Free Radical Polymerizations," *Journal of the American Chemical Society* 121, (1999), 3904-3920.

²⁷⁷ Connolly, T. J.; Scaiano, J. C. "Reactions of the "Stable" Nitroxide Radical Tempo. Relevance to "Living" Free Radical Polymerizations and Autopolymerization of Styrene," *Tetrahedron Letters* 38, (1997), 1133-1136.

²⁷⁸ Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K.; Saban, M. "Narrow Polydispersity Polystyrene by a Free-Radical Polymerization Process - Rate Enhancement," *Macromolecules* 27, (1994), 7228-7229: Veregin, R. P. N.; Odell, P. G.; Michalak, L. M.; Georges, M. K. "Mechanism of Rate Enhancement Using Organic Acids in Nitroxide-Mediated Living Free-Radical Polymerizations," *Macromolecules* 29, (1996), 4161-4163: Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. "Nitroxide Stable Free-Radical Mediated Free-Radical Polymerization - Autopolymerization," *Abstracts of Papers of the American Chemical Society* 208, (1994), 491-POLY.

effects on the resulting molecular weight distributions were observed at high monomer conversions. Further investigations by Georges et al. showed that organic acid salts such as 2-fluoro-1-methylpyridinium *p*-toluene sulfonate (FMPTS) exhibited an even greater enhancement of the polymerization rate.²⁷⁹ It was also determined that the source of the rate enhancement using FMPTS resulted from a decrease in the concentration of the nitroxide mediator. Hawker and coworkers pioneered the use of acylating agents such as acetic anhydride to directly affect the alkoxyamine bond energy and shift the mediation equilibrium.²⁸⁰ An increased polymerization rate was observed and the molecular weight distribution remained narrow within a limited molecular weight range.

The concentration of nitroxide mediator in the polymerization has also been employed to affect the rate of polymerization. Increasing the concentration of the nitroxide mediator resulted in a decrease in the resulting monomer conversion rate.²⁸¹ This result was consistent with the current mechanistic model of the SFRP system.²⁸² Goto and Fukuda investigated the use of added radical initiator to accelerate the rate of stable free radical polymerization.²⁸³ Addition of *tert*-butyl hydroperoxide increased the rate of styrene polymerization 3 fold without negatively affecting the molecular weight distribution.

²⁷⁹ Odell, P. G.; Veregin, R. P. N.; Michalak, L. M.; Brousmiche, D.; Georges, M. K. "Rate Enhancement of Living Free-Radical Polymerizations by an Organic-Acid Salt," *Macromolecules* 28, (1995), 8453-8455: Odell, P. G.; Veregin, R. P. N.; Michalak, L. M.; Georges, M. K. "Characteristics of the Stable Free Radical Polymerization of Styrene in the Presence of 2-Fluoro-1-Methylpyridinium P- Toluenesulfonate," *Macromolecules* 30, (1997), 2232-2237.

²⁸⁰ Malmstrom, E.; Miller, R. D.; Hawker, C. J. "Development of a New Class of Rate-Accelerating Additives for Nitroxide-Mediated 'Living' Free Radical Polymerization," *Tetrahedron* 53, (1997), 15225-15236.

²⁸¹ MacLeod, P. J.; Veregin, R. P. N.; Odell, P. G.; Georges, M. K. "Stable Free Radical Polymerization of Styrene: Controlling the Process with Low Levels of Nitroxide," *Macromolecules* 30, (1997), 2207-2208: Veregin, R. P. N.; Odell, P. G.; Michalak, L. M.; Georges, M. K. "The Pivotal Role of Excess Nitroxide Radical in Living Free Radical Polymerizations with Narrow Polydispersity," *Macromolecules* 29, (1996), 2746-2754: Lacroix-Desmazes, P.; Lutz, J. F.; Chauvin, F.; Severac, R.; Boutevin, B. "Living Radical Polymerization: Use of an Excess of Nitroxide as a Rate Moderator," *Macromolecules* 34, (2001), 8866-8871.

²⁸² Fukuda, T.; Terauchi, T. "Mechanism of "Living" Radical Polymerization Mediated by Stable Nitroxyl Radicals," *Chemistry Letters*, (1996), 293-294: Fukuda, T.; Terauchi, T.; Goto, A.; Ohno, K.; Tsujii, Y.; Miyamoto, T.; Kobatake, S.; Yamada, B. "Mechanisms and Kinetics of Nitroxide-Controlled Free Radical Polymerization," *Macromolecules* 29, (1996), 6393-6398.

²⁸³ Goto, A.; Fukuda, T. "Effects of Radical Initiator on Polymerization Rate and Polydispersity in Nitroxide-Controlled Free Radical Polymerization," *Macromolecules* 30, (1997), 4272-4277.

One of the most significant alterations to enhance the rate of SFRP polymerization was the development of novel nitroxide mediating agents.²⁸⁴ Altering the structure of the nitroxide mediator from a cyclic structure characteristic of 2,2,6,6-tetramethylpiperidyl-oxy (TEMPO) to an open structure found in the di-*tert*-butyl nitroxide (DBN) resulted in higher monomer conversion rates for styrene.²⁸⁵ The recently developed α -hydrogen containing nitroxides demonstrated a similar effect on the polymerization of styrene.²⁸⁶ In addition to the open structure, Hawker found that the functional groups attached to the nitroxide significantly affected the polymerization rate.²⁸⁷ After the initial efforts by Matyjaszewski demonstrated a rate enhancement using a phosphonic acid derivative of TEMPO,²⁸⁸ Hawker investigated a α -hydrido nitroxide that possessed a hydroxyl functionality. Earlier efforts also confirmed the tendency of hydrogen bonding to affect the reactivity of nitroxides.²⁸⁹ This report describes the investigation of the effects of the alkyl ester structure on the rate on monomer conversion in stable free radical polymerization processes.

²⁸⁴ Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. "Development of a Universal Alkoxyamine for "Living" Free Radical Polymerizations," *Journal of the American Chemical Society* 121, (1999), 3904-3920; Grimaldi, S.; Finet, J. P.; Le Moigne, F.; Zeghdaoui, A.; Tordo, P.; Benoit, D.; Fontanille, M.; Gnanou, Y. "Acyclic Beta-Phosphonylated Nitroxides: A New Series of Counter-Radicals for "Living"/Controlled Free Radical Polymerization," *Macromolecules* 33, (2000), 1141-1147.

²⁸⁵ Kazmaier, P. M.; Moffat, K. A.; Georges, M. K.; Veregin, R. P. N.; Hamer, G. K. "Free-Radical Polymerization for Narrow-Polydispersity Resins - Semiempirical Molecular-Orbital Calculations as a Criterion for Selecting Stable Free-Radical Reversible Terminators," *Macromolecules* 28, (1995), 1841-1846.

²⁸⁶ Grimaldi, S.; Finet, J. P.; Le Moigne, F.; Zeghdaoui, A.; Tordo, P.; Benoit, D.; Fontanille, M.; Gnanou, Y. "Acyclic Beta-Phosphonylated Nitroxides: A New Series of Counter-Radicals for "Living"/Controlled Free Radical Polymerization," *Macromolecules* 33, (2000), 1141-1147.

²⁸⁷ Harth, E.; Van Horn, B.; Hawker, C. J. "Acceleration in Nitroxide Mediated 'Living' Free Radical Polymerizations," *Chemical Communications*, (2001), 823-824.

²⁸⁸ Matyjaszewski, K.; Gaynor, S. G.; Greszta, D.; Mardare, D.; Shigemoto, T.; Wang, J. S. "Unimolecular and Bimolecular Exchange-Reactions in Controlled Radical Polymerization," *Macromolecular Symposia* 95, (1995), 217-231.

²⁸⁹ Beckwith, A. L. J.; Bowry, V. W.; Ingold, K. U. "Kinetics of Nitroxide Radical Trapping .1. Solvent Effects," *Journal of the American Chemical Society* 114, (1992), 4983-4992; Studer, A. "Tin-Free Radical Cyclization Reactions Using the Persistent Radical Effect," *Angewandte Chemie-International Edition* 39, (2000), 1108-1111.

6.3 Experimental

6.3.1 Material

The alkyl acrylate monomers were purchased from Aldrich and deinhibited using a neutral alumina column prior to polymerization. 2,2'-Azobisisobutyronitrile (AIBN) and dodecanol were purchased from Aldrich and used as received. The nitroxide mediator, *N-tert-butyl-N*-[1-diethylphosphono(2,2-dimethylpropyl)]nitroxide (DEPN), was synthesized using a method previously described.²⁹⁰

6.3.2 Characterization

¹H NMR spectra were collected on a Varian Unity-400 spectrometer in CDCl₃ at ambient temperature. Molecular weights were determined at 40 °C in chloroform (HPLC grade) at 1 mL/min using polystyrene standards on a Waters 717+ Autosampler SEC equipped with 3 in-line PLgel 5 μm MIXED-C columns, a Waters 410 differential RI detector and an in-line Wyatt Technologies miniDAWN multiple angle laser light scattering (MALLS). *In situ* FTIR monitoring was performed with an ASI Applied Systems ReactIR™ 1000 reaction analysis system with a stainless steel DiComp™ probe.²⁹¹ A comparison of peak height versus a common baseline point was performed to eliminate data scatter due to baseline drift. Melt rheology was performed on a TA Instruments AR1000 rheometer at 50 °C in oscillatory mode with a 2% strain. Tack testing was accomplished using a TA.XT2i Texture Analyzer (Texture Technologies Corp. Scarsdale, NY/Stable Micro Systems, Godalming, Surrey, UK) with a stainless steel probe and a pull of rate of 2 mm/s and a 1 s dwell time. Thermal behavior was evaluated on a Pyris Perkin Elmer DSC under N₂ atmosphere using controlled heating and cooling rates.

²⁹⁰ Grimaldi, S.; Finet, J. P.; Le Moigne, F.; Zeghdaoui, A.; Tordo, P.; Benoit, D.; Fontanille, M.; Gnanou, Y. "Acyclic Beta-Phosphonylated Nitroxides: A New Series of Counter-Radicals for "Living"/Controlled Free Radical Polymerization," *Macromolecules* 33, (2000), 1141-1147.

²⁹¹ Pasquale, A. J.; Long, T. E. "Real-Time Monitoring of the Stable Free Radical Polymerization of Styrene Via in-Situ Mid-Infrared Spectroscopy," *Macromolecules* 32, (1999), 7954-7957; Pasquale, A. J.; Long, T. E. "Synthesis of Star-Shaped Polystyrenes Via Nitroxide-Mediated Stable Free-Radical Polymerization," *Journal of Polymer Science Part a-Polymer Chemistry* 39, (2001), 216-223.

6.3.3 Stable Free Radical Polymerization of Alkyl Acrylates Monitored Using in situ FTIR Spectroscopy

A typical polymerization of n-butyl acrylate is described. AIBN (0.107 mmol) and DEPN (0.269 mol) were added to a 100 mL round-bottomed flask with a magnetic stir bar. n-Butyl acrylate (15 mL) was then added to the AIBN/DEPN reaction mixture via syringe. The reaction vessel was sealed and placed in a $-78\text{ }^{\circ}\text{C}$ IPA/dry ice bath. The reaction mixture was subjected to at least three freeze thaw cycles to remove oxygen and nitrogen was added to the degassed reaction flask. The contents of the reaction vessel were subsequently cannulated to a sealed, nitrogen filled reaction flask equipped with a FTIR insertion probe. A preheated $130\text{ }^{\circ}\text{C}$ oil bath was raised to the reaction vessel and data collection was commenced acquiring one spectrum every 2 min for 4 h. The reaction mixture was diluted with THF and precipitated into methanol. The isolated polymers were dried in the vacuum oven at $65\text{ }^{\circ}\text{C}$ for 48 h.

6.3.4 Stable Free Radical Copolymerization of n-Butyl Acrylate and 2-Hydroxyethyl Acrylate Monitored Using in situ FTIR Spectroscopy

AIBN (0.071 mmol) and DEPN (0.179 mol) were added to a 100 mL round-bottomed flask with a magnetic stir bar. n-Butyl acrylate (25.8 mL) and 2-hydroxyethyl acrylate (HEA) (2.3 mL) were then added to the AIBN/DEPN reaction mixture via syringe. The reaction vessel was sealed and placed in a $-78\text{ }^{\circ}\text{C}$ IPA/dry ice bath. The reaction mixture was subjected to at least three freeze thaw cycles for degassing and nitrogen was added to the degassed reaction flask. The contents of the reaction vessel were subsequently cannulated to a sealed, nitrogen filled reaction flask equipped with a FTIR insertion probe. A preheated $130\text{ }^{\circ}\text{C}$ oil bath was raised to the reaction vessel and data collection was commenced with the acquisition of one spectrum every 2 min for 4 h. The polymerization mixture was diluted with THF and precipitated into a methanol:water mixture (5:1). The isolated polymers were dried in the vacuum oven at $65\text{ }^{\circ}\text{C}$ for 48 h.

6.3.5 Dodecanol Catalyzed Stable Free Radical Polymerization of n-Butyl Acrylate Monitored Using *in situ* FTIR Spectroscopy

AIBN (0.071 mmol), DEPN (0.179 mol), and dodecanol (8.908 mmol) were added to a 100 mL round-bottomed flask with a magnetic stir bar. n-Butyl acrylate (26.5 mL) was then added to the AIBN/DEPN reaction mixture via syringe. The reaction vessel was sealed and placed in a $-78\text{ }^{\circ}\text{C}$ IPA/dry ice bath. The reaction mixture was subjected to at least three freeze thaw cycles to remove oxygen and nitrogen was added to the degassed reaction flask. The contents of the reaction vessel were subsequently cannulated to a sealed, nitrogen filled reaction flask equipped with a FTIR insertion probe. A preheated $130\text{ }^{\circ}\text{C}$ oil bath was raised to the reaction vessel and data collection was commenced acquiring one spectrum every 2 min for 4 h. The reaction mixture was diluted with THF and precipitated into methanol. The isolated polymers were dried in the vacuum oven at $65\text{ }^{\circ}\text{C}$ for 48 h.

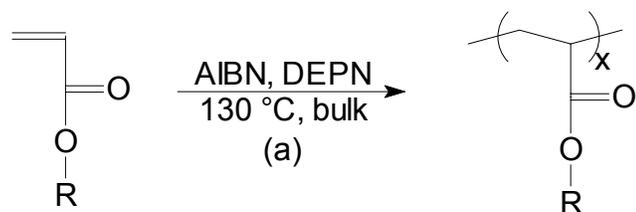
6.4 Results and Discussion

6.4.1 Effect of Alkyl Ester Chain Length on SFRP Kinetics

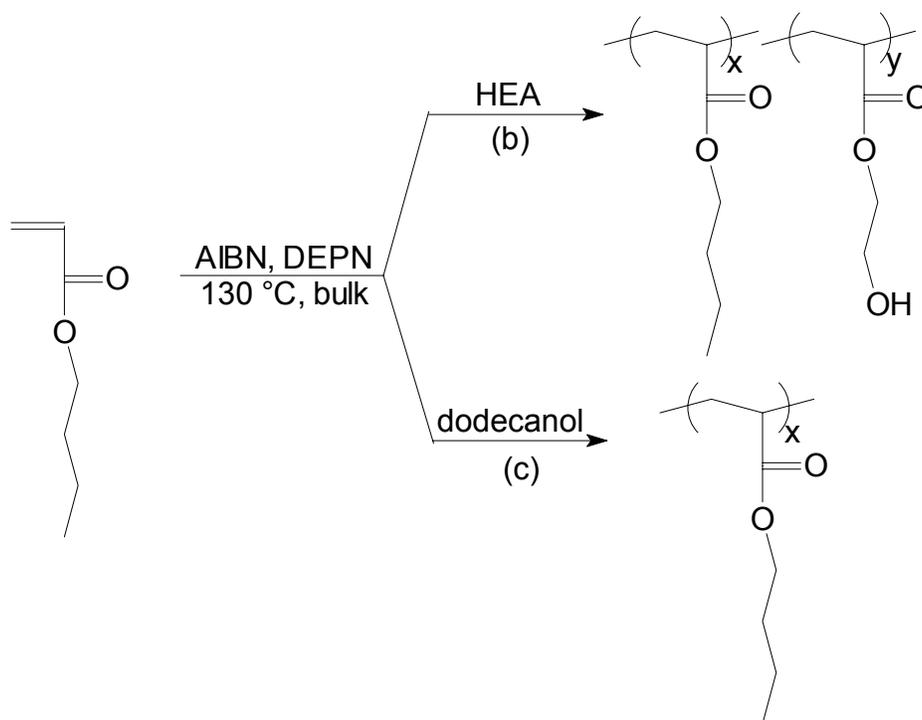
Previous studies of SFRP kinetics have examined the electronic and steric effects associated with the alkoxyamine C—ON bond. While a distinct effect due to the introduction of steric strain around the C—ON bond from an open structure nitroxide moiety such as DEPN or DBN was reported, no one has examined the possibility of steric effects arising from bulky monomer functionalities has not been examined.²⁹² A variety of alkyl acrylate monomers with different alkyl ester chain sizes were polymerized in the presence of DEPN (Scheme 6.1(a)). The molar ratio of DEPN to AIBN was maintained at 2.5 for all of the polymerizations.

The monomer conversions for n-butyl, *t*-butyl, 2-ethylhexyl, and lauryl acrylate were monitored in real-time using *in situ* FTIR spectroscopy. In particular, the C—H wag absorbance of the monomer at 968 cm^{-1} was utilized to determine the monomer

²⁹² Goto, A.; Fukuda, T. "Comparative Study on Activation Rate Constants for Some Styrene/Nitroxide Systems," *Macromolecular Chemistry and Physics* 201, (2000), 2138-2142; Goto, A.; Kwak, Y.; Yoshikawa, C.; Tsujii, Y.; Sugiura, Y.; Fukuda, T. "Comparative Study on Decomposition Rate Constants for Some Alkoxyamines," *Macromolecules* 35, (2002), 3520-3525.



R= n-butyl, t-butyl, 2-ethylhexyl, lauryl



Scheme 6.1: Stable free radical polymerizations of various alkyl acrylates.

concentration relative to the initial value. The degree of conversion was maintained at ~10% for all polymerizations to avoid complications due to polymerization viscosity issues. A comparison of the monomer disappearance profiles for n-butyl, 2-ethylhexyl and lauryl acrylate exhibited no noticeable trends suggesting that the alkyl ester chain length does not significantly affect the activation-deactivation equilibrium controlling the SFRP process (Figure 6.1). In addition, the pseudo first order kinetics for these monomers were determined (Figure 6.2) and the resulting observed rate constants are shown in Table 6.1. The rate constant values exhibited little difference and no distinct trend based on chain length size. A comparison of n-butyl and *t*-butyl acrylate demonstrated the effect of concentrating more steric bulk around the propagating radical with the *t*-butyl group. However, examination of the polymerization kinetics also revealed no significant difference between the observed rate constants. The resulting polymer products all exhibited narrow molecular weight distributions ranging from 1.09 to 1.19 suggesting the polymerizations proceeded in a controlled manner.

6.4.2 Effect of Hydroxyl Containing Acrylic Monomer on SFRP Kinetics

Copolymerizations of n-butyl acrylate and 2-hydroxyethyl acrylate (HEA) were studied to investigate the electronic factors that may affect the polymerization (Scheme 6.1b). HEA was chosen as a comonomer because its ester alkyl side chain was similar in size to the n-butyl acrylate alkyl side group. Moreover, the HEA monomer was expected to possess a similar rate of polymerization in a conventional free radical system. The molar ratio of DEPN to AIBN for all copolymerizations was held at 2.5:1.0. Analysis of the resulting polymerization kinetics shown in Figure 6.3 revealed a distinct trend associated with the concentration of the hydroxyl containing monomer in the polymerization. The observable IR absorbances attributable to nBA and HEA were not resolved. Therefore, the overall monomer conversion was monitored using the C-H deformation associated with the acrylate double bond at 864 cm^{-1} . The addition of 10 mol% HEA to the polymerization resulted in little or no difference in the rate of monomer conversion compared to the n-butyl acrylate homopolymerization. The rate of monomer conversion did, however, increase as the concentration of HEA was increased to 20 and 30 mol%. The addition of 40 mol% HEA to the copolymerization showed an

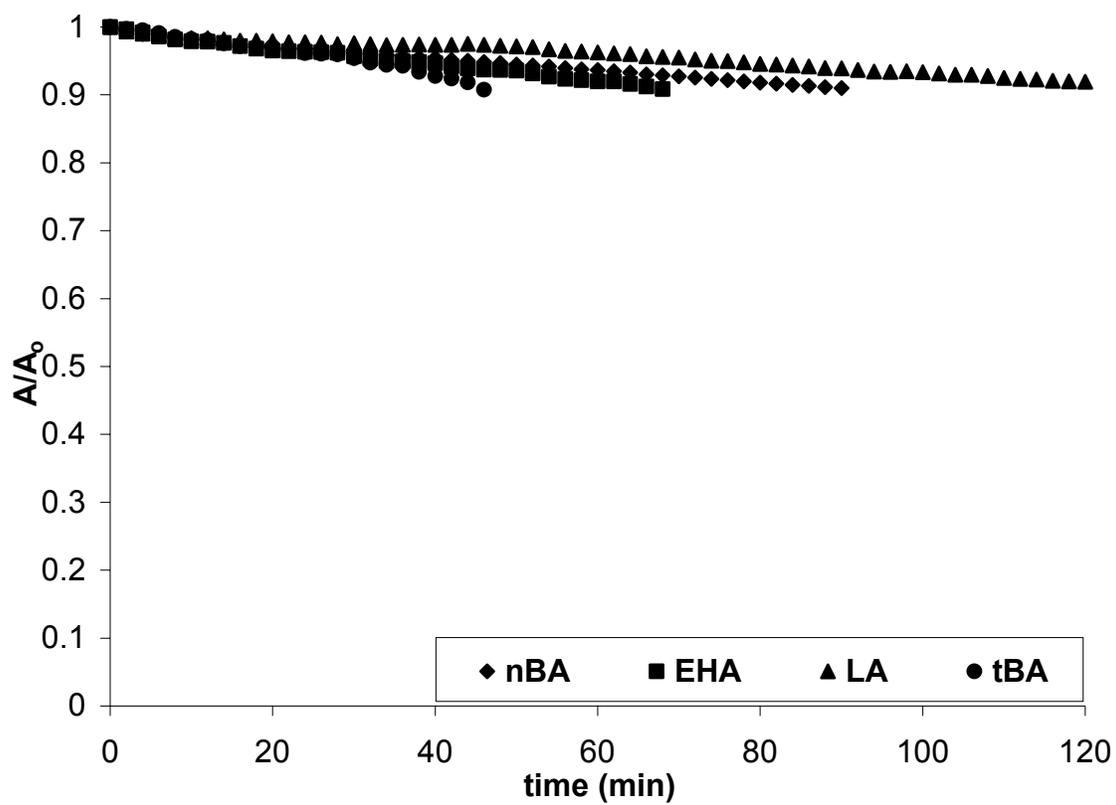


Figure 6.1: Monomer conversion profiles for the SFRP of alkyl acrylates.

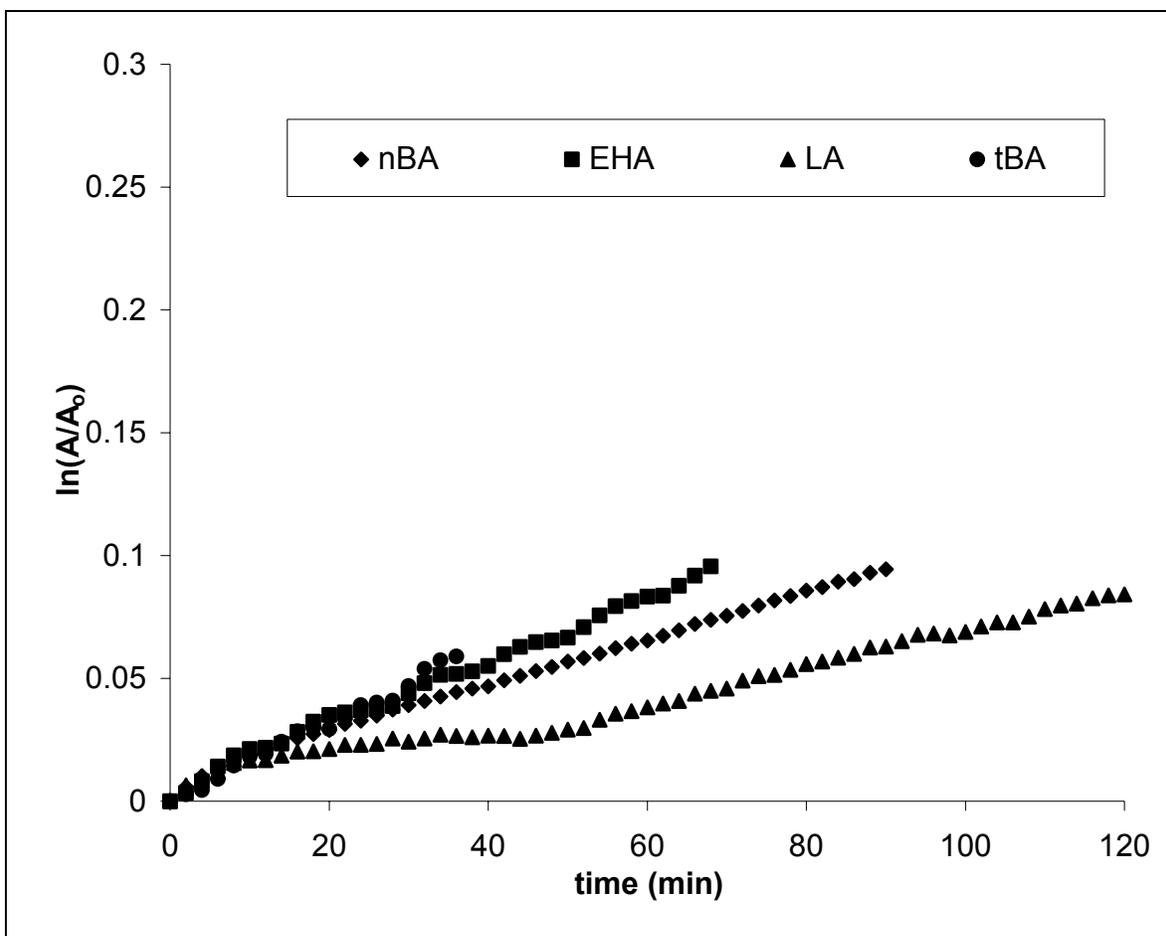


Figure 6.2: Pseudo 1st order kinetic plots for the SFRP of alkyl acrylates.

Table 6.1: Pseudo 1st order rate constants for the SFRP of n-butyl (nBA), 2-ethylhexyl (EHA), lauryl (LA) and *t*-butyl (*t*BA) acrylate determined using *in situ* FTIR.

Monomer	nBA	EHA	LA	<i>t</i> BA
$k_{\text{obs}} (\times 10^{-5} \text{ s}^{-1})$	1.61	2.17	1.01	2.68

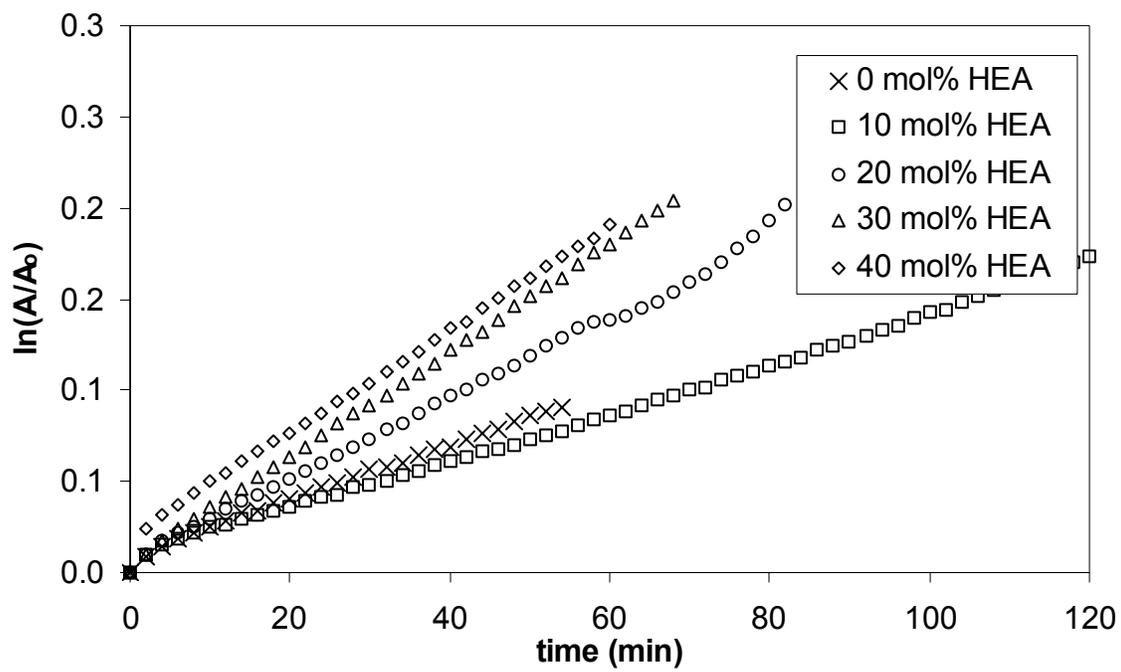


Figure 6.3: Pseudo 1st order kinetics plots for the stable free radical copolymerization of n-butyl acrylate and 2-hydroxyethyl acrylate.

overall monomer conversion rate constant identical to that observed with 30 mol% HEA in the monomer feed. The observed rate constants for the various copolymerizations are shown in Figure 6.4. The rate constant plateau suggested a saturation of the acceleration effect. The source of the polymerization rate enhancement was attributed to hydrogen bonding interactions between the hydroxyl group of HEA monomer and the nitroxide. The hydrogen bonding locked the nitroxide into an inactive state allowing the propagating radical to remain in the active uncapped state for a longer period of time (Figure 6.5) resulting in a greater number of monomer additions per activation-deactivation cycle.²⁹³ These results are consistent with earlier observations in the laboratories of Hawker and Matyjaszewski.²⁹⁴ The absence of rate enhancement with 10 mol% HEA may result due to an insufficient number of hydroxyl functionalities for interaction with the nitroxide mediators.

While the rate of the stable free radical polymerization increased with increasing concentration of the hydroxyl containing acrylate monomer, the controlled nature of the polymerization remained constant based on molecular weight distributions. Table 6.2 details the molecular weight results of the HEA/nBA copolymerizations in the presence of DEPN. Although FTIR absorbances for nBA and HEA were indistinguishable, ¹H NMR analysis of the resulting copolymers revealed macromolecules enriched with the hydroxyl containing monomer compared to the monomer feed ratio. For all copolymerizations, the molar percentage of HEA in the copolymer was almost 50% higher than what was charged in the monomer feed (Table 6.3). The polymerizations were terminated prior to full monomer conversion and the enrichment most likely occurred due to monomer reactivity ratios that favored the early addition of the HEA monomer to the polymer.

²⁹³ Beckwith, A. L. J.; Bowry, V. W.; Ingold, K. U. "Kinetics of Nitroxide Radical Trapping .1. Solvent Effects," *Journal of the American Chemical Society* 114, (1992), 4983-4992.

²⁹⁴ Harth, E.; Van Horn, B.; Hawker, C. J. "Acceleration in Nitroxide Mediated 'Living' Free Radical Polymerizations," *Chemical Communications*, (2001), 823-824; Matyjaszewski, K.; Gaynor, S. G.; Greszta, D.; Mardare, D.; Shigemoto, T.; Wang, J. S. "Unimolecular and Bimolecular Exchange-Reactions in Controlled Radical Polymerization," *Macromolecular Symposia* 95, (1995), 217-231.

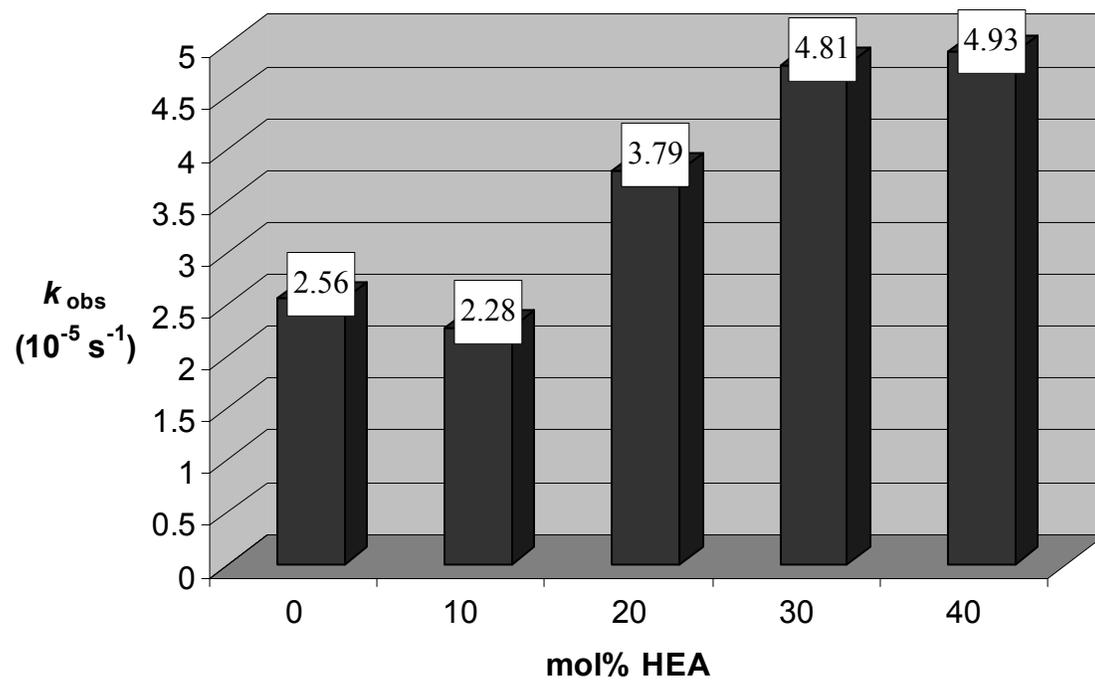


Figure 6.4: Pseudo 1st order rate constants for the nBA/HEA copolymerizations.

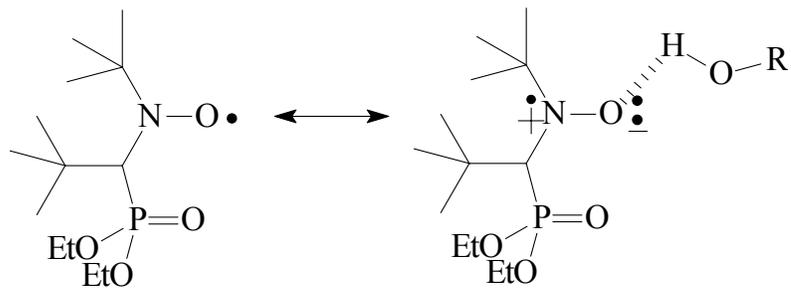


Figure 6.5: Resonance forms associated with the DEPNO nitroxide and stabilization resulting from hydrogen bonding.

Table 6.2: Molecular weight of HEA/nBA copolymers.

Monomer Feed Ratio		M_n^a	M_w/M_n^a
HEA	nBA		
0	100	72700	1.22
10	90	81100	1.22
20	80	47100	1.25
30	70	70300	1.12
40	60	108300	1.22

^a determined using GPC/RI/MALLS

Table 6.3: ^1H NMR analysis of HEA/nBA copolymers.

Monomer Feed Ratio		Copolymer Composition ^a	
HEA	nBA	HEA	nBA
0	100	0	100
10	90	14	86
20	80	28	72
30	70	40	60
40	60	51	49

^a determined using ^1H NMR spectroscopy

6.4.3 Dodecanol Catalyzed Stable Free Radical Polymerization of n-Butyl Acrylate

Based upon the results observed during the copolymerization of HEA and n-butyl acrylate, polymerizations with added amounts of dodecanol were studied to investigate catalysis of the SFRP process using a hydrogen bonding hydroxyl group (Scheme 6.1c). Dodecanol was chosen to avoid volatilization during the high temperature SFRP reactions. The molar ratio of nitroxide to dodecanol was systematically altered and the resulting polymerizations were monitored using *in situ* FTIR. Molar ratios of 0, 50 and 112 were studied and, as expected, increasing the concentration of the dodecanol resulted in an acceleration of the monomer conversion and the corresponding kinetics (Figure 6.6). The observed rate constants steadily increased with greater concentrations of dodecanol (Table 6.4). Interestingly, the rate enhancement induced upon addition of dodecanol was greater than that of equimolar amounts of HEA. The inclusion of HEA in the polymer chain may have limited hydroxyl group mobility and reduced the resulting rate enhancement. Deleterious effects on the controlled nature of the polymerization process were absent based on GPC analysis of the polymer products. The molecular weights of the resulting macromolecules ranged from 45K-60K g/mol with molecular weight distributions of 1.08-1.29. Molecular weights and molecular weight distributions exhibited no systematic trend based on the amount of dodecanol employed to catalyze the polymerization.

Table 6.4: Rate constants for n-butyl acrylate homopolymerizations catalyzed with dodecanol.

ROH:DEPN molar ratio	0	50	112
k_{obs} ($\times 10^{-5} \text{ s}^{-1}$)	2.50	3.83	5.17

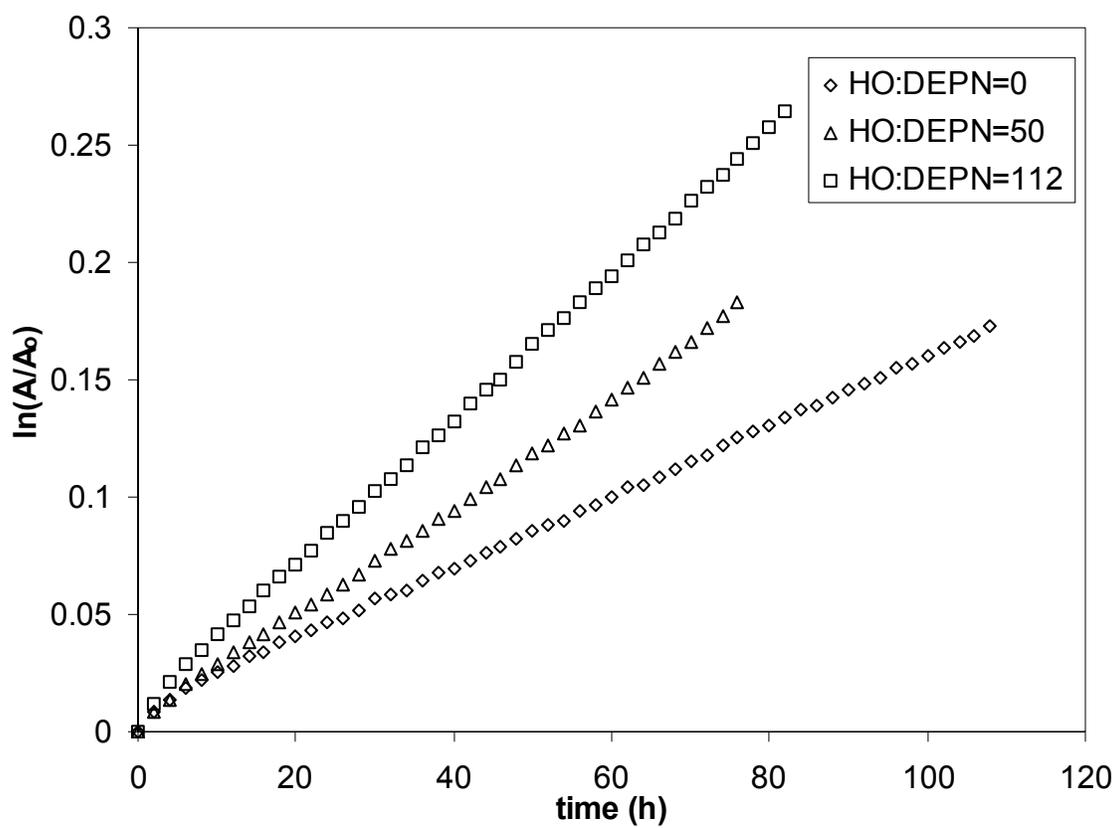


Figure 6.6: Pseudo 1st order kinetic plots of dodecanol catalyzed SFRP for n-butyl acrylate.

6.5 Mechanical Properties Analysis of HEA and nBA Copolymers

The random copolymer possessing 0-52 mol% HEA based on NMR analysis were examined using melt rheology to investigate the presence and effect of hydrogen bonding in the copolymers due to the presence of the HEA hydroxyl. The increasing incorporation of HEA in the copolymer resulted in an increase in the T_g of the copolymers (Table 6.5). A plot of HEA incorporation in the polymer product versus the resulting T_g was linear (Figure 6.7). In addition, extrapolation of the relationship between HEA molar percent and T_g revealed a poly(HEA) homopolymer T_g of $-10\text{ }^\circ\text{C}$ that correlated well with the T_g of a HEA homopolymer determined using DSC ($-9\text{ }^\circ\text{C}$). The copolymers, exhibiting similar molecular weights and narrow molecular weight distributions from GPC analysis, were analyzed with an isothermal frequency sweep at $50\text{ }^\circ\text{C}$ well above the T_g of all the copolymers. Examination of the zero shear viscosities estimated based on extrapolation of the rheological curves demonstrated a significant effect due to the increased incorporation of HEA in the copolymer (Figure 6.8). The increasing concentration of HEA resulted in a increase in the observed zero shear viscosity. Moreover, a decrease in the relaxation times for the copolymers was observed as the concentration of HEA in the copolymers was increased (Figure 6.9). These results suggested the presence of some degree of hydrogen bonding via interaction of the hydroxyl functionality. In addition to the rheological analysis, tack testing of the HEA and nBA copolymers was also performed. The copolymers with larger amounts of incorporated HEA demonstrated higher peak pull off forces and greater peak areas (Figure 6.10). The higher pull off forces suggested enhanced interaction with the probe. The peak areas, which are related to the energy necessary to debond the probe, demonstrated increasing values with increasing HEA content due to greater resistance to deformation. This increased resistance further suggested that the polymer was behaving like a higher molecular weight macromolecule possibly due to hydrogen bonding interactions among the HEA repeat units.

6.6 Conclusions

The stable free radical polymerizations of various alkyl acrylate monomers were investigated using real-time FTIR spectroscopic techniques. The varying sizes of

Table 6.5: nBA and HEA copolymers synthesized via DEPN mediated SFRP.

Copolymer Composition		M_n	M_w/M_n	T_g (°C)
HEA	nBA			
0	100	55K	1.16	-48
13	87	68K	1.36	-42
28	72	63K	1.24	-34
40	60	62K	1.19	-32
52	48	65K	1.25	-29

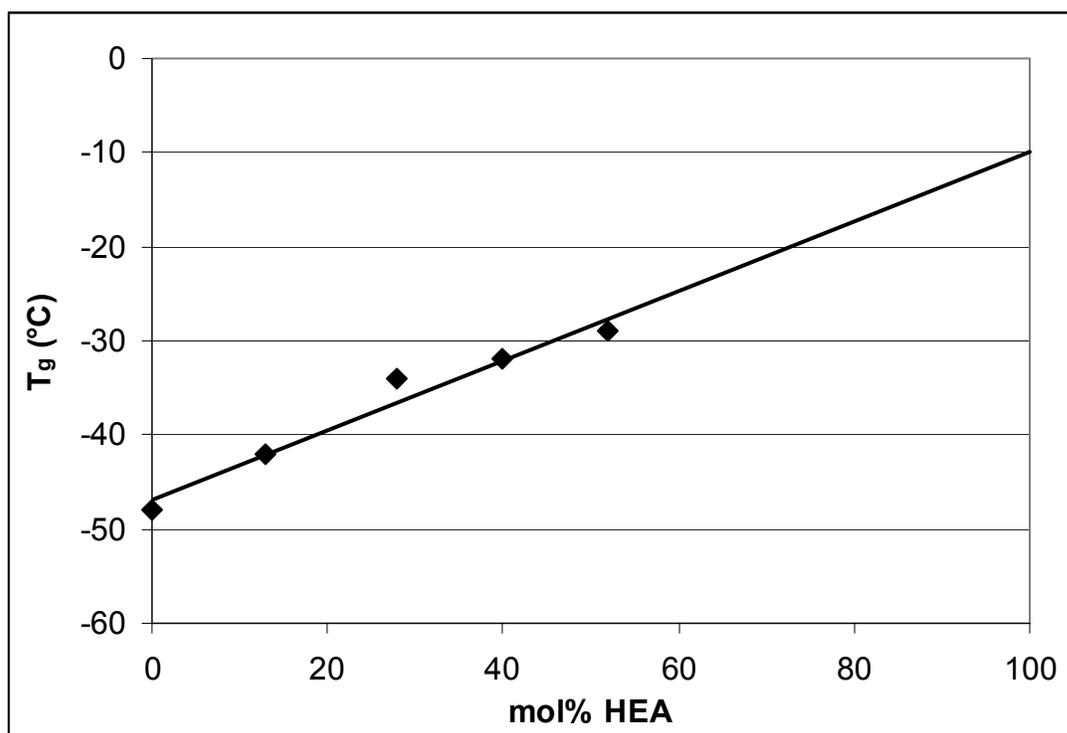


Figure 6.7: Plot of T_g versus mol% HEA in nBA and HEA copolymers.

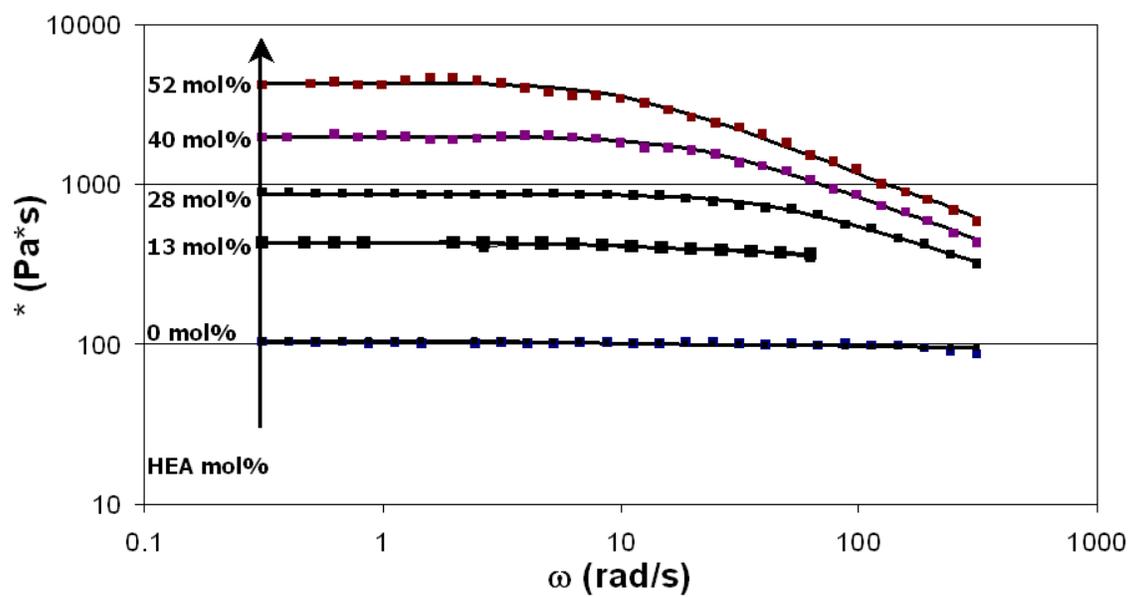


Figure 6.8: Melt rheology of nBA and HEA copolymers synthesized via SFRP

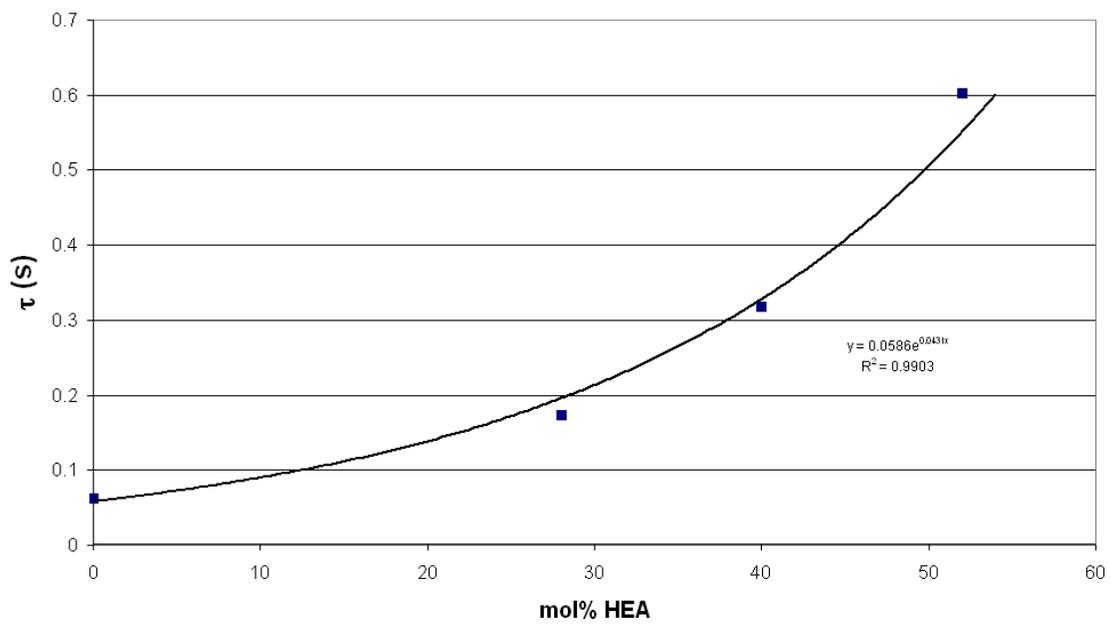


Figure 6.9: Correlation between relaxation time (τ) and the concentration of HEA in the copolymer.

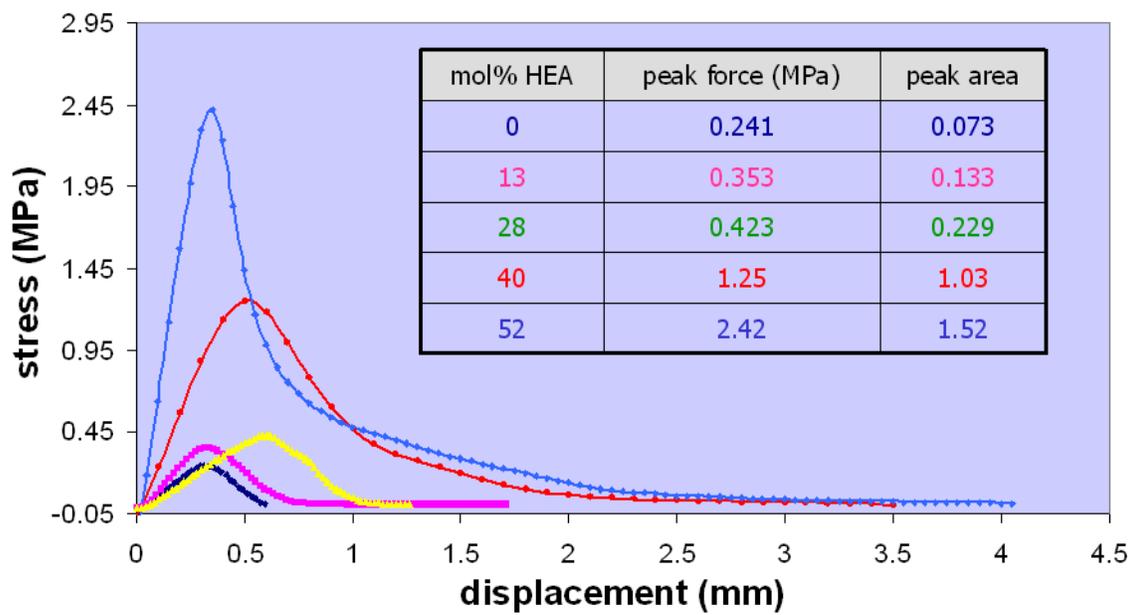


Figure 6.10: Tack testing of nBA and HEA random copolymers.

aliphatic alkyl ester chains exhibited no significant effect on the rate of the polymerization. On the contrary, inclusion of the hydroxyl containing HEA monomer in a copolymerization with n-butyl acrylate resulted in acceleration of the monomer conversion and polymerization rate. A similar phenomenon was observed upon addition of dodecanol to a n-butyl acrylate homopolymerization. Moreover, the rate enhancement due to dodecanol was greater than that observed with the HEA monomer. It was determined that the incorporation of the hydroxyl functionality in the stable free radical polymerization of the acrylate monomers shifted the equilibrium prolonging the lifetime of the active intermediates and resulting in more monomer additions per activation-deactivation cycle.

6.7 Acknowledgements

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Chapter 7 : Synthesis and Characterization of Acrylic Amphiphilic Blocks via Living Anionic and Stable Free Radical Polymerization Methodologies

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7.1 Abstract

The synthesis of amphiphilic block copolymers composed of alkyl acrylate monomers was investigated using the stable free radical polymerization process. The size of the resulting block sequences was restricted using the control of the SFRP and *in situ* FTIR monitoring. The molecular weight of each monomer sequence within the block copolymers was investigated using NMR, FTIR and GPC. The resulting polymer products were subjected to hydrolysis using catalytic amounts of *para*-toluene sulfonic acid converting the *t*-butyl functionalities into carboxylic acid groups. Thermal transitions for the alkyl acrylate triblock copolymers before and after modification were examined using DSC and revealed the presence of a low temperature glass transition temperature indicative of a microphase separated system. Further investigation of the acrylate copolymer using DMA and AFM confirmed the presence of a two-phase system exhibiting a soft EHA matrix filled with hard acrylic acid domains. In addition, SAXS was employed to further examine the long range order present in the system and results from AFM correlated well with data derived from the SAXS analysis.

7.2 Introduction

The growing complexity of advanced technology has demanded specifically tailored polymeric materials for individual applications. Typically, anionic

polymerization methodologies offer the ability to accurately control the monomer composition and the resulting polymer architecture.²⁹⁵ However, the reactive nature of the anionic propagating species renders it incompatible with many monomer families. This functional group intolerance coupled with rigorous laboratory techniques prompted an investigation into free radical polymerization as an alternative to prepare well-defined macromolecules. Stable free radical polymerization (SFRP), atom transfer radical polymerization (ATRP) and reversible addition fragmentation transfer polymerization (RAFT) have all recently emerged as potential alternatives to anionic polymerization.²⁹⁶ All the controlled free radical techniques operate based on an equilibrium between dormant and active chains. The equilibrium, which lies heavily in favor of the dormant unreactive state, serves to limit appreciable levels of chain transfer and chain termination that typically lead to broadened polydispersities in conventional free radical polymerization. The three techniques differ in the type of mediating agent that reversibly caps the propagating radical. The ATRP system is based on a reversible redox reaction that involves a halogen exchange between the polymer chain end and a transition metal catalyst, typically copper. The RAFT technique uses thio-containing molecules to mediate the polymerization. The SFRP system employs a stable free radical nitroxide species to reversibly react with the propagating radical chain. This nitroxide will not couple with itself or other oxygen centered radical and reacts at diffusion-controlled rates with carbon-centered radicals.

The polymerization of acrylic monomers allows the introduction of a wide array of possible polarities. Acrylic polymerization utilizing anionic methods is tedious and requires the use of special initiators and reaction processes due to the propensity of side

²⁹⁵ Webster, O. W. "Living Polymerization Methods," *Science* 251, (1991), 887-893; Frontini, G. L.; Elicabe, G. E.; Meira, G. R. "Optimal Periodic Control of a Continuous Living Anionic- Polymerization .2. New Theoretical Results," *Journal of Applied Polymer Science* 33, (1987), 2165-2177; Szwarc, M. "'Living" Polymers," *Nature* 178, (1956), 1168-1169.

²⁹⁶ Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. "Narrow Molecular-Weight Resins by a Free-Radical Polymerization Process," *Macromolecules* 26, (1993), 2987-2988; Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Moad, G.; Thang, S. H. "Living Radical Polymerization with Reversible Addition- Fragmentation Chain Transfer (Raft Polymerization) Using Dithiocarbamates as Chain Transfer Agents," *Macromolecules* 32, (1999), 6977-6980; Wang, J. S.; Matyjaszewski, K. "Controlled Living Radical Polymerization - Halogen Atom- Transfer Radical Polymerization Promoted by a Cu(I)Cu(II) Redox Process," *Macromolecules* 28, (1995), 7901-7910.

reactions associated with the monomer carbonyl functionality.²⁹⁷ The advent of controlled free radical techniques like SFRP has made well-defined acrylic copolymers a viable possibility.²⁹⁸ Synthetic developments in nitroxide mediating agents lead to the discovery of a new family of nitroxides possessing an α -hydrogen that enables efficiently controlled polymerization of acrylate monomers.²⁹⁹ Various researchers have investigated the synthesis of well-defined block copolymers utilizing the more efficient nitroxide mediators.³⁰⁰ This report describes the synthesis of an amphiphilic acrylic block copolymes system. Amphiphilic polymer systems have garnered research attention for use as emulsion and dispersion stabilizers as well as in blend compatibilization.³⁰¹ The SFRP technique was utilized to construct the well-defined alkyl acrylate precursor block copolymer. *In situ* FTIR polymerization monitoring was employed to precisely manipulate the degree of polymerization achieved in each polymerization step. The resulting block copolymer was subjected to *para*-toluene sulfonic acid catalyzed hydrolysis to yield a macromolecule possessing a central hydrophobic block bounded with two hydrophilic carboxylic acid containing blocks.

²⁹⁷ Wiles, D. M. *In Structure and Mechanism in Vinyl Polymerization*, ed. K. F. ODriscoll (New York: Marcel Dekker, 1969).

²⁹⁸ Grimaldi, S.; Finet, J. P.; Le Moigne, F.; Zeghdaoui, A.; Tordo, P.; Benoit, D.; Fontanille, M.; Gnanou, Y. "Acyclic Beta-Phosphonylated Nitroxides: A New Series of Counter-Radicals for "Living"/Controlled Free Radical Polymerization," *Macromolecules* 33, (2000), 1141-1147; Benoit, D.; Grimaldi, S.; Robin, S.; Finet, J. P.; Tordo, P.; Gnanou, Y. "Kinetics and Mechanism of Controlled Free-Radical Polymerization of Styrene and N-Butyl Acrylate in the Presence of an Acyclic Beta-Phosphonylated Nitroxide," *Journal of the American Chemical Society* 122, (2000), 5929-5939; Robin, S.; Gnanou, Y. "Triblock Copolymers Based on Styrene and N-Butyl Acrylate by Nitroxide-Mediated Radical Polymerization: Problems and Solutions," *Macromolecular Symposia* 165, (2001), 43-53.

²⁹⁹ Benoit, D.; Grimaldi, S.; Finet, J. P.; Tordo, P.; Fontanille, M.; Gnanou, Y. "Controlled Free-Radical Polymerization in the Presence of a Novel Asymmetric Nitroxyl Radical," *Abstracts of Papers of the American Chemical Society* 213, (1997), 465-POLY; Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. "Development of a Universal Alkoxyamine for "Living" Free Radical Polymerizations," *Journal of the American Chemical Society* 121, (1999), 3904-3920.

³⁰⁰ Robin, S.; Gnanou, Y. "Triblock Copolymers Based on Styrene and N-Butyl Acrylate by Nitroxide-Mediated Radical Polymerization: Problems and Solutions," *Macromolecular Symposia* 165, (2001), 43-53; Robin, S.; Guerret, O.; Couturier, J. L.; Pirri, R.; Gnanou, Y. "Synthesis and Characterization of Poly(Styrene-B-N-Butyl Acrylate-B-Styrene) Triblock Copolymers Using a Dialkoxyamine as Initiator," *Macromolecules* 35, (2002), 3844-3848.

³⁰¹ *Amphoteric Surfactants*, ed. C. L. Hilton (New York: Marcel Dekker, 1982); Zushun, X.; Changfeng, Y.; Shiyuan, C.; Linxian, F. "Study on the Micellization of Amphiphilic Graft Copolymer Ps-G-Peo in Toluene," *Polymer Bulletin* 44, (2000), 215-222; Janssen, H. M.; Peeters, E.; Zundert, M. F. v.; Genderen, H. M. v.; Meijer, E. W. "Unconventional, Amphiphilic Polymers Based on Chiral Poly(Ethylene Oxide) Derivatives. I. Synthesis and Characterization," *Macromolecules* 30, (1997), 8113-8128.

7.3 Experimental

7.3.1 Materials

2-Ethylhexyl acrylate (EHA) and *t*-butyl acrylate (tBA) monomers were purchased from Aldrich. The acrylate monomers were deinhibited using a neutral alumina column and subsequently sparged and stored under nitrogen. 2,2-Azobisisobutyronitrile (AIBN), dioxane and *para*-toluene sulfonic acid (*p*TSA) were purchased from Aldrich and used as received. The nitroxide mediator, DEPN, and the alkoxyamine were synthesized according to the methods previously described.

7.3.2 Instrumentation

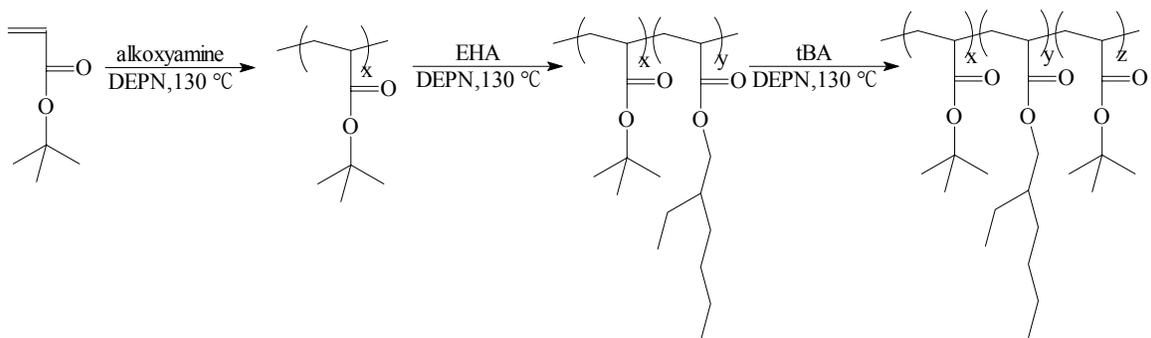
¹H NMR spectra were collected on a Varian Unity-400 spectrometer in CDCl₃ at ambient temperature. Molecular weights were determined at 40 °C in THF (ACS grade) at 1 mL/min using polystyrene standards on a Waters SEC equipped with 3 in-line PLgel 5 μm MIXED-C columns with an autosampler, a 410 RI detector, and an inline Wyatt Technologies miniDawn multiple angle laser light scatterer (MALLS). *In situ* FTIR monitoring was performed with an ASI Mettler-Toledo ReactIR 1000 apparatus with a stainless steel dicomp insertion probe. A comparison of peak height versus a common baseline point was performed to eliminate data scatter due to baseline drift. Atomic force microscopy (AFM) was performed on a Digital Instruments Dimension 3000 AFM using a TAP300 probe from Nanodevices Metrology Probes. The analysis was performed in tapping mode at 1 Hz scan rate. AFM samples were prepared via spin coating onto piranha treated silicon wafers from 1.0 wt% solutions at 2000-5000 rpm. Small angle X-ray scattering (SAXS) was accomplished using a small-angle X-ray scattering camera with a sample-to-detector distance of 62.3 cm, pinhole collimation, and a Bruker Hi-Star multiwire area detector. The X-rays were generated at 2.4 kW and monochromated using pyrolytic graphite. The data were corrected for detector anomalies and azimuthally averaged into intensity versus *q* format where *q* is defined as $4\pi\sin(\theta)/\lambda$.

7.3.3 Synthesis of Poly(*t*-butyl acrylate-*b*-2-ethylhexyl acrylate-*b*-*t*-butyl acrylate) via Stable Free Radical Polymerization

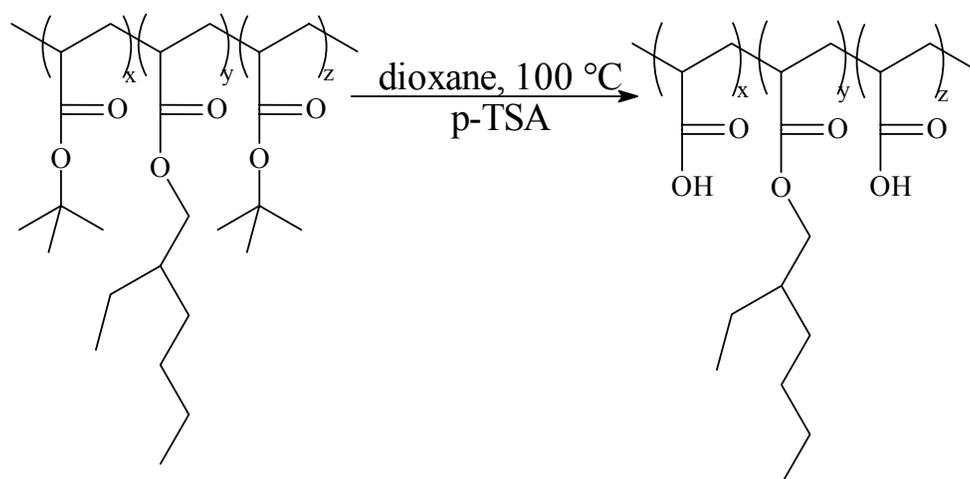
The alkoxyamine (0.85 g) and nitroxide mediator (0.23 g) were added to a 100 mL 3-neck round-bottomed flask with a special neck to accommodate the FTIR probe. A stir bar was added to the reaction system and it was sealed with septa and copper wire. The reaction vessel was purged with nitrogen for 30-45 minutes. Highly degassed *t*-butyl acrylate (25 mL) was added to the reaction mixture via syringe. A 130 °C oil bath was raised to the FTIR reaction flask and data collection was commenced at one spectrum every two minutes. The conversion was monitored and the reaction was stopped to yield the desired molecular weight polymer product. The reaction mixture was cooled, subsequently vented and diluted with THF. The polymer product was precipitated into methanol and dried in the vacuum oven for 24 h at 65 °C. The subsequent EHA and *t*BA blocks were synthesized in a similar fashion utilizing the polymer product from the previous step as the alkoxyamine initiator for the polymerization. (Scheme 7.1)

7.3.4 Hydrolysis of *t*-Butyl Group to Produce Carboxylic Acid Group

The deprotection of the acrylate triblock copolymer is described (Scheme 7.2). The poly(*t*-butyl acrylate-*b*-2-ethylhexyl acrylate-*b*-*t*-butyl acrylate) copolymer (10.5 g) was added to a 100 mL round-bottomed 2-neck flask with a stir bar. *p*TSA was added to the reaction flask at 5.0 wt% compared to the *t*-butyl acrylate monomer (0.53 g). Finally, dioxane was added to the flask (110 mL). The reaction vessel was equipped with a cold water condenser and a nitrogen inlet/outlet system. A 100 °C oil bath was raised to the reaction flask and the reaction was allowed to proceed for 48 h. The dioxane was removed via vacuum stripping and the resulting polymer was washed with water multiple times to remove the acid catalyst and dried in the vacuum oven at 85 °C for 48 h.



Scheme 7.1: Three step synthesis of alkyl acrylate triblock copolymer via SFRP.



Scheme 7.2: Hydrolysis of *t*-butyl groups to yield carboxylic acid functionalities.

7.4 Results and Discussion

7.4.1 Synthesis of Amphiphilic Acrylate Triblock Copolymer via Stable Free Radical Polymerization

Unlike anionic methodologies that allow block copolymerization in a single reaction, the block copolymers synthesized with SFRP processes required three individual polymerization steps. However, the SFRP method enabled a less complicated reaction process for the synthesis of the acrylate triblock copolymer. The initial *t*-butyl acrylate homopolymer was synthesized using a preformed alkoxyamine and supplemental DEPN mediator. The excess nitroxide served to slow the rate of monomer conversion associated with the rapid acrylate polymerizations. The polymerization was performed in a reaction vessel equipped with an *in situ* FTIR probe to monitor the monomer conversion. Monitoring the monomer conversion allowed control of the resulting polymer molecular weight. Figure 7.1 details the monomer disappearance profile for the initial *t*-butyl acrylate homopolymer. The C—H wag absorbance associated with the monomer double bond was monitored at 984 cm^{-1} . A distinct increase in the absorbance was observed in the disappearance profile that was due to a removal of the heat from the reaction vessel resulting in a shift in the distribution and an observed increase the IR absorbance. The sharp increase signified the end of the polymerization due to reduced polymerization temperatures. The polymer product was isolated and the molecular weight was determined using GPC. The polymer was then used as a macroinitiator for the polymerization of 2-ethylhexyl acrylate to produce a poly(*t*-butyl acrylate-*b*-2-ethylhexyl acrylate) copolymer. FTIR spectroscopy was used to monitor the monomer conversion (984 cm^{-1}) in the synthesis of each polymer block. After molecular weight determination, the diblock copolymer was employed as a macroinitiator for the final *t*-butyl acrylate polymerization to yield the desired triblock copolymer. Examination of the GPC chromatograms (Figure 7.2) showed shifting of the curves indicative of initiation of the polymerization via the macroinitiator.

It was also observed in the molecular weight analysis that a broadening of the molecular weight distribution occurred with each subsequent polymerization from 1.10 to 1.49. This suggested that some of the macroinitiators may not have initiated during the

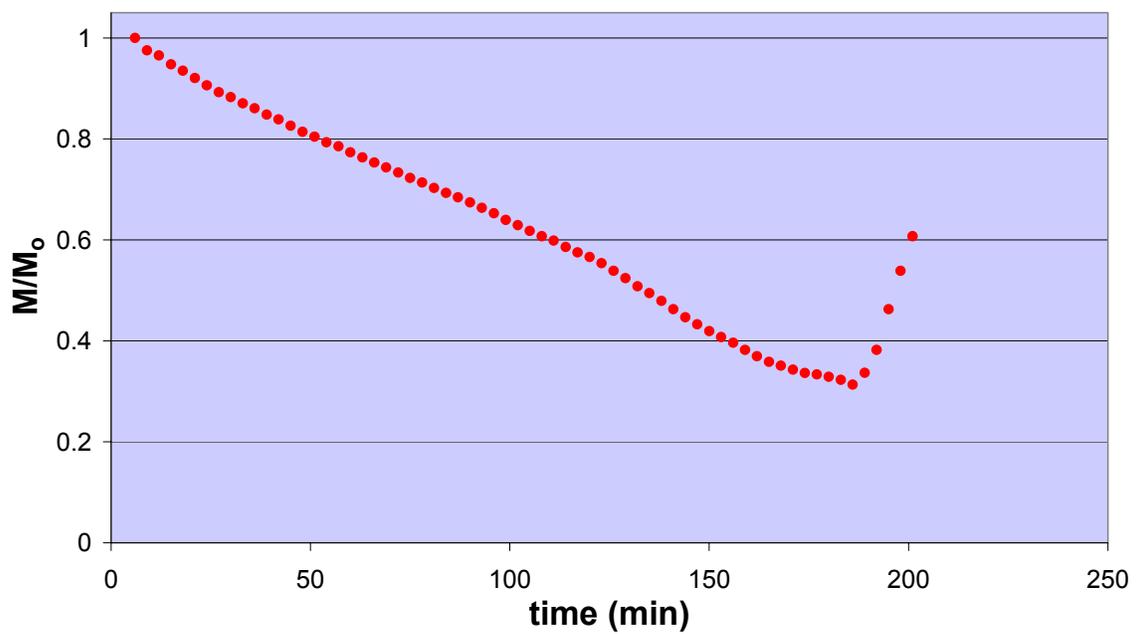


Figure 7.1: Monomer disappearance profile for tBA monomer monitoring the C—H wag absorbance at 984 cm^{-1} .

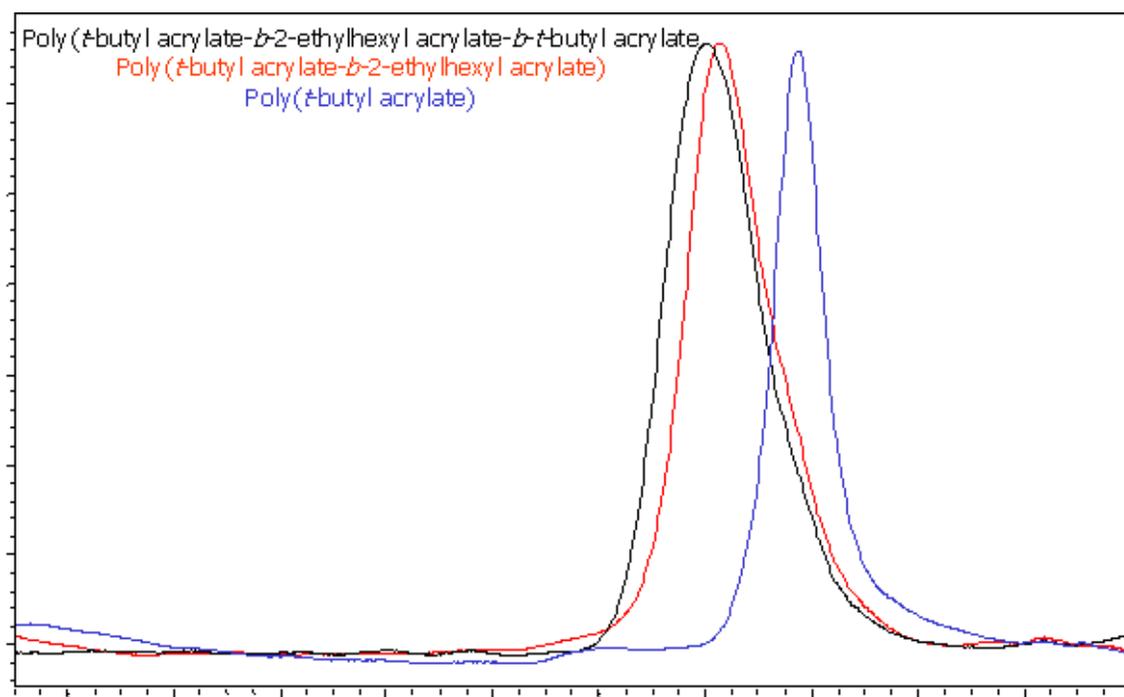


Figure 7.2: GPC chromatograms of polymers utilized in the acrylate triblock copolymer formation.

polymerization resulting in residual macroinitiator. The extent of inactivity of the macroinitiators was minimized as a result of low monomer conversion in each polymerization leading to nitroxide end group integrity in the isolated polymer products. The resulting block sizes were investigated using NMR, GPC and FTIR. The determined molecular weights for NMR and FTIR were based on an initial molecular weight determined using GPC. Analysis of the product molecular weight determined using FTIR, NMR and GPC showed good agreement among the three techniques and the block copolymer was determined to have a composition of 20K-38K-17K (tBA-EHA-tBA). The observed broadening of molecular weight distribution prompted an investigation of the nitroxide chain end integrity. Two alkyl acrylate copolymers were synthesized with similar molecular weight (7K and 12K) using the SFRP technique with DEPN mediation. The monomer conversion of one sample was maintained at a low level (~35 %) while the other sample was allowed to polymerize to high monomer conversion (~80 %). The two polymers were employed as macroinitiators for the polymerization of another alkyl acrylate monomer. GPC analysis of the resulting block copolymers revealed a monomodal distribution in the copolymer derived from the macroinitiator with low monomer conversion (Figure 7.3). On the other hand, the GPC chromatogram for the block copolymer initiated with the high conversion macroinitiator revealed a distinct low molecular weight shoulder attributed to macroinitiating species with no terminal nitroxide functionality incapable of chain extending (Figure 7.4). This result indicated that polymerizations with high monomer conversion approaching 80% yield macromolecules with less than 100% end group integrity.

Further investigation of the nitroxide chain end was performed with a post-polymerization nitroxide chain end functionalization. A low molecular polystyrene homopolymer (~2.5K) was dissolved in chlorobenzene with a slight molar excess of diphenylethylene (DPE). The reaction mixture was heated to 130 °C for 24 h. ¹H NMR analysis of the resulting polymer product revealed a disappearance of the resonances associated with the terminal methyne adjacent to the nitroxide chain end. Unfortunately, the resonances associated with the attachment of a DPE group to the polymer chain end were not resolved from the other polymeric signals in the ¹H NMR spectrum. In order to

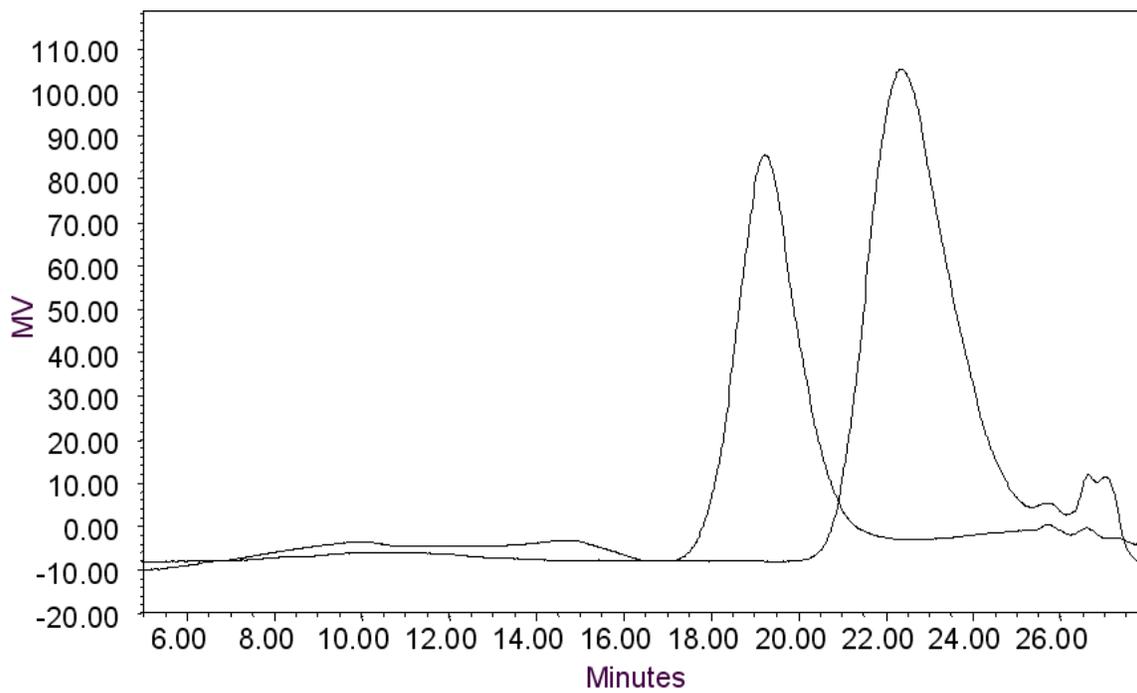


Figure 7.3: GPC chromatograms for block copolymers initiated with low monomer conversion macroinitiator.

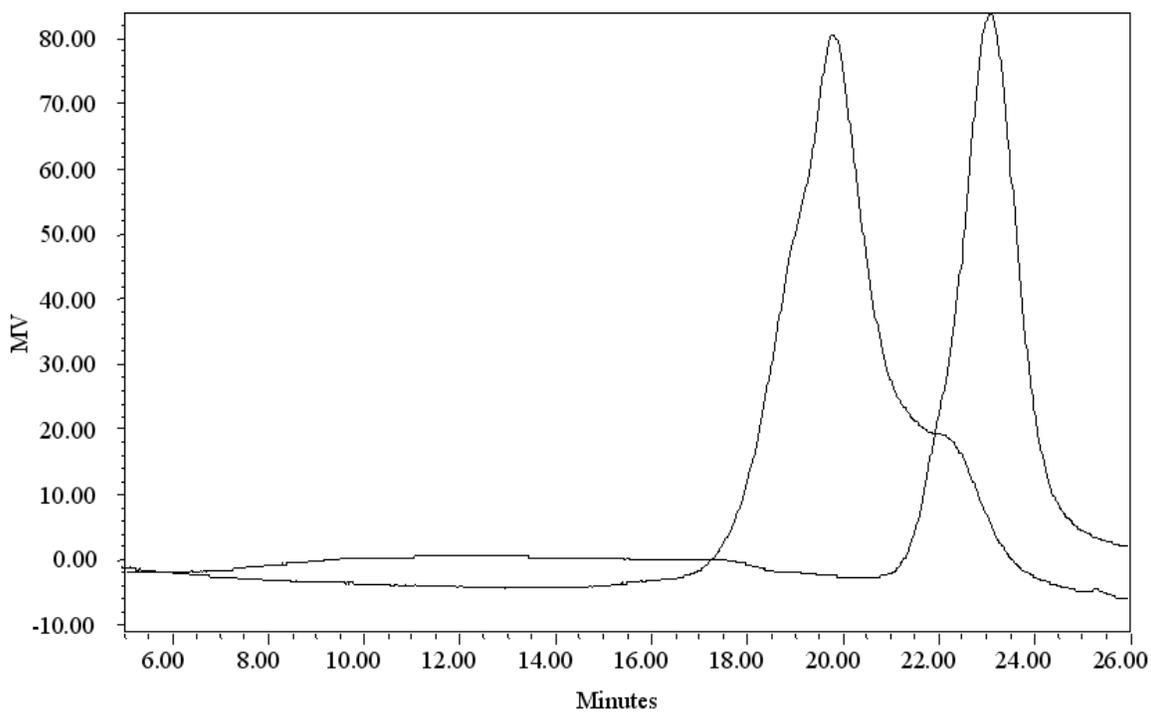


Figure 7.4: GPC chromatograms for block copolymers initiated with high monomer conversion macroinitiator.

observe the attachment of the DPE molecule to the end of the polymer chain, a DPE functionalized with *t*-butyldimethylsilyl protected hydroxyl groups *para* to the ethylene attachments was employed in the functionalization reaction (Figure 7.5). The functional DPE was added to the reaction mixture and reacted at 130 °C for 24 h. ¹H NMR analysis of the purified modification product again showed the disappearance of all resonances associated with TEMPO attachment at the polymer chain end. Moreover, resonances at 0.2 ppm and 1.0 ppm associated with the methyl and *t*-butyl groups attached to the silicon were observed (Figure 7.6). Comparison of the peak integrations indicated that approximately one of every four polystyrene macromolecules possessed a functionalized DPE chain end. The BPO initiator chain end was unaffected by the reaction conditions as indicated in the NMR analysis. Optimization of the reaction conditions may allow higher levels of chain end functionalization.

The final triblock copolymer was dissolved in dioxane with 5 wt% *p*TSA and reacted at reflux for 48 h. In addition, some the poly(*t*-butyl acrylate-*b*-2-ethylhexyl acrylate) diblock copolymer was also dissolved in dioxane and subjected to hydrolysis under identical reaction conditions. ¹H NMR analysis of both hydrolysis products confirmed the cleavage of 100% of the *t*-butyl groups (1.5 ppm) as well as the appearance of a small carboxylic acid resonance at approximately 12 ppm. Moreover, FTIR was used to observe a change in the carbonyl region (1600-1800 cm⁻¹) and the hydroxyl region (3100-3400 cm⁻¹) associated the conversion from the *t*-butyl group to the carboxylic acid group (Figure 7.7 & Figure 7.8). In both the diblock and triblock copolymers, a broadening of the carbonyl region was observed. Also, a broad peak was observed in the higher energy region of the spectrum attributable to the presence a hydrogen bonded hydroxyl group.

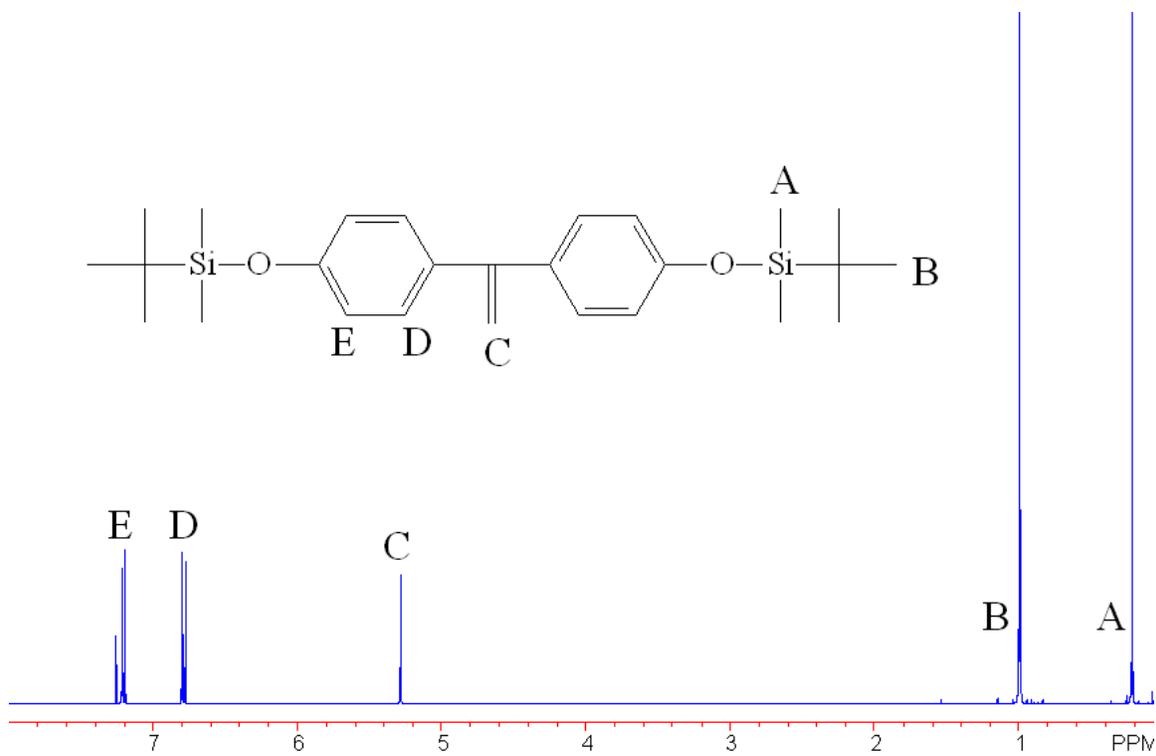


Figure 7.5: ¹H NMR spectrum for *t*-butyldimethyl silyl functionalized diphenylethylene.

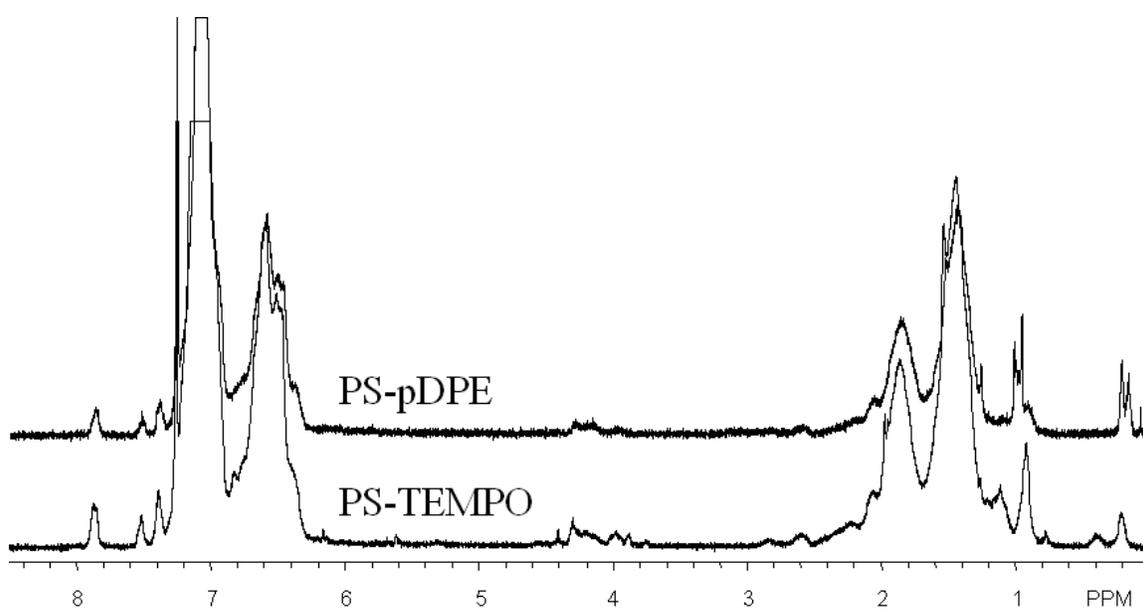


Figure 7.6: Comparison of ^1H NMR spectra of polystyrene terminated with TEMPO and polystyrene reacted with protect DPE (pDPE).

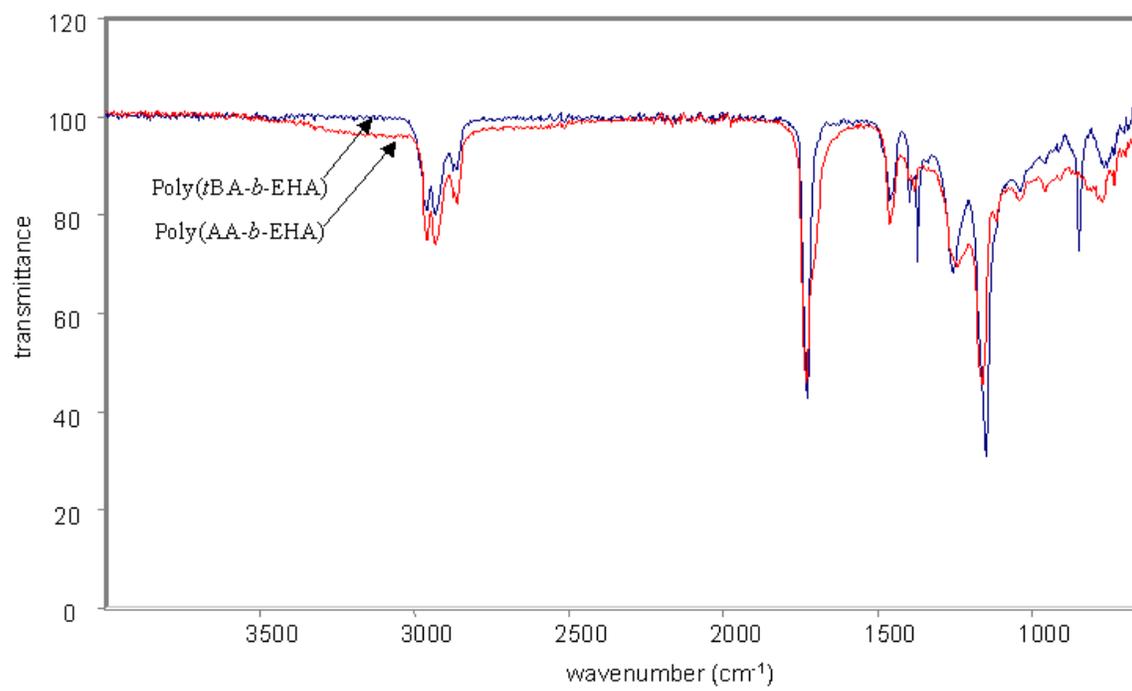


Figure 7.7: FTIR spectra of diblock copolymers before and after *t*-butyl group cleavage.

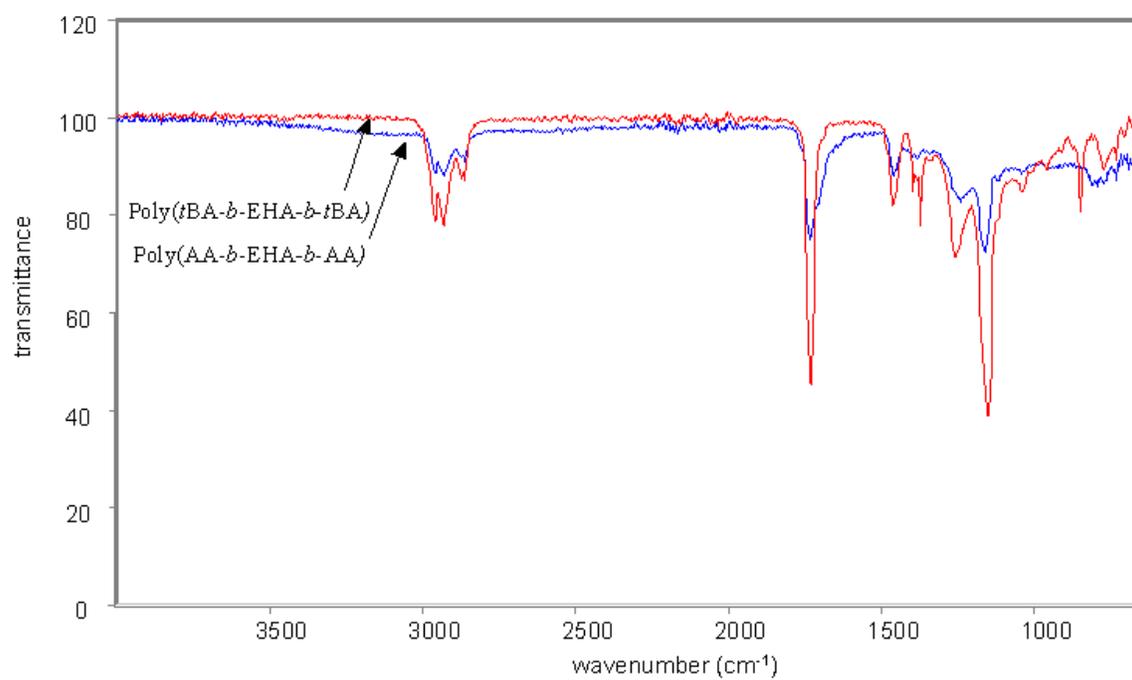


Figure 7.8: FTIR spectra of triblock copolymers before and after *t*-butyl group cleavage.

7.4.2 Characterization of Amphiphilic Acrylate Triblock Copolymer

The acrylic acid (AA) containing triblock and diblock copolymers were initially analyzed using DSC in an attempt to observe the two expected glass transitions. However, only the low T_g observed at $-65\text{ }^\circ\text{C}$ and $-70\text{ }^\circ\text{C}$ in the diblock and triblock, respectively, associated with the EHA central block was evident. On the other hand, DSC analysis of the precursor polymers containing the *t*BA sequences revealed both a low temperature poly(EHA) glass transition at $-64\text{ }^\circ\text{C}$ and a higher temperature T_g transition at $36\text{ }^\circ\text{C}$ associated with the *t*BA blocks. Dielectric analysis (DEA) was also employed to analyze the thermal transitions of the acrylic acid block copolymers. Again, only a low glass transition characteristic of EHA block was observable at approximately $-55\text{ }^\circ\text{C}$. Higher temperatures near the expected acrylic acid block T_g resulted in unreasonable signal intensities due to high ionic conductivity on the AA segments. In addition to DEA, dynamic mechanical analysis was employed to observe the thermal transitions. The experiment was run with a 1 Hz tensile frequency at a $5\text{ }^\circ\text{C}/\text{min}$ heating rate. The plot of $\tan \delta$ versus temperature exhibited the expected low temperature transition of EHA at $-50\text{ }^\circ\text{C}$ and also a high temperature transition attributed to the relaxation of the acrylic acid blocks at $150\text{ }^\circ\text{C}$ (Figure 7.9). The presence of two thermal T_g transitions strongly suggested a microphase-separated polymer morphology. In addition to the two α relaxations (T_g), a β relaxation typical of acrylic polymer systems was also observed at $60\text{ }^\circ\text{C}$ in the DMA trace.³⁰²

The microphase morphology was further investigated using tapping mode atomic force microscopy to directly observe the presence of a two-phase system. The large difference in T_g 's enabled detection of hard and soft phases in the AFM analysis. The microphase separated morphology was detectable in both the diblock and triblock copolymers including the precursor *t*-butyl acrylate containing block copolymers containing *t*-butyl acrylate functionalities. The AA containing copolymers were dissolved in a mixture of dioxane and THF (1:1) and spun coat onto pirhana treated

³⁰² Diaz-Calleja, R.; Riande, E.; Roman, J. S. "Dynamic-Mechanical Behavior of Phenyl and Chlorophenyl Esters of Poly(Acrylic Acid)," *Macromolecules* 24, (1991), 1854-1858; Okrasa, L.; Boiteux, G.; Ulanski, J.; Seytre, G. "Molecular Relaxation in Anisotropic Composites Based on (Hydroxypropyl)Cellulose and Acrylic Polymer," *Polymer* 42, (2001), 3817-3825.

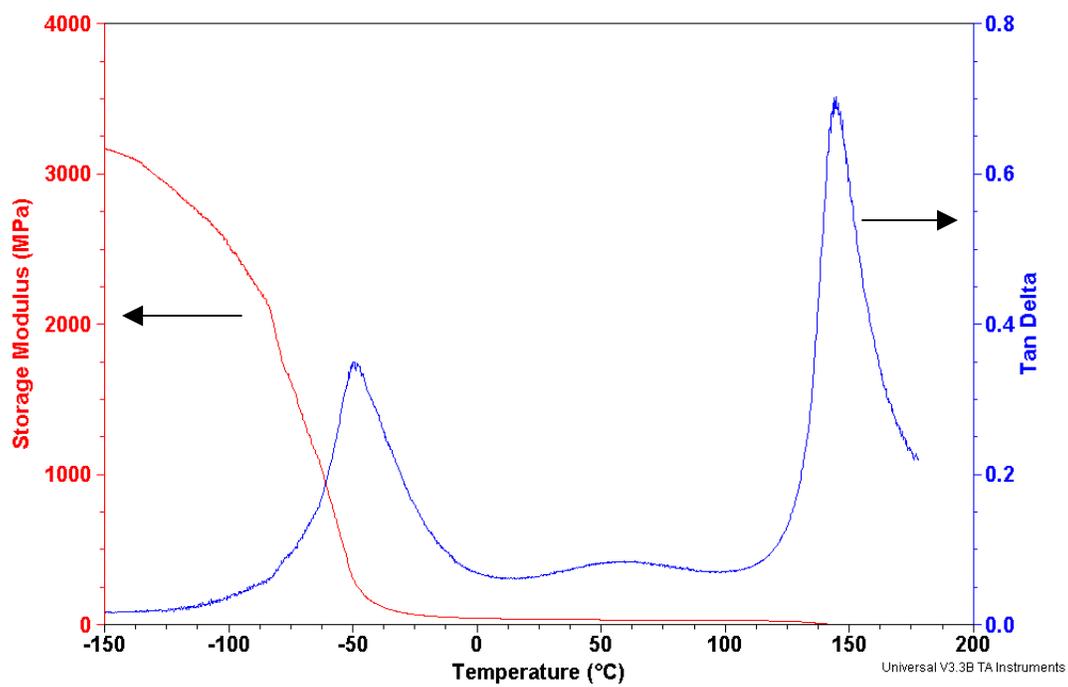


Figure 7.9: Dynamic mechanical analysis of the poly(AA-*b*-EHA-*b*-AA) triblock copolymer at 1 Hz and 5 °C/min heating rate.

silicon wafers at approximately 2000 rpm. The precursor *t*-butyl acrylate copolymers were spun coat out of a chloroform solution at approximately 4000 rpm. Analysis of the resulting AFM micrographs for the precursor polymers revealed the presence of different phases. It appeared that a hard and soft phase were present as well as an intermediate phase resulting from the mixing of the hard and soft segments represented as the brown regions in Figure 7.10. Moreover, the mixed phase was present in a significantly higher percentage in the diblock copolymer possibly indicating a greater propensity for phase mixing. Conversion of the *t*-butyl functionality to a carboxylic acid functionality resulted in a shift in the weight fractions of hard and soft phases in the polymer. The AFM micrographs of the acrylic acid containing triblock and diblock copolymer are shown in Figure 7.11 and demonstrated a different microphase separated morphology. The phase image revealed the presence of two distinct phases; a hard phase associated with acrylic acid shown in the light color surrounded by a soft matrix attributed to 2-ethylhexyl acrylate shown in the dark color. The acrylic acid segments resulted in small spheres distributed throughout the 2-ethylhexyl acrylate continuous phase. The presence of the intermediate mixed phase was not observable. However, large areas of 2-ethylhexyl acrylate aggregation were observed and did not contain any of the randomly distributed hard domains. Although distinct phases were observed, the micrographs did not exhibit well-defined long range ordering. The slightly broad molecular weight distributions observed in GPC (~ 1.50) indicated that the block lengths for all the polymers were not completely identical. In addition, residual monomer in the macroinitiator would have resulted in a tapering effect leading to further mixing of the phases.

Further analysis of the polymeric morphology was accomplished using small angle X-ray scattering. The sample polymers were analyzed in an orientation normal and parallel to the plane of film formation to elucidate any domain ordering within the film.

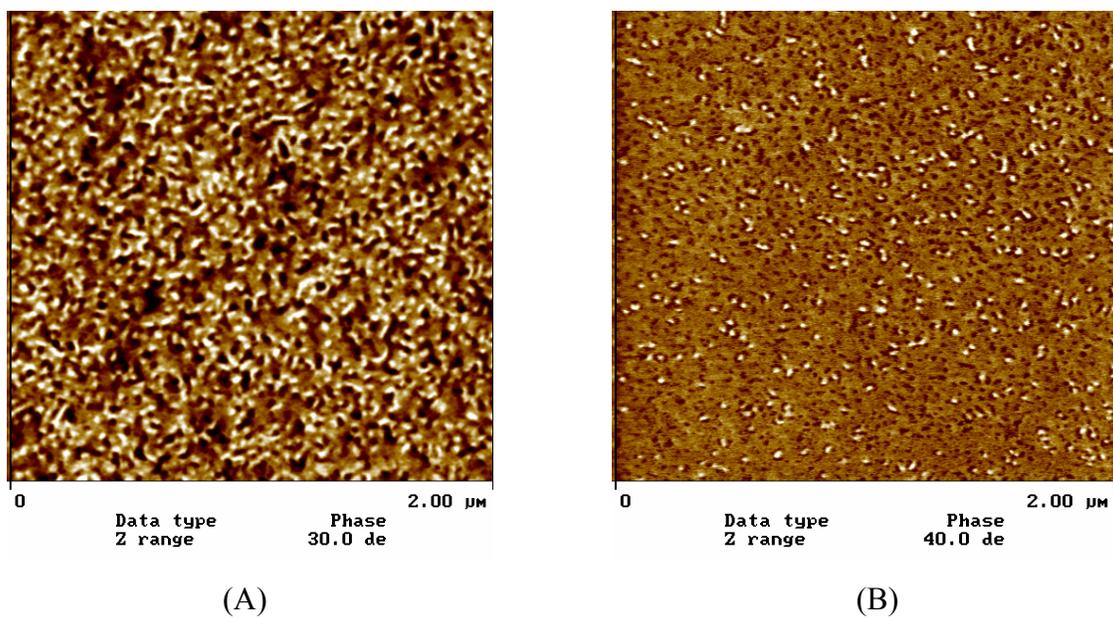


Figure 7.10: AFM micrographs of poly(*t*-butyl acrylate-*b*-2-ethylhexyl acrylate-*b*-*t*-butyl acrylate) (20K-45K-17K) (A) and poly(*t*-butyl acrylate-*b*-2-ethylhexyl acrylate) (20K-40K) (B).

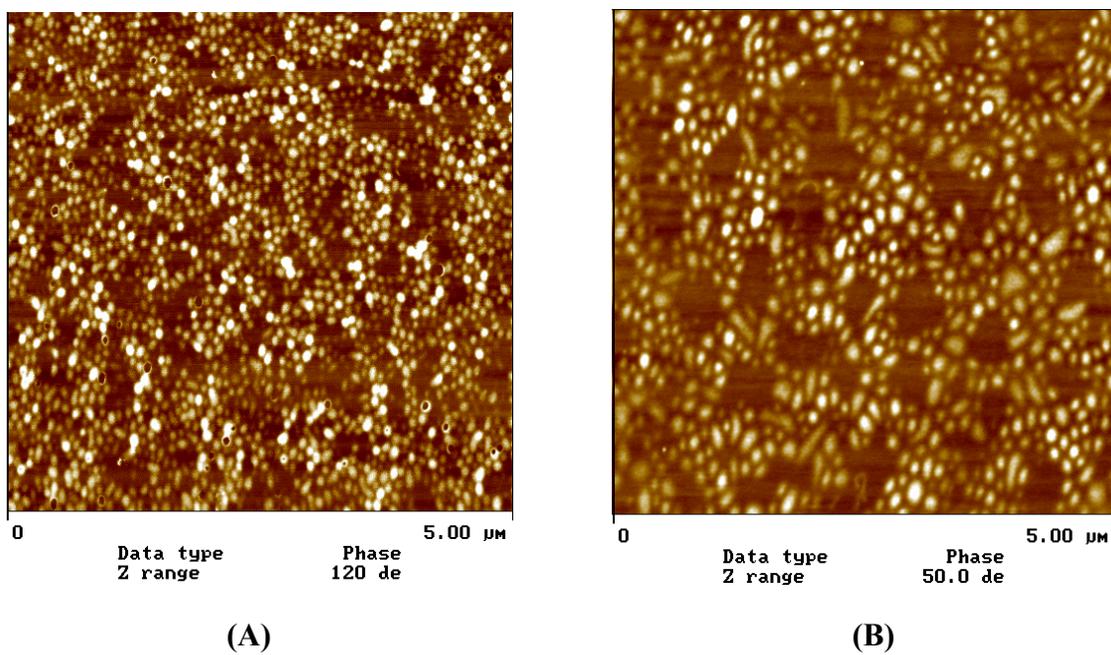


Figure 7.11: AFM micrograph of poly(acrylic acid-*b*-2-ethylhexyl acrylate-*b*-acrylic acid) (11K-45K-10K) (A) and poly(acrylic acid-*b*-2-ethylhexyl acrylate) (10K-50K) copolymers in the unannealed state.

The peak values for the SAXS analysis of the various block copolymers determined using SAXS analysis are detailed in Table 7.1. The primary interference peaks could be observed. The presence of some secondary peaks indicated possible long range order in the system; however, significant noise observed in the scattering curve reduced the reliability of the secondary peak signals. The spacing (d) was calculated based on the primary interference peak observed in the scattering data. Moreover, the spacing was also calculated based on the AFM analysis accomplished by measuring the distance between the center of the hard domains using a ruler. The compiled data is shown in Table 7.1 In addition, the actual SAXS traces for the precursor and deprotected triblock copolymers are shown in Figure 7.12, Figure 7.13, Figure 7.14, and Figure 7.15.

Table 7.1: Small angle X-ray scattering peak values for acrylic triblock copolymers.

	Poly(<i>t</i> BA- <i>b</i> -EHA)	Poly(<i>t</i> BA- <i>b</i> -EHA- <i>b</i> - <i>t</i> BA)	Poly(AA- <i>b</i> -EHA)	Poly(AA- <i>b</i> -EHA- <i>b</i> -AA)
q	0.0178	0.0160	0.010	0.0124
d*	352 Å	392 Å	628 Å	506 Å
d**	395 Å	555 Å	1570 Å	985 Å

* based on SAXS analysis ** based on AFM analysis

The microphase separation observed in the triblock copolymer sometimes leads to mechanical integrity where the phase separated domains act as physical crosslinks. Consequently, the amphiphilic triblock copolymer was cast into films and molded into dogbone samples for tensile testing. A typical stress-strain curve for the acrylic acid containing triblock copolymer is shown in Figure 7.16. The triblock copolymer exhibited little mechanical integrity achieving elongations only on the order of 15-20 percent. The Young's modulus determined using the initial slope of the curve was approximately 1.6 Mpa. The modulus and elongation values were not comparable to typical values for other

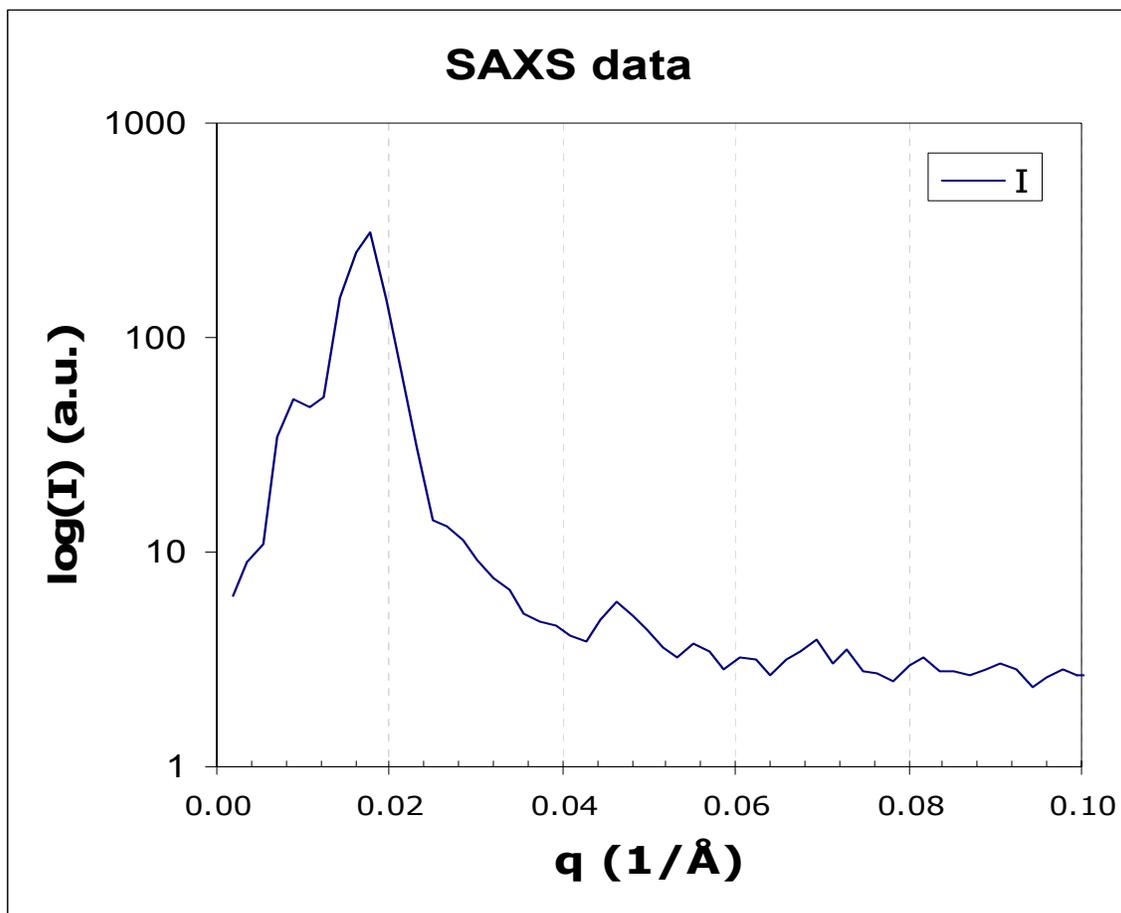


Figure 7.12: SAXS analysis of poly(*t*BA-*b*-EHA) (20K-40K).

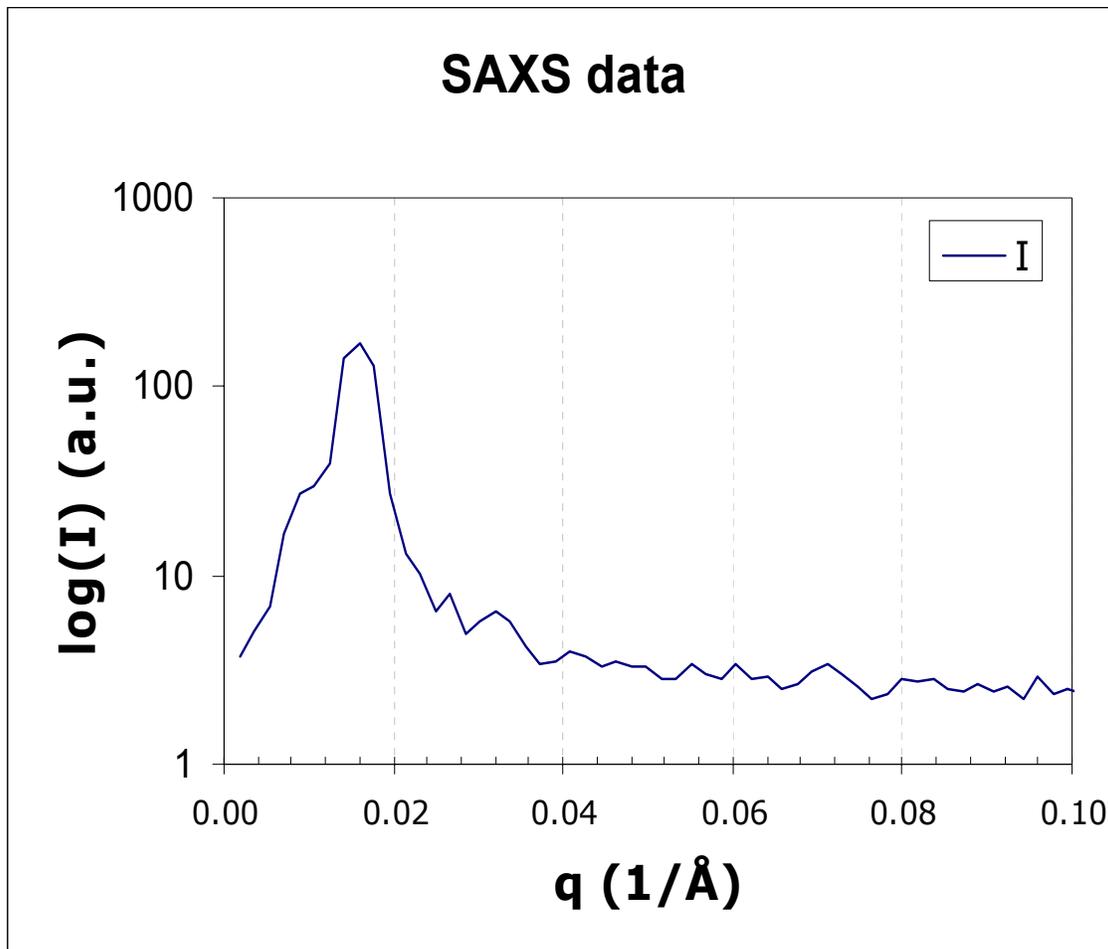


Figure 7.13: SAXS analysis of poly(*t*BA-*b*-EHA-*b*-*t*BA) (20K-38K-17K).

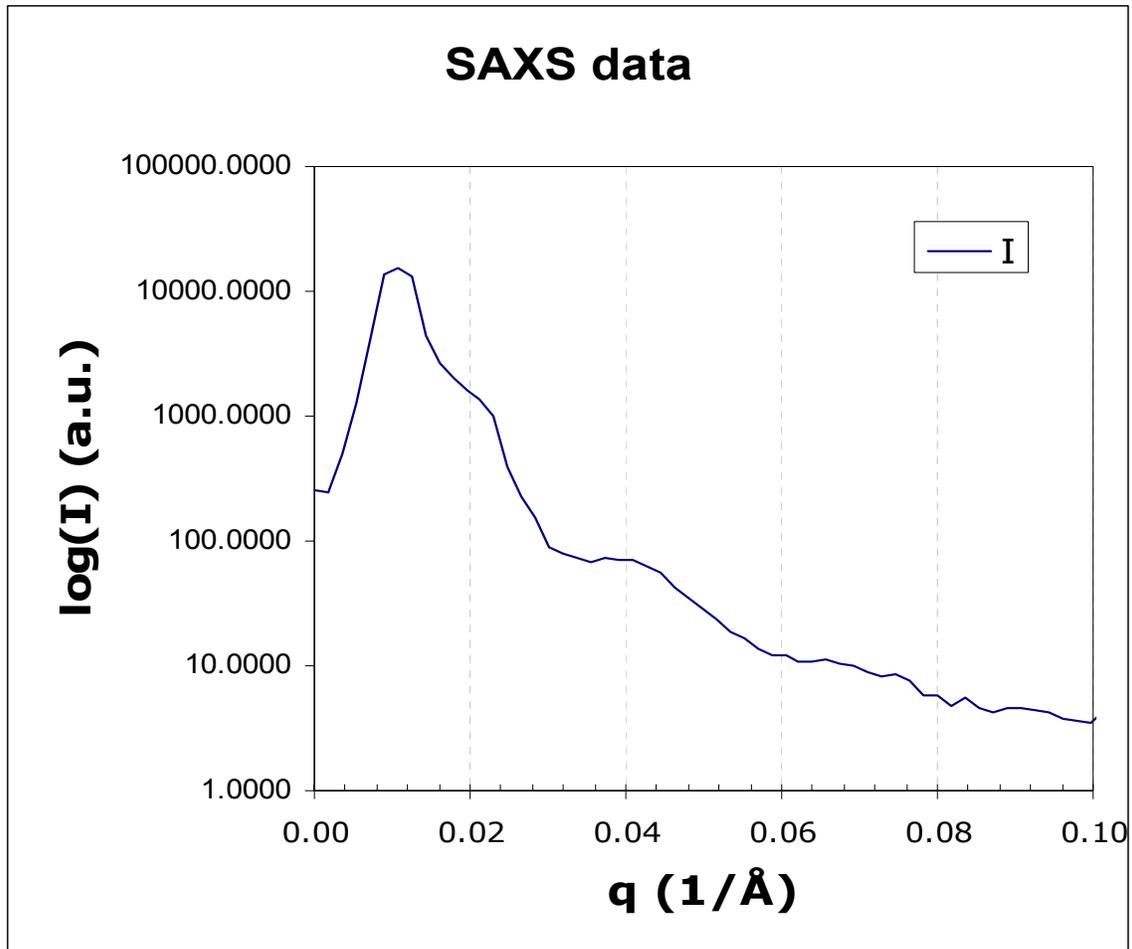


Figure 7.14: SAXS analysis of poly(AA-*b*-EHA) (11K-40K).

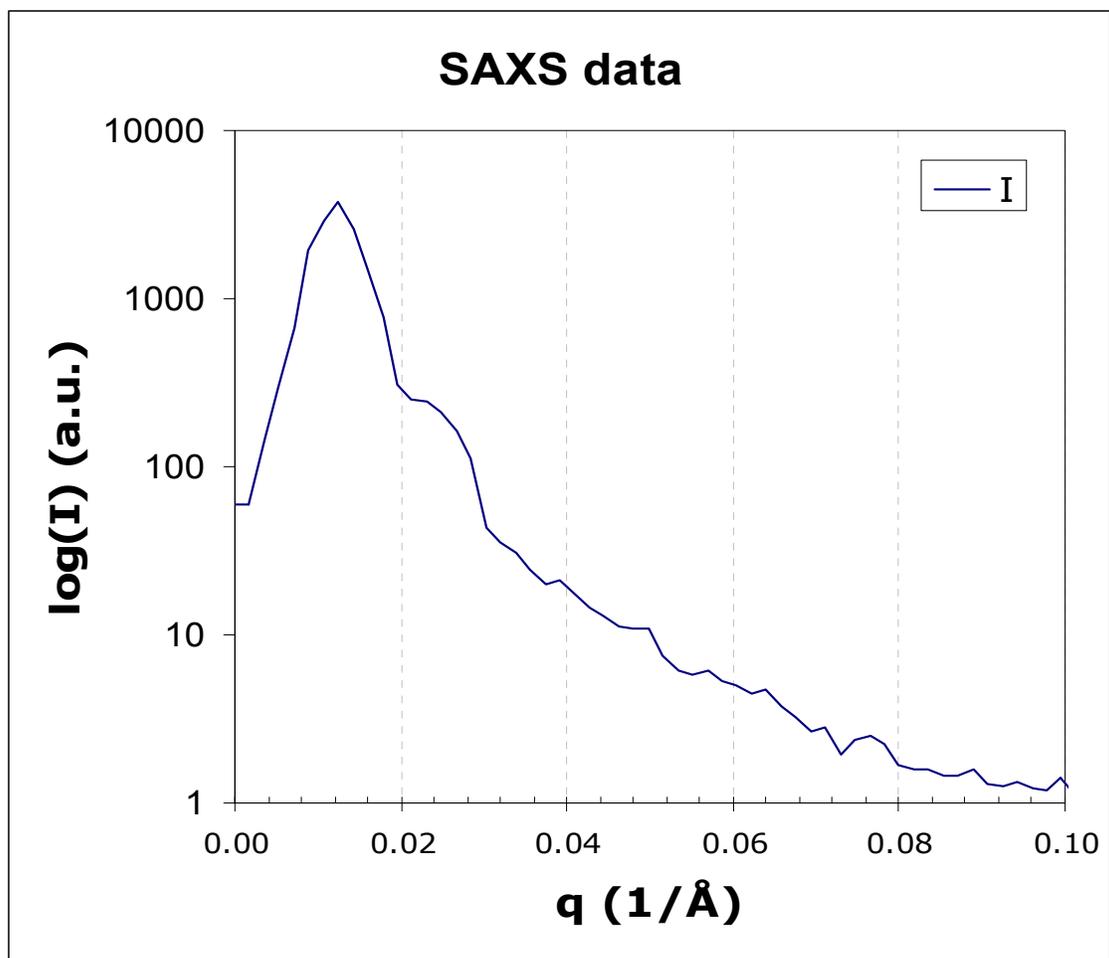


Figure 7.15: SAXS analysis of poly(AA-*b*-EHA-*b*-AA) (11K-38K-10K).

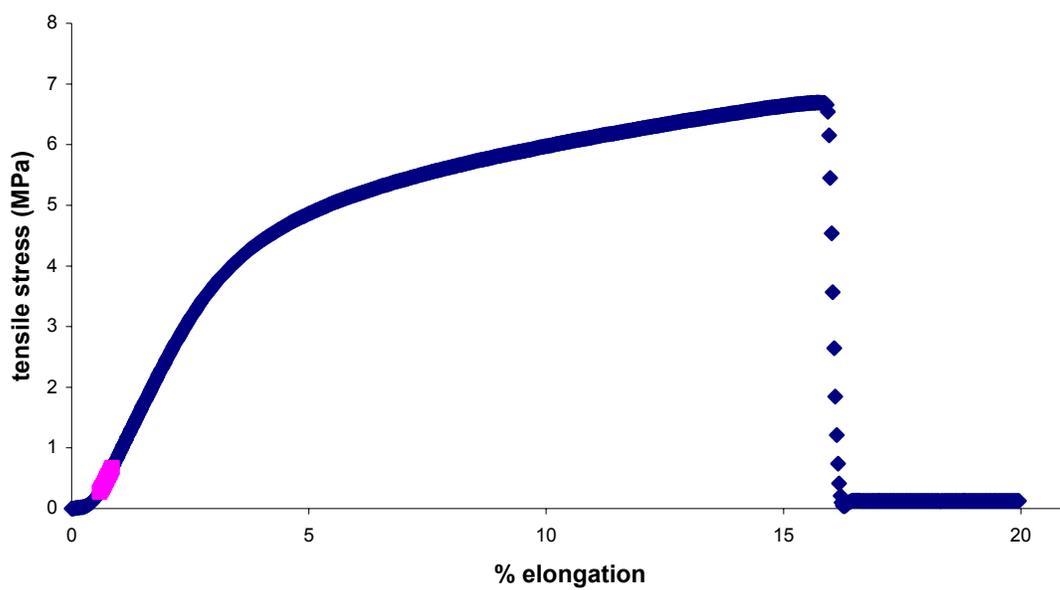


Figure 7.16: Stress-strain curve for poly(acrylic acid-*b*-2-ethylhexyl acrylate-*b*-acrylic acid) (11K-47K-11K) triblock copolymer.

thermoplastic elastomers such as Kraton, which can achieve elongations of 1500%. The lack of substantial mechanical integrity was possibly due to the short length of the blocks. Chain entanglements are necessary to create any mechanical strength. The molecular weight for entanglements for acrylate polymers is relatively high at values typically greater than 20,000 g/mol. The outer acrylic acid blocks were expected to act as the physical crosslinking sites, but the low molecular weight prevented any substantial entanglements rendering the physical crosslinking incapable of withstanding any applied mechanical stress. Triblock copolymers with higher molecular weight outer acrylic acid sequences would potentially improve the mechanical properties associated with this copolymer system. In addition to insufficient block lengths, plasticization due to water absorption may have affected the resulting copolymer mechanical properties. TGA analysis was used to examine the level of water contained in the block copolymers and showed small but significant percentages with the triblock (~2.7%) absorbing more than the diblock (~1.6%) due to larger amounts of the hygroscopic acrylic acid sequences.

7.5 Conclusions

The synthesis of amphiphilic copolymers based on alkyl acrylate monomer compositions was achieved via stable free radical polymerization methodologies. The resulting alkyl acrylate triblock copolymers were converted to amphiphilic copolymer system via acid catalyzed hydrolysis of the *t*-butyl group to a carboxylic acid functionality. DSC data for the amphiphilic triblock copolymers suggested a microphase separated morphology. Moreover, DMA of the acrylate analogue showed two distinct T_g 's. AFM and SAXS experiments confirmed the presence of a two-phase system.

7.6 Acknowledgements

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Chapter 8 : Synthesis and Characterization of Macromolecules Containing Photocrosslinkable Cinnamate Functionality

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8.1 Abstract

Multicomponent acrylate random copolymers were synthesized via conventional free radical polymerization methodologies to incorporate maleic anhydride or 2-hydroxyethyl acrylate units into the polymer backbone. The anhydride and hydroxyl functionality were subsequently reacted with photoactive cinnamate derivative possessing an appropriate functional group. The ring opening reaction associated with maleic anhydride modification resulted in attachment of the photoactive cinnamate functionality to the polymer backbone and the production of an adjacent carboxylic acid functionality. The post-polymerization modification conditions were optimized to yield greater than 50 % of the anhydride units being converted. The pendant hydroxyl group characteristic of 2-hydroxyethyl acrylate was reacted with cinnamoyl chloride to attach the photoactive cinnamate group. The photoactive macromolecules were subjected to irradiation (>300 nm) resulting in crosslinked polymeric materials. UV-Vis and gel fraction measurements were used to investigate the extent and effectiveness of the reaction.

Key words: UV crosslinkable, free radical polymerization, photodimerization, polymer modification

8.2 Introduction

Crosslinked materials have found various applications such as structural materials as well as hydrogels. Conventional crosslinking methods have typically employed chain

type reaction involving a reactive species such as a radical or cation.³⁰³ The extent of such reactions is difficult to control and often requires the introduction of thermal or light energy and an initiator to start the crosslinking reaction. Alternative methods for crosslinking polymers have sought to eliminate the need for thermal energy and special initiators and include photoactivated crosslinking developed by Plambeck in the 1950's.³⁰⁴ Some photoinduced crosslinking processes employ a photoinitiator to produce radicals capable of polymerizing vinyl groups present in the polymer matrix. Photoinitiated crosslinking has been used extensively in acrylic based adhesives, most recently to afford releasable polymeric adhesives.³⁰⁵

In addition to photoinitiated radical crosslinking of the polymer, novel functional groups that can crosslink via non-radical radiation pathways have also been examined and include coumarins and cinnamate compounds as well as several others.³⁰⁶ The first synthetic photoreactive polymers resulted from work done by Minsk and coworkers on the photodimerization of poly(vinyl cinnamate).³⁰⁷ The photocrosslinking route for the

³⁰³ Nakano, S.; Endo, T. "Thermal Cationic Curing with Benzylammonium Salts," *Progress in Organic Coatings* 22, (1993), 287-300: Keller, R. C. "Peroxide Curing of Ethylene Propylene Elastomers," *Rubber Chemistry and Technology* 61, (1988), 238-254: Peacock, A. J. "The Efficiency of Cross-Linking Linear Polyethylene by Using Dicumyl Peroxide," *Polymer Communications* 28, (1987), 259-260: Staeger, M.; Finot, E.; Brachais, C. H.; Auguste, S.; Durand, H. "Surface Investigation of Adhesive Formulation Consisting of Uv Sensitive Triblock Poly(Styrene-B-Butadiene-B-Styrene) Copolymer," *Applied Surface Science* 185, (2002), 231-242.

³⁰⁴ L. Plambeck, J. "Photographic Preparation of Relief Images," (U.S. Patent # 2,760,863: 1956).

³⁰⁵ Boyne, J. M.; Millan, E. J.; Webster, I. "Peeling Performance of a Novel Light Switchable Pressure-Sensitive Adhesive," *International Journal of Adhesion and Adhesives* 21, (2001), 49-53: Chivers, R. A.; Webster, I., "Investigations into the Mechanism of Adhesion of a Novel Light-Deactivatable Pressure-Sensitive-Adhesive" (paper presented at the Adhesion '99, Cambridge, UK, 1999): Webster, I. "The Development of a Pressure-Sensitive Adhesive for Trauma-Free Removal," *International Journal of Adhesion and Adhesives* 19, (1999), 29-34: Dowbenko, R., "Radiation Curing," in *Handbook of Pressure Sensitive Adhesive Technology*, ed. Donatas Satas (New York: Van Nostrand Reinhold, 1989).

³⁰⁶ Kuckling, D.; Adler, H. J. P.; Arndt, K. F.; Hoffmann, J.; Plotner, M.; Wolff, T. "Photocrosslinking of Thin Films of Temperature-Sensitive Polymers," *Polymers for Advanced Technologies* 10, (1999), 345-352: Kuckling, D.; Ivanova, I. G.; Adler, H. J. P.; Wolff, T. "Photochemical Switching of Hydrogel Film Properties," *Polymer* 43, (2002), 1813-1820: Schonberg, A.; Latif, N.; Moubasher, R.; Awad, W. "Photochemical Reactions. Part Xv. (a) Photopolymerization of Coumarins and Related Substances. (B) Photo-Addition and -Reduction Processes or Aromatic Ketones," *Journal of the Chemical Society*, (1950), 374-379: Zahir, S. "Studies in the Photodimerization of the Diglycidyl Ether of 4,4'-Dihydroxychalcone," *Journal of Applied Polymer Science* 23, (1979), 1355-1372: Choi, D. H.; Oh, S. J. "Photochemical Reactions of a Dimethacrylate Compound Containing a Chalcone Moiety in the Main Chain," *European Polymer Journal* 38, (2002), 1559-1564.

³⁰⁷ E. Robertson, W. D., L. Minsk "Photosensitive Polymers. Ii. Sensitization of Poly(Vinyl Cinnamate)," *Journal of Applied Polymer Science* 2, (1959), 308-311: L. M. Minsk, J. G. S., W. P. Van Deusen, & J. F.

coumarin and cinnamate molecules involves the formation of a cyclobutane ring via a [2+2] cycloaddition (Scheme 8.1).³⁰⁸ Cinnamate derivatives have recently been utilized to crosslink a number of acrylic liquid crystalline polymers with significant success.³⁰⁹ The advantage to the cycloaddition crosslinking process is the reduction of postcure events induced via addition of reactive elements. In addition, the cycloaddition pathway is not thermally allowed.³¹⁰

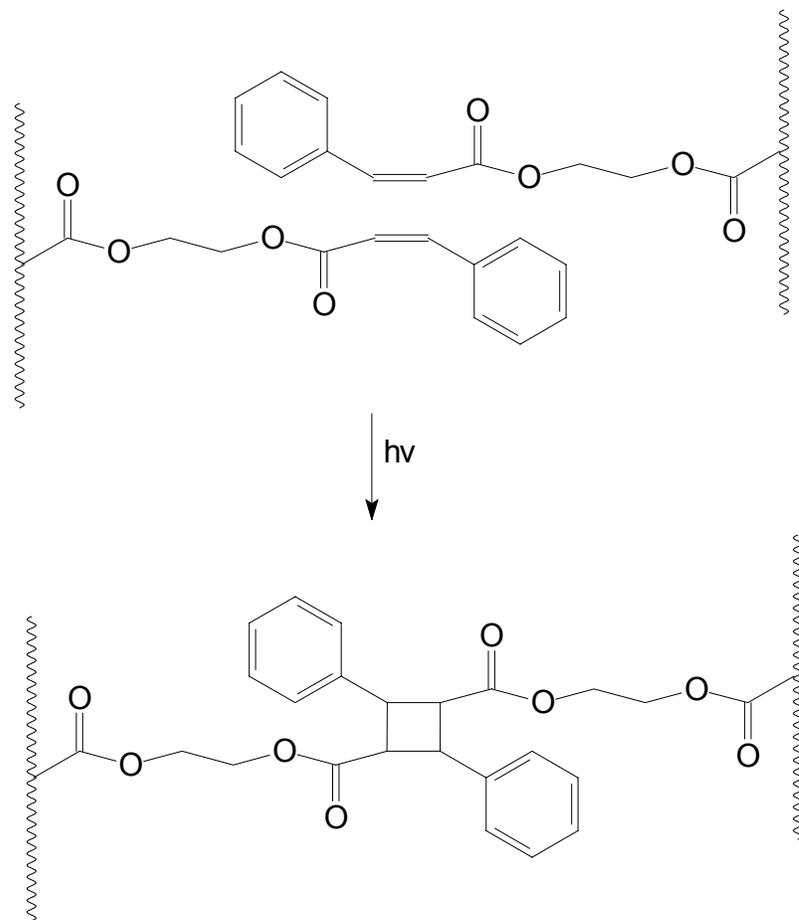
This report describes the synthesis of functional acrylate multicomponent copolymers and the modification to incorporate a photoactive crosslinking cinnamate functionality. The photoactive groups were introduced via two reaction pathways, an acid chloride reaction and a ring opening of a cyclic anhydride. The photoactive polymers were evaluated for their performance in adhesive applications after irradiation.

Wright "Photosensitive Polymers. I. Cinnamate Esters of Poly(Vinyl Alcohol) and Cellulose," *Journal of Applied Polymer Science* 2, (1959), 302-307; L. M. Minsk, W. P. V. D., & E. M. Robertson "Photosensitization of Polymers," (U.S. Patent # 2,670,285: 1954); L. M. Minsk, W. P. V. D., & E. M. Robertson "Photosensitization of Polymeric Cinnamic Esters," (U.S. Patent # 2,670,286: 1954); L. M. Minsk, W. P. V. D., & E. M. Robertson "Photosensitization of Cinnamate Acid Esters," (U.S. Patent # 2,670,287: 1954).

³⁰⁸ Zheng, Y.; Micic, M.; Mello, S. V.; Mabrouki, M.; Andreopoulos, F. M.; Konka, V.; Pham, S. M.; Leblanc, R. M. "Peg-Based Hydrogel Synthesis Via the Photodimerization of Anthracene Groups," *Macromolecules* 35, (2002), 5228-5234; Reiser, A. *Photoreactive Polymers: The Science and Technology of Resists* (Wiley-Interscience, 1989).

³⁰⁹ Chae, B.; Lee, S. W.; Ree, M.; Jung, Y. M.; Kim, S. B. "Photoreaction and Molecular Reorientation in a Nanoscaled Film of Poly(Methyl 4-(Methacryloyloxy)Cinnamate) Studied by Two-Dimensional Ftir and Uv Correlation Spectroscopy," *Langmuir* 19, (2003), 687-695; Ichimura, K.; Akita, Y.; Akiyama, H.; Kudo, K.; Hayashi, Y. "Photoreactivity of Polymers with Regioisomeric Cinnamate Side Chains and Their Ability to Regulate Liquid Crystal Alignment," *Macromolecules* 30, (1997), 903-911; Jackson, P. O.; Karapinar, R.; O'Neill, M.; Hindmarsh, P.; Owen, G. J.; Kelly, S. M., "Alignment of Coumarin-Containing Polymers for Liquid Crystal Displays" (paper presented at the Proceedings of SPIE-The International Society for Optical Engineering, 1999); Jantas, R.; Wodka, T.; Janowska, G. "Macro-Azo-Initiators Having Cinnamate End Groups: Synthesis, Characterization and Photopolymerization with 2-Hydroxyethyl Methacrylate," *Polimery* 46, (2001), 812-816; Kawatsuki, N.; Kawakami, T.; Yamamoto, T. "A Photoinduced Birefringent Film with a High Orientational Order Obtained from a Novel Polymer Liquid Crystal," *Advanced Materials* 13, (2001), 1337-1339; Kim, H. T.; Park, J. K. "Thermal Degradation of Poly(Vinyl Cinnamate)," *Polymer Bulletin* 41, (1998), 325-331; Kimura, T.; Kim, J.-Y.; Fukuda, T.; Matsuda, H. "Uv-Curable Azobenzene Polymer Bearing Photo-Crosslinkable Moiety for Stabilization of Photo-Fabricated Surface Relief Structure," *Macromolecular Chemistry and Physics* 2002, (2002), 2344-2350; Lazarev, V. V.; Barberi, R.; Iovane, M.; Papalino, L.; Blinov, L. M. "Dynamics of Liquid Crystal Azimuthal Anchoring at a Poly (Vinyl Cinnamate) Interface Measured in Situ During Polarized Uv Light Irradiation," *Liquid Crystals* 29, (2002), 273-279; Oriol, L.; Pinol, M.; Serrano, J. L.; Tejedor, R. M. "Synthesis, Characterization and Photoreactivity of Liquid Crystalline Cinnamates," *Journal of Photochemistry and Photobiology a-Chemistry* 155, (2003), 37-45.

³¹⁰ Kim, H. T.; Park, J. K. "Thermal Degradation of Poly(Vinyl Cinnamate)," *Polymer Bulletin* 41, (1998), 325-331.



Scheme 8.1: Photoinduced dimerization of cinnamate functionality attached to a polymer chain.

The photodimerization reaction was monitored and the post irradiation characteristics of the polymers were examined.

8.3 Experimental

8.3.1 Materials

n-Butyl (nBA), 2-hydroxyethyl (HEA), methyl (MA), and 2-ethylhexyl acrylate (EHA) were provided by Avery Dennison Chemical Company and passed through a neutral alumina column prior to use to remove radical inhibitors. Maleic anhydride (MAH) and 2,2'-azobisisobutyronitrile (AIBN) were purchased from Aldrich and used as received. Ethylene glycol, triethyl amine and cinnamoyl chloride were purchased from Acros. The ethylene glycol was dried in a vacuum oven for 24 h at 80 °C prior to use.

8.3.2 Instrumentation

¹H NMR spectra were collected on a Varian Unity-400 spectrometer in CDCl₃ at ambient temperature. Molecular weights were determined at 40 °C in chloroform (HPLC grade) at 1 mL/min using polystyrene standards on a Waters SEC equipped with 3 in-line PLgel 5 μm MIXED-C columns with an autosampler, a 410 RI detector and an inline Wyatt Technologies miniDawn multiple angle laser light scatterer (MALLS). *In situ* FTIR monitoring was performed with an ASI Mettler-Toledo ReactIR 1000 apparatus with a stainless steel dicomp insertion probe.³¹¹ A comparison of peak height versus a common baseline point was performed to eliminate data scatter due to baseline drift. UV-Vis spectroscopy was performed using an Analytical Instrument Systems Inc. spectrometer equipped with fiber optic cables, a DT1000CE light source, and an Ocean Optics USB2000 UV-Vis detector. Irradiations were performed on a Fusion UV Systems Inc. mercury microwave source with a P300MT power supply and a adjustable conveyor belt. Light intensities were measured using an EIT Inc. UV power puck.

³¹¹ Pasquale, A. J.; Long, T. E. "Real-Time Monitoring of the Stable Free Radical Polymerization of Styrene Via in-Situ Mid-Infrared Spectroscopy," *Macromolecules* 32, (1999), 7954-7957; Pasquale, A. J.; Long, T. E. "Synthesis of Star-Shaped Polystyrenes Via Nitroxide-Mediated Stable Free-Radical Polymerization," *Journal of Polymer Science Part a-Polymer Chemistry* 39, (2001), 216-223.

8.3.3 Synthesis of Maleic Anhydride Containing Acrylic Copolymer

The synthesis of a typical MAH multi-component copolymer is described. The methyl (2.4 g), n-butyl (11.2 g), and 2-ethylhexyl acrylate (6.8 g) monomers were added to a 250 mL round-bottomed flask with a magnetic stir bar. Maleic anhydride (1.64 g) was then added to the reaction flask. The reaction mixture was then diluted with ethyl acetate (33 mL). Finally, the initiator, AIBN (88.2 mg), was added to the reaction vessel. The reaction mixture was sparged with nitrogen for 15 minutes. The polymerization vessel was subsequently equipped with a water condenser and a nitrogen inlet/outlet. The flask was placed in an 85 °C oil bath with a magnetic stirrer and allowed to polymerize for 24 h. The polymer was diluted with ethyl acetate (25 mL) and precipitated into methanol. The isolated polymer product was dried in the vacuum oven at 65 °C for 24 h. The HEA containing copolymers were synthesized in a similar fashion with the MAH molar percent being substituted with HEA.

8.3.4 Synthesis of Aliphatic Hydroxyl Cinnamate Derivative

The synthesis of the ethylene glycol based cinnamate derivative is described. Triethyl amine (33.1 g) was added to freshly distilled acetone (50 mL) in a 250 mL 2-neck round-bottomed flask with a magnetic stir bar. Ethylene glycol (44.5 g) was added to the triethyl amine solution. One neck was fitted with a nitrogen outlet and the other neck was fitted with a 250 mL addition funnel sealed with a rubber septum. The flask was placed in an ice cooled 0 °C bath. An acetone (75 mL) solution of cinnamoyl chloride (27.1 g) was also prepared in a separate flask. The cinnamoyl chloride solution was then added to the addition funnel. A nitrogen inlet was inserted into the addition funnel septum and the cinnamoyl chloride solution was added dropwise to the ethylene glycol solution over 30 min. The reaction began to turn a light yellow color and precipitation of the triethylamine salt was observed. After 16 h, the reaction mixture was filtered through filter paper and the residual acetone solvent was removed *in vacuo*. The reaction mixture was redissolved in dichloromethane and washed with water five times to remove the residual salt. The dichloromethane was dried with magnesium sulfate and removed. The product was collected as an orange-yellow oil in 92% yield. A hexane diol derivatized cinnamate was prepared in a similar manner.

8.3.5 Modification of the Maleic Anhydride Containing Copolymers

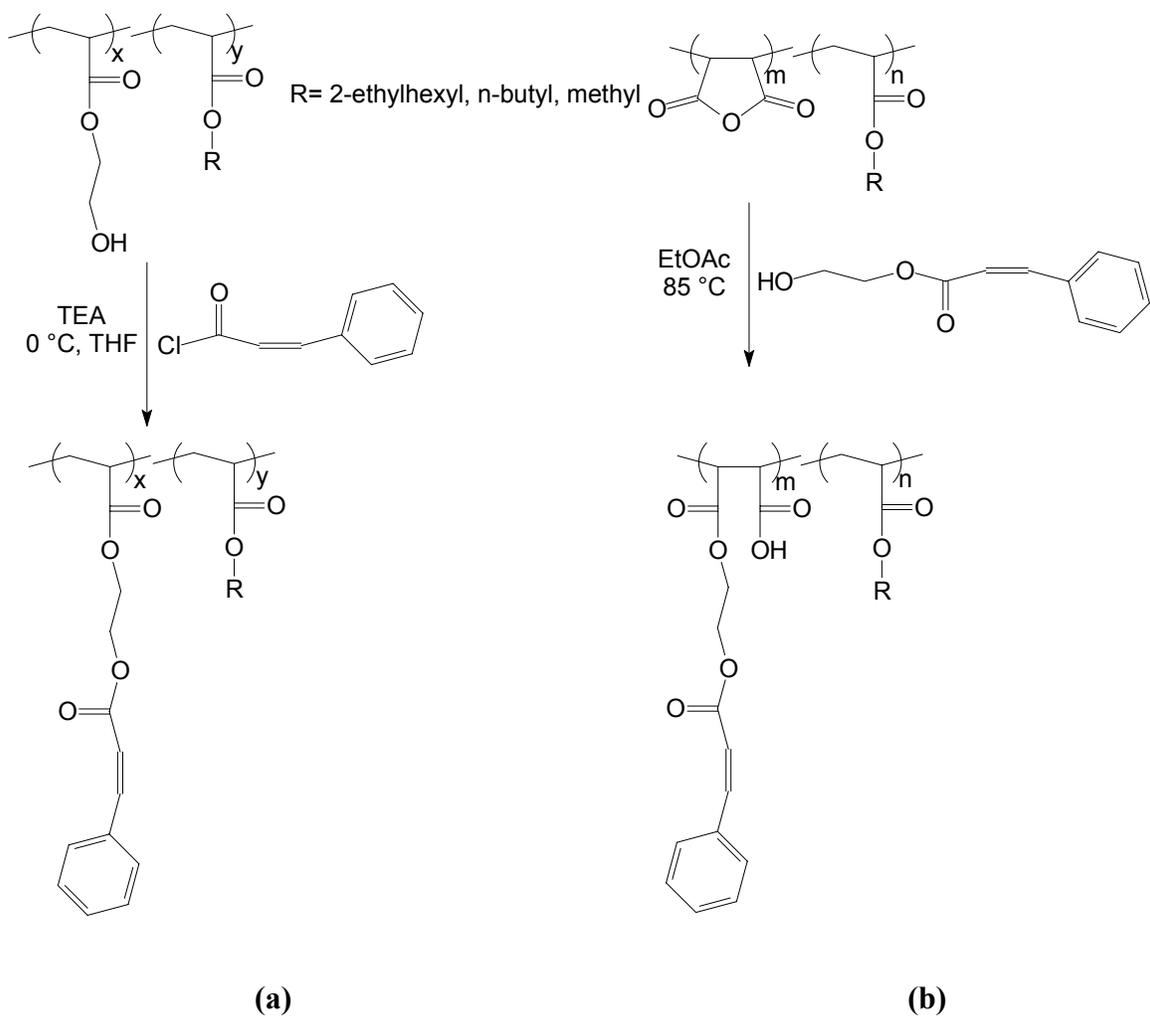
The unprecipitated polymer in solution (8.36 g) was transferred to a 100 mL round-bottomed flask with a magnetic stir bar. The purified ethylene glycol cinnamate derivative (2 g) was added to the reaction flask. Ethyl acetate was also added to the reaction mixture to produce a 50 wt% solids solution. The flask was equipped with a water condenser and nitrogen atmosphere. The ethyl acetate reaction mixture was refluxed at 85 °C for 16 h. The modified polymer product was precipitated into methanol and dried in the vacuum oven at 65 °C for 24 h. Modification of the HEA containing copolymer was accomplished using cinnamoyl chloride to react in a facile manner with the pendant hydroxyl functionality.

8.4 Results and Discussion

8.4.1 Synthesis and Modification of HEA Containing Random Copolymers

The HEA copolymers were synthesized via a conventional free radical solution polymerization in ethyl acetate. AIBN was employed to initiate the polymerization and was added at 0.7 wt% compared to the total monomer weight. The resulting macromolecule exhibited a weight average molecular weight of 650K with a molecular weight distribution of 3.7. The composition of the copolymers were examined using ¹H and ¹³C NMR spectroscopy and corresponded well with the feed ratios. The copolymers typically possessed 53 mol% EHA and 22 mol% nBA with varying amounts of methyl acrylate and hydroxyethyl acrylate. Typical compositions exhibited 10-20 mol% of the hydroxyl functional HEA.

Modification of these copolymers proceeded via an acid chloride reaction between the hydroxyl group of HEA and cinnamoyl chloride (Scheme 8.2a). Manipulation of the molar ratio of hydroxyl functionality and cinnamoyl was utilized to control the level of functionalization. Triethyl amine was employed as an acid trap and was added in a 10% excess compared to the acid chloride to promote full conversion. The HEA hydroxyl functionality was converted at 33%, 66% and 100% to the photoactive cinnamate group. ¹H NMR of the modified polymers shown in Figure 8.1 confirmed the



Scheme 8.2: Post-polymerization introduction of photoactive cinnamate functional groups.

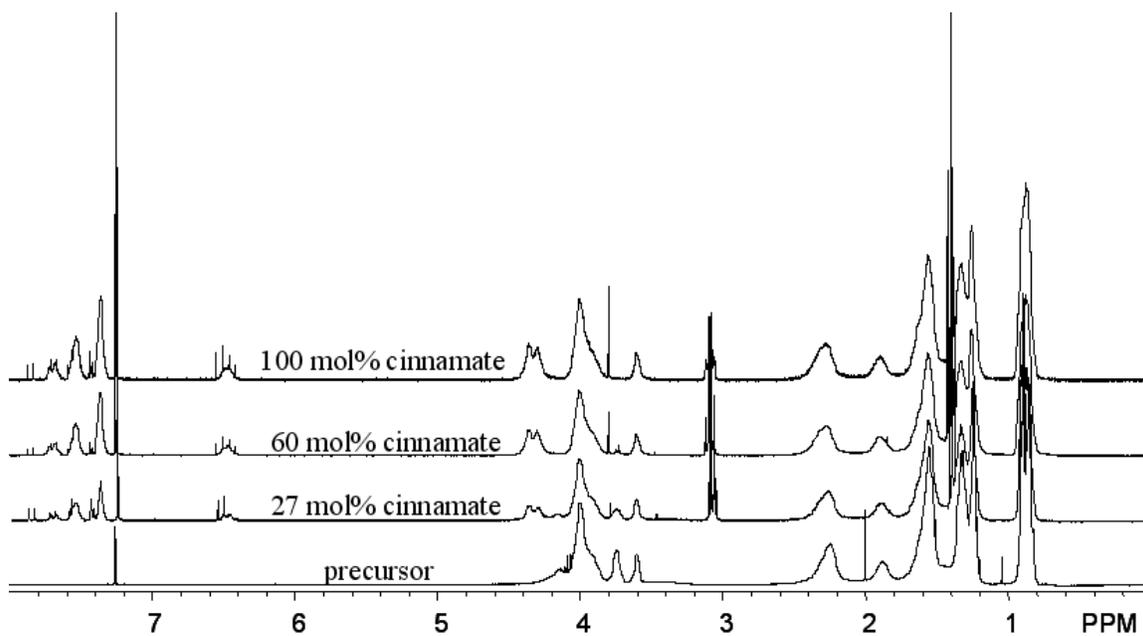


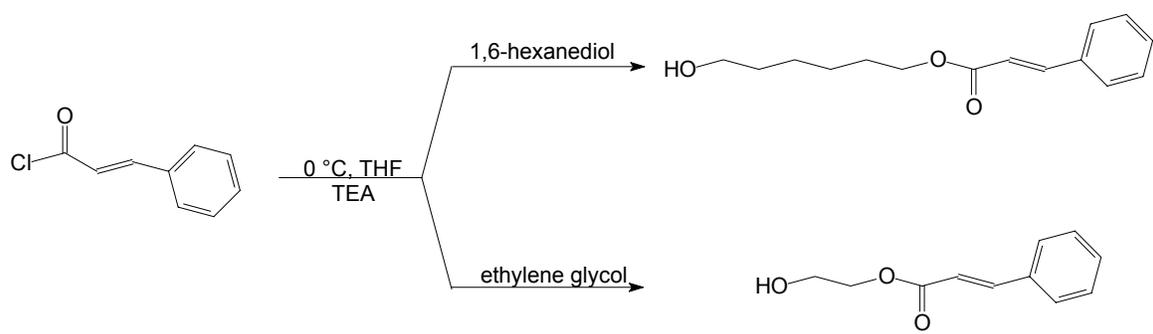
Figure 8.1: ^1H NMR spectra of the precursor hydroxyl containing copolymer and the subsequent functionalized cinnamate copolymers.

presence of different levels of the cinnamate functionalities. The resonances associated with the cinnamate group are apparent at 6.5 ppm and from 7.3-7.6 ppm. In addition, the methylene adjacent to the hydroxyl functionality shifted downfield upon modification and formation of an adjacent ester linkage. The disappearance of the methylene adjacent to the hydroxyl at 3.75 ppm was observed along with the corresponding appearance of the methylene resonance adjacent to an ester linkage at approximately 4.3 ppm. Moreover, a new signal was observed in the UV-Vis spectra of the polymer characteristic of the double bond absorbance associated with a cinnamate functionality at 278 nm.

8.4.2 Synthesis and Modification of MAH Containing Random Copolymers

The MAH multicomponent copolymers were synthesized in a similar fashion to the HEA copolymers via free radical solution polymerization in ethyl acetate using AIBN initiator at 0.7 wt% compared to the monomer weight. The resulting macromolecules exhibited weight average molecular weights ranging from 130K to 320K with molecular weight distributions of 2.5-4.1 typical of free radical polymerizations involving alkyl acrylate monomers. The composition of the copolymers were investigated using ^1H and ^{13}C NMR and corresponded well with the initial monomer feed ratios. The copolymers typically possessed 52 mol% EHA and 22 mol% nBA with varying amounts of methyl acrylate and maleic anhydride. Typical polymer compositions possessed 10-15 mol% of the maleic anhydride monomer.

In addition to the copolymer compositions, cinnamate derivatives possessing an aliphatic hydroxyl functionality were synthesized. Cinnamate functionalized molecules based on 1,6-hexanediol and ethylene glycol were synthesized via an acid chloride reaction and the corresponding diol (Scheme 8.3). The molar excess of the diol was maintained at a high level to ensure no significant functionalization of both hydroxyl groups and both reaction products were isolated in approximately 80 % yield. The hexanediol reaction required a molar ratio of 3:1 of the diol compared to the acid chloride, which corresponded a 500% molar excess of the hydroxyl functionality. The ^1H NMR shown in Figure 8.2a confirmed the molecular structure of the cinnamoyl chloride and hexanediol product (HD-Cinn) and also indicated that less than 3 mol% of the



Scheme 8.3: Synthesis of cinnamate based alcohols with different aliphatic spacers.

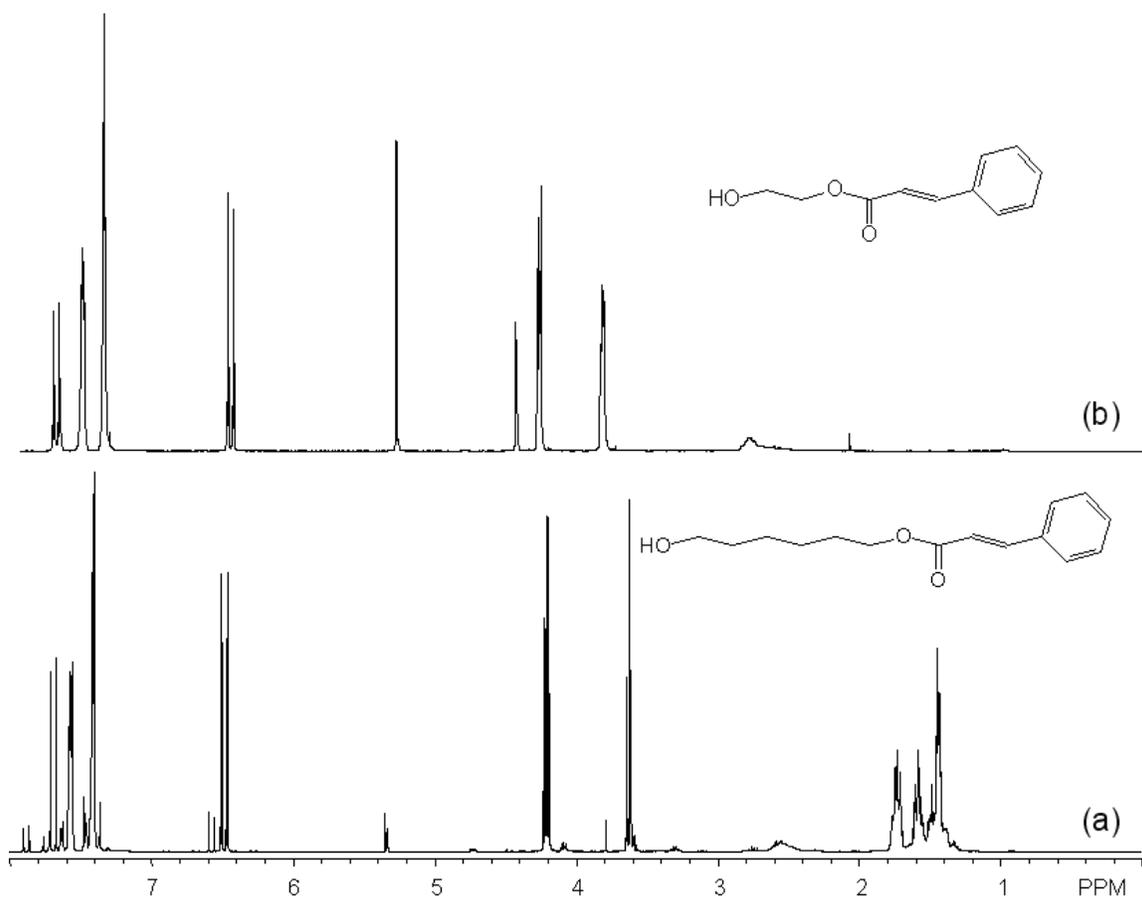


Figure 8.2: ^1H NMR spectra of the synthesized cinnamate derivatives possessing an aliphatic hydroxyl functionality.

product was difunctionalized with cinnamate. The ethylene glycol derivative (EG-Cinn) exhibited a greater propensity to difunctionalize. Molar ratios from 1.5:1 up to 6:1 were investigated and the percentage of difunctionalized diol steadily decreased with the increase in molar ratio (Table 8.1). Consequently, a molar ratio of 6:1 was employed to obtain the product with only 9.5% difunctional. The ^1H NMR of the purified product is shown in Figure 8.2b.

The synthesized cinnamate derivatives were subsequently employed in a ring opening reaction of the maleic anhydride unit found in the polymer backbone (Scheme 8.2b). The modifications were performed in ethyl acetate at 85 °C for 24 h. The modification reaction resulted in attachment of a cinnamate functionality attached to the polymer backbone via an aliphatic spacer consisting of 2 or 6 methylene units. Moreover, a carboxylic acid was formed directly adjacent to the cinnamate group. ^1H NMR was utilized to confirm the attachment of the photoactive group and determined the level of functionalization. Resonances characteristic of the cinnamate functionality were observed at 6.5ppm and at 7.3-7.6 ppm (Figure 8.3). Moreover, the appearance of a new methylene resonance was observed at 4.3 ppm corresponding to the methylene adjacent to the newly formed ester linkage.

The effect of monomer composition on the modification reaction was investigated using copolymers of maleic anhydride and a single additional monomer. Copolymers of maleic anhydride with methyl, n-butyl, and 2-ethylhexyl acrylate were prepared in a manner identical to the multicomponent copolymer systems. Molecular weights of the resulting copolymers ranged from 70,000 g/mol to 300,000 g/mol with relatively broad molecular weight distributions (1.93-3.03). The bicomponent copolymers were functionalized in a 10 wt% ethyl acetate solution at 85 °C using a 1.5:1.0 molar ratio of cinnamate derivative to anhydride functionality. ^1H NMR was employed to study the different levels of functionalization for the copolymers. Table 8.2 highlights the percent conversion anhydride ring opening corresponding to polymer modification. The n-butyl acrylate and 2-ethylhexyl acrylate copolymers exhibited only slight degrees of

Table 8.1: The effect of the molar ratio of acid chloride to ethylene glycol on the level of difunctionalization.

Molar Ratio		
Cinnamoyl Chloride	Ethylene Glycol	mol% difunctionalized ^a
1	1.5	35
1	4	14
1	6	9.5

^alevel of difunctionalization determined using ¹H NMR

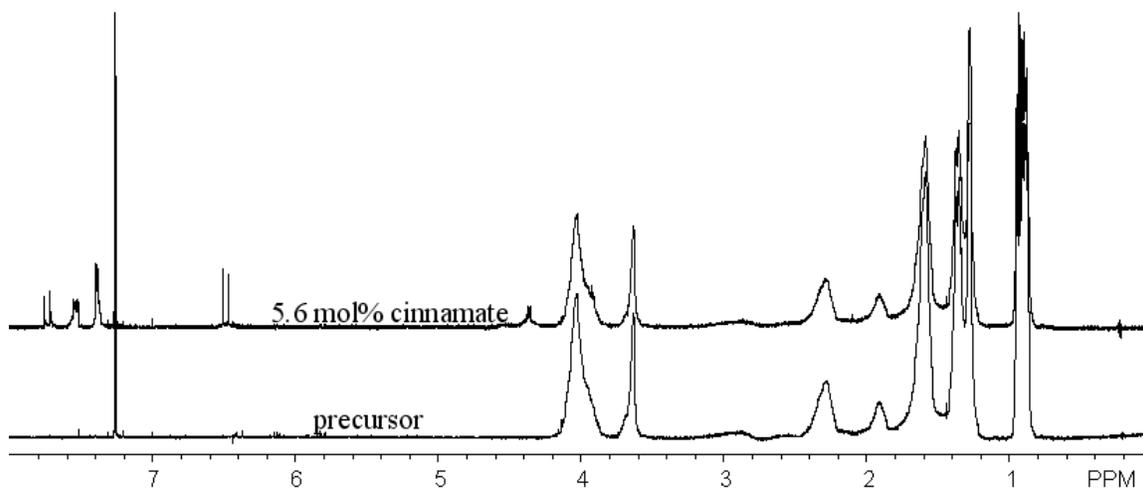


Figure 8.3: ^1H NMR spectra detailing the introduction of photoactive cinnamate groups via an anhydride ring opening reaction.

Table 8.2: Levels of cinnamate functionalization with an ethylene spacer in the bicomponent copolymers of alkyl acrylate and maleic anhydride.

alkyl acrylate	MAH:EG-Cinn	mol% cinnamate ^a	MAH conversion
methyl acrylate	1.5:1.0	4.0 ^b	40 %
n-butyl acrylate	1.5:1.0	<1.0	<10 %
2-ethylhexyl acrylate	1.5:1.0	<1.0	<10 %

^a degree of cinnamate functionalization determined using ¹H NMR spectroscopy

^b methyl acrylate copolymer modification resulted in a slightly crosslinked system and calculated mol% cinnamate is based on soluble fraction

modification. On the other hand, the methyl acrylate copolymer possessed a high level of cinnamate functionalization. This result suggested that steric crowding from the larger alkyl ester chains of n-butyl and 2-ethylhexyl acrylate inhibit the modification reaction.

Further investigation of the modification reaction involved use of the multicomponent copolymers and examined the effect of solvent concentration and the molar ratio of the reactants. The initial solvent concentration was reduced from 90 wt% ethyl acetate to 50 wt% ethyl acetate. The reduction in solvent resulted in an increase in the degree of functionalization from 1.1 mol% to 2.5 mol%. This level of functionalization corresponded to conversions of the anhydride ring opening of 11% and 25%. It is unclear at this time whether the enhanced reaction performance was a function of concentration or a reduction in alternative reactive sites for the hydroxyl nucleophile. Alternative solvent systems will be explored to elucidate this possibility. In addition to the solvent concentration, the concentration of the cinnamate alcohol was altered to improve the degree of modification. The molar ratios of alcohol to anhydride functionality were varied from 1.5:1.0 to 4.5:1.0 and the results are presented in Table 8.3. As expected, an increased concentration of the photoactive alcohol yielded a higher level of conversion. Conversions of 56% and 64% for the ring opening reaction were achieved. Again ^1H NMR was utilized to monitor the extent of polymer modification.

8.4.3 Irradiation and Evaluation of the Photocrosslinking Process

The optimized conditions for the hydroxyl and anhydride post polymerization modifications were used to produce polymers possessing desired degrees of photoactive functionality. The polymeric materials were cast as films (5-9 μm) from chloroform onto specific substrates depending on the method for analysis. Subsequently, the cast films were exposed to UV irradiation via a conveyor system that carried the sample under a microwave UV source. The irradiation process involved exposure to two different UV microwave bulbs. The first pass was exposure to an H bulb that emits radiation primarily in the UVC region of the spectrum. The next six passes under the D bulb exposed the sample to light primarily in the UVA region and is referred to as the postcure step.

Table 8.3: Effect of molar ratio of the cinnamate derivative to maleic anhydride on the level of maleic anhydride modification.

EG-Cinn:MAH molar ratio	mol% cinnamate ^a	MAH conversion
1.5	2.5	25
3.0	3.8	38
4.5	5.6	56

^adegree of cinnamate functionalization determined using ¹H NMR

Three HEA based copolymers functionalized at levels of 6, 11, and 18 mol% cinnamate were exposed to UV irradiation. UV-Vis spectroscopy was used to monitor the disappearance of the double bond involved in the photodimerization reaction. A λ_{\max} for the double bond absorbance was observed at 278 nm. The double bond conversion profiles showed approximately 20-25% conversion based on UV-Vis spectroscopy (Figure 8.4). The double bond conversion was similar regardless of the level of cinnamate conversion. Only the copolymer functionalized with 18 mol% cinnamate exhibited a slightly reduced degree of conversion; however, this result may be due to UV-Vis spectroscopic analysis performed outside the linear Beer-Lambert region. In addition, gel fraction measurements were performed on the irradiated samples. The gel fractions for the polymer samples exposed to the postcure step were similar within the standard deviation of the measurement. However, increasing levels of cinnamate functionalization resulted in lower gel fractions (Figure 8.5). The lower levels of gelled polymer were likely due to an increase in the percentage of intramolecular dimerization in the highly functionalized copolymers. Lower cinnamate levels prevented intramolecular dimerization and promoted the intermolecular process because having fewer cinnamate functionalities per polymer chain reduced the chances of same chain cinnamate dimerization. Contrary to intermolecular dimerizations, intramolecular dimerizations resulted in cyclization of sections of the polymer chain with no significant increase in the molecular weight.

The optimized modification conditions were utilized to produce MAH based copolymers with approximately 2.5 mol%, 3.8 mol%, 5.6 mol%, and 6.4 mol% cinnamate functionality with the ethylene glycol derivative. The double bond disappearance profiles for the different functionalized copolymers are shown in Figure 8.6. The initial UV exposure under the H bulb resulted in a significant decrease in the concentration of the photoactive double. Subsequent passes under the D bulb associated with the postcure steps resulted only a slight decrease in the λ_{\max} absorbance. The corresponding gel fraction measurements revealed crosslinking trends opposite those observed with the HEA based copolymers. The increased functionalization resulted in

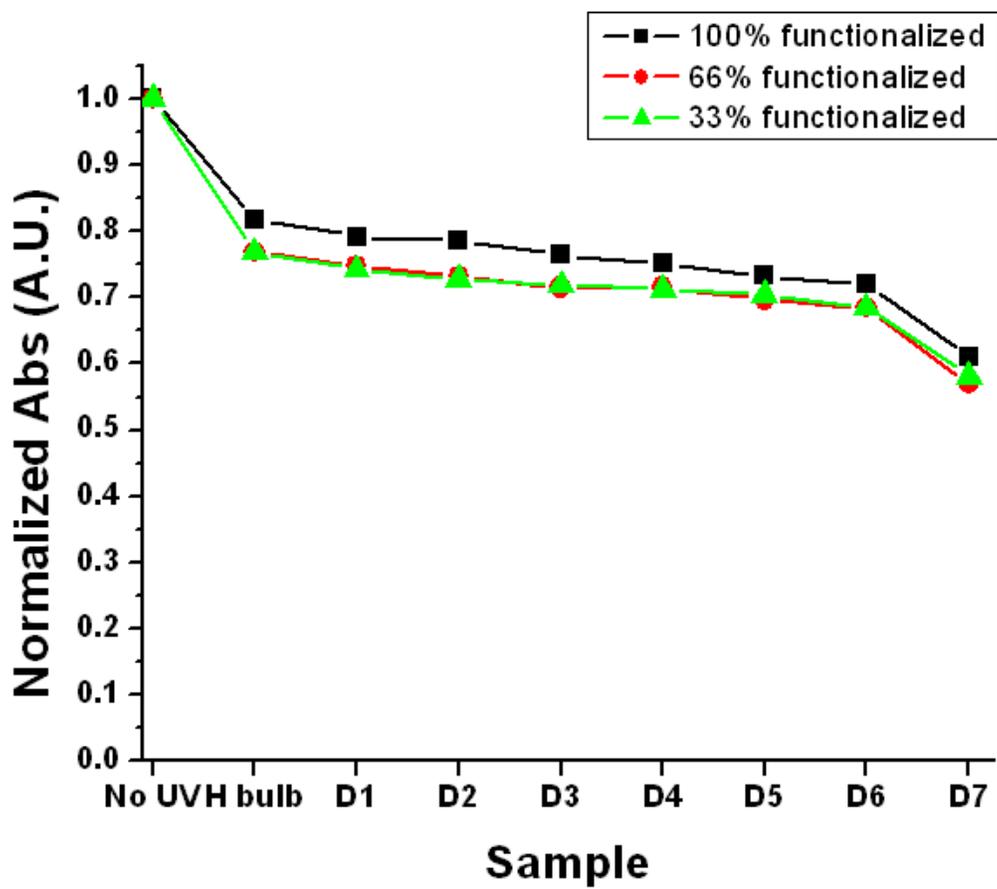


Figure 8.4: Double bond consumption profiles based on UV-Vis spectroscopy for cinnamate modified copolymers.

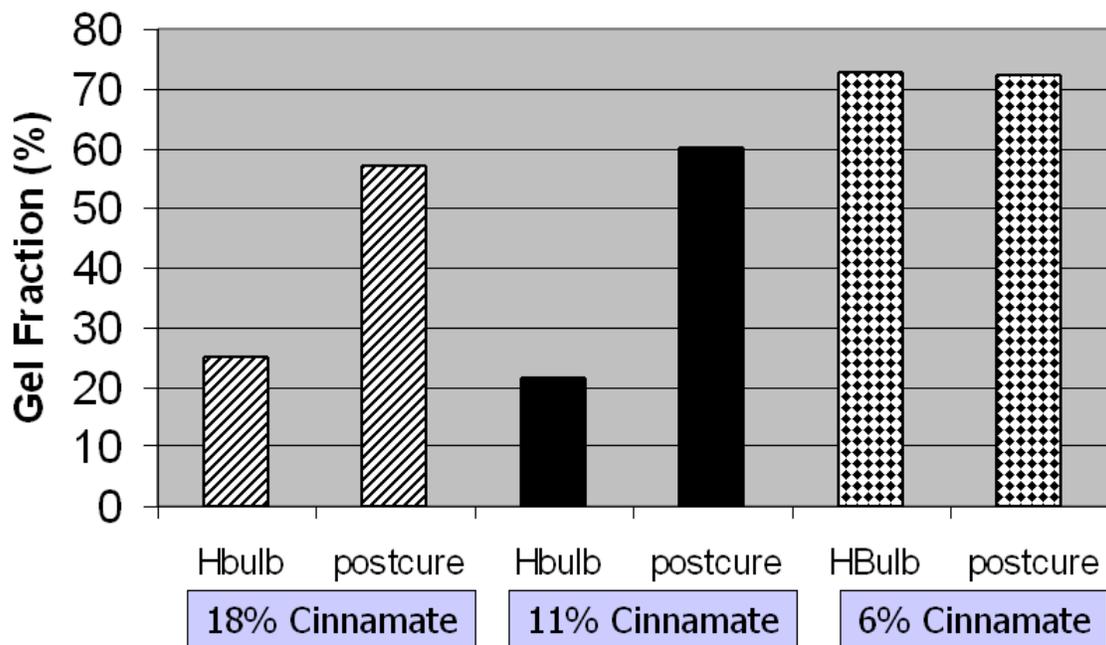


Figure 8.5: Gel fractions of cinnamate functionalized HEA-containing polymers after H bulb and postcure irradiation.

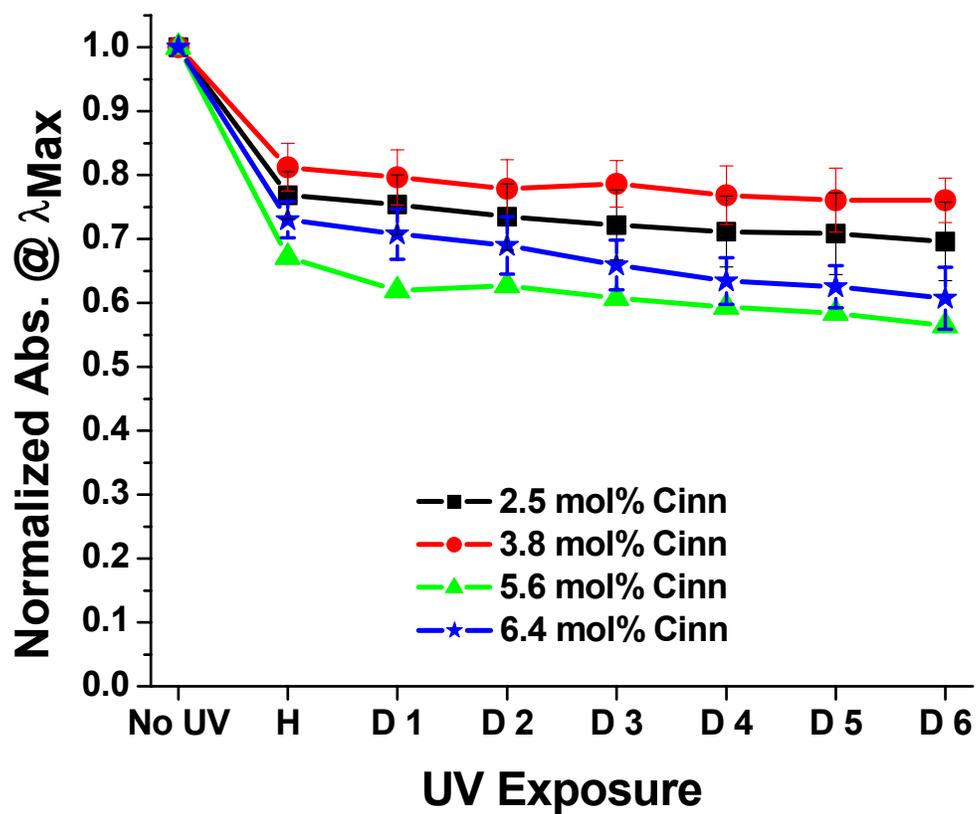


Figure 8.6: Double bond disappearance profiles for the functionalized MAH-containing polymers functionalized copolymers are shown.

higher initial gel fractions upon exposure with the H bulb. The postcure gel fractions (Figure 8.7) for the three samples were similar indicating that higher dosages of UV radiation lead to the same degree of the intermolecular crosslinking. However, higher initial cinnamate content served to improve the level of crosslinking achieved on the initial pass. It was thought that higher degrees of functionalization would reveal similar trends to that observed in the HEA copolymer series. There seems to exist an optimum level of cinnamate functionality that leads to high levels of intermolecular reactions and lower levels of intramolecular dimerization.

Adhesive performance for the functionalized copolymers was evaluated using an ASTM standard peel test. The peel force and mechanism of failure were monitored. An aluminum peel wheel was used to allow 90° peel testing. Samples exposed to no irradiation, a single H bulb pass, and six D bulb passes were examined (Figure 8.8). The initial radiation exposure resulted in an increase in the peel force. However, the postcure process resulted in lower peel forces. The initial increase was attributed to an increase in the resistance to deformation resulting from the photo-induced crosslinking. The subsequent decline in peel strength was attributed to a surface effect. The six postcure passes effectively crosslinked the surface of the adhesive and thereby reduced the tackiness of the polymer leading to a reduction in peel strength. In all cases, the apparent mode of failure was adhesive.

8.5 Conclusions

The copolymer compositions containing 2-hydroxyethyl acrylate and maleic anhydride represent viable precursor polymers for the introduction of a photoactive cinnamate group via an acid chloride reaction and an anhydride ring opening reaction, respectively. The level of functionalization was controlled using various modification parameters. In the HEA based copolymers, 100% conversion of the hydroxyl functionality was achieved. Approximately, up to 65% of the MAH functionalities were converted to photoactive groups. Moreover, irradiation of the photoactive polymers resulted in highly crosslinked polymer systems. UV-Vis spectroscopy and gel fraction

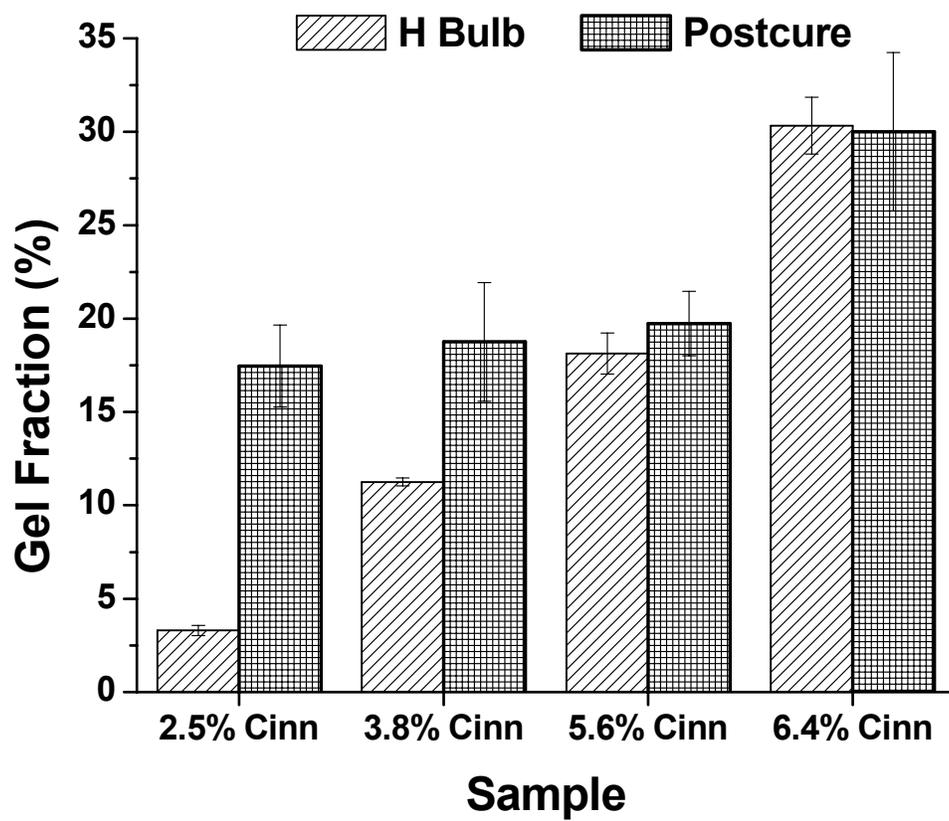


Figure 8.7: Gel fractions of cinnamate functionalized MAH-containing polymers after H bulb and postcure irradiation.

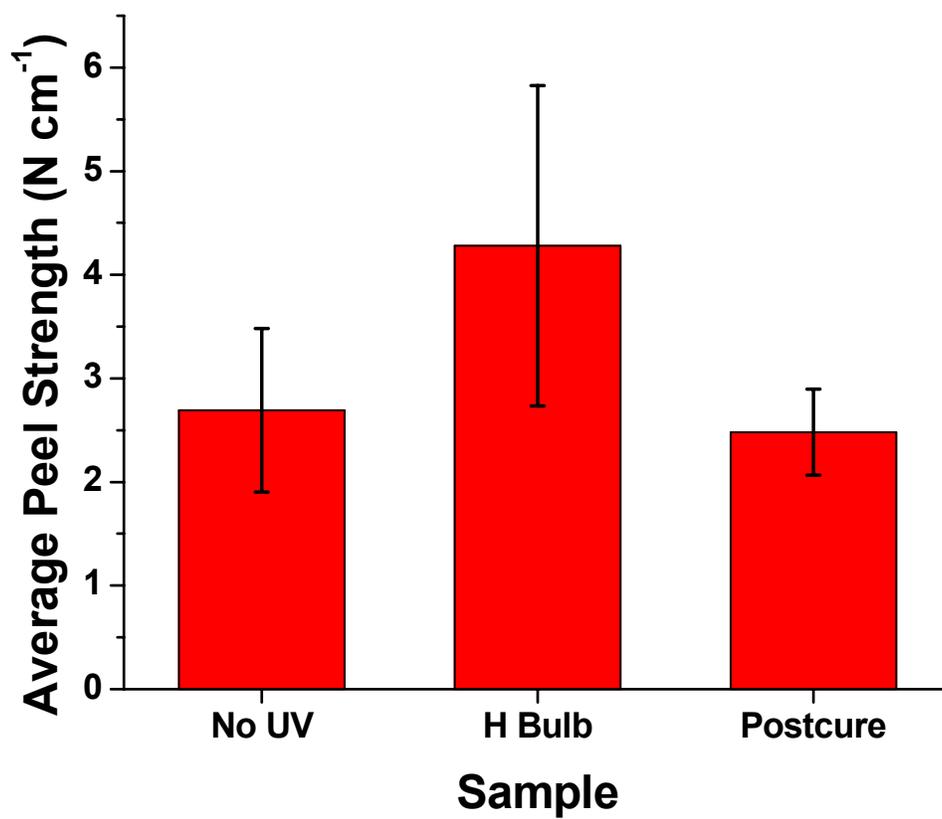


Figure 8.8: Average peel strengths of 6.4 mol% cinnamate functionalized MAH-containing polymer as cast, after H bulb and postcure irradiation.

measurements were utilized to evaluate the extent and characteristics of the photocrosslinking process.

8.6 Acknowledgements

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Chapter 9 : Future Work

9.1 Investigations of Amphiphilic Block Copolymer Synthesis via Stable Free Radical Polymerization Processes

- Expand on previous efforts via production of block copolymers of acrylic acid (AA) and 2-ethylhexyl acrylate (EHA) with larger block lengths approaching M_c
 - Increase AA sequence length to increase rigidity and water solubility (20K, 40K, 60K block lengths)
 - Increase EHA sequence length to make copolymer softer for adhesive applications (60K, 80K, 100K block lengths)
 - Simultaneously change the lengths of both AA and EHA to impart different viscoelastic properties
 - Investigate other monomers such as dimethyl acrylamide as substitutes for AA to construct hydrophilic blocks.
- Investigate resulting copolymer compositions using mechanical properties analysis
 - Peel testing, DMA, melt and solution rheology, DSC to examine microphase separation and association different phases
 - Neutralize carboxylic acid groups with NaOH or other appropriate base and reexamine resulting mechanical properties

9.2 Well-defined Hydroxyl Copolymer Systems via the Stable Free Radical Polymerization Methodology

- Synthesize model copolymers possessing identical percent hydroxyl composition but different locations of the hydroxyl functionality in the copolymer
 - Employ random copolymers containing various amount of HEA in a comparison with well-defined triblock copolymers
 - Synthesize poly((HEA-*co*-nBA)-*b*-nBA-*b*-(HEA-*co*-nBA)) with block lengths 20K-40K-20K

- Synthesize poly(nBA-*b*-(HEA-*co*-nBA)-*b*-nBA) with block lengths 20K-40K-20K
- Examine resulting morphology and rheological properties
- Use the model systems as precursor scaffolds for systematic examination of hydrogen bonding (DNA base pairs) and branching (long chain aliphatics) via attachment through the hydroxyl group

9.3 Novel Polymer Architectures Using the Stable Free Radical Polymerization Technique

- Synthesize block copolymers with structure, poly((HEA-*co*-nBA)-*b*-nBA) where the HEA containing block is short (<5K) and the pure nBA block is large (>50K)
- Modify the hydroxyl group via attachment of a photoactive species like cinnamates or coumarin
 - Irradiate the resulting copolymer to yield a star shaped copolymer that is reversible depending on the wavelength of light irradiation
- Modify the hydroxyl group via attachment of a strong complementary or self-complementary hydrogen bonding species
 - Mix polymer or polymers to produce star structures that possess similar or different arms and can be broken down by the addition of solvent or heat

Chapter 10 : Overall Conclusions

The stable free radical polymerization methodology was employed in the synthesis of a variety of tailored macromolecular systems. Initially, the SFRP technique was employed in an attempt to synthesize well-defined 2-vinylnaphthalene homopolymers. However, using *in situ* FTIR spectroscopy to monitor the polymerization in a real time fashion revealed similar polymerization kinetics in reactions performed with or without the TEMPO mediator. A novel modified Mayo mechanism for 2VN was proposed as a source of thermally generated radical initiators. An Arrhenius analysis of the thermal polymerization processes associated with styrene and 2-vinylnaphthalene revealed a significantly reduced activation energy necessary for the 2VN process. The styrene thermal polymerization process required almost 30 kJ/mol more energy for activation than the 2VN system.

Based on the determined thermal polymerization activation energies for styrene and 2VN, it was demonstrated that 2VN in small quantities could function as an initiator in the controlled free radical polymerization of styrene. A systematic increase in the concentration of 2VN compared to styrene resulted in a reduction in the molecular weight of the resulting polystyrene homopolymer. Polymerization variable such as temperature and molar ratio of initiator to mediator were investigated to optimize the 2VN initiated polymerizations. The resulting polymer products exhibited a distinct UV absorbance associated with the 2VN initiating species. As the molecular weight of the polymer decreased, the concentration of the initiator end group increased. Both UV-Vis and ¹H NMR spectroscopy was utilized to confirm the presence of the initiator and mediator end groups.

The facile two step synthesis of a triblock copolymer was accomplished using a novel dinitroxide mediating agent. Reaction of hydroxyl-TEMPO with 1,6-hexamethylene diisocyanate yielded a dinitroxide compound whose structure was confirmed with ¹H NMR. The use of the dinitroxide in a styrene polymerization resulted in homopolymers with an internal bisalkoxyamine linkage. This precursor was used to initiate the polymerization of *t*-butyl styrene resulting in a triblock copolymer. It was

also observed that mediation using the dinitroxide resulted in an enhanced degree of nitroxide degradation compared to conventional mononitroxides such as TEMPO. This enhancement was attributed to a shift in the mediation equilibrium resulting in greater amounts of free nitroxide and polymeric radicals. This result highlighted the necessity to possess a mediation equilibrium that lies heavily in favor of the dormant polymer species in order to achieve controlled polymerizations.

The *in situ* FTIR monitoring technique was employed in the synthesis of a novel nitroxide mediating agent, DEPN. The two-step nitroxide synthesis was monitored using the *in situ* FTIR technique to optimize the reaction conditions. This nitroxide mediator was then used in the stable free radical polymerization of various alkyl acrylate monomers. The SFRP technique in concert with *in situ* FTIR was utilized to construct a well-defined triblock copolymer with a central EHA block and two surrounding *t*BA segments. This tailored triblock copolymer, poly(*t*BA-*b*-EHA-*b*-*t*BA) (20K-38K-17K), was subsequently treated with pTSA to remove the *t*-butyl groups resulting in two outer acrylic acid sequences. The polymer product exhibited a microphase separated morphology based on DSC, DEA, and DMA analysis. Moreover, AFM and SAXS analysis was employed to directly observe the morphology of the copolymers.

In addition to carboxylic acid functionalities, hydroxyl functionalities were also incorporated into acrylate polymers in a controlled manner via addition of HEA to the monomer feed. A series of random copolymers with various molar concentrations of HEA and nBA were synthesized using the DEPN mediator. Molar ratios of 0-40 mol% HEA in the monomer feed were polymerized while monitoring the reactions using *in situ* FTIR spectroscopy. Polymerization kinetics based on acrylate monomer disappearance profiles revealed a significant acceleration of monomer conversions rates upon increasing the concentration of HEA in the polymerization. Addition of small amounts of dodecanol to the polymerization resulted in a similar acceleration of monomer conversion rate; however, the dodecanol demonstrated a greater rate enhancement for smaller quantities. ¹H NMR analysis of the copolymer products revealed an enrichment of HEA in the copolymer composition compared to the monomer feed. This result was attributed to

monomer reactivity ratios that favor preferential addition of the HEA monomer. Melt rheology and tack testing also demonstrated a significant effect due to the presence of the hydroxyl functionality. Copolymers with increasing amounts of HEA demonstrated increasing zero-shear viscosities and increased forces during tack analysis.

A series of multi-component acrylate copolymers containing HEA or MAH were synthesized. The resulting copolymers were modified after polymerization to attach a photoactive cinnamate functionality. Controlling the modification reaction conditions including temperature, solvent concentration and reagent molar ratio enabled the synthesis of copolymers with controlled levels of photoactive functionality. The modified copolymers were irradiated using a high power microwave source to induce non-radical photodimerization. The photodimerization process was monitored using UV-Vis spectroscopy to observe the disappearance of the photoactive double bond. In addition, gel fraction measurements and peel testing were performed to monitor the effects of the photodimerization process on the polymer properties.

Chapter 11 : Vita of Jeremy Richard Lizotte

Jeremy Richard Lizotte, son of Richard and Joyce Lizotte, was born on May 21, 1977 in Charlottetown, Prince Edward Island, Canada. He was raised in Roanoke Rapids, NC. He graduated from Roanoke Rapids High School in May of 1995. In August of the same year, he began his undergraduate studies at the University of North Carolina at Chapel Hill. In May 1999, he graduated from UNC-CH with a B.S. degree in Chemistry. In the fall of 1999, he began work as a graduate student in the Ph.D. program in the Department of Chemistry at Virginia Polytechnic Institute and State University in Blacksburg, VA. Upon completion of his Ph.D. degree in September of 2003, he will be employed with Eastman Chemical Company as a Senior Research Chemist in the Polymer Synthesis Research and Development Laboratory at Kingsport, Tennessee.