

Synthesis and Characterization of Branched Macromolecules for High Performance Elastomers, Fibers, and Films

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Dissertation submitted to the faculty of the Virginia Polytechnic Institute and State
University in partial fulfillment of the requirements for the degree of

Doctor of Philosophy
In
Chemistry

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November 16, 2005
Blacksburg Virginia

Keywords: Step-growth polymerization, $A_2 + B_3$ polymerization, polyester, polyurethane,
branching, hyperbranched, highly branched, elastomer, ionomer

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ABSTRACT

An $A_2 + B_3$ polymerization for the synthesis of hyperbranched polymers was altered using oligomeric precursors in place of either one or both of the monomer pairs to synthesize highly branched macromolecules. Unique topologies that are intermediates between long-chain branched and hyperbranched structures were obtained and the term “highly branched” was used to define these novel architectures. Various types of highly branched polymers, such as polyurethanes, poly(urethane urea)s, poly(ether ester)s, and poly(arylene ether)s were synthesized using the oligomeric $A_2 + B_3$ strategy. The molar mass of the oligomeric precursor permitted the control of the molar mass between branch points, which led to interesting macromolecular properties, such as superior mechanical performance to conventional hyperbranched polymers, disrupted crystallinity, improved processibility, and a multitude of functional end groups.

Highly branched poly(urethane urea)s and polyurethanes exhibited microphase-separated morphologies as denoted by dynamic mechanical analysis. The similarity in soft segment glass transition behavior and mechanical properties of the branched systems with that of the linear analogues suggested these materials have considerable promise for a variety of applications. When a polycaprolactone triol was utilized as the B_3 oligomer for the synthesis of highly branched polyurethane elastomers, the high degree of branching resulted in a completely amorphous soft segment, whereas the linear analogue with equivalent soft segment molar mass retained the crystallinity of polycaprolactone segment.

Oligomeric $A_2 + B_3$ methodology was further utilized to tailor the degree of branching of poly(ether ester)s that were developed based on slow addition of dilute solution of poly(ethylene glycol) (PEG) (A_2) to a dilute solution of 1,3,5-benzenetricarbonyl trichloride (B_3) at room temperature in the presence of triethylamine.

A revised definition of the degree of branching was proposed to accurately describe the branched poly(ether ester)s and the degree of branching decreased as the molar mass of the PEG diols was increased. Moreover, branched poly(arylene ether)s were prepared via a similar oligomeric $A_2 + B_3$ polymerization of phenol endcapped telechelic poly(arylene ether sulfone) oligomers (A_2) and tris(4-fluorophenyl) phosphine oxide (B_3) in solution. Highly branched poly(ether ester)s were also synthesized in the melt phase using the oligomeric $A_2 + B_3$ polymerization strategy. Melt polymerization effectively limited the cyclization reactions, which are common in $A_2 + B_3$ polymerizations in solution, and overcame the need for large amounts of polymerization solvent typical of $A_2 + B_3$ systems.

Finally, a new family of telechelic polyester ionomers was synthesized based on phosphonium bromide salt end groups and branching allowed the incorporation of higher levels of ionic end groups compared to linear analogues.

Acknowledgements

I would like to express my sincere gratitude to my advisor, Dr. Timothy E. Long, for his encouragement and tremendous support throughout my graduate career. I appreciate his patience and confidence in me from the first day. I would like to thank my current and former committee members, Dr. James E. McGrath, Dr. Judy S. Riffle, Dr. Alan R. Esker, and Dr. S. Richard Turner, Dr. Donald J. Leo, for their valuable time and guidance during my graduate studies at Virginia Tech.

I would like to recognize all Long group members, particularly my colleagues I have worked with: Jeremy Lizotte, Dave Williamson, Casey Elkins, Brian Mather, Afia Karikari, Kalpana Viswanathan, Tomonori Saito, Gözde Öztürk, Matt McKee, and Ann Fornof. I would particularly like to thank Qin Lin for his initiative support and mentorship when I first stepped into the polyester world. I would also like to thank Cheryl Heisey for helping me all the time with patience.

I have met wonderful Turkish colleagues in Blacksburg, thanks to Emre Işın and Ayşen Tulpar for their support and friendship. My thanks especially go to my colleague and my roommate, Ufuk Karabıyık, who has made life easier and more fun during my graduate life.

I would like to thank my high school teacher, Mustafa Ateş, for teaching me chemistry, guiding me to chemistry, and seeing the unseen in basic science. I would like to send my gratitude to İskender and Emel Yılgör, my professors at Koç University, who always encouraged and supported me throughout my undergraduate and graduate studies.

I can't just thank my parents, Mustafa and Fatma Ünal, and my brother, Erhan Ünal, who have always trusted in me and supported me from the first day. I would not have been where I am today without my family. Finally, I would like to thank my fiancé, Hayriye Özhalıcı, for coming into my life, teaching me things I would never have learned, and being there to support me.

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Chapter 1: Introduction

1.1 Dissertation Overview

Tailored branching significantly influences the physical properties, rheology, and processing behavior of macromolecules. Numerous studies on polymer structure-property relationships have shown that controlled branching provides a useful tool for the preparation of polymeric materials with a multitude of functional endgroups and enhanced processibility. Classical hyperbranched polymers have unique characteristics such as low solution and melt viscosity, low hydrodynamic volume, good solubility, and a multitude of functional end groups. However, the lack of entanglements due to very short distance between branch points results in poor mechanical properties and stymies industrial applications of hyperbranched polymers. Research objectives will address the utility of new approaches to synthesize branched macromolecules that have unique thermal and physical properties, along with characteristics of hyperbranched polymers. Polymerization of functionally symmetric monomer pairs such as A_2 and B_3 type monomers has received great attention in the last decade as a conventional approach to synthesize hyperbranched polymers.¹ The wide range commercially available A_2 and B_3 monomers allowed tailoring the polymer structure due to various choices of monomer pairs and provided more facile routes to many families of hyperbranched polymers.

Our recent efforts have focused on substituting one of the monomer pairs with functionally symmetric, oligomeric precursors as a means of controlling the distance between the branch points, which led to remarkable physical properties compared to conventional hyperbranched polymers. Topologies that are intermediates between long-chain branched and hyperbranched were obtained. This dissertation examines the synthesis and characterization of step-growth polymers with unique branched architectures. Chapter two is a relevant literature pertaining to the synthesis of branched macromolecules, particularly long-chain branched and hyperbranched, via step-growth polymerization.

Chapter three describes the synthesis of novel, segmented, branched poly(urethane urea) elastomers that were obtained through oligomeric $A_2 + B_3$ polymerization. This

¹ Voit, B., *J. Polym. Sci. Polym. Chem.* **2005**, 43, 2679.

approach utilizes an isocyanate end-capped polyether (PPO or PTMO) as an oligomeric A_2 , and a B_3 triamine monomer, and produces highly branched, segmented poly(urethane urea)s with mechanical properties comparable to their linear analogues. This novel approach can easily be extended to a large number of telechelic oligomers (A_2) including poly(dimethylsiloxane) (PDMS) or poly(ethylene glycol) and trifunctional monomer (B_3) combinations for the preparation of a wide range of polymeric materials from elastomers to engineering thermoplastics. In order to better understand the polymer structure development in this approach, experimental studies were performed to monitor the molecular weight and polydispersity as a function of oligomeric A_2 addition and influence of solution concentration on the structural development.

Chapter four describes the synthesis of potentially biodegradable, polycaprolactone based, highly branched poly(ester urethane)s. Commercially viable, functionally symmetric A_2 and B_3 oligomeric precursors were utilized to achieve a highly branched topology. Optimization of the reaction conditions and a detailed comparison of the unique thermal and mechanical properties of highly branched poly(ester urethane)s with their linear analogues are reported.

Chapter five describes the preparation of poly(ether ester)s with different degrees of branching via the oligomeric A_2 with B_3 methodology. These novel branched architectures are both fundamentally interesting and commercially viable. The one-step oligomeric A_2 and B_3 methodology based on PEG diols offers a more facile approach to products with improved properties and performance. The introduction of branching in the polymer backbone disrupted crystallinity and completely amorphous polymers with a PEG segment were obtained. In addition, new applications such as highly branched poly(ether ester)s with photoactive ethyl acrylate end groups were also demonstrated to obtain photo-cross-linkable precursors.

Chapter six describes the oligomeric $A_2 + B_3$ polymerization in the melt phase. Highly branched poly(ether ester) via cyclization-free, melt condensation of poly(propylene glycol) (A_2 oligomer) and trimethyl 1,3,5-benzenetricarboxylate (TMT, B_3 monomer). The conversion of each monomer was monitored during the polymerization to understand the onset of gelation in the melt phase. Moreover, the

introduction of a monofunctional comonomer is reported as a novel strategy to avoid gelation in $A_2 + B_3$ polymerization.

Chapter seven describes preparation of poly(arylene ether)s of various branched topologies. Poly(arylene ether)s are a family of high performance engineering polymers with a relatively high glass transition temperature, high thermal stability, good mechanical properties, and excellent resistance to hydrolysis and oxidation. The synthetic methodology and molar mass characterization of the branched poly(arylene ether sulfone)s are described in detail.

Chapter eight describes the synthesis of novel ionic endcapping reagents and corresponding linear and branched telechelic polyester ionomers based on phosphonium salts. Phosphonium salt containing telechelic polyester ionomers were reported as attractive alternatives to more thermally labile ammonium based analogues. Chapter nine describes the synthesis and characterization of phosphonium based cationic polymers via conventional free radical polymerization.

Chapter 2: Literature Review

2.1 Long-Chain Branched Polymers

Partially Taken From:

McKee, M. G.; Unal, S.; Wilkes, G. L.; Long, T. E. "Branched Polyesters: Recent Advances in Synthesis and Performance." *Prog. Polym. Sci.* **2005**, *30*, 507-519.

2.1.1 Introduction

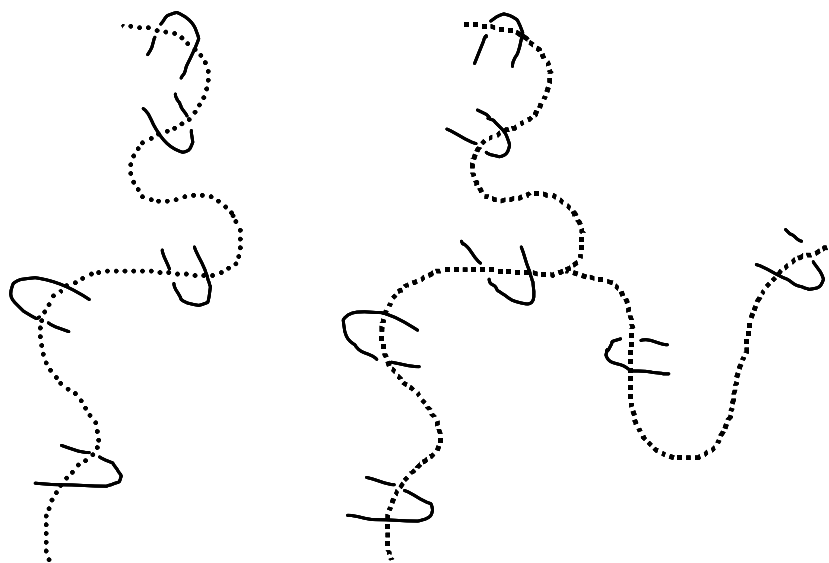
Branched polymers are characterized by the presence of branch points or the presence of more than two end groups and comprise a class of polymers between linear polymers and polymer networks. Although undesirable branching can occur in many polymerization reactions, controlled branching is readily achieved.² In fact, numerous studies on polymer structure-property relationships have shown that branched polymers display enhanced properties and performance for certain applications.³ Long-chain branched polymers offer significantly different physical properties than linear polymers and polymer networks. For example, a low concentration of long chain branching in the polymer backbone influences melt rheology, mechanical behavior, and solution properties, while large degrees of branching readily affects crystallinity.^{4,5} The strong influence of only one long chain branch per chain can be visualized by looking at Figure 2-1. The "slip-links" along the polymer backbone represent entanglements with other chains. The linear polymer is free to diffuse along a tube imposed by other chains, while it is obvious from Figure 2-1b that the mobility of the long-chain branched polymer is restricted, and must diffuse through some other mechanism. Thus, it is not surprising that long-chain branched polymers exhibit very different properties where chain entanglements play a role.

² Roovers, J.; Comanita, B., *Adv. Polym. Sci.* **1999**, *142*, 179.

³ Quirk, R. P.; Lee, Y.; Kim, J., In *Star and Hyperbranched Polymer*, Mishra, M. K.; Kobayashi, S., Eds. Marcel Dekker: New York, 1999; pp 1-25.

⁴ Shroff, R. N.; Mavridis, H., *Macromolecules* **1999**, *32*, 8454.

⁵ Pitsikalis, M.; Pispas, S.; Mays, J. W.; Hadjichristidis, N., *Adv. Polym. Sci.* **1998**, *135*, 1.



a) Linear entangled chain

b) Long chain branched entangled chain

Figure 2-1. Cartoon representing entangled linear chains (a) and long chain branched chains (b). The slip links represent entanglements due to other polymers.

It is widely documented that a high degree of branching in a polymer backbone provides enhanced solubility, lower viscosity and lower crystallinity, for the case of symmetric chains that readily crystallize, than a linear polymer of equal molecular weight.⁶ Therefore, a fundamental understanding of branching and how it influences polymer properties is essential for tailoring a polymeric material for high performance applications. Numerous types of branched polymers can be prepared using different polymerization techniques. In a living polymerization, multifunctional initiators or multifunctional linking agents yield well-defined star-branched polymers. Alkyl lithium initiators are particularly efficient types of multifunctional initiators, and polyfunctional silyl halides are highly efficient multifunctional linking agents.³ Comb polymers, which contain extensive branching along the polymer backbone, are synthesized in the presence of a polyfunctional coupling agent. Polyfunctional or multifunctional monomers of a functionality greater than two result in randomly branched polymers. Randomly branched polymers are often prepared by step-growth or chain polymerization in the presence of a multifunctional comonomer.² Highly branched (hyperbranched) polymers are prepared without gelation via the self condensation of an AB_x monomer containing

⁶ Tande, B. M.; Wagner, N. J.; Mackay, M. E.; Hawker, C. J.; Jenng, M., *Macromolecules* **2001**, 34, 8580.

one “A” functional group, and two or more “B” functional groups that are capable of co-reacting. Unlike dendrimers, which exhibit a regular, tree-like branch structure from a central core, hyperbranched polymers contain linear segments (defects) due to a more randomly branched architecture. Hyperbranched polymers are generally produced more easily than dendrimers and exhibit several similar properties.^{7,8}

The effect of branching on polymers prepared by chain-growth polymerization and single site catalyzed polymerizations has received significant attention. However, structure/property relationships for branched polyesters are limited and further studies are needed.⁹ Polyesters offer good mechanical and thermal properties and high chemical resistance at relatively low cost. Many polyesters, such as poly(ethylene terephthalate) (PET), polycarbonates, biodegradable aliphatic polyesters, and liquid crystalline polyesters are commercially available.¹⁰ PET is utilized for a wide range of applications including injection-molding and blow-molding.¹¹ Processing of some polyesters, however, is limited due to insufficient melt strength and melt viscosity. For example, while aliphatic polyesters such as poly(butylene adipate) (PBA) and poly(butylene succinate) (PBS) decompose rapidly under natural environmental conditions and are replacing some commodity polymers due to environmental concerns, processing these resins is often difficult due to low melt strength and melt viscosity.¹² Thus, many researchers have focused on modifying polyesters for enhanced melt strength and melt viscosity by introducing long chain branches into the polyester backbone. In this review, the synthetic methods for preparing various long-chain branched polyesters are reported. Moreover, the influence of branching on polyester properties for new high performance applications is discussed.

⁷ Malmström, E.; Hult, A., *Macromolecules* **1996**, 29, 1222.

⁸ Lin, Q.; Long, T. E., *Macromolecules* **2003**, 36, 9809.

⁹ Malmberg, A.; Kokko, E.; Lofgren, B.; Seppala, J. V., *Macromolecules* **1998**, 31, 8448.

¹⁰ Hsieh, T. T.; Tiu, C.; Hsieh, K. H.; Simon, G. P., *J. Appl. Polym. Sci.* **2000**, 77, 2319.

¹¹ Bikiaris, D. N.; Karayannidis, G. P., *Polym. Int.* **2003**, 52, 1230.

¹² Möck, A.; Burgath, A.; Hanselmann, R.; Frey, H., *Macromolecules* **2001**, 34, 7692, Anderson, K. S.; Hillmeyer, M. A., *Macromolecules* **2004**, 37, 1857.

2.1.2 Synthesis of Long-Chain Branched Polyesters

2.1.2.1 Introduction

Multifunctional comonomer branching agents are introduced into polycondensation reactions to obtain long-chain branched polyesters. Unlike short chain branches (SCB), a long chain branch (LCB) is long enough to entangle with other chains in the melt and concentrated solutions thereby drastically altering the flow properties. The critical molecular weight (M_c) is the minimum molecular weight at which a polymer chain entangles, as often measured by the molecular weight dependence of viscosity.¹³ The value M_c separates two regimes in the dependence of zero shear rate viscosity (η_0) on weight average molecular weight (M_w) for linear chains. Below M_c the value of η_0 scales directly with M_w and above M_c η_0 scales with $M_w^{3.4}$. Changes in M_c for a given polymer match changes in the entanglement molecular weight (M_e) which is determined from the plateau modulus (G_N^0) as shown in Equation 2-1,

$$M_e = \frac{\rho RT}{G_N^0}$$

Equation 2-1

where ρ is the polymer melt density, R is the gas constant, and T is the temperature. Fetters *et al.* related M_c and M_e through the packing length (p), which is proportional to the cross-sectional area of a polymer chain.¹⁴ Values of M_c were reported in the literature for several linear polyesters, including PET (3300 g/mol), poly(decamethylene succinate) (4600 g/mol), poly(decamethylene adipate) (4400 g/mol), and poly(decamethylene sebacate) (4500 g/mol).¹⁵

Hudson *et al.* showed that long-chain branching in the polymer backbone permits control over the rheology of the polymer.¹⁶ More recent studies on the modification of polyesters with long-chain branching have involved the use of PET, an engineering thermoplastic, with good thermal and mechanical stability, high chemical resistance, and

¹³ Ferry, J. D., *Viscoelastic Properties of Polymers*. 3rd ed.; Wiley: New York, 1980.

¹⁴ Fetters, L. J.; Lohse, D. J.; Graessley, W. W., *J. Polym. Sci. Part B: Polym. Phys.* **1999**, 37, 1023.

¹⁵ Zang, Y. H.; Carreau, P. J., *J. Appl. Polym. Sci.* **1991**, 42, 1965.

¹⁶ Hudson, N.; MacDonald, W. A.; Neilson, A.; Richards, R. W.; Sherrington, D. C., *Macromolecules* **2000**, 33, 9255.

ease of processing.^{11,17} Early work by Manaresi *et al.* describes the preparation of long-chain branched PET using low levels of trimesic acid.¹⁸ Intrinsic viscosity measurements and the extent of reaction were reported along with the degree of branching.

It is well known that polycondensation reactions with multifunctional comonomers may form an infinite molecular weight polymer network, or gel, above a certain multifunctional comonomer concentration or at high conversions. The onset of gelation occurs at a critical point of conversion during the polymerization, and is dependent on the degree of functionality and the concentration of the multi-functional ($f > 2$) branching agent. For example, polyester networks are prepared using dicarboxylic acids and tri- or tetrafunctional monomers.¹⁹ The critical extent of reaction (α_c) at which a polymer is predicted to form a gel is shown in Equation 2-2.

$$\alpha_c = \frac{1}{[r + rp(f - 2)]^{1/2}}$$

Equation 2-2

This equation is valid for polymerization mixtures with bifunctional A and B monomers and a multi-functional A monomer. In Equation 2-2, r is the ratio of A functional groups to B functional groups and p is the ratio of A functional groups with $f > 2$ to the total number of A groups. Low concentrations of multifunctional comonomers are used at low conversions to obtain long chain branching, and this method has yielded low molecular weight polymers. Neff *et al.* suggested the use of a monofunctional comonomer together with bifunctional and multifunctional monomers to overcome the gelation problem in high multifunctional comonomer concentrations or at high conversions.²⁰ Manaresi *et al.* were first to report the preparation and characterization of PETs synthesized in the presence of a high content (>1 mol %) of trifunctional comonomer (trimethyl trimesate), as well as monofunctional comonomers (methyl 2-benzoylbenzoate).²¹ Rosu *et al.* reported branched PETs using multifunctional and

¹⁷ Yoon, K. H.; Min, B. G.; Park, O. O., *Polym. Int.* **2002**, 51, 134.

¹⁸ Manerasi, P.; Parrini, P.; Semeghini, G. L.; de Fornarasi, E., *Polymer* **1976**, 17, 595.

¹⁹ Nagata, M., *Macromolecules* **1997**, 30, 6525.

²⁰ Neff, B. L.; Overton, J. R., *ACS Polym. Prepr.* **1982**, 23, 130.

²¹ Manerasi, P.; Munari, A.; Pilati, F.; Alfonso, G. C.; Russo, S.; Sartirana, L., *Polymer* **1986**, 27, 955.

monofunctional comonomers and subsequent solid-state polymerization was employed to increase the molecular weight of the final product.²²

Jayakannan and Ramakrishna synthesized high molecular weight branched PETs through the copolymerization of an A₂ monomer with small amounts of an AB₂ monomer.²³ However, as discussed in detail later in this review, insoluble crosslinked polymers were obtained at higher conversions. Hudson *et al.* synthesized and characterized branched PETs to study the balance between the branching reagents and endcapping reagents.¹⁶ The objective of their study was to examine various branching agents used for PETs and other polyesters and their influence on polymer properties, both with and without an endcapping reagent. Molecular weight was controlled via endcapping reagents on branched polyesters using a variety of branching agents.

More recently, Yoon *et al.* studied the effects of multifunctional comonomers such as trimethylolethane (TME) and pentaerythritol on the properties of PET copolymers.¹⁷ Molecular weights increased with increasing comonomer content while the molecular weight distribution broadened. Although solid-state mechanical properties did not differ significantly from linear analogues, the branched copolymers exhibited earlier shear-thinning onset in the melt compared to linear PET. Moreover, the crystallization rates of the copolymers decreased with increasing comonomer content as would be expected. Similar to branched PETs, branched poly(butylene isophthalate) (PBI) and poly(butylene terephthalate) (PBT) were synthesized and characterized to investigate their melt and crystallization properties. Linear and branched PBIs were synthesized from dimethylisophthalate (DMI) and 1,4-butanediol (BD) in the presence of trifunctional comonomers.²⁴ Branched PBTs were synthesized by incorporating the trifunctional comonomer, 1,3,5-tricarboxymethylbenzene.²⁵

High molecular weight branched aliphatic polyesters such as poly(ethylene succinate), poly(butylene succinate) (PBS), and poly(butylene adipate) (PBA), known as Bionolle™ polymers, were also prepared.²⁶ Bionolle™ polymers are used in a variety of applications, including film blowing, blow molding, extrusion coating and extrusion

²² Rosu, R. F.; Shanks, R. A.; Bhattacharya, S. N., *Polym. Intern.* **1997**, 42, 267.

²³ Jayakannan, M.; Ramakrishnan, S., *J. Polym. Sci. Part A: Polym. Chem.* **1998**, 36, 309.

²⁴ Bogdanov, B.; Toncheva, V.; Schact, E.; Finelli, L.; Sarti, B.; Scandola, M., *Polymer* **1999**, 40, 3171.

²⁵ Righetti, M. C.; Munari, A., *Macromol. Chem. Phys.* **1997**, 198, 363.

²⁶ Fujimaki, T., *Polym. Degr. Stab.* **1998**, 59, 209.

foaming.²⁷ Han *et al.* described synthetic conditions and thermal and mechanical properties for high molecular weight branched PBAs.¹² Ramakrishnan *et al.* reported the synthesis of a series of branched thermotropic liquid crystalline polyesters and their structural features.²⁸ Other novel branched polyesters such as branched poly(3-hydroxybenzoates) and poly(4-ethyleneoxy benzoate) were synthesized by Kricheldorf *et al.* and Ramakrishnan *et al.* respectively.^{29,30}

2.1.2.2 Synthesis of Branched Polyesters via A₂ and B₂ Monomers in the Presence of A_n or B_n (n>2) Monomers

The most common method for synthesizing branched polyesters is via the addition of small amounts of tri- or tetrafunctional comonomers to the polymerization. Manaresi *et al.* first reported the synthesis of branched PETs from dimethyl terephthalate (DMT) and ethylene glycol (EG) using a trifunctional branching agent, trimethyl trimesate (Equation 2-2).¹⁸

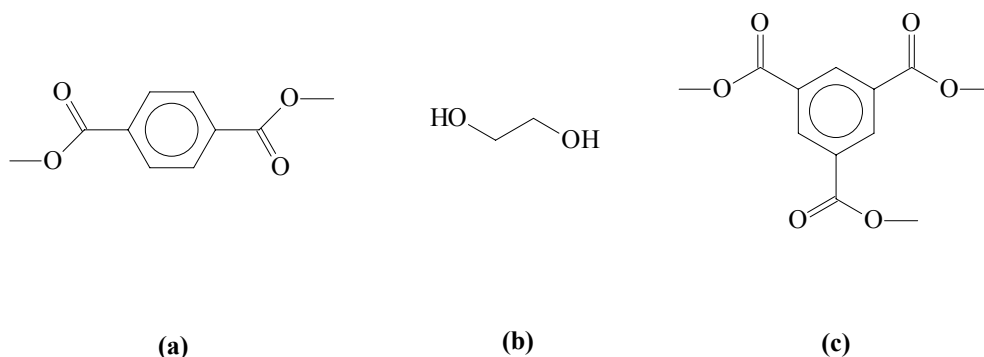


Figure 2-2. Bifunctional and trifunctional monomers used in the synthesis of branched PET. (a) dimethyl terephthalate (DMT), (b) ethylene glycol (EG), (c) trimethyl trimesate (Trimethyl 1,3,5-benzenetriesters) (TMT).

To prevent gelation, only small amounts (< 2%) of the trifunctional branching agent were used and the influence of long chain branching on PET properties was also reported. Although Manaresi *et al.* did not report the absolute molecular weights of the polymers, intrinsic viscosities in *o*-chlorophenol at 25 °C and the extents of reaction by end-group

²⁷ Yoshikawa, K.; Ofuji, N.; Umaizumi, M.; Moteki, Y.; Fujimaki, T., *Polymer* **1996**, 7, 1281.

²⁸ Kumar, A.; Ramakrishnan, S., *J. Polym. Sci. Part A: Polym. Chem.* **1996**, 34, 839.

²⁹ Kricheldorf, H. R.; Lubers, D., *Macromol. Chem. Phys.* **1995**, 196, 1549.

³⁰ Jayakannan, M.; Ramakrishnan, S., *J. Polym. Sci. Part A: Polym. Chem.* **1998**, 36, 309.

analysis were reported. After ester-interchange, only one type of functional group remained, i.e. the hydroxyl group of the hydroxy ethyl ester (Figure 2-3).

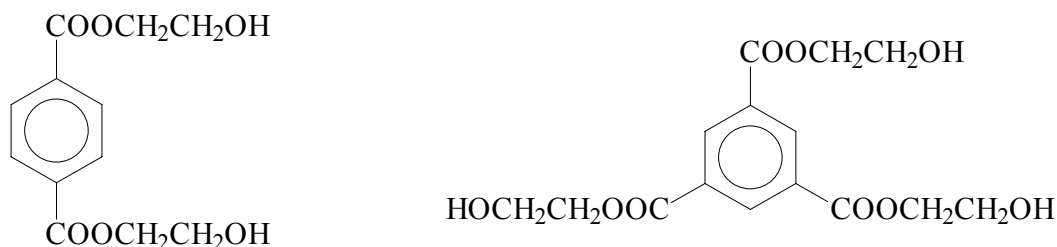


Figure 2-3. Hydroxy ethyl esters formed after the ester-interchange step during the polycondensation of PET.

In the subsequent polycondensation step, high molecular weight PET is formed via the evolution of ethylene glycol (Figure 2-4).

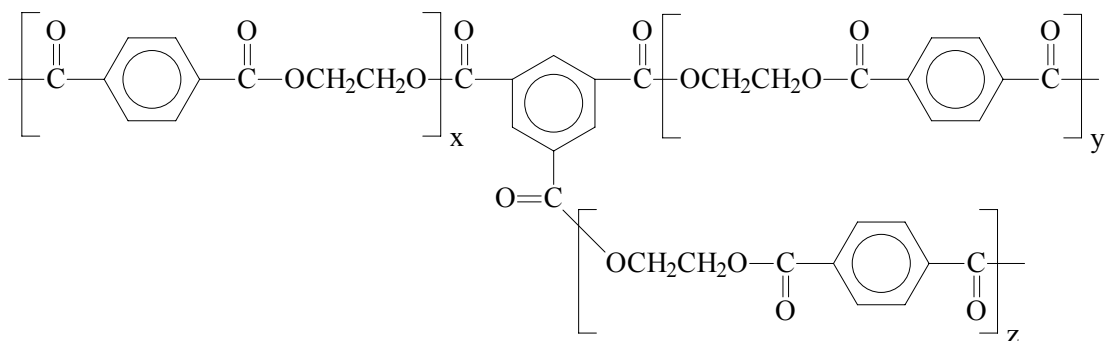


Figure 2-4. Structure of randomly branched PET.

Weisskopf used different trifunctional agents to synthesize high molecular weight branched PETs.³¹ Trimethylolpropane (TMP) was used as a trifunctional branching agent and pentaerythritol was a suitable tetrafunctional branching agent. Trimethylolethane (TME) and trimesic acid were also used as multifunctional comonomers (Figure 2-5). Hess *et al.* recently described the syntheses of both linear and branched PETs.³² Branched PETs were obtained via the ester-interchange route starting from DMT and a 2.5 M excess of EG. The reactions were performed in a stainless-steel reactor with different amounts (0.07 to 0.43 mol % with respect to DMT) of

³¹ Weisskopf, K., *J. Appl. Polym. Sci.* **1990**, 39, 2141.

³² Hess, C.; Hirt, P.; Oppermann, W. J., *J. Appl. Polym. Sci.* **1999**, 74, 728.

trimethylolpropane (TMP) (branching agent, Figure 2-5a) present during the transesterification step. Transesterification was catalyzed with the addition of manganese acetate at a maximum temperature of 230 °C. Following transesterification, polycondensation was catalyzed by antimony acetate at a maximum temperature of 290 °C under vacuum.

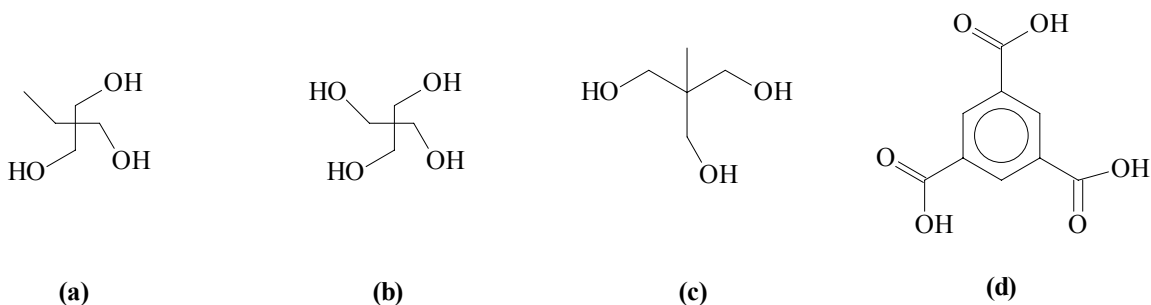


Figure 2-5. Trifunctional and tetrafunctional branching agents used in the synthesis of branched PET (a) trimethylolpropane (TMP), (b) pentaerythritol, (c) trimethylolpropane (TME), and (d) trimesic acid (TMA).

Yoon *et al.* synthesized branched PETs in a similar manner with TME as a branching agent at concentrations from 0.04 to 0.15 mol%.¹⁷ Titanium isopropoxide was used as the catalyst for the polycondensation reaction. High molecular weight PET copolymers were obtained with broad molecular weight distributions. The thermal properties of the copolymers were not significantly influenced by the comonomers due to the low concentrations; however the branched PET displayed enhanced zero shear rate viscosity (η_0) and shear thinning behavior. In a similar fashion, branched PBI and PBT samples were prepared using A₂, B₂, and A₃/B₃ type monomers. Branched PBIs were synthesized with the trifunctional branching agent tris(hydroxyethyl) isocyanurate (THEIC) during the polymerization reaction of dimethyl isophthalate (DMI) with 1,4-butanediol (BD) in the presence of a Ti(OBu)₄ catalyst (

Figure 2-6).²⁴ The branched PBIs were prepared via a two step polycondensation reaction. In the first step, the reaction temperature was raised from 140 to 200 °C and held at 200 °C until about 90% of the theoretical amount of methanol was collected. In the second step, the pressure was reduced and the temperature was maintained in the range of 200-230 °C. The temperature was maintained lower than normally employed for

polyesters, such as PBT, to prevent side reactions. Compositional and structural characterization included elemental analysis, mass spectroscopy, ^1H NMR spectroscopy, HPLC, and end group analysis. Linear and branched PBTs were also recently synthesized using DMT and BD as bifunctional monomers and trimethyl trimesate (TMT) as a trifunctional comonomer.²⁵ Using titanium tetrabutoxide at 250 °C in the second step yielded randomly branched PBTs.²⁷

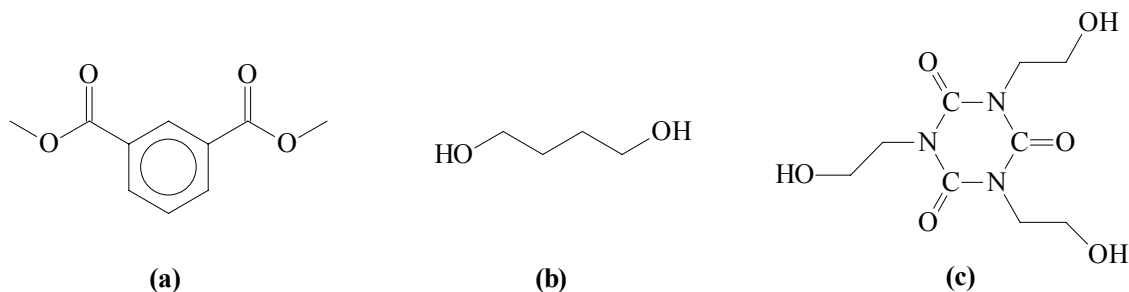


Figure 2-6. Bifunctional and trifunctional monomers used in the synthesis of branched PBI. (a) dimethyl isophthalate (DMI), (b) 1,4-butanediol (BD), and (c) tris(hydroxyethyl) isocyanurate (THEIC).

Han *et al.* synthesized high molecular weight branched PBAs from aliphatic dicarboxylic acids and glycols in the presence of glycerol or pentaerythritol.¹² The influence of reaction parameters such as catalyst concentration, reaction time, temperature, and concentration of branching agent on molecular weight was examined. These branched PBAs were prepared via the synthesis of linear PBA from adipic acid and BD in the presence of a titanium(IV) isopropoxide (TIP) catalyst and a triethylamine (TEA) cocatalyst. The resulting linear polymer was reacted with adipic acid in the presence of TIP to obtain prepolymers with carboxylic acid end groups. In a second step, the carboxylic acid terminated PBA prepolymers were condensed with the branching agent (glycerol or pentaerythritol) in the presence of TIP to obtain branched PBS. Han *et al.* studied molecular weight with respect to multifunctional comonomer concentration and showed that both the molecular weight and the molecular weight distribution of branched PBAs increased with increasing concentration of glycerol up to 0.6 wt% relative to the PBA prepolymer. The gel content of the branched PBAs also increased with increasing glycerol concentration up to 0.6 wt%. Surprisingly, 0.9 wt% or more

glycerol resulted in lower gel content and lower molecular weights. The authors did not offer an explanation for this dependence of gel content and molecular weight on branching content.

When branched PBAs were prepared with either glycerol or pentaerythritol, it was found that the molecular weight of branched PBAs with pentaerythritol was higher due to the higher degree of functionality. The introduction of a branching agent, TMP, to the polycondensation system of succinic acid and BD resulted in high molecular weight randomly branched poly(butylene succinate) (PBS).³³ The esterification was conducted using a 1.0 to 1.1 ratio of succinic acid to BD under nitrogen in the presence of a titanium isopropoxide catalyst. The temperature was raised from 140 to 200 °C as water was removed. The ensuing polycondensation step was performed by introducing 0.1 – 0.5 wt% of TMP to the reaction mixture at 140 °C. The reaction temperature was raised to 240 °C and the reaction was completed at a pressure less than 1 Torr. Absolute molecular weights and molecular weight distributions were determined using SEC (size exclusion chromatography) with a multi-angle laser light-scattering (MALLS) detector. The molecular weight distribution and the weight average molecular weight increased with increasing amounts of TMP, while the number-average molecular weight decreased.

It is possible to synthesize numerous types of branched polyesters by introducing A_3/B_3 or A_4/B_4 monomers into a polymerization of A_2 and B_2 monomers that involve transesterification and polycondensation. Long chain branched polymers generally have higher weight average molecular weights and broader molecular weight distributions compared with linear polymers synthesized at equivalent reaction conditions. In fact, a high level of multifunctional comonomer results in insoluble crosslinked systems or high gel content. Long chain branching strongly influences thermal, mechanical, and rheological behaviors of polymers as discussed in subsequent sections.

2.1.2.3 Synthesis of Branched Polyesters via A_2 and B_2 Monomers in the Presence of A_n or B_n ($n>2$) Monomers and a Monofunctional Endcapping Reagent

The introduction of long chain branches in polyesters is accomplished using low levels of a multifunctional comonomer and low conversions since gelation occurs at high levels of multifunctional comonomer and at higher conversions. However, the use of

³³ Jikei, M.; Kakimoto, M. A., *High Perform. Polym.* **2001**, 13, S33.

monofunctional comonomers in the presence of bifunctional and multifunctional monomers prevents or decreases gel content, and high molecular weight polymers with long chain branches are attainable at higher conversions. Neff *et al.* incorporated a monofunctional reagent as a chain terminator to prevent or decrease gel formation.²⁰ Branched PETs were synthesized from DMT, EG, and diethylene glycol (DEG) as bifunctional monomers, with trimellitic anhydride as the branching agent and stearic acid as a monofunctional reagent (Figure 2-7). Manaresi *et al.* synthesized highly branched PETs using a two step polycondensation reaction in the presence of a monofunctional comonomer, methyl 2-benzoylbenzoate, with bifunctional monomers, DMT and EG, and the trifunctional monomer, trimethyl trimesate (Figure 2-2).²¹ Munari *et al.* used a monofunctional comonomer to shift the gel point to higher percent conversions, and no gelation occurred when the ratio of monofunctional monomer to trifunctional monomer was greater than 3. When the ratio was less than 3, the gel point was reached at lower conversions. Methyl 2-benzoylbenzoate was used as the monofunctional comonomer, and polycondensation temperatures caused an approximately 30 wt % loss of monofunctional comonomer.

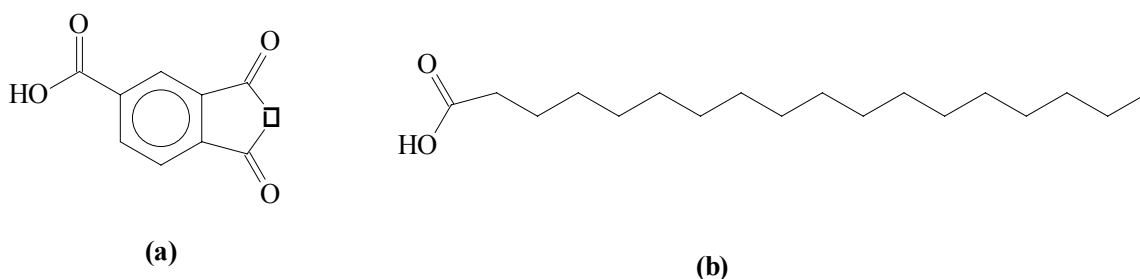


Figure 2-7. Trifunctional and monofunctional comonomers used by Neff *et al.* in the synthesis of branched PETs. (a) trimellitic anhydride, and (b) stearic acid.

Rosu *et al.* recently reported the synthesis and characterization of high molecular weight branched PETs that were prepared using a two step polycondensation reaction in the presence of monofunctional dodecanol or benzyl alcohol, DMT and EG, and multifunctional monomers, glycerol or pentaerythritol.²² The polymers with glycerol and pentaerythritol displayed different degrees of branching as pentaerythritol has four primary alcohol groups, while glycerol has two primary and one secondary alcohol group.

Therefore, the degree of branching was expected to be higher with pentaerythritol. In addition to two-step polycondensation reactions, solid-state polymerization was used to obtain high molecular weights. Solid-state polymerization increases polyester molecular weight, while avoiding thermal degradation.^{34,35} This method enables the preparation of linear and branched ultra-high-molecular-weight PETs with intrinsic viscosities of more than 2 dl/g (which corresponds to number-average molecular weights of 110,000 g/mole approximately).³⁶ Solid-state polymerization of PET is typically conducted 15-35 °C below the melting point of the polymer for various times.³⁴ It is also possible to perform these reactions at various temperatures (220, 230, 235 °C) under vacuum.³⁵ Rosu *et al.* reported molecular weight control for branched PETs when the reaction time in the solid-state polymerization step was controlled and specific compositions of reagents were used.²² The branched PETs were characterized by solution viscometry, thermal analysis, and melt rheology.

Recently, Hudson *et al.* studied branched PETs based on various branching agents and different endcapping reagent compositions.¹⁶ Branched PETs were prepared using conventional polycondensation reactions with a monofunctional monomer and various multifunctional monomers with DMT and EG or bis(2-hydroxyethyl) terephthalate. In addition to branching agents such as glycerol, pentaerythritol, and benzene-1,3,5-tricarboxylic acid (trimesic acid), Hudson *et al.* used benzene-1,2,4,5-tetracarboxylic acid, dipentaerythritol, and tripentaerythritol as branching agents with the endcapping reagent benzyl alcohol (Figure 2-8). A wide range of branched PETs (with various branching agents) as well as their compositions with and without the presence of an endcapping reagent were subsequently reported. The polymers were characterized using FTIR and ¹H NMR spectroscopy, light scattering, dilute solution viscometry, and melt rheology to investigate the influence of branching on solution and melt properties.

³⁴ Felgner, P. L.; Barenholz, Y.; Behr, J. P.; Cheng, S. H.; Cullis, P.; Huang, L.; Jesse, J. A.; Seymour, L.; Szoka Jr, F. C.; Thierry, A. R.; Wagner, E.; Wu, G., *Hum. Gene Ther.* **1997**, 8, 511.

³⁵ Karayannidis, G. P.; Kokkalas, E.; Bikiaris, D. N., *J. Appl. Polym. Sci.* **1995**, 56, 405.

³⁶ Tate, S.; Ishimaru, F., *Polymer* **1995**, 36, 353.

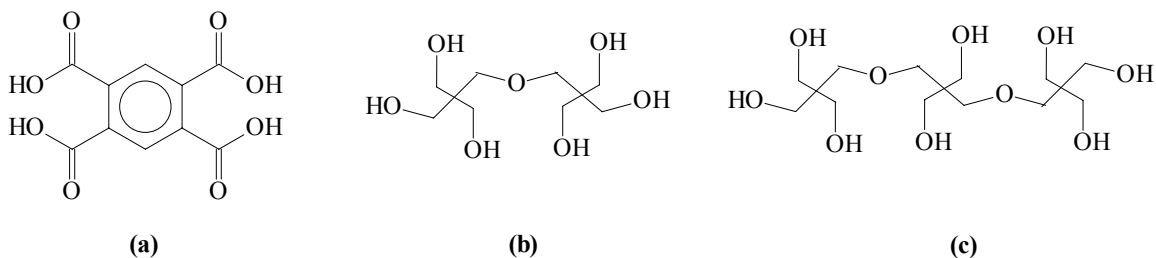


Figure 2-8. Branching agents used by Hudson *et al.* (a) benzene-1,2,4,5-tetracarboxylic acid, (b) dipentaerythritol, and (c) tripentaerythritol.

Although end-group modification of linear PETs for enhanced solubility and blend compatibility was previously reported, Kim and Oh investigated the effect of functional end groups on the physical properties of PETs by synthesizing hydroxyl and carboxylic acid end-capped linear and branched PETs.³⁷ The end-capped polymers were characterized using NMR spectroscopy, viscosity measurements, SEC, and thermal analysis. The high molecular weight branched PETs ($M_w > 100,000$) had broad molecular weight distributions, and diethylene glycol (DEG) units were present in the polymer backbone, which was attributed to side reactions of ethylene glycol during polycondensation.

2.1.2.4 Synthesis of Branched Polyesters via AB Monomers in the Presence of A₂B Monomers

An alternate method for synthesizing branched polyesters involves the copolymerization of A₂/B₂ or AB monomers with AB₂/A₂B monomers. Ramakrishnan *et al.* reported the synthesis and characterization of branched and “kinked” PETs through the copolymerization of an A₂ monomer with small amounts of an AB₂ monomer.²³ The term “kinked” describes linear disruption in the PET backbone due to meta substitution of the aromatic group. Therefore, in order to understand the influence of kinks, linear and branched polymers were also prepared. Branched and kinked PETs were synthesized using melt polymerization of bis-(2-hydroxyethyl) terephthalate (BHET) as A₂ monomer and ethyl bis-3,5-(2-hydroxyethoxy)benzoate (EBHEB) as the AB₂ monomer (Figure 2-9). Linear and kinked PETs were synthesized via the polycondensation of a BHET monomer with a 3-(2-hydroxyethoxy) benzoate (E3HEB) monomer that has a 1,3

³⁷ Kricheldorf, H. R.; Bohme, S.; Schwarz, G.; Kruger, R. P.; Schulz, G., *Macromolecules* **2001**, 34, 8886.

connectivity rather than a 1,4 connectivity, and the reaction was terminated early to prevent gel formation. Early gel formation was attributed to the fact that the EBHEB monomer behaved similarly to an A₃ type instead of AB₂, primarily due to the polycondensation reaction. Therefore, BHET was able to react with all three sites of EBHEB during polycondensation, which resulted in gel formation during the early stages of the polymerization. Unfortunately, stopping the reaction early to avoid gelation yielded low molecular weight polymers.

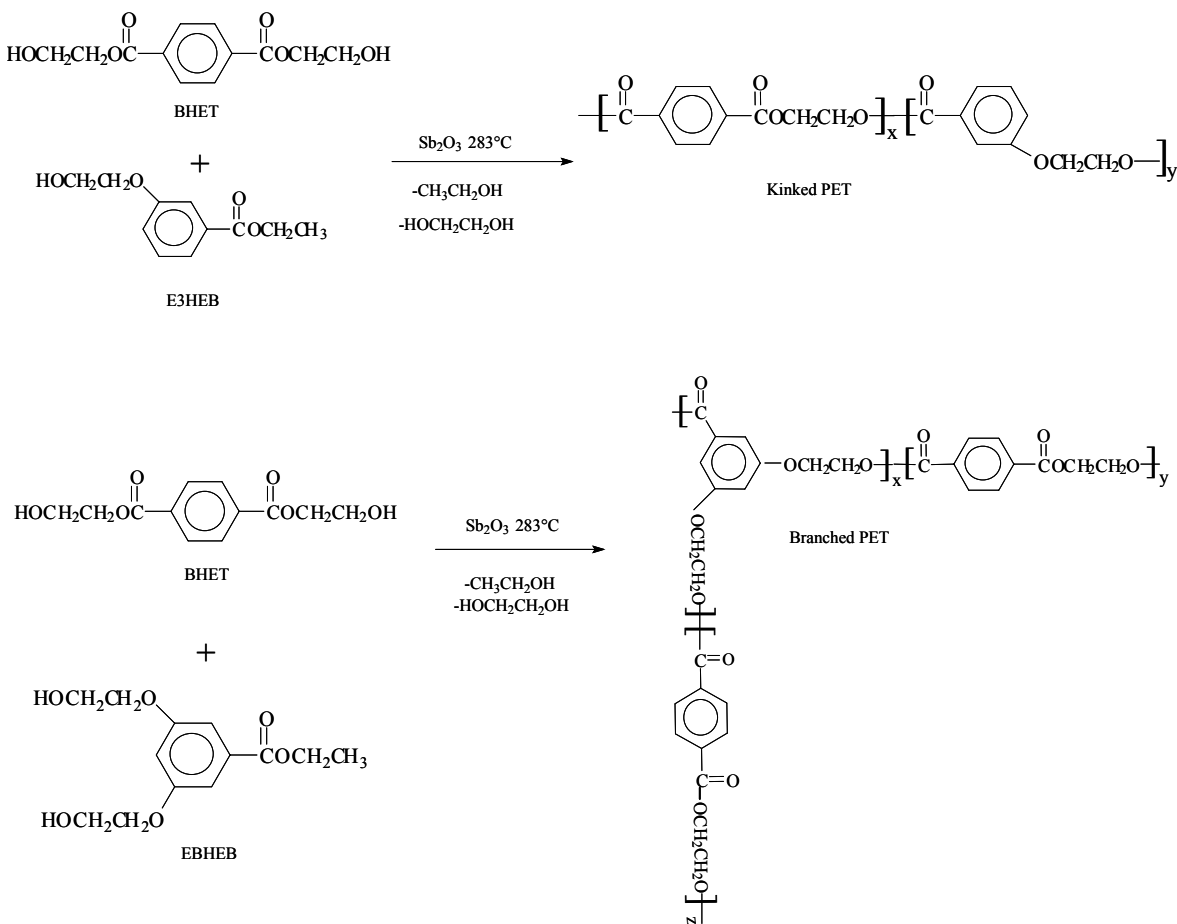


Figure 2-9. Reaction schemes for the synthesis of branched and kinked PETs.

In addition to PETs, poly(4-ethyleneoxy benzoate) was synthesized using ethyl 4-(2-hydroxyethoxy) benzoate (E4HEB) as AB monomer and EBHEB as AB₂ monomer.³⁰ Crosslinked polymers were formed at branching agent levels higher than 50 mol %. When compared to branched PETs, the branching content in these materials was higher

and therefore a wider range of branched polymers were prepared to study the effect of branching on the thermal properties. Kricheldorf *et al.* prepared linear, long chain branched, and hyperbranched poly(3-hydroxy-benzoates) via condensation of acid chlorides, 3-(trimethylsiloxy) benzoyl chloride as an AB type monomer, and 3,5-(bistrimethylsiloxy) benzoyl chloride as AB₂ type monomer.²⁹

2.2 Hyperbranched Polymers

2.2.1 Introduction

Hyperbranched polymers began to seriously attract the attention of scientists in the early 1990s, although Flory first described the synthesis of highly branched polymers by the self condensation of AB₂ type monomers or condensation of AB and AB₂ type monomers in 1952.³⁸ The term “hyperbranched” was first coined by Webster and Kim in the late 1980s, referring to a dendrimer-like structure with very high chain branching.³⁹ Hyperbranched (also termed as highly branched) polymers were not deemed to be very promising at first, probably due to their poor mechanical properties, broad molecular weights, and non-entangled/non-crystalline behavior.^{40,41} However, after discovering the unique properties and developing appropriate techniques for synthesizing dendrimers in the mid 1980s, hyperbranched molecules started to become an alternative to dendrimers because of their relative ease of preparation and lower cost. Although dendrimers have a well-defined structure, they require a step-wise synthesis of the molecules, while hyperbranched molecules can be synthesized in one step. Hyperbranched molecules are believed to have properties similar to dendrimers even though they possess some defects on the polymer backbone.^{7,42} Relatively few studies were initially reported in the open literature on the synthesis of highly branched polymers.^{43,44}

³⁸ Flory, P. J., *J. Am. Chem. Soc.* **1952**, 74, 2718. Flory, P. J., *Principles of Polymer Chemistry*. Cornell University Press: Ithaca, NY, 1953.

³⁹ Voit, B., *J. Polym. Sci. Part A: Polym. Chem.* **2000**, 38, 2505.

⁴⁰ Hult, A.; Johansson, M.; Malmström, E., *Adv. Polym. Sci.* **1998**, 143, 1.

⁴¹ Jikei, M.; Chon, S. H.; Kakimoto, M. A.; Kawauchi, S.; Imase, T.; Watanebe, J., *Macromolecules* **1999**, 32, 2061.

⁴² Kim, Y. H., In *Polymeric Materials Encyclopedia*, Salamone, J. C., Ed. CRC Press: New York, 1996; pp 3049-3053.

⁴³ Kricheldorf, H. R.; Zhang, Q. Z.; Schwarz, G., *Polymer* **1982**, 23, 1821. Kim, Y. H.; Webster, O. W., *ACS Polym. Prepr.* **1988**, 29, 310. Kim, Y. H.; Webster, O. W., *J. Am. Chem. Soc.* **1990**, 112, 4592.

⁴⁴ Hawker, C. J.; Lee, R.; J., F. J. M., *J. Am. Chem. Soc.* **1991**, 113, 4583.

Hyperbranched polymers are known to possess properties similar to dendrimers, such as low viscosity, good solubility, unique thermal properties and good chemical reactivity.⁴⁵ Dendritic molecules have low viscosities because of their less entangled structure due to their spherical shape. Most hyperbranched polymers are amorphous, although crystalline hyperbranched polymers do exist. There are many unreacted chain ends in hyperbranched polymers, and the polymer properties are highly dependent on the nature of the end groups. Therefore, modifying the end groups provides a viable means of controlling the properties of these polymers.

The growing interest in hyperbranched polymers is due to their unique properties such as low viscosity and high functionality, which make hyperbranched polymers useful in several applications, such as functional crosslinkers, additives, modifiers in adhesives, coatings, structured hydrogels and dental composites.^{40,46} Hyperbranched polymers have also become useful in nanotechnology, for use as building blocks for nanoscale reaction parts, in biochemistry and biomedical applications, which include drug and gene delivery components, and finally in organic synthesis such as recyclable catalysts or high-loading supports.^{46,47}

2.2.2 Synthetic Routes to Hyperbranched Polymers

Hyperbranched polymers can be synthesized using condensation polymerization, ring opening polymerization,⁴⁸ and addition polymerization.^{46, 49} Various types of hyperbranched polymers including polyphenylenes, polyesters, polyethers, poly(ether ketones), poly(ether sulfones), polyamides, poly(ether imides), polyurethanes, polyureas, and polysiloxanes are synthesized using condensation polymerization.^{39,45,47,50}

As described by Flory (1952), hyperbranched polymers can be prepared by the self condensation of AB_n type monomers, where A and B units react with each other and

⁴⁵ Jikei, M.; Kakimoto, M. A., *High Perform. Polym.* **2001**, 13, S33.

⁴⁶ Burgath, A.; Sunder, A.; Frey, H., *Macromol. Chem. Phys.* **2000**, 201, 782. Mezzenga, R.; Boogh, L.; Månson, J.-A. E., *Composites Science and Technology* **2001**, 61, 787. Haag, R., *Chem. Eur. J.* **2001**, 7, 327.

⁴⁷ Kim, Y. H., *J. Polym. Sci. Part A: Polym. Chem.* **1998**, 36, 1685.

⁴⁸ Burgath, A.; Sunder, A.; Frey, H., *Macromol. Chem. Phys.* **2000**, 201, 782.

⁴⁹ Hawker, C. J.; Lee, R.; J., F. J. M., *J. Am. Chem. Soc.* **1991**, 113, 4583. Tokar, R.; Kubisa, P.; Penczek, S., *Macromolecules* **1994**, 27, 320. Burgath, A.; Sunder, A.; Frey, H., *Macromol. Chem. Phys.* **2000**, 201, 782. Sunder, A.; Mülhaupt, R.; Frey, H., *Macromolecules* **2000**, 33, 309.

⁵⁰ Gao, C.; Yan, D., *Prog. Polym. Sci.* **2004**, 29, 183.

n is equal to or greater than 2.³⁸ After hyperbranched polymers gained further recognition, several varieties of hyperbranched polyesters were synthesized and characterized using many different methods (Figure 2-10). Specifically, hyperbranched polyesters were prepared by self-condensation of different types AB₂ type monomers,^{44,51} condensation of AB₂ type monomer in the presence of a B_f type core molecule,⁵² condensation of AB₂/AB₃ type monomers with AB type monomers with different functionalities,^{29,43,53} or co-condensation of A₂ and B₃ type monomers. The last method has been a new synthetic strategy for the synthesis of hyperbranched polymers and there are several studies reported on the synthesis different types of hyperbranched polymers via polymerization of functionally symmetric A₂ and B₃ monomer pairs.

⁵¹ Gooden, J. K.; Gross, M. L.; Mueller, A.; Stefanescu, A. D.; Wooley, K. L., *J. Am. Chem. Soc.* **1998**, 120, 10180. Turner, S. R.; Voit, B. I.; Mourey, T. H., *Macromolecules* **1993**, 26, 2617. Turner, S. R.; Walter, F.; Voit, B. I.; Mourey, T. H., *Macromolecules* **1994**, 27, 1611. Gooden, J. K.; Gross, M. L.; Mueller, A.; Stefanescu, A. D.; Wooley, K. L., *J. Am. Chem. Soc.* **1998**, 120, 10180. Massa, D. J.; Shriner, K. A.; Turner, S. R.; Voit, B. I., *Macromolecules* **1995**, 28, 3214. Spindler, R.; Frechet, J. M. J., *Macromolecules* **1993**, 26, 4809. Hult, A.; Johansson, M.; Malmstrom, E., *Adv. Polym. Sci.* **1999**, 143, 1. Kumar, A.; Ramakrishnan, S., *J. Polym. Sci. Part A: Polym. Chem.* **1996**, 34, 839. Bolton, D. H.; Wooley, K. L., *J. Polym. Sci. Part A: Polym. Chem.* **2002**, 40, 823. Chu, F.; Hawker, C. J.; Pomery, P. J.; Hill, D. J. T., *J. Polym. Sci. Part A: Polym. Chem.* **1997**, 36, 1627. Hahn, S. W.; Yun, Y. K.; Jin, J. I., *Macromolecules* **1998**, 31, 6417. Schmaljohann, D.; Voit, B., *Macromol. Theory Simul.* **2003**, 12, 679. Schmaljohann, D.; Voit, B., *Macromol. Theory Simul.* **2003**, 12, 679. Parker, D.; Feast, W. J., *Macromolecules* **2001**, 34, 2048. Choi, J.; Kwak, S. Y., *Macromolecules* **2004**, 37, 3745.

⁵² Hult, A.; Johansson, M.; Malmstrom, E., *Adv. Polym. Sci.* **1999**, 143, 1. Möck, A.; Burgath, A.; Hanselmann, R.; Frey, H., *Macromolecules* **2001**, 34, 7692.

⁵³ Kricheldorf, H. R.; Stöber, O.; Lübbers, D., *Macromolecules* **1995**, 28, 2118. Kricheldorf, H. R.; Stukenbrock, T., *Polymer* **1997**, 38, 3373. Kricheldorf, H. R., *Macromol. Symp.* **1997**, 122, 15. Kricheldorf, H. R.; Stukenbrock, T., *J. Polym. Sci. Part A: Polym. Chem.* **1998**, 36, 31. Kricheldorf, H. R.; Stukenbrock, T., *J. Polym. Sci. Part A: Polym. Chem.* **1998**, 36, 2347. Kricheldorf, H. R.; Bolender, O.; Wollheim, T., *Macromolecules* **1999**, 32, 3878. Reina, A.; Gerken, A.; Zemann, U.; Kricheldorf, H. R., *Macromol. Chem. Phys.* **1999**, 200, 1784. Möck, A.; Burgath, A.; Hanselmann, R.; Frey, H., *Macromolecules* **2001**, 34, 7692. Gao, C.; Yan, D.; Zhu, X.; Huang, W., *Polymer* **2001**, 42, 7603.

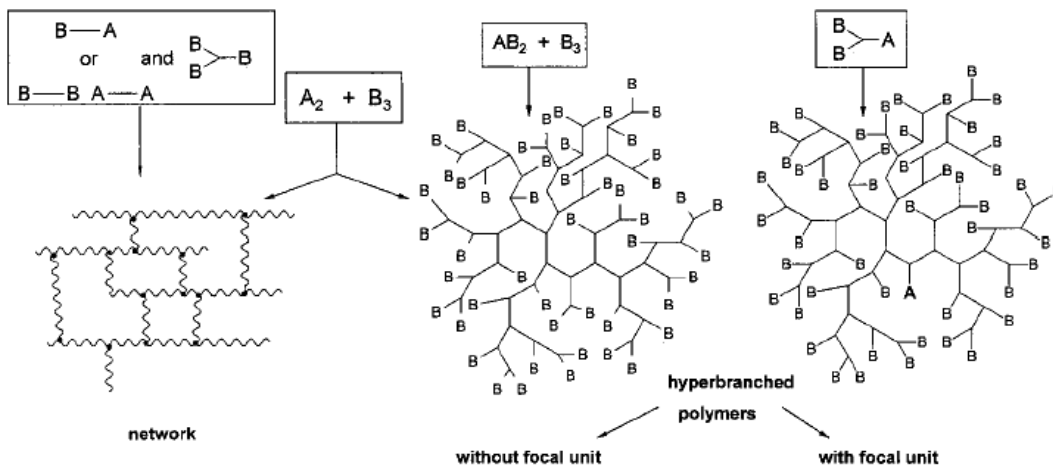


Figure 2-10. Synthetic methods for hyperbranched polymers.

2.2.3 Synthesis of Hyperbranched Polymers via Polymerization of Functionally Symmetric Monomer Pairs

2.2.3.1 Introduction

AB_n type monomers that contain one “A” functional group and *n* “B” functional groups undergo self-polycondensation or copolymerize with AB type monomers to generate hyperbranched polymers.³⁸ However, the limited commercial availability of functionally non-symmetric AB and AB_n type monomers has precluded industrial implementation. Polymerization of functionally symmetric monomer pairs such as A₂ and B_x (*x* ≥ 3) has emerged as an alternative approach to the classic AB_n type polymerization to synthesize hyperbranched polymers.^{54,55} Various combinations of functionally symmetric monomer pairs are possible including A₂ and B₄, A₃ and B₃, and A₂ and B₃; however A₂ and B₃ polymerization, also termed as A₂ + B₃, has received significant attention in the last decade as a more facile approach to synthesize hyperbranched polymers. Several types of difunctional (A₂) and trifunctional monomers (B₃) are commercially available, or much less effort is required to synthesize A₂ and B₃ monomers compared to AB_n monomers. The wide range commercially available A₂ and B₃ monomers also allow tailoring the polymer structure due to various choices of

⁵⁴ Jikei, M.; Chon, S. H.; Kakimoto, M. A.; Kawauchi, S.; Imase, T.; Watanebe, J., *Macromolecules* **1999**, 32, 2061.

⁵⁵ Emrick, T.; Chang, H. T.; Fréchet, J. M. J., *Macromolecules* **1999**, 32, 6380. Emrick, T.; Chang, H. T.; Fréchet, J. M. J., *J. Polym. Sci. Part A: Polym. Chem.* **2000**, 38, 4850.

monomer pairs and provide more facile routes to many families of hyperbranched polymers. Moreover, the risk of premature polymerization in some AB and AB_n type monomers is insignificant in the polymerization of separate functionally symmetric monomer pairs.⁵⁶

According to Flory's well-established theory, the direct polymerization of A₂ and B₃ monomers is a crosslinking strategy that results in a sol-gel system dependant on the A₂:B₃ molar ratio and functional group conversion.³⁸ Despite the high risk of gelation, the potential of A₂ + B₃ polymerization for many industrial applications has encouraged scientists to devote significant attention to the determination of reaction parameters to avoid gelation. The first two pioneering reports that described the synthesis of hyperbranched polymers using the A₂ + B₃ polymerization appeared in 1999. Kakimoto and coworkers reported the synthesis of hyperbranched aromatic polyamides which were derived from commercially available aromatic diamines (A₂) and trimesic acid (B₃).⁵⁴ In addition, Fréchet and coworkers demonstrated the synthesis of hyperbranched polyether epoxies via proton-transfer polymerization from 1,2,7,8-diepoxyoctane (A₂) and 1,1,1-tris(hydroxymethyl)ethane (B₃) using various molar ratios of A₂ and B₃.⁵⁵ Stopping the reactions immediately prior to gelation resulted in soluble, network-like products with reasonable molar mass and high degrees of branching, which resembled hyperbranched polymers.

After these two pioneering reports, several families of hyperbranched polymers, such as aromatic polyamides,⁵⁷ polyimides,^{58, 59} poly(ether sulfone)s,⁶⁰ poly(arylene ether)s,⁶¹ polyesters,^{62, 63} and polycarbonates,⁶⁴ were reported via the A₂ + B₃

⁵⁶ Voit, B., *J. Polym. Sci. Part A: Polym. Chem.* **2000**, 38, 2505.

⁵⁷ Russo, S.; Boulares, A.; Da Rin, A., *Macromol. Symp.* **1999**, 143, 309. Monticelli, O.; Mariani, A.; Voit, B.; Komber, H.; Mendichi, R.; Pitto, V.; Tabuani, D.; Russo, S., *High Perform. Polym.* **2001**, 13, S45. Monticelli, O.; Mariani, A.; Voit, B.; Komber, H.; Mendichi, R.; Pitto, V.; Tabuani, D.; Russo, S., *High Perform. Polym.* **2001**, 13, S45.

⁵⁸ Fang, J. F.; Kita, H.; Okamoto, K. I., *Macromolecules* **2000**, 33, 4639. Liu, Y.; Chung, T. S., *J. Polym. Sci. Part A: Polym. Chem.* **2002**, 40, 4563. Chen, H.; Yin, J., *Polym. Bull.* **2003**, 49, 313. Chen, H.; Yin, J., *J. Polym. Sci. Part A: Polym. Chem.* **2004**, 42, 1735. Köytepe, s.; Paşahan, A.; Ekinçi, E.; Seçkin, T., *Europ. Polym. J.* **2005**, 41, 121.

⁵⁹ Hao, J.; Jikei, M.; Kakimoto, M. A., *Macromolecules* **2002**, 35, 5372. Hao, J.; Jikei, M.; Kakimoto, M. A., *Macromol. Symp.* **2003**, 199, 233. Hao, J.; Jikei, M.; Kakimoto, M. A., *Macromolecules* **2003**, 36, 3519.

⁶⁰ Kricheldorf, H. R.; Vakhtangishvili, L.; Fritsch, D. J., *J. Polym. Sci. Part A: Polym. Chem.* **2002**, 40, 2967. Kricheldorf, H. R.; Fritsch, D. J.; Vakhtangishvili, L.; Schwarz, G., *Macromolecules* **2003**, 36, 4347.

⁶¹ Czupik, M.; Fossum, E., *J. Polym. Sci. Part A: Polym. Chem.* **2003**, 41, 3871.

polymerization. $A_2 + B_3$ addition reactions were also reported for the preparation of various hyperbranched polymers via Michael addition.^{56, 65, 66} The classic $A_2 + B_3$ approach was altered with monomer pairs such as $AA^* + B_3$, $A_2 + B^*B_2$, or $AA^* + B^*B_2$ to control the hyperbranched structure formation, where A and A^* or B and B^* were the same or similar type of functional groups exhibiting different reactivities.^{50, 67} These types of monomer pairs are not solely functionally symmetric and are, therefore excluded from this report.

Many researchers have asserted that various factors account for avoiding gelation and generating fully soluble, hyperbranched products. These factors include the formation of reactive intermediates that resemble the AB_2 type monomers,⁵⁴ partial conversion of functional groups,⁵⁵ slow addition of one monomer to another,⁶² significant levels of cyclization reactions,⁶⁰ and reactivity differences between identical functional groups within the same molecule.^{59, 63} If one or more of these factors arise, $A_2 + B_3$ polymerization deviates from ideal crosslinking conditions and the polymerizations results in high molar mass highly branched structures. In this review, the theoretical treatment of $A_2 + B_3$ polymerization and synthetic methods for preparing various gel-free hyperbranched polymers from functionally symmetrical monomer pairs are reported. Moreover, the influence of reaction parameters and the factors that mitigate gelation for new families of gel-free hyperbranched polymers are discussed.

2.2.3.2 Theoretical Treatment of $A_2 + B_3$ Polymerization

Flory first introduced the theory of gelation for nonlinear polymers in 1952.³⁸ According to this theory, polymerizations that contain multifunctional monomers (monomer units with functionalities higher than two) generate a three-dimensional network at a certain monomer conversion for a given stoichiometric ratio of functional groups. Therefore, treatment of $A_2 + B_3$ polymerization according to this theory and

⁶² Lin, Q.; Long, T. E., *Macromolecules* **2003**, 36, 9809.

⁶³ Stumbe, J.; Bruchmann, B., *Macromol. Rapid Commun.* **2004**, 25, 921.

⁶⁴ Scheel, A.; Komber, H.; Voit, B., *Macromol. Symp.* **2004**, 210, 101.

⁶⁵ Liu, Y. L.; Tsai, S. H.; Wu, C. S.; Jeng, R. J., *J. Polym. Sci. Part A: Polym. Chem.* **2004**, 42, 5921.

⁶⁶ Tang, L. M.; Fang, Y.; Feng, J., *Polymer Journal (Tokyo)* **2005**, 37, 255.

⁶⁷ Yan, D.; Gao, C., *Macromolecules* **2000**, 33, 7693. Gao, C.; Yan, D.; Zhu, X.; Huang, W., *Polymer* **2001**, 42, 7603. Gao, C.; Tang, W.; Yan, D., *J. Polym. Sci. Part A: Polym. Chem.* **2002**, 40, 2340. Liu, Y.; Wu, D.; Ma, Y.; Tang, G.; Wang, S.; He, C.; Chung, T.; Goh, S., *Chem. Comm.* **2003**, 2630. Zheng, Z.; Pan, C.; Wang, D.; Liu, Y., *Macromol. Chem. Phys.* **2005**, 206, 2182.

determination of the gel point are essential to synthesize gel-free hyperbranched polymers. In a nonlinear polymerization system, such as $A_2 + B_3$, a branching coefficient, α , is defined as the probability that a given functional group of a branch unit (B_3) is linked to another branch unit. In general, α can be calculated from the ratio of the “A” and “B” functional groups and the extent of reaction at a given time. In the case of an $A_2 + B_3$ polymerization, α can be calculated using Equation 2-3,

$$\alpha = r \times p_A^2 = p_B^2 / r$$

Equation 2-3

where r is the ratio of A to B groups (A:B), and p_B and p_A are the fraction of A and B groups that have reacted. Another important term is the critical branching coefficient (α_c), which defines the gel point. For a given r value, α increases as a function of the extent of reaction. An infinite network is formed when α reaches a critical value, α_c . The critical branching coefficient (α_c) is calculated as;

$$\alpha_c = \frac{1}{(f-1)}$$

Equation 2-4

where f denotes the average functionality of multifunctional monomers in the system. Therefore, α_c becomes 0.5 for an $A_2 + B_3$ polymerization since only trifunctional monomer is present as a multifunctional monomer. During polymerization, a fully soluble product is present when $\alpha < \alpha_c$, and a sol-gel mixture begins to appear when $\alpha > \alpha_c$. As calculated from Equation 1, the maximum α value is equal to one, which resembles a fully crosslinked system. The value of α can also be correlated to the degree of branching of a product, which apparently increases as a function of monomer conversion. In addition, the weight fractions of sol-gel are proportional to α in the $\alpha_c < \alpha < 1$ regime. In an $A_2 + B_3$ polymerization, it is important to calculate the critical conversion of A and B groups (p_{Ac} and p_{Bc}) at the gel point for various r values, based on Equation 2-3 and Equation 2-4. Table 2-1 summarizes the critical conversion of A and B groups for various A to B ratios. As the molar ratio of A to B functional groups is increased, the gel

point is reached sooner, at a lower monomer conversion, and gelation becomes more difficult to avoid.

Table 2-1. Calculation of gel point in $A_2 + B_3$ polymerization ($\alpha_c=0.5$) for various monomer ratios using Equation 2-3 and Equation 2-4.

$A_2:B_3$	$r = A:B$	p_{Ac}	p_{Bc}
0.75:1.00	0.50	1.000	0.500
0.90:1.00	0.60	0.913	0.548
1.00:1.00	0.67	0.866	0.577
1.25:1.00	0.83	0.775	0.645
1.50:1.00	1.00	0.707	0.707
2.00:1.00	1.33	0.612	0.816
3.00:1.00	2.00	0.500	1.000

It should be noted that Flory's well-established theory on gelation is based on the following assumptions: (1) the reactivity of the functional groups remains constant during polymerization, (2) the reactions do not involve cyclization, and (3) the polymerization is restricted to the reaction between A and B groups. As discussed later, deviations from these assumptions may shift the gel point to higher conversions and avoid gelation, resulting in high molar mass, highly branched structures.⁵⁹

Other than Flory's theory for gel formation, there are few significant reports on the theoretical treatment of $A_2 + B_3$ polymerizations. Voit and Schmaljohann reported a theoretical simulation of structural development and reported the influence of several factors such as composition, kinetics, and monomer addition on the resulting hyperbranched polymer via the $A_2 + B_3$ polymerization.⁶⁸ Seven types of different structural units, such as substructures of linear, dendritic, and terminal units, were identified based on different monomer sequences and adjacent groups of each structural unit. Initial monomer composition played an important role in determining the ratio of these structural units in the final product. The structural units and monomer sequences as

⁶⁸ Schmaljohann, D.; Voit, B., *Macromol. Theory Simul.* **2003**, 12, 679.

predicted in theoretical calculations were also reported experimentally using detailed NMR spectroscopic analysis.⁶⁹

Determination of the degree of branching is an essential metric for hyperbranched polymers. Several equations were developed earlier to define the structure of hyperbranched polymers based on the self-condensation of AB₂ monomers.^{39,45} The degree of branching (DB(Fréchet)) was described as the ratio of the sum of fully branched and terminal units to the total number of units,⁴⁴

$$DB = (D + T)/(D + T + L)$$

Equation 2-5

where D, T, and L correspond to the total number of dendritic, terminal, and linear units, respectively, and $D + T + L = 1$. Frey and coworkers alternatively defined the degree of branching (DB(Frey)) according to Equation 2-6.⁷⁰

$$DB = 2D/(2D + T)$$

Equation 2-6

In most cases, these equations are also applicable to the products of A₂ + B₃ polymerization.

Voit and Schmaljohann reported theoretical calculations at various monomer compositions demonstrating that higher degrees of branching (DB(Frey)) are achieved at higher A₂ to B₃ monomer ratios. Gelation occurs at p_A values as the A₂ to B₃ monomer ratio is increased (Figure 2-11).⁶⁸ The discontinuity in each plot indicates the gel point at a corresponding p_A . Differences in the reaction rate constants for the conversion of the A₂ monomer influenced the degree of branching, and slow addition of either both monomers or just the B₃ monomer had the strongest effect on the resulting higher DB. In all cases, high conversion without gelation was critical for high molar mass products.

Recent reports in our laboratories provided a comparative study of experimental results and theoretical simulations for the synthesis of highly branched, segmented poly(urethane urea)s (HB-PUU), where a dilute solution of an A₂ oligomer (polyether

⁶⁹ Monticelli, O.; Mariani, A.; Voit, B.; Komber, H.; Mendichi, R.; Pitto, V.; Tabuani, D.; Russo, S., *High Perform. Polym.* **2001**, 13, S45.

⁷⁰ Hölter, D.; Burgath, A.; Frey, H., *Acta Polym.* **1997**, 48, 30.

diisocyanate) was slowly added into a B₃ (triamine)solution.⁷¹ The HB-PUU molar mass increase was monitored as a function of A₂ addition using SEC analysis. The experimental procedure was modeled using Monte-Carlo (MC) simulations to better understand the molar mass increase and structure development.

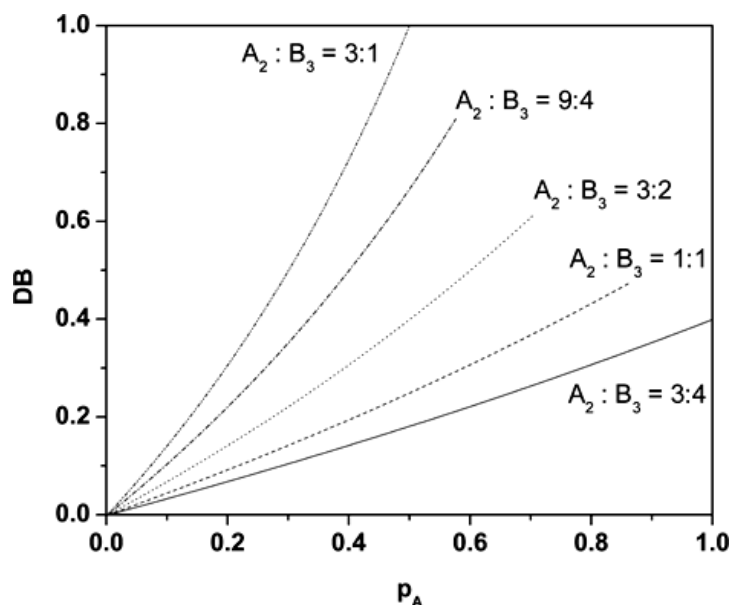


Figure 2-11. Theoretical simulation of DB versus conversion of A functional groups (p_A) for various A₂:B₃ monomer ratios.⁶⁸

Similar to the experimental procedure, N molecules of A₂ were sequentially added into N molecules of B₃. When MC simulations were employed in the absence of cyclization, reactions between A and B groups on the same molecule were not allowed. However, as discussed later, cyclization is a very important factor that accounts for deviations from theoretical assumptions and a significant shift in the gel point during the synthesis of hyperbranched polymers.^{60,72,73} It is well known that dilute solutions favor cyclization reactions and cyclic macromolecules are generally prepared under very dilute conditions (~below 5% solids).

In an attempt to simulate experimental conditions, a cyclization parameter (γ) was introduced based on selected probabilities for the reaction between A and B groups

⁷¹ McKee, M.; Unal, S.; Wilkes, G. L.; Long, T. E., *Prog. Polym. Sci.* **2005**, 30, 507.

⁷² Kricheldorf, H. R.; Schwarz, G., *Macromol. Rapid Commun.* **2003**, 24, 359. Kricheldorf, H. R.; Hobzova, R.; Schwarz, G.; Vakhtangishvili, L., *Macromolecules* **2005**, 38, 1736.

⁷³ Burgath, A.; Sunder, A.; Frey, H., *Macromol. Chem. Phys.* **2000**, 201, 782.

within the same molecule. The value of γ varied between 0 (no cyclization) and 1 (highest cyclization ratio) and the structural characteristics such as the molar mass, polydispersity, degree of branching, and number of cycles per molecule were monitored. The experimental and theoretical molar mass data are plotted in Figure 2.⁷¹ The experimental values for the polymerizations at 25% solids in Figure 2(a) agree fairly well with the simulations at low cyclization ratios ($\gamma=0-0.001$). At lower concentrations (10% solids) that are known to promote cyclization experimental values agreed very well with the theoretical data at a higher cyclization ratio ($\gamma=0.1$). Figure 2(b) shows that cyclization also plays an important role in the polydispersity of the final products. MC simulations suggest that higher polydispersities are achieved at lower cyclization ratios. In summary, MC simulations with a cyclization parameter f clearly demonstrated that cyclization reactions have a great influence on the final polymer product in the slow addition of an A_2 monomer to a B_3 monomer.

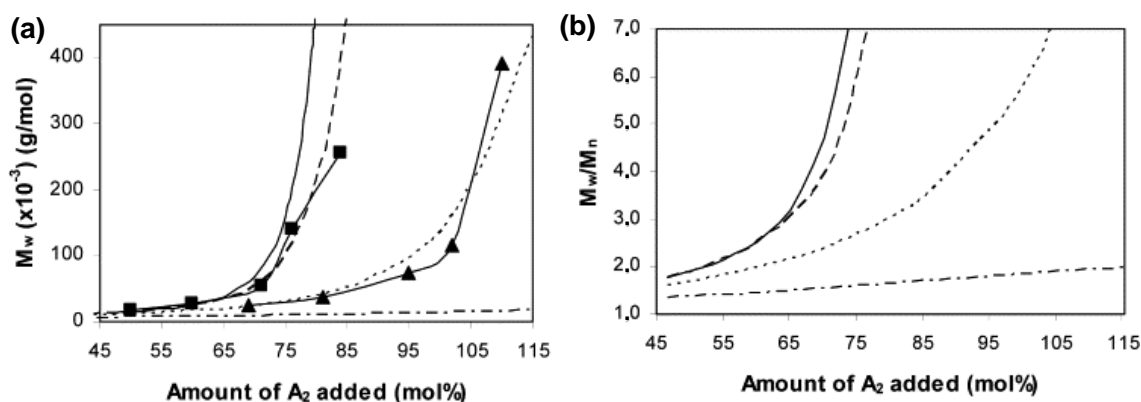


Figure 2-12. Comparison of experimental and simulation results on the development of (a) weight average molar mass and (b) polydispersity as a function of A_2 addition and cyclization ratio. Experimental data: Molar masses from SEC analysis. Polymerization conducted in (■) 25 wt %, (▲) 10 wt % by solids. Simulation data: (—) $\gamma=0$, (---) $\gamma=0.01$, (- - -) $\gamma=0.1$, and (- - - -) $\gamma=1$.

2.2.3.3 Polymerization of Symmetrical Monomer Pairs

2.2.3.3.1 Hyperbranched Polyamides

Kakimoto and coworkers reported the direct polycondensation of aromatic diamines (A_2) and trimesic acid (B_3) as a new approach to synthesize hyperbranched

aromatic polyamides as shown in Figure 2-13.⁷⁴ Equimolar amounts of diamines and trimesic acid were polymerized ($A_2:B_3 = 1:1$, $A:B = 2:3$) in the presence of triphenyl phosphite and pyridine as the condensation agents and NMP as the solvent. While the reaction mixture with a 1:1 molar ratio of monomers was expected to crosslink at $P_{Ac} = 86.6\%$, no gelation was experimentally observed. This apparent discrepancy was explained by the formation of an 'A-ab-(B')₂ type intermediate when the reaction was kinetically controlled, and the first condensation reaction of A_2 and B_3 was faster than subsequent propagation (Figure 2-13). This intermediate resembled the common AB_2 type molecule, and the polymerization of this intermediate proceeded without gelation.

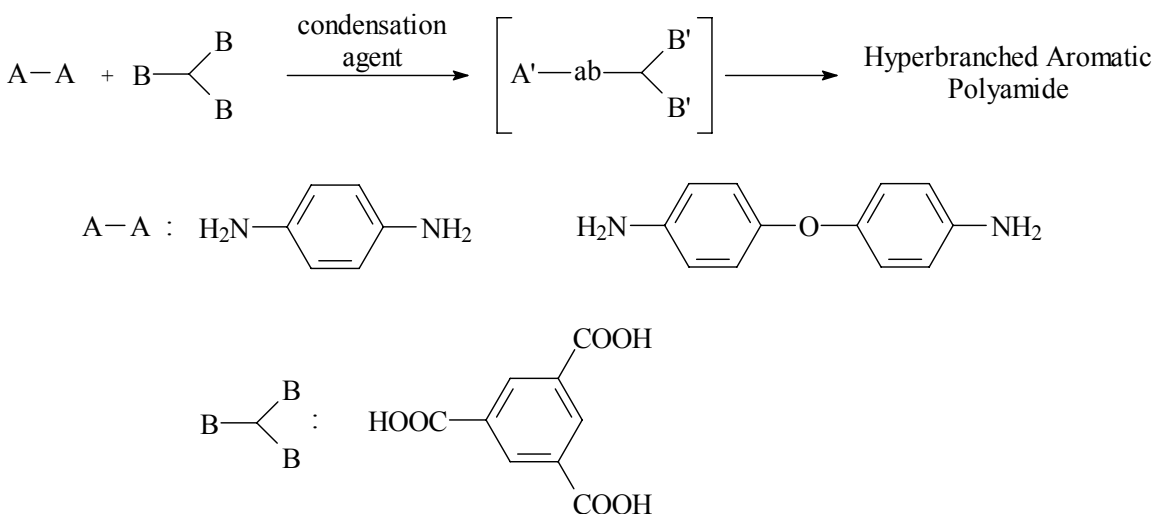


Figure 2-13. Synthesis of hyperbranched aromatic polyamides from aromatic diamines (A_2) and trimesic acid (B_3).

Gel-free products were only prepared in dilute solutions (as low as 4 wt %), and gelation was inevitable when the amount of solvent was reduced. Jikei and Kakimoto compared the structural features of hyperbranched aromatic polyamides that were prepared using both $A_2 + B_3$ and AB_2 polymerizations.⁷⁴ ¹³C NMR spectroscopy revealed that although both polymers had similar DB values, hyperbranched polyamides from $A_2 + B_3$ had a larger number of dendritic units relative to terminal units, whereas the number of dendritic and terminal units was nearly equal in hyperbranched polyamides

⁷⁴ Jikei, M.; Kakimoto, M. A., *High Perform. Polym.* **2001**, 13, S33.

from AB₂ polymerization. Therefore, A₂ + B₃ polymers had higher inherent viscosities than the more conventional AB₂ polymers.

Russo, Voit, Komber, and coworkers subsequently reported the synthesis of hyperbranched aromatic polyamides via A₂ + B₃ polymerization and studied the influence of various reaction parameters such as initial monomer ratio on gel formation and final polymer structure.^{57,75,76} When the polymerizations were stopped prior to gelation for A₂:B₃ = 1:1 (A:B=2:3) and A₂:B₃ = 3:2 (A:B = 1) ratios, the number and nature of endgroups, as well as the degree of branching, varied. Stopping the reaction immediately prior to gelation resulted in partial monomer conversion. Therefore, final products possessed both amine (A) and carboxylic acid (B) endgroups, and the relative number of these endgroups depended on the initial ratio of A₂ and B₃.

Detailed ¹H, ¹³C, and 2D NMR spectroscopic analyses were used to characterize the microstructures present in a hyperbranched aromatic polyamide.⁶⁹ Various structural units were assigned in a hyperbranched aromatic polyamide, based on the monomer sequence and the nature of the endgroups as shown in Figure 2-14. In the early stages of the polymerization, only AB₂, A₂B, and A₃ type structures form (Figure 2-14, top row). The reaction of an A group in the top row with a B functionality transforms this group to A', which connects two B₃ units. In general, products from A₂ + B₃ were similar to products of AB₂ polymerization in terms of intrinsic viscosity and thermal properties, but possessed different ratios of structural units. DB also varied and deviated from the classic 50% value for AB₂ polymers due to differences in the structural units with varying A₂:B₃ ratio. Finally, polymerization of A₂ and B₃ monomers in a ratio of 0.71:1.00 (A:B=0.5) yielded only low molar mass oligomers with a low fraction of dendritic units.

Hyperbranched aromatic polyamides were evaluated as potential supporting materials for protein immobilization⁷⁵ and palladium nanoparticles.⁷⁶ When the hyperbranched polyamides were used as the polymeric matrix in a solution containing Pd nanoparticles, the interaction between the amine endgroups and the metallic precursor (PdCl₂) tailored the stability of the solution. The number of amine groups affected the

⁷⁵ Cosulich, M. E.; Russo, S.; Pasquale, S.; Mariani, A., *Polymer* **2000**, 41, 4951.

⁷⁶ Monticelli, O.; Mariani, A.; Voit, B.; Komber, H.; Mendichi, R.; Pitto, V.; Tabuani, D.; Russo, S., *High Perform. Polym.* **2001**, 13, S45. Monticelli, O.; Mariani, A.; Voit, B.; Komber, H.; Mendichi, R.; Pitto, V.; Tabuani, D.; Russo, S., *High Perform. Polym.* **2001**, 13, S45. Monticelli, O.; Russo, S.; Campagna, R.; Voit, B., *Polymer* **2005**, 46, 3597.

extent of nanoparticle stability in solution. The Pd nanoparticle solutions were stable up to 5 months under optimized conditions using an $A_2 + B_3$ hyperbranched polyamide as the polymeric matrix.

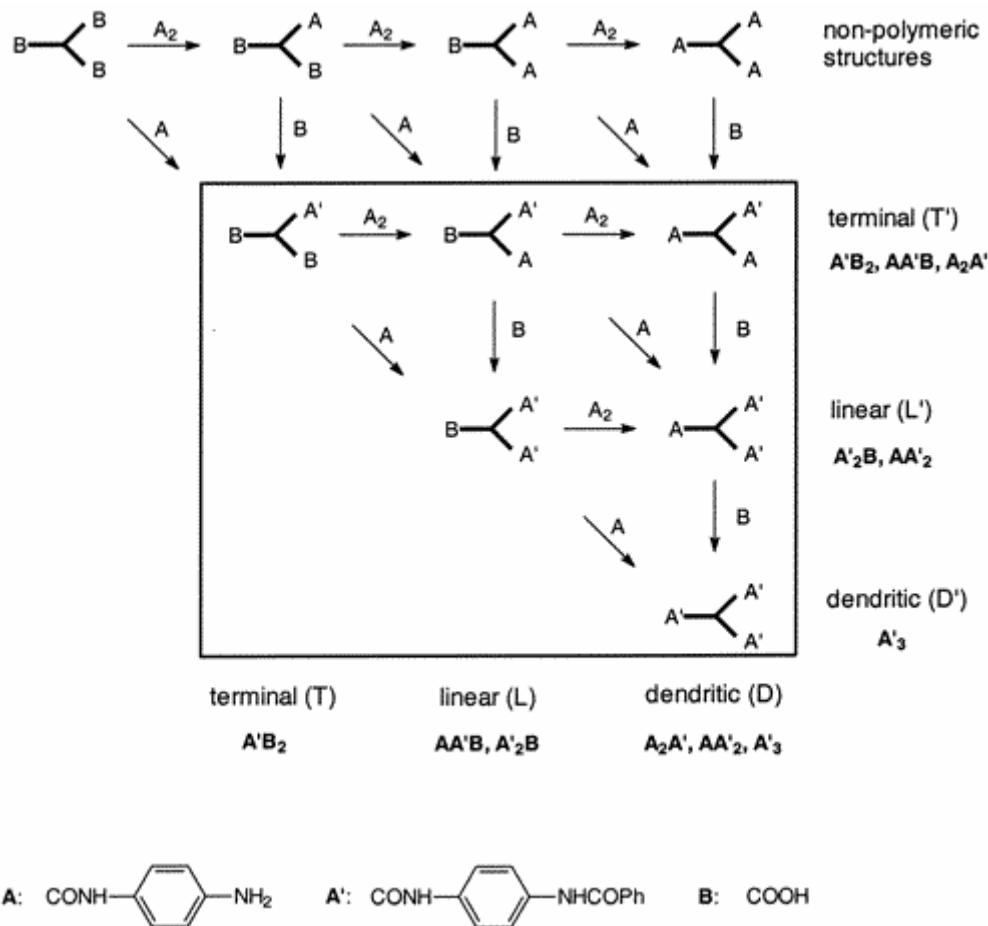


Figure 2-14. Structural units and reaction pathways for the polycondensation of *p*-phenylenediamine (A_2) and trimesic acid (B_3).⁶⁹

2.2.3.3.2 Hyperbranched Polyimides

Synthesis of hyperbranched aromatic polyimides using A_2 and B_3 monomers (Figure 2-15) was reported by Okamoto *et al.* for the first time using a series of commercially available dianhydrides (A_2) and a triamine, tris(4-aminophenyl)amine (TAPA, B_3), synthesized from tris(4-nitrophenyl)amine in one step.⁵⁸ Previously, preparation of wholly aromatic hyperbranched polyimides using the conventional AB_2 polymerization was not feasible due to the high reaction rates between anhydrides and

amines. A functionally nonsymmetric monomer that possesses two complimentary reactive sites such as anhydride and amine would not exist due to premature reaction.

In the polymerization of dianhydrides (A_2) and triamines (B_3), different orders of monomer addition resulted in hyperbranched polymers with different endgroups. In the first approach, a dianhydride (A_2) solution was added to a TAPA (B_3) solution in a 1:1 molar ratio, resulting in an amine terminated hyperbranched polyimide with DB values ranging from 64 to 72% depending on the dianhydride selection.

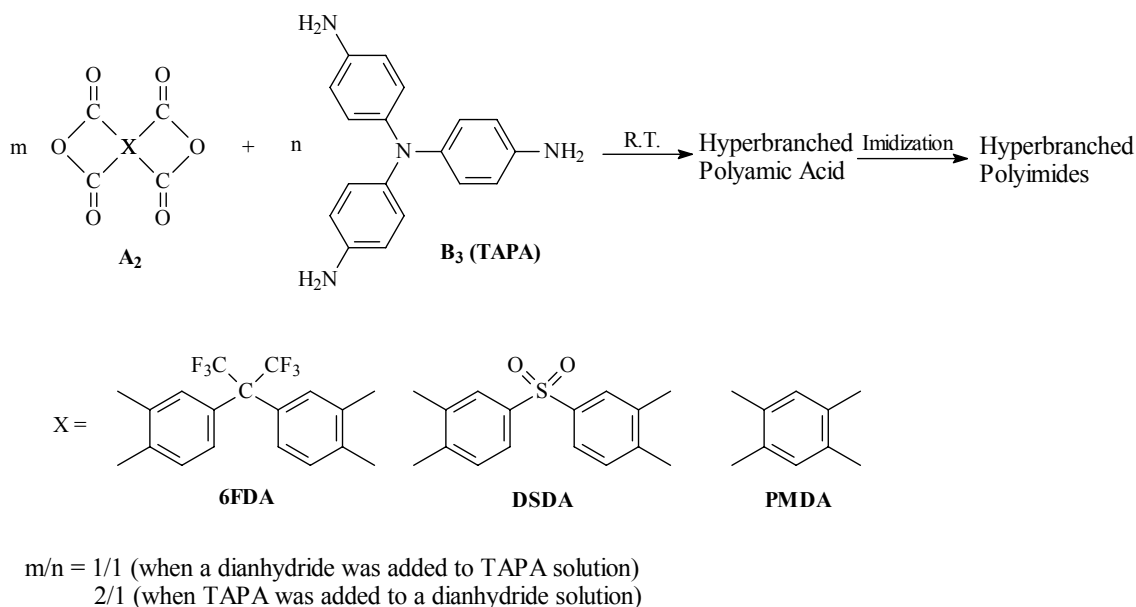


Figure 2-15. Synthesis of wholly aromatic hyperbranched polyimides from A_2 and B_3 monomers.

The final product, that was derived from 6FDA (Figure 2-15), had a weight average molar mass of 37,000 and a polydispersity of 5.8. Slow addition of a TAPA (B_3) solution into a dianhydride (A_2) solution at $A_2:B_3=2:1$ ($A:B = 4:3$) ratio resulted in wholly branched, anhydride-terminated polyimides. The final product that was derived from DSDA (Figure 2-15) had a weight average molar mass of 150,000 and a polydispersity of 18. Gelation occurred immediately when the rate of monomer addition was too fast, or the monomers were mixed at the onset of the reaction. In both approaches, higher monomer concentrations in solution resulted in gelation and were maintained below a critical concentration value to avoid gelation.

Despite the fact that slow addition of one monomer into another at an optimized molar ratio seemed to avoid gelation, significant effort was not devoted to understand the apparent discrepancy with Flory's theory behind the formation of fully soluble products. Kakimoto *et al.* subsequently reported a non-ideal $A_2 + B_3$ polymerization approach to prepare hyperbranched polyimides using a more convenient polymerization strategy.⁵⁹ Two novel B_3 monomers, tri(phthalic anhydride) and tri(phthalic acid methyl ester), were synthesized for this purpose (Figure 2-16).

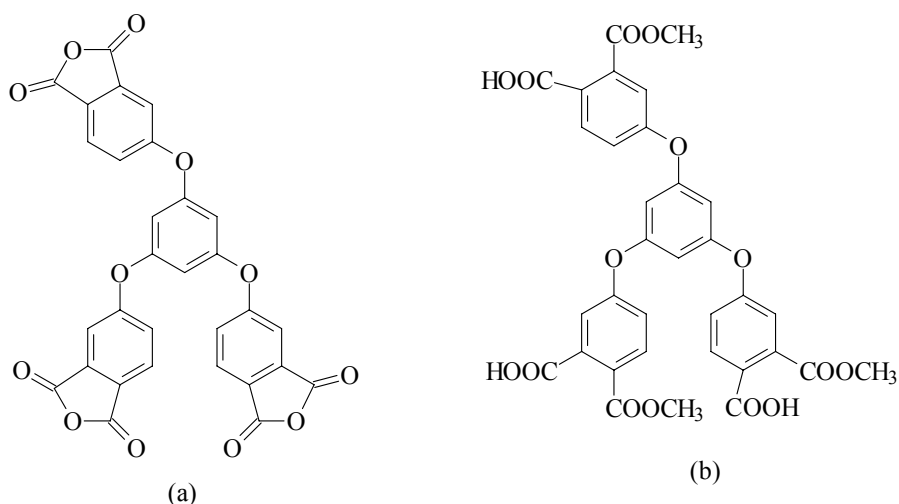


Figure 2-16. B_3 monomers used by Kakimoto *et al.* (a) tri(phthalic anhydride), (b) tri(phthalic acid methyl ester).

Polymerization of 1,4-phenylenediamine (A_2) and tri(phthalic anhydride) (B_3) resembled an ideal $A_2 + B_3$ polymerization; however, it was difficult to assess the preferred monomer addition strategy, i.e., mixed monomers at the onset or A_2 monomer addition into B_3 due to high reactivity.⁵⁹ The final products had limited solubilities in common organic solvents. Therefore, a non-ideal $A_2 + B_3$ system was preferred to prepare hyperbranched polyimides from 1,4-phenylenediamine (A_2) and tri(phthalic acid methyl ester) (B_3) in the presence of a condensation agent (DBOP). The presence of the condensation agent effectively prevented the carboxylic acid groups from reacting with amine nucleophiles at once; two different competing active intermediates were formed early in the polymerization that were reactive toward amine nucleophiles, one having a lower tendency for reaction.

Deviation from the assumption that functional group reactivity remains constant during polymerization clearly avoids gelation in a non-ideal $A_2 + B_3$ polymerization. Monomer concentration was effectively optimized to obtain polyimides with a high DB. The content of dendritic units increased as the monomer concentration was increased, and above a critical concentration (0.08 g/mL), high molar mass products with high DB (above 50%) were obtained.

Two hyperbranched polymers, one derived from non-ideal $A_2 + B_3$ monomer pairs and one derived from an AB_2 monomer, had the same repeating unit, but distinct physical properties.⁵⁹ Hyperbranched polymers from the non-ideal $A_2 + B_3$ polymerization had a much higher inherent viscosity and formed self-standing films with superior mechanical properties relative to the AB_2 self-condensation product. These studies revealed that chain entanglements were present to some extent in the non-ideal $A_2 + B_3$ polymerization. As shown in Figure 2-17, this was attributed to the formation of linear oligomers at early stages of non-ideal $A_2 + B_3$ polymerization, resulting in loose-packing and a lower branching density compared to the AB_2 self-condensation product.⁵⁹

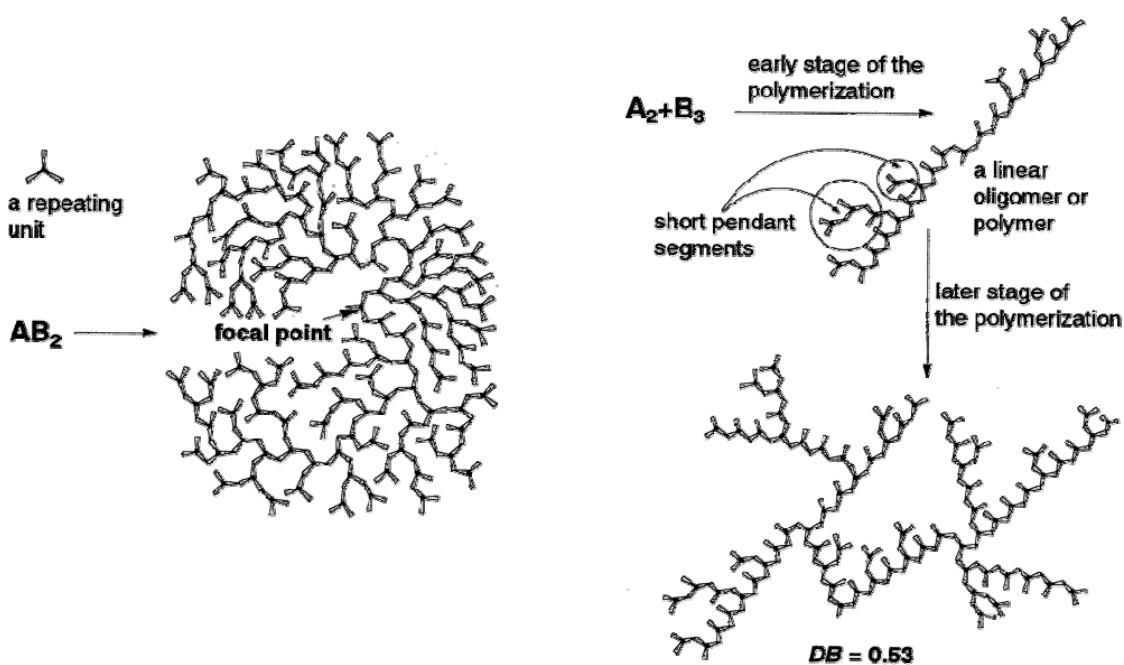


Figure 2-17. Molecular topologies of hyperbranched polyimides by AB_2 self-condensation and non-ideal $A_2 + B_3$ polymerization.⁵⁹

2.2.3.3.3 Hyperbranched Polyethers

Kricheldorf *et al.* studied the $A_2 + B_3$ polymerization and used matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF/MS) as a powerful tool for the analysis of these complex reaction mixtures. Detailed MALDI-TOF/MS studies on various step-growth polymers, such as polyesters, polyamides, polyimides, polycarbonates, poly(ether sulfone)s, and poly(ether ketone)s, demonstrated that cyclization competes with chain growth during all stages of a step-growth polymerization (even for linear polymers) and at all concentrations.⁷² MALDI-TOF/MS characterization revealed that the final structure of the $A_2 + B_3$ polymerization products is very sensitive to cyclization reactions. Extensive cyclization during the $A_2 + B_3$ polymerization avoids gelation, and produce branched polymers with cyclic building blocks or a mixture of branched and multicyclic polymers.^{60,72}

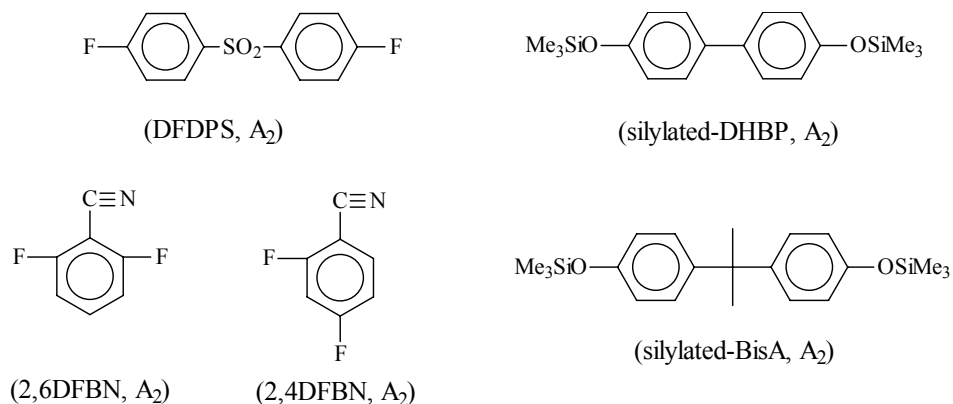


Figure 2-18. Chemical structure of A_2 monomers commonly used by Kricheldorf *et al.*

When 4,4'-difluorodiphenyl sulfone (DFDPS, A_2 , Figure 2-18) and 1,1,1-tris(4-hydroxyphenyl)ethane (THPE, B_3 , Figure 2-19) were polymerized in a 1:1 molar ratio to prepare poly(ether sulfone)s, gelation was avoided, and MALDI-TOF/MS detected significant fractions of cyclic components.⁶⁰ An excess of 10 mol% DFDPS (A_2) resulted in gelation when polymerized with THPE (B_3), while polymerization of DFDPS (A_2) with silylated-THPE (Figure 2-19, B_3) at molar ratios of $A_2:B_3 = 1.0:1.0$ or $1.1:1.0$ did not result in gelation. As expected, the $A_2:B_3 = 1.1:1.0$ ratio yielded higher molar mass products. An increase in the $A_2:B_3$ ratio to $1.2:1.0$ resulted in gelation.

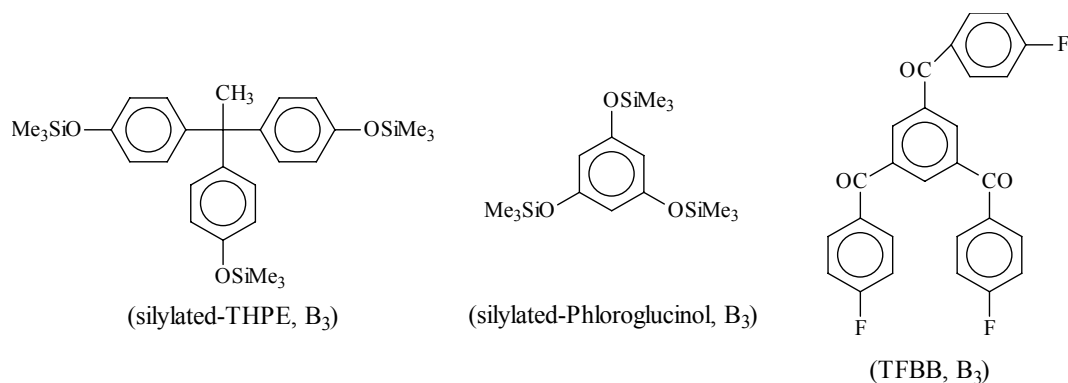


Figure 2-19. Chemical structure of B₃ monomers used by Kricheldorf *et al.*

MALDI-TOF/MS revealed the presence of significant fractions of cyclic components detectable up to a degree of polymerization of 16 (C16) (Figure 2-20 (a)). More complex cyclic structures, such as bicyclic oligo(ether sulfone)s (Figure 2-20 (b)) were also detected using MALDI-TOF/MS.

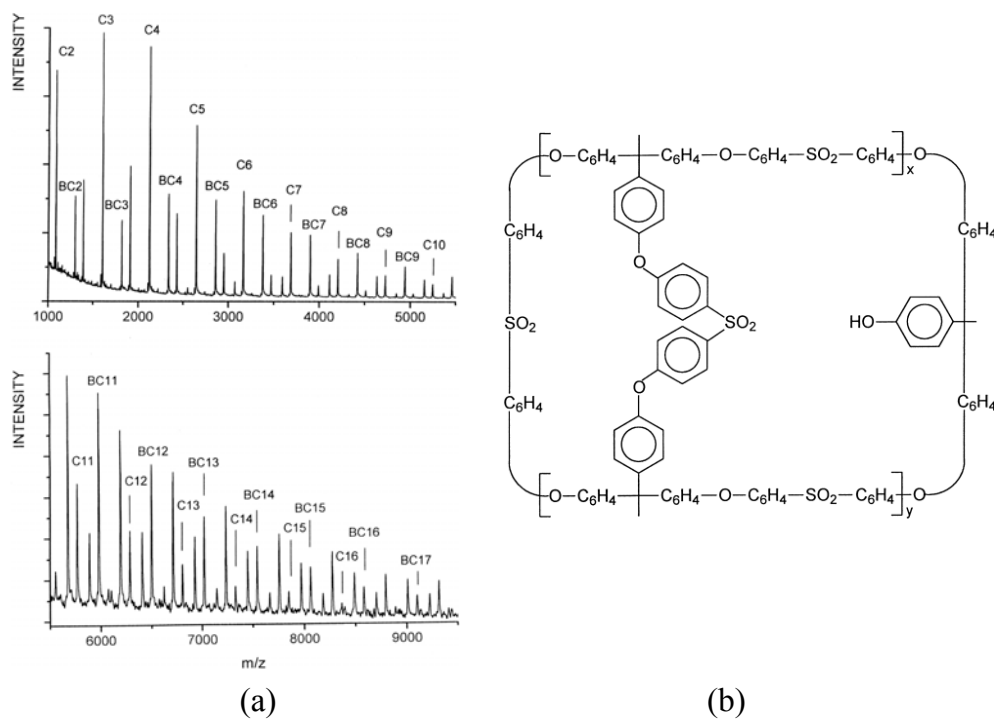


Figure 2-20. (a) Typical MALDI-TOF mass spectrum of a hyperbranched poly(ether sulfone) from DFDPS (A₂) and silylated-THPE (B₃) with A₂:B₃ = 1.1:1.0 (b) Proposed bridged cyclic (bicyclic) oligo(ether sulfone)s detected (labeled as BC).

Kricheldorf and coworkers also established a nomenclature, B_xC_Y in order to denote the number of “bridge units” (x) and total number of repeating units (Y).⁶⁰ In a similar fashion, MALDI-TOF revealed a high degree of cyclization and a significant fraction of multicyclic product that was derived from a 1:1 ratio of DFDPS (A₂, Figure 2-18) and silylated phloroglucinol (B₃, Figure 2-19). Gelation was observed when 30 mol % excess of DFDPS (A₂) was added. The final branched and cross-linked polymers mainly consisted of cyclic building blocks.⁸⁹

The influence of chain stiffness also plays an important role on the extent of cyclization. 1,3,5-tris(4-fluorobenzoyl)benzene (TFBB, B₃, Figure 2-19) was polymerized with silylated diphenols (DHBP and BisA as A₂, Figure 2-18) of varying chain stiffness to synthesize poly(ether ketone)s.⁷² Polymerization of TFBB (B₃) with silylated-DHBP showed a lower cyclization tendency and resulted in partially cross-linked products even at a 1:1 ratio of A₂:B₃, whereas cyclic and multicyclic poly(ether ketone)s were obtained up to a 1.3:1.0 = A₂:B₃ ratio without gelation when silylated-BisA was used. Kricheldorf *et al.* also reported the influence of structural isomerism on cyclization in A₂ + B₃ polymerization.⁷² Polycondensation of silylated-THPE (B₃, Figure 2-19) with either 2,6-difluorobenzonitrile (2,6DFBN, A₂) or 2,4-difluorobenzonitrile (2,4DFBN, A₂) (Figure 2-18) in a 1:1 molar ratio produced completely soluble polyethers. Gelation was observed with a 10 mol % increase in 2,6DFBN, whereas completely soluble products were obtained even with a 50 mol% excess of 2,4DFBN. Such a difference in cyclization tendency was attributed to the different isomer conformations favored by energy minimization.

Czupik and Fossum reported the synthesis of a series of hyperbranched poly(arylene ether phosphine oxide)s (HB-PAEPOs) via the polymerization of a variety of bisphenols (A₂) and tris(4-fluorophenyl)phosphine oxide (TFPO, B₃, Figure 2-21).⁶¹ The influence of various reaction parameters, such as A₂ monomer reactivity, A:B ratio (A₂:B₃), addition mode, solvent, and concentration, on the final molar mass, polydispersity, and DB was studied. The B₃ monomer, TFPO, was synthesized to provide a spectroscopic handle (³¹P NMR) to study the development of branching during the reaction. Polymerization of bisphenol-A (A₂, Figure 2-21, 2a) with TFPO (B₃) in toluene/N-methyl pyrrolidone (NMP) at a A₂:B₃ = 1:1 molar ratio yielded products with

weight average molar mass values as high as 220,000 g/mol. When the A₂:B₃ ratio was increased, a significant decrease in the time required to reach the gel point was observed. Monomer concentration in solution also affected the final properties of the products. Decreasing the concentration from 0.176 to 0.050 mol/L resulted in low molar mass products and a gel point was not reached, which is indicative of extensive cyclization reactions that are promoted in dilute solution. When a bisphenol-A (A₂) solution was added to a TFPO (B₃) solution over 6 h to achieve a A₂:B₃ = 1:1 ratio, the weight average molar mass increased to 299,000 g/mol with a polydispersity of 24. In contrast, only 85% of TFPO (B₃) solution could be added to the bisphenol-A (A₂) solution before the gel point was reached.

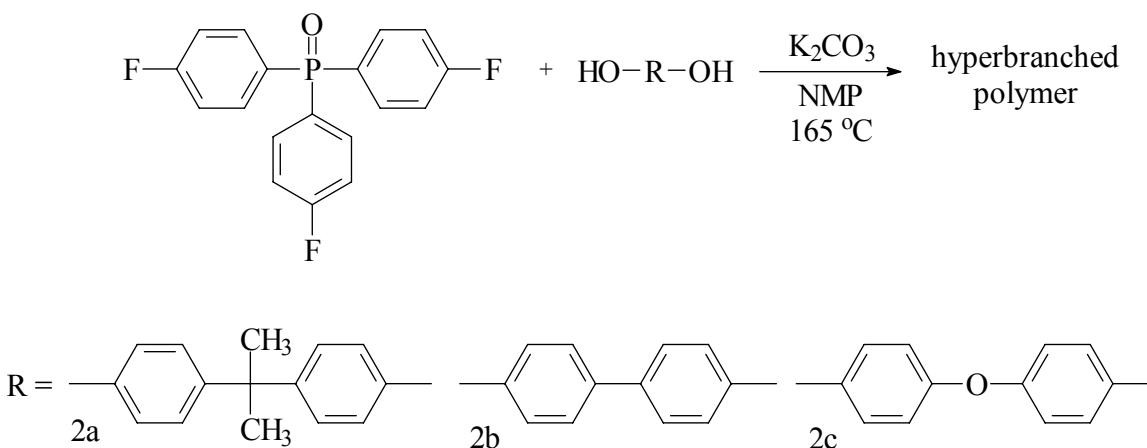


Figure 2-21. Synthesis of hyperbranched poly(arylene ether phosphine oxide)s (HB-PAEPOs) via the polymerization of a variety of bisphenols as A₂ and tris(4-fluorophenyl)phosphine oxide (TFPO) as B₃.

As depicted in Figure 2-22, ³¹P NMR allowed the investigation of the branched structure of the final products. When A₂ was added to B₃, DB was monitored over time using ³¹P NMR spectroscopy. The final polymeric product had a DB value of 54%. In contrast, the final soluble product obtained from the slow addition of B₃ to A₂ had a DB value of 70% when only 80% of B₃ was added. Reactions under more dilute conditions also resulted in similar DB values; however, the presence of a downfield signal was more significant (Figure 2-22, right (f)) and attributed to intermolecular cyclization products.

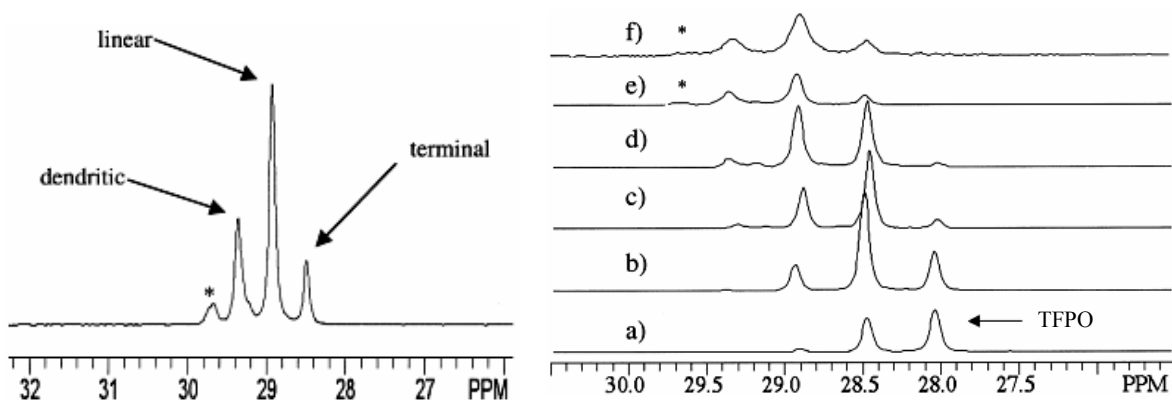


Figure 2-22. (left) Typical ^{31}P NMR spectrum of a HB-PAEPO and (right) ^{31}P NMR spectra at various reaction times of HB-PAEPO synthesized via the slow addition of A_2 into B_3 .

2.2.3.3.4 Hyperbranched Polyesters

Long *et al.* reported the synthesis of hyperbranched aromatic polyesters via the slow addition of a dilute bisphenol-A (A_2) solution into a dilute 1,3,5-benzenetricarbonyl trichloride (BTC, B_3) solution at room temperature (Figure 2-23).⁶² The molar ratio of $\text{A}_2:\text{B}_3$ was maintained at 1:1 and the maximum final monomer concentration was ~ 0.08 mol/L to obtain gel-free products. The residual acid chloride functional groups (B) were further reacted with methanol to obtain methyl ester terminated hyperbranched aromatic polyesters. ^1H NMR spectroscopy revealed a DB value of $\sim 50\%$ with the aid of model dendritic, terminal, and linear compounds for chemical shift assignments. Final products had moderate molar masses with polymodal SEC traces, which is a characteristic of hyperbranched polymers.

While the vast majority of hyperbranched polymers in the literature are synthesized in solution, a few studies report $\text{A}_2 + \text{B}_3$ polymerization in the melt phase.^{55,63,77} Synthesis of hyperbranched aliphatic polyesters via the melt polymerization of adipic acid (A_2) and glycerol (B_3) is an example of a non-ideal $\text{A}_2 + \text{B}_3$ system.⁶³ Molar ratios of $\text{A}_2:\text{B}_3$ from 1:1 to 2:1 were utilized to obtain hyperbranched products, and the molar mass increased with increasing $\text{A}_2:\text{B}_3$ ratio. The absence of gelation even at $\text{A}_2:\text{B}_3 = 2:1$ suggests a distinct reactivity difference between the primary and the secondary alcohols on glycerol (B_3), and hence glycerol acts as a B_2B^* type monomer.

⁷⁷ Lusic, H.; Fossum, E., *Polym. Prep. Div. Polym. Sci.* **2003**, 44, 858.

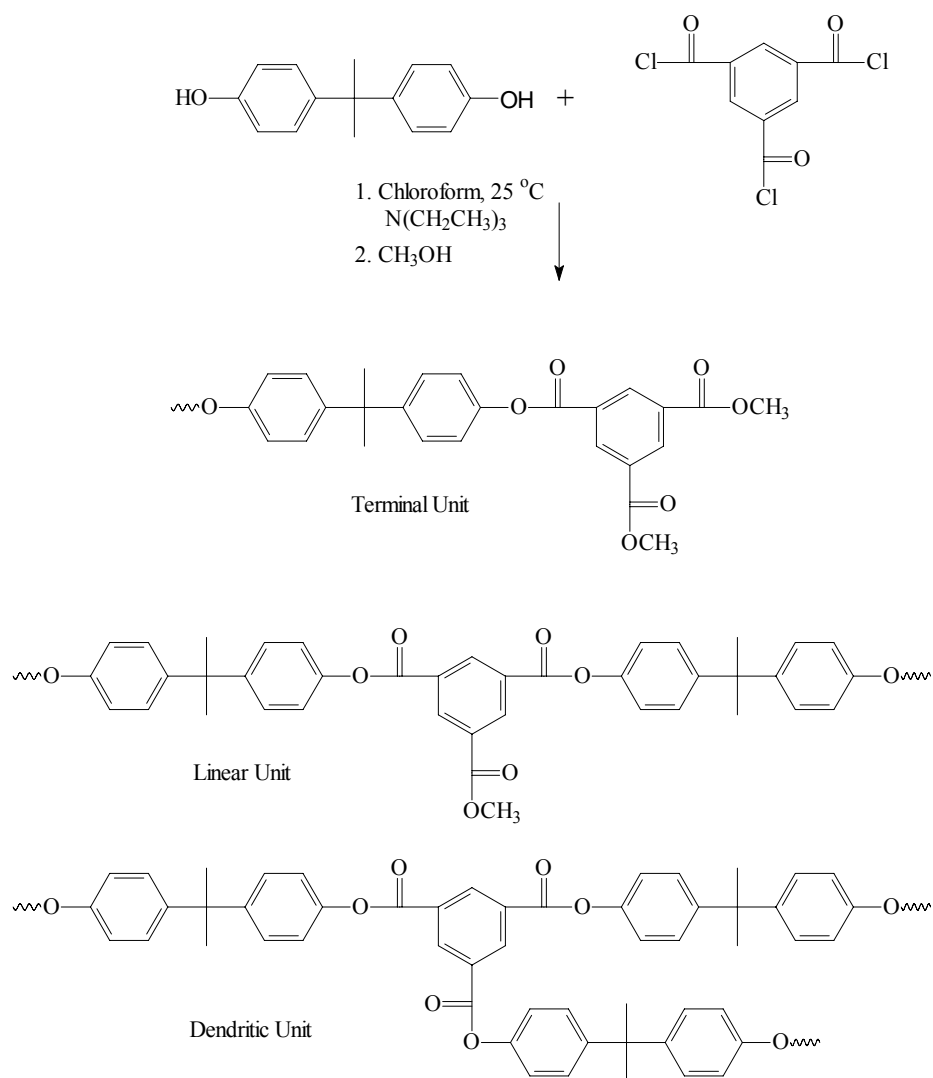


Figure 2-23. Synthesis of methyl ester terminated hyperbranched polyarylesters via polymerization of A₂ and B₃ monomers.

2.2.3.3.5 Hyperbranched Polycarbonates

The reaction of a bis(carbonylimidazolide) (A₂) with triethanolamine (B₃) in the presence of a catalytic amount of KOH resulted in hyperbranched thermolabile polycarbonates (Figure 2-24).⁶⁴ ¹H and ¹³C NMR spectroscopic analyses effectively differentiated reacted and unreacted monomers in the final product mixture. The unreacted B₃ monomer showed different chemical shifts than the bB₂ and b₂B units (Figure 2-24) where b denotes the reacted B group.

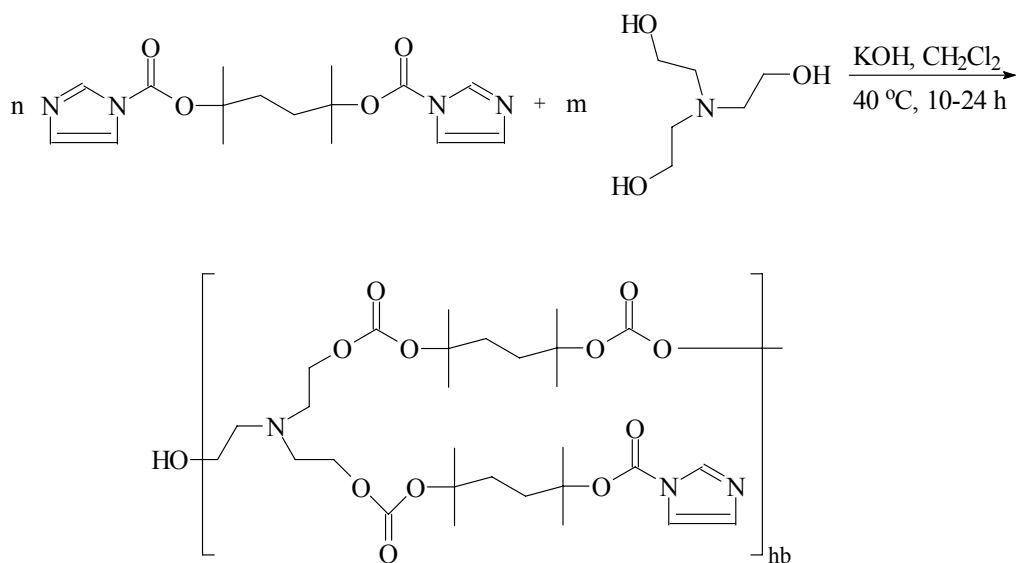


Figure 2-24. Synthesis of a hyperbranched polycarbonate via $A_2 + B_3$ polymerization.

Similarly, unreacted (A_2), half-reacted (aA), and fully-reacted (a_2) bis(carbonylimidazolide) units were differentiated. 2D NMR spectroscopy detected cyclic structures in the final product and the cyclic content increased with decreasing monomer concentration during polymerization. The final product that contained carbonate groups had a T_g of $-14\text{ }^\circ\text{C}$ and decomposed completely into volatile products above $200\text{ }^\circ\text{C}$. Thus, the decomposition behavior of these compact and globular hyperbranched polycarbonates may find application as templates for the preparation of nanoporous polymeric materials.

2.2.3.4 Proton Transfer Polymerization of A_2 and B_3 Monomers

Fréchet and coworkers authored one of the two pioneering reports on the synthesis of hyperbranched polymers via $A_2 + B_3$ polymerization.⁵⁵ Hyperbranched aliphatic polyethers containing epoxy chain-ends were synthesized via proton-transfer polymerization from A_2 and B_3 monomer pairs, such as a diol (A_2) and a triepoxide (B_3) or a diepoxide (A_2) and a triol (B_3). Hyperbranched polymers were obtained before gelation by stopping the reactions prior to full monomer conversion, which, otherwise would result in gelation in the bulk. It was also proposed that the $A_2 + B_3$ polymerization of triepoxide (B_3), synthesized from the reaction of a triol (1,1,1-tris(hydroxymethyl)ethane) and excess epichlorohydrin, with a diol (1,4-butanediol, A_2)

produced an AB₂ diepoxyalcohol intermediate as depicted in Figure 2-25.⁷⁶ The polymers isolated prior to the gel point had polydispersities greater than 20 and separation of the final product from the residual low molar mass impurities was not feasible.

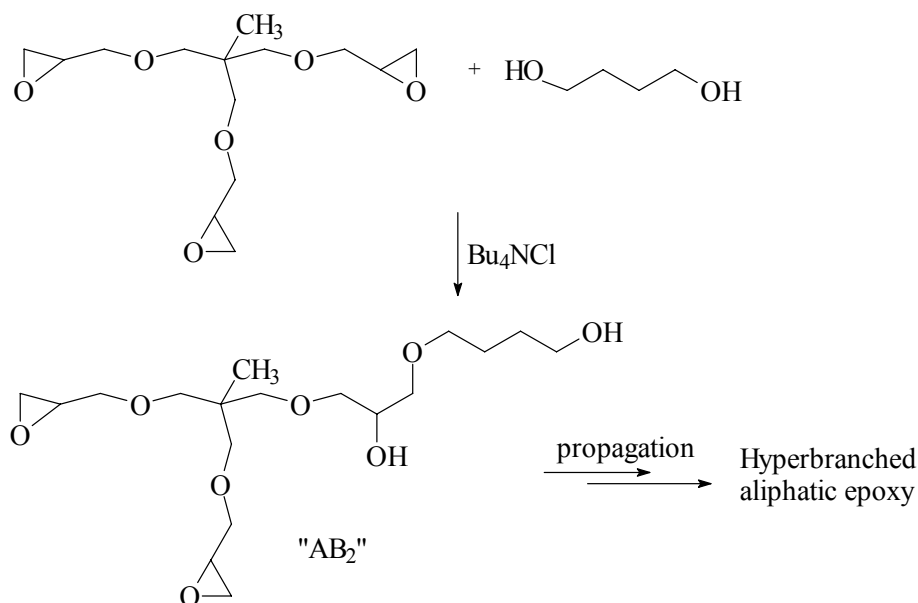


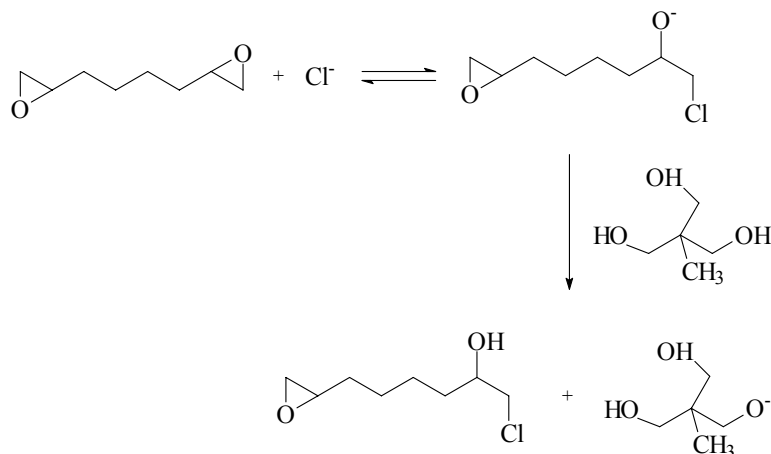
Figure 2-25. Formation of an AB₂ type diepoxyalcohol in the synthesis of hyperbranched polyethers via the proton transfer polymerization of a triepoxide (B₃) and 1,4-butanediol (A₂).

Thus, A₂ + B₃ polymerization of diepoxides with triols was alternatively reported to prepare hyperbranched aliphatic polyether epoxies.⁵⁵ In order to achieve epoxy chain-ends, the ratio of diepoxide to triol (A₂:B₃) was maintained between 1.5:1 and 3:1. Initially, a secondary alkoxide was formed by the addition of chloride ion to diepoxide (A₂). Subsequently, a primary alkoxide was generated by proton exchange between the secondary alkoxide and the triol (B₃) as shown in Figure 2-26, followed by propagation to produce hyperbranched aliphatic polyether epoxies.

Step-growth polyaddition kinetics was observed when molar mass was monitored as a function of reaction time. Hyperbranched products derived at a molar ratio of A₂:B₃ = 3:1 resulted in the highest DB and possessed epoxide chain-ends, with a glass transition temperature of -20 °C. Thermogravimetric analysis showed a thermal degradation onset of 305 °C with a 50% weight loss at 395 °C. Furthermore, hydroxyl groups on the

hyperbranched aliphatic polyether epoxies were successfully functionalized to silyl, hexyl ester, and carbamate groups, which resulted in increased hydrophobicity due to hydrocarbon substituents for each derivatization.

1) Generation of primary alkoxide:



2) Propagation:

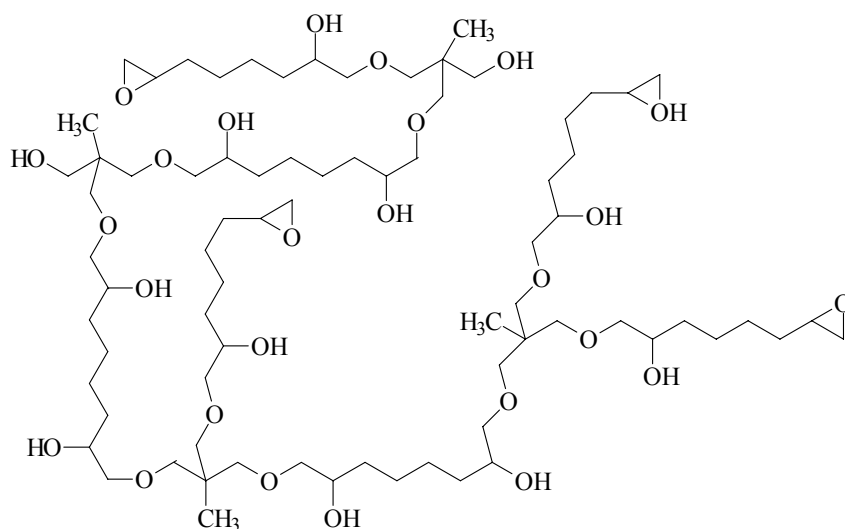


Figure 2-26. Formation of a primary alkoxide by proton transfer and propagation steps during the $A_2 + B_3$ polymerization of a diepoxide and triol.

Fréchet and coworkers similarly reported the synthesis of a hyperbranched polyether that possessed multiple pendant porphyrin units. A bisphenolic porphyrin served as an A_2 monomer (Figure 2-27) and was polymerized with a triepoxide (B_3) via proton

transfer. Porphyrin chromophores offer promise in the construction of optoelectronic devices.⁷⁸

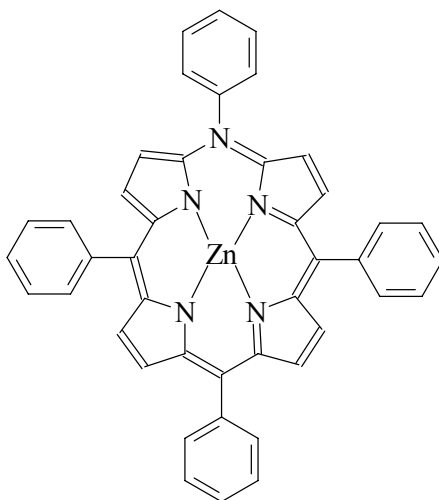


Figure 2-27. Chemical structure of bisphenolic porphyrin as an A_2 monomer.

2.2.3.5 Michael Addition Polymerization of A_2 and B_3 Monomers

Michael addition reactions between functionally symmetric monomer pairs have been successfully demonstrated to prepare hyperbranched polymers.^{56,65,66} Voit and coworkers reported the synthesis of hyperbranched polythioethers via the Michael addition of dithiol (A_2) to a trivinyl compound (B_3 , Figure 2-28).⁵⁶ Due to the high reactivity of thiol toward vinyl groups AB_2 type monomers do not appear suitable for the synthesis of hyperbranched polythioethers. In an $A_2 + B_3$ polymerization of a dithiol and a trivinyl monomer, suppression of gelation was attributed to cyclization reactions resulting in products with crown ether structures suitable for metal salt binding.

Hyperbranched poly(ester amine)s with terminal acrylate groups were prepared via a Michael addition between piperazine (A_2) and trimethylolpropanetriacrylate (TMPTA, B_3 , Figure 2-29).⁶⁶ The TMPTA (B_3) solution was added to a piperazine (A_2) solution in an ice bath over 1 h. The reaction temperature was subsequently increased and maintained at 30 °C for 48 h. Fully soluble, hyperbranched products were obtained below 10 wt % monomer concentrations in THF, whereas higher concentrations resulted in gelation in very short reaction times.

⁷⁸ Hecht, S.; Emrick, T.; Fréchet, J. M. J., *Chem. Comm.* **2000**, 4, 313.

Liu *et al.* synthesized hyperbranched polyaspartimides via the Michael addition reaction of bismaleimides (A_2) and triamines (B_3) as shown in Figure 2-30.⁶⁵ High monomer concentrations (0.76 M) resulted in a crosslinked product. Therefore, a lower monomer concentration (0.19 M) was selected to avoid gelation. Among the two bismaleimides (Figure 2-30), BMDM showed a higher reactivity than BEMM, due to steric and inductive effects arising from alkyl substituents.

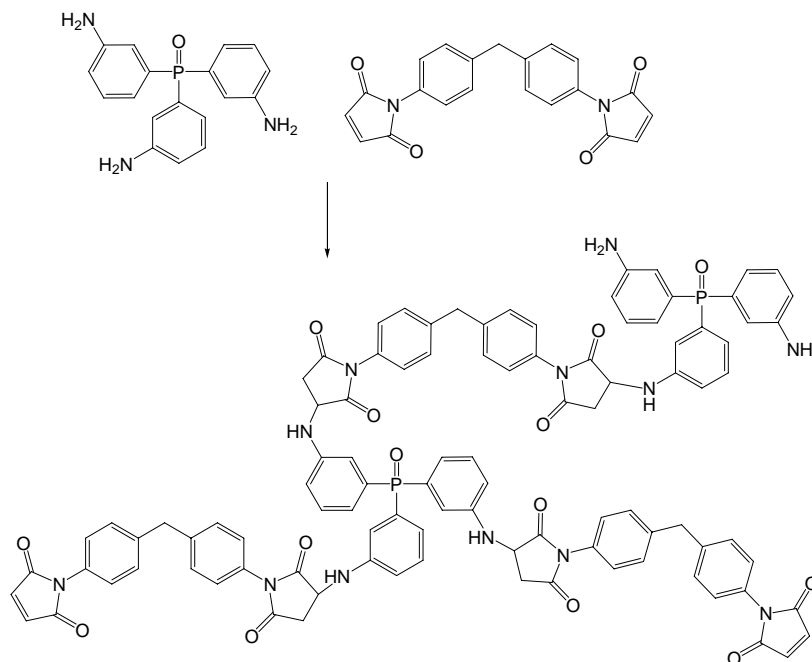


Figure 2-30. Synthesis of hyperbranched polyaspartimides via the Michael addition of A_2 and B_3 monomers.

The DB (Fréchet) ranging from 51 to 69% indicated a hyperbranched structure. Hyperbranched polyaspartimides had glass transition temperatures above 200 °C. Thermogravimetric analysis revealed good thermal stabilities for both products. The hyperbranched polymers derived from TAPPO were thermally stable up to 370 °C under both air and nitrogen and showed high char yields.

2.2.4 Conclusions

Polymerization of functionally symmetric monomer pairs such as A_2 and B_3 monomers received great attention in the last decade due to commercial availability of these monomers, despite the high risk of gelation. Several research groups reported the

successful polymerization of A_2 and B_3 monomers and optimized reaction conditions avoided gelation to prepare hyperbranched polymers including polyamides, polyimides, polyethers, polyesters, and polycarbonates. Important reaction conditions to avoid gelation were the solution concentration, $A_2:B_3$ molar ratio, order of monomer addition, and relative reactivity of the functional groups. Concentration of the polymerization medium played the most important role since dilute solution conditions promoted cyclization reactions and shifted critical monomer conversions for gelation to higher values. At an optimized concentration of monomers, gelation was successfully mitigated even at molar ratios $A_2:B_3 = 1:1$. Mixing the monomers at the polymerization onset, or slow addition of one onto another influenced the gelation incidence, as well as the final structure of the branched polymers. In addition to the most common polycondensation reactions, other types of reactions, such as the proton transfer polymerization, and Michael addition of A_2 and B_3 monomers were also demonstrated to synthesize hyperbranched polymers. In an attempt to further understand the synthesis and structure-property relationships in $A_2 + B_3$ hyperbranched polymers, this review provides an overview of the recent synthetic approaches to the polymerization of A_2 and B_3 type, functionally symmetric monomers pairs.

Chapter 3: A New Generation of Highly Branched Polymers: Hyperbranched, Segmented Poly(urethane urea) Elastomers

Taken From:

Unal, S.; Yilgor, I.; Yilgor, E.; Sheth, J. P.; Wilkes, G. L.; Long, T. E. "A New Generation of Highly Branched Polymers: Hyperbranched, Segmented Poly(urethane urea) Elastomers." *Macromolecules* **2004**, *37*, 7081-7084.

Unal, S.; Oguz, C.; Yilgor, E.; Gallivan, M.; Long, T. E.; Yilgor, I. "Understanding the Structure Development in Hyperbranched Polymers Prepared by Oligomeric $A_2 + B_3$ Approach: Comparison of Experimental Results and Simulations." *Polymer* **2005**, *46*, 4533-4543.

3.1 Abstract

Novel segmented hyperbranched polymers were obtained through oligomeric $A_2 + B_3$ chemistry. An isocyanate terminated polyether oligomer (A_2) was slowly added into a triamine (B_3) in order to achieve high molecular weight, gel-free products. These compositions exhibited microphase-separated morphologies as denoted by DMA. The similarity in soft segment glass transition behavior and strain hardening character of the hyperbranched systems with that of the linear system suggests such hyperbranched materials have considerable promise for structural applications. Structure development in these systems was investigated by monitoring the molecular weight and polydispersity as a function of amount of A_2 added into B_3 . Experimental studies at various solution concentrations showed a strong influence of concentration on the gel point and the extent of cyclization in the final products.

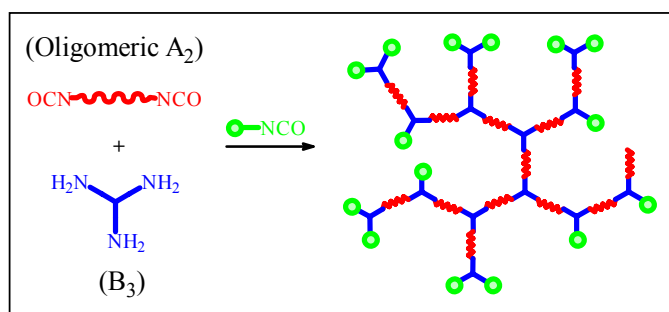


Figure 3-1. Oligomeric $A_2 + B_3$ approach to hyperbranched, segmented polymers.

3.2 Introduction

Highly branched polymers, which include dendritic, hyperbranched, or multibranch systems, exhibit interesting and versatile performance. Interest in branched macromolecules is due to several unique properties when compared with their linear analogues, which include low solution and melt viscosities, improved solubilities, and the presence of a large number of functional end groups that offers the possibility for further modification for various high-performance applications. On the other hand, several important structural drawbacks of hyperbranched polymers, with the exclusion of dendrimers, include broad molecular weight distributions, irregular arm growth (branching), and a statistical distribution of functional end groups throughout the macromolecule. More importantly, hyperbranched polymers generally display inferior mechanical properties when compared to their linear analogues since segment lengths are much shorter than the critical molecular weight for entanglement (M_c). A number of excellent reviews are available in the literature, which describes the synthetic methodologies for the preparation of a wide variety of hyperbranched and dendritic macromolecules using condensation, addition, and ring-opening polymerizations and their properties.⁷⁹

Linear, segmented polyurethanes or thermoplastic polyurethanes (TPU), which consist of alternating hard and soft segments, represent a commercially interesting and versatile class of polymeric materials.⁸⁰ Thus, TPUs are quite suitable for a wide range of applications in many diverse fields, ranging from protective coatings to elastomeric fibers and biomaterials.⁸¹ Superior mechanical and thermal properties of TPUs are attributed to microphase-separated morphologies and strong hydrogen bonding between the hard segment domains.⁸² Early reports of the successful preparation of hyperbranched polyurethanes appeared in 1993 when Spindler and Fréchet disclosed AB₂

⁷⁹ Kim, Y. H., *J. Polym. Sci. Part A: Polym. Chem.* **1998**, 36, 1685. Voit, B., *J. Polym. Sci. Part A: Polym. Chem.* **2000**, 38, 2505. Roovers, J.; Comanita, B., *Adv. Polym. Sci.* **1999**, 142, 179. Hult, A.; Johansson, M.; Malmstrom, E., *Adv. Polym. Sci.* **1999**, 143, 1. Freire, J., *J. Adv. Polym. Sci.* **1999**, 143, 35. Jikei, M.; Kakimoto, M. A., *High Perform. Polym.* **2001**, 13, S33.

⁸⁰ Hepburn, C., *Polyurethane Elastomers*. Elsevier Sci. Publ.: Essex, 1992. Lelah, M. D.; Cooper, S. L., *Polyurethanes in Medicine*. CRC Press: Boca Raton, FL, 1986. Oertel, G., *Polyurethanes Handbook*. Hanser Publishers: Munich, 1994.

⁸¹ Woods, G., *The ICI Polyurethanes Book*. John Wiley: New York, 1990.

⁸² Cooper, S. L.; Tobolsky, A. W., *J. Appl. Polym. Sci.* **1996**, 10, 1837. Yilgor, E.; Yilgor, I., *Polymer* **2001**, 42, 7953. Aneja, A.; Wilkes, G. L., *Polymer* **2003**, 44, 7221.

type monomers which contained a single hydroxyl (A) and two blocked isocyanate groups (B₂).⁸³ Polymerization was conducted in refluxing THF in the presence of catalytic amounts of dibutyltin dilaurate to produce a high molecular weight product, which was subsequently end-capped with an aliphatic alcohol.

Kumar and Ramakrishnan⁸⁴ prepared an AB₂ type monomer and reported the preparation of wholly aromatic hyperbranched polyurethanes using 3,5-dihydroxybenzoyl azide in a Curtius type rearrangement reaction. Moreover, they also reported the one-pot synthesis of hyperbranched polyurethanes containing di- and triethylene oxide spacer segments.⁸⁵ The starting material was 3,5-bis(ω -hydroxy oligoethyleneoxy)benzoyl azide, which is a classical AB₂ type monomer. The ether spacer segments consisted of short di- and tri(ethylene oxide) units. In a similar fashion, Hong *et al.*⁸⁶ also reported the preparation of hyperbranched polyurethanes which were derived from AB₂ monomers that contained very short ethylene oxide units. Several other reports on the preparation of hyperbranched polyurethanes using AB₂ monomers⁸⁷ and others are also available.⁸⁸ More recently, Bruchmann and Schrepp described a one-step methodology for the preparation of hyperbranched poly(urethane urea)s, utilizing commercially available A₂ and B₃ type monomers.⁸⁹ A₂ monomer was a diisocyanate (isophorone diisocyanate or toluene diisocyanate), and the B₃ monomer was an aminoalkanediol.

The preparation and structure-property behavior of linear segmented thermoplastic poly(urethane urea)s (TPUU) and polyureas with different soft segments have received significant attention over the past three decades.⁸⁰ Recently, we disclosed the preparation of segmented, hyperbranched elastomers and engineering thermoplastics which displayed mechanical properties comparable to their linear analogues.⁹⁰ In the present report, a simple oligomeric A₂+B₃ approach will be described for the preparation of segmented,

⁸³ Spindler, R.; Frechet, J. M. J., *Macromolecules* **1993**, 26, 4809.

⁸⁴ Kumar, A.; Ramakrishnan, S., *Chem. Comm.* **1993**, 1453.

⁸⁵ Kumar, A.; Ramakrishnan, S., *J. Polym. Sci. Part A: Polym. Chem.* **1996**, 34, 839.

⁸⁶ Hong, L.; Cui, Y.; Wang, X.; Tang, X., *J. Polym. Sci. Part A: Polym. Chem.* **2002**, 40, 344.

⁸⁷ Davis, N.; Rannard, S., *Polym. Mater. Sci. Eng.* **1997**, 77, 63. Versteegen, R. M.; Sijbesma, R. P.;

Meijer, E. W., *Polym. Prepr.* **1999**, 40 (2), 839. Taylor, R. T.; Paupailboon, U., *Tetrahedron Lett.* **1998**, 39, 8005.

⁸⁸ Feast, W. J.; Rannard, S. P.; Stoddart, A., *Macromolecules* **2003**, 36, 9704. Stumbe, J.; Bruchmann, B., *Macromol. Rapid Commun.* **2004**, 25, 921. Stumbe, J.; Bruchmann, B., *Macromol. Rapid Commun.* **2004**, 25, 921. Gao, C.; Yan, D., *Macromolecules* **2003**, 36, 613.

⁸⁹ Stumbe, J.; Bruchmann, B., *Macromol. Rapid Commun.* **2004**, 25, 921.

⁹⁰ Unal, S.; Yilgor, I.; Yilgor, E.; Sheth, J. P.; Wilkes, G. L.; Long, T. E., *Macromolecules* **2004**, 37, 7081.

hyperbranched polyureas and poly(urethane urea)s with mechanical properties comparable to their linear analogues. This approach utilizes an isocyanate end-capped polyether (PPO or PTMO) as an oligomeric A₂ monomer, and a B₃ triamine monomer. This novel approach can easily be extended to a large number of telechelic oligomers (A₂) including poly(dimethylsiloxane) (PDMS) or poly(ethylene glycol) and trifunctional monomer (B₃) combinations for the preparation of a wide range of polymeric materials from elastomers to engineering thermoplastics. In order to better understand the polymer structure development in this approach, experimental studies were performed to monitor the molecular weight and polydispersity as a function of oligomeric A₂ addition and influence of solution concentration on the gel point.

3.3 Experimental

3.3.1 Materials

Bis(4-isocyanatocyclohexyl)methane (HMDI) (Bayer) and cyclohexyl isocyanate (CHI) (Aldrich) with purities greater than 99.5% were used. Poly(tetramethylene oxide) (PTMO) oligomers (Terathane, Du Pont) with number-average molecular weights (M_n) of 2000 (PTMO2) and 3500 g/mol (PTMO3) and α,ω -amine terminated poly(propylene oxide) oligomer (PPO) (Jeffamine D-2000, Huntsman) with M_n of 2000 g/mol (PPO2) were used as received. Tris(2-aminoethyl)amine (TRIS) (Aldrich), a poly(oxyalkylene)triamine (Jeffamine T-403, Huntsman) (ATA), 2-methyl-1,5-diaminopentane (MDAP) (Dytek A, Du Pont), HPLC grade isopropyl alcohol (IPA), and tetrahydrofuran (THF) (Aldrich) were all used as received. Chemical structures of triamines are depicted in Figure 3-2.

3.3.2 Characterization

IR spectra were obtained on a Nicolet NEXUS 670 FTIR spectrometer with a resolution of 2 cm⁻¹, using thin films cast on KBr disks. Size-exclusion chromatography (SEC) was conducted on a Waters system that was equipped with three in-line PLgel 5 mm Mixed-C columns, an autosampler, a 410 RI detector, a Viscotek 270 dual detector, and an in-line Wyatt Technologies miniDawn multiple angle laser light scattering (MALLS) detector at 40 °C in tetrahydrofuran (THF) at 1 mL min⁻¹ using polystyrene

standards. Absolute molecular weights were obtained from MALLS detector. Because of its insolubility in THF, the SEC of the linear TPUU (PTMO2-MDAP) was conducted on a Waters system equipped with Styragel HT columns and an RI detector in *N*-methyl-2-pyrrolidone (NMP) containing 0.05 M LiBr, at 40 °C with a flow rate of 1 mL/min. Dynamic mechanical analysis (DMA) was conducted on Seiko DMS210. Samples were quenched from room temperature to -125 °C and thereafter subjected to a heating rate of 2 °C/min and 1 Hz. A Perkin-Elmer Pyris-1 instrument was used for differential scanning calorimetry (DSC) analysis at 10 °C/min under a helium atmosphere, and all reported data were obtained from the second heating. Stress-strain tests were conducted on an Instron 4400R using dog-bone-shaped samples with 2.9 mm width, 10 mm grip separation distance, and 25 mm/min cross-head speed.

3.3.3 Synthesis of Hyperbranched, Segmented Poly(urethane urea)s

All reactions were conducted in three-necked, round-bottomed flasks that were equipped with an overhead stirrer, addition funnel, and nitrogen inlet. Isocyanate end-capped PTMOs (A₂, Figure 3-3) were prepared in bulk at 80 °C with 50 ppm dibutyltin dilaurate as the catalyst. Isocyanate end-capping reactions of amine terminated PPO were performed in IPA at room temperature by the dropwise addition of the oligomer solution into the HMDI solution in 15-20 min.⁹¹ Quantitative conversions were confirmed using FTIR spectroscopy (Nicolet Nexus 870 FT-IR). The segmented hyperbranched polyureas based on PPO were prepared in IPA. PTMO-based polymers were prepared in THF/IPA (25/75 vol/vol). Both polymers were synthesized by the dropwise addition of the A₂ (isocyanate terminated PTMO or PPO) solution into a solution of B₃ (TRIS or ATA, Figure 3-2) at room temperature. Reactions were conducted in dilute solutions, typically at 10-15% solids with very strong agitation. Since equimolar amounts of A₂ and B₃ (or in terms of equivalents $[A]/[B] = 2/3 = 0.67$) were used, [B] was always in excess, and gelation was not observed during the reactions.

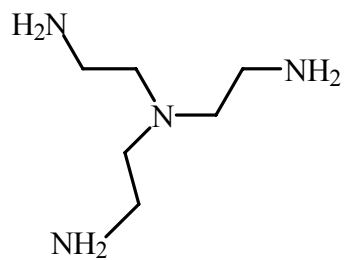
⁹¹ Yilgor, E.; Atilla, G. E.; Ekin, A.; Kurt, P.; Yilgor, I., *Polymer* **2003**, 44, 7787.

3.3.4 Monitoring the Structure Development in Hyperbranched, Segmented Poly(urethane urea)s using SEC

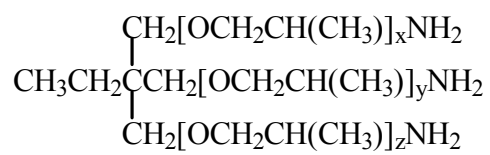
In experiments where the influence of solution concentration on gelation and cyclization was investigated, HMDI was used as (A_2 , Figure 3-3) and ATA as (B_3 , Figure 3-2). In these experiments IPA was used as the reaction solvent and reactions were conducted at room temperature under very strong agitation. HMDI (A_2) and ATA (B_3) were separately dissolved in IPA at the specific concentration at which the reactions would be conducted. ATA (B_3) solution was introduced into the reactor and the HMDI (A_2) solution into the addition funnel. HMDI (A_2) solution was added into the reactor dropwise until the gelation is observed. Duration of the experiments was usually less than 30 minutes to ensure very small reaction between IPA and HMDI.⁹² Stoichiometric amount of HMDI (A_2) added at the gel point was determined for reactions carried out at various solution concentrations from 5 to 25 wt % solids. Dual reactions were performed to determine the reproducibility. Amount of cyclization at each concentration was determined by subtracting the theoretical amount of A_2 needed at the gel point (75.0%) from the amount of A_2 used to reach the gel point experimentally.

In order to monitor the molecular weight increase and the polydispersity of the products, hyperbranched poly(urethane urea)s were synthesized via the slow addition of isocyanate-terminated PTMO (A_2) solution into ATA (B_3) solution at two different concentrations; 10 and 25 wt % solids. Samples were withdrawn from the reactor at different amounts of A_2 addition and end capped with CHI prior to analysis by size-exclusion chromatography (SEC).

⁹² Unal, S.; Yilgor, I.; Yilgor, E.; Sheth, J. P.; Wilkes, G. L.; Long, T. E., *Macromolecules* **2004**, 37, 7081.



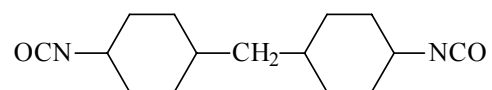
(a)



(b)

Figure 3-2. Chemical structures of triamines used: (a) tris(2-aminoethyl)amine (TRIS), (b) poly(oxyalkylene)triamine (ATA), where $x + y + z = 5.3$ and $M_w = 440$ g/mol.

Bis(4-isocyanatocyclohexyl)methane (HMDI)



HMDI end-capped PTMO

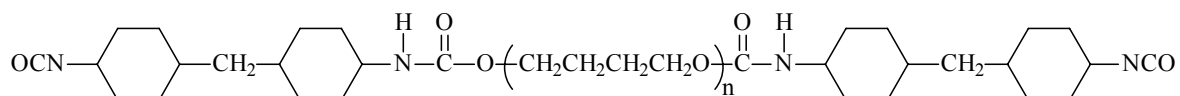


Figure 3-3. Chemical structures of monomeric and oligomeric A₂ reagents.

3.4 Results and Discussion

3.4.1 Synthesis and Characterization

Segmented, hyperbranched poly(urethane urea) elastomers were prepared using an oligomeric A_2+B_3 approach, where isocyanate end-capped PTMO oligomers (A_2) were slowly added to a triamine (B_3) solution at room temperature. It is well-known that aliphatic amines react with isocyanates instantaneously at room temperature.^{80,91} Table 3-1 summarizes the growth of the number- and weight-average molecular weights of the polymeric products for a PTMO2 + ATA ($A_2 + B_3$)-based system as a function of the amount of added A_2 . As expected, a gradual increase in M_n was observed as more A_2 was added to B_3 in the polymerization reactor.

It is also interesting to note that a dramatic increase in molecular weight distribution (M_w/M_n) of the product was observed as A_2 was added. This observation supports the formation of branched systems. Assuming complete reaction of A groups with B groups upon addition, the gel point for the system, where $[A_2] = [B_3]$, is at $p_A = 0.87$ or $p_B = 0.58$ (neglecting internal cyclization),⁹³ where p_A and p_B are the conversion of A and B groups, respectively. Table 3-1 shows that gelation was observed above $p_B = 0.75$, which was much higher than the critical value of 0.58. This clearly indicated internal cyclization, which is typical for $A_2 + B_3$ polymerizations.^{79,93,94} The data presented in Table 3-1 support the formation of fully soluble, hyperbranched segmented polymers under these reaction conditions. Chemical compositions of the segmented, hyperbranched PUUs and the corresponding linear TPUU are provided in Table 3-2. Representative average molecular weights and molecular weight distributions (M_w/M_n) of the hyperbranched polymers are provided in Table 3-3. Again, these results clearly indicate the formation of high molecular weight polymers with broad molecular weight distributions, which are typical for hyperbranched polymers.

⁹³ Flory, P. J., *J. Am. Chem. Soc.* **1952**, 74, 2718. Flory, P. J., *Principles of Polymer Chemistry*. Cornell University Press: Ithaca, NY, 1953.

⁹⁴ Kricheldorf, H. B., *Macromol. Symp.* **2003**, 199, 15. Kricheldorf, H. B.; Vakhtangishvili, L.; Schwartz, G.; Krueger, R. P., *Macromolecules* **2003**, 36, 5551.

Table 3-1. Average molecular weight and molecular weight distribution (M_w/M_n) of the polymers formed for PTMO2 + ATA ($A_2 + B_3$) system as a function of the amount of A_2 added and corresponding B_3 conversion (p_B).

$[A_2]$	$[B_3]$	p_B	M_n (g/mol)	M_w (g/mol)	M_w/M_n
0.69	1.00	0.46	16000	24000	1.50
0.81	1.00	0.54	17000	37000	2.18
0.95	1.00	0.64	26000	75000	2.88
1.02	1.00	0.68	28000	116000	4.14
1.10	1.00	0.74	63000	390000	6.19
1.12	1.00	0.75	Gel	Gel	--

Table 3-2. Chemical compositions of segmented, hyperbranched poly(urethane urea)s and a homologous linear TPUU (PTMO2-MDAP) (* = no CHI end-capping).

sample	HMDI (g)	soft segment		triamine		CHI (g)	HS (%)
		M _n (g/mol)	amount (g)	type	amount (g)		
PTMO2-ATA*	17.70	2000	67.50	ATA	14.85	--	33
PTMO2-ATA	17.00	2000	64.70	ATA	14.25	4.05	35
PTMO3-ATA	11.45	3500	76.25	ATA	9.60	2.70	24
PPO2-ATA	17.00	2000	64.70	ATA	14.25	4.05	35
PTMO2-TRIS	18.80	2000	71.55	TRIS	5.20	4.45	28
PTMO2-MDAP*	26.90	2000	65.00	MDAP	8.10	--	35

Table 3-3. Average molecular weight and molecular weight distribution (M_w/M_n) of various segmented hyperbranched polymers ($[A]/[B] = 0.67$) end-capped with CHI and a homologous linear TPUU (* = no CHI end-capping).

sample	M_n (g/mol)	M_w (g/mol)	M_w/M_n
PTMO2-ATA	33000	111000	3.36
PTMO3-ATA	42500	179000	4.21
PPO2-ATA	25000	110000	4.40
PTMO2-MDAP*	27000	42000	1.56

These novel, segmented, hyperbranched polymers also display excellent thermomechanical and tensile properties as a function of the chemical composition. Figure 3-4 depicts the comparative DMA behavior of hyperbranched elastomers, PTMO2-ATA* (uncapped), PTMO2-ATA and PTMO2-TRIS (both end-capped with CHI), and the linear TPUU (PTMO2-MDAP). It should be noted that PTMO2- and ATA-based hyperbranched elastomers (PTMO-ATA and PTMO-ATA*) and the linear TPUU (PTMO2-MDAP) have similar hard segment contents while the hyperbranched elastomers PTMO3-ATA and PTMO2-TRIS have a lower amount of hard segment content. All polymers displayed two-phase behavior with the PTMO soft segment transition occurring at approximately -75 °C. As depicted in Figure 3-5, DSC analysis of PTMO2-ATA and PTMO2-MDAP also showed similar soft segment transitions at -77 and -78 °C, respectively, and a significant shift from the pure PTMO T_g (-79 °C) was not observed. The linear TPUU exhibited a much more extended rubbery plateau reaching to about 200 °C and a higher plateau modulus than the hyperbranched polymers. While a lower plateau modulus could suggest a lower entanglement density, it must be recognized that these hyperbranched polymers have an equal to or lower amount of hard segment content compared to the linear analogue; however, a lower $\tan \delta$ magnitude is observed at the same T_g peak. If it is presumed that this observation is only attributed to entanglement, then why is the magnitude of the PTMO transition depressed compared to the linear analogue? This was presumed to be due to some phase mixing that may account for the changes in plateau modulus. Detailed studies are currently underway in order to better understand this interesting phenomenon in these novel hyperbranched elastomers. As expected, a urea end-capped segmented hyperbranched polymer (PTMO2-ATA) displayed better thermomechanical integrity than its uncapped homologue (PTMO2-ATA*) due to increased hydrogen bonding from the strong end group interactions. In fact, such interactions are also reflected in the more extended rubbery plateau of the end-capped polymer, which reaches to nearly 100 °C, whereas the uncapped analogue only extends to about 50 °C. In addition to end-capping, a significant influence of the triamine structure on the thermomechanical behavior was observed based on the DMA analysis of the urea end-capped, TRIS-based polymer (PTMO2-TRIS), which displayed a well-developed rubbery plateau extending to approximately 75 °C as shown in Figure 3-4.

Stress-strain curves and the data for both linear and hyperbranched TPUUs are shown in Figure 3-6. The linear TPUU, which contained 35 wt % urea hard segments, as expected, was a very strong elastomer with a modulus of 25.5 MPa, tensile strength of 42.0 MPa, and an elongation at break value of 620%. The uncapped segmented hyperbranched elastomer based on ATA trimer (PTMO2-ATA*) was weak and displayed modulus and tensile strength values of 1.50 and 3.10 MPa, respectively, but extended to over 1100% at break. It is important to note that although this sample is not end-capped with CHI, it still displays excellent recovery following 1100% elongation. Urea end-capping (PTMO2-ATA) improved the tensile properties significantly and resulted in the formation of a relatively strong elastomer which displayed modulus and tensile strength values of 5.3 and 15.7 MPa, respectively, and an elongation at break value over 1000%. Similar to the uncapped homologue (PTMO2-ATA*), following the 1100% elongation, PTMO2-ATA also exhibits excellent recovery. This behavior is an important signature in providing valuable information about entanglements and relaxation time features in these novel elastomers. A detailed investigation of the hysteresis behavior of the segmented hyperbranched poly(urethane urea)s is in progress. It is noted that the chemical structure of the triamine had a significant influence on the mechanical properties. As shown in Figure 3-6, a urea end-capped PTMO2-TRIS based hyperbranched PUU displayed a modulus of 11.2 MPa, an ultimate tensile strength of 38.2 MPa, and an elongation at break of 1000%, although it contained a lower urea hard segment content of 28 wt % compared to PTMO2-ATA (35 wt %). As can be noted from Figure 3-6, the tensile behavior of the PTMO2-TRIS-based hyperbranched PUU approaches that of the linear sample (PTMO2-MDAP) despite the fact that this sample contains only 28 wt % hard segments as compared to the 35 wt % in the linear sample. It is also interesting to note that the hyperbranched system exhibits strain-induced crystallization when the sample is uniaxially stretched and held at an extension ratio of 4.5x (as confirmed using wide-angle x-ray scattering). Strain-induced crystallization of PTMO ($M_w > \text{ca. } 2000 \text{ g/mol}$) in linear segmented copolymers is widely known in the literature and forms the basis of many commercial applications of such materials.⁹⁵

⁹⁵ Legge, N. R.; Holden, G.; Schroeder, H. E., *Thermoplastic Elastomers: A Comprehensive Review*. Hanser Publishers: New York, 1987.

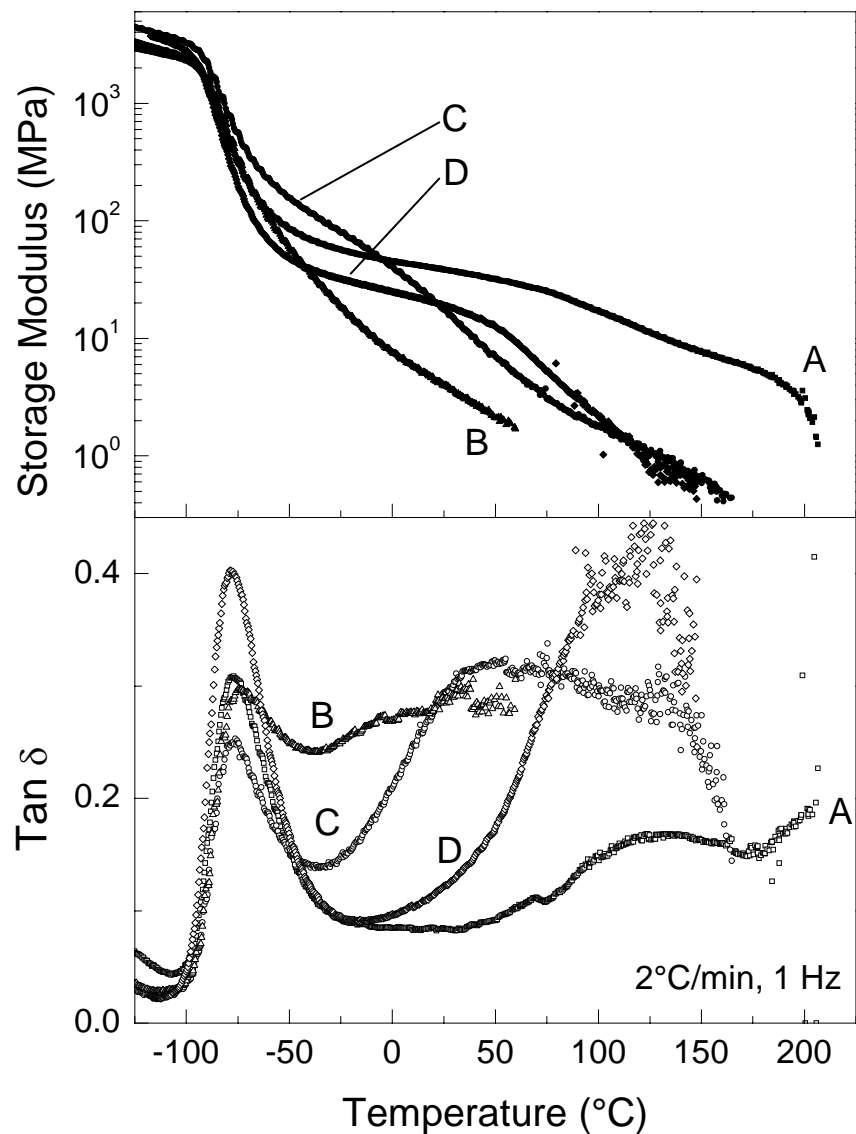


Figure 3-4. Dynamic mechanical behavior of hyperbranched, segmented poly(urethane urea) elastomers and a linear TPUU. (top) storage modulus-temperature curves and (bottom) $\tan \delta$ -temperature curves (A) PTMO2-MDAP*, (B) PTMO2-ATA*, (C) PTMO2-ATA, and (D) PTMO2-TRIS (* = no CHI end-capping).

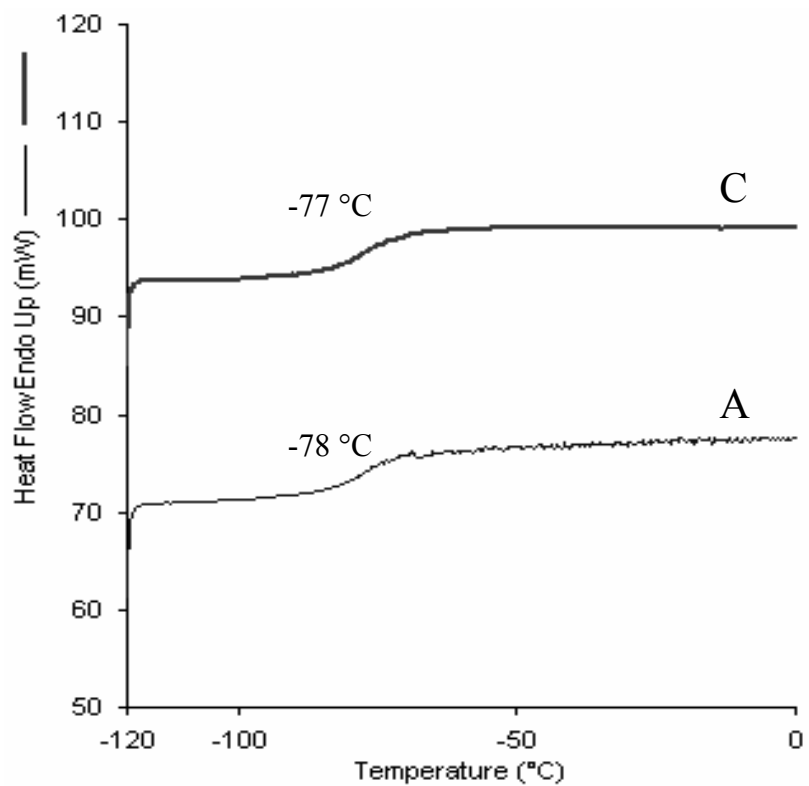


Figure 3-5. Differential scanning calorimetry of a hyperbranched, segmented PUU elastomer and a linear TPUU: (A) PTMO2-MDAP*, (C) PTMO2-ATA.

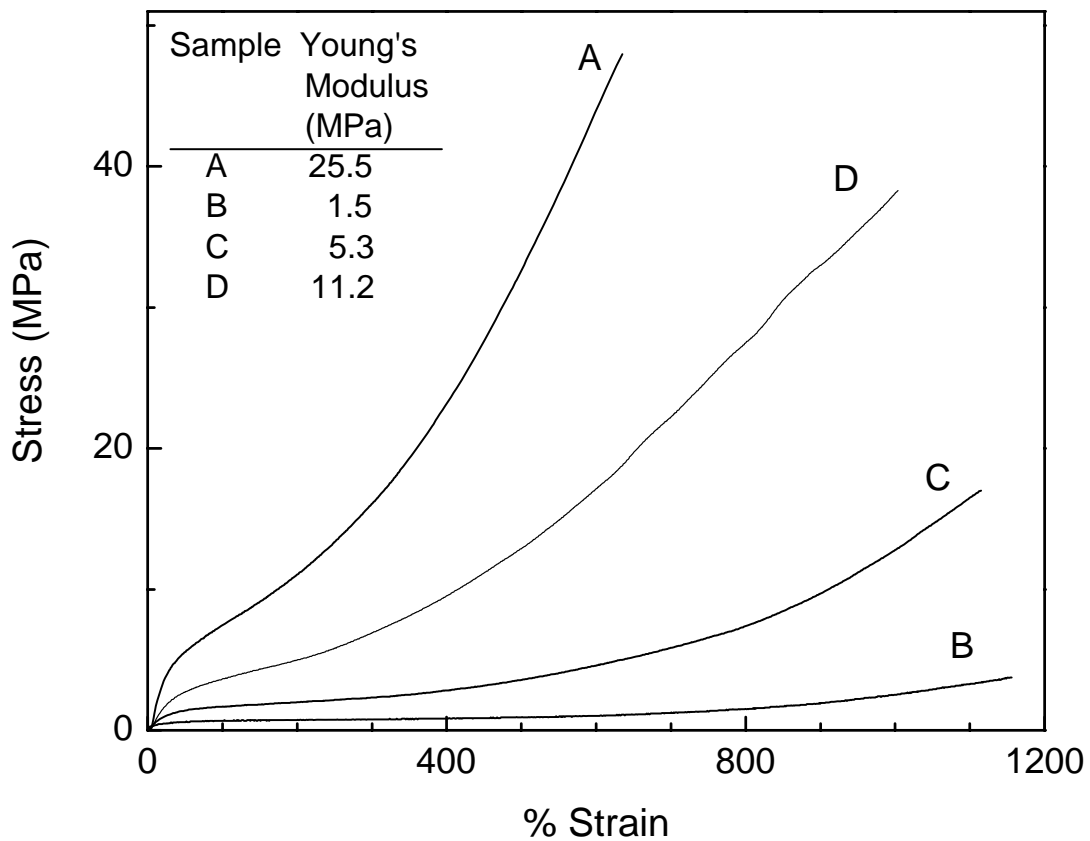


Figure 3-6. Comparison of the stress-strain behavior of hyperbranched, segmented poly(urethane urea) elastomers and a homologous linear TPUU: (A) PTMO2-MDAP*, (B) PTMO2-ATA*, (C) PTMO2-ATA and (D) PTMO2-TRIS (* = no CHI end-capping).

3.4.2 Understanding the Structure Development

The polymerization procedure, where A_2 was added slowly onto B_3 , is quite different than the conventional procedures employed for the preparation of step-growth polymers, which usually involves the addition of all reactants into the reactor at the beginning of the reaction. Slow addition of A_2 onto a large excess of B_3 is expected to provide a more controlled topology during polymer formation. It will also reduce the formation of side reactions and more importantly the risk of gel formation during reactions, since the stoichiometric balance of the reactants will be controlled throughout the reaction.

Flory has demonstrated that depending on the stoichiometry of the monomers and extent of reaction, step-growth polymerization reactions involving a mixture of difunctional (A_2) and trifunctional (B_3) monomers lead to the formation of hyperbranched or crosslinked polymers.⁹³ According to Flory, for an A_2+B_3 system with all monomers initially present in the reaction mixture, assuming no side reactions (or no cyclization), the monomer conversions at gel point can be calculated by using the following equations:^{93,96}

$$\alpha_c = \frac{1}{f-1}$$

Equation 3-1

$$\alpha = \frac{rp_A^2\rho}{1-rp_A^2(1-\rho)}$$

Equation 3-2

where (α) is the probability of branching, (α_c) is the probability of branching for gelation, (f) functionality of the branched units, (p_A and p_B) are the extent of reaction for A and B type monomers, (ρ) is the ratio of A groups on branch units to all A groups in the reaction mixture, and (r) is the ratio of the A groups to that of B groups. Flory showed that when $\alpha < \alpha_c$, gel formation is impossible, but may be possible when $\alpha > \alpha_c$.⁹³

⁹⁶ Flory, P. J., *Chem. Rev.* **1946**, 39, 137.

For an $A_2 + B_3$ system, where equimolar amounts of A_2 and B_3 are initially present in the reaction mixture; $f = 3$, $\alpha_c = 1/2$ and $r = 2/3$. Since all of our B groups are on branching units (B_3) $\rho = 1$. Assuming that $\alpha = \alpha_c$ at the gel point:

$$\alpha_c = r p_A^2 = \frac{p_B^2}{r}$$

Equation 3-3

Substituting the values of $\alpha_c = 1/2$ and $r = 2/3$ in Equation 3-3, $p_A = 0.866$ and $p_B = 0.577$ are calculated. This shows that in an $A_2 + B_3$ system, where equimolar amounts of A_2 and B_3 are initially present in the reaction mixture, the gelation will take place when 57.7% of the B_3 monomer or 86.6% of the A_2 monomer has reacted. Alternatively, when the concentrations of A groups and B groups are equal ($r = 1$), then theoretically, $p_A = p_B = 0.707$ at the gel point.

In the idealized limit of slow A_2 addition into a large excess of B_3 , each B group would be found in one of two possible states: (1) the B group is on an unreacted B_3 monomer, or (2) the B group has reacted with an A_2 , which has also reacted with another B_3 . Thus, the branching coefficient α is simply the conversion of B_3 , referred to by Flory as p_B . For the limit of slow A_2 addition, we define the conversion of A_2 as $p_A = 3/2 p_B$, which is the molar percent of A_2 added into the reactor when compared with the number of moles of B_3 present in the reactor. Thus, at the critical point for gel formation, $p_B = 0.50$ and $p_A = 0.75$. It is important to note that Flory's results apply only under the assumption that no cyclization has occurred, which is an unrealistic assumption at the gel point, as also noted by Flory. Furthermore, the condition $\alpha_c > 1/2$ does not indicate that a gel has formed, but only that gel formation may be possible.

3.4.2.1 Influence of Concentration of Polymerization Medium on Gel Point and Extent of Cyclization

As discussed above, in $A_2 + B_3$ polymerizations that are conducted in bulk (no solvent effect) with all monomers added together into the reactor, theoretical gel point is at 86.6% conversion of A or 57.7% conversion of B groups.^{93, 97} However, as

⁹⁷ Jikei, M.; Kakimoto, M. A., *High Perform. Polym.* **2001**, 13, S33.

demonstrated by various groups,^{98,99} in kinetically controlled polycondensation reactions cyclization competes with linear polymer formation. When the polymerization is carried out in solution, there is even more tendency to form cyclic oligomers and/or macromolecules due to the well known cage effect.¹⁰⁰ Increase in the amount of cyclic species is also observed in thermodynamically controlled ring-chain equilibration reactions.¹⁰¹ In order to understand the influence of the solvent concentration on gelation and cyclization during the preparation of highly branched polymers by oligomeric $A_2 + B_3$ approach, we conducted experiments by varying the solution concentration between 5 and 25% solids. A major difference in our approach is the slow addition of A_2 onto B_3 . As discussed above, in this case, the theoretical gel point is at 75% conversion of A or 50% conversion of B. In other reports,^{98,99,101} either AB_n type monomers were used or A_2 and B_3 were mixed together at the beginning of the polymerization reactions.

During our experiments A_2 (HMDI) and B_3 (ATA) solutions were prepared separately at specific concentrations (Table 3-4). B_3 solution is introduced into the reactor and A_2 solution into a graduated addition funnel. A_2 is added drop-wise onto B_3 solution under strong agitation. A_2 addition was continued until gelation. Amount of A_2 added at the gel point was determined at each concentration. The results are provided on Table 3-4, where the concentration of the reaction medium, amount of A_2 added and estimated level of cyclization are tabulated at each concentration. Experiments at 10, 15 and 20% solids were conducted twice to ensure the reproducibility of the experiments, which is clearly demonstrated when the results are compared. The amount of A_2 added is the molar percent of A_2 added into the reactor when compared with the number of moles of B_3 present in the reactor. Under ideal conditions in slow A_2 addition on B_3 , gelation is expected at 75% of A_2 addition. It is interesting to note that when the reaction is carried out at a fairly high solution concentration of 25% solids by weight, gelation takes place at 88.6% A_2 addition, which is higher than the amount expected by the theoretical

⁹⁸ Kricheldorf, H. R.; Schwartz, G., *Macromol. Rapid Comm.* **2003**, 24, 359. Kricheldorf, H. R., *Macromolecules* **2003**, 36, 2302.

⁹⁹ Gooden, J. K.; Gross, M. L.; Mueller, A.; Stefanescu, A. D.; Wooley, K. L., *J. Am. Chem. Soc.* **1998**, 120, 10180. Martinez, C. A.; Hay, A. S., *J. Polym. Sci. Part A: Polym. Chem.* **1997**, 35, 2015.

¹⁰⁰ Ziegler, K., *Ber. Dtsch. Chem. Ges.* **1934**, 67A, 139.

¹⁰¹ Jacobsen, H.; Stockmayer, W. H., *J. Chem. Phys.* **1950**, 18, 1600. Jacobsen, H.; Beckmann, C. O.; Stockmayer, W. H., *J. Chem. Phys.* **1950**, 18, 1607. Semlyen, J. A., *Large Ring Molecules*. Wiley: New York, 1996.

calculations. When the concentration of the reaction medium is reduced to 20% solids by weight, gel point is reached at about 93.8% A₂ addition, which is again, much higher than the theoretical value. These results clearly indicate the extensive amount of intramolecular cyclization during polymerization reactions in solution. As the concentration of the reaction medium is further reduced to 15, 10 and 7.5% solids by weight, the amount of A₂ needed for gelation steadily increases to 97, 107.5 and 120.5%. When the reaction is carried out at a concentration of 5% solids by weight, gelation is never observed even though a very large stoichiometric excess of A₂ is added into the system! We believe this observation can only be explained by cyclization. In Table 3-4, an estimate of the extent of cyclization for reactions at different concentrations is provided in the last column. Cyclization was calculated by subtracting the theoretical amount of A₂ needed for gelation (75%) from the amount of A₂ needed to reach the gel point experimentally.

Table 3-4. Influence of the concentration of reaction medium on cyclization and gel point in hyperbranched polyureas formed by the slow addition of HMDI (A₂) onto ATA (B₃) in IPA at 23 °C.

solution concentration		A ₂ added at gel point (%)	estimated cyclization (%)
weight (%)	volume (%)		
25	19.7	88.6	13.6
20	15.5	94.3	19.3
20	15.5	93.3	18.3
15	11.5	97.0	22.0
15	11.5	97.4	22.4
10	7.5	107.6	32.6
10	7.5	107.5	32.5
7.5	5.6	120.5	45.6
5.0	3.7	>150 (no gel)	very high

3.4.2.2 SEC Studies on Determination of Polymer Molecular Weight as a Function of A₂ Addition

After determination of the experimental gel points in A₂ + B₃ polymerization as a function of the solution concentration using low molecular weight A₂ (HMDI) and B₃ (ATA) monomers, we started investigating the development of polymer molecular weight and gel point as a function of oligomeric A₂ addition into B₃. In these experiments A₂ was an isocyanate end-capped PTMO-2000, which was obtained by the reaction of PTMO-2000 with a two-fold excess of HMDI and B₃ was ATA. Chemical structures of these compounds are provided in Figure 3-2 and Figure 3-3. Isocyanate end-capped oligomeric A₂ shown in Figure 3-3, is the ideal structure. Actual A₂ has a distribution of molecular weights and some unreacted HMDI.

In order to monitor the growth in the molecular weight of the polymers formed, samples were withdrawn from the reactor at different amounts of A₂ addition and end-capped with CHI prior to SEC analysis. Dendritic and hyperbranched structures are known to have different mass–hydrodynamic volume relationship compared to linear polymer standards that are used in SEC measurements. It should be noted that all SEC data reported in this manuscript are from MALLS detector. However, as we discuss in the manuscript, in our case, these highly branched structures also have linear segments between branch units, resembling structures between hyperbranched and long-chain branched polymers. Several hyperbranched poly(urethane urea)s that were synthesized using the exact same methodology were also examined in hexafluoroisopropanol and both the molecular weight and the molecular weight distribution values were very close to the results obtained in THF.¹⁰² Several studies that were reported on a variety of hyperbranched structures and their SEC characterization also demonstrated that SEC-viscometry can be useful.^{103, 104} Van Benthem and co-workers analyzed the size exclusion chromatography fractions of bis(2-hydroxypropyl)amide based hyperbranched polyesteramides by MALDI-TOF/MS, and confirmed that the masses measured were identical to those measured by SEC equipped with a viscometry detection. Recent review

¹⁰² Sheth, J. P.; Unal, S.; Yilgor, E.; Yilgor, I.; Beyer, F. L.; Long, T. E.; Wilkes, G. L., *Polymer* **2005**, 46, 10180.

¹⁰³ van Benthem, R. A. T. M.; Meijerink, N.; Geladé, E.; Koster, C. G. D.; Muscat, D.; Froehling, P. E.; Hendriks, P. H. M.; Vermeulen, C. J. A. A.; Zwartkruis, T. J. G., *Macromolecules* **2001**, 34, 3559.

¹⁰⁴ Unal, S.; Lin, Q.; Mourey, T. H.; Long, T. E., *Macromolecules* **2005**, 38, 3246.

by Mourey also provides several examples on the agreement in the molecular weight measurements of hyperbranched polymers by SEC and other direct methods.¹⁰⁴

SEC chromatographs provided in Figure 3-7 show the change in the molecular weight of the polymer formed as a function of oligomeric A₂ addition into B₃, where the concentration of the polymerization medium was constant at 25% solids by weight. Interestingly, gel point in this system was also observed at 89.0% A₂ addition, which is very similar to that of HMDI + ATA system described above, where experimental gel point was at 88.6% A₂ addition. Therefore, in SEC curves provided in Figure 3-7, the highest level of A₂ incorporation was 84%. M_n and M_w values obtained from light scattering detector are tabulated in Table 3-5. SEC curves clearly show the increase in the molecular weight of the polymer formed as a function of the amount of A₂ addition. SEC chromatograms shown in Figure 3-7 have two major peaks. The small peak centered at the elution volume of 24.5 min, which is due to B₃, becomes smaller as more A₂ is added. This is expected since B₃ concentration in the reaction mixture is reduced as it reacts with A₂. The large peak, which is due to the polymer formed, moves to lower elution volumes (minutes) as more A₂ reacts with B₃ and molecular weight of the polymer increases. SEC peaks are very symmetrical until very high levels of A₂ addition. This is a good indication which shows that slow addition of A₂ into B₃ results in homogeneous polymer growth. At 76% A₂ addition SEC curve shows a shoulder at lower elution volumes, indicating the formation of small amount of very high molecular weight polymer. At 84% A₂ addition two well defined shoulders can be seen on the SEC curve between 14 and 16 min elution volume. This is very typical for hyperbranched systems, where formation of very high molecular weight polymers are observed as the stoichiometric ratio of [A₂]/[B₃] approaches to the gel point,⁷⁹ which is at 75.0% A₂ addition during this reaction, as discussed before. When average M_n and M_w and molecular weight distribution or polydispersity index (PI = M_w/M_n) values for the polymers are examined (Table 3-5), a slow growth in M_n and M_w, typical of step-growth polymerization reactions are observed. Initially PI values of the oligomers/polymers formed are also around 1.5, also typical for condensation reactions. However, as more A₂ is added into the system and reacted with B₃, PI values of the polymer formed start increasing rapidly to 2.20, 4.06 and 5.88 at 71, 76 and 84% A₂ addition, respectively.

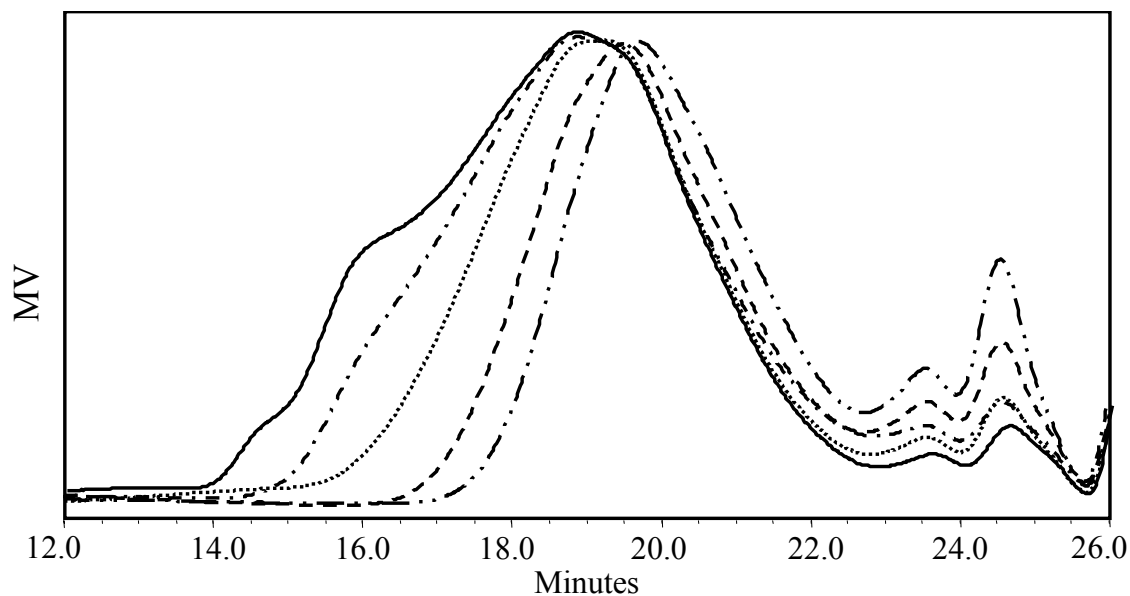


Figure 3-7. Monitoring the molecular weight development in oligomeric $A_2 + B_3$ polymerization as a function of mole percent of A_2 addition in the reaction between isocyanate end-capped PTMO-2k + ATA; in THF/IPA (25/75 wt/wt); concentration of the reaction medium 25% solids by weight.

(- · · -) 50%, (- - -) 60%, (· · · ·) 71%, (- · - · -) 76% and (————) 84% A_2 addition.

Table 3-5. Average molecular weights and molecular weight distributions of the polymers formed as a function of the amount of A₂ addition during the reaction of isocyanate terminated PTMO (A₂) and ATA (B₃). Concentration of reaction medium is 25% solids by weight.

sample	A₂ addition (%)	M_n (g/mol)	M_w (g/mol)	M_w/M_n
PUU-25-1	50	11,700	17,600	1.50
PUU-25-2	60	16,670	26,200	1.57
PUU-25-3	71	24,900	54,800	2.20
PUU-25-4	76	24,700	141,000	5.71
PUU-25-5	84	43,400	255,000	5.88
PUU-25-6	89	Gel	Gel	--

This is a clear indication of the formation of highly branched polymers, which typically show fairly high PI values.¹⁰⁵ Table 3-6 summarizes the SEC results on average molecular weights and molecular weight distributions of the polymers formed as a function of the amount of oligomeric A₂ addition during the reaction of isocyanate terminated PTMO (A₂) and ATA (B₃), where the concentration of reaction medium was 10% solids by weight. As A₂ is added and reacted with B₃, a gradual increase in M_n, M_w, and PI is observed, similar to that of 25% solid system discussed above. After 95% A₂ addition the increase M_n, M_w, and PI become more drastic due to the formation of highly branched polymers. Gel point in these experiments is observed at 112% of the A₂ addition (i.e. [A₂]/[B₃]=1.12). This is also in very good agreement with the low molecular weight A₂ (HMDI) + B₃ (ATA) system, where gel point was observed at 107.5% A₂ addition (i.e. [A₂]/[B₃]=1.075).

Figure 3-8 provides a direct comparison of the change in M_w as a function of oligomeric A₂ addition for polymerization reactions conducted at concentrations of 10 and 25% solids by weight. It is important to note that in both reactions the increase in M_w follows a very similar profile. The only difference is in the amount of A₂ needed to achieve similar M_w values for reactions carried out at different solution concentrations, due to dilution effects. In the reaction carried out at 25% solids, M_w values of the polymers formed are fairly low, less than 50,000 g/mol, until about 65% A₂ addition. Then as more A₂ is added a sharp upturn is observed and M_w reaches to 255,000 g/mol at 84% A₂ addition. A very similar behavior is observed in reactions conducted at 10% solids. As we have discussed in detail above, since the extent of cyclization is much higher at 10% solution than that of 25%, SEC results show formation of fairly low molecular weight polymers until about 85% A₂ addition, where M_w reaches to about 50,000 g/mol. At 95% and 102% A₂ additions M_w reaches to 75,000 and 116,000 g/mol, respectively. Then there is a very sharp increase in M_w, reaching to 392,000 g/mol at 110% A₂ addition.

Figure 3-9 provides a comparison of the change in PI for oligomeric A₂ + B₃ polymerization reactions conducted at concentrations of 10 and 25% solids by weight. In early stages of polymerization reactions, due to the stoichiometry of the mixture, where

¹⁰⁵ Gao, C.; Yan, D., *Prog. Polym. Sci.* **2004**, 29, 183.

B_3 is in large excess, mainly B_3 terminated oligomers and polymers with low degrees of branching are produced. As a result in both 10 and 25% reactions PIs are below 2.0, typical for step-growth polymers. However, as the amount of A_2 incorporation increases a dramatic increase in PI values, which goes to about 6.0 are observed. This is a clear indication of the formation of highly branched polymers.

Table 3-6. Average molecular weights and molecular weight distributions of the polymers formed as a function of the amount of A₂ addition during the reaction of isocyanate end-capped PTMO (A₂) and ATA (B₃). Concentration of reaction medium is 10% solids by weight.

sample	A₂ addition (%)	M_n (g/mol)	M_w (g/mol)	M_w/M_n
PUU-10-1	69	16,200	23,900	1.48
PUU-10-2	81	16,600	37,000	2.23
PUU-10-3	95	26,300	74,700	2.84
PUU-10-4	102	25,200	116,000	4.60
PUU-10-5	110	63,000	392,000	6.22
PUU-10-6	112	Gel	Gel	--

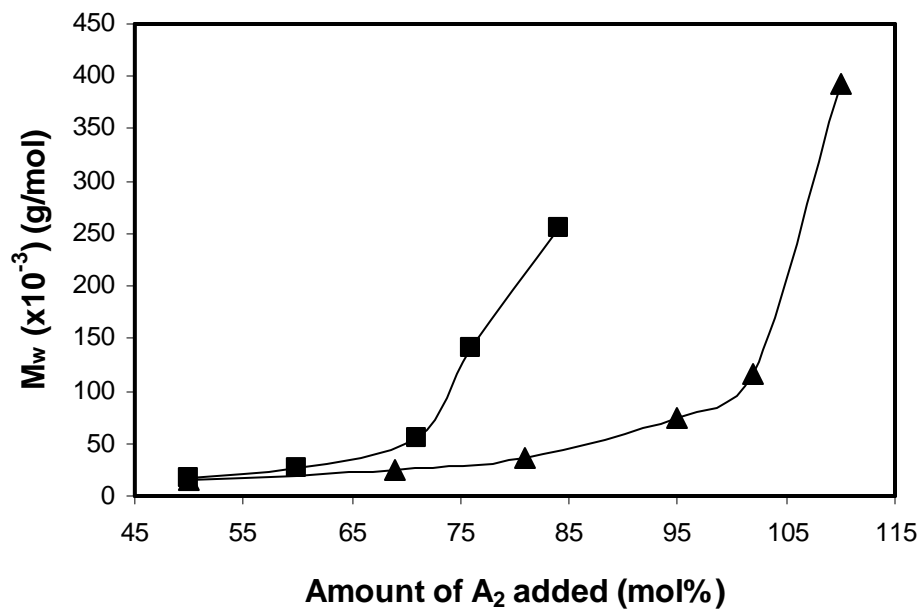


Figure 3-8. Comparison of the change in M_w as a function of oligomeric A_2 addition for polymerization reactions conducted at concentrations of 10% (▲) and 25% (■) solids by weight.

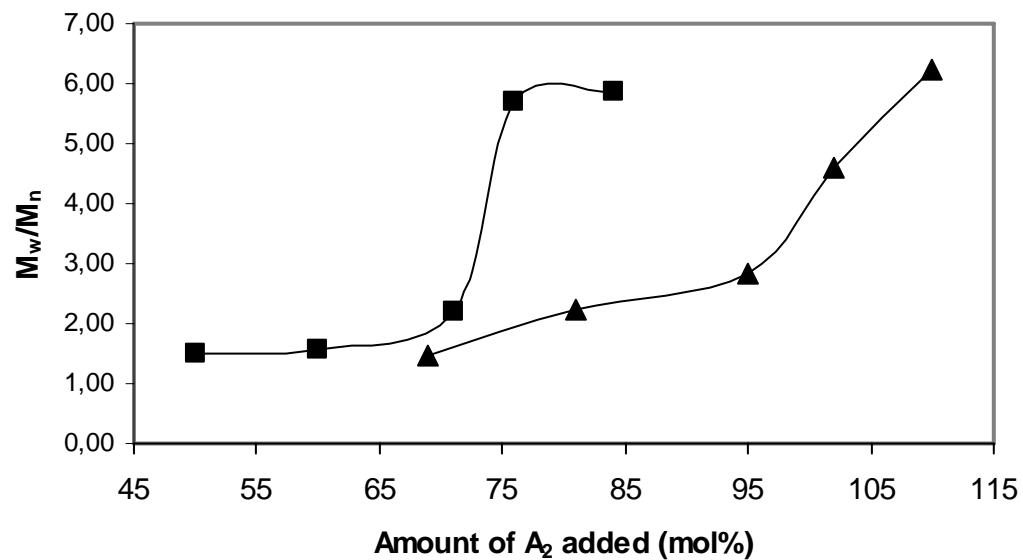


Figure 3-9. Comparison of the change in polydispersity (M_w/M_n) as a function of oligomeric A_2 addition for polymerization reactions conducted at concentrations of (\blacktriangle) 10% and (\blacksquare) 25% solids by weight.

3.5 Conclusions

Novel segmented hyperbranched polymers were obtained through oligomeric $A_2 + B_3$ chemistry. An isocyanate terminated polyether oligomer (A_2) was slowly added into a triamine (B_3) in order to achieve high molecular weight, gel-free products. These compositions exhibited microphase-separated morphologies as denoted by DMA. The similarity in soft segment glass transition behavior and strain hardening character of the hyperbranched systems with that of the linear system suggests such hyperbranched materials have considerable promise for structural applications. Formation of highly branched, segmented poly(urethane urea)s based on oligomeric $A_2 + B_3$ approach, where oligomeric A_2 is slowly added onto B_3 was investigated. SEC results clearly demonstrated the formation of high molecular weight segmented copolymers with high polydispersity values, typical of highly branched polymers. When polymerization reactions are conducted in dilute solutions no gelation was observed even at stoichiometric ratios of $[A_2]/[B_3]$ well beyond the theoretical gel point of 0.75. This was attributed to high degree of cyclization in dilute solutions.

3.6 Acknowledgements

This material is based upon work supported in part by the U.S. Army Research Laboratory and U.S. Army Research Office under Grant DAAD 19-02-1-0275 Macromolecular Architecture for Performance (MAP) MURI.

Chapter 4: Synthesis and Characterization of Poly(caprolactone) based, Highly Branched Segmented Poly(ester urethane)s

4.1 Abstract

Highly branched, segmented poly(ester urethane)s were synthesized via the polymerization of A_2 and B_3 type oligomers. The conventional two-step methodology (prepolymer synthesis + chain extension) to synthesize linear polyurethanes was not practical to synthesize highly branched polyurethanes. Thus, a new methodology was utilized, where an isocyanate functional A_2 hard segment was synthesized and polymerized with a B_3 soft segment. A branched polycaprolactone, PCL-triol was utilized as the B_3 oligomer. DMA and DSC analysis demonstrated that the PCL segment was completely amorphous in branched poly(ester urethane)s, whereas the crystallinity of PCL was retained to some extent in a linear analogue with equivalent soft segment molar mass. Stress-strain analysis revealed that the highly branched materials had slightly poorer mechanical performance than a linear analogue; however, showed lower hysteresis. Finally, poly(ester urethane) networks were prepared from a highly branched precursor, using a diisocyanate as the crosslinking agent.

4.2 Introduction

Segmented thermoplastic polyurethanes (TPU) and poly(urethane urea)s (TPUU) are important classes of polymeric materials that are widely used as high performance elastomers, fibers, coatings, adhesives, and biomaterials.^{106,107} The chemical composition of thermoplastic TPUs and TPUUs that consists of alternating soft and hard segments provides flexibility to tune the mechanical and thermal properties.¹⁰⁸ For example, the high performance of TPU and TPUU elastomers is attributed to the microphase separation between the hard and soft segments, with a continuous soft phase and strong hydrogen bonding interactions within urethane or urea hard domains. Therefore, the length of each segment plays an important role in microphase separation. In segmented copolymers, polyether, polyester, or polydimethylsiloxane oligomers that have low glass transition temperatures form the soft segment.

Polycaprolactone (PCL) polyols are widely used in the synthesis of TPUs and TPUUs, providing superior thermal and mechanical properties in various applications in the area of coatings, adhesives, shaped thermoplastics, and biomaterials.^{109, 110} Susceptibility of PCL to hydrolysis or to enzymatic activity of body components (biodegradation) renders PCL-based TPU and TPUUs candidates for biocompatible and biodegradable materials. These types of materials are widely used as vascular prostheses, artificial skins, pericardial patches, soft-tissue adhesives, drug delivery devices, scaffolds for tissue engineering, and artificial bones.¹¹¹ A drawback of using PCL as a soft segment in TPU or TPUU elastomers is the high degree of crystallinity of the PCL soft segment. The molar mass of PCL segment in TPUs and TPUUs is generally limited (varying from 500 to 2000 g/mol) due to the possibility of an undesirable crystalline phase in the high

¹⁰⁶ Woods, G., *The ICI Polyurethanes Book*. John Wiley: New York, 1990.

¹⁰⁷ Yilgor, E.; Yilgor, I., *Polymer* **2001**, 42, 7953.

¹⁰⁸ Hepburn, C., *Polyurethane Elastomers*. Elsevier Sci. Publ.: Essex, 1992.

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molar mass PCL segment.^{112,113} The crystallinity of PCL is disrupted when low molar mass PCL is used as the soft segment, however, low molar mass soft segments would damage the desirable microphase separated morphology that is essential for elastomers, and induce a significant extent of microphase mixing with the hard segment. On the other hand, systems based on higher molar mass PCL soft segment may possess a microphase separated morphology; however, a crystalline PCL phase becomes inevitable particularly after long aging times. Moreover, biodegradation behavior of PCL based TPUs is also dependent on the PCL soft segment molar mass.¹¹⁴

We have previously reported the preparation of segmented, highly branched PUU elastomers via the oligomeric $A_2 + B_3$ approach.¹¹⁵ Highly branched PUUs that were based on poly(tetramethylene oxide) (PTMO) displayed acceptable mechanical properties that were comparable to their linear analogues. In addition, large number of functional end groups permitted further chemical processes to enhance the performance of these PUUs. Moreover, these branched PUUs had significantly lower solution and melt viscosities compared to their linear analogues, which is a tremendous advantage in terms of processibility. Our recent efforts have focused on the preparation of highly branched PUs based on PCL soft segment. Herein, we report the synthesis and characterization of highly branched poly(ester urethane)s (HB-PEU) via an oligomeric $A_2 + B_3$ strategy. This approach utilizes commercially viable, functionally symmetric A_2 and B_3 monomers or oligomeric precursors to achieve a highly branched topology. The molar mass of the oligomeric precursors dictates the distance between each branch point and allows various topologies ranging from linear to hyperbranched. Optimization of the reaction conditions and a detailed comparison of the thermal and mechanical properties of HB-PEUs with their linear analogues are reported.

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4.3 Experimental

4.3.1 Materials

Bis(4-isocyanatocyclohexyl)methane (HMDI) (Bayer) with purities of >99.5% were used. PCL polyols (PCL-diol2k and PCL-triol2k) with M_n of 2000 were kindly donated by Solvay S.A. Molar mass of PCL polyols were confirmed by end-group titrations and ^1H NMR spectroscopic analyses. 1,4-butanediol (BD) and dibutyltin dilaurate (DBTDL) were purchased from Aldrich. Solvent, anhydrous dimethylacrylamide (DMAc, Aldrich), was used as received.

4.3.2 Characterization

Size exclusion chromatography (SEC) measurements were conducted on a Waters system that was equipped with three in-line PLgel 5 mm Mixed-C columns, an autosampler, a 410 RI detector, a Viscotek 270 dual detector, and an in-line Wyatt Technologies miniDawn multiple angle laser light scattering (MALLS) detector, at 40 °C in THF with a flow rate of 1 mL min⁻¹ using polystyrene standards. Molar masses were obtained from viscosity data based on universal calibration. Thermal analyses were conducted using a Perkin-Elmer Pyris 1 cryogenic differential scanning calorimeter (DSC) at a heating rate of 10 °C/min under a helium atmosphere. The first heat data were obtained upon cooling the sample from 25 to -120 °C and heating up to 80 °C at 10 °C/min. Dynamic mechanical analysis (DMA) was performed with a TA Instruments DMA 2980. The samples were quenched from room temperature to -125 °C and subjected to a heating rate of 2 °C/min and 1 Hz. MALDI-TOF/MS analyses were performed on a Kompact SEQ instrument using 100-180 power setting in positive ion linear mode. Laser wavelength was 337 nm, and the accelerating voltage was 20 kV in delayed extraction mode. The targets were prepared from a tetrahydrofuran (THF) solution with dithranol as the matrix and sodium iodide as the cationization reagent. The concentration of the matrix (dithranol) was 30 mg/mL, and the cationization reagent concentration was 2 mg/mL. Analytes were dissolved in THF at 10 mg/mL, and the analyte:matrix ratio was 2:5. ASI REACTIR 1000 was used for FTIR spectroscopy. Stress-strain tests were conducted on an Instron 5500 using dog-bone-shaped samples with 2.9 mm width, 10 mm grip separation distance, and 25 mm/min cross-head speed.

4.3.3 Synthesis of Branched Poly(ester urethane)s

Branched poly(ester urethane)s were synthesized using a two-step methodology. The first step involved the synthesis of an A₂ oligomer via the reaction of BD with excess HMDI in DMAc (~50 wt%). This reaction was conducted by dissolving HMDI and BD in a 2.05:1.00 molar ratio in DMAc at a 50% solution in a 3-neck flask, which was equipped with a nitrogen inlet, a condenser, and an overhead mechanical stirrer. The reaction was allowed to proceed at 80 °C in the presence of DBTDL (50 ppm) as catalyst for 2 h (Scheme 4-1). FTIR spectroscopy was used to confirm the completion of the reaction. Next step included mixing freshly prepared A₂, and B₃ oligomers (PCL-triol2k, Figure 4-1), where A₂:B₃ molar ratio was varied as shown in Table 4-1 and overall concentration of both reagents was maintained at 50 wt% in DMAc. As summarized in Table 4-1, three different methodologies, (I) mixing A₂ and B₃ at the polymerization onset, (II) slow addition of A₂ into B₃, (III) slow addition of B₃ into A₂ were used. The reactions were allowed to proceed for 24 h at 80 °C and followed by FTIR spectroscopy. HB-PEU films that were used for characterization were cast from DMAc solution and dried in vacuum at 80 °C until a constant weight was reached. The samples listed in Table 4-1 were identified as: HB-PEU-*x*, where HB denotes highly branched, PEU denotes poly(ester urethane), and *x* denotes the sample entry.

4.3.4 Synthesis of Linear Poly(ester urethane)s

A linear poly(ester urethane) (L-PEU) was synthesized via the conventional two-step methodology (prepolymer + chain extension).¹⁰⁷ A prepolymer of isocyanate terminated PCL-diol2k that was synthesized in bulk at 80 °C in the presence of DBTDL (50 ppm) was chain extended with BD at a 60 wt % solution in DMAc. The reaction was allowed to proceed for 24 h at 80 °C and quantitative conversions were confirmed using FTIR spectroscopy. The L-PEU film that was used for characterization was cast from DMAc solution and dried in vacuum at 80 °C until a constant weight was reached.

Table 4-1. Composition, synthetic routes, and SEC results for linear and highly branched poly(ester urethane)s.

sample	HS ^a (wt %)	route	A ₂ :B ₃	M _w (g/mol)	M _w /M _n	g'
HB-PEU-1	19	I	0.8:1.0	18,200	10.1	0.62
HB-PEU-2	23	I	1.0:1.0	167,000	8.0	0.36
HB-PEU-3	23	I	1.0:1.0	207,000	6.0	0.26
HB-PEU-4	27	I	1.2:1.0	gel	gel	gel
HB-PEU-5	27	I	1.2:1.0	- ^{b,c}	-	-
HB-PEU-6	23	II	1.0:1.0	28,000	1.7	0.57
HB-PEU-7	23	III	1.0:1.0	gel	gel	gel
L-PEU-1	24	I	-	37,900	1.9	0.97

^a Hard segment content = 100*(HMDI+BD)/(HMDI+BD+PCL);

^b Polymerization medium diluted to ~10 wt % after 3 h;

^c Limited solubility in THF.

Route I: A₂ and B₃ were mixed at the polymerization onset.

Route II: A₂ was added dropwise into B₃.

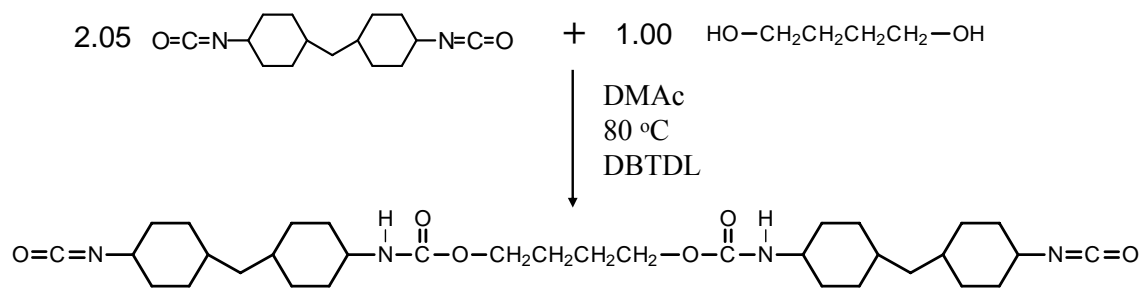
Route III: B₃ was added dropwise into A₂.

4.4 Results and Discussion

4.4.1 Synthesis of Poly(ester urethane)s

4.4.1.1 Synthesis of A_2 Oligomer

HB-PEUs were synthesized using a two-step methodology. The first step consisted of the synthesis of an isocyanate terminated A_2 oligomer. As shown in Scheme 4-1, the reaction of excess HMDI with BD is expected to yield an A_2 oligomer, which is a mixture of isocyanate terminated products with different degrees of polymerizations. MALDI-TOF/MS analysis confirmed the predominance of the desired A_2 oligomer in Scheme 4-1, with low fractions of higher degrees of polymerizations. As revealed by MALDI-TOF/MS (Figure 4-2), the final A_2 oligomer had a polydispersity of ~ 1.15 , which demonstrates that the A_2 product shown in Scheme 4-1 is the most plausible structure (Figure 4-2). The isocyanate terminated A_2 oligomer product was reacted with excess 1-butanol to eliminate highly reactive isocyanate end groups prior to MALDI-TOF/MS analysis. It should be noted butanediol was completely endcapped with isocyanate since MALDI-TOF did not detect any undesirable products, such as mono-end-capped butanediol. However, endcapping with 1-butanol was not 100%, and multiple peaks in Figure 4-2 are due to A_2 with di- or monosubstituted (butyl) chain ends.



Scheme 4-1. Synthesis of the A₂ oligomer.

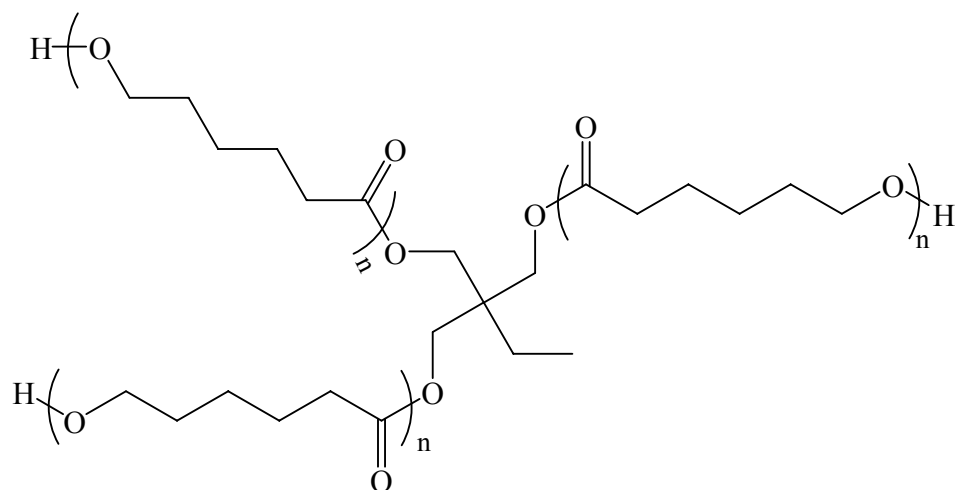


Figure 4-1. Chemical structure of the B₃ oligomer, polycaprolactone triol (PCL-triol2k).

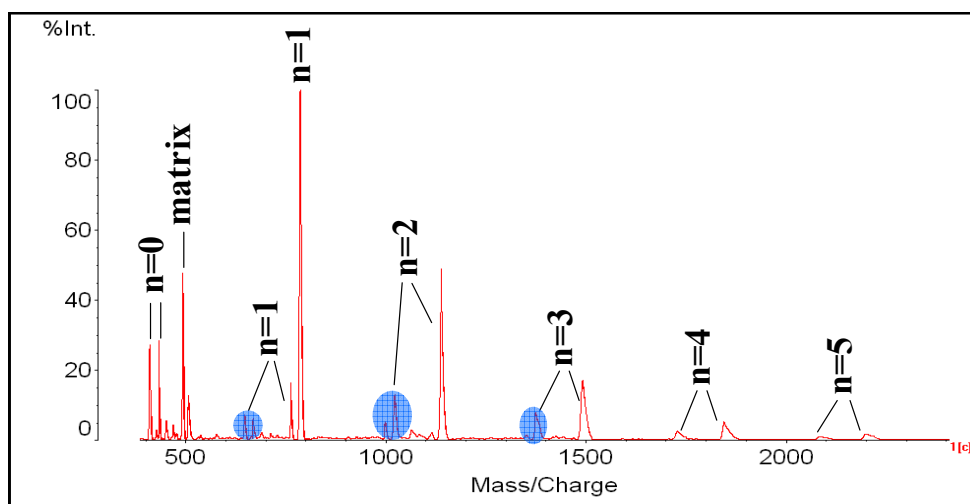
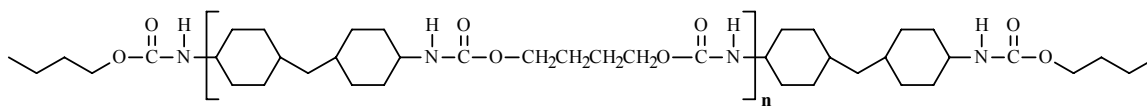


Figure 4-2. MALDI-TOF/MS analysis of A₂ oligomer with M_w/M_n = 1.15.

4.4.1.2 Polymerization

The second step involved the polymerization of a freshly synthesized A₂ oligomer with PCL-triol2k (B₃, Figure 4-1). As depicted in Scheme 4-2, polymerization of A₂ and B₃ oligomers generates a highly branched topology with a high concentration of branching within the soft segment. The final architecture in Scheme 4-2 is unlike that of highly branched PUUs we previously synthesized via the same methodology, where the branch points were located at the hard segment.

It is well established that controlled reaction conditions, such as the solution concentration, molar ratio and addition order of monomers, relative reactivity of the functional groups, and preferred partial monomer conversion effectively avoids gelation in an A₂ + B₃ polymerization.¹¹⁶ Thus, it was essential to optimize the reaction conditions to obtain gel-free, fully soluble products in our studies. As summarized in Table 4-1, two variables, the order of monomer addition, and molar ratio of A₂:B₃ were systematically changed. The polymerization of A₂ and B₃ monomers could proceed via three different routes; (I) mixing A₂ and B₃ at the onset of the reaction, (II) slow addition of A₂ into B₃, or (III) slow addition of B₃ into A₂.^{116,117} We have previously shown that due to the fast reaction rates between acid chlorides and alcohols,^{116,118} as well as isocyanates and amines,¹¹⁵ slow addition of A₂ into B₃ was the only feasible route to obtain gel-free, highly branched products. In this case, a slower reaction rate between the isocyanate and alcohol allowed us to study the influence of the three different routes on the properties of final products. Mixing A₂ and B₃ monomers at a 1.0:1.0 molar ratio at the onset of the polymerization (I) yielded high molar mass products with very high polydispersities (HB-PEU-2 and HB-PEU-3). On the other hand, route II yielded lower molar mass products with much lower polydispersities (HB-PEU-6, Table 4-1). Finally, route III resulted in gelation (HB-PEU-7) due to the formation of mostly dendritic units at early stages of the polymerization upon slow addition of the B₃ to an excess A₂, as also reported previously.

The molar ratio of the A₂:B₃ is another important parameter that influences the properties of final products. Theoretically, as the ratio of A₂:B₃ increases, the probability

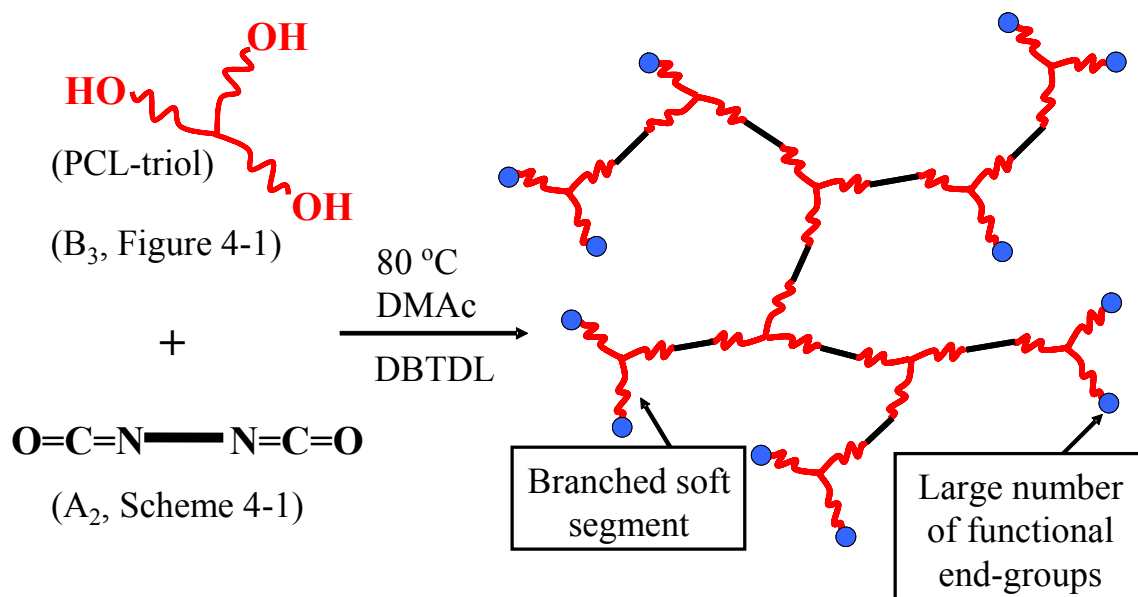
¹¹⁶ Unal, S.; Lin, Q.; Mourey, T. H.; Long, T. E., *Macromolecules* **2005**, 38, 3246.

¹¹⁷ Czupik, M.; Fossum, E., *J. Polym. Sci. Part A: Polym. Chem.* **2003**, 41, 3871.

¹¹⁸ Lin, Q.; Long, T. E., *Macromolecules* **2003**, 36, 9809.

of gelation also increases. During the synthesis, a 1.0:1.0 ratio of monomers yielded gel free, highly branched products (HB-PEU-2 and HB-PEU-3). As expected, when a lower ratio of A₂ to B₃ (0.8:1.0) was mixed at the onset of the reaction (HB-PEU-1), lower molar mass products were obtained. On the other hand, polymerization of A₂ and B₃ monomers with a ratio of 1.2:1.0 (HB-PEU-4) resulted in gelation. However, dilution of the polymerization medium to ~10 solids wt % during the synthesis of (HB-PEU-5, A₂:B₃ = 1.2:1.0) upon the viscosity increase in 3 h resulted in a highly viscous, fully soluble product. Although the final product was soluble in the polymerization solvent, DMAc, SEC characterization in THF was not possible due to very high molar mass. The absence of gelation was attributed to the cyclization reactions that were promoted by further dilution of the polymerization medium. SEC curves and the Mark-Houwink plots from the SEC-viscosity data for linear and highly branched PEUs indicated a much broader molar mass distributions for HB-PEUs compared to the linear analogue (Figure 4-3). Such high molar mass distributions were expected in highly branched polymers synthesized via A₂ + B₃ methodology. Moreover, the Mark-Houwink plots for L-PEU and HB-PEU-2 revealed the influence of the branching on the solution viscosity behavior of macromolecules, showing that the HB-PEU-2 had a lower solution viscosity than the linear analogue at any equivalent molar mass.

Dilute solution viscosity of branched polymers was rationalized determining the branching index value (g') which is an indirect method of characterizing the degree of branching. The value g' was calculated using the equation; $g' = [\eta]_{\text{branched}}/[\eta]_{\text{linear}}$ where $[\eta]_{\text{branched}}$ and $[\eta]_{\text{linear}}$ are the intrinsic viscosities of branched and linear polymers of equivalent molar masses. For any branched polymer, $[\eta]_{\text{linear}}$ was calculated using the Mark-Houwink equation ($[\eta]_{\text{linear}} = KM_w^a$), where K and a values are obtained from the SEC-viscosity for a linear analogue. The g' values close to unity indicate that the polymer is linear and this value decreases as the branching increases. For the L-PEU, the g' value was 0.97, whereas HB-PEUs had much lower g' values (as low as 0.25), indicating higher degrees of branching compared to L-PEUs (Table 4-1). HB-PEU-1 that was synthesized at A₂:B₃ = 0.8:1.0 ratio had a g' value of 0.62, whereas HB-PEU-6 that was synthesized via the slow addition of A₂ into B₃ had a g' value of 0.57. These two values indicate the formation of products with slightly branched topologies rather than highly branched under these conditions.



Scheme 4-2. Synthesis of highly branched poly(ester urethane)s via oligomeric $A_2 + B_3$ polymerization.

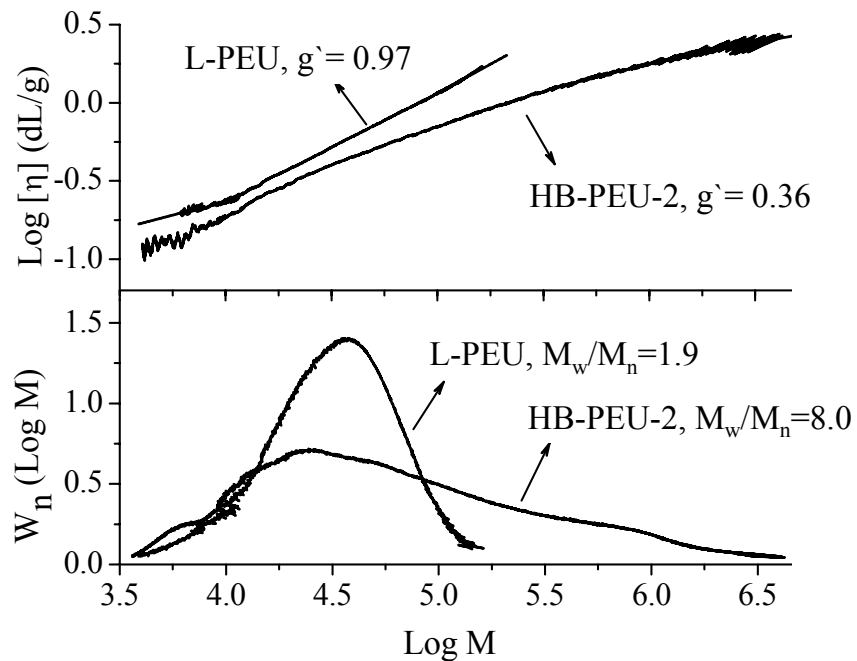


Figure 4-3. Mark-Houwink plots and SEC traces for highly branched and linear poly(ester urethane)s.

4.4.2 Characterization of Poly(ester urethane)s

4.4.2.1 Differential Scanning Calorimetry and Dynamic Mechanical Analyses

As mentioned earlier, one of the major drawbacks of using high molar mass PCL soft segments in TPU elastomers is the high degree of crystallinity of PCL. In order to investigate the influence of branching on the crystallization behavior of PCL soft segment, first heat DSC and DMA results were evaluated. Figure 4-4 shows the first heat DSC results for HB-PEU-3 and the L-PEU after one week of storage at room temperature. Both polymers showed a soft segment glass transition temperature (T_g) approximately at -50 °C. In addition, L-PEU showed a melting transition at 37 °C, whereas HB-PEU-3 was completely amorphous. This observation was not surprising according to the first heat data for the PCL-triol2k and PCL-diol2k precursors in Table 4-2. The first heat ΔC_p and ΔH_m values for PCL-triol2k and PCL-diol2k revealed that both precursors were semicrystalline; however, PCL-triol2k had a lower degree of crystallinity than the PCL-diol2k precursor. It has been also reported previously that topological changes dramatically influence the crystallization behavior of PCL.¹¹⁹ The first heat results were more reliable in terms of truly understanding the crystallization behavior of PCL. Second heat DSC results showed a completely amorphous soft segment for both L-PEU and HB-PEUs; however, after aging for one week, a crystalline phase appeared in L-PEU upon the first heat, indicating a slow crystallization behavior of PCL in urethane copolymers. The soft segment T_g for the L-PEU and HB-PEUs was slightly higher compared to the pure soft segment precursors (-65 °C), and this behavior was attributed to the mobility restrictions on the soft segment due to covalently linked urethane hard segments. Solution cast films of the L-PEU and HB-PEUs were characterized using DMA after 4 months of storage at room temperature. As shown in Figure 4-5, both L-PEU and HB-PEUs showed a soft segment T_g around -32 °C. The linear analogue had a higher storage modulus of the rubbery plateau until ~50 °C, and began to decrease due to the melting of the PCL crystalline phase. On the other hand, the branched products, HB-PEU-3 and HB-PEU-5 did not display any melting transition, indicating the absence of a PCL crystalline phase in highly branched products even after 4 months of storage. Finally, an increase was observed in $\tan \delta$ peak for the products, after ~75 °C due to softening of the hard segment.

¹¹⁹ Choi, J.; Kwak, S. Y., *Macromolecules* **2004**, 37, 3745.

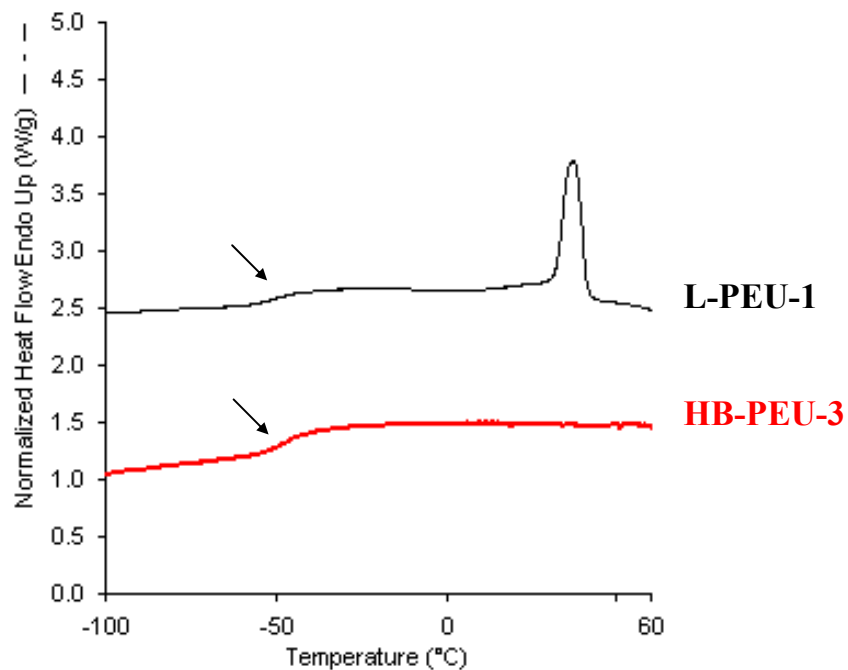


Figure 4-4. Differential scanning calorimetry of linear and highly branched poly(ether ester)s; 1st heat after 1 week of storage.

Table 4-2. 1st heat differential scanning calorimetry results for pure PCL soft segment precursors and corresponding linear or highly branched poly(ether ester)s.

Sample	T _g (°C)	ΔC_p (J/g °C)	T _m (°C)	ΔH_m (J/g)
PCL-triol2k	-65	0.67	25, 38	96.8, 82.9
PCL-diol2k	-67	0.33	50	204.8
HB-PEU-3	-52	1.23	-	-
HB-PEU-6	-48	1.53	-	-
L-PEU-1	-50	0.81	37	54.8

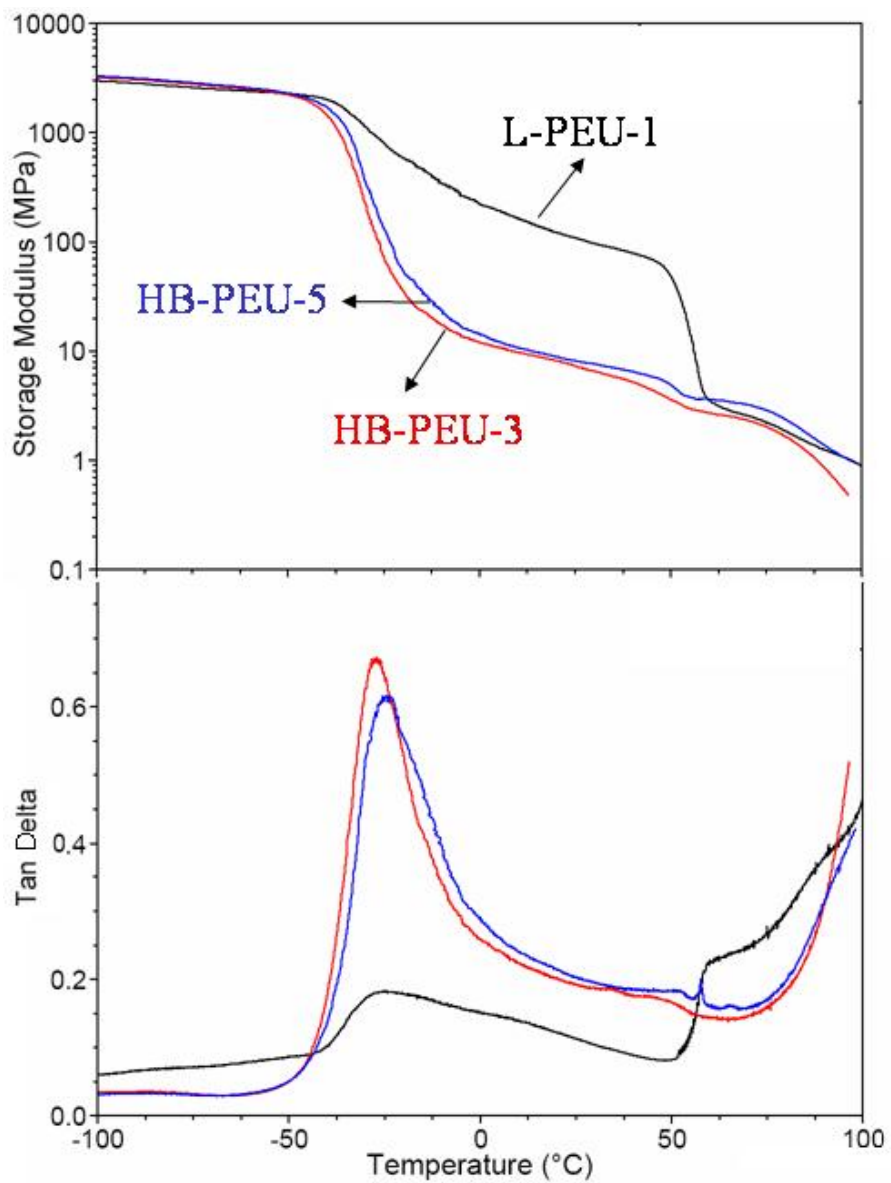


Figure 4-5. DMA response of linear and highly branched poly(ester urethane)s.

4.4.2.2 Mechanical Properties

The stress-strain results of the L-PEU and HB-PEUs are presented in Figure 4-6. Both linear and branched samples showed similar elongations at break; however, L-PEU showed a higher tensile strength and Young's modulus than the two HB-PEUs. Higher tensile strength and Young's modulus of the linear analogue was attributed to the presence of a PCL crystalline phase, which acted as another type of hard block in the polymer matrix. In return, the branched samples showed better recovery upon elongation, whereas the linear sample showed longer recovery times, due to the disruption of the crystallinity and slow re-crystallization of PCL.

The accessibility of the large number of functional end groups in HB-PEUs was demonstrated in Figure 4-7. A poly(ester urethane) network was prepared from a highly branched poly(ester urethane) precursor (HB-PEU-3) reacting a branched poly(ether ester) precursor with a diisocyanate at a stoichiometric ratio of hydroxyl and isocyanate groups and casting on a mold. Crosslinking was performed at 80 °C, and the final product had ~92% gel, which demonstrated that these low viscosity, highly functional materials have promising in coatings applications. Figure 4-8 demonstrates the dramatic increase in the mechanical performance of the poly(ester urethane) network.

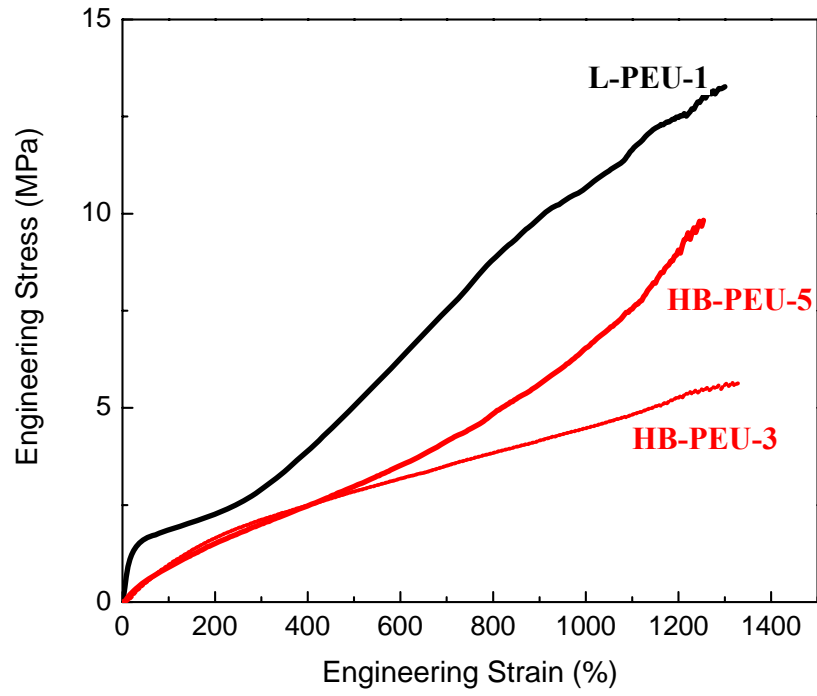


Figure 4-6. Stress-strain behavior of linear and highly branched poly(ether ester)s.

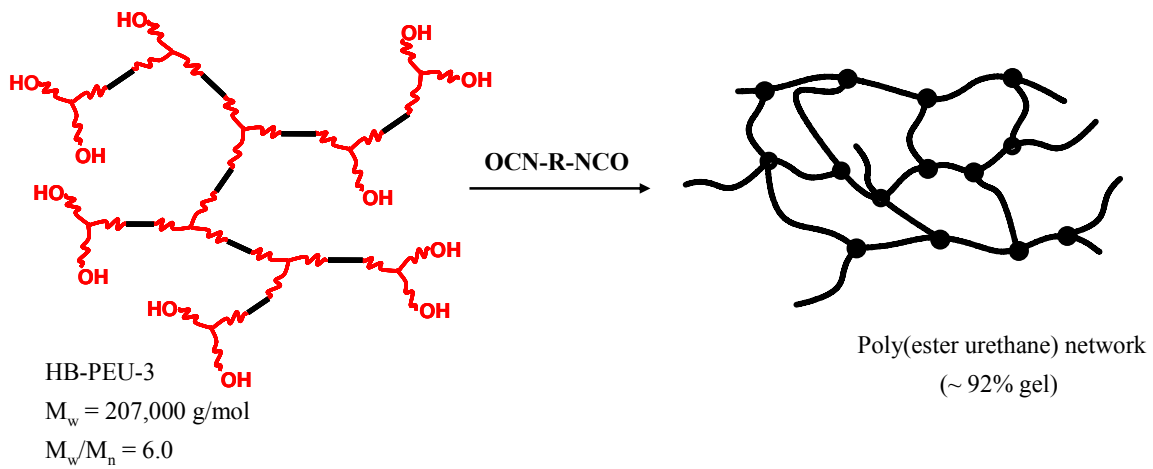


Figure 4-7. Preparation of a poly(ester urethane) network from a highly branched precursor.

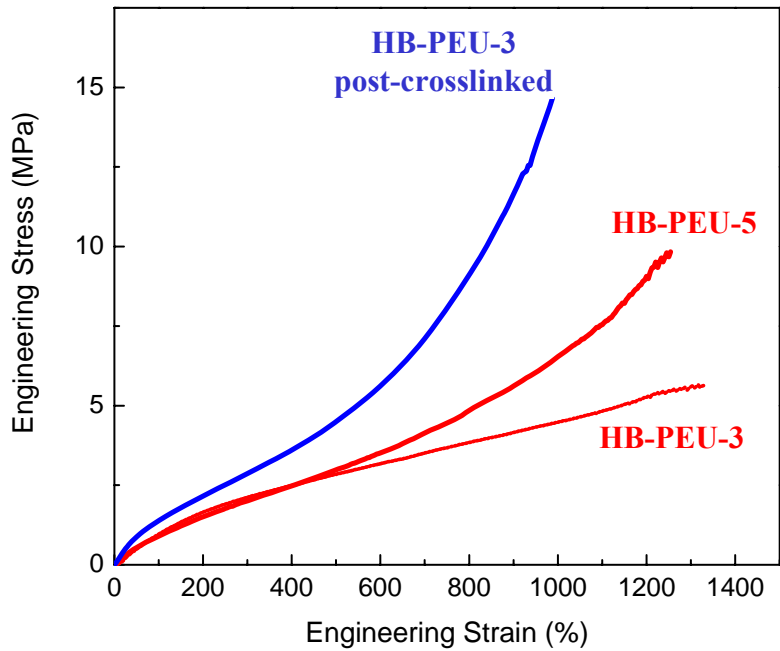


Figure 4-8. Stress-strain behavior of a poly(ester urethane) network and prepared from a high branched precursor (HB-PEU-3).

4.5 Conclusions

Polycaprolactone (PCL) based, highly branched poly(ester urethane)s were synthesized using the oligomeric $A_2 + B_3$ polymerization. Reaction conditions were optimized in order to obtain a fully soluble, highly branched structure. A branched PCL, PCL-triol was utilized as the B_3 oligomer, whereas an isocyanate functional A_2 oligomer was freshly synthesized and utilized. DMA and DSC analysis demonstrated that the PCL segment was completely amorphous in branched poly(ester urethane)s, whereas the crystallinity of PCL was retained to some extent in a linear analogue with equivalent soft segment molar mass. Therefore, it was clearly demonstrated that a branched soft segment allows the incorporation of higher molar mass PCL soft segments, which also dramatically reduces the solution viscosity and increases the number of functional end groups in these materials. In return, highly branched materials showed slightly poorer mechanical performance than the linear analogue; however, crystalline PCL phase contributed to the tensile strength and Young's modulus of the linear analogue. Finally, accessibility and utility of functional end groups were demonstrated by preparing a poly(ester urethane) network from a highly branched precursor.

4.6 Acknowledgements

This material is based upon work supported in part by the U.S. Army Research Laboratory and U.S. Army Research Office under Grant DAAD 19-02-1-0275 Macromolecular Architecture for Performance (MAP) MURI. The authors also thank Eastman Chemical Company for financial support.

Chapter 5: Tailoring the Degree of Branching: Preparation of Poly(ether ester)s via Copolymerization of Poly(ethylene glycol) Oligomers (A₂) and 1,3,5-benzenetricarbonyl trichloride (B₃)

Taken From:

Unal, S.; Lin, Q.; Mourey, T. H.; Long, T. E. "Tailoring the Degree of Branching: Preparation of Poly(ether ester)s via Copolymerization of Poly(ethylene glycol) Oligomers (A₂) and 1,3,5-benzenetricarbonyl trichloride (B₃).” *Macromolecules* **2005**, *38*, 3246-3254.

5.1 Abstract

A novel approach to tailor the degree of branching of poly(ether ester)s was developed based on the copolymerization of oligomeric A₂ and B₃ monomers. A dilute solution of poly(ethylene glycol) (PEG) (A₂) was added slowly to a dilute solution of 1,3,5-benzenetricarbonyl trichloride (B₃) at room temperature in the presence of triethylamine to prepare high molar mass gel-free products. PEG diols of various molar masses permitted the control of the degree of branching and an investigation of the effect of the distance between branch points. ¹H NMR spectroscopy indicated a classical degree of branching (DB) of 69% for a highly branched poly(ether ester) derived from 200 g/mol PEG diol. A revised definition of the degree of branching was proposed to accurately describe the branched poly(ether ester)s and the degree of branching decreased as the molar mass of the PEG diols was increased. The effects of branching and the length of the PEG segments on the thermal properties of the highly branched polymers were investigated using differential scanning calorimetry (DSC). Amorphous branched poly(ether ester)s were obtained using PEG diols with number average molar masses of either 200 or 600 g/mol. In-situ functionalization of the terminal acyl halide units with 2-hydroxyethyl acrylate provided novel photo-cross-linkable precursors.

5.2 Introduction

Tailored topology exerts a pronounced effect on the thermal, mechanical, and rheological properties of macromolecules.^{120,121} For example, high-density polyethylene (HDPE) and low density polyethylene (LDPE) are composed of nearly identical repeat units, which, however, exhibit dramatically different properties. Tailoring the extent and nature of branching in macromolecules has led to exquisite control of many physical properties. Branching during chain polymerization has received significant attention, and polyethylenes, for example, with diverse topologies that range from linear to dendritic structures are attainable via systematic changes in catalysts and reaction conditions.¹²⁰ Branching during step-growth polymerization also received considerable initial attention in the late 1970s for the preparation of unique branched architectures.¹²² Linear macromolecules are typically prepared via step-growth copolymerization of either AB monomers or a combination of A₂ and B₂ monomers. On the other hand, highly branched polymers, such as hyperbranched polymers, are often prepared via the self-condensation of AB_n monomers.^{123,124} Although Flory first described the synthesis of highly branched polymers via the self-condensation of AB₂ monomers or copolymerization of AB and AB₂ monomers in 1952,¹²⁵ hyperbranched polymers have received significant and renewed attention since the early 1990s. Webster and Kim first coined the term

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¹²⁴ Hawker, C. J.; Lee, R.; J., F. J. M., *J. Am. Chem. Soc.* **1991**, 113, 4583. Turner, S. R.; Voit, B. I.; Mourey, T. H., *Macromolecules* **1993**, 26, 2617. Gooden, J. K.; Gross, M. L.; Mueller, A.; Stefanescu, A. D.; Wooley, K. L., *J. Am. Chem. Soc.* **1998**, 120, 10180. Turner, S. R.; Walter, F.; Voit, B. I.; Mourey, T. H., *Macromolecules* **1994**, 27, 1611. Hult, A.; Johansson, M.; Malmstrom, E., *Adv. Polym. Sci.* **1999**, 143, 1. Kumar, A.; Ramakrishnan, S., *J. Polym. Sci. Part A: Polym. Chem.* **1996**, 34, 839. Bolton, D. H.; Wooley, K. L., *J. Polym. Sci. Part A: Polym. Chem.* **2002**, 40, 823. Hahn, S. W.; Yun, Y. K.; Jin, J. I., *Macromolecules* **1998**, 31, 6417. Emrick, T.; Chang, H. T.; Fréchet, J. M. J., *Macromolecules* **1999**, 32, 6380. Eichman, J. D.; Bielinska, A. U.; Kukowska-Latallo, J. F.; Baker, J., J. R., *PSTT* **2000**, 3, 232. Kunamaneni, S.; Buzza, D. M. A.; Parker, D.; Feast, W. J., *J. Mater. Chem.* **2003**, 13, 2749.

¹²⁵ Flory, P. J., *J. Am. Chem. Soc.* **1952**, 74, 2718. Flory, P. J., *Principles of Polymer Chemistry*. Cornell University Press: Ithaca, NY, 1953.

“hyperbranched” in the late 1980s, which referred to a dendrimer-like structure with a very high degree of branching.¹²⁶ Hyperbranched polymers are expected to exhibit inferior mechanical properties due to poor molar mass control and a lack of significant chain entanglements.¹²⁷ However, the continued discovery of many synthetic strategies for hyperbranched polymers and the realization of unique applications for highly branched polymers has resulted in the application of hyperbranched polymers as low-cost additives, dispersants, and compatibilizers.¹²⁸

Other commercially viable, synthetic methods were reported earlier for the preparation of polymers with degrees of branching that range between linear and hyperbranched polymers. For example, copolymerization of A₂ and B₂ monomers with a low level of a B₃ monomer (<2 mol %) typically results in products with a very low degree of branching.¹²⁹ Gelation prevents the incorporation of higher levels of B₃ monomers that are required to obtain higher levels of branching. Flory also proposed the copolymerization of AB and AB₂ monomers and the corresponding degree of branching of the final structures.¹²⁵ This synthetic method does not result in gelation and the molar ratio of AB to AB₂ monomers controls the degree of branching. Several families of polymers with different degrees of branching were prepared earlier based on this methodology and the effects of branching on the physical properties were thoroughly investigated.¹³⁰ However, the limited availability of functionally nonsymmetrical AB

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and AB₂ monomers has prevented many industrial applications, and more facile synthetic methods are needed for further exploration of branching in macromolecules.

Recently, alternative methodologies to the polymerization of AB_n monomers for the preparation of hyperbranched polymers have received attention, and it was demonstrated that the copolymerization of A₂ and B₃ monomers proceeds without gelation.¹³¹ In addition, A₂ and B₃ monomers are more readily available than AB and AB₂ monomers, which provides more facile routes to several families of hyperbranched polymers. Our recent efforts have also focused on A₂ with B₃ synthetic methodologies in order to control the degree of branching in highly branched copolymers.¹³² However, our approach involves the use of oligomers as A₂ or B₃ monomers for copolymerization without gelation. Although the reaction methodology is similar to the polymerization of low molar mass A₂ and B₃ monomers, the degree of branching was effectively tailored via the oligomeric A₂ or B₃ molar mass. Thus, macromolecules with a range of branched topologies were prepared without AB or AB_n monomers. Moreover, the final products exhibited a well-defined distance between B units due to the use of relatively narrow molar mass distribution A₂ oligomers. In contrast, branched polymers that are derived from the copolymerization of AB and AB_n monomers have a more ill-defined chain length between branch points.

This paper specifically describes the preparation of poly(ether ester)s with different degrees of branching via an oligomeric A₂ with B₃ methodology. These novel branched architectures are both fundamentally interesting and commercially viable.

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¹³² McKee, M.; Unal, S.; Wilkes, G. L.; Long, T. E., *Prog. Polym. Sci.* **2005**, 30, 507.

Poly(ethylene glycol) (PEG) is a semicrystalline, water soluble thermoplastic that is used in a wide range of applications such as biocompatible materials, drug and gene delivery, optical devices, cosmetics, and thermoplastic elastomers.¹³³ Poly(ethylene oxide)s that contain alkali metal salts also exhibit acceptable mechanical properties and ionic conductivity.¹³⁴ Hawker and co-workers have reported the preparation of hyperbranched poly(ether ester)s as a new class of ion conducting materials via AB₂ condensation.¹³⁵ The introduction of branching in the polymer backbone disrupted crystallinity and completely amorphous polymers were obtained. However, a multistep synthesis of complex AB₂ monomers was required prior to polymerization, and the distance between branch points was significantly less than the critical molar mass for entanglement. The one-step oligomeric A₂ and B₃ methodology based on PEG diols offers a more facile approach to products with improved properties and performance. In addition, new applications such as highly branched poly(ether ester)s with ethyl acrylate end groups were also prepared to obtain photo-cross-linkable precursors.

5.3 Experimental

5.3.1 Materials

Ethylene glycol (EG), diethylene glycol (DEG), poly(ethylene glycol) (PEG) (M_n: 200, 600, 2000, and 3400 g/mol), 1,3,5-benzenetricarbonyltrichloride (BTC) (99%), anhydrous triethylamine (TEA) (99%), dimethyl isophthalate (DMI), titanium tetraisopropoxide (99%), 2-hydroxyethyl acrylate (96%) (2-HEA), phenol (99+%), and 2,2-dimethoxy-2-phenylacetophenone (DMPA) (99%) were purchased from Aldrich. Chloroform was purchased from Burdick and Jackson (high purity), and methanol was purchased from EM Science. Chloroform and TEA were stirred over calcium hydride and distilled under nitrogen. EG, DEG, and PEG diols were dried in a vacuum oven (0.50 mmHg) at 70 °C for 18 h prior to polymerization. All other reagents were used as received unless otherwise stated.

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¹³⁵ Hawker, C. J.; Lee, R.; J., F. J. M., *J. Am. Chem. Soc.* **1991**, 113, 4583.

5.3.2 Characterization

^1H NMR spectroscopic analyses were performed on a Varian Unity 400 MHz spectrometer at ambient temperature. Size-exclusion chromatography (SEC) with viscometry detection (Viscotek model 110) in *N,N*-dimethylformamide (DMF) containing 0.01 M lithium nitrate at 35 °C using three Polymer Standards Services Gram Linear 8 x 300 mm columns was used to determine molar mass. Absolute molar masses were calculated from viscosity data based on a universal calibration curve that was constructed from narrow molar mass distribution poly(methyl methacrylate) standards. Thermal transition temperatures were determined using a Perkin-Elmer Pyris-1 at 10 °C/min under a helium atmosphere, and all reported data were obtained from the second heating. MALDI-TOF/MS analyses were performed on a Kompact SEQ instrument using 100-180 power setting in positive ion linear mode. Laser wavelength was 337 nm, and the accelerating voltage was 20 kV in delayed extraction mode. The targets were prepared from a tetrahydrofuran (THF) solution with dithranol as the matrix and potassium trifluoroacetate as the cationization reagent. The concentration of the matrix, dithranol, was 10 g/L, and the cationization reagent concentration was 1 g/L. Polymer samples were also dissolved in THF at 10 g/L, and the three solutions were mixed at a ratio of 8:1:1 matrix:salt:polymer.

5.3.3 Synthesis of Linear Poly(ether ester)s

Linear poly(ether ester)s were termed as L-xxx, L denoting linear, and xxx denoting the PEG precursor M_n . For the synthesis of L-200, a single neck, 250 mL round-bottomed flask was charged with 10.00 g of DMI (0.051 mol) and 10.30 g of PEG-200 (0.051 mol). Titanium tetraisopropoxide (20 ppm) was added to facilitate transesterification. The reaction flask, which contained the monomers and the catalyst, was degassed using vacuum and nitrogen three times and subsequently heated to 180 °C. The reactor was maintained at 180 °C for 2 h, and the temperature was increased to 200 °C over 2 h. Vacuum was applied (0.5 mmHg) for 30 min to ensure the removal of methanol. The product (L-200) was used as received. A similar synthetic method was used to prepare linear poly(ether ester)s from PEG-600 (L-600) and PEG-2000 (L-2000)

with the exception that equimolar amounts of PEG-600 and PEG-2000 were used with DMI.

5.3.4 Synthesis of Branched Poly(ether ester)s with Methyl Ester Terminal Groups

Methyl ester terminated, branched poly(ether ester)s were termed as HB-xxx-Me-y, HB denoting highly branched, xxx denoting the PEG precursor M_n , Me denoting methyl ester terminal groups, y denoting sample number. For the synthesis of HB-200-Me-1, BTC (10.00 g, 0.038 mol) was dissolved in 70 mL of freshly distilled chloroform in a dried, 250 mL two-necked flask equipped with a magnetic stir bar and addition funnel. PEG-200 (7.54 g, 0.038 mol) and TEA (11.41 g, 0.113 mol) were dissolved in 80 mL of freshly distilled chloroform and transferred into the addition funnel. The oligomer solution was slowly added to the reaction flask over 2 h, and a homogeneous reaction was maintained at ambient temperature for 24 h. Excess methanol was subsequently added to quench the terminal acid chloride end groups, and the homogeneous solution was stirred for 6 h. The solution was washed with deionized water three times and precipitated into hexane at $\sim 0^\circ\text{C}$. A waxy, pale yellow product was collected, and dried at 60°C in a vacuum oven for 24 h. Typical yields ranged from 90 to 95%. ^1H NMR (chloroform-*d*, ppm): 8.70-8.95 (3H, aromatic protons from BTC), 3.50-4.60 (4H, protons from PEG, 3H, protons from methyl ester terminal unit), 4.44 (-NCH₂CH₃), 1.42 (-NCH₂CH₃). ^{13}C NMR (chloroform-*d*, ppm): 164.9 (O=C-OCH₃, methyl ester end groups), 164.4 (O=C-OCH₂CH₂-), 134.2 and 130.7 (BTC), 70.3, 68.7, and 64.4 (PEG), 52.3 (-OCH₃, methyl ester end groups), 61.4 and 13.9 (-NCH₂CH₃, TEA salt).

A similar synthetic method was used to prepare methyl ester terminated, branched poly(ether ester)s from PEG-600 (HB-600-Me-y), PEG-2000 (HB-2000-Me-y), and PEG-3400 (HB-3400-Me) with the exception that PEG-600, PEG-2000, and PEG-3400 were used as A₂ oligomers at the concentrations and reaction times in Table 5-1.

5.3.5 Synthesis of Branched Poly(ether ester)s with Phenyl Ester Terminal Groups

Phenyl ester terminated, branched poly(ether ester)s were termed as HB-xxx-Ph, HB denoting highly branched, xxx denoting the A₂ precursor, Ph denoting phenyl ester terminal groups. The synthesis of HB-200-Ph was similar to HB-200-Me-1 preparation with the exception that phenol (3.57 g, 0.038 mol) was dissolved in 10 mL of freshly

distilled chloroform and added dropwise into the reaction flask over 30 min in place of the excess methanol. The homogeneous solution was stirred for 12 h, subsequently washed with deionized water three times and precipitated into hexane at $\sim 0^{\circ}\text{C}$. A waxy, pale yellow product was collected and dried at 60°C in a vacuum oven for 24 h. ^1H NMR (chloroform-*d*, ppm): 8.70-9.15 (3H, aromatic protons from BTC), 6.80-7.60 (aromatic protons from phenyl ester terminal unit), 3.50-4.60 (4H, protons from PEG), 4.44 (-NCH₂CH₃), 1.42 (-NCH₂CH₃). ^{13}C NMR (chloroform-*d*, ppm): 164.4 (O=C-OCH₂CH₂-), 163.1 (O=C-O-Ar, phenyl ester end groups), 150.2, 130.2, 125.9, and 121.1 (O=C-O-Ar, phenyl ester end groups) 134.2 and 130.7 (BTC), 70.3, 68.7, and 64.4 (PEG), 61.4 and 13.9 (-NCH₂CH₃, TEA salt).

A similar synthetic method was used to prepare phenyl ester terminated, branched poly(ether ester)s from EG, DEG, and PEG-600 with the exception that with the exception that equimolar amounts of each were used as A₂ oligomers (at 0.40 M) to prepare HB-EG-Ph, HB-DEG-Ph, and HB-600-Ph, respectively.

5.3.6 Synthesis of Branched Poly(ether ester)s with Ethyl Acrylate (25 mol%) and Methyl Ester (75 mol%) Terminal Groups, and Subsequent Photo-cross-linking using UV-Light

Highly branched poly(ether ester)s with 25 to 100 mol% ethyl acrylate terminal groups were termed as HB-200-EA-y, HB denoting “highly branched”, 200 denoting PEG-200 precursor, EA denoting ethyl acrylate terminal groups, y denoting sample number. For the synthesis of HB-200-EA-1, BTC (10.00 g, 0.038 mol) was dissolved in 35 mL of freshly distilled chloroform in a dried, 250 mL two-necked flask equipped with a magnetic stir bar and addition funnel. PEG-200 (7.54 g, 0.038 mol) and TEA (11.41 g, 0.113 mol) were dissolved in 60 mL of freshly distilled chloroform and transferred into the addition funnel. The solution was slowly added to the reaction flask over 2 h, and the homogeneous reaction was maintained at ambient temperature for 12 h. The functionalization of branched polymers with 2-HEA, isolation processes, and the polymer film preparation were conducted with minimized light exposure; the reaction flask and addition funnel were covered with aluminum foil to avoid exposure to laboratory light. 2-HEA (1.10 g, 0.01 mol) was dissolved in 5 mL of freshly distilled chloroform and added to the reaction flask dropwise over 10 min. The homogeneous reaction was

maintained at ambient temperature for 6 h, excess methanol was added to quench the remaining terminal acid chloride end groups, and the homogeneous solution was stirred for 6 h. The solution was washed with deionized water three times and precipitated into hexane at ~ 0 °C. A waxy, pale yellow product was collected and dried at room temperature in a vacuum oven for 96 h. ^1H NMR (chloroform-*d*, ppm): 8.70-8.95 (3H, aromatic protons from BTC), 3.50-4.60 (4H, protons from PEG, 3H, protons from 75 mol % methyl ester terminal unit, 4H, protons from 25 mol% ethyl acrylate terminal unit, $-\text{OCH}_2\text{CH}_2\text{OCOCHCH}_2$), 5.80-6.50 (3H, protons from 25 mol% ethyl acrylate terminal unit, $-\text{OCH}_2\text{CH}_2\text{OCOCHCH}_2$), 4.44 ($-\text{NCH}_2\text{CH}_3$), 1.42 ($-\text{NCH}_2\text{CH}_3$).

A 30 wt % solution of dried polymer was prepared in chloroform, and 4 wt % DMPA was added. Thin films were directly cast onto glass slides from the homogeneous solution and allowed to stand at ambient temperature for 24 h in the absence of light. The average thickness of the polymer films was ~ 12 μm . Completely dried films on glass slides were passed through a Fusion UV system (model LC-6B benchtop conveyor) at 10 ft/min at approximately 3.73 W/cm^2 (UVA) to initiate photo-cross-linking. Soxhlet extraction with chloroform was performed for 24 h on the photo-cross-linked films, and the gel content was determined upon drying at 60 °C.

Table 5-1. Characterization data for linear and highly branched poly(ether ester)s.

sample	A ₂ ^a (g/mol)	[M] ^b (mol/L)	M _n (g/mol)	M _w (g/mol)	M _z (g/mol)	[η] ^d (dL/g)	α ^e	T _g (°C)	T _c (°C)	T _m (°C)
HB-200-Me-1	200	0.25	1230	12300	56500	0.065	0.284	-17	-	-
HB-200-Me-2	200	0.40	1470	17500	74600	0.074	0.330	-15	-	-
HB-200-Me-3 ^c	200	0.40	1260	16200	73900	0.060	0.265	-17	-	-
HB-200-Me-4	200	0.45	780	9410	55500	0.063	0.288	-14	-	-
L-200	200	-	5970	15900	24800	0.176	0.569	-22	-	-
HB-600-Me-1	600	0.10	1420	4240	11900	0.071	0.411	-53	-10	4
HB-600-Me-2	600	0.12	1660	9860	29600	0.100	0.396	-50	-	-
HB-600-Me-3	600	0.16	2070	32600	171000	0.172	0.416	-53	-	-
L-600	600	-	3940	11300	17400	0.172	0.581	-51	-19	8
HB-2000-Me-1	2000	0.10	6050	27100	81000	0.259	0.513	-43	-	40
HB-2000-Me-2	2000	0.12	5360	23800	68000	0.238	0.498	-51	-	40
HB-2000-Me-3	2000	0.15	2130	7060	15000	0.148	0.490	-42	-	40
L-2000	2000	-	7550	17100	25100	0.256	0.621	-	-	47
HB-3400-Me	3400	0.10	9860	35200	120000	0.340	0.550	-	-	47

^aNumber-average molar mass of PEG diols as A₂ oligomers;

^bFinal concentration in highly branched poly(ether ester) synthesis;

^cReaction time was 12 h;

^d*N,N*-Dimethylformamide/0.01 M LiNO₃, 35 °C;

^eα=Mark-Houwink exponent.

5.4 Results and Discussion

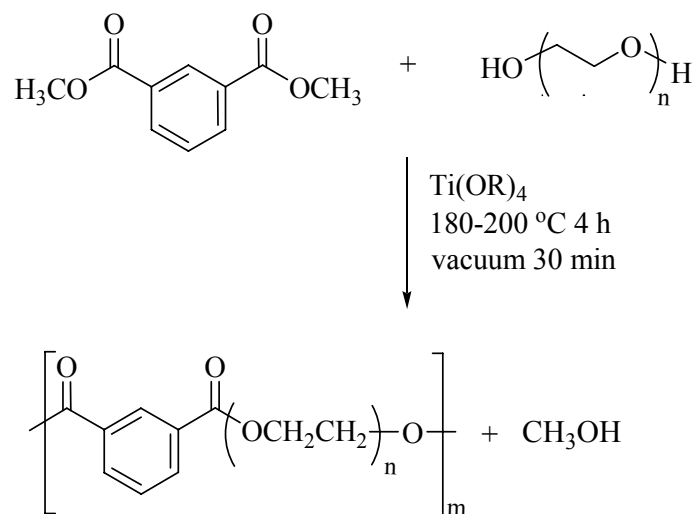
5.4.1 Polymerization

Two methods of step-growth polymerization were used to prepare poly(ether ester)s with degrees of branching ranging from linear analogues to highly branched polymers. Linear analogues with various distances between ester units were prepared via melt polymerization of DMI and PEG diols (Scheme 5-1). Compared to previous polyester products that were prepared using a similar methodology,¹³⁶ relatively low molar mass products were desired, and the linear analogues had absolute weight-average molar masses that were comparable to branched products prepared via the copolymerization of A₂ oligomers and a B₃ monomer (Table 5-1). A low amount of a trifunctional agent (typically 0.1–1.0 mol %) may be incorporated to prepare lightly branched polyesters via melt polymerization; however, gelation occurs at relatively low concentrations of trifunctional agent (>1.5 mol %), and a high degree of branching is not achievable.¹³⁷ To prepare highly branched polymers without gelation, the copolymerization of various molar mass PEG diols (A₂ oligomers) and a B₃ monomer was conducted in dilute solution. In an attempt to control the distance between branch points, PEG diols that have molar masses ranging from 200 to 3400 g/mol with very low molar mass distributions were used as A₂ oligomers (Table 5-2). Earlier studies have shown that copolymerization of low molar mass A₂ and B₃ monomers will result in a network. Moreover, a slow addition of A₂ to B₃ monomer in dilute solution avoids gelation, and hyperbranched aromatic polyesters were prepared earlier in a controlled fashion via low molar mass A₂ and B₃ copolymerization.¹³⁸ Thus, copolymerization of oligomeric A₂ with B₃ monomers for the preparation of branched poly(ether ester)s was utilized in our laboratories based on the slow addition approach (Scheme 5-2).

¹³⁶ Lin, Q.; Long, T. E., *Macromolecules* **2003**, 36, 9809. Lin, Q.; Long, T. E., *Macromolecules* **2003**, 36, 9809. Kang, H.; Lin, Q.; Armentrout, R. S.; Long, T. E., *Macromolecules* **2002**, 35, 8738. Kang, H.; Lin, Q.; Armentrout, R. S.; Long, T. E., *Macromolecules* **2002**, 35, 8738.

¹³⁷ McKee, M.; Colby, R. H.; Wilkes, G. L.; Long, T. E., *Macromolecules* **2004**, 37, 1760.

¹³⁸ Lin, Q.; Long, T. E., *Macromolecules* **2003**, 36, 9809. Lin, Q.; Long, T. E., *Macromolecules* **2003**, 36, 9809.



Scheme 5-1. Synthesis of linear poly(ether ester)s via melt polymerization.

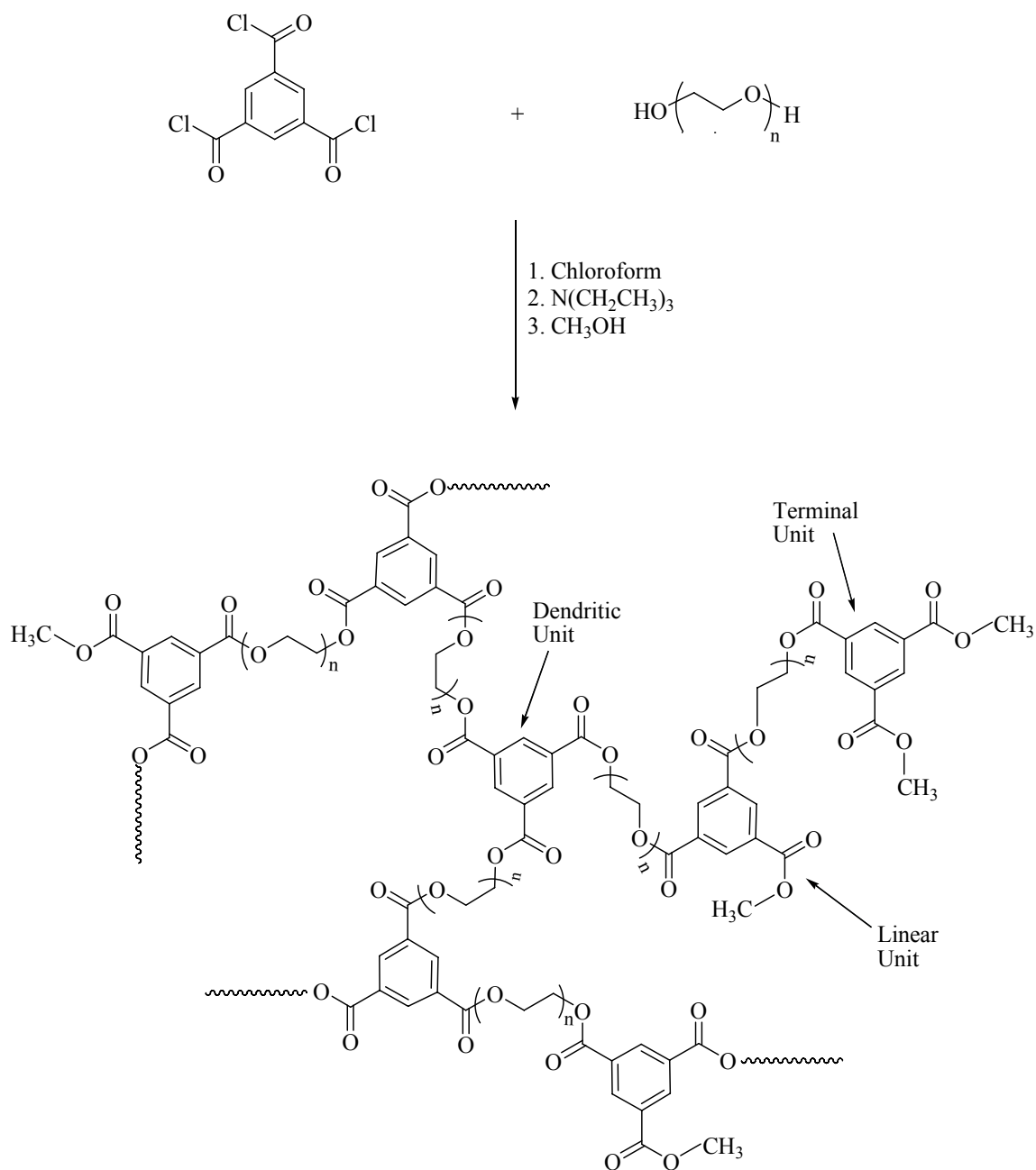
Table 5-2. Characterization of PEG diols as A₂ oligomers.

A₂ (g/mol)	n^a	M_w/M_n	T_g (°C)	ΔC_p (J/g °C)	T_m (°C)	ΔH (kJ/g)
200	4.1	1.02 ^b	-85	3.0	-	-
600	13.2	1.02 ^b	-58	0.8	20	0.37
2000	45.0	1.05 ^c	-	-	52	0.47
3400	76.8	1.07 ^c	-	-	53, 59	0.09, 0.35

^aAverage number of repeat units;

^bDetermined by MALDI-TOF/MS analysis;

^cDetermined by SEC analysis.



Scheme 5-2. Synthesis of methyl ester terminated highly branched poly(ether ester)s via polymerization of A_2 and B_3 monomers.

Others have reported reaction conditions that influence the final product in low molar mass A_2 and B_3 polymerization in dilute solution, and the type of solvent, order of monomer addition, monomer reactivity, reaction temperature, monomer concentration, reaction time, molar ratio of the monomers, and terminal groups are important parameters.¹³¹ In our studies, chloroform was a suitable solvent for the oligomeric A_2 and B_3 copolymerization as both the starting materials, and the branched products were completely soluble in chloroform. The order of monomer addition was necessary to maintain a homogeneous, gel-free solution, and this observation was consistent with our earlier reports.¹³⁸ When a dilute solution of B_3 monomer was added to a dilute solution of A_2 oligomer, highly cross-linked products were obtained regardless of the rate of addition. In contrast, slow addition of the oligomeric A_2 solution to the B_3 solution yielded branched polymers. Recently, Fossum and Czupik demonstrated that the development of branched structures was dependent on the order of monomer addition.¹³¹ When the A_2 monomer solution was added to the B_3 monomer solution, the initial products had linear topologies due to the excess of B_3 monomers. Slightly branched products were subsequently formed, and finally highly branched products formed through the continued addition of A_2 monomer. On the other hand, when the B_3 monomer solution was added to the A_2 monomer solution, the initial product was highly branched. In contrast to these earlier studies, the enhanced acid chloride reactivity in our approach significantly increased the risk of premature gelation. As a result, only the slow addition of PEG diol (A_2 oligomer) solution to the BTC (B_3) monomer solution was suitable for the preparation of highly branched products in the absence of gelation.

The polymerizations were conducted at room temperature, which is typical for the reaction of an acid chloride with an alcohol in the presence of TEA. As summarized in Table 5-1, monomer concentration, [M], has no obvious influence on the molar mass and the polydispersity of the final products. In general, the molar mass increases with increasing [M] for PEG-600, decreases with increasing [M] for PEG-2000, and changes non-systematically for the samples derived from PEG-200. HB-2000-Me-3 (0.15 M) had a considerably lower molar mass than HB-2000-Me-1 (0.10 M) and HB-2000-Me-2 (0.12 M). Lower molar mass HB-2000-Me-3 was attributed to limited solubility of the A_2 oligomer and the branched products at higher concentrations. TEA salt that is generated

during polymerization may also affect solubility during polymerization. At 0.18 M final monomer concentration for PEG-2000, premature gelation occurred during the polymerization. Similarly, gelation was observed at 0.50 and 0.18 M final monomer concentrations when PEG-200 and PEG-600 were used, respectively. In most cases, reactions were allowed to proceed for 24 h to ensure complete conversion; however, a branched polymer that was derived from PEG-200 was allowed to polymerize for 12 h (HB-200-Me-3) and a similar molar mass and polydispersity were obtained (HB-200-Me-2). Molar mass distributions broaden with increasing weight-average molar mass, as shown in Figure 5-1. Typical examples of Mark-Houwink plots (Figure 5-2) illustrate the effects of A_2 monomer length on dilute solution viscosity. Linear poly(ether ester) that was derived from PEG-2000 (L-2000) had a higher viscosity than linear poly(ether ester) derived from PEG-200 (L-200) at equivalent molar mass, indicating a more highly swollen or a less dense structure. A linear polymer derived from PEG-600 (L-600) (not shown) is intermediate between L-200 and L-2000. Highly branched poly(ether ester)s that were derived from PEG-200 had lower viscosities at equivalent molar mass than their linear analogues. The difference between the viscosities of linear and highly branched poly(ether ester)s derived from PEG-2000 is also apparent in Figure 5-2; however, it is less than the PEG-200 example, indicating a less highly branched structure. Highly branched poly(ether ester)s that are derived from PEG-600 (not shown) are also intermediate between the polymers derived from PEG-200 and PEG-2000. The slope of each curve in Figure 5-2 provides the Mark-Houwink constant (α), for each sample, which are also listed in Table 5-1. The value of α is known to be between 0.65 and 0.75 for linear random coils in a good solvent, whereas the value is approximately 0.25 for hyperbranched structures.[17,1926] The value of α was in the range of 0.55-0.62 for linear poly(ether ester)s (L-200, L-600, L-2000). Highly branched poly(ether ester)s derived from PEG-200 (HB-200-Me) had much lower α values (approaching 0.25), which indicated a more compact, or highly branched structures. As the distance between the B_3 units was increased to 600 (HB-600-Me) and 2000 (HB-2000-Me), α values increased, and approached values of linear analogues, which indicated that the branching decreased as the length of A_2 oligomer was increased. As reported previously, the intersection of the branched and linear curves determines the approximate distance

between the branch points.¹³⁹ As shown in Figure 5-2, such intersection occurs at $M > 5000$ for L-2000 and HB-2000-Me. The molar mass distribution of L-200 does not extend low enough to observe this intersection; however, if extended, the distance between the branch points would be much less than the PEG-2000 example. Overall, the viscosity of highly branched poly(ether ester)s compared to the linear analogues is consistent with the formation of branched architectures that differ in molar mass between branch points.

¹³⁹ Lusignan, C. P.; Mourey, T. H.; Wilson, J. C.; Colby, R. H., *Physical Review E* **1999**, 60, 5657.

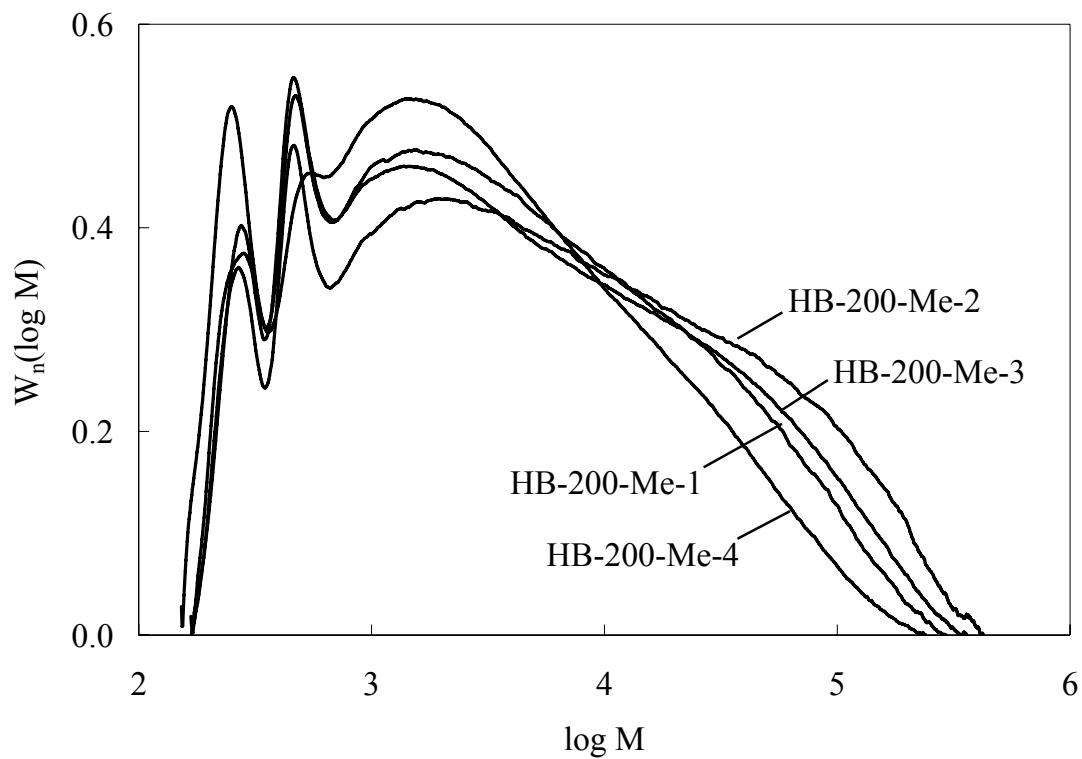


Figure 5-1. Molar mass distributions for highly branched poly(ether ester)s based on PEG-200.

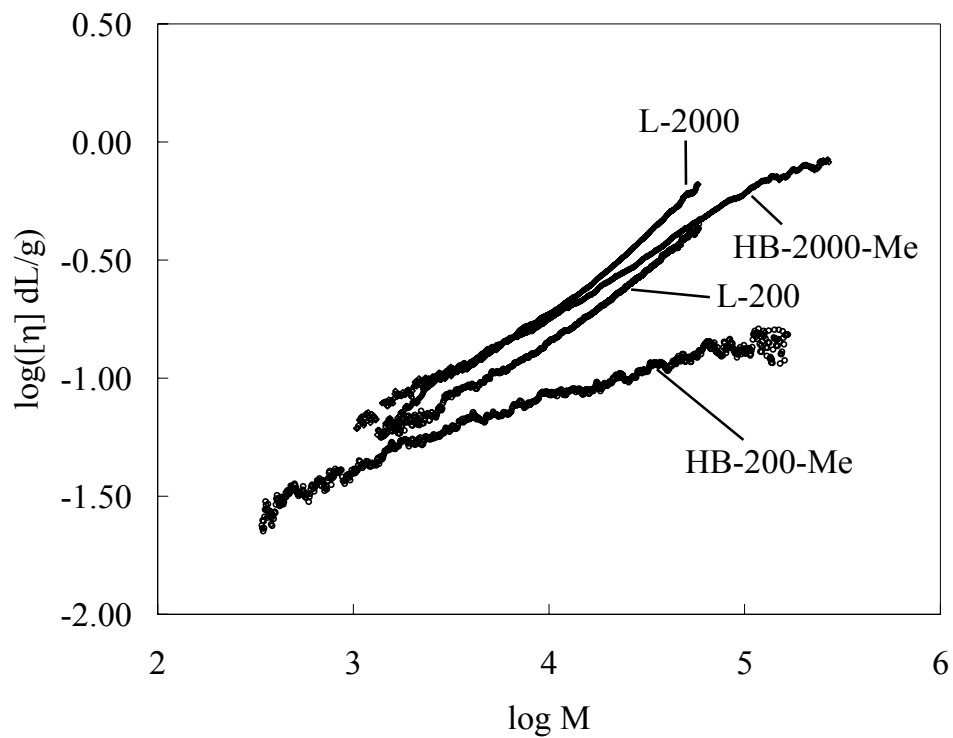


Figure 5-2. Mark-Houwink plots for PEG-200 and PEG-2000 based linear and highly branched poly(ether ester)s.

An explanation that accounts for successful polymerization of A_2 and B_3 monomers without gelation remains unclear. According to Flory, only low molar mass products are obtained since gelation occurs at very low monomer conversions.¹²⁵ However, Flory's theory is based on the following assumptions: (1) the reactivity of the functional groups remains constant during polymerization, and (2) the reactions do not involve cyclization. Deviations from these assumptions shift the gel point to higher conversions and the polymerizations result in high molar mass, highly branched structures.¹³¹ Jikei and co-workers proposed that when a reaction was kinetically controlled, the first condensation reaction of A_2 and B_3 was faster than subsequent propagation and A-ab- B_2 type intermediates were formed.¹³¹ Kricheldorf and co-workers reported that cyclization during polymerization was the major factor responsible for the gel point shift, and various cyclic species were identified using MALDI-TOF analysis.¹³¹ In our studies, highly reactive acid chloride groups were used as B units, and it was assumed that cyclization prevented gelation in dilute solution. As a result of cyclization, a relatively large amount of low molar mass species is expected in the final product. As shown in Figure 5-3, MALDI-TOF analysis of HB-200-Me-2 indicated the complete consumption of PEG precursor and the presence of low molar mass species in the 600–1000 m/z range. The molar mass distribution in Figure 5-3 arises from the molar mass distribution of PEG-200 precursor with a mass difference of ~44 Da. Because of the molar mass distribution that arises from the PEG-200 precursor, a confident assignment of the chemical structures for these low molar mass species was not possible. However, these low molar mass compounds are presumed to be oligomeric or cyclic structures, which are characteristic of $A_2 + B_3$ polymerization. The critical concentrations for gelation when various molar mass PEG diols were used as A_2 oligomers also supported the occurrence of cyclization. In a previous report, when bisphenol A, a relatively rigid diol, was used as the A_2 monomer, the critical concentration (0.08 M) for gelation was significantly lower.¹³⁸ Consequently, it was assumed that cyclization was less pronounced for bisphenol A due to limited conformational mobility relative to PEG diols, and the higher final monomer concentrations that were required to obtain gel-free high molar mass products from A_2 oligomers suggested the occurrence of cyclization.

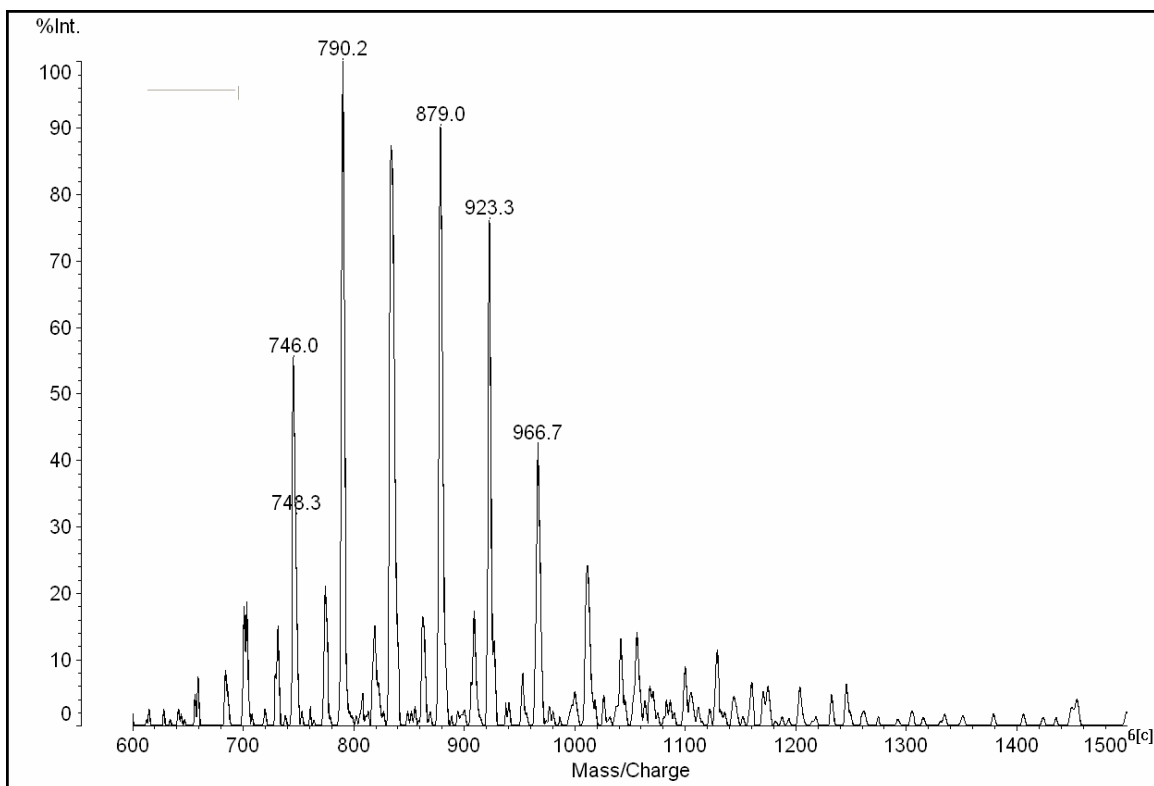


Figure 5-3. MALDI-TOF spectrum of HB-200-Me-2.

In-situ functionalization of the highly branched polymers was a powerful tool, especially at a molar ratio of $A_2:B_3 = 1:1$. A 1:1 molar ratio of $A_2:B_3$ corresponds to a 2:3 stoichiometric ratio of functional groups ($[A]:[B]$), and it was expected that the excess acid chloride functional groups were the terminal groups on the final branched polymers. The terminal acid chloride groups were reacted with methanol via in-situ functionalization to obtain methyl ester end groups, and structural characterization of the final products (Figure 5-4) was attempted using ^1H NMR spectroscopy. ^1H NMR spectroscopic analysis was not quantitative with respect to the concentration of end groups in the methyl ester-terminated poly(ether ester)s; the resonances that were indicative of methyl ester protons (3.5 ppm) and poly(ethylene glycol) protons (3.5-4.5 ppm) overlapped. Moreover, ^1H NMR spectroscopy did not provide quantitative analysis of the dendritic, terminal, and linear units in the polymer backbone due to overlap of the aromatic protons corresponding to each unit. Thus, phenyl ester terminal groups, as described below, were pursued to determine the degree of branching. ^1H NMR spectroscopy also indicated the presence of low levels of residual TEA salts (5-8 mol %, 1.42 and 4.44 ppm) after purification (Figure 5-4).

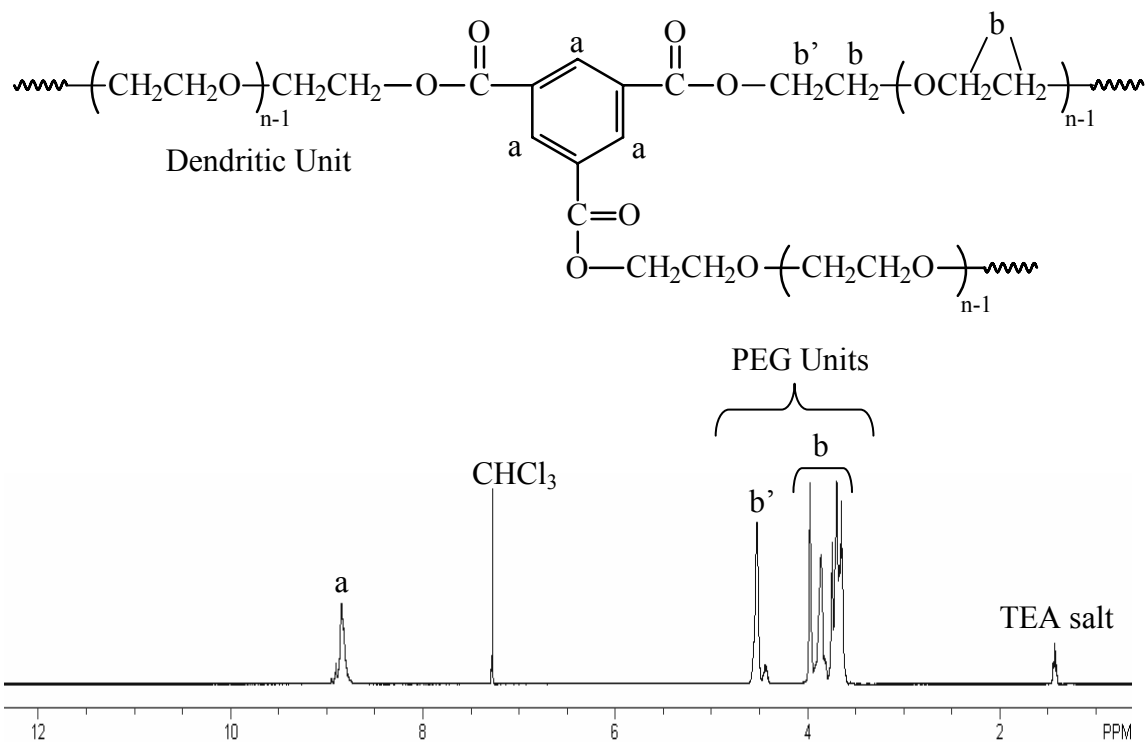


Figure 5-4. ¹H NMR spectrum of a methyl ester terminated highly branched poly(ether ester) (HB-200-Me-2, 400 MHz, CDCl₃).

5.4.2 Degree of Branching

Several equations were developed earlier to define the structure of hyperbranched polymers based on the self-condensation of AB₂ monomers.^{123,126} In most cases, these equations are also applicable to the products of A₂ and B₃ polymerization. If the highly branched products, which contain the oligomeric A₂ unit, were considered hyperbranched in a fashion similar to earlier poly(arylene ester)s,¹³⁸ then each oligomer between two branch points was considered a single repeat unit. Thus, the degree of branching based on BTC units was calculated according to the Fréchet definition.¹⁴⁰ The degree of branching (DB) was described as the ratio of the sum of all fully branched and terminal units to the total number of units

$$DB = (D + T)/(D + T + L)$$

Equation 5-1

where D, T, and L correspond to total number of dendritic, terminal, and linear units, respectively. To determine the degree of branching in these branched poly(ether ester)s, acid chloride terminal units were reacted with phenol to afford phenyl ester-terminated poly(ether ester)s. The phenyl ring has increased electron-withdrawing capability relative to alkyl ester end groups. Thus, the phenyl ester end groups provided a higher resolution of the aromatic protons that corresponded to dendritic, terminal, and linear units and permitted an improved deconvolution of the resonances in the aromatic region (Figure 5-5). Resonances were assigned based on our earlier model compounds for hyperbranched poly(arylene ester)s.¹³⁸ Moreover, ¹³C NMR spectroscopy of methyl ester-terminated poly(ether ester)s (Figure 5-6) and phenyl ester-terminated poly(ether ester)s (Figure 5-7) confirmed the structure and the quantity of both end groups. In this study, the chemical structures of the products were intermediate between linear and highly branched topologies since the A₂ oligomers have a relatively high molar mass. The Fréchet definition accurately described the branching structures only when each oligomer between the branch points was considered as a single repeat unit. Using Equation 5-1, the degree of branching of the poly(ether ester)s that were derived from EG,

¹⁴⁰ Hawker, C. J.; Lee, R.; J., F. J. M., *J. Am. Chem. Soc.* **1991**, 113, 4583.

DEG, PEG-200, and PEG-600 ranged from 62 to 69 mol % (Table 5-3). To properly characterize the oligomeric A₂ and B₃ products herein, Equation 5-1 was revised as,

$$DB = (D + T)/(D + T + L + n)$$

Equation 5-2

where n was defined as the number of repeat units in the linear oligomer when D + T + L = 1 and they were defined as the dendritic, terminal, and linear units of BTC, respectively. As a result, the degree of branching of poly(ether ester)s that were derived from EG, DEG, and PEG oligomers decreased dramatically. As summarized in Table 5-3, the degree of branching for branched poly(ether ester)s decreased as the molar mass of PEG oligomers increased. Consequently, the oligomeric A₂ and B₃ polymerization was an effective method to prepare polymers with a range of DB values.

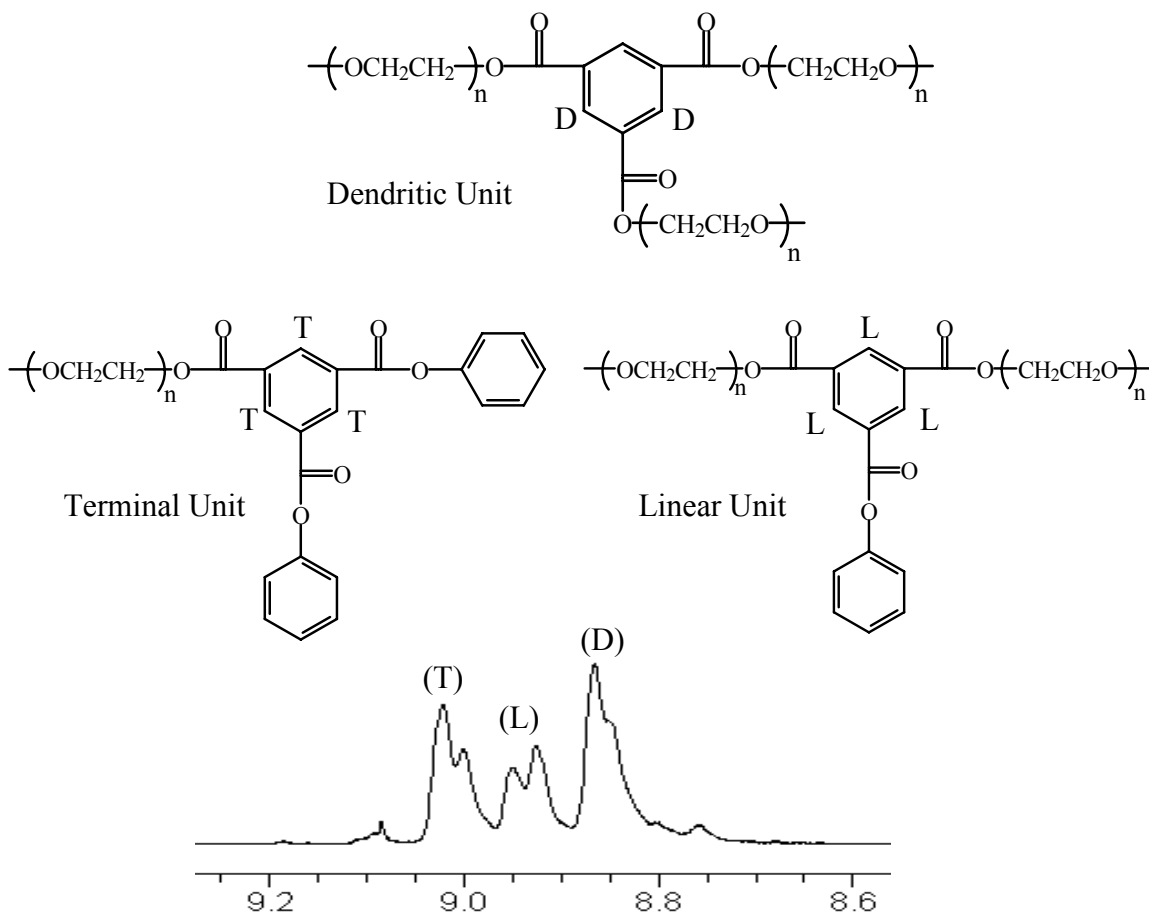


Figure 5-5. Aromatic region of ¹H NMR spectrum of a phenyl ester-terminated highly branched poly(ether ester) (HB-200-Ph, 400 MHz, CDCl₃).

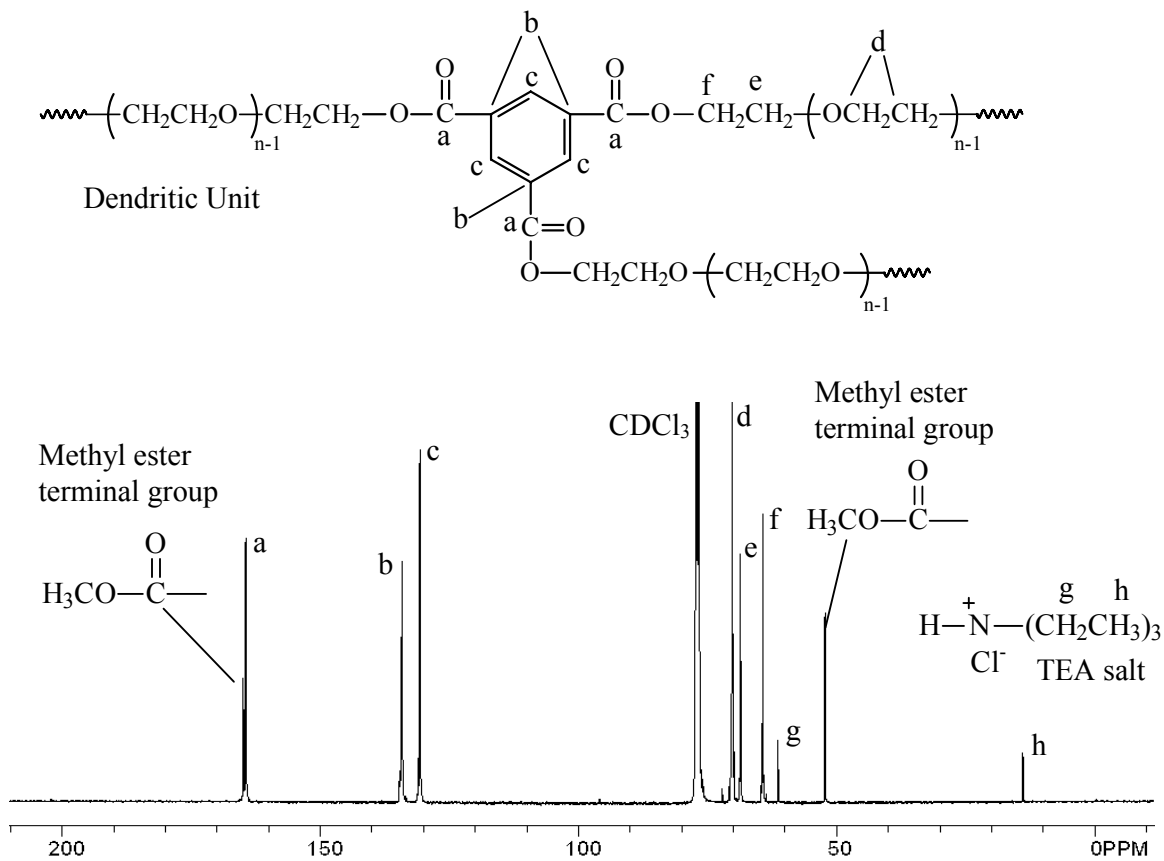


Figure 5-6. ¹³C NMR spectrum of a methyl ester terminated highly branched poly(ether ester) (HB-200-Me-2, 400 MHz, CDCl₃).

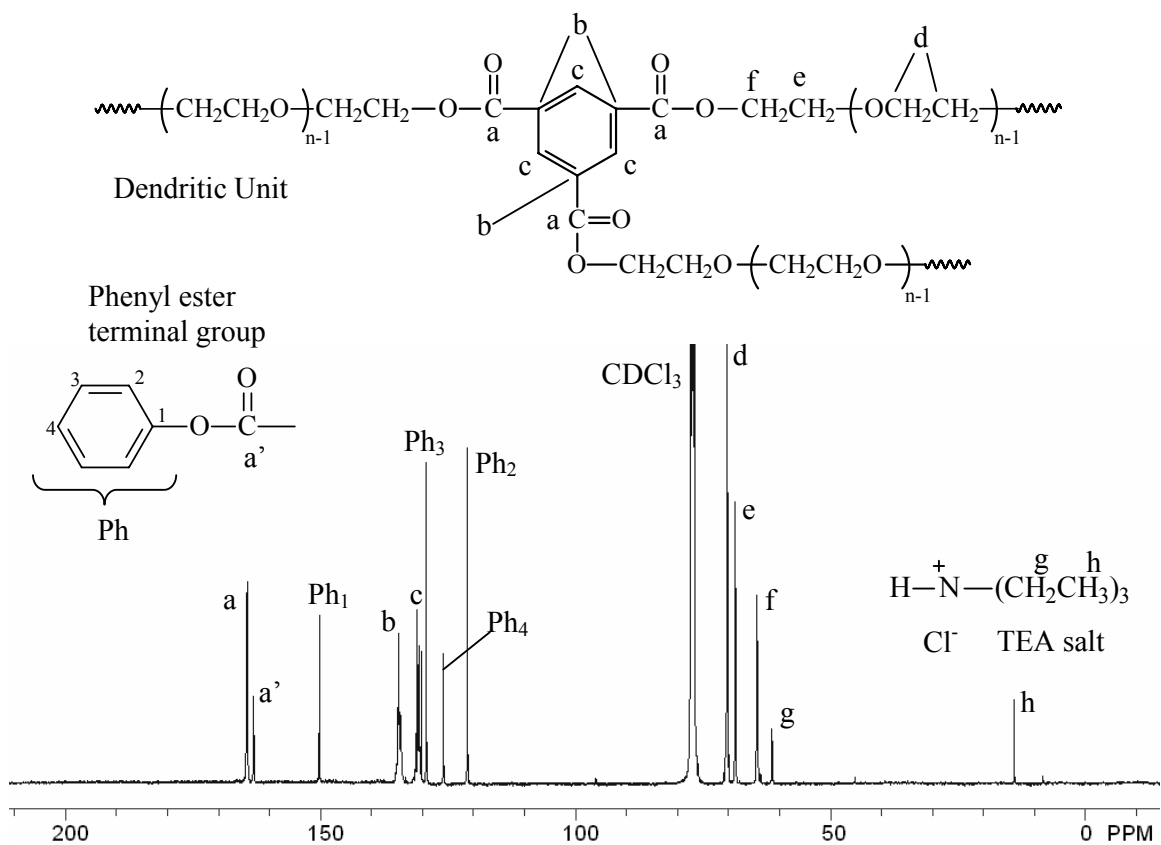


Figure 5-7. ¹³C NMR spectrum of a phenyl ester terminated highly branched poly(ether ester) (HB-200-Ph, 400 MHz, CDCl₃).

Table 5-3. The degree of branching of highly branched poly(ether ester)s using a revised equation

sample	A₂	n^a	classical DB (%)	revised DB (%)
HB-EG-Ph	Ethylene glycol	1.0	62	31
HB-DEG-Ph	Diethylene glycol	2.0	63	21
HB-200-Ph	PEG-200	4.1	69	14
HB-600-Ph	PEG-600	13.2	66	5

^aAverage number of repeat units in A₂ precursors

5.4.3 Thermal Analysis

The PEG oligomers with number-average molar masses (M_n) of 200 and 600 g/mol have glass transition temperatures (T_g) of -85 and -58 °C, respectively (Table 5-2). In addition, PEG-600 has a melting temperature (T_m) of 20 °C. Branched poly(ether ester)s derived from PEG-200 had glass transition temperatures ranging from -14 to -17 °C (Table 5-1). As expected, because of the presence of aromatic branch points (62-69 mol %), the branched poly(ether ester)s had higher glass transition temperatures than the precursor oligomers and linear analogues based on PEG-200 (L-200) also exhibited a T_g that was relatively close to the highly branched polymer (-22 °C).

Highly branched poly(ether ester)s that were prepared using an oligomeric A_2 with longer ethylene glycol chains (PEG-600) exhibited interesting thermal behavior depending on the final molar mass. The lower molar mass HB-600-Me-1 was semicrystalline with a T_g of -51 °C, crystallization temperature (T_c) of -10 °C, and a T_m of 4 °C. Similarly, a distinct crystallization and a melting peak were observed for the linear L-600. The linear and low molar mass branched poly(ether ester)s derived from PEG-600 had slower crystallization rates than the PEG-600 precursor. As the molar mass of the branched poly(ether ester) increased, the crystalline melting peak disappeared. Indeed, HB-600-Me-2 and HB-600-Me-3 exhibited a T_g of -50 and -53 °C, respectively; however, a T_c and T_m were not detected using identical DSC conditions.

The PEG-2000 and PEG-3400 precursors were highly crystalline and exhibited a T_m of 52 and 53-59 °C, respectively. It was reported earlier¹³⁵ that higher molar mass, linear poly(ethylene oxide)s ($M_n = 15000$ g/mol) also have a T_g at -67 °C, however, a T_g was not evident for the PEG-2000 and PEG-3400 precursors under the DSC conditions used in this study. The linear poly(ether ester) based on PEG-2000 (L-2000) was also semicrystalline with a T_m of 47 °C. However, the branched poly(ether ester)s based on PEG-2000 (HB-2000-Me-1, HB-2000-Me-2, and HB-2000-Me-3) had T_g values ranging from -42 to -51 °C and a depressed T_m at 40 °C relative to both the A_2 oligomer (PEG-2000) and the linear poly(ether ester) based on PEG-2000 (L-2000). These results are consistent with the crystallization behavior of branched polymers.¹²⁶ As the chain length of PEG precursor was increased to 3400 g/mol, only a depressed T_m at 47 °C was

observed for the branched poly(ether ester) (HB-3400-Me) when compared to the PEG-3400 precursor with T_m of 53 and 59 °C. As clearly shown, highly branched poly(ether ester)s have a lower degree of crystallinity. Decreased crystallinity of PEG based ion conducting polymeric materials is an important phenomenon in terms of providing enhanced ion mobility.¹³⁴ A more detailed investigation of the morphology of this family of branched polymers and ion conductivity measurements will be reported in the future.

5.4.4 UV-Crosslinking

As summarized in Table 5-4, the branched poly(ether ester)s cross-linked during isolation of the products when the polymer contained 50 mol % (HB-200-EA-2) and 100 mol % (HB-200-EA-3) ethyl acrylate terminal groups. The branched poly(ether ester) with 25 mol % ethyl acrylate terminal groups (HB-200-EA-1) was isolated successfully without premature cross-linking. Soxhlet extraction using chloroform was subsequently conducted after the UV-cross-linking of HB-200-EA-1. The UV-cross-linked films typically contained 80 wt % gel. In addition, the T_g increased from -12 to 13 °C upon cross-linking, and a less tacky, free-standing film was prepared.

Table 5-4. Summary of UV-cross-linking experiments of highly branched poly(ether ester) with ethylacrylate terminal groups

sample	ethyl acrylate terminal groups (mol %)	A₂ (g/mol)	[M] (g/mol)	T_g (°C)^a	gel (%)^b	T_g (°C)^b
HB-200-EA-1	25	200	0.45	-12	81	13
HB-200-EA-2	50	200	0.45	premature crosslinking		
HB-200-EA-3	100	200	0.45	premature crosslinking		

^aBefore UV-cross-linking;

^bAfter UV-cross-linking.

5.5 Conclusions

Oligomeric A_2 and B_3 polymerization is an effective method to control the degree of branching. A series of poly(ether ester)s with various degrees of branching were prepared via the addition of a dilute solution of PEG oligomer to a dilute solution of triacid chloride in the presence of TEA. The reaction conditions such as solvent, order of monomer addition, monomer reactivity, temperature, monomer concentration, reaction time, and type of terminal groups exerted pronounced effects on the properties of the branched copolymers. A revised equation was proposed to accurately determine the degree of branching of the final products, and the calculated results demonstrated that the degree of branching of highly branched poly(ether ester)s decreased with an increase in the molar mass of the oligomeric A_2 precursor. The relationship between intrinsic viscosity and molar mass also supported that products that were derived from lower molar mass PEG diols had more highly branched structures. Branched poly(ether ester)s based on PEG-200 and PEG-600 precursors were amorphous, and semicrystalline polymers were obtained from the higher molar mass PEG precursors (PEG-2000 or PEG-3400). Moreover, the branched polymers from PEG-200 were in-situ functionalized to obtain ethyl acrylate-terminated polymers. The ethyl acrylate-terminated polymers were UV-cross-linked to form less tacky, free-standing films with high gel contents.

5.6 Acknowledgements

This material is based upon work supported in part by the U.S. Army Research Laboratory and U.S. Army Research Office under Grant DAAD 19-02-1-0275 Macromolecular Architecture for Performance (MAP) MURI. The authors also thank Eastman Chemical Company for financial support.

Chapter 6: Highly Branched Poly(ether ester)s via Cyclization-Free Melt Condensation of A₂ Oligomers and B₃ Monomers

Taken From:

Unal, S.; Long, T. E. "Highly Branched Poly(ether ester)s via Cyclization-Free Melt Condensation of A₂ Oligomers and B₃ Monomers." *Macromolecules* **2005**, *submitted for publication*.

6.1 Abstract

This manuscript reports the first synthesis of A₂ + B₃ highly branched polyesters with the minimal formation of cyclics in the absence of a polymerization solvent. Highly branched poly(ether ester)s were synthesized in the melt phase using an oligomeric A₂ + B₃ polymerization strategy. Condensation of poly(propylene glycol) (M_n ~1060 g/mol) and trimethyl 1,3,5-benzenetricarboxylate in the presence of titanium tetraisopropoxide generated highly branched structures with high molar mass when the reaction was stopped immediately prior to the gel point. Size exclusion chromatography (SEC) and ¹H NMR spectroscopy were used to monitor molar mass as a function of monomer conversion and to determine the gel point. Monomer conversions at both the theoretical and experimental gel points for an A₂:B₃ = 1:1 molar ratio agreed well. Thus, cyclization reactions, which are common in A₂ + B₃ polymerization in solution, were negligible in the melt phase. The degree of branching (DB) increased with an increase in monomer conversion and molar mass, and the final product contained 20% dendritic units. Monofunctional endcapping reagents were also used to avoid gelation in the melt phase, and high molar mass final products were obtained with nearly quantitative monomer conversion in the absence of gelation. The presence of a monofunctional comonomer did not affect the molar mass increase or the formation of branched structures due to desirable ester interchange reactions.

6.2 Introduction

Hyperbranched polymers have emerged as popular alternatives to dendrimers in the last 15 years.^{141,142} Dendrimers are perfectly branched macromolecules that are synthesized via multi-step divergent or convergent methods¹⁴³ whereas hyperbranched polymers possess structural irregularities, but are typically synthesized with much less effort.^{141,142} Despite few irregularities in branching, hyperbranched macromolecules possess similar characteristics to dendrimers such as low hydrodynamic volume, low solution and melt viscosity, good solubility, a multitude of functional endgroups, and non-entangled chains.^{141,142} Initial studies focused on the synthesis of hyperbranched polymers via the self-condensation of AB_n (n ≥ 2) type monomers.^{141,142,144} Although several studies reported the synthesis and characterization of various types of hyperbranched step-growth polymers via the self-condensation of AB_n type monomers,^{141,142} limited availability of these functionally nonsymmetrical monomers has stymied industrial applications and fundamental studies of branching in macromolecules.

Polymerization of functionally symmetric monomer pairs such as A₂ and B₃ type monomers has also received great attention in the last decade as a convenient approach to synthesize hyperbranched polymers.^{142,145,146} Significant effort has been devoted to understanding the influence of the reaction parameters on gel formation in A₂ + B₃ systems, and gelation is retarded at optimum A₂:B₃ molar ratios (generally 1.0 or higher) to obtain high molar mass products. For example, gelation is predicted at 86.6% A group conversion (57.7% with respect to B) for a 1:1 molar ratio of A₂:B₃ monomers (A:B=2:3) that are homogeneously mixed at the onset of polymerization.¹⁴⁴ A few common strategies are used to avoid gelation in A₂ + B₃ polymerization. Stopping the reaction immediately prior to gelation results in partial conversion of functional groups; however,

¹⁴¹ Jikei, M.; Kakimoto, M. A., *Prog. Polym. Sci.* **2001**, 26, 1233. Kim, Y. H., *J. Polym. Sci. Part A: Polym. Chem.* **1998**, 36, 1685. Voit, B., *J. Polym. Sci. Part A: Polym. Chem.* **2000**, 38, 2505.

¹⁴² Gao, C.; Yan, D., *Prog. Polym. Sci.* **2004**, 29, 183.

¹⁴³ Fischer, M.; Vögtle, F., *Angew. Chem.* **1999**, 111, 934.

¹⁴⁴ Flory, P. J., *J. Am. Chem. Soc.* **1952**, 74, 2718. Flory, P. J., *Principles of Polymer Chemistry*. Cornell University Press: Ithaca, NY, 1953.

¹⁴⁵ Jikei, M.; Chon, S. H.; Kakimoto, M. A.; Kawauchi, S.; Imase, T.; Watanebe, J., *Macromolecules* **1999**, 32, 2061.

¹⁴⁶ Emrick, T.; Chang, H. T.; Fréchet, J. M. J., *Macromolecules* **1999**, 32, 6380. Emrick, T.; Chang, H. T.; Fréchet, J. M. J., *J. Polym. Sci. Part A: Polym. Chem.* **2000**, 38, 4850.

fully soluble highly branched products are prepared.^{145,146} Polymerization in dilute solution promotes cyclization reactions, which effectively avoid gelation, and the reaction proceeds with complete consumption of the limiting reagents.^{147,148} Slow addition of one monomer into the reaction mixture is also commonly employed especially for highly reactive monomer pairs.^{149,150} The slow addition strategy is generally related to one of the first two techniques, either the functional groups are only partially converted or cyclization reactions occur.¹⁴⁸ Finally, non-ideal conditions tailor the relative reactivity of one of the functional A or B groups on A₂ or B₃ resulting in AA* or B₂B* monomers.¹⁵¹ A* and B* groups exhibit different reactivities than A and B groups, respectively.

The vast majority of hyperbranched polymers via A₂ + B₃ polymerization reported in the literature were synthesized in solution. However, only two studies reported polycondensation of A₂ and B₃ monomers in the melt phase.^{152,153} For example, melt polymerization of adipic acid (A₂) and glycerol (B₃) resulted in highly branched aliphatic polyesters without gelation.¹⁵³ However, glycerol bears two primary alcohols and a secondary, which possess significantly different reactivity in the polymerization. Hence, glycerol effectively acts as a B₂B* monomer and gelation is avoided even at molar ratios of A₂:B₃ = 2:1. Other than polycondensation of A₂ and B₃ monomers, Fréchet and coworkers reported the synthesis of aliphatic polyether epoxies in bulk via the proton transfer polymerization from a diepoxide (A₂) and triol (B₃).¹⁴⁶ A feed molar ratio of A₂:B₃ = 3:1 was employed to introduce epoxide chain-ends. Polymerizations were stopped before the full conversion of limiting reagents prior to gelation and the molar mass increase was monitored with time.

¹⁴⁷ Kricheldorf, H. R.; Vakhtangishvili, L.; Fritsch, D. J., *J. Polym. Sci. Part A: Polym. Chem.* **2002**, 40, 2967.

¹⁴⁸ McKee, M.; Unal, S.; Wilkes, G. L.; Long, T. E., *Prog. Polym. Sci.* **2005**, 30, 507. McKee, M.; Unal, S.; Wilkes, G. L.; Long, T. E., *Prog. Polym. Sci.* **2005**, 30, 507. McKee, M.; Unal, S.; Wilkes, G. L.; Long, T. E., *Prog. Polym. Sci.* **2005**, 30, 507.

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¹⁵² Lusic, H.; Fossum, E., *Polym. Prep. Div. Polym. Sci.* **2003**, 44, 858.

¹⁵³ Stumbe, J.; Bruchmann, B., *Macromol. Rapid Commun.* **2004**, 25, 921.

This manuscript describes the synthesis of a highly branched poly(ether ester) via the melt condensation of poly(propylene glycol) (A_2 oligomer) and trimethyl 1,3,5-benzenetricarboxylate (TMT, B_3 monomer). The conversion of each monomer was monitored during the polymerization to understand the onset of gelation in the melt phase. The equal reactivity of the B_3 monomer does not promote a B_2B^* scenario and oligomeric A_2 provides the opportunity for entanglements between branch points. Finally, the introduction of a monofunctional comonomer is reported as a novel strategy to avoid gelation in $A_2 + B_3$ polymerization.

6.3 Experimental

6.3.1 Materials

Poly(propylene glycol) (PPG-1000, $M_n = 1060$ g/mol by ^1H NMR) was kindly donated by Bayer MaterialScience. Trimethyl 1,3,5-benzenetricarboxylate (98%) (TMT), dodecanol (DD), poly(propylene glycol) monobutyl ether (PPG-M-1000, $M_n = 1200$ g/mol by ^1H NMR), dimethyl terephthalate (DMT), and titanium tetraisopropoxide (99%) were purchased from Aldrich. PPG-1000 and PPG-M-1000 were dried in a vacuum oven (0.50 mmHg) at 50 °C for 18 h. TMT was purified by sublimation at 150 °C. All other reagents were used as received unless otherwise stated.

6.3.2 Characterization

^1H NMR spectroscopic analyses were performed on a Varian Unity 400 MHz spectrometer at ambient temperature. Triple detection size-exclusion chromatography (SEC) was conducted in THF (40 °C, 1 mL min $^{-1}$, polystyrene standards) on a Waters 717 Autosampler equipped with three in-line PLgel 5 mm Mixed-C columns, Waters 410 RI detector, Viscotek 270 dual detector, and in-line Wyatt Technology miniDAWN multiple angle laser light scattering (MALLS) detector. Thermal transition temperatures were determined using a Perkin Elmer Pyris-1 at 10 °C/min under helium, and reported data were obtained from the second heating.

6.3.3 Synthesis of Highly Branched Poly(ether ester)s

TMT (5.00 g, 19.82 mmol) and PPG-1000 (21.01 g, 19.82 mmol) were added to a 100-mL, two-necked, flask equipped with an overhead mechanical stirrer, nitrogen inlet, and condenser. Titanium tetraisopropoxide (60 ppm) was added to facilitate transesterification. The reaction flask was degassed using vacuum and nitrogen three times and subsequently heated to 150 °C. The reactor was maintained at 150 °C for 2 h, and the temperature was increased to 180 °C over 4 h. Vacuum was gradually applied (0.30 mmHg) and the reaction proceeded for 1 h at 180 °C. Aliquots (0.40 g) of the reaction mixture were removed at different reaction times and analyzed using ¹H NMR spectroscopy and SEC to monitor molar mass and monomer conversion.

Two methods (I and II) were used to synthesize both poly(propylene glycol) endcapped highly branched poly(ether ester)s (HBPEE-PPG) and dodecyl ester endcapped highly branched poly(ether ester)s (HBPEE-DD). In the first method (I), the endcapping reagent was introduced at the onset of polymerization. For the synthesis of HBPEE-PPG-I, PPG-M-1000 (11.89 g, 9.91 mmol) was added to the reaction flask with TMT (2.50 g, 9.91 mmol), PPG-1000 (10.51 g, 9.91 mmol), and titanium tetraisopropoxide (60 ppm). The same multistep temperature sequence was used as above with the exception that the reaction was allowed to proceed for 4 h at 180 °C in the second step and vacuum was applied for 4 h at 180 °C in the third step. HBPEE-DD-I was synthesized using the identical procedure as HBPEE-PPG-I with the exception that DD (1.85 g, 9.91 mmol) was initially added to the reaction flask in place of the PPG-M-1000. In the second method (II), the DD endcapping reagent was introduced at a later stage of polymerization. For the synthesis of HBPEE-DD-II, TMT (2.50 g, 9.91 mmol), PPG-1000 (10.51 g, 9.91 mmol), and titanium tetraisopropoxide (60 ppm) were added to the reaction flask and allowed to react at 150 °C for 2 h. Temperature was increased to 180 °C over 4 h and vacuum was gradually applied (0.30 mmHg) for 10 min. The reaction was paused and DD (1.85 g, 9.91 mmol) was added to the reaction flask. The reaction flask was maintained at 180 °C for 2 h and gradual vacuum was applied (0.30 mmHg) for 4 h.

6.3.4 Synthesis of Linear Poly(ether ester)s

A single neck, 100-mL round-bottomed flask equipped with an overhead mechanical stirrer, nitrogen inlet, and condenser was charged with DMT (5.25 g, 27.04 mmol) and PPG-1000 (27.29 g, 25.75 mmol). Titanium tetraisopropoxide (60 ppm) was added to facilitate transesterification. The reaction flask was degassed under vacuum and nitrogen three times and subsequently heated to 180 °C. The reactor was maintained at 180 °C for 4 h, and the temperature was increased to 200 °C over 2 h. Vacuum was applied (0.5 mmHg) for another 1 h to ensure the removal of methanol.

6.4 Results and Discussion

6.4.1 Polymerization

Conventional transesterification was used to prepare highly branched poly(ether ester)s in the melt phase using titanium tetraisopropoxide as catalyst. We previously reported the polymerization of poly(ethylene glycol) (PEG, A₂ oligomer) with B₃ acyl halides in dilute solution to prepare highly branched poly(ether ester)s.¹⁴⁸ Variations in the molar mass of the PEG oligomer controlled the distance between branch points. However, synthesis in dilute solution, which is generally associated with a significant amount of cyclization, resulted in a complex mixture of high molar mass, highly branched, polymers and low molar mass oligomers or cyclic compounds. Thus, melt polymerization was employed to overcome the need for large quantities of polymerization solvent, eliminate highly reactive acyl halides, and to limit the formation of low molar mass products.

Various commercial polyesters that are commonly used as engineering thermoplastics, such as poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), and various polyether based polyesters (i.e. Hytrel), are synthesized in the melt phase at temperatures ranging from 180 to 290 °C.^{154,155} Polymerizations in the current study were conducted at relatively lower temperatures to avoid degradation of the polyether-based A₂ oligomer (PPG-1000). ¹H NMR spectroscopy of the final products

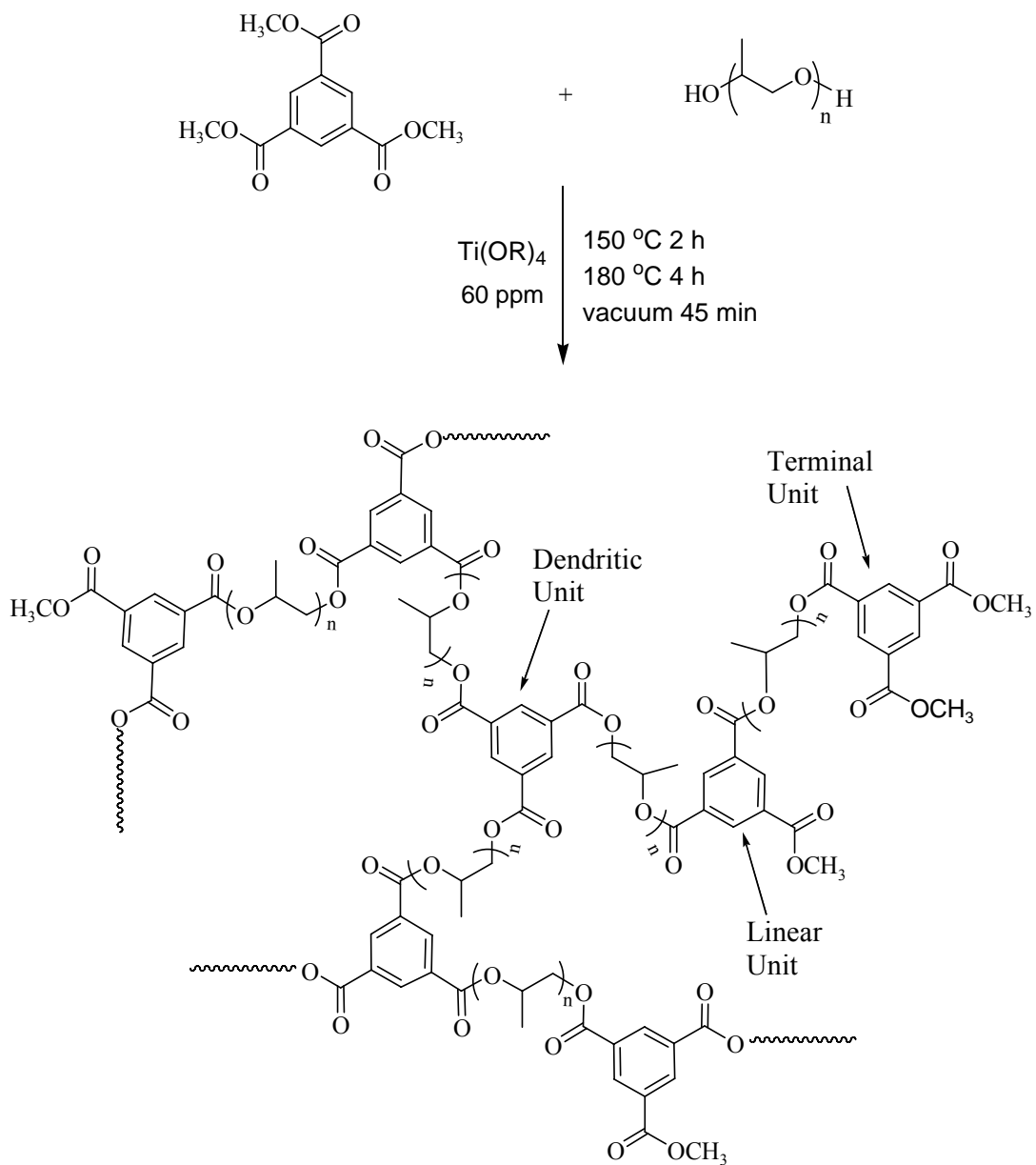
¹⁵⁴ Scheirs, J.; Long, T. E., *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters*. John Wiley & Sons, Ltd.: West Sussex, 2003. Witsipie, W. K., In *Polymerization Reactions and New Polymers*, Platzer, N., Ed. American Chemical Society: Washington, DC, 1973; p 39.

¹⁵⁵ McKee, M.; Unal, S.; Wilkes, G. L.; Long, T. E., *Prog. Polym. Sci.* **2005**, 30, 507.

did not reveal any unexpected resonances due to thermal degradation. Moreover, thermogravimetric analysis (TGA) also ensured no weight loss at polymerization temperatures.

PPG-1000 A₂ oligomer and TMT B₃ monomer were polymerized in a 1:1 molar ratio using a multistep temperature sequence in the presence of a transesterification catalyst as shown in Scheme 6-1. A lower initial temperature (150 °C) was required to ensure the reaction of TMT with PPG-1000 and minimize stoichiometric changes due to TMT sublimation. After 2 h at 150 °C, the reaction temperature was raised to 180 °C over 4 h and a homogeneous reaction mixture was observed. Slight vacuum was applied for 45 min to ensure the removal of condensation by-products and to obtain higher monomer conversions.

Aliquots of the reaction mixture were removed at different times during the course of the reaction and analyzed using ¹H NMR spectroscopy and SEC. PPG-1000 has characteristic NMR resonances that shift upon reaction with TMT (Figure 6-1(a)). In particular, the methyne resonances (3.88 ppm) and the resonances of the methyl groups that are adjacent to the hydroxyl end groups (1.08 ppm) shift slightly downfield (to 5.28 and 1.33 ppm, respectively). These two resonances were used to calculate the extent of reaction and monomer conversion for each sample. In addition, methyl ester resonances (3.93 ppm), which were expected to decrease as the reaction proceeded, were used to further confirm the calculations. Finally, aromatic resonances due to TMT were used to verify that the initial A₂:B₃ = 1:1 molar ratio was maintained throughout the reaction. Figure 6-1(b) shows the ¹H NMR spectrum of the reaction product at 85% hydroxyl (A) group conversion (*p*_A). Thus, ¹H NMR spectroscopy was a powerful tool to characterize reaction products and extent of reaction. Linear analogues of the highly branched poly(ether ester)s were synthesized for comparative purposes using dimethyl terephthalate (DMT), which was a suitable B₂ version of TMT (B₃). A 5% excess of DMT was charged to the reaction flask due to minor sublimation during the early stages of the reaction at 180 °C.



Scheme 6-1. Synthesis of highly branched poly(ether ester)s via melt condensation of PPG-1000 (A₂) and TMT (B₃).

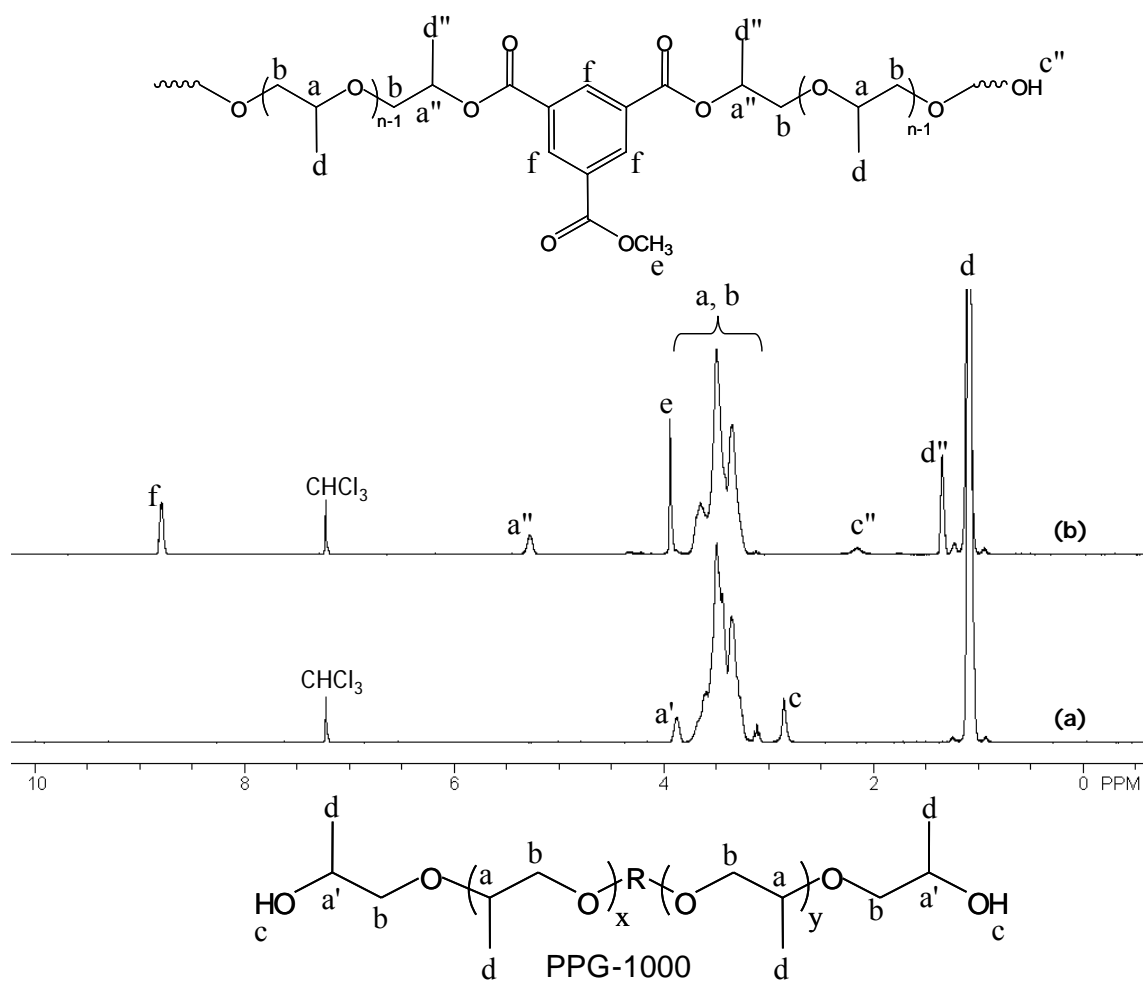


Figure 6-1. ^1H NMR spectra of (a) PPG-1000 and (b) reaction product at 86% conversion of hydroxyl (A) groups (400 MHz, CDCl_3).

SEC and ^1H NMR spectroscopy allowed us to monitor the molar mass increase as a function of monomer conversion. Figure 6-2 is a plot of absolute weight average molar mass as a function of the percent conversion of hydroxyl (p_A) and methyl ester (p_B) groups. The reaction resembled a typical step-growth polymerization with a dramatic increase in molar mass at $p_A = 80 - 85\%$ and $p_B = 53 - 57\%$. Gelation occurred at a critical monomer conversion, which is depicted in Figure 2 using a dotted line. A sudden increase in melt viscosity was also observed and associated with incidence of gelation. Multiple reactions were performed to determine the exact gel point and ensure reproducibility. A final soluble product was reproducibly obtained immediately prior to gelation at $p_A = 90\%$ and $p_B = 60\%$, and solubility tests confirmed that the product at $p_A = 90\%$ was fully soluble. SEC analysis of highly branched poly(ether ester)s revealed an absolute weight average molar mass (M_w) of 450,000 g/mol, which is exceptionally high for a step-growth polymerization. Fréchet and coworkers also monitored the molar mass increase hyperbranched aliphatic polyether epoxies via $A_2 + B_3$ proton transfer polymerization and observed a similar step-growth behavior.¹⁴⁶ However, a molar ratio of $A_2:B_3 = 3:1$ was employed, which would result in gelation at moderately lower monomer conversions, and a relationship between the monomer conversion and gel point was not established. In our studies, the experimental critical monomer conversion values for gelation ($p_A = 90\%$, $p_B = 60\%$) correlated well with the theoretical calculations ($p_{Ac} = 87\%$, $p_{Bc} = 58\%$) for an $A_2:B_3 = 1:1$ system. Close agreement between experimental and theoretical results indicated that there were negligible cyclization reactions that would have accounted for a delayed gel point. Figure 6-3 is a plot of polydispersity versus monomer conversion for the same series of samples. Polydispersity increased as a function of reaction extent and reached a maximum value of 13.7. The SEC traces in Figure 6-4 clearly show a polymodal distribution with a growing fraction of high molar mass hyperbranched polymer and a decreasing fraction of low molar mass oligomers with increasing monomer conversion. As expected for an $A_2 + B_3$ polymerization process, the final product ($p_A = 90\%$) showed multiple shoulders at the high molar mass elution times.

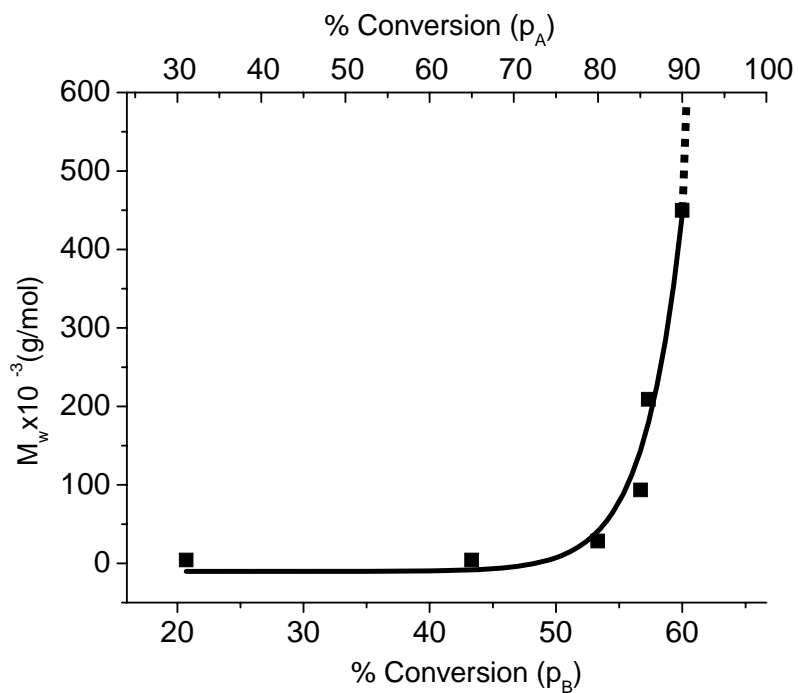


Figure 6-2. Weight average molar mass as a function of monomer conversion.

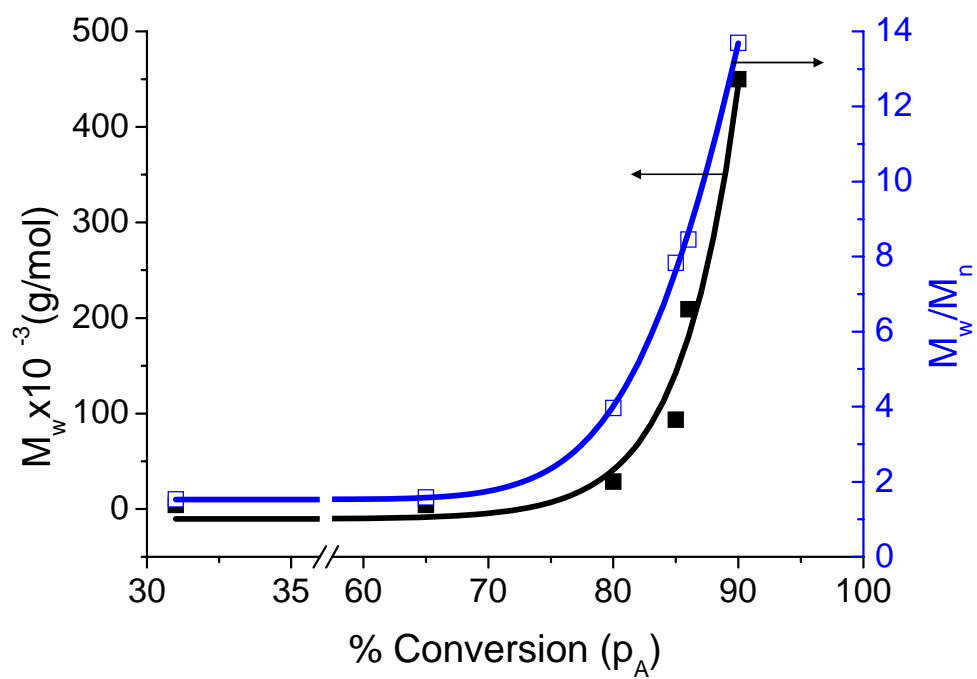


Figure 6-3. Weight average molar mass and polydispersity as a function of monomer conversion.

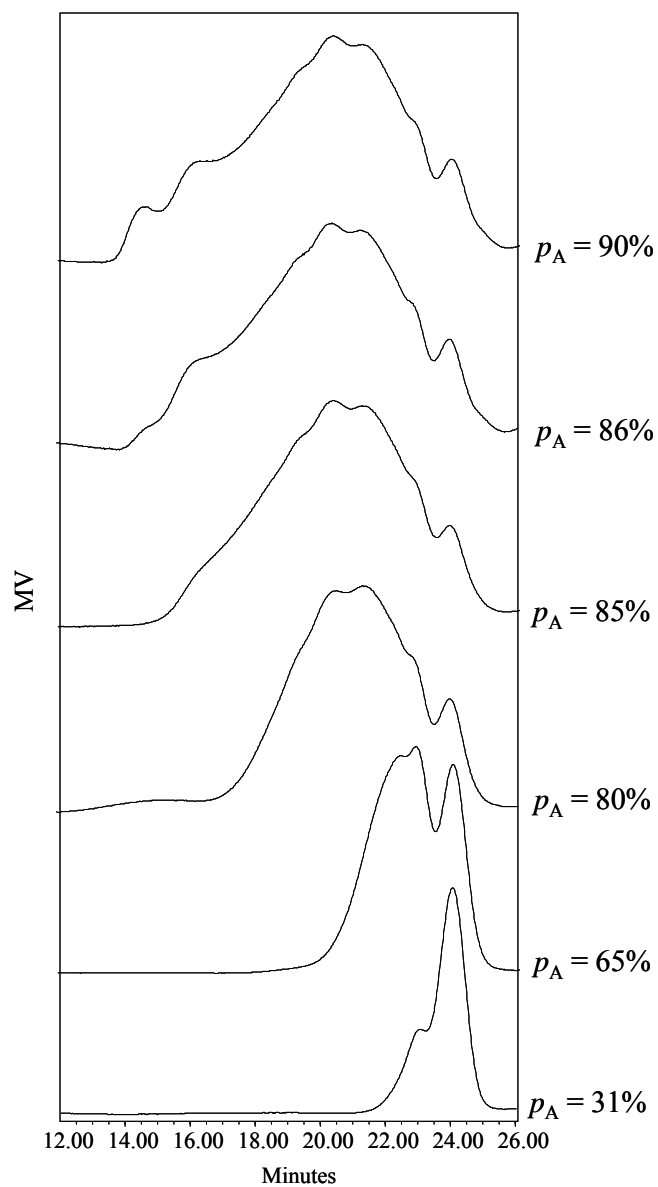


Figure 6-4. SEC traces of highly branched poly(ether ester)s as a function of monomer conversion.

6.4.2 Synthesis of Highly Branched Poly(ether ester)s with Monofunctional Endcapping Reagents to Avoid Gelation

Low levels of trifunctional agent (typically 0.1 – 1.0 mol %) are commonly used to synthesize lightly branched (long-chain branched) condensation polymers via the conventional $A_2 + B_2$ methodology, and it is widely recognized that the introduction of monofunctional comonomers prevents gelation and allows higher levels of branching.¹⁵⁵ However, $A_2 + B_3$ polymerization enables the incorporation of equimolar levels of multifunctional reagents, which is a significantly higher level of branching than $A_2 + B_2$ methodologies in the presence of B_3 .

In a novel strategy, either poly(propylene glycol) monobutyl ether (PPG-M-1000) or dodecanol (DD) were introduced as endcapping reagents (monofunctional comonomers, A) in hyperbranched polymers to avoid gelation during $A_2 + B_3$ polymerization. Both endcapping strategies allowed the polymerization to proceed to very high conversions (p_A and $p_B \geq 98\%$) without gelation, while in the absence of endcapping, gelation occurred at $p_A = \sim 90\%$ and $p_B = \sim 60\%$. PPG-M-1000 (A monomer) was introduced into the reaction flask at the onset of polymerization to synthesize HBPEE-PPG-I. The molar ratio of monomers was set at $A_2:B_3:A = 1:1:1$, targeting the endcapping of all residual methyl ester functionalities that are expected in an $A_2:B_3 = 1:1$ system. Additional polymerization time was required to ensure complete monomer conversion. Gelation was not observed after 2 h at 150 °C, 4 h at 180 °C, and 4 h under vacuum (180 °C). ¹H NMR spectroscopy of the final product indicated p_A and $p_B > 98\%$. As summarized in Table 6-1, the final product (HBPEE-PPG-I) had a weight average molar mass of 416,000 and polydispersity of 23.3.

When DD was used as the endcapping reagent (A) and added to the reaction flask at the onset of polymerization, the reaction resulted in gelation (HBPEE-DD-I). ¹H NMR analysis of the product indicated a 15% DD loss during polymerization, which was presumed to favor gelation. Therefore, when DD was used as the endcapping reagent (A), an alternate strategy, endcapping during polymerization, was utilized. In this approach, the polymerization was started using A_2 oligomer and B_3 monomer only, and DD (A monomer) was added to the reaction flask at a later stage of the polymerization ($p_B = \sim 56\%$, $p_A = \sim 84\%$ at the time of A introduction). A sharp decrease in p_A was expected

upon DD addition because of an increase in the concentration of unreacted A functional groups (hydroxyl). Following the addition of DD, the reaction proceeded for 2 h at 180 °C and vacuum was applied for 4 h. ¹H NMR spectroscopy of the final product (HBPEE-DD-II) revealed p_A and p_B of ~98%. The final polymer was gel-free and fully soluble with M_w of 302,000 g/mol and polydispersity of 14.2 (Table 6-1).

6.4.3 Characterization of Branching

Degree of branching (DB), which is defined as the ratio of dendritic and terminal units to the sum of all dendritic, linear, and terminal units, is a convenient method to characterize branching in hyperbranched polymers.¹⁵⁶ In a hyperbranched polymer that is synthesized via AB₂ polymerization, the approximate distribution of dendritic, terminal, and linear fractions is expected to be 25, 25, and 50%, respectively, resulting in a DB = ~50%. This approach does not properly characterize our systems due to the presence of oligomeric sequences rather than single monomer units between each branch point. Nevertheless, it provides useful information on the branching efficiency of the B₃ monomer and describes the branched structures when each oligomer between the branch points is considered as a single repeat unit. Detailed investigation of the ¹H NMR spectra of each sample at different conversions demonstrated the formation of dendritic, linear, and terminal units as a function of monomer conversion (Figure 6-5). At early stages of the polymerization ($p_A = 31\%$), only terminal and linear units were present. As the reaction proceeded, a dendritic shoulder (8.78 ppm) was more significant especially through the end of the reaction. Each spectrum in Figure 6-5 was processed using the NUTS NMR utility and overlapping aromatic resonances were deconvoluted using a line fitting procedure and optimizing various parameters (frequency, height, width at half height, and ratio of Lorentzian/Gaussian lineshape). Deconvolution of each resonance in Figure 6-5 revealed that the final product ($p_A = 90\%$) had ~20% dendritic units, which is slightly lower than 25% dendritic fraction that is anticipated in a hyperbranched polymer synthesized via AB₂ polymerization at 100% conversion of A groups. However, it should be noted that the feed molar ratio of A and B groups and monomer conversion is expected to play an important role on the distribution of dendritic, linear, terminal units in

¹⁵⁶ Hawker, C. J.; Lee, R.; J., F. J. M., *J. Am. Chem. Soc.* **1991**, 113, 4583.

an $A_2 + B_3$ polymerization. Therefore, 20% dendritic fraction is acceptable at 90% and 60% conversion of A and B groups, respectively.

The branching index (g'), which is derived from SEC viscometric data, was also used to characterize branching.¹⁵⁷ The value g' provides a direct comparison of the hydrodynamic volume of a branched molecule with its linear analogue, and is calculated as $g' = \frac{[\eta]_{\text{branched}}}{[\eta]_{\text{linear}}}$ where $[\eta]_{\text{branched}}$ and $[\eta]_{\text{linear}}$ are the intrinsic viscosities of branched and linear polymers of equivalent weight average molar mass. The g' values are closer to unity for linear polymers and decrease as branching increases. In order to calculate g' for any branched polymer, $[\eta]_{\text{branched}}$ is obtained directly from SEC, and $[\eta]_{\text{linear}}$ is calculated at an equivalent molar mass using the Mark-Houwink equation ($[\eta]_{\text{linear}} = K \times M_w^a$) with appropriate K and a values. The Mark-Houwink relationship $[\eta]_{\text{linear}} = 10^{-3.45} \times M_w^{0.65}$ was established using SEC for the linear poly(ether ester) in this study. Figure 6-6 depicts g' and weight average molar mass as a function of monomer conversion. Only linear structures formed at early stages of polymerization ($p_A < \sim 70\%$). Branching increased above $p_A = 70\%$ and g' ultimately reached a value of 0.27, which indicated a highly branched polymer.

A monofunctional reagent is theoretically expected to terminate some of the B functionalities and decrease the branching probability of a B_3 unit, resulting in a less branched structure. Furthermore, introducing the endcapping reagent late in the polymerization rather than at the onset is expected to yield a more highly branched polymer due to the formation of a branched intermediate prior to addition of the endcapping reagent. However, characterization of highly branched poly(ether ester)s that were synthesized in the presence of monofunctional endcapping reagents suggested that these considerations were not influential during the polymerization. The highly branched poly(ether ester)s that were synthesized in the presence of monofunctional endcapping reagents had g' values (Table 6-1) similar to the final product that was synthesized in the absence of endcapping reagent and obtained immediately prior to gelation ($p_A = 90\%$, $p_B = 60\%$). This suggested that the presence of a monofunctional reagent did not significantly influence the formation of branched structures. Moreover, the point at

¹⁵⁷ McKee, M.; Colby, R. H.; Wilkes, G. L.; Long, T. E., *Macromolecules* **2004**, 37, 1760.

which the monofunctional endcapping reagent was introduced (at the onset of polymerization versus at a later stage) did not alter the final structure. Such discrepancies between theoretical considerations and g' data were attributed to ester interchange reactions. Clearly, B functionalities that have reacted with the endcapping reagent continue to undergo ester-interchange with unreacted A groups. Thus, a non-ideal $A_2 + B_3$ system was envisioned, where a B_3 monomer reacted with an endcapping reagent and formed a B_2B^* type intermediate (B^* denotes the reacted B group that undergoes ester-interchange at a lower rate). In this system, the final products are expected to branch randomly, regardless of the presence of an endcapping reagent or the point in the polymerization at which the endcapping reagent is introduced.

Table 6-1. Characterization data for highly branched poly(ether ester)s that were synthesized using endcapping strategies.

sample	endcapping reagent (A)	A ₂ :B ₃ :A ^c	M _w (g/mol)	M _w /M _n	g'
HBPEE-PPG-I	PPG-M-1000 ^a	1:1:1	416,000	23.3	0.23
HBPEE-DD-I	Dodecanol ^a	1:1:1 ^d	crosslinked product		
HBPEE-DD-II	Dodecanol ^b	1:1:1	302,000	14.2	0.27

^a introduced at the onset of polymerization;

^b introduced during the polymerization (at $p_B = \sim 56\%$);

^c molar feed ratio;

^d ¹H NMR analysis indicated 15% loss of DD (A) during polymerization.

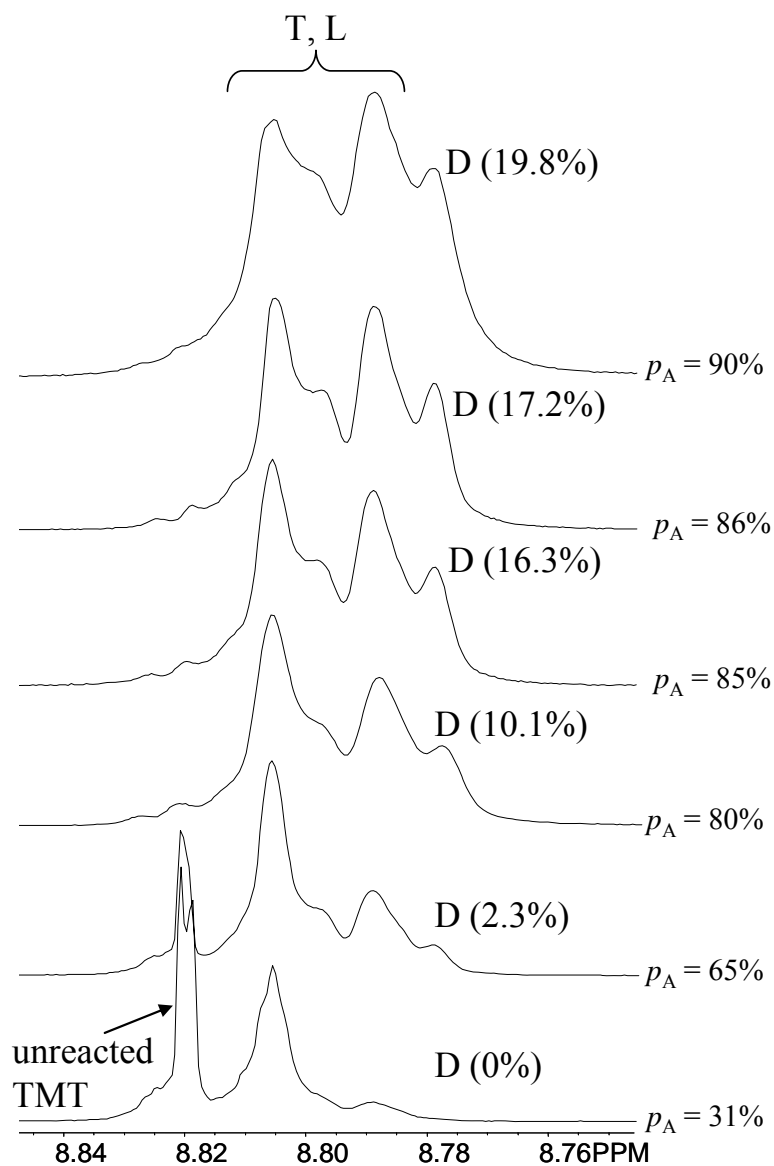


Figure 6-5. ¹H NMR spectra of aromatic region of highly branched poly(ether ester)s provide information on the structural changes and branching at various monomer conversions.

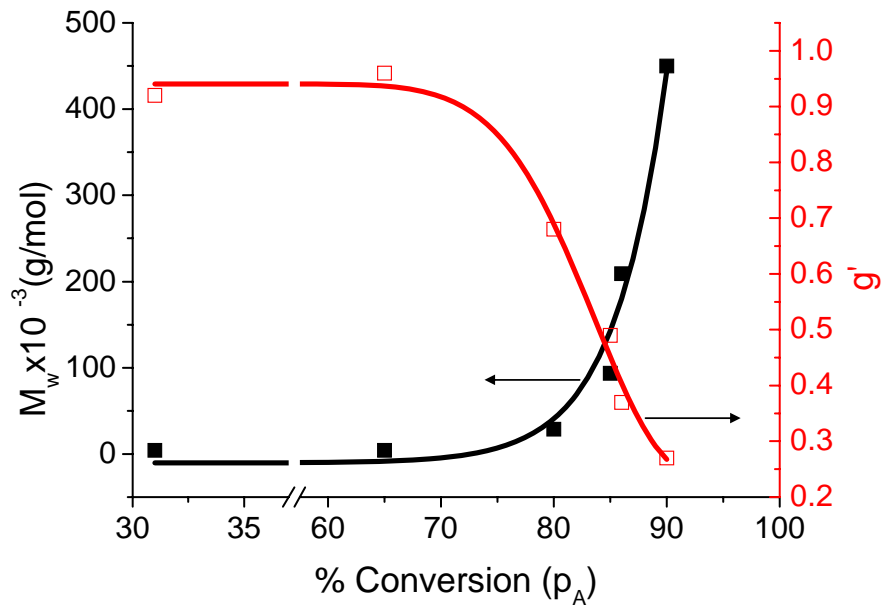


Figure 6-6. Branching index (g') as a function of monomer conversion.

6.5 Conclusions

Melt condensation of an A₂ oligomer (poly(propylene glycol)) with a B₃ monomer (trimethyl 1,3,5-benzenetricarboxylate) resulted in gelation at ~90% conversion of A ($p_A = 90\%$) and ~60% conversion of B groups ($p_B = 60\%$). However, fully soluble, highly branched, products with M_w of ~450,000 g/mol and M_w/M_n of 13.7 were obtained by stopping the reaction immediately prior to the gel point. The close approximation between the experimental ($p_A = 90\%$, $p_B = 60\%$) and theoretical ($p_{Ac} = 87\%$, $p_{Bc} = 58\%$) gel points suggested that cyclization reactions, which would inhibit gelation even at 100% conversion of A groups, were not significant in the melt phase. Moreover, gelation was successfully avoided when monofunctional endcapping reagents were introduced to the reaction flask either at the onset of polymerization or during the reaction. Greater than 98% of the A and B functionalities were consumed. The B functionalities that reacted with the endcapping reagent continued to undergo ester-interchange and reacted with unreacted A groups. As a result, the final products were similar to highly branched polymers that were synthesized in the absence of an endcapping reagent, and the point at which the monofunctional endcapping reagent was introduced (at the onset of polymerization versus at a later stage) did not influence the final structure.

6.6 Acknowledgements

This material is based upon work supported in part by the U.S. Army Research Laboratory and U.S. Army Research Office under grant number DAAD 19-02-1-0275 Macromolecular Architecture for Performance (MAP) MURI. The authors also thank Eastman Chemical Company for financial support.

Chapter 7: Highly Branched Poly(arylene ether)s via Oligomeric A₂ + B₃ Strategies

Taken From:

Lin, Q.; Unal, S.; Fornof, A. R.; Yilgor, I.; Long, T. E. "Highly Branched Poly(arylene ether)s via Oligomeric A₂ + B₃ Strategies." *Macromol. Chem. Phys.* **2005**, submitted for publication.

7.1 Abstract

Branched poly(arylene ether)s were prepared in an oligomeric A₂ + B₃ polymerization of phenol endcapped telechelic poly(arylene ether sulfone) oligomers (A₂) and tris(4-fluorophenyl) phosphine oxide (B₃). The molar mass of the A₂ oligomer significantly influenced the onset of gelation and the degree of branching (DB). A high level of cyclization during polymerization of low molar mass A₂ oligomers (U₃ = 660 and U₆ = 1200 g/mol) led to a high conversion of functional groups in the absence of gelation, and the level of cyclization reactions in the polymerization decreased as the molar mass of the A₂ oligomer was increased. The pronounced steric effect in the polymerization of higher molar mass A₂ oligomers (U₈ = 1800 and U₁₆ = 3400 g/mol) resulted in low reactivity of the third aryl fluoride in the B₃ monomer. As a result, only slightly branched (U₈ = 1800 g/mol) or nearly linear (U₁₆ = 3400 g/mol) high molar mass products were obtained with higher molar mass A₂ oligomers. The branched polymers exhibited lower Mark-Houwink exponents and intrinsic viscosities relative to linear analogs, and differences between the branched polymers and linear analogs were less significant as the molar mass of the A₂ oligomers was increased due to a decrease in the overall degree of branching.

7.2 Introduction

It is well recognized that molecular topology and architecture exert significant influences on polymer physical properties and potential applications.^{158,159} For example, hyperbranched polymers exhibit several unique properties, including low solution and melt viscosities, enhanced solubility, and the presence of a large number of functional end groups for further modification¹⁶⁰ as compared to linear analogs. However, the application of hyperbranched polymers as conventional structural materials is limited due to inadequate mechanical strength, which is attributed to a lack of chain entanglements among the low molar mass branches. Controlling the molar mass between branch points ensures chain entanglement and provides an opportunity to develop structural materials with acceptable mechanical properties and superior processibility.

Significant progress in the control of branch length was accomplished earlier for chain polymerization; for example, derivatives of polyethylene, polystyrene and poly(alkyl methacrylate)s with branching degrees ranging from linear (0%) to dendritic (100%) structures were prepared using diverse strategies.^{158,161} However, there has been less progress in the control of branch length in step-growth polymerization. For example, $A_2 + B_2 + B_3$ or $AB + B_n$ ($n \geq 3$) polymerizations offer facile synthetic approaches to influence topology.^{162,163} However, high risk of gelation prevents incorporation of a high

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level (> 3 mol %) of B_3 monomer in the absence of monofunctional reagents, which limits the degree of branching and significantly influences the physical properties of the final product.

Copolymerization of AB and AB_2 monomers is an effective strategy to manipulate branch length without the risk of gelation.^{164,165} However, few AB and AB_2 monomers are available commercially due to tedious synthetic approaches for asymmetric functionality. Moreover, the statistical distribution of segments results in broad compositional distributions, and the concept of average segment length does not accurately describe the structures.¹⁶⁵ As a result, the development of facile alternative approaches for the preparation of highly branched polymers with acceptable mechanical properties based on readily available monomers will promote significant progress in this field.

Recently, the polymerization of A_2 and B_3 monomers without gelation attracted significant attention as a facile approach to hyperbranched polymers.¹⁶⁶ Our current efforts focus on extending this low molar mass monomer method to manipulate the molar mass between branch points.¹⁶⁷ Different molar mass oligomers are suitable as A_2 monomers to control the branch length. Moreover, A_2 oligomers define the molar mass between B units relative to the entanglement molar mass and regularity is improved compared to polymers that are derived from the copolymerization of AB and AB_2 monomers.

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¹⁶⁴ Flory, P. J., *J. Am. Chem. Soc.* **1952**, 74, 2718, Flory, P. J., *Principles of Polymer Chemistry*. Cornell University Press: Ithaca, NY, 1953, Kricheldorf, H. R.; Zhang, Q. Z.; Schwarz, G., *Polymer* **1982**, 23, 1821, Choi, J.; Kwak, S. Y., *Macromolecules* **2004**, 37, 3745, Kunamaneni, S.; Buzza, D. M. A.; Parker, D.; Feast, W. J., *J. Mater. Chem.* **2003**, 13, 2749, Sendjarevic, I.; McHugh, A.; Markoski, L. J.; Moore, J. S., *Macromolecules* **2001**, 34, 8811.

¹⁶⁵ Hawker, C. J.; Lee, R.; J., F. J. M., *J. Am. Chem. Soc.* **1991**, 113, 4583, Frey, H.; Holter, D., *Acta Polym.* **1999**, 50, 67., Sendjarevic, I.; Liberatore, M. W.; McHugh, A. J.; Markoski, L. J.; Moore, J. S., *J. Rheol.* **2001**, 45, 1245.

¹⁶⁶ Lin, Q.; Long, T. E., *Macromolecules* **2003**, 36, 9809, Jikei, M.; Chon, S. H.; Kakimoto, M. A.; Kawachi, S.; Imase, T.; Watanebe, J., *Macromolecules* **1999**, 32, 2061, Emrick, T.; Chang, H. T.; Fréchet, J. M. J., *Macromolecules* **1999**, 32, 6380, Monticelli, O.; Mariani, A.; Voit, B.; Komber, H.; Mendichi, R.; Pitto, V.; Tabuani, D.; Russo, S., *High Perform. Polym.* **2001**, 13, S45, Fang, J. F.; Kita, H.; Okamoto, K. I., *Macromolecules* **2000**, 33, 4639, Kricheldorf, H. R.; Vakhtangishvili, L.; Fritsch, D. J., *J. Polym. Sci. Part A: Polym. Chem.* **2002**, 40, 2967, Kricheldorf, H. R.; Fritsch, D. J.; Vakhtangishvili, L.; Schwarz, G., *Macromolecules* **2003**, 36, 4347, Yan, D.; Gao, C., *Macromolecules* **2000**, 33, 7693, Komber, H.; Voit, B. I.; Monticelli, O.; Russo, S., *Macromolecules* **2000**, 34, 5487.

¹⁶⁷ McKee, M.; Unal, S.; Wilkes, G. L.; Long, T. E., *Prog. Polym. Sci.* **2005**, 30, 507.

Poly(arylene ether)s are a family of high performance engineering polymers with a relatively high glass transition temperature, high thermal stability, good mechanical properties, and excellent resistance to hydrolysis and oxidation.¹⁶⁸ Important commercial ketone and sulfone containing poly(arylene ether)s include bisphenol-A polysulfone (UDEL[®], Solvay Advanced Polymers), poly(ether sulfone) (Radel[®] PES, Solvay Advanced Polymers; Ultrason[®] PES, BASF), and poly(ether ether ketone) (Vicat[®] PEEK, Vicat PLC; Unitrex[®] PEEK, Nytef Plastics). These polymers exhibit very high melt viscosities due to their high glass transition temperatures and, consequently, are difficult to melt process into miniaturized devices.¹⁶³ Common approaches that improve the flow of thermoplastic polymers, such as the addition of flow promoters, have limited effect on melt viscosity.¹⁶³

Earlier studies of branched poly(arylene ether ketone)s via the copolymerization of AB and AB₂ monomers demonstrated that the incorporation of branches effectively modifies polymer physical properties,¹⁶⁴ and branching was also an effective means to control melt flow.¹⁶³ Moreover, despite the rigidity of poly(arylene ether)s, entanglement molar mass is fairly low in the range of approximately 2000-3000 g/mol.¹⁶⁸ This relatively low entanglement molar mass ensures sufficient chain entanglement for mechanical integrity when branch points are incorporated to improve processibility.

Herein, a novel synthetic methodology is reported for the preparation of poly(arylene ether)s of various branched topologies. The synthetic methodology and molar mass characterization of the branched poly(arylene ether sulfone)s are described in detail. The influence of topology on glass transition temperature, melt rheology, and mechanical properties will be reported in a future publication.

7.3 Experimental

7.3.1 Materials

DMSO and toluene were purchased from Aldrich, dried over calcium hydride, and distilled immediately prior to use. Monomer grade 4,4'-dichlorodiphenylsulfone (DCDPS) and linear poly(ether sulfone) (UDEL[®] P-1700) were graciously provided by

¹⁶⁸ Kloss, J.; Munaro, M.; De Souza, G. P.; Gulmine, J. V.; Wang, S. H.; Zawadzki, S.; Akcelrud, L., *J. Polym. Sci.: Part A Polym. Chem.* **2002**, 40, 4117.

BP Amoco, and monomer grade bisphenol-A (BisA) was kindly supplied by Dow Chemical Company. Potassium carbonate was purchased from Aldrich. The monomers and potassium carbonate were dried under vacuum (0.5 mmHg) at 80 °C for 18 h prior to use. The B₃ monomer, tris(4-fluorophenyl) phosphine oxide (TFPPO), was prepared according to previously published procedures.^{169,170}

7.3.2 Characterization

¹H, ¹³C, ¹⁹F and ³¹P NMR spectroscopic analyses were performed on a Varian Unity 400 MHz spectrometer at ambient temperature. Triple detection size-exclusion chromatography (SEC) was conducted in HPLC grade chloroform (40 °C, 1 mL min⁻¹, polystyrene standards) on a Waters 717 Autosampler equipped with three in-line PLgel 5 mm Mixed-C columns, Waters 410 RI detector, Viscotek 270 dual detector, and in-line Wyatt Technology miniDAWN multiple angle laser light scattering (MALLS) detector.

7.3.3 Synthesis of Phenol Terminated Telechelic Poly(arylene ether sulfone) Oligomers (A₂ Oligomers)

DCDPS, BisA, potassium carbonate, dry DMSO, and dry toluene were introduced into a three-necked, round-bottomed flask at different molar ratios to obtain precursor A₂ oligomers of targeted molar mass (Table 7-1). The reaction flask was equipped with a condenser, mechanical stirrer, and dry nitrogen inlet. The reactor temperature was raised to 135–140 °C for 2 h to remove a toluene/water azeotrope with a Dean–Stark trap and ensure anhydrous reaction conditions. The temperature was subsequently raised to 170 °C, and the reaction was allowed to proceed for 6 h. The reactor was cooled to 25 °C under ambient conditions, and the reaction mixture was poured into a water/acetic acid solution (90/10 v/v) under strong agitation to precipitate the oligomer. The A₂ oligomers were collected using a filter funnel and dried in an 80 °C vacuum oven for 24 h. The A₂ oligomers were classified as U-x, where (x) denotes the average number of repeat units in the oligomer (Table 7-1).

¹⁶⁹ Kloss, J.; Munaro, M.; De Souza, G. P.; Gulmine, J. V.; Wang, S. H.; Zawadzki, S.; Akcelrud, L., *J. Polym. Sci.: Part A Polym. Chem.* **2002**, 40, 4117.

¹⁷⁰ Bernal, D. P.; Bedrossian, L.; Collins, K.; Fossum, E., *Macromolecules* **2003**, 36, 333.

7.3.4 Synthesis of Branched Poly(arylene ether sulfone)s

A₂ oligomer, B₃ monomer, potassium carbonate, dry DMSO, and dry toluene were added to a three-necked, round-bottomed, flask equipped with a condenser, mechanical stirrer, and dry nitrogen inlet (Table 7-2). Subsequent steps were identical to those for the preparation of the A₂ oligomers. The branched products were termed BPES-x-y, where x denotes the number of repeat units of the A₂ oligomer and y denotes the different reaction conditions as summarized in Table 7-2. ¹H-NMR (CDCl₃): δ = 6.95 – 6.99 (d); 7.00 – 7.08 (d); 7.25 -7.30 (d); 7.15 -7.23 (m); 7.56 -7.63 (m); 7.65 – 7.73 (m); 7.85 -7.91 (d).

7.4 Results and Discussion

7.4.1 Synthesis of A₂ Oligomers

The degree of polymerization (X_n) of phenol end-capped telechelic poly(arylene ether) oligomers is determined based on the monomer molar ratio according to Equation 1:¹⁷¹

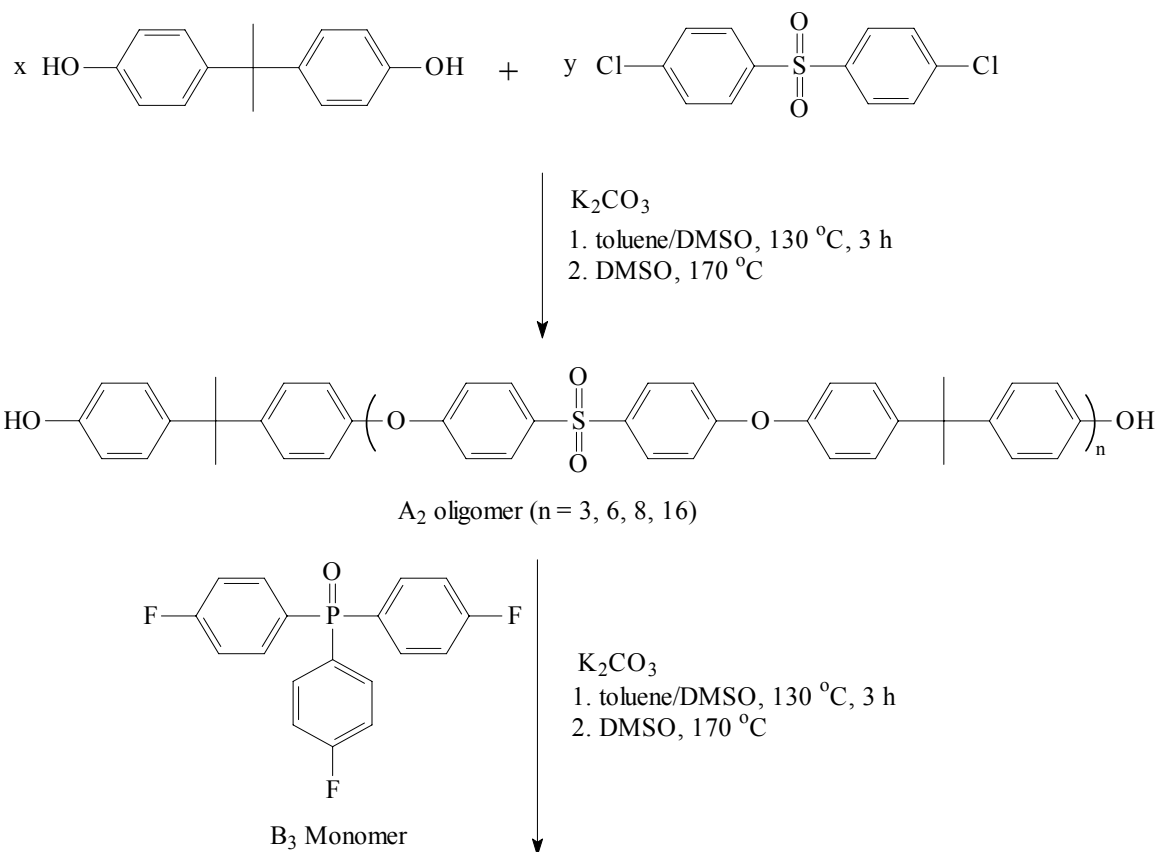
$$\bar{X}_n = \frac{1+r}{1-r}$$

Equation 7-1

where $r = \frac{N_a}{N_b}$ and N_a and N_b denote the moles of functional a and b groups, respectively.

Phenol end-capped telechelic poly(arylene ether) A₂ oligomers of well-defined molar mass were prepared (Scheme 7-1), and the number average molar mass of the oligomers was determined based on ¹H NMR endgroup analysis (Figure 7-1). SEC was also used to determine the molar mass and polydispersity of the higher molar mass oligomers. The predicted X_n values calculated using Equation 1 agreed well with experimental ¹H NMR and SEC data (Table 7-1).

¹⁷¹ Hedrick, J. L.; Yilgor, I.; Jurek, M.; Hedrick, J. C.; Wilkes, G. L.; McGrath, J. E., *Polymer* **1991**, 32, 2020.



Branched Poly(arylene ether sulfone)s

Scheme 7-1. Synthesis of phenol terminated telechelic poly(arylene ether sulfone) oligomers and polymerization with B₃ monomer to obtain branched poly(arylene ether sulfone)s.

Table 7-1. Composition and molar mass data for A₂ oligomers.

A₂ oligomer	BisA:DCDPS (molar ratio)	M_n^a (theo)	M_n^b (NMR)	M_n^c (MALLS)	M_w/M_n	a^d
U ₃	2:1	660	720	-	-	-
U ₆	5:3	1,200	1,080	1,330	1.62	-
U ₈	9:7	1,800	1,780	2,300	2.12	0.61
U ₁₆	15:17	3,400	3,320	3,600	2.20	0.56

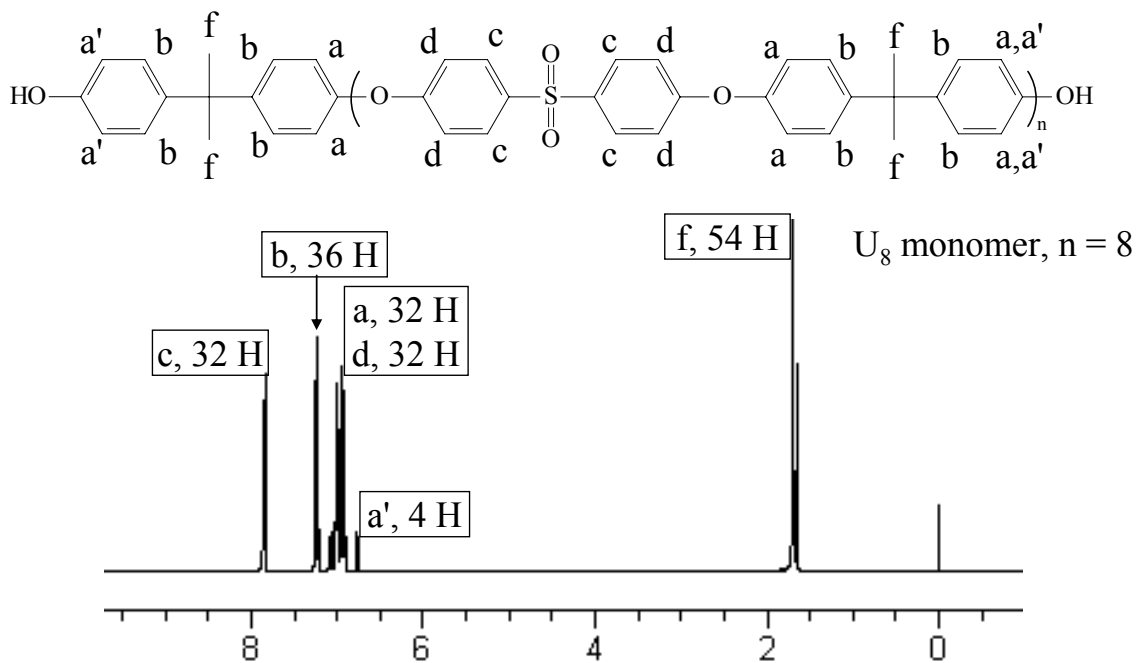


Figure 7-1. ¹H NMR spectrum of U8 A₂ oligomer.

7.4.2 Polymerization

According to Flory's well-established theories, $A_2 + B_3$ polymerizations yield networks and only low molar mass sol fractions are obtained prior to gelation.¹⁶⁴ Flory's theories are, however, based on the assumptions that cyclization does not occur and that the reactivity of the functional groups remains constant throughout the polymerization. It is well documented that polymerizations typically deviate from these two assumptions.^{166, 172} Indeed, it is possible to prepare high molar mass, highly branched, polymers without gelation using the $A_2 + B_3$ methodology at reaction conditions that typically promote cyclization.¹⁶⁶

The reaction of a B_3 monomer is depicted in Figure 7-2 and k_1 , k_2 and k_3 denote the rate constants of the three consecutive reactions of the B_3 monomer. The first reaction produces a terminal unit, the second a linear unit, and the third a dendritic unit. In Flory's theory, k_1 , k_2 and k_3 are assumed identical, which may hold during the initial stage of a polymerization involving highly reactive functional groups such as tri(acyl chloride) and a diol.¹⁶⁶ However, in most cases, the reactivity of the functional groups decreases dramatically as the polymerization proceeds due to additional steric effects of adjacent polymer chains, which was termed earlier as the kinetic excluded-volume effect (Figure 7-3).¹⁷² Despite dilute solution conditions in a good solvent, polymeric functional groups exhibit a significantly lower reactivity than unreacted monomers and low molar mass analogs. As a result, k_1 is always greater than k_2 and k_3 . Moreover, polymer end groups generally exhibit a higher reactivity than those along the length of the polymer chain due to a lower kinetic excluded-volume effect (Figure 7-3). Thus, it is presumed that k_2 is also greater than k_3 .

For $A_2 + B_3$ polymerization processes, a moderate k_3 value leads to branched products without gelation. If k_3 is slightly smaller than k_2 , only lightly branched products are obtained and the risk of gelation is very small. However, if k_3 is comparable to k_2 or

¹⁷² Choi, J.; Kwak, S. Y., *Macromolecules* **2004**, *37*, 3745, Fang, J. F.; Kita, H.; Okamoto, K. I., *Macromolecules* **2000**, *33*, 4639, Black, P. E.; Worsfold, D. J., *J. Polym. Sci. Part A: Polym. Chem.* **1981**, *19*, 1481., Worsfold, D. J., *J. Polym. Sci. Part A: Polym. Chem.* **1983**, *21*, 2271., Kloss, J.; Munaro, M.; De Souza, G. P.; Gulmine, J. V.; Wang, S. H.; Zawadzki, S.; Akcelrud, L., *J. Polym. Sci.: Part A Polym. Chem.* **2002**, *40*, 4117., Jeon, H. K.; Macosko, C. W.; Moon, B. M.; Hoyer, T. R.; Yin, Z., *Macromolecules* **2004**, *37*, 2563.

k_1 , the products have a higher degree of branching with a greater risk of gelation. The fraction of dendritic units in the final products provides a reasonable estimate of the magnitude of k_3 . Several equations were proposed earlier to define the degree of branching (DB) of the products from AB_n monomers, including the following equation as introduced by Fréchet:

$$DB = (D + T)/(D + T + L)$$

Equation 7-2

where D, T, and L are the molar fractions of incorporated AB_n units as dendritic, terminal, and linear units, respectively.¹⁵⁶ Although Equation 7-2 accurately describes hyperbranched products from AB_n monomers, it does not accurately characterize slightly branched products. The fraction of dendritic units, which is related to the magnitude of k_3 , is proposed as a novel parameter to characterize branching efficiency.

For highly reactive monomers and irreversible reactions such as the reaction of tri(acid chloride) with a diol, k_1 , k_2 , and k_3 should be essentially equal in the initial stage of the reaction. In fact, our earlier efforts have shown that high molar mass, highly branched, products were obtained via the slow addition of A_2 monomers to a B_3 solution.^{167,173} Significant cyclization maintained the solubility of the final products and delayed the onset of gelation. Kricheldorf and coworkers have also clearly demonstrated that cyclization competes with $A_2 + B_3$ polymerization, and cyclics are always present in the final product.^{174,175} In addition, significant cyclization reactions were disclosed in the preparation of linear poly(arylene ether sulfone)s based on bisphenol-A and 4,4'-dichlorodiphenylsulfone.¹⁷⁵ Thus, the incidence of cyclization reactions in step-growth polymerization leads to gel free, high molar mass, hyperbranched poly(arylene ether)s via $A_2 + B_3$ polymerization.¹⁶⁶

¹⁷³ McKee, M.; Unal, S.; Wilkes, G. L.; Long, T. E., *Prog. Polym. Sci.* **2005**, 30, 507.

¹⁷⁴ Kricheldorf, H. R.; Schwarz, G., *Macromol. Rapid Comm.* **2003**, 24, 359.

¹⁷⁵ Kricheldorf, H. R.; Bohme, S.; Schwarz, G.; Kruger, R. P.; Schulz, G., *Macromolecules* **2001**, 34, 8886.

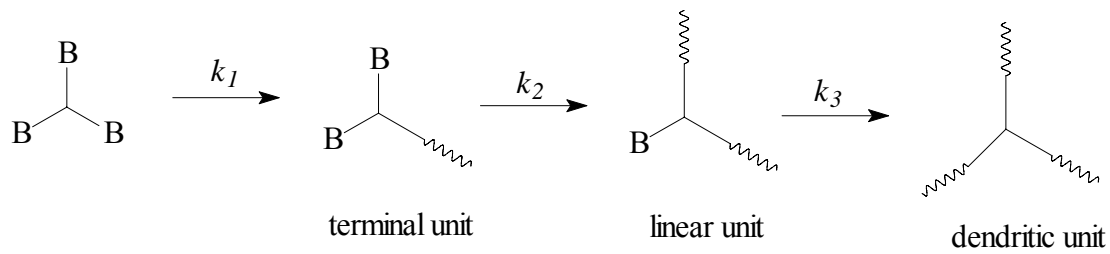


Figure 7-2. Reaction of B_3 monomer.

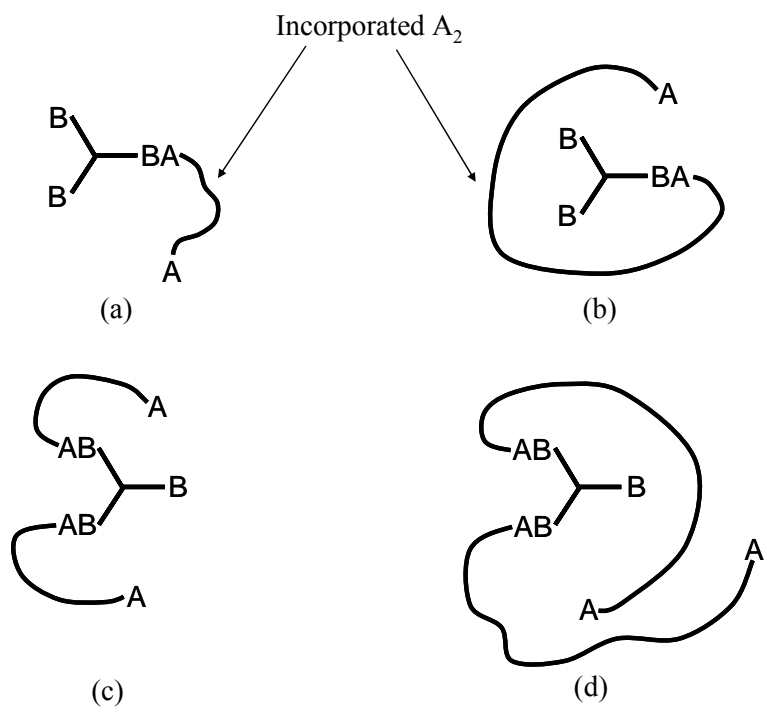


Figure 7-3. Kinetic excluded-volume effect with A_2 oligomers of varying molar mass.

(a), (c): low molar mass A_2 ; (b), (d): high molar mass A_2 .

Fossum and Czupik used ^{31}P NMR spectroscopy to confirm that significant cyclization reactions led to high molar mass hyperbranched poly(arylene ether)s in the polymerization of low molar mass A_2 and B_3 monomers.¹⁷⁶ Thus, hyperbranched products derived from A_2 and B_3 monomers will contain one or more cyclic structures in each hyperbranched molecule if significant cyclization reactions occur during the polymerization. However, it remains difficult to precisely characterize the average number of cyclic structures in hyperbranched molecules. Although kinetic factors and cyclization favor the formation of soluble polymers during $\text{A}_2 + \text{B}_3$ polymerization, these earlier efforts demonstrated that it is essential to select suitable reaction conditions in order to avoid gelation.

Phenol end-capped telechelic poly(arylene ether) A_2 oligomers of various molar masses and a tris(4-fluorophenyl) phosphine oxide B_3 monomer (TFPPO) were polymerized as shown in Scheme 7-1. The TFPPO B_3 monomer provided an important analytical advantage as the final dendritic, linear, and terminal unit in the branched polymer products exhibited significantly different chemical shifts in the ^{31}P NMR spectra (Figure 7-4).^{170,176} This desirable spectroscopic tag allowed an investigation of the branched structures as a function of B_3 conversion. Moreover, the B_3 monomer, terminal units, and linear units also exhibited different chemical shifts in the ^{19}F NMR spectrum (Figure 7-5), which provided a complementary method to confirm the ^{31}P NMR results.

When the low molar mass BisA was used as A_2 monomer, 0.20 M monomer solutions proceeded without gelation for a long period at 170 °C (HBPEs). Aliquots (2 mL) of the homogeneous reaction solution were removed every 15 min and ^{31}P and ^{19}F NMR spectroscopy of the precipitated products demonstrated that the products reached a degree of branching of 51% with approximately 27% dendritic units after the first 15 min of reaction time (Table 7-2). This result suggests the functional groups were highly reactive with k_1 , k_2 and k_3 approximately equal in the initial stage. A ^{31}P NMR resonance presumed due to cyclic products (28.8 ppm) appeared in the initial stage of the reaction, and the relative amount decreased slightly as the polymerization proceeded (Figure 7-4).¹⁷⁶ The high critical concentration for gelation and the ^{31}P NMR resonance for the cyclic product confirmed that significant cyclization prevented gelation.¹⁷⁶

¹⁷⁶ Czupik, M.; Fossum, E., *J. Polym. Sci. Part A: Polym. Chem.* **2003**, 41, 3871.

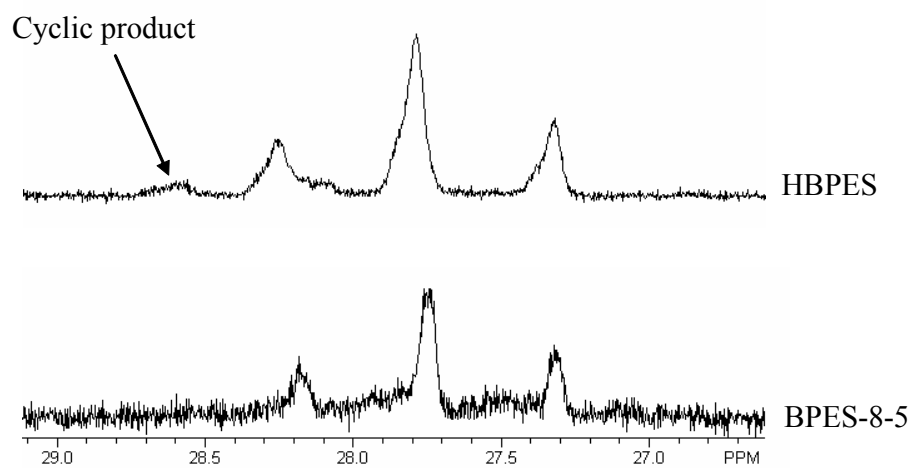


Figure 7-4. ^{31}P NMR spectra of hyperbranched (HB PES) and slightly branched (BPES-8-5) poly(arylene ether)s.

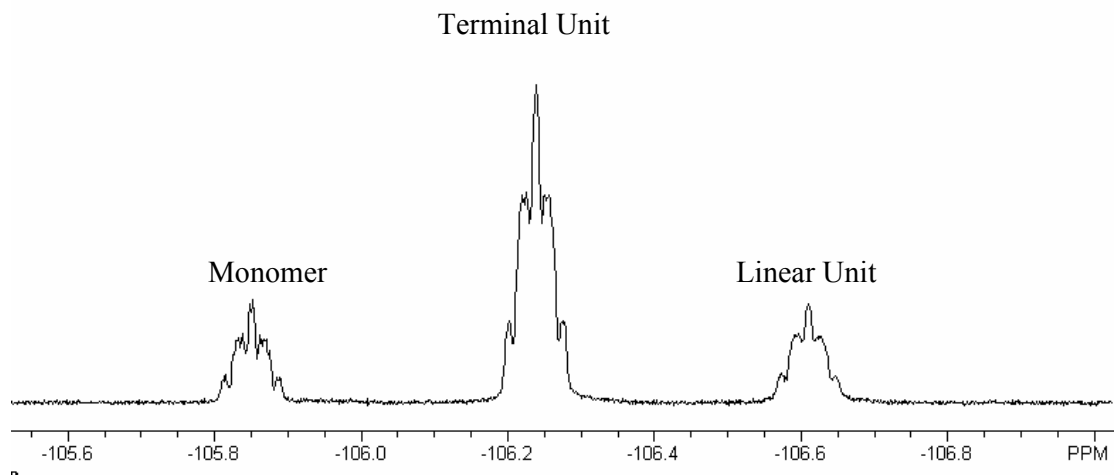


Figure 7-5. ^{19}F NMR spectroscopy is a complementary method to confirm the ^{31}P NMR results. Residual B_3 monomer, terminal units, and linear units exhibit different chemical shifts in the ^{19}F NMR spectrum (BPES-8-1).

Table 7-2. Reaction conditions, composition, molar mass data, and solution behavior of poly(arylene ether)s of various architectures.

sample	[M]	A ₂ :B ₃	A:B	t (h)	M _n ^a (g/mol)	M _w (g/mol)	a	[η] (dL/g)	g'	D	T	L	DB (%)	L _{A2}	DB _G (%)	predicted topology ^b
							(SEC)	(SEC)	(SEC)	³¹ P NMR			(Eqn 2)	(Eqn 4)	(Eqn 3)	
HBPES	0.20	1:1	2:3	8	15,700	19,200	0.14	0.03	0.11	0.27	0.24	0.49	51	0	51	HB
BPES-3-1	0.10	1:1	2:3	16	4,000	10,400	0.41	0.10	0.17	0.24	0.22	0.54	46	3	12	MB
BPES-6-1	0.10	1:1	2:3	16	13,800	34,500	0.44	0.10	0.23	0.17	0.32	0.51	49	6	7	MB
BPES-8-1	0.20	1:1	2:3	4	10,700	19,000	-	-	-	-	-	-	-	-	-	-
BPES-8-2	0.10	1:1	2:3	8	9,400	31,900	0.57	0.25	0.61	0.08	0.44	0.48	52	8	6	SB
BPES-8-3	0.10	1:1	2:3	16	20,500	65,300	0.50	0.28	0.43	0.09	0.38	0.53	47	8	5	SB
BPES-8-4	0.10	3:2	1:1	8	7,000	44,600	0.55	0.28	0.55	0.17	0.39	0.44	56	12	4	SB
BPES-8-5	0.10	3:2	1:1	16	101,000	175,000	0.61	0.67	0.63	0.33	0.15	0.52	48	12	4	SB
BPES-8-6	0.10	3:1	2:1	4	7,200	14,200	0.47	0.12	0.50	100	0	0	100	24	4	SB
BPES-16-1	0.05	1:1	2:3	8	9,500	45,000	0.54	0.29	-	0	0.59	0.41	-	-	-	Linear
BPES-16-2	0.05	1:1	2:3	16	32,200	147,000	0.55	0.38	-	0	0.46	0.54	-	-	-	Linear
UDEL [®]	-	-	-	-	16,100	43,400	0.65	0.46	0.94	-	-	-	-	-	-	Linear
LPES-1	-	-	1:1	-	130,000	233,000	1.10	0.89	-	-	-	-	-	-	-	Linear

^a Chloroform, 40 °C, viscometric detector;

^b Topology predictions based on Mark-Houwink constants and DB_G:(HB) hyperbranched, (MB) moderately branched, (SB) slightly branched.

Gelation was observed within 2 or 3 h at 170 °C with 0.20 M solutions of the lower molar mass oligomers ($U_3 = 660$ g/mol, $U_6 = 1200$ g/mol). As summarized in Table 7-2, high molar mass products (BPES-3-1 and BPES-6-1) were prepared without gelation using 0.10 M solutions of the U_3 and U_6 oligomers, and the fraction of dendritic units based on ^{31}P NMR spectroscopy in the BPES-3-1 (24%) and BPES-6-1 (17%) products were lower than that for the HBPEs hyperbranched polymer (27%). It is proposed that the higher molar mass A_2 oligomers resulted in a greater kinetic excluded-volume effect (Figure 7-3), which resulted in a lower k_3 and a corresponding lower degree of branching. Moreover, the resonance related to low molar mass cyclic structures was not observed in the ^{31}P NMR spectra, which also indicates cyclization decreased as the molar mass of the A_2 oligomers was increased. Although the lower k_3 decreased the risk of gelation, it did not sufficiently offset the increased risk of gelation due to the decreased cyclization. As a result, a more dilute solution ($A_2 = 0.10$ M) was necessary to increase cyclization and further decrease k_3 to avoid gelation.

A 0.20 M solution of U_8 at 170 °C resulted in a high solution viscosity in 3 h. Gelation did not occur and the product (BPES-8-1) remained soluble. ^{31}P and ^{19}F NMR spectroscopies demonstrated that the conversion of B_3 monomer was low, and the product contained both polymer and residual monomers (Table 7-2 and Figure 7-5). A 0.10 M U_8 solution was used to further reduce solution viscosity and achieve a higher monomer conversion (BPES-8-2), and ^{31}P and ^{19}F NMR analyses revealed a lower fraction of dendritic units ($\sim 8\%$, Table 7-2) at the $A_2:B_3 = 1:1$ ($A:B = 3:2$) ratio. SEC did not reveal significant cyclization (Figure 7-6), and the absence of gelation was mainly attributed to a lower branching efficiency due to a pronounced kinetic excluded-volume effect with the moderate molar mass U_8 oligomer at low concentrations.

A very high viscosity was achieved in a short reaction time with the U_{16} as A_2 oligomer, and a small fraction of high molar mass product was obtained at low monomer conversion. A more dilute, 0.05 M solution, was used to further reduce the solution viscosity and achieve higher monomer conversion (BPES-16-1 and BPES-16-2). ^{31}P and ^{19}F NMR spectroscopy revealed no dendritic units presumably due to the high kinetic excluded-volume effect. SEC analysis also confirmed that this low monomer concentration led to significant cyclization (Figure 7-7). The cyclic products had lower

molar mass than the starting A₂ oligomers (3400 g/mol) indicating the major mechanism for the formation of low molar mass cyclic products in such a dilute solution was “back-biting degradation”.¹⁶⁵ Thus, the products based on the U₁₆ A₂ oligomer were complex blends containing both high molar mass linear polymers and a high fraction of low molar mass cyclics.

The mode of monomer addition plays an important role in gelation.¹⁷⁶ In this study the B₃ monomer and A₂ oligomer were combined at the onset of the reaction. In contrast, when the B₃ monomer is slowly added to a solution of A₂ oligomer, the concentration of B₃ monomer is extremely low during the initial stages of the reaction. As a result, a higher conversion of third B functional groups in the middle of the forming polymer results in gelation after only a small amount of B₃ monomer is added to the A₂ solution. A significant kinetic excluded-volume effect and lower branching efficiency were observed with the moderate molar mass oligomers in the current work; however, an increase in the concentration of A functionality may partially offset this negative effect.

Increasing the A₂:B₃ molar ratio from 1:1 to 3:2 (A:B molar ratio from 2:3 to 1:1) with the U₈ A₂ oligomer resulted in a higher fraction of dendritic units and a shorter reaction time to achieve high molar mass products (Table 7-2). When the A₂:B₃ molar ratio was increased to 3:1 (A:B = 2:1), gelation occurred in 8 h (BPES-8-6). The sol fraction was isolated upon extraction, and ³¹P NMR spectroscopy demonstrated a single resonance assigned to the dendritic unit. SEC analysis and ¹H NMR spectroscopy indicated a product with M_n = 7,200 g/mol, M_w = 14,000 g/mol, and phenolic end groups. As discussed earlier, the branching efficiency determined using ³¹P NMR spectroscopy only describes the branched structures based on the B₃ units and does not consider the A₂ oligomer branch point dilution. Thus, when an oligomeric A₂ is used, it is necessary to normalize the degree of branching by taking into account the number of linear repeat units in each A₂ oligomer. A revised equation was proposed to characterize the global degree of branching.¹⁷³

$$DB_G = \frac{D_{B_3} + T_{B_3}}{D_{B_3} + L_{B_3} + T_{B_3} + L_{A_2}}$$

Equation 7-3

where, D_{B_3} , L_{B_3} , and T_{B_3} denote the molar fractions of incorporated B_3 units as dendritic, linear, and terminal units, respectively. When $D_{B_3} + L_{B_3} + T_{B_3} = 1$, L_{A_2} denotes the number of normalized repeat units in the A_2 oligomer:

$$L_{A_2} = n \times \frac{[A_2]}{[B_3]}$$

Equation 7-4

where n denotes the number of repeat units in the A_2 oligomer and $\frac{[A_2]}{[B_3]}$ denotes the molar ratio of A_2 and B_3 monomers in the reaction. For example, $L_{A_2} = 3$ for a product synthesized from the U_3 A_2 oligomer at a 1:1 $[A_2]:[B_3]$ molar ratio. When U_8 is used as the A_2 oligomer, L_{A_2} values for $[A_2]:[B_3]=1:1, 3:2,$ and $3:1$ are 8, 12, and 24, respectively.

If the branching efficiency is constant, the global degree of branching, DB_G , decreases as the molar mass of the A_2 oligomer and L_{A_2} are increased. The calculated DB_G values are listed in Table 7-2. A series of poly(arylene ether sulfone)s of various architectures were achieved including a hyperbranched polymer based on low molar mass BisA (HBPEs), moderately branched polymers without significant entanglements (BPES-3-1 and BPES-6-1), and slightly branched polymers (BPES-8-1, BPES-8-5, and BPES-8-6). These poly(arylene ether sulfone)s of various topologies will provide a unique opportunity to investigate the influence of architecture on polymer physical properties.

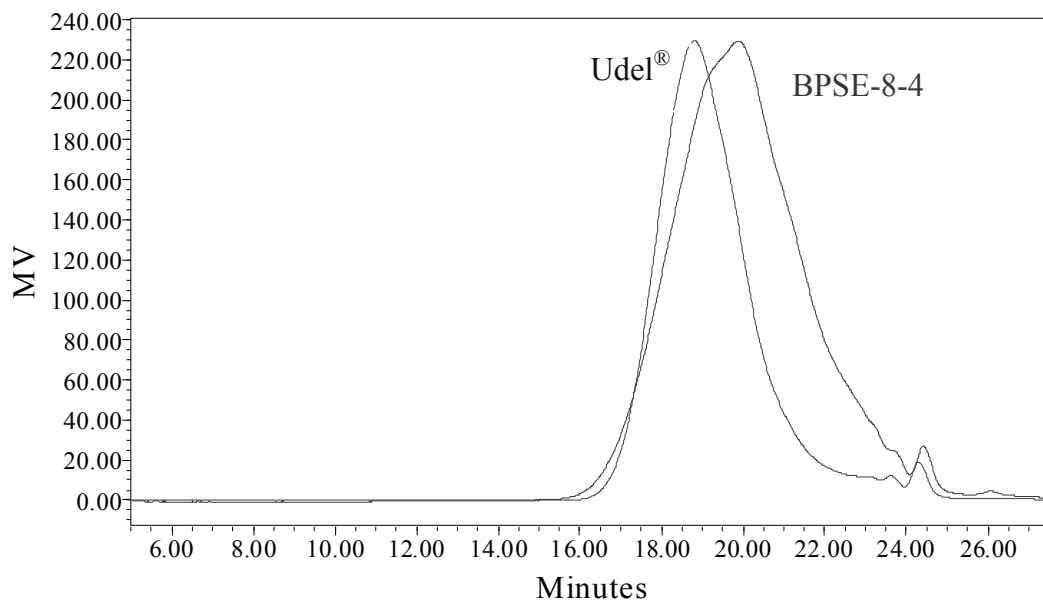


Figure 7-6. SEC curves demonstrate the equivalent molar mass and cyclic fractions of UDEL[®] and BPES-8-4.

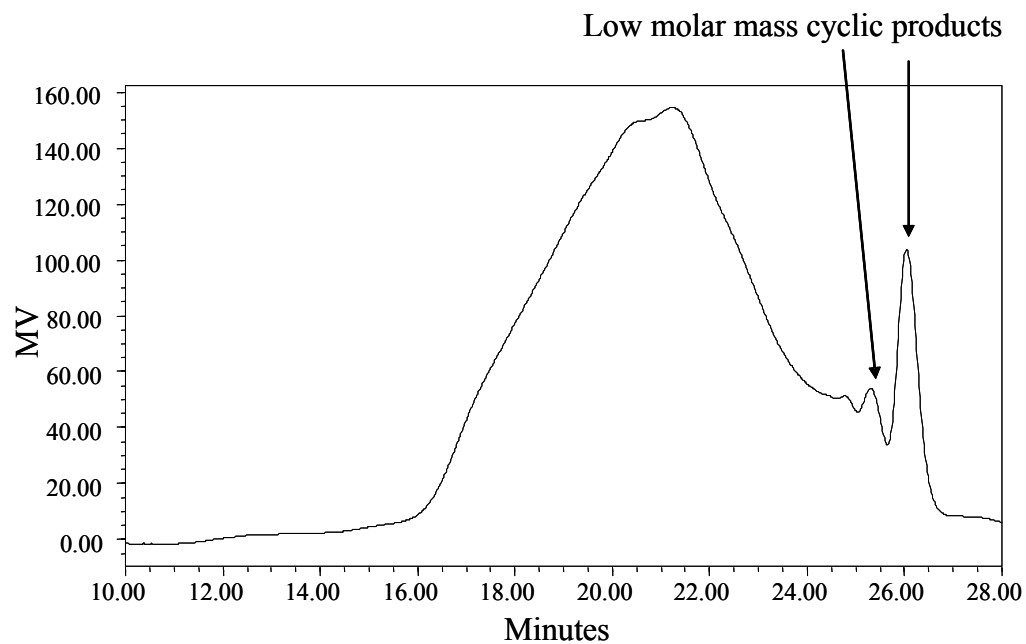


Figure 7-7. SEC curve for BPES-16-1, a mixture of high molar mass products and a high fraction of low molar mass cyclic products.

7.4.3 SEC Investigation

Size exclusion chromatography (SEC) data were obtained using the well established triple-detection technique, which employs refractive index (RI), intrinsic viscosity (IV), and light scattering detectors for the elucidation of product composition, molar mass distributions and dilute solution behavior. The weight average molar mass values obtained using the viscometric detector (Table 7-2) were in good agreement with multiple angle laser light scattering (MALLS) based values.

The high molar mass A₂ oligomers led to high molar mass products in a short time. The SEC curves for UDEL and the linear LPES-1 sample exhibited two distinct symmetric peaks; the smaller peak at approximately 24 min was attributed to low molar mass cyclic products. Both the weight average molar mass and the SEC curve of the slightly branched BPES-8-4 (44,600 g/mol) were similar to UDEL (43,400 g/mol) (Figure 7-6). The hyperbranched polymer based on BisA (HB PES) exhibited a multimodal curve due to the existence of high fractions of low molar mass cyclic products (Figure 7-8).¹⁷⁶ The fraction of low molar mass cyclic products decreased when the molar mass of the A₂ oligomer was increased (BPES-6-1), suggesting a decrease in cyclization (Figure 7-8).

MALLS and viscometry data were used to measure the Mark-Houwink exponent (a), intrinsic viscosity ([η]), radius of gyration ($\langle R_g^2 \rangle^{1/2}$), and viscometric radius (R_η) of the products. Contraction factors were used as previously described to characterize the change in dimension of a coil of a given molar mass.^{161,177}

$$g' = \frac{[\eta]_{br}}{[\eta]_l}$$

Equation 7-5

$$g = \frac{(\langle R_g^2 \rangle^{1/2})_{br}}{(\langle R_g^2 \rangle^{1/2})_l}$$

Equation 7-6

$$\rho = \frac{R_\eta}{\langle R_g^2 \rangle^{1/2}}$$

Equation 7-7

¹⁷⁷ McKee, M.; Colby, R. H.; Wilkes, G. L.; Long, T. E., *Macromolecules* **2004**, 37, 1760.

where *br* denotes the branched polymer and *l* denotes the linear polymer of equivalent molar mass. The *g'* factor provides the difference in the hydrodynamic volume between the branched and linear polymers. The *g* factor provides information on the geometrical shrinkage/expansion of the molecule. The ρ parameter discloses the difference in molecular geometry and hydrodynamic dimensions due to the branched structure.¹⁷⁷

The branched polymers exhibited lower intrinsic viscosities and Mark-Houwink exponents than the linear analogs (Table 7-2). The Mark-Houwink exponent increased as the molar mass of the A₂ oligomer was increased due to a decrease in the global degree of branching. The relationship between intrinsic viscosity and weight average molar mass (*M_w*) for a moderate molar mass linear polymer was based on earlier SEC-viscometric data for UDEL:

$$[\eta]_l = 4 \times 10^{-4} \times M_w^{0.65}$$

Equation 7-8

Equation 7-8 was used to calculate $[\eta]_l$ values for linear analogs for each of the branched polymers. The measured $[\eta]_{br}$ and calculated $[\eta]_l$ values were then used to calculate *g'* according to Equation 7-5. As expected, the *g'* values (Table 7-2) demonstrated that branching significantly decreased the hydrodynamic volume. Moreover, the slightly branched BPES-8-5 exhibited a lower Mark-Houwink exponent than the LPES-1 linear analog (Table 7-2), which is expected due to the lower hydrodynamic radius of the branched polymer.

The slightly branched BPES-8-4 and linear UDEL samples and the slightly branched BPES-8-5 and linear LPES-1 samples have equivalent *M_w* and fractions of low molar mass cyclic structures, respectively, which provides a unique opportunity to investigate the influence of branching on polymer coils in dilute solutions (Table 7-3). The *g'* contraction factor for UDEL is 0.94, which is reasonably close to the expected value of 1.0 for a completely linear polymer. The analogous branched BPES-8-4 has a *g'* of only 0.55, which indicates a significant amount of branching (Table 7-2). A low *g'*, 0.63, was also observed for the BPES-8-5 polymer. While only “slightly branched” relative to hyperbranched polymers, it is evident based on *g'* values that these poly(arylene ether sulfone)s are significantly branched when compared to traditional step growth polymers with added trifunctional branching agent.¹⁷⁷

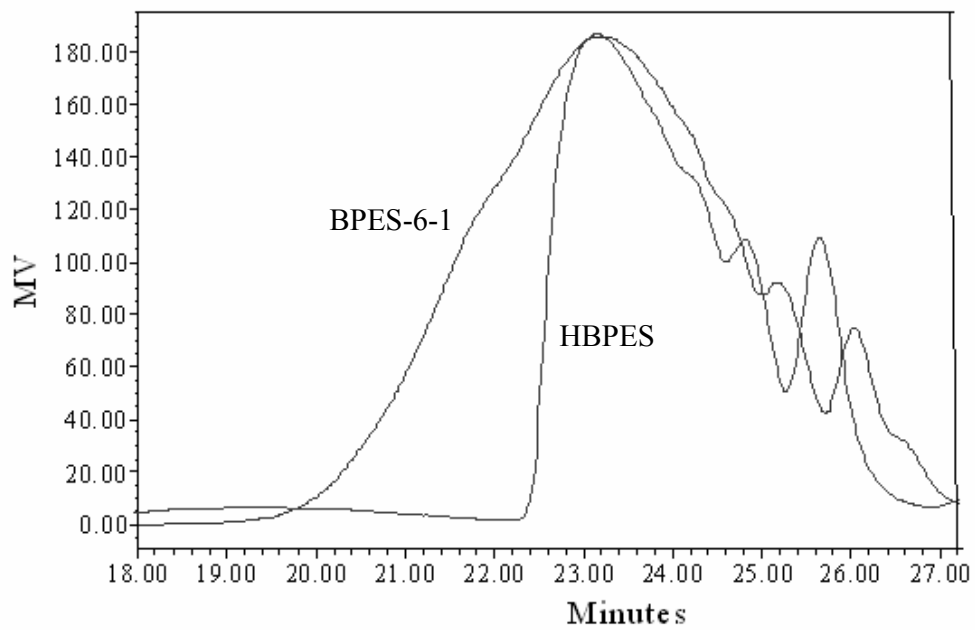


Figure 7-8. SEC curves of a hyperbranched poly(arylene ether phosphine oxide) (HB PES) and a moderately branched poly(arylene ether sulfone)s (BPES-6-1).

Table 7-3. “Shrinking” factors of poly(arylene ether sulfone)s.

sample	M_w^a (g/mol)	g	ρ
BPES-8-4	44,100	0.85	0.77
UDEL [®]	43,500	1.00	0.83
BPES-8-5	148,000	1.00	0.42
LPES-1	150,000	1.08	0.74

^a Chloroform, 40 °C, MALLS.

7.5 Conclusions

Poly(arylene ether)s of various architectures were prepared via an oligomeric $A_2 + B_3$ polymerization. Hyperbranched, moderately branched, slightly branched, and linear topologies were achieved. When bisphenol-A and low molar mass oligomers were used as A_2 , pronounced cyclic reactions led to branched products without gelation. The significance of the cyclic reactions decreased as the molar mass of the A_2 oligomers was increased. When moderate molar mass oligomers were used as A_2 monomers, a kinetic excluded-volume effect resulted in a low branching efficiency. An increase in the concentration of A_2 oligomer significantly improved the branching efficiency. In most cases, this synthetic strategy did not broaden the molar mass distribution. In fact, the branched BPES-8-4 product was generally of equivalent molar mass and contained a similar fraction of low molar mass cyclic products as the commercial UDEL. The branched structures effectively decreased the solution viscosity, and the influences of branched structure on other physical properties such as glass transition temperature, melt rheology, and mechanical properties will be reported in the near future.

7.6 Acknowledgements

This material is based upon work supported by the U.S. Army Research Laboratory under grant number DAAD 19-02-1-0275 Macromolecular Architecture for Performance (MAP) MURI. The authors also thank Prof. James E. McGrath and Dr. William L. Harrison, Department of Chemistry, Virginia Polytechnic Institute and State University for providing the high molar mass poly(arylene ether sulfone) and for helpful discussions. The materials from BP Amoco and Dow Chemical Company are greatly appreciated.

Chapter 8: Synthesis of Phosphonium-Based Telechelic Polyester Ionomers

8.1 Abstract

This chapter reports the synthesis of a new family of telechelic polyester ionomers based on phosphonium bromide salts. Novel cationic endcapping reagents, which possess phosphonium bromide sites and benzoic acid or ethyl ester functionalities, were synthesized. Thermogravimetric analysis revealed that the phosphonium-based ionic compounds had higher thermal stabilities than the ammonium-based analogues. These endcapping reagents were introduced to the melt polyesterification at temperatures ranging from 220 °C to 275 °C for the synthesis of linear or branched polyester ionomers. ^1H and ^{31}P NMR spectroscopic analyses confirmed the quantitative incorporation of the ionic endgroups and the absence of significant degradation due to the endcapping reagents. Branching enabled the enhancement of ionic chain end concentrations and preliminary transmission electron microscopic analysis indicated the presence of ionic aggregates in a branched telechelic polyester ionomer with 5 mol % ionic chain ends.

8.2 Introduction

Low concentrations of covalently bonded ionic groups are known to dramatically affect the physical and rheological properties of organic polymers. Ionomers containing less than 15 mol % ionic groups form a class of materials with improved mechanical and thermal properties, compared to nonionic, high molar-mass analogues. These dramatic changes in the performance of ionomers are attributed to the formation of ionic aggregates that act as thermoreversible crosslink points in the organic polymer matrix. Control of the size and the structure of these ionic aggregates offers a wide variety of advantages such as controlled melt processibility, improved thermal stability at typical processing conditions, and improved miscibility with inorganic additives.^{178,179}

Telechelic ionomers are synthesized via placement of the ionic groups at the chain ends and are commonly utilized as model ionomers since the molar mass between ionic aggregates is well-defined.^{180,181} In step-growth polymerization, copolymerization of A₂ and B₂ monomers with a low level of a monofunctional comonomer (endcapping reagent) typically results in chain-end functionalized products.¹⁸² Previous studies in our laboratories have included the synthesis and characterization of telechelic poly(ethylene terephthalate) (PET) sodiosulfonate ionomers derived from sodium salts of 3-sulfobenzoic acid. Our studies have shown that ionic end groups have a significant influence on the thermal and rheological performance of PET. However, these ionic aggregates persisted in the melt phase and hindered processibility. Most studies on

¹⁷⁸ Tant, M. R.; Mauritz, M. R.; Wilkes, G. L., *Ionomers: Synthesis, Structure, Properties and Applications*. Blackie Academic & Professional: New York, 1997.

¹⁷⁹ Eisenberg, A.; Kim, M., *Ion-Containing Polymers*. Academic Press: New York, 1977; Eisenberg, A.; S., K. J., *Introduction to Ionomers*. Wiley: New York, 1998.

¹⁸⁰ Broze, G.; Jerome, R.; Teyssie, P.; Marco, G., *Polym. Bull.* **1981**, 4, 241. Broze, G.; Jerome, R.; Teyssie, P.; Gallot, B., *J. Polym. Sci., Polym. Lett. Ed.* **1981**, 19, 415. Broze, G.; Jerome, R.; Teyssie, P., *Macromolecules* **1981**, 14, 224. Broze, G.; Jerome, R.; Teyssie, P., *Macromolecules* **1982**, 15, 920. Jerome, R., In *Telecheloc Polymers: Synthesis and Applications*, Goethals, E. J., Ed. CRC Press, Inc.: Boca Raton, FL, 1989; p Chapter 11.

¹⁸¹ Boykin, T. C.; Moore, R. B., *Poly. Eng. Sci.* **1998**, 38, 1658. Boykin, T. C.; Moore, R. B., *Polym. Prepr.* **1998**, 39, 393. Barber, G. D.; Carter, C. M.; Moore, R. B., *Polym. Mater. Eng.* **2000**, 82, 241. Ng, C. W. A.; Lindway, M. J.; MacKnight, W. J., *Macromolecules* **1994**, 27, 7. Ng, C. W. A.; MacKnight, W. J., *Macromolecules* **1996**, 29, 2421.

¹⁸² Kang, H.; Lin, Q.; Armentrout, R. S.; Long, T. E., *Macromolecules* **2002**, 35, 8738.

ionomers have focused on random polyester ionomers in which ionic groups are randomly distributed as pendant groups along the polymer chain.¹⁸³

This study describes the synthesis of novel ionic endcapping reagents and corresponding linear and branched telechelic polyester ionomers based on phosphonium salts. SEC and NMR spectroscopy reveal the formation of well-defined, phosphonium salt containing telechelic ionomers, and TEM indicates the formation of ionic aggregates. Phosphonium-based ionomers are attractive alternatives to more thermally labile ammonium based analogues.

8.3 Experimental

8.3.1 Materials

Trioctylphosphine (TOP, 90%), triphenylphosphine (TPP, 99%), 4-bromobenzoic acid (98%), ethyl 6-bromohexanoate (99%), nickel(II) bromide (98%), dimethyl terephthalate (DMT, 99%), dimethyl isophthalate (DMI, 98%), and trimethyl 1,3,5-benzenetricarboxylate (TMT, 98%) were purchased from Aldrich and used as received. Ethylene glycol (EG) was purchased from J.T. Baker and used as received. Titanium tetra(isopropoxide) (99%) and antimony(III) oxide (99%) were purchased from Aldrich. The preparation of catalyst solutions for polyester synthesis was described in a previous report.^[ref] Tetraoctylphosphonium bromide (TrOPBr) and tetraoctylammonium bromide (TrOABr) were purchased from TCI America.

8.3.2 Characterization

Solution ¹H (400 MHz) and ³¹P NMR (200 MHz) spectroscopic analyses were performed on a Varian Inova spectrometer at ambient temperature. Size-exclusion chromatography (SEC) with viscometry detection (Viscotek Model 110; two Polymer Laboratories Plgel mixed-C columns) in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) containing 0.01 M tetraethylammonium nitrate at 45 °C was used to determine molar mass. Absolute molar masses were calculated from the viscosity data and a universal calibration curve was constructed from narrow molar mass distribution poly(methyl methacrylate) standards. Thermogravimetric analysis (TGA) was performed on a Perkin-

¹⁸³ Greener, J.; Gillmore, J. R.; Daly, R. C., *Macromolecules* **1993**, 26, 6416.

Elmer TGA 7 under a nitrogen atmosphere at a heating rate of 10 °C /min. Thermal transition temperatures were determined using a Perkin-Elmer Pyris-1 differential scanning calorimeter (DSC) at 10 °C/min under a helium atmosphere, and all reported data were obtained from the second heating. Transmission electron micrographs (TEM) were obtained using a Philips 420T with 100kV accelerating voltage.

8.3.3 Synthesis of (*p*-Carboxyphenyl)trioctyl phosphonium bromide (I-Oc)

A double-neck, 100-mL, round-bottomed flask, which was equipped with an overhead mechanical stirrer and argon inlet, was charged with nickel(II) bromide (1.52 g, 6.86 mmol) and degassed consecutively using argon and slight vacuum. TOP (30.00 g, 80.94 mmol) and 4-bromobenzoic acid (16.28 g, 80.94 mmol) were added, and the reaction mixture was heated to 170 °C under argon. The reaction was maintained at 170 °C for 18 h. The dark green product mixture was dissolved in 100 mL of chloroform and filtered through a fritted Buchner funnel. A by-product, biphenyl-4,4'-dicarboxylic acid, was collected and discarded upon filtration. The dark green chloroform solution was washed with acidic water (pH = 5) three times, and the solution turned yellow. Upon removal of residual water in chloroform using sodium sulfate, the product was precipitated in ethyl ether. A white, solid product was collected and dried at 50 °C in a vacuum oven for 8 h. The product was recrystallized from acetone five times until no yellow color was detected upon dissolution in hot acetone. The white crystals were dried at 60 °C in a vacuum oven for 24 h. Typical yields ranged from 55 to 60%.

8.3.4 Synthesis of (5-Ethoxycarbonyl pentyl)trioctyl phosphonium bromide (II-Oc)

A double-neck, 100-mL, round-bottomed flask, which was equipped with a condenser and nitrogen inlet, was charged with ethyl 6-bromohexanoate (4.83 g, 21.65 mmol) and TOP (8.04 g, 21.65 mmol). The reaction mixture was heated to 80 °C under nitrogen and maintained at 80 °C for 45 min until a clear, homogeneous reaction mixture was obtained. The reaction temperature was increased to 120 °C over 1 h and maintained for 2 h. Finally, the reaction was maintained at 140 °C for another 2 h. The pale yellow, viscous liquid was cooled to room temperature and washed with *n*-hexane and ethyl ether three times, consecutively. The final product was dried at 120 °C in a vacuum oven for 24 h. A pale yellow viscous liquid was obtained. Typical yields were ~ 80 %.

8.3.5 Synthesis of (5-Ethoxycarbonyl pentyl)triphenyl phosphonium bromide (II-Ph)

A double-neck, 100 mL, round-bottomed flask, which was equipped with a condenser and nitrogen inlet, was charged with ethyl 6-bromohexanoate (5.20 g, 23.31 mmol) and TPP (6.11 g, 23.31 mmol). The reaction mixture was heated to 120 °C under nitrogen over 1 h, and a clear, homogeneous reaction mixture was obtained. The reaction was maintained at 120 °C for 5 h and at 140 °C for another 5 h. The pale yellow viscous liquid product mixture was cooled to room temperature and washed with n-hexane and ethyl ether three times, consecutively. The final product was dried at 120 °C in a vacuum oven for 24 h. A pale yellow, viscous liquid was obtained. Typical yields were ~ 70 %.

8.3.6 Synthesis of Linear Telechelic Polyester Ionomers

Linear telechelic polyester ionomers were synthesized via the polycondensation of a poly(ethylene terephthalate)-co-poly(ethylene isophthalate) (PET-co-PEI) oligomeric precursor and a phosphonium-based endcapping reagent. The samples listed in Table 8-1 were identified as: LPETI-*x*, where L denotes linear, PETI denotes PET-co-PEI, and *x* denotes the sample entry. The amorphous PET-co-PEI oligomer was prepared via the melt condensation of DMT (25.25 g, 130 mmol), DMI (25.25 g, 130 mmol), and EG (32.28 g, 520 mmol). Both titanium tetraisopropoxide (30 ppm) and antimony(III) oxide (200 ppm) were added to facilitate ester exchange and subsequent polycondensation.

The reactor consisted of a 250-mL, round-bottomed flask equipped with an overhead mechanical stirrer, nitrogen inlet, and condenser. The reaction flask containing the monomers and catalysts was degassed using vacuum and nitrogen three times and subsequently heated to 190 °C. The reactor was maintained at 190 °C for 2 h, and the temperature was increased to 220 °C over 2 h. The reaction was allowed to proceed for 30 min at 275 °C. Vacuum was gradually applied to 0.30 mmHg, and polycondensation continued for 15 min at 275 °C. Corresponding telechelic PET-co-PEI ionomers were prepared via the subsequent melt condensation of the freshly prepared PET-co-PEI oligomer and the endcapping reagents. A desired amount of the endcapping reagent (Table 8-1) was added to the reaction flask containing the PET-co-PEI oligomer at room temperature. For the synthesis of L-PETI-1 and L-PETI-2, the reaction flask was degassed, subsequently heated to 250 °C, and maintained at 250 °C for 30 min. The

temperature was increased to 275 °C, and the reaction was allowed to proceed for 30 min at 275 °C. Vacuum was gradually applied to 0.20 mmHg, and polycondensation continued for 2 h at 275 °C. For the synthesis of L-PETI-4 and L-PETI-5, the temperature was increased to 220 °C upon the addition of the endcapping reagent and maintained at 220 °C for 30 h. The temperature was increased to 250 °C, allowed to proceed for 30 min, vacuum was applied for 2h, and polycondensation continued for 2 h at 250 °C.

L-PETI-3 was alternatively synthesized by introducing a desired amount of the endcapping reagent (Table 8-1) to the reaction flask at the beginning of the polymerization with DMI, DMT, EG, and catalysts. The reaction flask containing the monomers, endcapping reagent, and catalysts was degassed using vacuum and nitrogen three times and subsequently heated to 190 °C. The reactor was maintained at 190 °C for 2 h, and the temperature was increased to 220 °C over 2 h. The reaction was allowed to proceed for 30 min at 275 °C. Vacuum was gradually applied to 0.30 mmHg, and polycondensation continued for 2 h min at 275 °C.

8.3.7 Synthesis of Branched Telechelic Polyester Ionomers

The samples listed in Table 8-1 were identified as: BPETI-*x*, where B denotes branched, PETI denotes PET-co-PEI, and *x* denotes the sample entry. The synthesis of the branched PET-co-PEI oligomer was similar to the synthesis of the linear PET-co-PEI oligomer with the exception that a desired amount (2 or 3 mol %, Table 8-1) of TMT branching agent was added to the DMT, DMI, and EG mixture at the beginning of the reaction. The branched telechelic PET-co-PEI ionomers were synthesized via the melt condensation of the freshly prepared branched PET-co-PEI oligomer and the desired amount of I-Oc endcapping reagent (3.0 or 5 mol %, Table 8-1); the melt condensation methodology was identical to that used to prepare the L-PETI-1 and L-PETI-2 samples.

Table 8-1. Composition and molar mass data of linear and branched telechelic polyester ionomers.

sample	endcapping reagent		branching agent (TMT) (mol %)	polycond. temp. ^b (°C)	M _n (g/mol)	M _w (g/mol)	M _w /M _n
	type	(mol %)					
LPETI-1	I-Oc	1.0	-	275	14,500	25,600	1.77
LPETI-2	I-Oc	3.0	-	275	6,000	10,600	1.77
LPETI-3 ^a	I-Oc	3.0	-	275	5,500	10,100	1.84
LPETI-4	II-Oc	3.0	-	250	5,400	9,400	1.76
LPETI-5	II-Ph	3.0	-	250	6,000	9,600	1.60
BPETI-1	I-Oc	3.0	2.0	275	4,900	18,400	3.73
BPETI-2	I-Oc	5.0	3.0	275	2,000	5,400	2.76

^a The endcapping reagent was introduced to the reaction mixture at the onset of polymerization;

^b Polymerization temperature after the endcapping reagent was introduced.

8.4 Results and Discussion

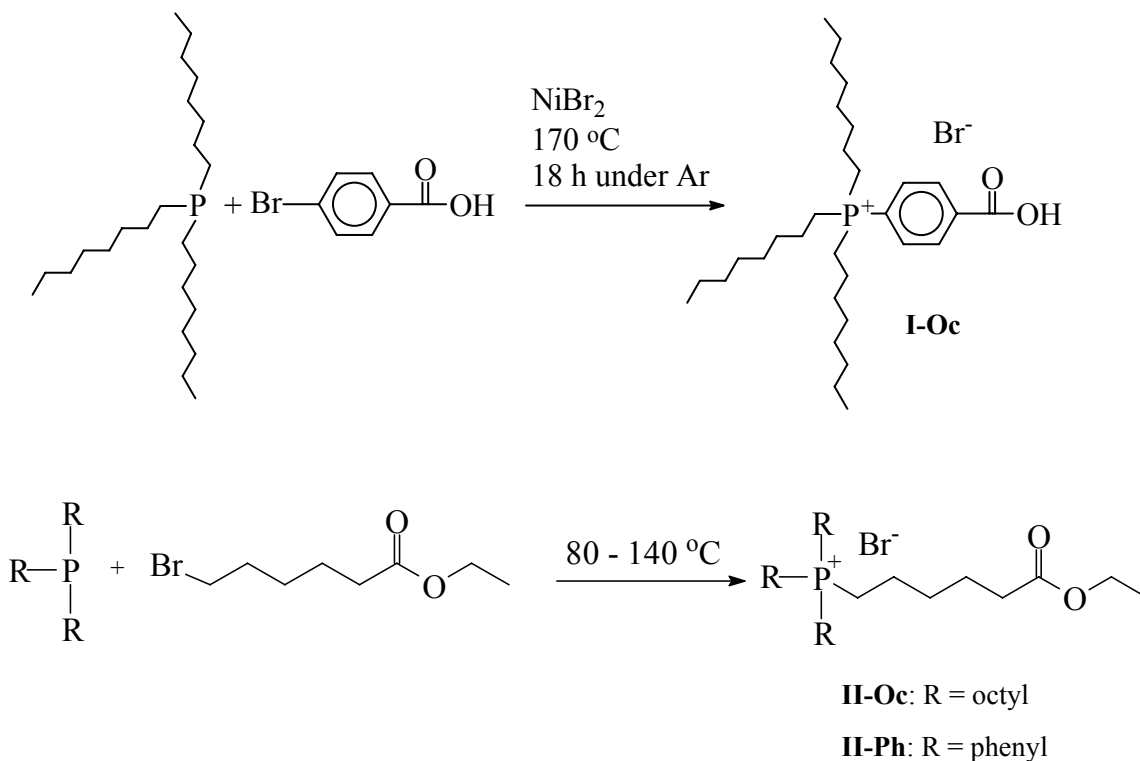
8.4.1 Synthesis of Phosphonium Bromide-Based Endcapping Reagents

Most of the earlier studies on ionomers with main chains bearing a cationic group focused on quaternary ammonium salt-based systems with limited thermal stabilities above 200 °C. The incorporation of such ammonium salts in organic polymers, such as polyesters that require high synthesis and processing temperatures is not feasible. Thus, our studies focused on the synthesis of phosphonium salt containing endcapping reagents that readily undergo transesterification reactions at temperatures ranging from 190 to 275 °C over 2 to 3 h.

The endcapping reagent (*p*-carboxyphenyl)trioctyl phosphonium bromide, I-Oc, was synthesized via an oxidative addition and reductive elimination reaction¹⁸⁴ in the presence of nickel (II) bromide as a catalyst (Scheme 8-1). The endcapping reagents, (5-ethoxycarbonyl pentyl)triphenyl phosphonium bromide (II-Ph) and (5-ethoxycarbonyl pentyl)trioctyl phosphonium bromide (II-Oc), were synthesized via a S_N2 reaction mechanism with moderately high yields (Scheme 8-1). As shown in Figure 8-1, the thermal stability of the I-Oc phosphonium salt endcapping reagent using thermogravimetric analysis (TGA) was greater than tetraoctylammonium bromide (TrOABr). Tetraoctylphosphonium bromide (TrOPBr) and the endcapping reagent (I-Oc) based on phosphonium salt showed similar thermal stabilities with thermal degradations started after 339 and 327 °C, respectively, whereas the model ammonium salt (TrAPBr) exhibited a degradation onset at 173 °C. Moreover, isothermal TGA of I-Oc also showed a weight loss of <5% after 2 h at 275 °C under a nitrogen atmosphere, revealing that I-Oc was suitable as an endcapping reagent for polyester synthesis at temperatures up to 275 °C. This demonstrates that phosphonium based ionomers provide definitive advantages in thermal stability compared to ammonium functionalized polymers. Figure 8-2 depicts the thermogravimetric analysis of II-Oc and II-Ph. Both the II-Oc and II-Ph endcapping reagents exhibited a degradation onset above ~260 °C, slightly lower than I-Oc; however, as discussed in the polymerization section, both the II-

¹⁸⁴ Horner, H.; Duda, U. M., *Tetrahedron Letters* **1970**, 59, 5177.

Oc and II-Ph endcapping reagents were successfully polymerized without any significant thermal degradation.



Scheme 8-1. Synthesis of phosphonium bromide-based monofunctional endcapping reagents.

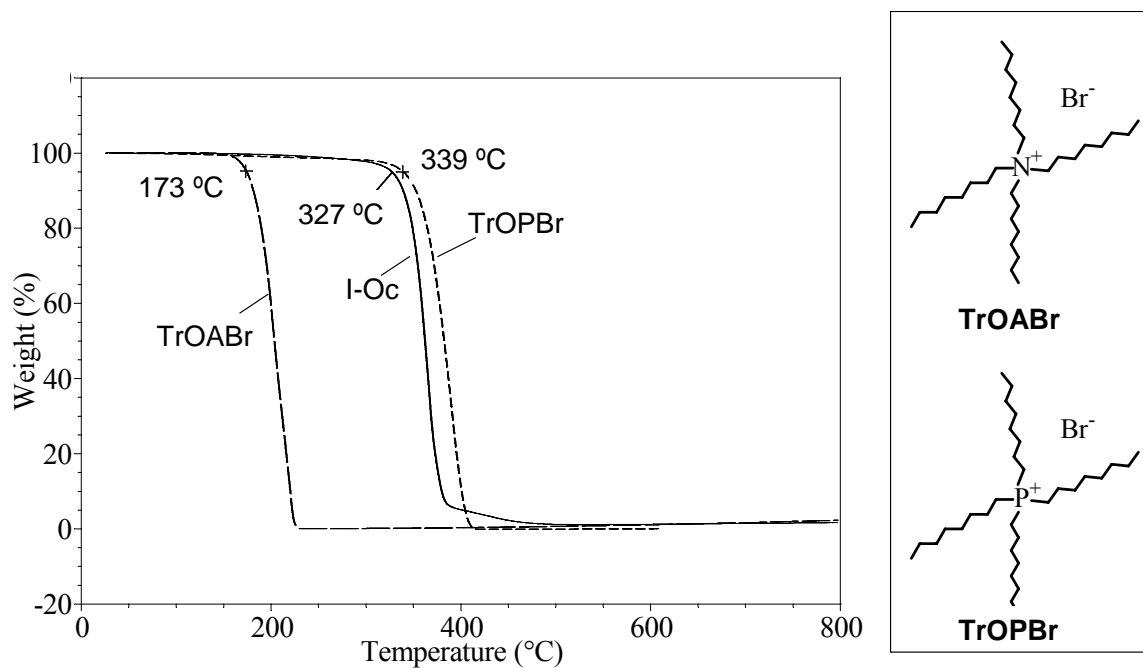


Figure 8-1. Thermogravimetric analysis of I-Oc and two model ionic compounds, tetraoctylphosphonium bromide (TrOPBr) and tetraoctylammonium bromide (TrOABr).

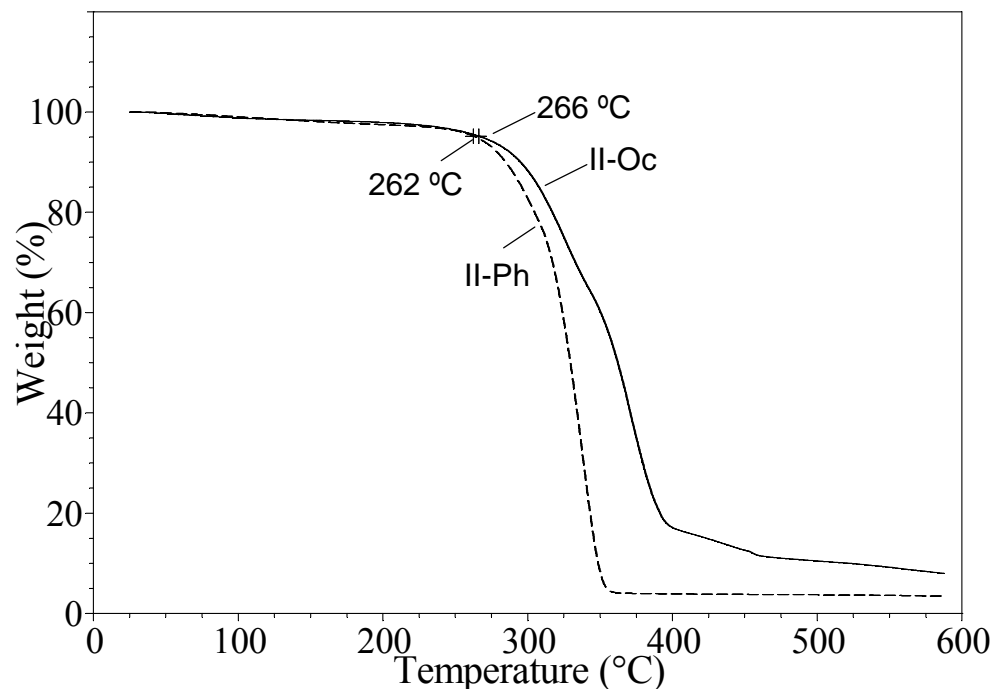
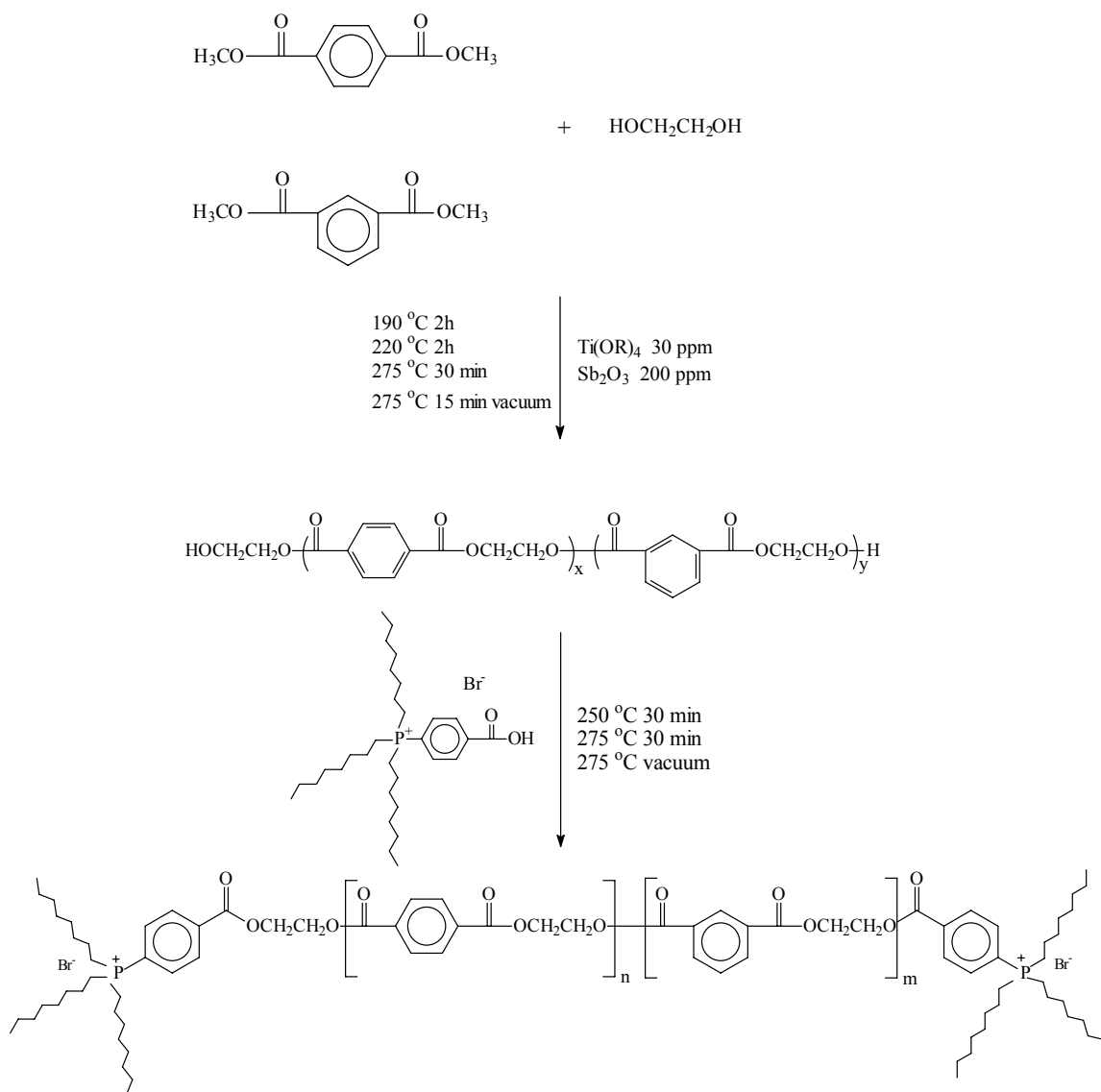


Figure 8-2. Thermogravimetric analysis of II-Oc and II-Ph synthesized via S_N2 reaction.

8.4.2 Polymerization

A two-step methodology was followed for the synthesis of the telechelic polyester ionomers. First, a hydroxyl terminated, linear or branched PET-co-PEI oligomer was synthesized using the multistep temperature sequence described in Scheme 8-2, and subsequently allowed to undergo polycondensation in the presence of a phosphonium endcapping reagent. As summarized in Table 8-1, the second polycondensation step was maintained at 275 °C with the I-Oc endcapping reagent due to thermal stability considerations. The ^1H NMR spectrum of the phosphonium endcapping reagent (I-Oc) and a corresponding polyester ionomer (L-PETI-2) are shown in Figure 8-3. Resonances that are characteristic of protons on the endcapping reagent are clearly visible in both spectra, demonstrating the successful incorporation of the ionic site at the chain ends. ^{31}P NMR spectroscopic analysis confirmed the presence of the phosphonium salt on the polymer chain ends. Figure 8-4 shows the ^{31}P NMR spectra of trioctylphosphine (TOP), the corresponding cationic endcapping reagent (I-Oc), and the telechelic polyester ionomer that was derived from I-Oc. It is clear that the cationic phosphorous was preserved at the polymer chain ends, and neither oxidation nor reduction of the phosphorous center, which are possible side reactions at high temperatures, significantly occurred during the polymerization.

In order to verify the validity of the two step-methodology (oligomer synthesis and endcapping), L-PETI-3 was synthesized by introducing the endcapping reagent (I-Oc) at the onset of polymerization. Thus, the polymerization was performed in one-step, and all monomers were mixed at the beginning of the polymerization. As summarized in Table 8-1, equivalent amounts of endcapping reagent were charged (3 mol %) during the synthesis of L-PETI-2 and L-PETI-3, but two-step versus one-step methodologies were investigated, respectively. Similar molar masses were obtained from size exclusion chromatography (SEC) of L-PETI-2 and L-PETI-3, which indicated that the two-step methodology was as efficient as the one-step methodology in terms of incorporating ionic groups at the polymer chain ends. The endcapping reagent is less likely to undergo degradation in the two-step strategy as reaction times are dramatically reduced. Thus, the two-step methodology was employed for the synthesis of the polyester ionomers.



Scheme 8-2. Synthesis of telechelic polyester ionomers via the polycondensation of a hydroxyl terminated polyester oligomer and ionic endcapping reagent (I-Oc).

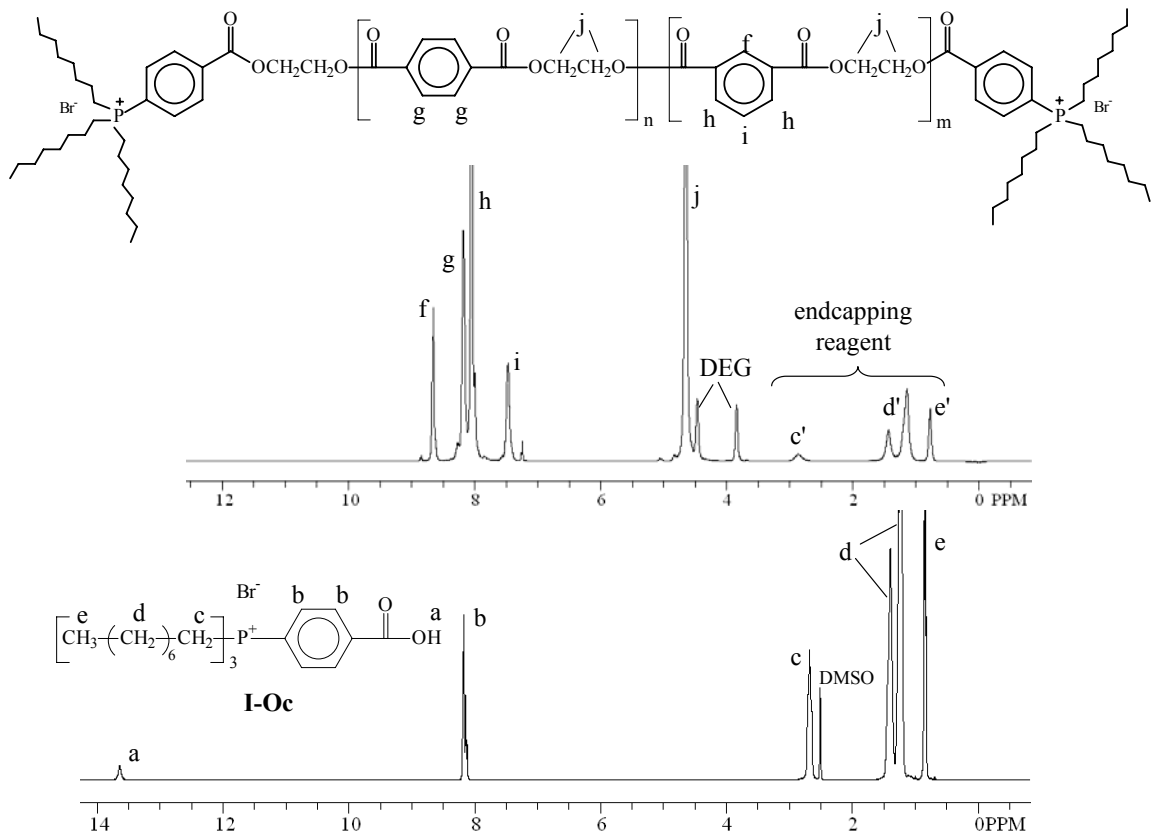


Figure 8-3. ¹H NMR spectra of I-Oc and a corresponding telechelic polyester ionomer (L-PETI-2).

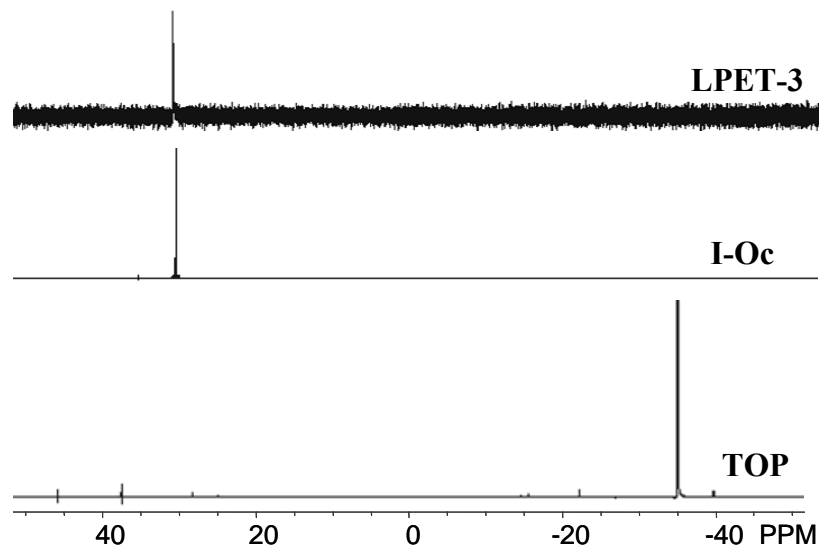


Figure 8-4. ^{31}P spectra of trioctylphosphine (TOP), phosphonium salt (I-Oc), and a corresponding polyester ionomer (L-PETI-2).

As expected, SEC analysis of L-PETI-1 and L-PETI-2 revealed a decrease in molar mass with increasing amounts of endcapping reagent. As summarized in Table 8-1, the lower thermal stabilities of the II-Oc and II-Ph endcapping reagents compared to I-Oc dictated that L-PETI-4 and L-PETI-5 were synthesized at relatively lower temperatures. Figure 8-5 shows the ^1H NMR spectra of II-Ph and the corresponding telechelic polyester ionomer. Both the aliphatic octyl and aromatic resonances of the endcapping reagent were preserved in the polyester ionomer. In addition, disappearance of the methyl proton resonances (Figure 8-5, peak a) on the ethyl ester group of II-Ph confirmed an efficient transesterification reaction and removal of ethanol. SEC characterization of L-PETI-4 and L-PETI-5 showed similar molar mass values relative to the ionomers that were derived from I-Oc (Table 8-1).

It is widely recognized that low levels of trifunctional agent (typically 0.1 – 1.0 mol %) are commonly used to synthesize lightly branched (long-chain branched) condensation polymers via the conventional $A_2 + B_2$ methodology.¹⁸⁵ It is also known that the addition of monofunctional comonomers with trifunctional agents eliminates the risk of gel formation. Branched telechelic polyester ionomers were synthesized in the presence of a trifunctional comonomer (TMT) and the phosphonium endcapping reagent (I-Oc). As expected, the polydispersities of B-PETI-1 and B-PETI-2 were higher than the linear analogues (Table 8-1). The weight average molar mass of a 2 mol % branched polyester ionomer with 3 mol % ionic chain ends (B-PETI-1) was dramatically higher than linear ionomers (L-PETI-1 and L-PETI-2) with equivalent ionic contents. On the other hand, branched B-PETI-2 with 5 mol % ionic chain ends showed similar molar mass values to linear ionomers with 3 mol % ionic chain ends. Thus, branching was effectively utilized to increase the ionic chain end concentration in telechelic polyester ionomers.

Transmission electron micrographs (TEM) of branched telechelic polyester ionomers (B-PETI-2) revealed a distinct morphological difference compared to polyesters that were synthesized in the absence of an ionic endcapping reagent (Figure 8-6). As reported previously, TEM and small angle x-ray scattering (SAXS) are widely used to characterize the morphology of ionomers.¹⁷⁹ Preliminary TEM analysis clearly

¹⁸⁵ McKee, M.; Unal, S.; Wilkes, G. L.; Long, T. E., *Prog. Polym. Sci.* **2005**, 30, 507.

indicated the formation of ionic aggregates in branched B-PETI-2 with 5 mol % ionic chain ends. SAXS analysis of telechelic polyester ionomers is currently underway and will be reported in a forthcoming manuscript.

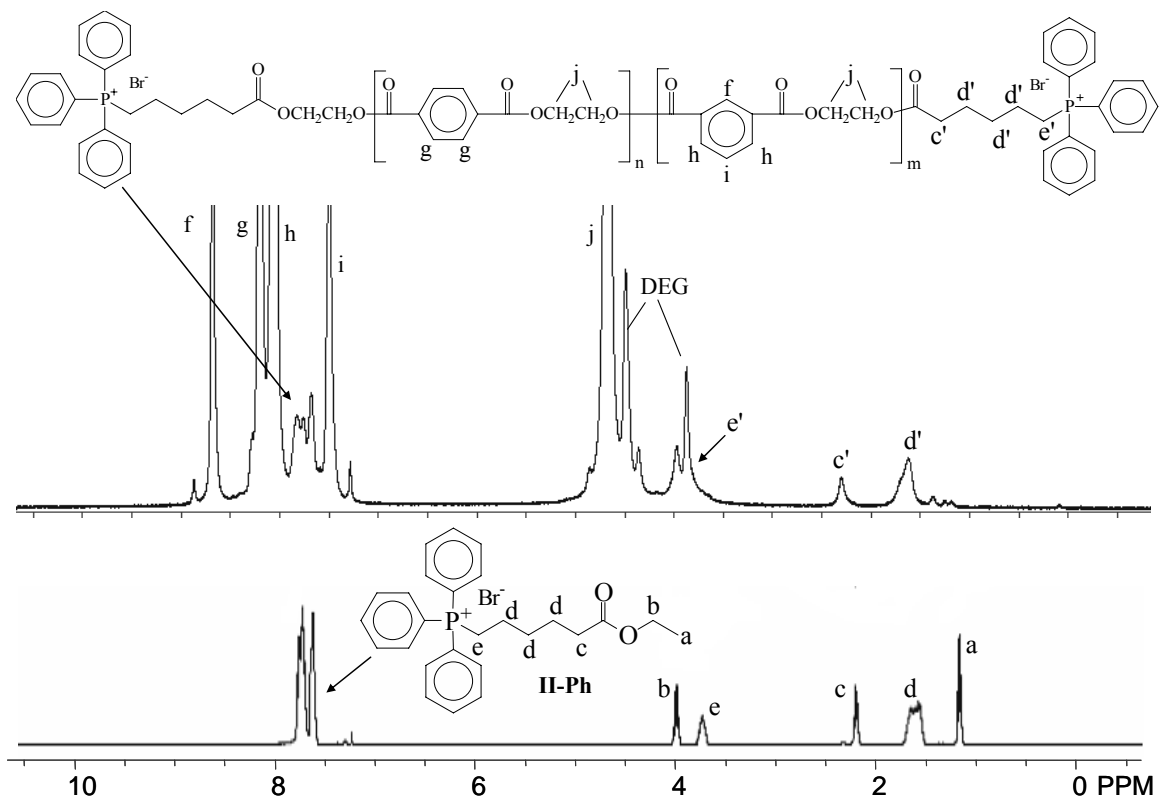


Figure 8-5. ^1H NMR spectra of II-Ph and a corresponding telechelic polyester ionomer (L-PETI-5).

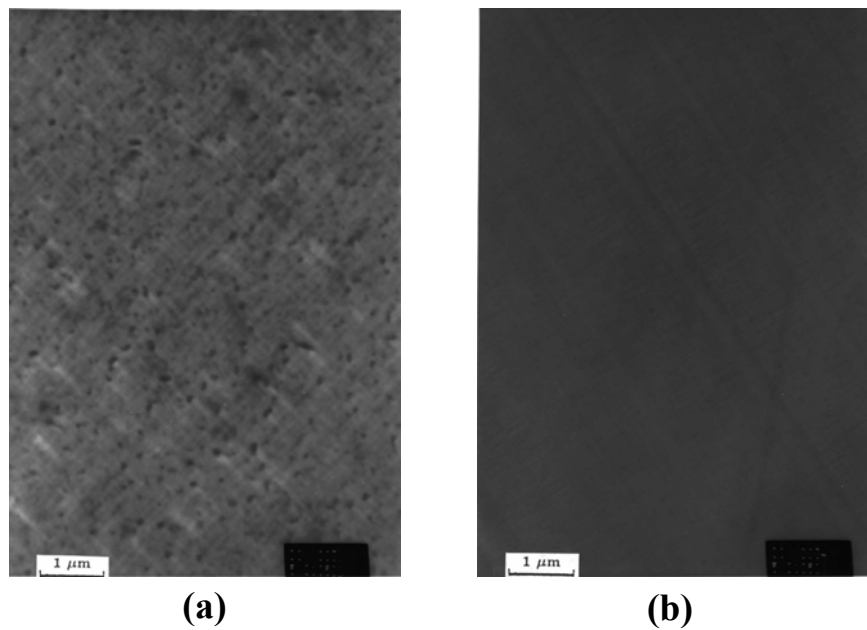


Figure 8-6. Transmission electron micrographs of (a) B-PETI-2, a branched telechelic polyester ionomer with 5 mol % ionic chain ends, and (b) a nonionic polyester control.

8.5 Conclusions

Thermally stable, novel phosphonium salt endcapping reagents bearing a phosphonium salt and a monofunctional site for transesterification were synthesized. Corresponding telechelic polyester ionomers with linear and branched topologies were prepared via the polycondensation of a hydroxyl terminated polyester oligomer and a phosphonium-based endcapping reagent. The introduction of low levels of a multifunctional comonomer as a branching agent allowed the synthesis of branched, telechelic polyester ionomers with moderate molar masses and ionic contents as high as 5 mol %. Preliminary TEM analysis of these polyester ionomers and comparison with nonionic polyester analogues indicated the formation of ionic aggregates in the polymer matrix. More detailed investigations of the solid state structures using SAXS and melt rheological studies will be reported in the future for these novel phosphonium based ionomers.

8.6 Acknowledgements

The authors acknowledge the generous support of Eastman Kodak Company, many insightful discussions with Dr. Cathy Fleischer, and SEC analyses by Dr. Thomas H. Mourey.

Chapter 9: Synthesis of a New Family of Phosphonium-Based Cationic Acrylic Polymers

Taken From:

Unal, S.; Palmer, C. M.; Long, T. E. "Synthesis of phosphonium-based acrylic ionomers" *Polym. Prep. (Am. Chem. Soc., Div. Polym. Chem.)* **2005**, *46*, 1064.

9.1 Abstract

Two new types of vinyl and methacrylate monomers that contain a phosphonium group were synthesized. Free radical polymerization of the vinyl monomer, trioctyl(vinyl)phosphonium bromide, resulted in relatively low molar mass cationic polymers due to poor stabilization of the propagating species. On the other hand, homopolymers of the new methacrylate monomer that bears a phosphonium salt as a pendant group formed self-standing, ductile films at room temperature. Moreover, copolymerization of this new monomer with 2-hydroxyethyl acrylate in a 50:50 molar ratio was also successful.

9.2 Introduction

The presence of ionic groups in organic polymers at various concentrations enables the control of the performance of polymeric materials. Various properties of polymers such as modulus, glass transition, viscosity, and melt strength are tailored by the incorporation of low concentrations (<15 mol%) of ionic groups.¹⁸⁶ On the other hand, polyelectrolytes, which contain higher contents of ionic groups (>15 mol %), comprise another important class of polymeric materials. Although numerous types of ionic polymers bearing anionic groups attached to the polymer backbone have been reported, only few types of cationic polymers are present in the literature. Among those, cationic polymers that are based on quaternary ammonium salts are the most common and widely used in gene therapy, nanotechnology, and surfactants.^{186,187}

Synthetic approaches reported in the literature to prepare cationic polymers that are based on phosphonium salts are very limited. Endo *et al.* reported the synthesis of polymeric phosphonium salts and their antibacterial activity more than 10 years ago.¹⁸⁸ Unfortunately, this class of polymers did not seem to attract a great deal of attention due to synthetic difficulties and relatively expensive chemistry. Herein, we report the synthesis and characterization of phosphonium based cationic polymers via conventional free radical polymerization. For this purpose, two types of vinyl and acrylate monomers that contain phosphonium groups were synthesized.

9.3 Experimental

9.3.1 Materials

Triethylphosphine (90%), 2-bromoethanol (98+%), 2-hydroxyethyl acrylate (2-HEA, 96%), 2-isocyanatoethylmethacrylate (98%), 2,2'-azobisisobutyronitrile (AIBN, 98%), N-N dimethylformamide (DMF, 99.8%), and dibutyltin dilaurate (95%, DBTDL) were purchased from Aldrich and used without further purification.

¹⁸⁶ Eisenberg, A.; S., K. J., *Introduction to Ionomers*. Wiley: New York, 1998.

¹⁸⁷ van de Wetering, P.; Cherng, J.-Y.; Talsma, H.; Hennick, W. E., *J. Cont. Rel.* **1997**, 49, 59. van de Wetering, P.; Cherng, J.-Y.; Talsma, H.; Crommelin, D. J. A.; Hennick, W. E., *J. Cont. Rel.* **1998**, 53, 145.

¹⁸⁸ Kanazawa, A.; Ikeda, T.; Endo, T., *J. Polym. Sci. Polym. Chem.* **1993**, 31, 335.

9.3.2 Characterization

Solution ^1H and ^{31}P NMR spectroscopic analyses were performed on a Varian Unity 400 spectrometer at ambient temperature. Size-exclusion chromatography (SEC) on Waters system equipped with Styragel HT columns and an RI detector in NMP containing 0.05 M LiBr, at 40 °C with a flow rate of 1 mL/min. Thermal analyses were conducted using a Perkin-Elmer Pyris 1 cryogenic DSC at a heating rate of 10 °C/min under a helium atmosphere, and all reported data were obtained from the second heating. ASI REACTIR 1000 was used for FTIR spectroscopy. MALDI-TOF/MS analyses were performed on a Kompact SEQ. The targets were prepared from a tetrahydrofuran (THF) solution with dithranol as the matrix and potassium trifluoroacetate as the cationization reagent.

9.3.3 Synthesis and Homopolymerization of Trioctyl(vinyl)phosphonium bromide

Trioctylphosphine (6.0 g, 16.2 mmol) and 2-bromoethanol (2.02 g, 16.2 mmol) were refluxed in bulk at 150 °C for 48 hours under nitrogen. The product mixture was poured into ethyl ether upon cooling and the mixture was stirred overnight. The product was filtered off and recrystallized from ethyl acetate. White crystals were collected and dried in vacuum oven for 24 h at 60 °C.

A 100-mL round bottom flask was charged with trioctyl(vinyl)phosphonium bromide (2.00 g, 4.2 mmol), DMF (3.00 g, 40 wt% solids), and AIBN (20 mg, 1 wt%). The flask was purged with nitrogen for 15 min, heated to 60 °C, and maintained for 24 hours.

9.3.4 Synthesis of Phosphonium-Based Cationic Methyl Methacrylate Monomer (PBrMMA)

9.3.4.1 Synthesis of (2-Hydroxyethyl)trioctylphosphonium bromide Precursor

A 100-mL double-neck round bottom flask was charged with trioctylphosphine (16.62 g, 44.8 mmol) and a magnetic stirrer. A condenser and an additional funnel charged with 2-bromoethanol (5.88 g, 47.0 mmol) were attached to the flask. 2-bromoethanol was added dropwise over 2 hours at 80 °C under nitrogen atmosphere. The temperature was raised to 120 °C and maintained 2 hours. Once cooled, the product was washed with hexane and ethyl ether subsequently to remove any unreacted reagents. A

colorless, clear ionic liquid was obtained upon drying in a vacuum oven at 60 °C overnight. (MALDI-TOF/MS: 415 *m/z*)

9.3.4.2 Synthesis of PBrMMA from (2-Hydroxyethyl)trioctylphosphonium bromide Precursor

A 100-mL round bottom flask was charged with (2-hydroxyethyl)trioctyl phosphonium bromide (3.02 g, 6.1 mmol), 2-isocyanatoethylmethacrylate (0.95 g, 6.1 mmol), and 50 ppm of DBTDL catalyst. The reaction was carried out at 70 °C for 5 hours and completion of the reaction was verified by FTIR spectroscopy.

9.3.5 Homopolymerization of PBrMMA

PBrMMA was polymerized via conventional free radical polymerization. A round bottom flask was charged with PBrMMA (1.89 g, 2.9 mmol), DMF (8.81 g), and AIBN (varied from 0.5 to 1.0 wt %) and purged with nitrogen for 15 min. The reaction was allowed to proceed at 60 °C for 24 h. The reaction mixture was diluted with 9.00 g of chloroform and the product was precipitated into hexane. Pale yellow, self-standing films were obtained upon drying on a Teflon mold in vacuum oven at 60 °C overnight.

9.3.6 Copolymerization of PBrMMA with 2-Hydroxyethyl acrylate (HEA)

PBrMMA (2.02 g, 3.1 mmol) was copolymerized with 2-HEA (3.6 g, 3.1 mmol) in DMF at 20 wt% solids. The reaction was carried out for 24 h under nitrogen using 1 wt% AIBN at 60 °C. The reaction mixture was diluted with chloroform and precipitated into hexane. The product was spread out on a Teflon plate and dried in vacuum oven at 60 °C for 24 h. A pale yellow, self-standing film of the product was obtained.

9.4 Results and Discussion

9.4.1 Synthesis and Homopolymerization of Trioctyl(vinyl)phosphonium bromide

The synthesis of trioctyl(vinyl)phosphonium bromide involved the elimination reaction between trioctylphosphine and 2-bromoethanol at 150 °C as depicted in Scheme 9-1. ¹H NMR spectroscopic analysis indicated the presence of olefinic peaks at 6.3 – 6.8 ppm as a result of the elimination reaction that is favored at high temperatures (Figure

9-1). Formation of water during the reaction was an evidence of the elimination reaction. ^{31}P NMR analysis also indicated the formation of a phosphonium salt (not shown).

Upon the successful synthesis, trioctyl(vinyl)phosphonium bromide was polymerized via conventional free radical polymerization in the presence of AIBN as the initiator (Scheme 9-2). SEC analysis of the final homopolymers indicated the formation of low molar mass cationic polymers with number average molar masses of 3000 to 4000 g/mol. Such low molar masses were attributed to the poor stabilization of the propagating species during the free radical reaction. Although the cationic homopolymers were low molar mass products, it is believed that trioctyl(vinyl)phosphonium bromide could be utilized as a cationic comonomer in various free radical polymerizations as well as crosslinking agents for unsaturated polymeric systems in order to introduce low concentrations of ionic moieties.

9.4.2 Synthesis of PBrMMA, Corresponding Cationic Homopolymers and Copolymers

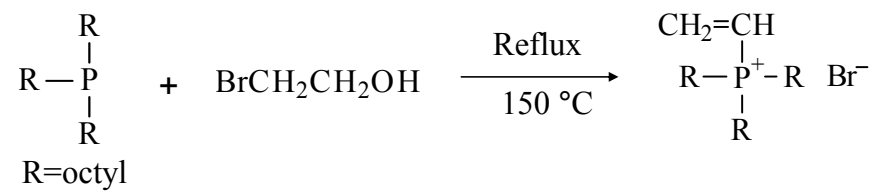
Because of low molar masses obtained from the homopolymerization of the vinyl phosphonium monomer, we have focused on the synthesis of methacrylate monomers bearing phosphonium groups. First, a phosphonium salt precursor, (2-hydroxyethyl)trioctyl phosphonium bromide was synthesized as shown in Scheme 3. The synthesis involved the slow addition of 2-bromoethanol to trioctylphosphine at 80 °C. Both the slow addition and lower temperature favored an $\text{S}_{\text{N}}2$ reaction mechanism yielding (2-hydroxyethyl)trioctyl phosphonium bromide precursor (Scheme 9-3). ^1H NMR spectroscopic analysis confirmed the structure of (2-hydroxyethyl)trioctyl phosphonium bromide indicating the presence of a hydroxyl peak as well as the absence of any olefinic peaks that would have formed in an elimination side reaction (Figure 9-2). MALDI-TOF/MS analysis also confirmed formation of the expected product: 415.0 m/z.

The second step was the synthesis of PBrMMA as depicted in Scheme 9-4. Equimolar amounts of (2-hydroxyethyl)trioctyl phosphonium bromide and 2-isocyanatoethyl methacrylate were reacted at 70 °C under the catalytic activity of DBTDL. As shown in Figure 9-3, FTIR spectroscopy verified the completion of the reaction in Scheme 9-4. Hydroxyl ($\sim 3400\text{ cm}^{-1}$) and isocyanate ($\sim 2270\text{ cm}^{-1}$) peaks in the initial reaction mixture disappeared after 5 h. Two new peaks due to formation of

urethane ($-NH$) were observed both at ~ 3300 and 1550 cm^{-1} . In addition to ester carbonyl ($C=O$) in the methacrylate unit, formation of the urethane carbonyl ($C=O$) resulted in increased intensity of the carbonyl peak at $\sim 1750\text{ cm}^{-1}$.

PBrMMA monomer was polymerized as shown in Scheme 9-5 via conventional free radical polymerization. When the polymerization was carried out in 35 wt% solids using 1.0 wt% initiator, the final product had a number average molar mass of 136,000 g/mol. Initiation of the polymerization using 0.5 wt% AIBN in DMF at 20 wt% solids resulted in a cationic homopolymer with number average molar mass of 27,000 g/mol. When PBrMMA was copolymerized with 2-HEA in a ratio molar of 25:75 (PBrMMA:2-HEA) an insoluble crosslinked product was obtained. In the case of the copolymerization of a 50:50 molar ratio of PBrMMA to 2-HEA in DMF at 20 wt% solids using 1.0 wt% AIBN, a soluble copolymer was obtained with a number average molar mass of 59,000 g/mol. Although SEC analysis indicated the formation of high molar mass products, molar mass distributions were in the range of 3.0 to 6.0 for these polymers. These high molar mass distributions were attributed to the polyelectrolyte backbone and its behavior in solution.

Both homopolymers of PBrMMA and the copolymer of PBrMMA and 2-HEA formed self-standing, ductile films at room temperature. DSC analysis indicated a glass transition temperature (T_g) of $40\text{ }^\circ\text{C}$ for homopolymers and $0\text{ }^\circ\text{C}$ for the copolymer with 2-HEA. It should be noted that in addition to the ionic groups that are believed to influence the thermal and mechanical properties, pendant urethane groups also influence the physical properties of these materials due to hydrogen bonding.



Scheme 9-1. Synthesis of trioctyl(vinyl)phosphonium bromide.

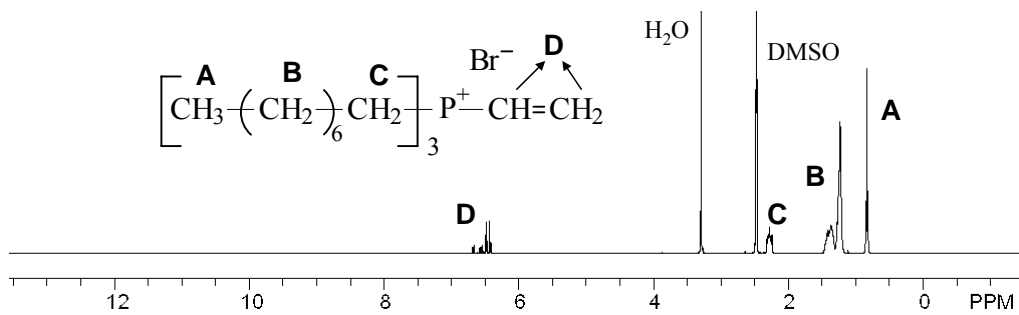
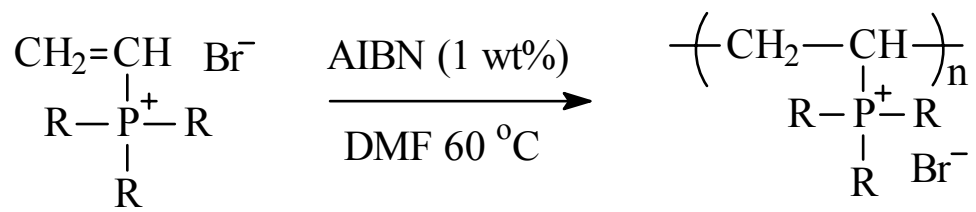
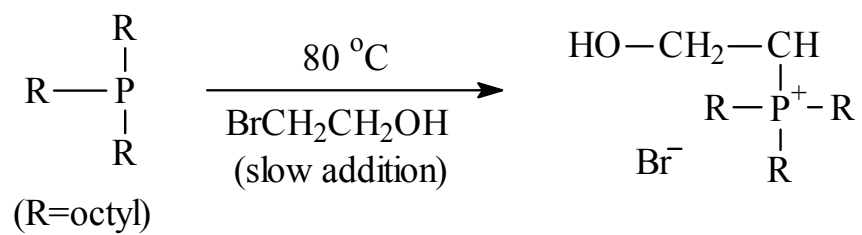


Figure 9-1. ^1H NMR characterization of trioctyl(vinyl)phosphonium bromide.



Scheme 9-2. Homopolymerization of trioctyl(vinyl)phosphonium bromide.



Scheme 9-3. Synthesis of (2-hydroxyethyl)trioctyl phosphonium bromide precursor.

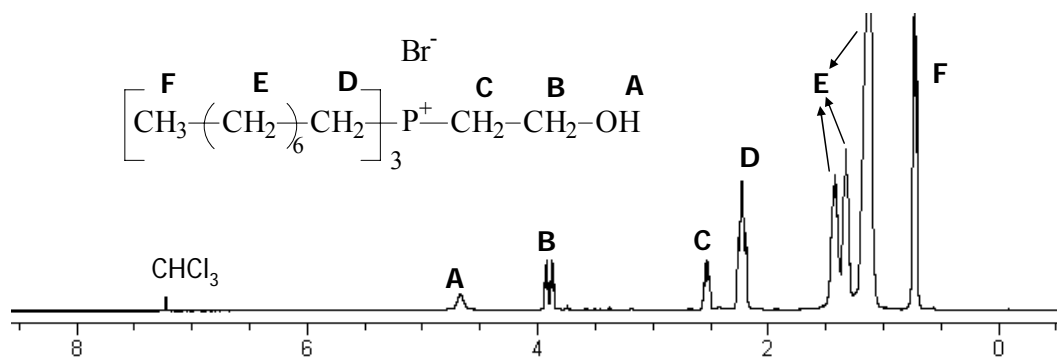
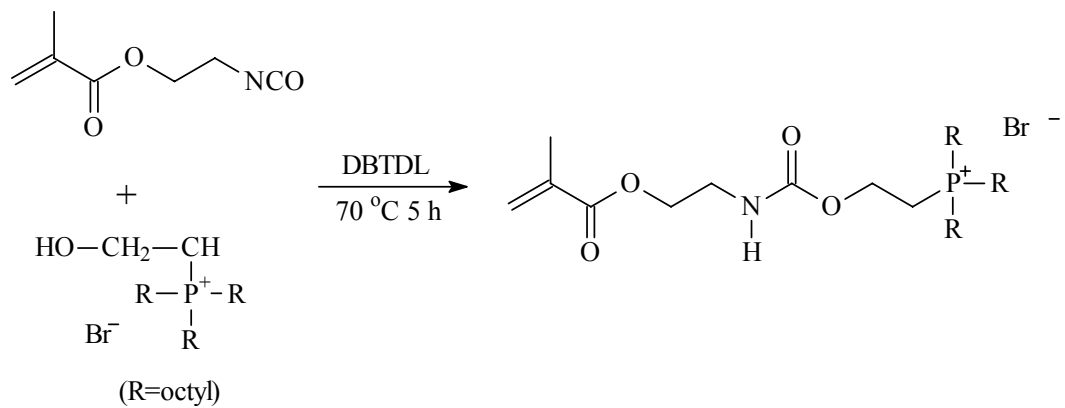


Figure 9-2. ^1H NMR spectrum of (2-hydroxyethyl)trioctyl phosphonium bromide precursor.



Scheme 9-4. Synthesis of phosphonium salt containing methyl methacrylate monomer (PBrMMA).

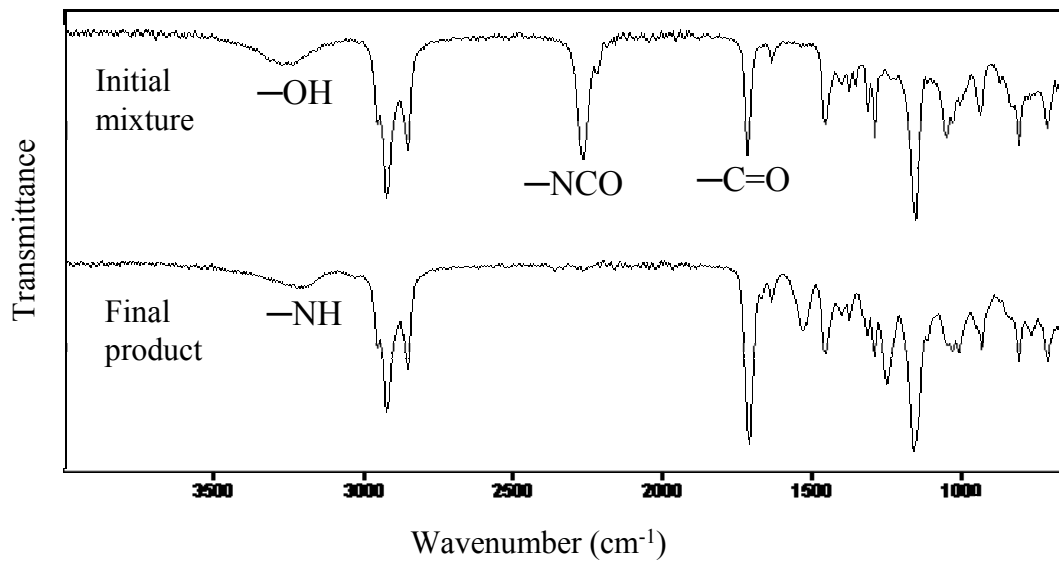
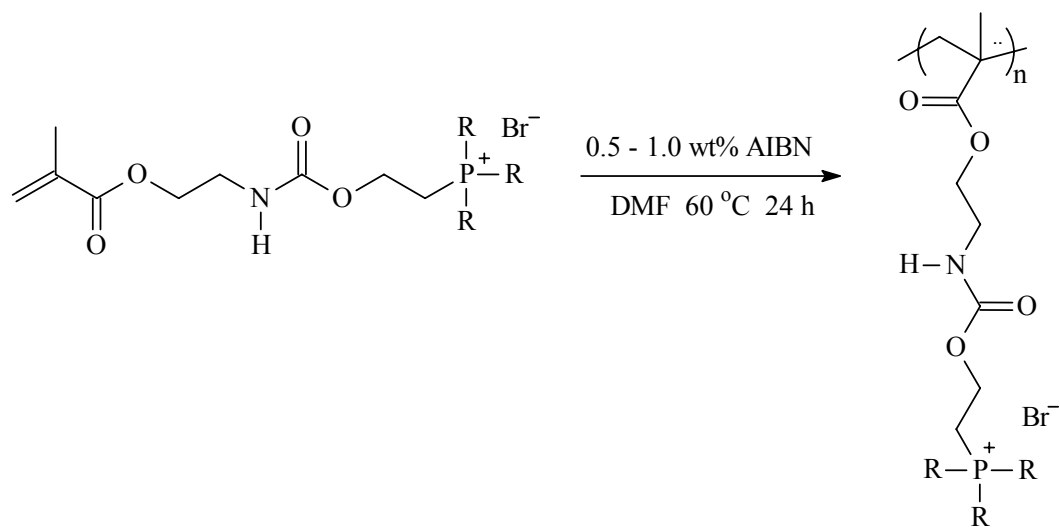


Figure 9-3. FTIR spectrum of PBrMMA.



Scheme 9-5. Homopolymerization of PBrMMA.

9.5 Conclusions

Two new types of vinyl and methacrylate monomers that contain a phosphonium group were synthesized. Free radical polymerization of the vinyl monomer, trioctyl(vinyl)phosphonium bromide, resulted in relatively low molar mass cationic polymers due to poor stabilization of the propagating species. On the other hand, homopolymers of the new methacrylate monomer that contained a phosphonium salt as a pendant group formed self-standing, ductile films at room temperature. Moreover, copolymerization of this new monomer with 2-hydroxyethyl acrylate in a 50:50 molar ratio was also successful.

9.6 Acknowledgements

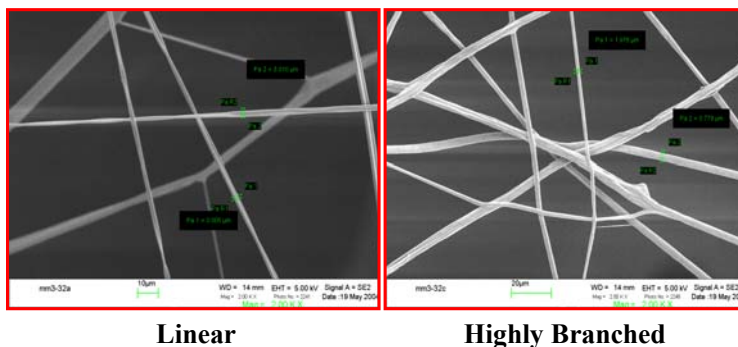
This material is based upon work supported by, or in part by, the U.S. Army Research Laboratory and the U.S. Army Research Office under the grant number DAAD19-02-1-0275 Macromolecular Architecture for Performance (MAP) MURI.

Chapter 10: Overall Conclusions

Unique macromolecular architectures that possess degrees of branching between long-chain branched and hyperbranched polymers were achieved via the placement of either one or both of the monomer pairs in a conventional $A_2 + B_3$ polymerization with oligomeric precursors. The molar mass of the oligomeric precursor permitted the control of the distance between branch points and dictated the final polymer properties. Highly branched step-growth polymers, such as segmented poly(urethane urea)s, poly(ester urethane)s, poly(ether ester)s, and poly(arylene ether)s retained the characteristics of a hyperbranched polymer, such as low solution and melt viscosity, low hydrodynamic volume, good solubility, and a multitude of functional end groups. In addition, these polymers showed versatile properties such as superior mechanical performance to hyperbranched polymers. Highly branched, segmented poly(urethane urea) elastomers exhibited microphase-separated morphologies as denoted by dynamic mechanical analysis. The similarity in soft segment glass transition behavior and strain hardening character of the branched systems with that of the linear analogues suggested these materials with improved processibilities have considerable promise for structural applications. Structural development was investigated by monitoring the molecular weight and polydispersity as a function of amount of A_2 added into B_3 . Experimental studies at various solution concentrations allowed the optimization of the reaction conditions to avoid gelation and achieve a high degree of branching. It was found that the slow addition of the isocyanate terminated polyether oligomer (A_2) to a triamine (B_3) was the most plausible strategy to avoid undesirable gelation. Recently, we reported electrospun highly branched poly(urethane urea)s that formed elastomeric fibrous mats and had superior elongation, which did not fail at 1300% elongation (Figure 10-1).¹⁸⁹ Because of lower solution viscosity of highly branched polymers than linear analogues, less solvent was required to electrospin highly branched poly(urethane urea)s relative to a linear analogue; nevertheless, both linear and highly branched fibrous mats had similar mechanical performances. Thus, these novel, highly branched, segmented poly(urethane urea) elastomers offered the improved processibility peculiar to hyperbranched polymers

¹⁸⁹ McKee, M. G.; Park, T.; Unal, S.; Yilgor, I.; Long, T. E., *Polymer* **2005**, 46, 2011.

and the advantageous mechanical performance multiphase morphology with linear soft segments between hard segment branch points.



Non-woven highly branched PUU mats exhibit elastomeric behavior.

Figure 10-1. Electrospun highly branched poly(urethane urea) fibers.

The oligomeric $A_2 + B_3$ approach was extended to the synthesis of potentially biodegradable, highly branched, segmented poly(ester urethane)s. DSC and DMA results revealed that a high degree of branching through the soft block resulted in a completely amorphous polycaprolactone segment. A linear analogue with equivalent soft segment molar mass retained the crystallinity of polycaprolactone segment to some extent. Stress-strain analysis revealed that the highly branched materials had slightly poorer mechanical performance than a linear analogue; however, showed lower hysteresis. Finally, accessibility of functional end groups on low viscosity, highly branched materials offered promising applications in coatings technology.

Oligomeric $A_2 + B_3$ methodology was further utilized to tailor the degree of branching of poly(ether ester)s that were developed based on slow addition of dilute solution of poly(ethylene glycol) (PEG) (A_2) to a dilute solution of 1,3,5-benzenetricarbonyl trichloride (B_3) at room temperature in the presence of triethylamine.

PEG diols of various molar masses permitted the control of the degree of branching and an investigation of the effect of the distance between branch points. ^1H NMR spectroscopy indicated a classical degree of branching (DB) of 69% for a highly branched poly(ether ester) derived from 200 g/mol PEG diol. A revised definition of the degree of branching was proposed to accurately describe the branched poly(ether ester)s and the degree of branching decreased as the molar mass of the PEG diols was increased. In-situ functionalization of the terminal acyl halide units with 2-hydroxyethyl acrylate provided novel photo-cross-linkable precursors.

Oligomeric $\text{A}_2 + \text{B}_3$ melt polymerization effectively overcame the common issues in $\text{A}_2 + \text{B}_3$ polymerization in solution. Cyclizations were limited in the melt phase, thus theoretical and experimental gel points agreed well. Highly branched products were obtained by stopping the reaction immediately prior to the gel point. Melt polymerization not only limited the cyclization, but also overcame the need for large amounts of polymerization solvent for $\text{A}_2 + \text{B}_3$ systems. Moreover, monofunctional endcapping reagents were introduced to avoid gelation in the melt phase, and high molar mass final products were obtained with nearly quantitative monomer conversion in the absence of gelation. The presence of a monofunctional comonomer did not affect the molar mass increase or the formation of branched structures due to desirable ester interchange reactions.

Branched poly(arylene ether)s were prepared via a similar oligomeric $\text{A}_2 + \text{B}_3$ polymerization of phenol endcapped telechelic poly(arylene ether sulfone) oligomers (A_2) and tris(4-fluorophenyl) phosphine oxide (B_3) in solution. The molar mass of the A_2 oligomer significantly influenced the onset of gelation and the degree of branching (DB). The branched polymers exhibited lower Mark-Houwink exponents and intrinsic viscosities relative to linear analogues, and differences between the branched polymers and linear analogues were less significant as the molar mass of the A_2 oligomers was increased due to a decrease in the overall degree of branching.

Furthermore, the functionality of branched macromolecules was tailored via the incorporation of ionic groups at the polymer chain ends. A new family of telechelic polyester ionomers was synthesized based on phosphonium bromide salts. Novel cationic endcapping reagents, which possessed phosphonium bromide sites and benzoic

acid or ethyl ester functionalities, were synthesized. Improved thermal stabilities of the phosphonium salts over ammonium analogues allowed the introduction of these endcapping reagents to the melt polyesterification at temperatures ranging from 220 °C to 275 °C for the synthesis of linear or branched polyester ionomers. Branching enabled the enhancement of ionic chain end concentrations and preliminary transmission electron microscopic analysis indicated the presence of ionic aggregates in a branched telechelic polyester ionomer with 5 mol % ionic chain ends. Finally, in order to investigate the behavior of phosphonium based cationic macromolecules, two new types of vinyl and methacrylate monomers that contained a phosphonium group were synthesized. Free radical polymerization of the vinyl monomer, trioctyl(vinyl)phosphonium bromide, resulted in relatively low molar mass cationic polymers due to poor stabilization of the propagating species. On the other hand, homopolymers of the new methacrylate monomer that bears a phosphonium salt as a pendant group formed self-standing, ductile films at room temperature. Moreover, copolymerization of this new monomer with 2-hydroxyethyl acrylate in a 50:50 molar ratio was also successful.

Chapter 11: Suggested Future Work

11.1 Polycaprolactone based, Highly Branched Poly(ester urethane)s

Polycaprolactone based polymeric materials are great candidates for biocompatible and biodegradable systems due to the susceptibility of polycaprolactone to hydrolysis or enzymatic degradation. Therefore, the influence of topology on the biodegradation behavior of polycaprolactone based poly(ester urethane) elastomers should be investigated. Biodegradation studies could be performed in phosphate buffer solution (PBS) at a neutral or acidic pH. Considering the fact that biodegradation more readily occurs in the amorphous phase rather than the crystalline phase, branched topology is expected to have a significant influence on the biodegradation behavior of polycaprolactone based poly(ester urethane) elastomers. In addition, the influence of the nature of end groups on the biodegradation of branched poly(ester urethane)s should be investigated. The chain end polarity could be easily tailored using monofunctional endcapping reagents for functionalization. Mechanical analysis and biodegradation studies of hydroxyl terminated versus alkyl chain terminated highly branched poly(ester urethane)s are expected to yield interesting results. Finally, labile comonomers may be incorporated to tune the biodegradation rate of poly(ester urethane)s. For example, using methyl 2,6-diisocyanatohexanoate (Figure xx), a novel, lysine-diisocyanate based comonomer, highly branched and poly(ester urethane)s could be synthesized and their biodegradation behavior as well as thermal and mechanical properties should be investigated.

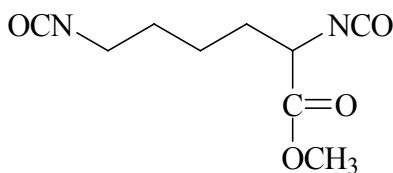


Figure 11-1. Chemical structure of lysine based diisocyanate as a potential comonomer in polyurethane synthesis.

11.2 Highly Branched Poly(ether ester)s

Initial adhesion studies with highly branched poly(ether ester)s, which were based on PEG-200 and had a glass transition temperature of $-20\text{ }^{\circ}\text{C}$, revealed that these materials have promising adhesive strength. Further studies should be performed on evaluating the adhesion properties of highly branched poly(ether ester)s. Blends of linear and highly branched poly(ether ester)s that are prepared to tune the adhesion/cohesion strength may be examined as potential pressure sensitive adhesives. Another important area that highly branched poly(ether ester)s have promising advantages is templates for metal salts in conductive materials. Poly(ethylene glycol) dissolves alkali metal salts and exhibits acceptable ionic conductivity. Disrupted crystallinity of poly(ethylene glycol) in highly branched poly(ether ester)s is expected to enhance the ion mobility in these materials and the multitude of the functional end groups may allow the preparation of photo-cross-linkable ion conducting materials.

Melt polymerization of A_2 and B_3 monomers has been demonstrated to be a cost-effective methodology for the synthesis of highly branched polyesters. The substitution of one of the monomer pairs with oligomeric precursors yields highly branched polymers with a well-defined distance between the branch points. Highly branched poly(ether ester)s with a controlled distance between the branch points are expected to exhibit interesting melt rheological behavior. Thus, two series of highly branched poly(ether ester)s, one with varying distance between branch points, the other with varying degree of branching should be synthesized and their melt rheology should be examined. Melt $A_2 + B_3$ polymerization can also be extended to the synthesis of other types of polyesters, such as polyether based polyester elastomers. The ratio of A_2 oligomer/ A_2 monomer will control the hard segment content, and yield polyester elastomers with improved processibility due to the branched structure.

11.3 Phosphonium-based Telechelic Polyester Ionomers

Further characterization of this new family of telechelic polyester ionomers should be performed. Critical polymer characterization strategies include melt and solution rheological analysis for direct comparisons of non-ionic control analogues with the

proposed telechelic polyester ionomers. Furthermore, initial studies have revealed that these telechelic polyester ionomers could be utilized as a compatibilizing agent for inorganic additives and organic polymers.

Chapter 12: Vita of Serkan Unal

Serkan Unal was born on October 6, 1978, in Tokat, Turkey. He graduated from Tokat Anatolian High School in June 1996 and began his undergraduate studies at Koc University, Istanbul, Turkey. He graduated from Koc University with a B.S. degree in Chemistry in June 2001. In August 2001, he began his graduate studies in the Chemistry Department at Virginia Polytechnic Institute and State University in Blacksburg, Virginia. Upon completion of his Ph.D. degree in December 2005, he will be employed with Bayer MaterialScience as an Associate Research Scientist in the CAS Innovations Department in Pittsburgh, Pennsylvania.