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POLYISOBUTYLENE-BASED MIKTO-ARM STAR POLYMERS SYNTHESIZED VIA QUASILIVING CATIONIC POLYMERIZATION AND ATOM TRANSFER RADICAL POLYMERIZATION

Lesli Krystin Breland
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by

Lesli Krystin Breland

A Dissertation Submitted to the Graduate Studies Office of The University of Southern Mississippi in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

August 2007
The University of Southern Mississippi

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This research pertains to the synthesis of mikto-arm star polymers created via quasiliving cationic polymerization (QCP) and atom transfer radical polymerization (ATRP). The first part of this work focuses on the synthesis of cationic initiators that contain latent functionalities for initiation of ATRP polymerizations.

In the second part of this work, well-defined copolymers of polyisobutylene (PIB) and polystyrene (PS) were created by cationic polymerization. After transformation of the initiating site, poly(tert-butyl acrylate) (PtBA) was synthesized via ATRP. This block was later hydrolyzed to form poly(acrylic acid) (PAA), which serves as a hydrophilic segment of the material. The polymers had narrow PDIs and target polymer compositions. However, molecular weights were higher than expected when low molecular weight polymers were targeted. This is attributed to a complexation between the Lewis acid, titanium tetrachloride (TiCl₄), and the carbonyl group in the initiators.
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CHAPTER I
ADVANCES IN LIVING CATIONIC AND ATOM TRANSFER RADICAL
POLYMERIZATIONS

The term living polymerization may be used to describe a variety of controlled chain polymerizations. An “ideal” living system is one in which the growing chain end propagates in the absence of chain transfer and termination. However, a truly living system is never fully achieved; chain transfer and termination do occur, but these chain-breaking events are negligible. The livingness of a system is best expressed by comparing the rate constant for propagation ($k_p$) to those for termination ($k_t$) and chain transfer ($k_{tr}$). Higher ratios (larger $k_p$) are characteristic of more living processes, with the ratio of an ideal polymerization being infinity.

Szwarc et al. reported the first living systems in 1956, when he polymerized styrene and isoprene anionically.\textsuperscript{1,2} The polymerizations illustrated 100% monomer conversion without chain termination, as indicated by the persistence of color in the reaction. Also, after the initial monomer was consumed, additional charges of monomer were added and the reaction proceeded to full conversion. This method led to the production of block copolymers of styrene and isoprene.

Living Carbocationic Polymerization

Living anionic polymerization was the first technique that was able to produce polymers with target $M_n$s and narrow PDIs when ionic species with differing reactivities were employed. This control over the polymerization was accomplished in the absence of detectable chain transfer or termination. It was thought that the concept of living
polymerization could not be extended to cationic processes, even though there were a variety of potentially applicable monomers, because in no case could all criteria for living polymerizations be met. Chain transfer in carbocationic polymerizations is highly likely because the hydrogen atoms in a position $\beta$ to the carbenium ion are very susceptible to abstraction by basic components of the polymerization system (Figure I.1). Thus, the lifetime of the cation is too short to create well-defined polymers and block copolymers. In order to create high molecular weight materials, this lifetime needs to be extended by eliminating chain transfer. Szwarc introduced the concept of an equilibrium by examining the shelf life of cations. He noted that several species participate in ionic reactions, such as free ions and ion pairs, and they usually co-exist in an equilibrium with each other (Figure I.2). The equilibrium constant is small, indicating that most of the chains are in the dormant state at any given time and cannot take part in termination or chain transfer reactions. However, the chains can be re-initiated to yield polymers of high molecular weight. When none of the species induce termination or chain transfer, the system is considered to be living.

The concept of using “dormant” and “active” species was first reported with the polymerization of tetrahydrofuran, where only the “active” species participated in propagation. A system containing oxonium ions that were in equilibrium with triflate ester initiators was reported to fine-tune the reaction rate and allow for macromolecular engineering. Also about this time, Johnson and Young found that addition of $I_2$ to vinyl alkyl ethers creates a diiodide species. A polymerization occurred where the molecular weight increased with monomer addition, and the polymers always contained covalently bound iodine. However, in these systems, control was less than that of anionic systems,
and the polymers exhibited broad PDIs, which indicates the presence of chain transfer. Thus, these polymerizations only exhibit “living-like” behavior. It is now generally accepted that most “living” cationic systems are indeed “quasiliving,” which is to say that chain ends can propagate indefinitely by causing chain transfer and termination events to be reversible. Through proper selection of counterions, salts, and electron-donating species, propagation by free ions is greatly reduced, creating more dormant chains and yielding much more controlled polymerizations.

The first example of a quasiliving cationic system to yield well-defined polymers was reported in 1984 by Higashimura and coworkers. The polymerization of isobutyl vinyl ether (IBVE) in n-hexane initiated with a HI/I₂ mixture had a molecular weight that increased directly with monomer conversion, and the PDI of the resulting material was <1.1. The livingness of the system was attributed to fast initiation that could not be achieved with I₂ alone, and the absence of chain transfer. Additionally, the polarity of the reaction medium affected livingness. When the solvent was changed to CH₂Cl₂, increased chain transfer was observed, indicating the presence of a higher concentration of active species.

Since the development of the HI/I₂ initiating system, other dual-component systems have been developed. The reaction components are based upon nucleophilic counterions using protic acids/Lewis acid systems, such as HI/ZnI₂. The proper selection of conditions and materials yields reactions that produce well-defined polymers. Lewis acids stronger than ZnI₂, such as TiCl₄ or SnCl₄, may also be used in the initiator systems. However, polymerizations of IBVE with these components were very fast and produced polymers with broad PDIs and uncontrolled molecular weights. The
uncontrolled nature was due to high solvent polarity and high Lewis acidity of the Lewis acid. Higashimura showed that these reactions could be transformed into quasiliving systems by the addition of an appropriate salt, such as tetraalkyl ammonium ($n$Bu$_4$N$^+$Y$^-$) or phosphonium ($n$Bu$_4$P$^+$Y$^-$) salts with nucleophilic anions ($Y^-$ = Cl, Br, I, CH$_3$CO$_2$). The authors attributed the transformation to the suppression of the ionic dissociation of the carbocation. The addition of salts can enhance the polymerization of less reactive monomers, such as styrene and isobutylene (IB), in the same manner.

The addition of certain bases, termed “electron donors (EDs),” to polymerizations containing strong Lewis acids also yielded quasiliving polymerizations. It was hypothesized that the EDs donated electrons to the carbocation, thus stabilizing the active center. Higashimura and coworkers reported that the addition of ethyl benzoate or ethyl acetate to previously uncontrolled polymerization of IBVE yielded well-defined polymers. Additional EDs such as tetrahydrofuran, dioxane, pyridine, and pyridine derivatives also improve the livingness of cationic polymerizations, effectively by stabilizing the carbocation, thus eliminating side reactions. Less reactive monomers, such as IB, require stronger bases to impart livingness. Examples of these are amides, esters, amines, sulfoxides, and pyridines, and because they are stronger, they are used in much smaller concentrations than the EDs used for IBVE polymerizations.

More recently, the “carbocation stabilization” theory has been questioned. Faust and coworkers showed that, in the polymerization of IB with cumyl-type initiators using TiCl$_4$ as Lewis acid, the ED 2,6-di-tert-butylpyridine (DTBP) did not complex with the chain end and only scavenged protic impurities. This was concluded because increasing...
the concentration of ED in the system did not change the polymerization rate, and ideally, the rate would slow if the ED complexed with the cation.\textsuperscript{22} The authors hypothesized that complexation did not occur due to steric hinderance from the bulky $t$-butyl groups and the pyridine only scavenged protic impurities that could cause unwanted initiation.

Storey and coworkers suggested that EDs not only act as protic scavengers, but they also contribute to the suppression of free-ion formation, which is critical for a quasiliving system.\textsuperscript{23} The polymerization of IB in the absence of additives yielded a polymer with bimodal distribution, indicating propagation by both paired and unpaired ions. Upon addition of EDs, polymerizations were more controlled and produced monomodal molecular weight distributions. Thus, it was stated that EDs served two purposes. The minor role was to scavenge protic impurities to prevent protic initiation, and the major role was suppression of free ions via the counteranion Ti\textsubscript{2}Cl\textsubscript{6}\textsuperscript{-}, which is formed from the onium salt product of proton scavenging.

While progress has been made toward cationic "living" systems, most reactions are considered to be quasiliving in nature. This is because there is indeed termination present in the reactions, but this termination is completely reversible. This allows the addition of more monomer to the system and yields polymerizations that have properties similar to truly living systems (i.e.- narrow molecular weight distributions and target molecular weights). Thus, the reactions appear to be "living".

Atom Transfer Radical Polymerization

The majority of commercially available polymers are produced by free-radical polymerization processes due to the less stringent reaction conditions and the wide variety of monomers that can be polymerized through the radical mechanism. However,
these polymers suffer from lack of control during the polymerization process, yielding materials with broad PDIs and molecular weights that do not meet targets. Radical polymerizations, unlike ionic polymerizations, have diffusion-controlled bimolecular termination reactions, which limit the polymer molecular weight and are difficult to prevent. In addition, consumption of the initiating species is slow and often incomplete during the course of the polymerization. These difficulties have been overcome through the advent of "living"/controlled free-radical (LCFRP) polymerization techniques. LCFRPs are similar to quasiliving carbocationic polymerizations in that an exchange between dormant species and active species contribute to the "livingness" of the polymerizations. However, the propagating species is a radical instead of a cation or anion. The general reaction scheme is illustrated in Figure 1.3.

One of the more robust controlled free radical polymerization techniques is atom transfer radical polymerization (ATRP). It is aptly named because the most important step of the reaction is the atom transfer between a dormant chain and a transition metal complex. This process finds its origins in a reaction called the Kharasch addition, and a similar reaction known as the atom transfer reversible addition reaction (ATRA). The primary difference between ATRA and ATRP is that in the polymerization process of ATRP, more than one monomer unit may add to the intermediate radical in an activation period versus the single addition in ATRA. The general scheme for ATRA/ATRP is illustrated in Figure 1.4. A ligated transition metal complex \((M^{n+}/L)\) undergoes a one-electron oxidation \((M^{n+1}/L)\) and abstracts a halogen atom from the chain end \((1)\) in the process. This abstraction leaves an intermediate radical \((2)\), which is responsible for propagation. In the presence of excess monomer \((3)\), we obtain \((4)\), which may then
be deactivated by reaction with (7) to yield the reversibly terminated oligomer (5). With proper selection of transition metal, ligand, initiator, monomer, and polymerization conditions, the resulting polymers in ATRP have molecular weights that increase linearly with conversion and narrow PDIs.

ATRP was developed by two different groups in 1995. Matyjaszewski and coworkers reported the polymerization of styrene and various acrylates by LCFRP using a transition metal species.24 The polymerizations proceeded via free radical intermediates with copper halide/2,2'-bipyridine catalysts. The resulting materials had target molecular weights and low PDIs (<1.5).

Simultaneously, Higashimura and coworkers reported a similar “living” free radical process.25 In this report, MMA was polymerized from CCl₄ using a combination of the catalyst complex RuCl₂ and triphenylphosphine (RuCl₂(PPh₃)₃) and a Lewis acid, methylaluminum bis(2,6-di-tert-butylphenoxide) (MeAl(ODBP)₂). The “living” character of the polymerization was demonstrated by a linear semilogarithmic plot of conversion versus time and a linear increase in molecular weight with conversion. The resulting polymers also had low PDIs (~ 1.3).

Since the successes of these experiments, a great deal of research has focused on the individual components of the ATRP process. The ligand, initiator, monomer, metal, and other additives and conditions have been studied in detail. The following will examine some of the highlights of this work.

Possibly the most important component of the ATRP system is the transition metal catalyst. Not only does it determine the position of the atom transfer equilibrium, but it is also responsible for the exchange between the dormant and active chain ends. As
with ionic polymerizations, the dormant species should be favored for controlled polymerizations. If a transition metal catalyst is to be effective, it must meet several requirements. First, the metal center must have at least two oxidation states separated by one electron, and the center must have a good affinity for halogens. Also, the coordination sphere around the metal should be able to accommodate a halogen when needed. The ligand should also complex strongly to the metal in order to effectively solubilize the metal. Finally, the system should be fine-tuned to favor the deactivation of the growing chain. Metals in groups 6-11 of the periodic table possess the required properties for ATRP. Though a variety of the metals have been used as catalysts, the more popular choices are Ru and Cu-based systems, particularly Cu(I) chloride and Cu(I) bromide. Ru-bases complexes are primarily used for MMA polymerizations, where Cu is much more versatile.

The role of the ligand in ATRP is to solubilize the metal catalyst and adjust the redox potential of the metal center for appropriate reactivity. The primary criterion for ligand selection is that it coordinates strongly with the metal so that solubility is highest. The two primary types of ligands are comprised of nitrogen or phosphorus. Nitrogen-based ligands work particularly well in copper-mediated ATRP, though they have been used in iron systems as well. For the Cu-based systems, the coordination chemistry of the metal complex affects the catalyst activity, and multidentate ligands have been developed to promote controlled polymerizations. A few of these are illustrated in Figure 1.5. It is important to note that steric hindrance of the nitrogen atoms or strong electron-withdrawing groups reduce the catalyst activity and efficiency.
Multidentate amines, such as tetramethylethylenediamine (TMEDA), N,N,N’ ,N’ ,N”-pentamethyldiethylenetriamine (PMDETA), and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), provide attractive alternatives to the first-used bypyridine-based ligands for several reasons, the most important being lower redox potentials between the copper and the simple amines. This yields higher rates of activation of the dormant halides, and thus, possibly higher rates of polymerization. These ligands have been used in the polymerization of monomers such as styrene, methyl acrylate, and methyl methacrylate.27

The activity of nitrogen-based ligands can vary with structure, but there are a few general guidelines that may be followed. First, activity decreases as the number of coordinating sites decreases and also as the number of linking carbons increases. Activity is also usually higher for bridged and cyclic systems such as (Me6TREN) than for linear systems, though this may lead to less control in the polymerization.28

Phosphorus-based ligands may be used to complex most transition metals used in ATRP, such as Ru, Fe, Ni, and Pa, but they are not efficient with Cu systems. The most frequently used of these ligands is PPh3, which has been used with a variety of transition metals. Though a variety of phosphorus-based ligands have been studied, only those that are both strongly basic and contain well-defined steric bulk display high activity and good control of polymerizations.26

A variety of monomers have been polymerized by ATRP, including styrenes, (meth)acrylates, (meth)acrylamides, and acrylonitrile. For a monomer to be polymerized by this process, it must contain a substituent that can stabilize the propagating radical.
ATRP of acrylates has been reported using Cu, Ru, and Fe-based systems, though Cu tends to be superior to the others. Acrylates with a variety of side chains are polymerizable with ATRP. Some of these include \( n \)-butyl acrylate, 2-hydroxyethyl acrylate, and glycidyl acrylate. Poly(\( t \)-butyl acrylate) (PtBA) can also be synthesized and then hydrolyzed to create the more hydrophilic poly(acrylic acid) (PAA).\(^{29}\) Acrylic acid itself cannot be polymerized by ATRP because the acid functionality can poison the catalyst by coordinating to the metal or by protonating the ligand.\(^{26}\) Thus, the protected form of the monomer must be used.

Methyl methacrylate (MMA) and other methacrylates have also been polymerized by ATRP with a larger variety of metal catalysts. This is because the dormant species of MMA is more easily activated and the reaction has a higher equilibrium rate constant than reactions involving monomers that form less stable radicals. In order to obtain controlled polymerizations and well-defined products, conditions that favor deactivation should be used. These include lower catalyst concentrations and higher amounts of solvent, which reduce the concentration of growing radicals. Ru catalysts are well suited for MMA polymerizations because they have higher redox potentials, which increase the rate of deactivation of the system.

Styrene and its derivatives have been successfully polymerized by ATRP using copper,\(^{24}\) iron,\(^{30}\) ruthenium,\(^{31}\) and rhenium\(^{32}\) catalysts, though the copper systems tend to be most popular. The suitability of the variety of catalysts is due to the stability of the secondary benzylic radical, which allows catalysts with both high and low redox potentials to be used. Styrenic polymerizations may be carried out in solvent or in the bulk, but non-polar solvents are recommended because they enhance the stability of the
halide end group.\textsuperscript{26} It has also been shown that the atom transfer equilibrium is shifted toward the active species for the polymerization of styrene derivatives containing electron withdrawing groups on the ring, resulting in faster polymerizations.\textsuperscript{33}

The primary function of the initiator in ATRP is to govern the molecular weight of the polymer by determining the number of growing chains. There are two important considerations when choosing an initiator. Initiation should be fast compared to propagation, and the probability of side reactions should be minimized. Alkyl halides are typically used as initiators, and they undergo homolytic bond cleavage to produce the propagating radical. Chlorines and bromines are the most effective halides for this process, though iodine has been used in some acrylic and styrenic polymerizations. Fluorine is not used because the C-F bond is too strong to undergo homolytic cleavage.\textsuperscript{26} Tertiary halides are better initiators than secondary or primary, and the same halide that is used in the initiator should be used in the metal salt. In general, the initiating group should form a radical of similar reactivity to that of the propagating chain. Some of the more common ones are illustrated in Figure 1.6.

ATRP is tolerant to many additives because the radical species does not react with many functional groups. This is a great advantage because it reduces the need to protect functionalities during the polymerization process. For example, the addition of water or other polar compounds had little effect on the control of both copper and ruthenium-mediated systems.\textsuperscript{26} ATRP is mildly sensitive to oxygen. Small amounts can be scavenged by the metal catalyst, but this reduces the effective catalyst concentration available for the polymerization. Just as this would decrease the reaction rate, some additives may actually increase the rate. For instance, Cu(0) oxidizes to Cu(I), which
would increase the catalyst concentration and, thus, the rate of the reaction.\textsuperscript{34} Cu(0) can simultaneously reduce excess Cu(II) to Cu(I) \emph{in situ}, which adds another element to the increased reaction rate. Adding iron powder to Fe(II) or Fe(III) salts yields similar results. In another example, the presence of a Lewis acid, such as aluminum alkoxide, is required for controlled polymerization of MMA when catalyzed by RuCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{3}.\textsuperscript{25} It is hypothesized that this is due to coordination of the aluminum with the carbonyl groups on both the chain end and monomer. Other additives which may increase the reaction rate are carboxylic acids\textsuperscript{35} and phenols.\textsuperscript{36}
**Figure 1.1** General termination events for “living” carbocationic polymerization of isobutylene

\[ \begin{align*}
\text{H} & \quad \text{CH}_3 \\
\text{C} \quad \text{C} \quad \Theta & \quad \text{X} \\
\text{H} & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*} \]

\[ \text{β-H abstraction} \quad \text{Chain transfer} \quad \text{Termination} \]

\[ \begin{align*}
\text{C} \quad \text{C} & \quad \text{X} \\
\text{H} & \quad \text{CH}_3 \\
\text{H} & \quad \text{CH}_3
\end{align*} \]

**Figure 1.2** Chain equilibrium between (a) dormant, (b) ion pair, (c) free-ion chains. P is the propagating chain end, X is the counterion, \( K_{\text{eq}} \) is the ionization equilibrium constant, and \( K_{\text{dis}} \) is the ion pair dissociation equilibrium constant.

\[ \begin{align*}
P_X & \quad \xrightleftharpoons{K_{\text{eq}}} \quad P \Theta X \Theta \\
\text{(a)} & \quad \text{(b)} & \quad \text{(c)}
\end{align*} \]
Figure 1.3 General scheme for controlled radical polymerizations.
Figure 1.4 General scheme for atom transfer radical addition (ATRA) or atom transfer radical polymerization (ATRP)
**Bipyridine-based**

![Image of bipy](image)

**Pyridinimine-based**

![Image of dHbipy](image)

**Amine-based**

![Image of TMEDA](image)

**Figure 1.5** Examples of nitrogen-based ligands used in Cu-mediated ATRP

**Figure 1.6** Examples of initiators used in ATRP

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CHAPTER II

POLYMER ARCHITECTURES PRODUCED BY “LIVING” POLYMERIZATION TECHNIQUES

Polymers with well-defined properties, such as target molecular weights and narrow PDIs, can be synthesized via a variety of living polymerization techniques. An overview of two of these, quasiliiving cationic polymerization and atom transfer radical polymerization, was presented in Chapter I. An equilibrium between the dormant and active chain ends exists in these polymerizations, and the inactive species is favored for controlled reactions. It is also possible to combine living polymerization techniques to yield block copolymers with well-defined segments and high functionalities. This enables the creation of materials that would not otherwise be able to be synthesized.

Initiators for living polymerizations may be monofunctional or multifunctional, and may be reacted to yield a variety of polymer architectures, such as stars, telechelic materials, or even crosslinked networks (Figure II.1). Termination of the polymerization yields predictable chain end functionalities and quantitative end group conversion. These functionalities may be further reacted to yield block copolymers.

The following discussion will focus on two architectures that are of specific interest in this work, block copolymers and star polymers.

Block Copolymers

Block copolymers synthesized via living polymerization techniques were first reported by Szwarc in 1956, with the production of poly(styrene-\(\beta\)-butadiene-\(\beta\)-styrene) (PS-PBD-PS) materials. This process involved the creation of PS-PBD diblocks...
initiated from a monofunctional initiator. After complete conversion of styrene monomer, the PBD block was created via sequential monomer addition. The resulting materials were then covalently linked using dichlorosilane to form the A-B-A triblock, where A and B represent the PS and PBD blocks, respectively. This process was later commercialized by Shell, who produced A-B and A-B-A copolymers of PS with either PBD or polyisoprene (PI).^{41}

The block copolymers created by Szwarc have become known as thermoplastic elastomers (TPEs). TPEs are typically block copolymers that contain glassy outer blocks and rubbery inner blocks, which are formed from hard and soft segments of the polymer, respectively. Due to the distinct separation of the phases, the copolymers have been shown to separate into nanophases.^{42} Minor phases of the outer blocks organize to form physical crosslinks in the materials (Figure II.2). At ambient temperatures, the materials behave as crosslinked rubbers due to this ordering. However, when heated above the glass transition temperature (Tg) of the outer blocks, the physical crosslinks are disrupted by long-range segmental motion, and the materials can be melt processed. When cooled again, the glassy characteristics reform and the stability of the material is regained.

Since this early work, TPEs with polyisobutylene (PIB) center blocks have been developed. There are several advantages to using PIB over the conventional isoprene or butadiene systems. First, the PIB chain is completely saturated, unlike PI and PBD, giving it higher thermal and oxidative stability. PIB also has increased packing ability and a bulky chain, which yield high barrier and high damping properties, respectively. PIB is inert toward sulfonation and other post-polymerization reactions,^{43} allowing selective modification of the PS blocks. Finally, PIB-based triblocks are synthesized
from difunctional initiators. This eliminates the need for coupling reactions that could result in incomplete linking and leave diblock contaminants in the system, which is sometimes seen in anionic reactions.

The incorporation of PIB as a center block material in cationic polymerization was first reported by Kennedy, who used p-chlorostyrene as the outer block material. The first report of poly(styrene-\textit{b}-isobutylene-\textit{b}-styrene) (PS-PIB-PS) triblock copolymer synthesis came the following year (Figure II.3). In each case, the sequential monomer addition technique employed by Szwarc was used to introduce the second monomer to the living chain end at complete conversion of the IB polymerization, forming the desired A-B-A architecture.

PS-PIB-PS block copolymer systems display important morphological properties due to their phase separation. Storey and coworkers found that morphology is dependent on volume percent (vol\%) of PS (Figure II.4). As the amount of PS in the material is increased, the morphology changes from spheres of PS dispersed in a continuous matrix of PIB to more continuous phases, such as cylinders or lamellar structures. For example, PS volume percentages of 20-40\% yield cylinders of PS, while slightly higher PS percentages display lamellar morphologies. Near the transitions from one morphology to another, mixed morphologies may be observed, such as the presence of both spheres and cylinders at 29\% or cylinders and lamellae at 37\%. DMA analysis also indicated the presence of two phases in the block copolymers by noting two Tgs. One occurred at $-55^\circ\text{C}$ and the other at $100-110^\circ\text{C}$, which represent the relaxations of the PIB and PS segments, respectively. The Tgs of the materials may also be observed by DSC, but the transitions are much more pronounced in DMA.
It should be noted that, although this section has focused primarily on A-B-A triblocks, A-B block copolymers may also be synthesized from initiators that contain two different functionalities. This is particularly useful in reactions that employ a combination of polymerization techniques. Well-defined polymers can be obtained as long as one of the initiating sites is protected or otherwise remains unreacted. The unreacted site may then be used to initiate a second polymerization. This concept will be examined further in the discussion of star polymers.

**Star Polymers**

A star polymer is defined as a macromolecular structure having branches radiating from a central core. An A-B or A-B-A block copolymer could, in theory, be termed a two-armed star, but the term “star polymer” is usually reserved for entities containing three or more arms, or branches. All of the branches may be composed of the same homopolymers, or the branches may be block copolymers. Star polymers within the latter group are often referred to as a star-block copolymer.

Star-block copolymers offer several advantages in physical properties over their linear counterparts. It has been suggested that they display improved tensile properties over the linear systems due to the presence of a central core, which acts as a permanent crosslink in the material. Secondly, star-block systems have more numerous arms than the linear polymers, which, in turn, mean more individual segments of each polymer. Because of the increased number of segments, the polymers organize to form more numerous glassy domains, or physical crosslinks, which add stability to the system. Finally, increasing the number of arms on a star polymer, while keeping the composition and molecular weight constant, shortens the arm length. The processability of the
polymer is increased because the shorter arms reduce the viscosity of the material by decreasing chain entanglements.\textsuperscript{49,50}

Two methods may be used to synthesize star polymers, and they are similar to synthetic routes for block copolymers. The \textit{core-first} method allows the polymer arms to be grown from a central core with multiple initiating sites; thus, the chain ends can remain reactive. For this method to produce well-defined, controlled polymers, all of the initiating sites must be equally reactive and have equal probability for reaction. Thus, the core species should be as architecturally symmetrical as possible (Figure II.5). Also, the initiator must be soluble in the reaction medium. If these criteria are not met, the arms of the star may have varying molecular weights, and some sites may not initiate at all.

The \textit{arm-first} method involves linking pre-formed arms to a central core molecule. This method usually does not allow further reactions to occur, and the final product must often be fractionated to remove the linear polymer contaminants. These contaminants most often result from the use of a stoichiometric excess of arm, which is used to ensure all linking sites on the core molecule. The primary advantage to this system is that the arms can be isolated and characterized before the star polymer is formed.

\textit{Mikto-arm Star Polymers}

Mikto-arm polymers are stars that contain chemically different arms (Figure II.6). The term “mikto” is rooted in the Greek word for “mixed.”\textsuperscript{48} Eschwey and Buchard published the first synthesis of mikto-arm stars in 1975,\textsuperscript{51} though the majority of work in this area has been accomplished in the last 20 years. The primary methods of synthesis
include anionic polymerization of the monomers and linking the pre-formed arms to a core molecule. These methods have been summarized in three different approaches.

The first method of mikto-arm polymer synthesis involves the production of star polymers by polymerizing a small amount of divinyl benzene from the living ends of an anionic polymeric chain. This leaves the same number of anions at the core as the number of arms, and a second monomer can then be polymerized from the core. This technique of arm-first then core-first polymerization has come to be known as the “in-out” method. Eschwey and coworkers first reported this method when they polymerized stars composed of styrene and isoprene. Rempp used this same approach 15 years later to polymerize acrylates and methacrylates. However, there are architectural restrictions in using this method in that only polymers of the $A_nB_n$ type may be created. Also, this linking process yields star molecules with a distribution of number of arms per molecule, about some average value.

The second approach has been used by both Swarc and Quirk to create $A_2B_2$ type stars. In this type of reaction, double 1,1-diphenylethylenes, such as 1,3-di(1-phenylethenyl) benzene or meta double 1,1-diphenylethylene (MDDPE), were used as linking agents for anionically created polymers. Upon addition of a second monomer, the 4-armed star was formed. Quirk was also able to synthesize some 3-armed star materials by using different isomers of the linking agent.

The final method, which has been used to create both $A_2B$ and $A_3B$ type stars, involves linking the arms with chlorosilanes. This technique has been used by several researchers, including Pennisi and Fetters, Mays, and Hadjichristidis et al. In each instance, one monomer (such as styrene) is polymerized and then reacted with an excess
of a multifunctional silane. In this way, each chain becomes capped with a chlorosilane residue that carries either 2 or 3 unreacted chlorosilane functions. Then, the second polymer is added. Again, a major drawback to this type of reaction is the purification and separation that must be done to remove any unwanted polymer segments.

Morphological investigations of mikto-arm star polymers illustrate that the architecture of the molecule greatly affects the microdomain structure of the material at a given volume fraction. In a study by Hadjichristidis and coworkers, diblock copolymers comprised of 50% PS in diblock form show lamellar morphologies.\textsuperscript{58} For the same fraction of PS in A\textsubscript{2}B and A\textsubscript{3}B stars, the morphologies shift to a triconnected cubic structure and a hexagonally packed cylindrical structure, respectively. The authors suggested that the shift in morphology may be due to overcrowding of the chains on one side of the interface.

Though the methods described above work fairly well for styryl and dienyl chain ends, it is difficult to create star architectures based on other polymers. Thus, it is necessary to use multi-functional initiators. The application of these initiators to create mikto-arm stars also allowed the use of various polymerization techniques, such as ATRP, where the arms of the stars could be grown outward from the core rather than linking the arms together. In 2002, Gnanou and coworkers reported the synthesis of AB\textsubscript{2} type polymers by ATRP.\textsuperscript{59} In this work, PS was synthesized and functionalized with a brominated branching agent that may initiate two different arms. PS or PtBA arms were then created from the new initiating sites via ATRP. Radical polymerization techniques have also been recently used with the “in-out” method to create mikto-arm stars.\textsuperscript{60} Figure
II.7 illustrates some initiators, or branching agents, that have been used to synthesize these hetero-armed materials.\textsuperscript{59,61}
Figure II.1 Examples of polymer architectures that may be synthesized via living polymerization techniques
Figure II.2 Cartoon illustration of phase separation in thermoplastic elastomers, such as PS-PIB-PS

Figure II.3 Synthesis of PS-PIB-PS triblocks via living carbocationic polymerization
**Figure II.4** Block copolymer morphologies of PS-PIB-PS triblocks as seen with increasing PS content.
Figure II.5 Initiators that have been used to create symmetrical star polymers
Figure II.6 Cartoon structures of some mikto-arm star polymer architectures
Figure II.7 Branching agents that have been used to synthesize mikto-arm star polymers
CHAPTER III
SYNTHESIS OF POLY(STYRENE-\textit{b}-ISOBUTYLENE-\textit{b}-ACRYLIC ACID) LINEAR TERPOLYMERS AND STAR POLYMERS FROM A MONOFUNCTIONAL CATIONIC INITIATOR

As discussed in the previous chapters, A-B-A triblock copolymers have received considerable attention over the years. Of particular interest in this work are PS-PIB-PS thermoplastic elastomers, which consist of rubbery inner blocks and glassy outer segments that phase-separate on the nanoscale.\(^{20, 40, 42, 45-47}\) While the PIB segment provides high barrier and dampening properties, the PS segments provide physical crosslinks that lend stability to the materials. Also, the PS blocks provide sites for further sulfonation and inorganic modification, which have been shown to increase the thermal and mechanical properties of the material relative to the precursor triblocks.\(^{43, 62-67}\)

One proposed application for sulfonated PS-PIB-PS materials is permselective membranes due to their proton (H\textsuperscript{+}) and water (H\textsubscript{2}O) transport properties.\(^{62, 63, 68, 69}\) This has been achieved by increasing the volume fraction of PS in the materials to the point where lamellar morphologies are formed. Sulfonation of a specific mol\% of the styrene repeat units induces hydrophilicity to the PS domain and provides a continuous pathway for H\textsuperscript{+} and H\textsubscript{2}O transport. While this has proven successful, it is believed that swelling the PS domain with water will eventually decrease the mechanical properties of the material. This potential problem was overcome by creating triphasic systems based on the PS-PIB-PS triblocks that have separate segments for the crosslinking phase and the
Pentablock terpolymers containing poly(acrylic acid) (PAA) outerblocks (PAA-PS-PIB-PS-PAA) were synthesized by chain extending the original A-B-A triblocks with tert-butyl acrylate and then hydrolyzing the side groups to yield the hydrophilic acid. PAA is incompatible with both PS and PIB; thus, the properties of those segments remain unaffected by the addition of the new blocks, and new or more complex morphologies may be obtained. These studies form the basis of the synthesis of novel star polymers containing blocks of polyisobutylene (PIB), poly(acrylic acid) (PAA), and optionally polystyrene (PS). The polymers will be created using a combination of quasiliving cationic polymerization and atom transfer radical polymerization. Schemes of the polymers that will be outlined in this chapter are illustrated in Figure III.1.

Experimental

Materials

Methyl 3,3-dimethyl-4-pentenoate was used as received from TCI America. Methyl magnesium bromide (3 M solution in diethyl ether), borane-tetrahydrofuran (THF) complex (1 M solution in THF), hydrogen peroxide (30 wt.% solution in water), acetic anhydride (99.5%), triethylamine (99.5%), methylcyclohexane (anhydrous, 99+%), 2,4-lutidine (DMP, 99+%), TiCl₄ (99.9%, packaged under N₂ in Sure-Seal bottles), potassium t-butoxide (95%), 2-bromoisobutyryl bromide (98%), 2-bromopropionyl bromide (98%), 2,2-bis(hydroxymethyl) propionic acid (98%), benzene (99.9%), phosphorus pentachloride (95%), Cu(I)Br (99.999%), anisole (99%), aluminum oxide (alumina, standard grade, activated, neutral, Brockmann I, ~150 mesh, 58 Å), DOWEX™MSC-1 macroporous ion-exchange resin (Dowex sodium, strong cation, 20-50
mesh) and toluene (anhydrous, 99.8%) were used as received from Sigma-Aldrich, Inc. Isobutylene (IB) and CH$_2$Cl (MeCl) (both BOC, 99.5%) were dried through columns packed with CaSO$_4$ and CaSO$_4$/4 Å molecular sieves, respectively. Ammonium chloride, hexane, sodium hydroxide, and ethyl ether were used as received from Fisher Chemical Co. Styrene, 2,6-di-tert-butylpyridine, tert-butyl acrylate (tBA), and THF were distilled from CaH$_2$ under reduced pressure. 1,1,4,7,7-Pentamethyldiethylenetriamine (PMDETA) (99%) from Sigma-Aldrich and distilled tert-butyl acrylate were sparged with dry N$_2$(g) for 20 min before use.

Real-time ATR-FTIR Monitoring of Block Copolymerization

Block copolymer formation was monitored using the ReactIR 1000 reaction analysis system (light conduit type) (ASI Applied Systems, Millersville, MD) equipped with a DiComp (diamond-composite) insertion probe, a general purpose type PR-11 platinum resistance thermometer (RTD), and a CN76000 series temperature controller (Omega Engineering, Stamford, CT). This instrument enabled the collection of infrared spectra of the polymerization components and monitoring of reaction temperature in real time. First, the polymerization of IB was monitored by following the diminution and eventual disappearance of the absorption at 887 cm$^{-1}$ associated with the $\equiv$CH$_2$ wag. By plotting peak height of the absorbance vs. time, a monomer decay profile for isobutylene was generated. The peak height at 887 cm$^{-1}$ at any time, $H_t$, less the reference peak height, $H_r$, measured prior to addition of monomer to the reactor, was assumed to be directly proportional to isobutylene monomer concentration. Analysis of styrenic monomer depletion was conducted similarly to that of isobutylene, using the peak at 907 cm$^{-1}$ associated with the $\equiv$CH$_2$ wag. However, the polymer chains were already
living at the time the styrenic monomer was introduced; therefore, \( H_0 \) could not be
directly measured and instead was set equal to the first-measured height of the 907 cm\(^{-1}\)
peak immediately after addition of the styrene monomer charge.

**Synthesis of 3,3,5-Trimethyl-5-chlorohexyl acetate (TMCHA)**

The initiator, 3,3,5-trimethyl-5-chlorohexyl acetate (TMCHA), was synthesized
using a variation of a previously reported procedure. The overall reaction scheme is
illustrated in Figure III.2. A representative procedure was as follows: To a 250 mL,
three-necked round-bottom flask equipped with a mechanical stirrer, nitrogen inlet/outlet,
and ice bath was charged 0.471 mol methyl magnesium bromide (157 mL of a 3M
solution in diethyl ether). Methyl 3,3-dimethyl-4-pentenoate (15 mL, 9.4x10\(^{-2}\) mol) was
added dropwise via syringe over 30 min. The reaction was stirred for 1.5 hours at 0\(^\circ\)C,
and then removed from the ice bath and stirred overnight at room temperature. The
vessel contents were poured into a mixture of 300 g ice and 25 g (0.47 mol) ammonium
chloride contained in a beaker. The resulting slurry was transferred to a separatory
funnel; the beaker was rinsed with de-ionized H\(_2\)O and diethyl ether, and the rinses were
added to the separatory funnel. The layers were separated and the organic layer was
dried over magnesium sulfate, filtered, and vacuum stripped to yield the liquid product,
5-hydroxy-3,3,5-trimethylhexene, in 68% yield (9.1 g).

Hydroboration-oxidation was carried out as follows: Borane-THF complex (70
mL, 7.0x10\(^{-2}\) mol) was charged to a 250 mL three-necked round-bottom flask equipped
with mechanical stirrer, external ice/water bath, and nitrogen inlet/outlet. 5-Hydroxy-
3,3,5-trimethylhexene (5.0 g, 3.5x10\(^{-2}\) mol), dissolved in 22.5 mL THF (20 wt.%
solution), was added dropwise via syringe to the reactor over 30 min. The reaction
proceeded for 5 h. Aqueous NaOH solution (23.5 mL, 3 M solution) was added to the reactor via syringe at a rate such that the temperature of the reactor did not exceed 45°C (~45 min). Then 8 g H₂O₂ (30 wt% solution in water) was added quickly to the reactor, and the reaction was allowed to proceed for an additional 75 min. The aqueous phase was saturated with potassium carbonate, and the organic layer was separated and washed several times with DI H₂O and dried over magnesium sulfate. Solvent was removed by vacuum stripping, and the liquid product, 1,5-dihydroxy-3,3,5-trimethylhexane (80% yield, 4.5 g), was dried under vacuum at ambient temperature.

Acetylation of the primary hydroxyl group of 1,5-dihydroxy-3,3,5-trimethylhexane was carried out as follows: To a 50 mL round-bottom flask equipped with condenser column, magnetic stir bar, and heating mantle were charged 10 g (6x10⁻² mol) 1,5-dihydroxy-3,3,5-trimethylhexane dissolved in 30 mL triethylamine and 6 g (6x10⁻² mol) acetic anhydride. The reaction was refluxed for 24 h, and then cooled, washed with de-ionized water and dried over magnesium sulfate, and the solvent was removed by vacuum stripping. The liquid product, 5-hydroxy-3,3,5-trimethylhexyl acetate, was obtained in 71% yield (8.9 g).

The final product (TMCHA) was produced by chlorination of the tertiary alcohol group. HCl, formed by dripping sulfuric acid over sodium chloride, was bubbled through a solution of 10 g 5-hydroxy-3,3,5-trimethylhexyl acetate in 30 mL methylene chloride for 5 h, while the temperature of the reactor was maintained at 0°C using an external ice/water bath. The reactor was removed from the ice/water bath, and excess HCl was neutralized by the addition of sodium bicarbonate. The resulting mixture was then stirred over magnesium sulfate. Next, the mixture was filtered, and the solvent was removed by
vacuum stripping. The liquid product, 3,3,5-trimethyl-5-chlorohexyl acetate, was obtained in 69% yield (7.5 g).

Synthesis of 2,2-Bis((2-bromo-2-methyl)propionatomethyl)propionyl chloride

The overall reaction scheme for the synthesis of the branching agent 2,2-bis((2-bromo-2-methyl)propionatomethyl)propionyl chloride is illustrated in Figure III.3. To a 250 mL 3-necked round bottom flask equipped with a magnetic stirbar and ice bath were charged 5.0 g (3.7x10^{-2} mol) 2,2-bis(hydroxymethyl) propionic acid and 80 mL THF. Then 10.4 mL (7.4x10^{-2} mol) triethylamine was added via syringe. The solution became homogeneous upon TEA addition. A solution of 9.3 mL (7.4x10^{-2} mol) 2-bromoisobutyryl bromide in 20 mL THF was added dropwise via syringe. The ice bath was removed, and the mixture was allowed to stir overnight at room temperature. The salts were then filtered off and the bulk of the solvent was removed by rotary evaporation and under direct vacuum until a soft white solid was formed. The product 2,2-bis((2-bromo-2-methyl)propionatomethyl)propionic acid (BPPA) was used without further purification (90% yield).

2,2-Bis((2-bromo-2-methyl)propionatomethyl)propionic acid was converted to an acid chloride as follows: To a 250 mL 3-necked round bottom flask equipped with mechanical stirbar were charged 11 g (2.4x10^{-2} mol) BPPA dissolved in 50 mL benzene. Then 6.7 g (3.2x10^{-2} mol) phosphorus pentachloride was added quickly to the reactor to minimize exposure to the atmosphere. The mixture was allowed to stir overnight at room temperature. Any salts that were formed were filtered off, and benzene was removed by vacuum stripping. The liquid product was washed with hexanes to remove excess PCI5. Excess salts were removed by filtration, and the brown liquid product 2,2-bis((2-bromo-
2-methyl)propionatomethyl)propionyl chloride (BPPC) was recovered by removing hexane under vacuum (75% yield).

**Synthesis of PIB and PIB-PS Copolymers Using Quasiliving Cationic Polymerization with Sequential Monomer Addition Techniques**

A representative procedure for the synthesis of PIB containing a blocked-hydroxyl head group is as follows: The DiComp probe was inserted into a 250 mL 4-necked round-bottom flask equipped with a platinum resistance thermometer, a stirring rod and bearing, and a Teflon paddle. The reactor was placed in the hexane/heptane bath and allowed to equilibrate to -70°C. Into the flask were charged 97.6 mL Hex (-70°C), 65.0 mL MeCl (-70°C), 0.06 mL (5.2x10^-4 mol) 2,4-lutidine, 0.04 mL (1.8x10^-4 mol) DtBP, and 0.07 g (3.4x10^-4 mol) TMCHA initiator. This mixture was allowed to stir for 15 min, after which several FTIR background spectra were collected. Then 14.3 mL (1.8x10^-1 mol) IB (-70°C) was added to the flask. Several monomer baseline spectra were obtained, and 1.2 mL (1.1x10^-2 mol) TiCl₄ (neat and at room temperature) was added to the flask. Once the IB achieved >99% conversion, the reaction was quenched with 50 mL pre-chilled MeOH. The molar concentrations of the reagents were as follows: [IB]₀=1.0 M, [TMCHA]₀=1.88x10^-3 M, [DtBP]₀=9.8x10^-4 M, [2,4-Lutidine]₀=2.9x10^-3 M, [TiCl₄]₀=6.0x10^-2 M. The IB spectral data acquisition was then aborted, and the reaction mixture was washed with methanol and water. The polymer was extracted with hexanes, and the organic phase was dried over magnesium sulfate, filtered, and vacuum stripped to remove the solvent. The polymer was dried in a vacuum oven at room temperature for several days.
The procedure was modified slightly for the synthesis of a PIB-PS block copolymer. The DiComp probe was inserted into a 1 L 4-necked round-bottom flask equipped with a platinum resistance thermometer, a stirring rod and bearing, and a Teflon paddle. The reactor was placed in the hexane/heptane bath and allowed to equilibrate to \(-70^\circ\text{C}\). Into the flask were charged 220 mL MCHex (-70°C), 146 mL MeCl (-70°C), 0.14 mL (1.2x10\(^{-3}\) mol) 2,4-lutidine, 0.08 mL (3x10\(^{-4}\) mol) DtBP, and 0.2 g (9x10\(^{-4}\) mol) TMCHA. This mixture was allowed to stir for 15 min, after which several background spectra were collected. Then 32 mL (4x10\(^{-1}\) mol) IB (-70°C) was added to the flask. Several monomer baseline spectra were obtained, and 1.5 mL (1.4x10\(^{-2}\) mol) TiCl\(_4\) (neat and at room temperature) was added to the flask. Once the IB achieved \(>99\%\) conversion, a 1-2 mL aliquot was taken and added to 10 mL pre-chilled MeOH. The molar concentrations of the reagents were as follows: \([\text{IB}]_0=1.0 \text{ M}, [\text{TMCHA}]_0=2\times10^{-3} \text{ M}, [\text{DtBP}]_0=1\times10^{-3} \text{ M}, [2,4-\text{Lutidine}]_0=3\times10^{-3} \text{ M}, [\text{TiCl}_4]_0=3.5\times10^{-2} \text{ M}\). The IB spectral data acquisition was then aborted, and the ReactIR was set up for the styrene reaction. A new set of scans was begun by acquiring several baseline spectra, followed by the addition of a pre-chilled solution of 48 mL (4.2x10\(^{-1}\) mol) styrene in 96 mL MCHex and 64 mL MeCl. When the reaction reached \(~50\%\) conversion, 60 mL pre-chilled MeOH was added to the reactor. The mixture was precipitated into 5x excess MeOH, and the solid product was filtered and dried in a vacuum oven at 25°C. The molar concentrations of styrene in the addition and in the total reaction were 2.0 M and 6.9x10\(^{-1}\) M, respectively.
Site transformation of the Macroinitiator.

The two-step site transformation was carried out using a variation of a previously reported procedure.\textsuperscript{72} A representative procedure, using a PIB-PS copolymer as the macroinitiator, is as follows: To deblock the hydroxyl group at the initiator fragment and simultaneously dehydrochlorinate the PS chain end, a three-necked round bottom flask, equipped with heating mantle, magnetic stirbar, and condensing column, was charged with PIB-PS (5.0 g, Mn=14,450 g/mol) dissolved in 50 mL distilled THF. The reactor was purged with N\textsubscript{2} and then equipped with a N\textsubscript{2} bubbler. Potassium tert-butoxide (0.16 g, 1.4x10\textsuperscript{-2} mol) dissolved in 5 mL THF was injected slowly via syringe. The reaction was refluxed overnight and cooled to room temperature, and the product was precipitated into an excess of 80/20 (v/v) MeOH/DI H\textsubscript{2}O. The solid product was filtered and dried in a vacuum oven at room temperature overnight (98% yield).

To incorporate a single bromine functionality onto the polymer chain end, the following procedure was employed: To a 250 mL three-necked round bottom flask equipped with magnetic stirbar, heating mantle, N\textsubscript{2} bubbler, and condenser column were charged hydroxy-functional PIB-PS (2.5 g, Mn=14,450 g/mol), 20 mL THF, 0.3 mL 2-bromopropionyl bromide (2.8x10\textsuperscript{-3} mol), and 0.3 mL triethylamine (2.2x10\textsuperscript{-3} mol). The reaction was refluxed for 48 h (adding THF as needed to maintain constant reaction volume), and the mixture was precipitated into excess MeOH/DI H\textsubscript{2}O (80/20 v/v). The solid product was dried overnight in a vacuum oven at room temperature to remove excess solvent (93% yield).

To incorporate dual bromine functionalities, the 2-bromopropionyl bromide was replaced with the branching agent 2,2-bis((2-bromo-2-methyl)propionatomethyl)
propionyl chloride. A representative procedure using a PIB macroinitiator is outlined as follows: The hydroxyl functionality of the initiator was deblocked as described above. To a 250 mL three-necked round bottom flask equipped with magnetic stirbar, heating mantle, \( \text{N}_2 \) bubbler, and condenser column were charged hydroxy-functional PIB (6.1 g, \( \text{Mn}=31,600 \text{ g/mol} \)), 150 mL THF, 0.98 g (2.1x10\(^{-3}\) mol) branching agent, and 0.36 mL triethylamine (2.6x10\(^{-3}\) mol). The reaction was refluxed for 48 h (adding THF as needed to maintain constant reaction volume). Hexanes were added to the slightly cooled mixture, and the solution was washed with de-ionized water. The organic layer was collected and dried over MgSO\(_4\) and then filtered, and the solvent was removed by vacuum stripping. The polymer was dried in a vacuum oven overnight at room temperature to remove any excess solvent.

*Synthesis of PtBA-PIB-PS Linear Terpolymers and Stars Using ATRP*

A representative procedure for the synthesis of a PtBA-PIB-PS terpolymer is as follows: To a 100 mL Kjeldahl style schlenk flask, equipped with magnetic stirbar and contained within a dry box, were charged 4.1x10\(^{-2}\) g (2.87x10\(^{-4}\) mol) CuBr, 2.3 g (1.6x10\(^{-4}\) mol) brominated PIB-PS, 15 mL toluene, 0.30 mL anisole, and 1.03 g (8.0x10\(^{-3}\) mol) tBA (sparged with \( \text{N}_2 \) for 30 min prior to use). The mixture was allowed to stir to solubilize the macroinitiator. The flask was then sealed with a rubber septum and cable tie and removed from the dry box. The flask was sparged with \( \text{N}_2 \) for 5 minutes. Then, 6.0x10\(^{-2}\) mL (2.87x10\(^{-4}\) mol) PMDETA (sparged with \( \text{N}_2 \) prior to use) was added to the reactor via syringe. An initial aliquot (0.1 mL, \( t=0 \)) was taken and quenched by freezing in liquid nitrogen (LN\(_2\)), and the reactor was submerged in an oil bath preheated to 90°C. Additional aliquots (0.1 mL) were taken at predetermined intervals via a \( \text{N}_2 \) purged...
syringe for kinetic analysis, and the reaction was quenched in LN\textsubscript{2} after 5.5 h. The polymer, dissolved in methylene chloride, was passed through a column consisting of a neutral alumina bottom layer and a DOWEX® MSC-1 ion-exchange resin top layer and precipitated into excess MeOH/DI H\textsubscript{2}O (80/20 v/v). The solid product was collected by vacuum filtration and dried under vacuum at room temperature overnight (96% yield).

This procedure was modified slightly to create a 3-armed star containing 2 PtBA arms. An example is as follows: To a 100 mL Kjeldahl style schlenk flask, equipped with magnetic stirbar and contained within a dry box, were charged \(4.0 \times 10^{-2} \text{ g} \ (2.8 \times 10^{-4} \text{ mol}) \) CuBr, \(2.1 \text{ g} \ (1.4 \times 10^{-4} \text{ mol}; \ 2.8 \times 10^{-4} \text{ mol ATRP initiating sites}) \) PIB-PS, \(10 \text{ mL} \) toluene, \(0.20 \text{ mL} \) anisole, and \(1.81 \text{ g} \ (1.4 \times 10^{-2} \text{ mol}) \) tBA (sparged with N\textsubscript{2} for 30 min prior to use). The mixture was allowed to stir to solubilize the macroinitiator. The flask was then sealed with a rubber septum and cable tie and removed from the dry box. The flask was sparged with N\textsubscript{2} for 5 minutes. Then, \(6.0 \times 10^{-2} \text{ mL} \ (2.87 \times 10^{-4} \text{ mol}) \) PMDETA (sparged with N\textsubscript{2} prior to use) was added to the reactor via syringe. An initial aliquot (0.1 mL, \(t=0\)) was taken and quenched by freezing in liquid nitrogen (LN\textsubscript{2}), and the reactor was submerged in an oil bath preheated to 90°C. Additional aliquots (0.1 mL) were taken at predetermined intervals via a N\textsubscript{2} purged syringe for kinetic analysis, and the reaction was quenched in LN\textsubscript{2} after 5.5 h. The polymer, dissolved in methylene chloride, was passed through a column consisting of a neutral alumina bottom layer and a DOWEX® MSC-1 ion-exchange resin top layer and precipitated into excess MeOH/DI H\textsubscript{2}O (80/20 v/v). The solid product was collected by vacuum filtration and dried under vacuum at room temperature overnight (96% yield).
Monomer conversion for all polymerizations was determined by $^1$H-NMR using anisole as an internal standard. Integration of the methoxy resonance in anisole (3.75 ppm) and the vinyl resonance in tBA (5.75-5.60 ppm) at predetermined time intervals allowed for the quantitative determination of tBA conversion. The aliquots were subsequently passed through a column of neutral alumina, vacuum dried, and analyzed by SEC.

Cleavage of tert-Butyl Acrylate Side Chains

The poly(tert-butyl acrylate) segments were converted to poly(acrylic acid) by cleaving the side chains. A representative procedure is as follows: A thin layer of PtBA-PIB-PS was spread in a heat-resistant dish and placed in a vacuum oven that was preheated to 130°C. After 48h, the dish was removed, and the polymer was cooled to room temperature to be collected.

Size Exclusion Chromatography (SEC)

Molecular weights and polydispersity index (PDI) of the purified polymers were determined using a SEC system equipped with a Waters Alliance 2690 Separations Module, an on-line multi-angle laser light scattering (MALLS) detector operating at 690nm (MiniDAWN™, Wyatt Technology Inc.), an interferometric refractometer (Optilab DSP™, Wyatt Technology Inc.) operating at 35°C, and one set of PLgel™ (Polymer Laboratories Inc.) SEC columns connected in series. Tetrahydrofuran (THF), freshly distilled from CaH₂, was employed as the mobile phase and was delivered at a flow rate of 1.0 mL/min. Sample concentrations were approximately 7 mg/mL with an injection loop volume of 100μL. Detector signals were simultaneously recorded and absolute molecular weights and polydispersity indices (PDIs) were calculated using
ASTRA™ software (Wyatt Technology Inc). The dn/dc value was calculated from the signal response of the Optilab DSP, assuming 100% mass recovery from the columns.

**Proton and Carbon Magnetic Resonance Spectroscopy (H and 13C-NMR)**

1H and 13C-NMR were used for the structural elucidation of the copolymers and block copolymer composition. 13C-NMR was also used to quantitatively monitor the disappearance of the tert-butyl ester groups in the deprotection of the polymers. Solution 1H and 13C-NMR spectra were obtained on a Varian Unity 300 MHz spectrometer using 5 mm o.d. tubes with sample concentrations of 5-7% and 15-20% (w/v), respectively, in deuterated chloroform (CDCl₃) (Aldrich Chemical Co.) containing 0.03% (v/v) tetramethylsilane as an internal reference. The 1H and 13C-NMR spectra were the Fourier transformation of 32 and 1000 transients, respectively. 13C-NMR spectra of the PAA-PS-PIB-PS-PAA BCPs were obtained using sample concentrations of 20% (w/v), in deuterated methyl sulfoxide/deuterated chloroform (10/90 v/v) (Aldrich Chemical Co.) containing 0.03% (v/v) tetramethylsilane as an internal reference.

**Fourier Transform-Infrared (FT-IR) Spectroscopy**

FT-IR spectroscopy was used to qualitatively monitor the disappearance of the tert-butyl ester groups in the deprotection of the polymer segments. FT-IR spectra were obtained using a Bruker Equinox 55 FT-IR spectrometer using 32 scans at 4 cm⁻¹ resolution. Polymer samples were cast onto a NaCl plate from THF and dried with N₂(g) before analysis. Data were collected using OPUS NT IR software.

**Differential Scanning Calorimetry**

Thermal transitions of the polymers were studied using a TA DSC Q100 analysis system and analyzed with TA Universal Analysis software. The samples were heated to
150°C, quenched to -90°C, and heated to 150°C at a rate of 10°C/min. The glass transition was taken as the temperature corresponding to transition mid-point in the first derivative curve.

Results and Discussion

*Synthesis of 3,3,5-Trimethyl-5-chlorohexyl acetate (TMCHA)*

The TMCHA initiator, which contains a cationic initiating site and a latent hydroxyl functionality, was synthesized in four steps from methyl 3,3-dimethyl-4-pentenoate. In the $^1$H NMR spectrum of the starting material (Figure III.4), the methoxy protons of the ester functionality appear at 3.6 ppm. After the Grignard reaction, the peak is no longer present, and peaks associated with the newly formed hydroxyl functionality are present further upfield, near 2 ppm (Figure III.5).

The hydroboration-oxidation reaction was the most difficult stage of the synthesis. Addition of the NaOH solution had to be carried out very slowly (1 or 2 drops at a time) to avoid pressure due to uncontrolled exotherm. As the NaOH was introduced, a frothy white precipitate formed on the surface of the liquid, but disappeared as the reaction proceeded. The ice bath was maintained over the entire 7 h reaction time to keep the reactor below 45°C. Upon completion of hydroboration-oxidation, the peaks associated with the olefinic protons at 5-6 ppm in Figure III.5 shifted upfield to positions characteristic of methylene units (~1.7 and 3.7 ppm), and a broader peak appeared at ~2.5 ppm representing the two hydroxyl protons (Figure III.6).

Upon protection of the hydroxyl functionality at the head of the initiator, a new peak associated with the methyl group of the acetate functionality appeared near 2 ppm, and the peak corresponding to the methylene protons nearest the ester group shifted...
slightly downfield (Figure III.7). Finally, when the tertiary hydroxyl group was
converted to a chloride functionality, the peak associated with the hydroxyl proton
disappeared and the adjacent methylene (e) and gem-dimethyl proton (f) shifted
downfield (Figure III.8). The starting material, three intermediates, and final product
were all liquids at room temperature.

**Synthesis of 2,2-Bis((2-bromo-2-methyl)propionatomethyl)propionyl chloride**

In the synthesis of the branching agent intermediate, BPPA, the solid white
starting product (2,2-bis(hydroxymethyl)propionic acid) was observed to go into solution
upon the addition of TEA. After stirring the reaction mixture, and again after removal of
the solvent, white salts were observed in the reactor. Upon removing any residual solvent
with a vacuum pump, the product was revealed as a soft, white solid obtained in \( \sim 90\% \)
yield. Figure III.9 illustrates the \(^1\)H NMR spectrum of the product. The methylene
protons centered at 4.3 ppm, and the methyl protons adjacent to bromine are located at
1.9 ppm. The acid proton may be seen as a small broad peak anywhere between 7 and 11
ppm. Peak (d), which represents the acid functionality in this NMR spectrum, is
identified as the broad peak underneath the sharp chloroform peak at 7.3. The peak near
1.3 ppm represents the methyl group nearest the acid functionality. The peaks between 3
and 4 ppm are attributed to some residual solvent and 2,2-bis(hydroxymethyl)propionic
acid. It is not important to completely free the sample of these impurities because they
disappear upon transformation to the acid chloride.

As the acid is converted to an acid chloride, the methylene peak near 4.3 shifts
slightly to \( \sim 4.4 \) ppm, and the methyl peak near 1.3 shifts to 1.45 ppm, as illustrated in the
\(^1\)H NMR spectrum in Figure III.10. Because these changes are very small, the primary
indication of conversion to the final product is the disappearance of the peak associated with the acid functionality. The color of the mixture changes from yellow to orange as the reaction proceeds, and the final product, BPPC, is a brown liquid obtained in ~75% yield.

Synthesis of PIB and PIB-PS Copolymers Using Quasiliving Cationic Polymerization with Sequential Monomer Addition Techniques

ATRP macroinitiators, either PIB homopolymer or, in some instances, PIB-PS were synthesized via quasiliving cationic polymerization using TMCHA as the initiator and TiCl4 as the coinitiator in a MCHex/MeCl (60/40 v/v) solvent system with DMP and DtBP as Lewis base additive and proton trap, respectively, at -70°C. At >99% conversion of the IB as determined by ATR-FTIR monitoring, an aliquot was removed for PIB block analysis by SEC, and then a 2.0 M charge of styrene in MCHex/MeCl was added to the reactor. The reaction was quenched at ~50% styrene conversion with prechilled methanol. The styrene polymerization was short-stopped in this manner to avoid side reactions that become important when the propagation reaction slows at high conversions. Styrene cationic polymerizations are not as living as those of IB, and the dominant side reaction is usually chain transfer to polymer in the form of electrophilic aromatic substitution involving a propagating cation and a phenyl ring on a polymer chain. The occurrence of this reaction is revealed by the presence of chain-coupled polymer. SEC analysis of the isolated polymers showed that there were no high molecular weight peaks that would indicate chain coupling, and thus this side reaction was avoided. The polymers also had narrow PDIs.
Table III.1 lists molecular weight and compositional data for the PIB intermediate blocks and PIB-PS copolymers, as well as PIB macrorinitiators that do not contain PS segments. Number average molecular weight of the PIB blocks by SEC ($M_{n,\text{PIB/sec}}$) was higher than theoretical, indicating low initiator efficiency ($I_{\text{eff}} = 0.56-0.72$). This phenomenon is apparently related to complexation of TiCl$_4$ with the carbonyl group in the initiator. Through analysis of a separate set of experiments that varied [TiCl$_4$] while keeping all other concentrations the same, it was determined that [TiCl$_4$] must exceed [TMCHA] by 100% to obtain complete conversion of IB in a reasonable amount of time (~4 h). Experiments that employed [TiCl$_4$] at 0.8 and 1.2x[TMCHA] showed no reaction by real-time IR after 1.5 h, and no polymer could be collected, indicating that the carbonyl group in the TMCHA interacts with the TiCl$_4$ and prohibits the reaction from occurring. Another set of experiments indicated that the initiation efficiency of TMCHA improved as the target molecular weight was increased, with efficiency being ~96% at a target Mn of 30,000 g/mol. Although the cause of low $I_{\text{eff}}$ with TMCHA is poorly understood, it was observed that initiation of styrene by quasiliving PIB was quantitative; thus by adjusting the [IB]/[TMCHA] ratio to compensate for the low $I_{\text{eff}}$ of TMCHA, the targeted compositions of the copolymers were achieved, and the initiator was successfully used to create the diblock system.

Figures III.11 and III.12 illustrate the $^1$H NMR spectra of the PIB-PS copolymer and PIB homopolymer, respectively. As shown, the end group regions associated with the initiator are comparable in the different samples. The primary difference is the absence of the peak associated with the terminal chloride in the PIB sample. These peaks are located at 1.68 and 1.96 ppm. Number average molecular weight of the PIB block...
and PIB macroinitiators were taken as the value determined by SEC. Number average molecular weight of the PS block from SEC \( (M_{n,PS(SEC)}) \) was calculated as the difference in molecular weight between the overall block copolymer \( (M_{n,PIB-PS(SEC)}) \) and \( M_{n,PIB(SEC)} \). Copolymer composition was determined by comparison of the relative intensities of the aromatic and aliphatic resonances, as described previously for PS-PIB-PS systems.\(^{42} \)

\( M_{n,PS(nmr)} \) was calculated using a variation of a previously reported equation (Equation III.1),\(^{42} \)

\[
M_{n,PS(nmr)} = M_{n,PIB(SEC)} \cdot \frac{W_{PS(nmr)}}{(100 - W_{PS(nmr)})}
\]

where \( W_{PS(nmr)} \) is the weight percent of PS as determined by \(^1\)H NMR spectroscopy of the copolymer. The weight percent of PS equation is used to determine copolymer composition\(^{42} \) and is illustrated in Equation III.2,

\[
w_{PS(NMR)} = \frac{M_{Si} \cdot Ar}{(M_{Si} \cdot Ar) + M_{IB}(5 \cdot Al - 3 \cdot Ar)/8} \times 100\%
\]

where \( M_{Si} \) and \( M_{IB} \) are the molecular weights of styrene and isobutylene monomer units, respectively, \( Ar \) is the area of the aromatic region, and \( Al \) is the area of the aliphatic region. As shown in Table 1, the two measures of PS block molecular weight were in excellent agreement.

**Site Transformation of the Macroinitiator**

The end groups of the PIB and PIB-PS macroinitiators were transformed in two steps to allow for ATRP initiation. The first involved application of the strong base potassium tert-butoxide to de-protect the hydroxyl functionality of the initiator fragment and simultaneously dehydrochlorinate the tail group. The base was introduced to the copolymer as a slurry in THF, and the mixture became homogeneous as the reaction...
Figure III.11 illustrates the resonances associated with the methylene protons nearest the protected hydroxyl group (a) and the proton nearest to the terminal chlorine atom (b) in the PIB-PS samples prior to reaction. The integrated areas of these two resonances were found to be in a ratio of approximately 2 to 1, as predicted based upon the structure of the copolymer. After reaction, peaks (a) and (b) are no longer present in the $^1$H NMR spectrum of PIB-PS (Figure III.13), and a new peak at ~3.7 ppm has appeared. This peak is associated with the methylene protons of the initiator fragment nearest to the hydroxyl group, and they correspond with the analogous protons of 1,5-dihydroxy-3,3,5-trimethylhexane, which is the product of the hydroboration-oxidation reaction in the initiator synthesis (Figure III.6). The same peak is present in the PIB sample (not shown).

The second step of site transformation involved the incorporation of an $\alpha$-bromo carbonyl species, such as 2-bromopropionyl bromide, for ATRP initiation. This reaction was facile but slow; 48 h were needed for complete conversion. Incorporation of 2-bromopropionyl bromide produces a linear polymer, and the $^1$H NMR spectrum of the product is shown in Figure III.14. This compound was used in the synthesis of PtBA-PIB-PS terpolymers. The inset of the NMR spectrum illustrates the shift of the methylene protons in the initiator downfield to near 4.2 ppm and the appearance of a peak associated with the methine proton next to the bromine head group. Incorporation of the branching agent BPPC instead of 2-bromopropionyl bromide produces a macroinitiator capable of forming a 3-armed star. 2-bromoisobutyryl bromide was used in the synthesis of the branching agent instead of 2-bromopropionyl bromide because it gives a cleaner product. This is because the symmetrical structure of 2-bromoisobutyryl bromide allows
some crystallization. Figure III.15 shows the $^1$H NMR spectrum of the site-transformed PIB homopolymer, which is representative; the peaks associated with the end groups are identical in a PIB-PS sample. The inset of the plot illustrates peaks at 4.75 ppm (b) and at 4.35 ppm (a), which represent the methylene protons of the branching agent and of the original initiator fragment, respectively. The peak (a) now appears as a pair of doublets instead of a triplet, possibly indicating that the two protons now reside in slightly different chemical environments due to hindered rotation caused by the bulky branching agent. Peak (c) represents the four methyl groups of the branching agent. Since this peak occurs near the aliphatic region of the spectrum, it can be seen more readily in the PIB homopolymers compared to PIB-PS.

**Synthesis of PtBA-PIB-PS Linear Terpolymers and Stars Using ATRP**

Tert-butyl acrylate was polymerized at 90°C under ATRP conditions in a N$_2$ atmosphere, using PMDETA as the nitrogen-containing ligand, Cu(I)Br as the catalyst, toluene as solvent, and anisole as an internal standard to monitor monomer conversion. The initiator was a PIB-PS diblock copolymer or PIB homopolymer modified as described above. Aliquots were removed at predetermined intervals to monitor conversion and for SEC analysis. Upon introduction of PMDETA, the reaction turned light green. As higher conversion was obtained, a darker green color developed.

Figures III.16 and III.17 show the $^1$H and $^{13}$C NMR spectra, respectively, of a representative triblock terpolymer (PtBA-PIB-PS). The resonances between 6.2-7.3 ppm and 0.5-2.0 ppm of the $^1$H NMR represent the aromatic and aliphatic protons (a and b), respectively, from the PS and PIB segments. Addition of the acrylate block was indicated by the appearance of a new resonance at ~2.2 ppm (c), which represents the...
methine proton of PtBA repeat units. The tert-butyl resonances are not visible because they overlap with the gem-dimethyl peaks from the PIB segment. Additionally, the ultimate methine proton at the end of the PtBA segment would normally be visible near 4.1 ppm. However, it was not observed in this sample due to low end group concentration and a small amount of residual solvent (peak x, anisole) that slightly overlaps the peak. The $^{13}$C NMR spectrum also indicates the presence of each of the three polymer segments. Of note are peaks associated with the gem-dimethyl groups and backbone methylene carbons of PIB (located at 32 and 60 ppm, respectively), the aromatic carbons of PS (125-128 and 146 ppm), and the carbonyl (174 ppm) and tert-butyl groups (28 and 80 ppm) of PtBA. The same appropriate resonances can be seen in PtBA$_2$-PIB copolymers.

Table III.2 illustrates the results of the ATRP reactions. Number average molecular weight of the terpolymer, $M_{n, PtBA-PIB-PS}$, was determined by SEC-MALLS. Terpolymer composition was calculated from $^1$H NMR data as described previously.$^{70}$ Molecular weight and compositional data were in excellent agreement for the terpolymers. However, because the peaks of PtBA and PIB overlap in $^1$H NMR, the composition of those copolymers cannot be calculated by NMR. Integrated peak areas of the aromatic and aliphatic regions in the $^1$H-NMR spectra of PIB-PS diblock copolymers, Ar$_c$ and Al$_c$, respectively, and PtBA-PIB-PS triblock terpolymers, Ar$_t$ and Al$_t$, respectively, were used to calculate the composition of the terpolymers. The method is based upon the fact that the IB/St repeat unit ratio is the same in both spectra:

$$\frac{N_{IB,c}}{N_{St,c}} = \frac{N_{IB,t}}{N_{St,t}}$$

Equation III.3
where, \( N_{\text{IB}} \) and \( N_{\text{IB,p}} \) are the number of moles of IB repeat units in the copolymer and terpolymer, respectively, and \( N_{\text{St}} \) and \( N_{\text{St,p}} \) are the number of moles of styrene repeat units in the copolymer and terpolymer, respectively. Because the integrations were calculated from two separate \(^1\text{H} \) NMR experiments, the integration values were normalized using the ratio, \( R_n \), of the peak areas for the aromatic regions of the two spectra, as follows:

\[
R_n = \frac{A_{\text{r}}} {A_{\text{c}}}
\]  

**Equation III.4**

In the copolymer, each styrene repeat unit contributes 5 protons to \( A_{\text{r}} \) and 3 protons to \( A_{\text{c}} \) and each IB repeat unit contributes 8 protons to \( A_{\text{c}} \). Therefore:

\[
N_{\text{St,c}} = K_c \frac{A_{\text{c}}}{5}
\]  

**Equation III.5**

\[
N_{\text{IB,c}} = K_c \frac{1}{8} \left( A_{\text{c}} - \frac{3}{5} A_{\text{r}} \right)
\]  

**Equation III.6**

where, \( K_c \) is the proportionality constant associated with integration of the copolymer spectrum. This constant will be able to be factored out in the final calculations; thus, a numerical value is not necessary.

In the triblock terpolymer, the styrene contribution is identical to that of the copolymer because PtBA does not contribute protons to the aromatic region of the NMR spectrum:

\[
N_{\text{St,i}} = K_i \frac{A_{\text{r}}}{5}
\]  

**Equation III.7**

where, \( K_i \) is the proportionality constant associated with integration of the terpolymer spectrum. Because \( N_{\text{IB}} \) is identical in each sample, \( N_{\text{IB,t}} \) may be obtained from Equation III.8 as follows:
Each tBA repeat unit contributes 12 protons to $A_l$. Therefore, the number of moles of tBA in the triblock terpolymer, $N_{tBA,t}$, is given as follows:

$$N_{tBA,t} = K_t \frac{1}{12} R_N \left[ A_l - R \left( A_l - \frac{3}{5} A_r \right) - \frac{3}{5} A_r \right]$$

Equation III.9

The mole fractions of each type of monomer unit in the triblock terpolymer may now be calculated directly from Equations III.7-III.9. Weight fractions of each type of monomer unit can be calculated using the appropriate repeat unit molecule weights, for example:

$$W_{tBA} = \frac{M_{tBA} N_{tBA,t}}{M_{St} N_{t} + M_{IB} N_{IB,t} + M_{tBA} N_{tBA,t}}$$

Equation III.10

where, $M_{tBA}$, $M_{St}$, and $M_{IB}$ are the repeat unit molecular weights for tert-butyl acrylate, styrene, and IB, respectively.

SEC traces (normalized intensity) representing each stage of the terpolymer synthesis sequence for a PtBA-PIB-PS linear terpolymer and a PtBA₂-PIB star, are shown in Figure III.18. For both samples, molecular weight as determined by MALLS increased with the addition of each block segment, as expected.

An FTIR spectrum (Figure III.19) of the PtBA-PIB-PS triblock was obtained to confirm the incorporation of the PtBA segment and eliminate the possibility of side-chain hydrolysis during the drying process. As illustrated, C=O and C-O stretches, which are characteristic of PtBA appear near 1730 cm\(^{-1}\) and 1150 cm\(^{-1}\), respectively. If the chains had hydrolyzed, slight shifts in these peaks, along with a broadening of the peak near 3000 cm\(^{-1}\) (which would represent the appearance of the acid group), would be observed.\(^{70}\)
Cleavage of tert-Butyl Acrylate Side Chains

An FTIR spectrum (Figure III.20) of the PAA-PIB-PS triblock is illustrated to identify the cleavage of the PtBA side chains to create the hydrophilic poly(acrylic acid). The polymer is characterized by a slight shift in the 1730 cm\(^{-1}\) stretch to 1715 cm\(^{-1}\) and the disappearance of the 1150 cm\(^{-1}\) peak. The peak near 3000 cm\(^{-1}\) also broadened, which is characteristic of the acid functional group, as stated above. This conversion to PAA was verified by \(^{13}\)C NMR spectroscopy because it is often difficult to obtain a good FTIR spectrum of the hydrolyzed polymer. The small peak representing the t-butyl groups that would be present at 28 ppm (Figure III.17) completely disappeared, as illustrated in Figure III.21.

Differential scanning calorimetry was also used to elucidate the cleavage of the tert-butyl groups as well as verify phase separation of the final material. DSC thermograms for PtBA-PIB-PS and PAA-PIB-PS are illustrated in Figure III.22. The glass transition for PIB was observed at -65°C in each sample. The appearance of distinctive transitions at higher temperatures along with the unchanged PIB transition gives a clear indication of phase separation.

Conclusions

In this study, both linear terpolymers and 3-armed stars that contain PAA-PIB-PS blocks were synthesized, along with stars containing only PIB and PAA segments. PIB and PS were created via quasiliving cationic polymerization from 3,3,5-trimethyl-5-chlorohexyl acetate, which contains a monofunctional cationic initiator and a latent hydroxyl functionality. The resulting polymers had target molecular weights and
compositions, as well as relatively low PDIs, as characterized by SEC. Copolymer compositions as determined by $^1$H NMR were in excellent agreement with GPC data.

The hydroxyl group in the initiator was subsequently deblocked and modified to incorporate either one or two ATRP initiating sites using 2-bromopropionyl bromide or a separately synthesized branching agent, respectively. The change from one site to two allowed for the formation of 3-armed stars instead of linear systems. ATRP of tBA was then carried out using CuBr and PMDETA in toluene. The resulting polymers had appropriate molecular weights, and compositions of the terpolymers that contained PS could be calculated from $^1$H NMR integrations. The compositions of polymers that contained only PIB and PtBA segments could not be calculated from NMR because the peaks overlap and there is no reference group present that could be used to ratio the areas from two different spectra. The clean polymers were finally hydrolyzed to yield two- and three-phase systems that contain a hydrophobic segment, a hydrophilic segment, and optionally a crosslinking segment. Verification of the hydrolysis was obtained through FTIR spectroscopy, $^{13}$C NMR analysis, and DSC. A reaction scheme of the entire polymerization process is illustrated in Figure III.23.
Table III.1  $M_n$, PDI, and composition data for PIB and PIB-PS copolymers

<table>
<thead>
<tr>
<th>Entry</th>
<th>PIB $M_n$ (g/mol)</th>
<th>PS $M_n$ (g/mol)</th>
<th>PDI</th>
<th>PIB $M_n$ (g/mol)</th>
<th>PS $M_n$ (g/mol)</th>
<th>Copolymer $M_n$ (g/mol)</th>
<th>PDI</th>
<th>Wt% PIB (NMR)</th>
<th>Wt% PS (NMR)</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>5,000</td>
<td>6,900</td>
<td>1.08</td>
<td>5,000</td>
<td>7,500</td>
<td>14,400</td>
<td>1.36</td>
<td>47.5</td>
<td>52.5</td>
</tr>
<tr>
<td>B</td>
<td>3,500</td>
<td>6,300</td>
<td>1.28</td>
<td>3,500</td>
<td>7,300</td>
<td>13,600</td>
<td>1.34</td>
<td>45.8</td>
<td>54.2</td>
</tr>
<tr>
<td>C</td>
<td>20,000</td>
<td>34,900</td>
<td>1.21</td>
<td>10,000</td>
<td>17,900</td>
<td>52,800</td>
<td>1.25</td>
<td>66.3</td>
<td>33.7</td>
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<td>30,000</td>
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<td>---</td>
<td>---</td>
<td>31,600</td>
<td>1.06</td>
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<td>0</td>
</tr>
<tr>
<td>E</td>
<td>7,500</td>
<td>9,200</td>
<td>1.07</td>
<td>---</td>
<td>---</td>
<td>9,200</td>
<td>1.07</td>
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Table III.2  $M_n$, PDI, and composition data for polymers containing PtBA segments

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<thead>
<tr>
<th>Entry</th>
<th>[C(l)]$_0$</th>
<th>Pzn.</th>
<th>Conv.</th>
<th>Homo/ Copolymer $M_n$ (g/mol)</th>
<th>PDI</th>
<th>Co/ Terpolymer $M_n$ (g/mol)</th>
<th>PDI</th>
<th>Wt% PIB (NMR)</th>
<th>Wt% PS (NMR)</th>
<th>Wt% PtBA (NMR)</th>
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<tbody>
<tr>
<td>A</td>
<td>1:1:1</td>
<td>300</td>
<td>85.6</td>
<td>14,400</td>
<td>1.36</td>
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<td>1.37</td>
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<td>36.2</td>
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<td>B</td>
<td>2:2:1</td>
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<td>41.9</td>
<td>14,400</td>
<td>1.36</td>
<td>21,600</td>
<td>1.38</td>
<td>33.6</td>
<td>36.6</td>
<td>29.7</td>
</tr>
<tr>
<td>C</td>
<td>1:1:1</td>
<td>275</td>
<td>54.0</td>
<td>13,600</td>
<td>1.34</td>
<td>18,100</td>
<td>1.36</td>
<td>37.6</td>
<td>44.7</td>
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</tr>
<tr>
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<td>1.36</td>
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<td>1.36</td>
<td>18,900</td>
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<td>31,600</td>
<td>1.06</td>
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<td>62.1</td>
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<td>1:1:1</td>
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<td>9,200</td>
<td>1.07</td>
<td>14,800</td>
<td>1.54</td>
<td>62.2</td>
<td>0</td>
<td>37.8</td>
</tr>
</tbody>
</table>

$a$ denotes linear terpolymers (PtBA-PIB-PS).
$b$ denotes PIB-PS-initiated star polymers containing 2 PtBA arms (PtBA$_2$-PIB-PS).
$c$ denotes PIB-initiated star polymers containing 2 PtBA arms (PtBA$_2$-PIB). Composition determined by SEC.
Figure III.1  Polymer architectures that have been initiated by TMCHA

Methyl 3,3-dimethyl-4-pentenoate

3,3,5-trimethyl-5-chlorohexyl acetate

Figure III.2  Overall scheme for the synthesis of 3,3,5-trimethyl-5-chlorohexyl acetate
Figure III.3 Overall scheme for the synthesis of 2,2-bis((2-bromo-2-methyl)propionatomethyl)propionyl chloride
Figure III.4 $^1$H NMR spectrum of methyl-3,3-dimethyl-4-pentenoate
Figure III.5 \( ^1H \) NMR spectrum of 5-hydroxy-3,3,5-trimethylhexene
Figure III.6 $^1$H NMR spectrum of 1,5-dihydroxy-3,3,5-trimethylhexane
Figure III.7 $^1$H NMR spectrum of 5-hydroxy-3,3,5-trimethylhexyl acetate
Figure III.8 $^1$H NMR spectrum of 3,3,5-trimethyl-5-chlorohexyl acetate
Figure III.9 $^1$H NMR spectrum of 2,2-bis((2-bromo-2-methyl)propionatomethyl) propionic acid
Figure III.10 $^1$H NMR spectrum of 2,2-bis((2-bromo-2-methyl)propionatomethyl) propionyl chloride
Figure III.11 $^1$H NMR spectrum of PIB-PS copolymer with expansion of the chain ends

(Table III.1, Entry A)
Figure III.12 $^1$H NMR spectrum of PIB with expansion of the chain end (Table III.1, Entry D)
Figure III.13 $^1$H NMR spectrum of deprotected PIB-PS, with inset illustrating the hydroxyl head group (Table III.1, Entry A)
Figure III.14 $^1$H NMR spectrum of brominated PIB-PS, with expansion of the head group region (Table III.1, Entry A)
Figure III.15 $^1$H NMR spectrum of branched PIB, with expansion of the end group region (Table III.1, Entry D)
Figure III.16 $^1$H NMR spectrum of PtBA-PIB-PS (Table III.2, Entry A)
Figure III.17 $^{13}$C NMR spectrum of PtBA-PIB-PS (Table III.2, Entry A)

Figure III.18 SEC traces of PIB and PtBA$_2$-PIB (Table III.2, Entry E [left]) and PIB, PIB-PS, and PtBA-PIB-PS (Table III.2, Entry A [right])

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Figure III.19 FTIR spectrum of PtBA-PIB-PS triblock terpolymer (Table III.2, Entry A)

Figure III.20 FTIR spectrum of PAA-PIB-PS triblock terpolymer (Table III.2, Entry A)
Figure III.21 $^{13}$C NMR spectrum of PAA-PIB-PS terpolymer. The arrow indicates the disappearance of the peak associated with the tert-butyl groups of PtBA.
Figure III.22 DSC thermograms of PtBA-PIB-PS and PAA-PIB-PS (Table III.2, Entry A)
Figure III.23 Overall reaction scheme for the synthesis of PAA-PIB-PS block terpolymers. PAA₂-PIB and PAA₂-PIB-PS star polymers may be prepared in the same manner by introducing 2,2-bis((2-bromo-2-methyl)propionatmethyl)propionyl chloride as a branching agent instead of 2-bromopropionyl bromide.
CHAPTER IV

SYNTHESIS OF POLY(ACRYLIC ACID)-POLY(ISOBUTYL-RYENE-\textit{b}-STYRENE)\textsubscript{2}

STAR POLYMERS FROM A DIFUNCTIONAL CATIONIC INITIATOR

As mentioned in earlier chapters, copolymers can be created using a combination of "living" polymerization techniques if one polymer can be appropriately functionalized to initiate a second polymerization. This may be accomplished by using multi-functional initiators or by appropriately functionalizing the prepolymer. The combination of cationic polymerization with ATRP to form PIB-based star polymers is of specific interest to this work.

A variety of monomers have been polymerized from chemically modified PIB macroinitiators. Several of these reactions involved converting allyl-terminated PIB to a primary alcohol through a hydroboration-oxidation reaction and then introducing a brominated species for ATRP initiation.\textsuperscript{73-75} Other reactions involve capping PIB with a transitional monomer that can initiate ATRP, such as styrene.\textsuperscript{76} Storey and coworkers extended this work to create pentablock terpolymers in which the PS segments are a significant part of the polymer rather than only a few units.\textsuperscript{70} In all of these methods, the PIB tail group was modified to create linear polymers or star-block copolymers. To our knowledge, multi-functional initiators have not been used to combine ATRP and cationic polymerization techniques.

This chapter discusses the use of a difunctional cationic initiator to create triblock copolymers based on PIB. A latent site on the initiator is then deblocked and used to initiate the polymerization of \textit{tert}-butyl acrylate. The result is a three- or four-armed star
polymer that contains two PIB-PS arms, which allow the material to act as a thermoplastic elastomer. ATRP is carried out in a manner similar to the “grafting from” technique for branched polymers. However, the arms will be radiating from one central core to form a mikto-arm star. Hydrolysis of the PtBA segments yields either PAA-(PIB-PS)₂ or PAA₂-(PIB-PS)₂ stars (Figure IV.1). In collaboration with the Mauritz research group, these architectures may be compared to the ABC and A₂B polymers discussed in the previous chapter.

Experimental

Materials

Triethylamine (99.5%), tetrahydrofuran (anhydrous, 99.9%), methylcyclohexane (anhydrous, 99+%), 2,4-lutidine (DMP, 99+%), TiCl₄ (99.9%, packaged under N₂ in Sure-Seal bottles), potassium t-butoxide (95%), 2-bromoisobutyryl bromide (98%), Cu(I)Br (99.999%), anisole (99%), aluminum chloride (99.99%), bromine (99.5+%), manganese(IV) oxide (>99%, particle size 60-230 mesh, aluminum oxide (alumina, standard grade, activated, neutral, Brockmann I, ~150 mesh, 58 Å), DOWEX®-MSC-1 macroporous ion-exchange resin (Dowex sodium, strong cation, 20-50 mesh) and toluene (anhydrous, 99.8%) were used as received from Sigma-Aldrich, Inc. Ethyl ether and hydrochloric acid were used as received from Fisher Scientific. Isobutylene (IB) and CH₃Cl (MeCl) (both BOC, 99.5%) were dried through columns packed with CaSO₄ and CaSO₄/4 Å molecular sieves, respectively. Styrene, 2,6-di-tert-butylpyridine, tert-butyl acrylate (tBA), and 1,3-diisopropylbenzene were distilled from CaH₂ under reduced pressure. 1,1,4,7,7-Pentamethyldiethylenetriamine (PMDETA) (99%) from Sigma-Aldrich and distilled tert-butyl acrylate (tBA) were sparged with dry N₂(g) for 20 min
before use. The synthesis of 3,3,5-trimethyl-5-chlorohexyl acetate\textsuperscript{77} (TMCHA) and 2,2-bis((2-bromo-2-methyl)propionatomethyl)propionyl chloride (BPPC) were outlined in Chapter III.

Real-time ATR-FTIR Monitoring of Block Copolymerization

Block copolymer formation was monitored using the ReactIR 1000 reaction analysis system (light conduit type) (ASI Applied Systems, Millersville, MD) equipped with a DiComp (diamond-composite) insertion probe, a general purpose type PR-11 platinum resistance thermometer (RTD), and a CN76000 series temperature controller (Omega Engineering, Stamford, CT). The light conduit and probe were contained within a glove box (Mbraun Labmaster 130) equipped with a hexane/heptane cold bath. This instrument enabled the collection of infrared spectra of the polymerization components and monitoring of reaction temperature in real time. First, the polymerization of IB was monitored by following the diminution and eventual disappearance of the absorption at 887 cm\textsuperscript{-1} associated with the \textsuperscript{=CH\textsubscript{2}} wag. By plotting peak height of the absorbance vs. time, a monomer decay profile for isobutylene was generated. The peak height at 887 cm\textsuperscript{-1} at any time, \(H_t\), less the reference peak height, \(H_r\), measured prior to addition of monomer to the reactor, was assumed to be directly proportional to isobutylene monomer concentration. Analysis of styrenic monomer depletion was conducted similarly to that of isobutylene, using the peak at 907 cm\textsuperscript{-1} associated with the \textsuperscript{=CH\textsubscript{2}} wag. However, the polymer chains were already living at the time the styrenic monomer was introduced; therefore, \(H_0\) could not be directly measured and instead was set equal to the first-measured height of the 907 cm\textsuperscript{-1} peak immediately after addition of the styrene monomer charge.

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**Synthesis of 1,3-di(2-bromo-2-propyl)-5-(1,1,3,3-tetramethyl-5-acyloxypentyl) benzene (HDCB)**

The difunctional cationic initiator HDCB was synthesized in two steps, and the overall reaction scheme is illustrated in Figure IV.2. A representative procedure for the Friedel-Crafts reaction is as follows: To a 3-necked 100 mL round bottom flask equipped with a magnetic stirbar and contained within a dry box were charged 3.02 g (2.26x10^2 mol) aluminum chloride immediately followed by 4.5 mL (2.37x10^2 mol) 1,3-diisopropyl benzene. The reactor was sealed, removed from the box, and equipped with a condenser column fitted with a calcium chloride drying column that vented into a flask of water. To the stirring mixture was charged 4 g (1.82x10^2 mol) 3,3,5-trimethyl-5-chlorohexyl acetate (TMCHA) slowly via syringe. The reaction was allowed to stir at room temperature until the evolution of gas bubbles ceased and then for 30 min more. The vessel contents were poured into a beaker containing 25 g ice and 5 mL hydrochloric acid. The organic component was extracted with ethyl ether and washed with DI H2O. The layers were separated and the organics were dried over MgSO4. The salts were filtered and excess solvent was removed by vacuum stripping. The product was then separated under vacuum using bulb-to-bulb distillation (Büchi glass oven B-585 [Kugel Rohr], oven temp.=130-150°C, rotation speed=50 rpm) to obtain the clear liquid product 1,3-diisopropyl-5-(1,1,3,3-tetramethyl-5-acyloxypentyl) benzene (30.9% yield).

In order to functionalize the initiator for cationic polymerization, the following bromination procedure was employed:78 To a 3-necked 250 mL round bottom flask equipped with magnetic stirbar were charged 1.95 g (5.6x10^2 mol) 1,3-diisopropyl-5-(1,1,3,3-tetramethyl-5-acyloxypentyl) benzene dissolved in 10 mL methylene chloride,
3.14 g (3.6×10^{-2} mol) manganese(IV) oxide, and 1.00 mL (1.9×10^{-2} mol) bromine. The mixture was allowed to stir at room temperature for 45 min. The solid manganese (IV) oxide was then filtered off. Excess solvent was removed from the liquid portion with a well-trapped vacuum pump to obtain the brown liquid product 1,3-di(2-bromo-2-propyl)-5-(1,1,3,3-tetramethyl-5-acetoxypentyl) benzene in 57% yield. The product was stored in the freezer until use.

*Synthesis of PS-PIB-PS Copolymers Using Quasiliving Cationic Polymerization with Sequential Monomer Addition Techniques*

The following outlines the synthesis of PS-PIB-PS triblock copolymers initiated by HDCB. The DiComp probe was inserted into a 250 mL 4-necked round-bottom flask equipped with a platinum resistance thermometer, a stirring rod and bearing, and a Teflon paddle. The reactor was placed in the hexane/heptane bath and allowed to equilibrate to −70°C. Into the flask were charged 48 mL MCHex (−70°C), 32 mL MeCl (−70°C), 0.03 mL (2.62×10^{-4} mol) 2,4-lutidine, 0.02 mL (8.73×10^{-5} mol) DtBP, and 1.01 g (2×10^{-3} mol) HDCB. This mixture was allowed to stir for 15 min, after which several background spectra were collected. Then 7.2 mL (8.9×10^{-2} mol) IB (−70°C) was added to the flask. Several monomer baseline spectra were obtained, and 1.5 mL (1.7×10^{-2} mol) TiCl₄ (neat and at room temperature) was added to the flask. Once the IB achieved >99% conversion, a 1-2 mL aliquot was taken and added to 10 mL pre-chilled MeOH. The molar concentrations of the reagents were as follows: [IB]₀=1.0 M, [HDCB]₀=2.25×10^{-2} M, [DtBP]₀=9.8×10^{-4} M, [2,4-Lutidine]₀=2.9×10^{-3} M, [TiCl₄]₀=1.5×10^{-1} M. The IB spectral data acquisition was then aborted, and the ReactIR was set up for the styrene reaction. A new set of scans was begun by acquiring several baseline spectra, followed
by the addition of a pre-chilled solution of 13 mL (1.1x10\(^{-1}\) mol) styrene in 61 mL MCHex and 41 mL MeCl. When the reaction reached ~50% conversion, 60 mL pre-chilled MeOH was added to the reactor. The mixture was precipitated into 5x excess MeOH, and the solid product was filtered and dried in a vacuum oven at 25°C. The molar concentrations of styrene in the addition and in the total reaction were 2.0 M and 5.6x10\(^{-1}\) M, respectively.

**Site transformation of the Macroinitiator**

The two-step site transformation was carried out using a variation of a previously reported procedure.\(^72\) A representative procedure is as follows: To deblock the hydroxyl group at the initiator fragment and simultaneously dehydrochlorinate the PS chain end, a three-necked round bottom flask equipped with heating mantle, magnetic stirbar, and condensing column, was charged with PS-PIB-PS (5 g, Mn=28,700 g/mol) dissolved in 60 mL anhydrous THF. The reactor was purged with \(N_2\) and then potassium tert-butoxide (0.12 g, 1.1x10\(^{-3}\) mol) dissolved in 5 mL THF was injected slowly via syringe. The reaction was refluxed 24 h and cooled to room temperature, and the product was precipitated into an excess of 80/20 (v/v) MeOH/DI \(H_2O\). The solid product was filtered and dried in a vacuum oven at room temperature overnight (92% yield).

To incorporate a single bromine functionality onto the polymer chain end, the following procedure was employed: To a 250 mL three-necked round bottom flask equipped with magnetic stirbar, heating mantle, and condenser column were charged hydroxy-functional PS-PIB-PS (2.0 g, Mn=28,700 g/mol), 40 mL THF, 0.09 mL 2-bromoisobutryl bromide (7.3x10\(^{-4}\) mol), and 0.1 mL triethylamine (7.3x10\(^{-4}\) mol). The reaction was refluxed for 48 h (adding THF as needed to maintain constant reaction
volume), and the mixture was precipitated into excess MeOH/DI H$_2$O (80/20 v/v). The solid product was dried overnight in a vacuum oven at room temperature to remove excess solvent (94% yield).

To incorporate dual bromine functionalities, the 2-bromoisobutyryl bromide was replaced with the branching agent 2,2-bis((2-bromo-2-methyl)propionatomethyl)propionyl chloride (BPPC). A representative procedure is outlined as follows: The hydroxyl functionality of the initiator was deblocked as described above. To a 250 mL three-necked round bottom flask equipped with magnetic stirbar, heating mantle, N$_2$ bubbler, and condenser column were charged hydroxy-functional PS-PIB-PS (2.0 g, Mn=28,700 g/mol), 60 mL THF, 0.31 g (6.8x10$^{-4}$ mol) BPPC, and 0.10 mL triethylamine (7.3x10$^{-4}$ mol). The reaction was refluxed for 48 h (adding THF as needed to maintain constant reaction volume). The mixture was precipitated into excess MeOH/DI H$_2$O (80/20 v/v). The solid product was dried overnight in a vacuum oven at room temperature to remove excess solvent (95% yield).

**Synthesis of PS-PIB-PS based stars**

A representative procedure for ATRP polymerization to create PtBA-(PIB-PS)$_2$ stars is as follows: To a 100 mL Kjeldahl style Schlenk flask, equipped with magnetic stirbar and contained within a dry box, were charged 4.1x10$^{-2}$ g (2.87x10$^{-4}$ mol) CuBr, 2.3 g (1.6x10$^{-4}$ mol) PS-PIB-PS, 15 mL toluene, 0.30 mL anisole, and 1.03 g (8.0x10$^{-3}$ mol) tBA (sparged with N$_2$ for 30 min prior to use). The mixture was allowed to stir to solubilize the macroinitiator. The flask was then sealed with a rubber septum and cable tie and removed from the dry box. The flask was sparged with N$_2$ for 5 minutes. Then, 6.0x10$^{-2}$ mL (2.87x10$^{-4}$ mol) PMDETA (sparged with N$_2$ prior to use) was added to the
reactor via syringe. An initial aliquot (0.1 mL, t=0) was taken and quenched by freezing in liquid nitrogen (LN2), and the reactor was submerged in an oil bath preheated to 90°C. Additional aliquots (0.1 mL) were taken at predetermined intervals via a N2 purged syringe for kinetic analysis, and the reaction was quenched in LN2 after 5.5 h. The polymer, dissolved in methylene chloride, was passed through a column consisting of a neutral alumina bottom layer and a DOWEX® MSC-1 ion-exchange resin top layer and precipitated into excess MeOH/DI H2O (80/20 v/v). The solid product was collected by vacuum filtration and dried under vacuum at room temperature overnight (96% yield).

This procedure was modified slightly to create a 4-armed star containing 2 PtBA arms. An example is as follows: To a 100 mL Kjeldahl style Schlenk flask, equipped with magnetic stirbar and contained within a dry box, were charged 4.0x10^{-2} g (2.8x10^{-4} mol) CuBr, 2.1 g (1.4x10^{-4} mol; 2.8x10^{-4} mol CE) PS-PIB-PS, 10 mL toluene, 0.20 mL anisole, and 1.81 g (1.4x10^{-2} mol) tBA (sparged with N2 for 30 min prior to use). The mixture was allowed to stir to solubilize the macroinitiator. The flask was then sealed with a rubber septum and cable tie and removed from the dry box. The flask was sparged with N2 for 5 minutes. Then, 6.0x10^{-2} mL (2.87x10^{-4} mol) PMDETA (sparged with N2 prior to use) was added to the reactor via syringe. An initial aliquot (0.1 mL, t=0) was taken and quenched by freezing in liquid nitrogen (LN2), and the reactor was submerged in an oil bath preheated to 90°C. Additional aliquots (0.1 mL) were taken at predetermined intervals via a N2 purged syringe for kinetic analysis, and the reaction was quenched in LN2 after 5.5 h. The polymer, dissolved in methylene chloride, was passed through a column consisting of a neutral alumina bottom layer and a DOWEX® MSC-1 ion-exchange resin top layer and precipitated into excess MeOH/DI H2O (80/20 v/v).
The solid product was collected by vacuum filtration and dried under vacuum at room temperature overnight (96% yield).

Monomer conversion for all polymerizations was determined by $^1$H-NMR using anisole as an internal standard. Integration of the methoxy resonance in anisole (3.75 ppm) and the vinyl resonance in tBA (5.75-5.60 ppm) at predetermined time intervals allowed for the quantitative determination of tBA conversion. The aliquots were subsequently passed through a column of neutral alumina, vacuum dried, and analyzed by SEC.

*Cleavage of tert-Butyl Acrylate Side Chains*

The poly(tert-butyl acrylate) segments were converted to poly(acrylic acid) by cleaving the side chains. A representative procedure is as follows: A thin layer of PtBA-PIB-PS was spread in a heat-resistant dish and placed in a vacuum oven that was preheated to 130°C. After 48h, the dish was removed, and the polymer was cooled to room temperature to be collected.

*Size Exclusion Chromatography (SEC)*

Molecular weights and polydispersity index (PDI) of the purified polymers were determined using a SEC system equipped with a Waters Alliance 2690 Separations Module, an on-line multi-angle laser light scattering (MALLS) detector operating at 690nm (MiniDAWN™, Wyatt Technology Inc.), an interferometric refractometer (Optilab DSP™, Wyatt Technology Inc.) operating at 35°C, and one set of PLgel™ (Polymer Laboratories Inc.) SEC columns connected in series. Tetrahydrofuran (THF), freshly distilled from CaH$_2$, was employed as the mobile phase and was delivered at a flow rate of 1.0 mL/min. Sample concentrations were approximately 7 mg/mL with an
injection loop volume of 100μL. Detector signals were simultaneously recorded and absolute molecular weights and polydispersity indices (PDIs) were calculated using ASTRA ™ software (Wyatt Technology Inc). The dn/dc value was calculated from the signal response of the Optilab DSP, assuming 100% mass recovery from the columns.

Proton and Carbon Magnetic Resonance Spectroscopy (H and 13C-NMR)

1H and 13C-NMR were used for the structural elucidation of the copolymers and block copolymer composition. 13C-NMR was also used to quantitatively monitor the disappearance of the tert-butyl ester groups in the deprotection of the polymers. Solution 1H and 13C-NMR spectra were obtained on a Varian Unity 300 MHz spectrometer using 5 mm o.d. tubes with sample concentrations of 5-7% and 15-20% (w/v), respectively, in deuterated chloroform (CDCl3) (Aldrich Chemical Co.) containing 0.03% (v/v) tetramethylsilane as an internal reference. The 1H and 13C-NMR spectra were the Fourier transformation of 32 and 1000 transients, respectively. 13C-NMR spectra of the PAA-PS-PIB-PS-PAA BCPs were obtained using sample concentrations of 20% (w/v), in deuterated methyl sulfoxide/deuterated chloroform (10/90 v/v) (Aldrich Chemical Co.) containing 0.03% (v/v) tetramethylsilane as an internal reference.

Fourier Transform-Infrared (FT-IR) Spectroscopy

FT-IR spectroscopy was used to qualitatively monitor the disappearance of the tert-butyl ester groups in the deprotection of the polymer segments. FT-IR spectra were obtained using a Bruker Equinox 55 FT-IR spectrometer using 32 scans at 4 cm⁻¹ resolution. Polymer samples were cast onto a NaCl plate from THF and dried with N2(g) before analysis. Data were collected using OPUS NT IR software.

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Differential Scanning Calorimetry

Thermal transitions of the polymers were studied using a TA DSC Q100 analysis system and analyzed with TA Universal Analysis software. The samples were heated to 150°C, quenched to -90°C, and heated to 150°C at a rate of 10°C/min. The glass transition was taken as the temperature corresponding to transition mid-point in the first derivative curve.

Results and Discussion

Synthesis of 1,3-di(2-bromo-2-propyl)-5-(1,1,3,3-tetramethyl-5-acetyloxypentyl) benzene (HDCB)

3,3,5-Trimethyl-5-chlorohexyl acetate was reacted with 1,3-diisopropylbenzene (DIPB) ($^1$H NMR illustrated in Figure IV.3) in a Friedel-Crafts reaction to create a difunctional cationic initiator. DIPB also served as the solvent for the reaction and was used in slight excess. However, it is difficult to separate the solvent from the reaction product; thus, very little excess solvent is used. The product is a yellow liquid after extraction with ethyl ether but becomes clear upon purification. Bulb-to-bulb distillation was used to separate the product. Two trap flasks were used in the set-up, with one trap placed inside the oven and one outside the oven. The outer trap was cooled with dry ice, and the oven temperature was ramped from 130°C to 150°C to collect the clear product. The $^1$H NMR spectrum of the product is illustrated in Figure IV.4. The triplet near 4.1 ppm (b) and the singlet at ~2 ppm (a) correspond to the methylene protons nearest the O atom and the methyl protons of the acetate group, respectively, of the TMCHA chain and can be verified by comparing the spectrum to that of TMCHA. The other peaks that are characteristic of TMCHA have shifted slightly due to new chemical environments. One
new peak that is of importance is the multiplet present at 2.9 ppm (i), which represents the methine protons of the isopropyl groups. Upon integration, this peak was found to be in a 1:1 ratio with the triplet at 4.1 ppm, which verifies the removal of any residual 1,3-diisopropylbenzene to leave pure product.

In order to introduce cationic initiating sites, the 1,3-diisopropyl-5-(1,1,3,3-tetramethyl-5-acetyloxypentyl) benzene intermediate product was brominated in the presence of manganese(IV) oxide. Upon introduction of bromine to the reactor, a large amount of HBr gas was formed, which was allowed to vent from the reactor directly into the fume hood. The product (1H NMR in Figure IV.5) is a viscous brown liquid. The primary change in the NMR spectrum is the disappearance of the peak associated with the methine protons, which have been replaced by the halogen.

Synthesis of PS-PIB-PS Copolymers Using Quasiliving Cationic Polymerization with Sequential Monomer Addition Techniques

ATRP macroinitiators containing a PIB center block and PS outer blocks were synthesized via quasiliving cationic polymerization using HDCB as the initiator and TiCl₄ as the coinitiator in a MCHex/MeCl (60/40 v/v) solvent system with DMP and DtBP as Lewis base additive and proton trap, respectively, at -70°C. At >99% conversion of the IB as determined by ATR-FTIR monitoring, an aliquot was removed for PIB block analysis by SEC, and then a 2.0 M charge of styrene in MCHex/MeCl was added to the reactor. The reaction was quenched at ~50% styrene conversion with prechilled methanol. The styrene polymerization was short-stopped in this manner to avoid electrophilic aromatic substitution reactions that can occur at high conversions. SEC analysis of the isolated polymers showed that there were no high molecular weight

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peaks that would indicate chain coupling, and thus this side reaction was avoided. The polymers also had fairly narrow PDIs, which indicates well-defined block copolymers.

Table IV.1 lists molecular weight and compositional data for the PIB intermediate blocks and PS-PIB-PS copolymers. Number average molecular weight of the PIB blocks by SEC ($M_{n,PIB(SEC)}$) was higher than theoretical, indicating low initiator efficiency. This phenomenon is expected because HDCB is created from the TMCHA initiator, and we see the same low efficiency with TMCHA. This is apparently related to complexation of TiCl$_4$ with the carbonyl group in the initiator. The initiation efficiency of HDCB increases as the monomer to growing chain end ratio increases, as does TMCHA.

Number average molecular weight of the PS block from SEC ($M_{n,PS(SEC)}$) was calculated as the difference in molecular weight between the overall block copolymer ($M_{n,PIB-PS(SEC)}$) and $M_{n,PIB(SEC)}$. Figure IV.6 illustrates the $^1$H NMR spectrum of the PS-PIB-PS copolymer, and the inset of the spectrum illustrates the chain end region of the triblock system. The two peaks near 4.4 ppm have comparable areas, as would be expected for this polymer architecture. The peaks are not very well defined because the end group concentration is very low, due to the molecular weight of the sample. Copolymer composition was determined by comparison of the relative intensities of the aromatic and aliphatic resonances of the $^1$H NMR spectrum, as described previously for PS-PIB-PS systems.\(^{42}\) $W_{PS(\text{nmr})}$ was calculated using a variation of a previously reported equation (Equation III.1),\(^{42}\)

$$M_{n,PS(\text{nmr})} = M_{n,PIB(SEC)} \cdot \frac{W_{PS(\text{nmr})}}{(100 - W_{PS(\text{nmr})})}$$

Equation IV.1

where $W_{PS(\text{nmr})}$ is the weight percent of PS as determined by $^1$H NMR of the copolymer (Eq. III.2). The weight percent of PIB is calculated by subtracting the weight percent of
PS from 100. The block length of each PS segment can also be calculated, as illustrated in Equation IV.2.

\[
M_{n,PS(nmr)} = M_{n,PIB(SEC)} \cdot \frac{W_{PS(nmr)}}{2(100 - W_{PS(nmr)})}
\]

Equation IV.2

As shown in Table 1, the two measures of PS block molecular weight were in excellent agreement.

**Site Transformation of the Macroinitiator**

The end groups of the PS-PIB-PS macroinitiators were transformed in two steps to allow for ATRP initiation. The first involved application of the strong base potassium tert-butoxide to de-protect the hydroxyl functionality of the initiator fragment and simultaneously dehydrobrominate the tail group. The base was introduced to the copolymer as a slurry in THF, and the mixture became homogeneous as the reaction proceeded. As shown in the \(^1\)H NMR spectrum of the product of this reaction (Figure IV.7), the peaks associated with the protected hydroxyl group in the initiator and the sec-benzyl chloride tail group have disappeared, and a new peak at ~3.75 ppm has appeared. This peak is associated with the methylene protons of the initiator fragment nearest to the hydroxyl group, and they correspond with the analogous protons of 1,5-dihydroxy-3,3,5-trimethylhexane, which is the product of the hydroboration-oxidation reaction in the initiator synthesis.

The second step of site transformation involved the incorporation of an \(\alpha\)-bromo carbonyl species, such as 2-bromoisobutyryl bromide, for ATRP initiation. This reaction was facile but slow; 48 h were needed for complete conversion. Incorporation of 2-bromoisobutyryl bromide produces an \(A_2B\) three-armed star, and the \(^1\)H NMR spectrum of the product is shown in Figure IV.8. This compound was used in the synthesis of
PtBA-(PIB-PS)$_2$ terpolymers. The inset of the NMR spectrum illustrates the shift of the methylene protons in the original initiator fragment downfield to near 4.4 ppm. Incorporation of the branching agent BPPC instead of 2-bromoisobutryl bromide produces a macroinitiator capable of forming a 4-armed star ($^1$H NMR shown in Figure IV.9). The inset of the plot illustrates a peak at 4.4 ppm (a), which represents the methylene protons of the initiator fragment (as in the monofunctional sample), and a peak associated with the methylene protons of the branching agent near 5.1 ppm (b).

**Synthesis of PtBA-PIB-PS Linear Terpolymers and Stars Using ATRP**

*Tert*-butyl acrylate was polymerized at 90°C under ATRP conditions in a N$_2$ atmosphere, using PMDETA as the nitrogen-containing ligand, Cu(I)Br as the catalyst, toluene as solvent, and anisole as an internal standard to monitor monomer conversion. The initiator was a PS-PIB-PS triblock copolymer modified as described above. Aliquots were removed at predetermined intervals to monitor conversion and for SEC analysis. Upon introduction of PMDETA, the reaction turned light green. As higher conversion was obtained, a darker green color developed. The overall conversion is low in these samples because the polymers are high molecular weight; thus, the chain end concentration is low. Longer polymerization times, as well as using more concentrated reactions, would have given higher conversion. However, the ATRP was successful.

Figures IV.10 and IV.11 show the $^1$H and $^{13}$C NMR spectra, respectively, of a representative terpolymer (PtBA$_2$-(PIB-PS)$_2$). The resonances between 6.2-7.3 ppm and 0.5-2.0 ppm of the $^1$H NMR represent the aromatic and aliphatic protons (a and b), respectively, from the PS and PIB segments. Addition of the acrylate block was indicated by the appearance of a new resonance at ~2.2 ppm (c), which represents the
methine proton of PtBA repeat units. The tert-butyl resonances are not visible because they overlap with the gem-dimethyl peaks from the PIB segment. Additionally, the ultimate methine proton at the end of the PtBA segment would normally be visible near 4.1 ppm. However, it was not observed in this sample due to low end group concentration. The $^{13}$C NMR spectrum also indicates the presence of each of the three polymer segments. Of note are peaks associated with the gem-dimethyl groups and backbone methylene carbons of PIB (located at 32 and 60 ppm, respectively), the aromatic carbons of PS (125-128 and 146 ppm), and the $t$-butyl groups (28 and 80 ppm) of PtBA. The peaks attributed to PtBA are very small, however, and only the peak at 28 ppm may be seen. The same appropriate resonances can be seen in PtBA-(PIB-PS)$_2$ copolymers.

Table III.2 illustrates the results of the ATRP reactions. Number average molecular weight of the terpolymer, $M_{n,\text{PtBA-PIB-PS}}$, was determined by SEC-MALLS. Terpolymer composition was calculated from $^1$H NMR data as described previously (Chapter III). Integrated peak areas of the aromatic and aliphatic regions in the $^1$H-NMR spectra of PS-PIB-PS triblock copolymers, $A_r$ and $A_l$, respectively, and PtBA-PIB-PS triblock terpolymers, $A_{rt}$ and $A_{lt}$, respectively, were used to calculate the composition of the terpolymers.

SEC traces (normalized intensity) representing each stage of the terpolymer synthesis sequence for a PtBA$_2$-(PIB-PS)$_2$ star are shown in Figure IV.12. Molecular weight as determined by MALLS increases with the addition of each block segment, as expected.
An FTIR spectrum (Figure IV.13) of the PtBA₂-(PIB-PS)₂ star was obtained to confirm the incorporation of the PtBA segment and eliminate the possibility of side-chain hydrolysis during the drying process. As illustrated, the C=O and C-O stretches appear near 1730 cm⁻¹ and 1150 cm⁻¹, respectively, which are characteristic of PtBA. If the chains had hydrolyzed, slight shifts in these peaks, along with a broadening of the peak near 3000 cm⁻¹ (which would represent the appearance of the acid group), would be observed.⁷⁰

Cleavage of tert-Butyl Acrylate Side Chains

An FTIR spectrum (Figure IV.14) of the PAA₂-(PIB-PS)₂ star is illustrated to identify the cleavage of the PtBA side chains to create the hydrophilic poly(acrylic acid). The polymer is characterized by a slight shift in the 1730 cm⁻¹ stretch to 1715 cm⁻¹ and the disappearance of the 1150 cm⁻¹ peak. This conversion to PAA was verified by¹³C NMR spectroscopy. The small peak representing the t-butyl groups that would be present at 28 ppm (Figure IV.11) completely disappeared, as illustrated in Figure IV.15.

Differential scanning calorimetry was performed on the hydrolyzed star polymers to verify cleavage of the t-butyl ester groups and elucidate phase separation. Figure IV.16 illustrates the DSC curve for a PAA₂-(PIB-PS)₂ star polymer. The glass transition of PIB is visible near -65°C, and the transition of PAA is seen just above 100°C. The presence of separate transitions illustrates complete phase separation.

Conclusions

In this study, both 3 and 4-armed stars that contain phase-separated segments of PAA, PIB, and PS were synthesized. PIB and PS were created via quasiliving cationic polymerization from 1,3-di(2-bromo-2-propyl)-5-(1,1,3,3-tetramethyl-5-acetyloxypropyl)
benzene (HDCB), which contains a difunctional cationic initiator and a latent hydroxyl functionality. The resulting polymers had target compositions, though the molecular weight was high, as well as relatively low PDIs, as characterized by SEC. Copolymer compositions as determined by $^1$H NMR were in excellent agreement with GPC data.

The hydroxyl group in the initiator was subsequently deblocked and modified to incorporate either one or two ATRP initiating sites using 2-bromoisobutyryl bromide or a separately synthesized branching agent, respectively. The change from one site to two allowed for the formation of 4-armed stars instead of 3-armed systems. ATRP of tBA was then carried out using CuBr and PMDETA in toluene. The resulting polymers had appropriate molecular weights, and compositions of the terpolymers could be calculated from $^1$H NMR integrations. The clean polymers were finally hydrolyzed to yield three-phase thermoplastic elastomers that contain a hydrophobic segment, a hydrophilic segment, and a crosslinking segment. Verification of the hydrolysis was obtained through FTIR spectroscopy, DSC, and $^{13}$C NMR analysis.
### Table IV.1 \( M_{\text{n}} \), PDI, and composition data for PS-PIB-PS triblock copolymers.

<table>
<thead>
<tr>
<th>Entry</th>
<th>PIB ( M_{\text{n,Tb}} ) (g/mol)</th>
<th>PIB ( M_{\text{n,SEC}} ) (g/mol)</th>
<th>PS ( M_{\text{n,Tb}} ) (g/mol)</th>
<th>PS ( M_{\text{n,SEC}} ) (g/mol)</th>
<th>PS ( M_{\text{n,NMR}} ) (g/mol)</th>
<th>Copolymer ( M_{\text{n}} ) (g/mol)</th>
<th>PDI</th>
<th>Wt% PIB (NMR)</th>
<th>Wt% PS (NMR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>30,000</td>
<td>70,700</td>
<td>10,000</td>
<td>5,400</td>
<td>8,000</td>
<td>75,400</td>
<td>1.19</td>
<td>89.8</td>
<td>10.2</td>
</tr>
<tr>
<td>B</td>
<td>10,000</td>
<td>33,300</td>
<td>5,000</td>
<td>22,300</td>
<td>23,600</td>
<td>55,600</td>
<td>1.33</td>
<td>58.8</td>
<td>41.2</td>
</tr>
<tr>
<td>C</td>
<td>3,000</td>
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<td>3,000</td>
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<td>17,300</td>
<td>28,700</td>
<td>1.26</td>
<td>42.3</td>
<td>57.7</td>
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</table>

### Table IV.2 \( M_{\text{n}} \), PDI, and composition data for star polymers containing PtBA segments.

<table>
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<tr>
<th>Entry</th>
<th>[Ligand] ( _0 ): Pzn.</th>
<th>([\text{Cu(I)Br}]_0): Time (min)</th>
<th>Conv. (%)</th>
<th>Copolymer ( M_{\text{n,SEC}} ) (g/mol)</th>
<th>PDI</th>
<th>Terpolymer ( M_{\text{n,SEC}} ) (g/mol)</th>
<th>PDI</th>
<th>Wt% PIB (NMR)</th>
<th>Wt% PS (NMR)</th>
<th>Wt% PtBA (NMR)</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>1:1:1</td>
<td>242</td>
<td>3.1</td>
<td>75,400</td>
<td>1.19</td>
<td>76,300</td>
<td>1.19</td>
<td>89.9</td>
<td>8.1</td>
<td>2.1</td>
</tr>
<tr>
<td>B</td>
<td>2:2:1</td>
<td>229</td>
<td>5.0</td>
<td>55,600</td>
<td>1.53</td>
<td>59,400</td>
<td>1.54</td>
<td>56.3</td>
<td>39.5</td>
<td>4.2</td>
</tr>
<tr>
<td>C</td>
<td>1:1:1</td>
<td>272</td>
<td>5.4</td>
<td>28,700</td>
<td>1.26</td>
<td>30,900</td>
<td>1.28</td>
<td>38.8</td>
<td>52.3</td>
<td>8.9</td>
</tr>
<tr>
<td>D</td>
<td>2:2:1</td>
<td>254</td>
<td>15.4</td>
<td>28,700</td>
<td>1.26</td>
<td>27,100</td>
<td>1.26</td>
<td>46.8</td>
<td>49.3</td>
<td>3.9</td>
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<tr>
<td>E</td>
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<td>1.53</td>
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<td>1.56</td>
<td>50.3</td>
<td>35.3</td>
<td>14.4</td>
</tr>
<tr>
<td>F</td>
<td>4:4:1</td>
<td>268</td>
<td>12.8</td>
<td>55,600</td>
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<td>56,600</td>
<td>1.53</td>
<td>54.3</td>
<td>38.1</td>
<td>7.6</td>
</tr>
</tbody>
</table>

\( a \) denotes \( A_2B_2 \) stars \([\text{PtBA}_2-(\text{PIB-PS})_2]\).  
\( b \) denotes \( A_2B \) stars \([\text{PtBA}-(\text{PIB-PS})_2]\).
Figure IV.1 Polymer architectures that may be synthesized from HDCB

Figure IV.2 Overall scheme for the synthesis of 1,3-di(2-bromo-2-propyl)-5-(1,1,3,3-tetramethyl-5-acetyloxypentyl) benzene (HDCB)
Figure IV.3 $^1$H NMR spectrum of 1,3-diisopropylbenzene
Figure IV.4 $^1$H NMR spectrum of 1,3-diisopropyl-5-(1,1,3,3-tetramethyl-5-acetyloxy-pentyl) benzene

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Figure IV.5 $^1$H NMR spectrum of 1,3-di(2-bromo-2-propyl)-5-(1,1,3,3-tetramethyl-5-acetyloxypropyl) benzene (HDCB)
Figure IV.6 $^1$H NMR spectrum of PS-PIB-PS with expansion of the chain ends (Table IV.1, Entry C)
Figure IV.7 $^1$H NMR spectrum of deprotected PS-PIB-PS with expansion of the initiating head group (Table IV.1, Entry C)
Figure IV.8 $^1$H NMR spectrum of PS-PIB-PS with expansion of the ATRP initiating site (Table IV.1, Entry C)
Figure IV.9 $^1$H NMR spectrum of branched PS-PIB-PS for dual ATRP initiation (Table IV.1, Entry C)
Figure IV.10 $^1$H NMR spectrum of PtBA$_2$-(PIB-PS)$_2$ (Table IV.2, Entry B)
Figure IV.11 $^{13}$C NMR spectrum of PtBA$_2$-(PIB-PS)$_2$ (Table IV.2, Entry B)
Figure IV.12 SEC traces of each segment of a star polymer: PIB, PS-PIB-PS, and PtBA$_2$-(PIB-PS)$_2$ (Table IV.2, Entry D)
Figure IV.13 FTIR spectrum of a PtBA\textsubscript{2}-(PIB-PS\textsubscript{2}) star polymer (Table IV.2, Entry B)
Figure IV.14 FTIR spectrum of star polymer after hydrolysis (PAA$_2$-(PIB-PS)$_2$) (Table IV.2, Entry B)
Figure IV.15 $^{13}$C NMR spectrum of PAA$_2$-(PIB-PS)$_2$ (Table IV.2, Entry B). The arrow indicates the disappearance of the peak at 28 ppm, which is associated with the $t$-butyl groups of PtBA.
Figure IV.16 DSC thermogram of a PAA$_2$-(PIB-PS)$_2$ star
APPENDIX

SYNTHESIS OF A PtBA-PIB-PS TERPOLYMER FROM AN INITIATOR CONTAINING A PRIMARY CHLORIDE

During our studies with the initiator 3,3,5-trimethyl-5-chlorohexyl acetate, low initiation efficiency was observed. As the target molecular weight of the samples was increased, the efficiency improved. This phenomenon has been discussed by other authors\textsuperscript{71,79} who report that this is caused by interaction of the carbonyl group with TiCl\textsubscript{4}. In order to alleviate this issue, we proposed to replace the acetate group of the initiator with a primary chloride. It is known that primary halides are generally ineffective initiators for cationic polymerizations because they are formed too slowly or in very low concentrations. This is due to the instability of the charge upon ionization. There have been a few reports of initiation by primary or secondary halides,\textsuperscript{80-82} but initiation more likely involves some other mechanism, such as adventitious water. Thus, the primary chloride to be incorporated into the initiator would not react to create a difunctional species.

This section discusses the synthesis of the initiator 3,3,5-Trimethyl-1,5-dichlorohexane (TMDCH) and its effectiveness in producing a linear terpolymer (PtBA-PIB-PS). The initiator is created from an intermediate product of TMCHA and contains a tertiary chloride that may initiate the cationic polymerization of IB and styrene. The primary chloride will then be converted to an ATRP initiating site for the synthesis of PtBA. From this experiment, the effectiveness of TMDCH as a cationic initiator can be compared to that of TMCHA.
Materials

Methyl 3,3-dimethyl-4-pentenoate was used as received from TCI America. Methyl magnesium bromide (3 M solution in diethyl ether), borane-tetrahydrofuran (THF) complex (1 M solution in THF), hydrogen peroxide (30 wt.% solution in water), triethylamine (99.5%), methylcyclohexane (anhydrous, 99+%), 2,4-lutidine (DMP, 99+%), TiCl4 (99.9%, packaged under N2 in Sure-Seal bottles), potassium t-butoxide (95%), 2-bromoisobutyryl bromide (98%), thionyl chloride (>99%), Cu(I)Br (99.999%), anisole (99%), aluminum oxide (alumina, standard grade, activated, neutral, Brockmann I, ~150 mesh, 58 Å), DOWEX®MSC-1 macroporous ion-exchange resin (Dowex sodium, strong cation, 20-50 mesh) and toluene (anhydrous, 99.8%) were used as received from Sigma-Aldrich, Inc. Isobutylene (IB) and CH3Cl (MeCl) (both BOC, 99.5%) were dried through columns packed with CaSO4 and CaSO4/4 Å molecular sieves, respectively. Ammonium chloride, sodium hydroxide, and ethyl ether were used as received from Fisher Chemical Co. Styrene, 2,6-di-tert-butylpyridine, tert-butyl acrylate, and THF were distilled from CaH2 under reduced pressure. 1,1,4,7,7-Pentamethyldiethylenetriamine (PMDETA) (99%) from Sigma-Aldrich and distilled tert-butyl acrylate (tBA) were sparged with dry N2(g) for 20 min before use.

Real-time ATR-FTIR Monitoring of Block Copolymerization

Block copolymer formation was monitored using the ReactIR 1000 reaction analysis system (light conduit type) (ASI Applied Systems, Millersville, MD) equipped with a DiComp (diamond-composite) insertion probe, a general purpose type PR-11 platinum resistance thermometer (RTD), and a CN76000 series temperature controller.
This instrument enabled the collection of infrared spectra of the polymerization components and monitoring of reaction temperature in real time. First, the polymerization of IB was monitored by following the diminution and eventual disappearance of the absorption at 887 cm$^{-1}$ associated with the $\equiv$CH$_2$ wag. By plotting peak height of the absorbance vs. time, a monomer decay profile for isobutylene was generated. The peak height at 887 cm$^{-1}$ at any time, $H_t$, less the reference peak height, $H_r$, measured prior to addition of monomer to the reactor, was assumed to be directly proportional to isobutylene monomer concentration. Analysis of styrenic monomer depletion was conducted similarly to that of isobutylene, using the peak at 907 cm$^{-1}$ associated with the $\equiv$CH$_2$ wag. However, the polymer chains were already living at the time the styrenic monomer was introduced; therefore, $H_0$ could not be directly measured and instead was set equal to the first-measured height of the 907 cm$^{-1}$ peak immediately after addition of the styrene monomer charge.

**Synthesis of 3,3,5-Trimethyl-1,5-dichlorohexane (TMDCH)**

The initiator, 3,3,5-trimethyl-1,5-dichlorohexane (TMDCH), was synthesized by chlorinating an intermediate product of TMCHA. The overall reaction scheme is illustrated in Figure V.1 and a representative procedure was as follows: To a 250 mL, three-necked round-bottom flask equipped with a mechanical stirrer, nitrogen inlet/outlet, and ice bath was charged 0.471 mol methyl magnesium bromide (157 mL of a 3M solution in diethyl ether). Methyl 3,3-dimethyl-4-pentenoate (15 mL, 9.4x10$^{-2}$ mol) was added dropwise via syringe over 30 min. The reaction was stirred for 1.5 hours at 0°C, and then removed from the ice bath and stirred overnight at room temperature. The vessel contents were poured into a mixture of 300 g ice and 25 g (0.47 mol) ammonium
chloride contained in a beaker. The resulting slurry was transferred to a separatory funnel; the beaker was rinsed with de-ionized H$_2$O and diethyl ether, and the rinses were added to the separatory funnel. The layers were separated and the organic layer was dried over magnesium sulfate, filtered, and vacuum stripped to yield the liquid product, 5-hydroxy-3,3,5-trimethylhexene, in 68% yield (9.1 g).

Hydroboration-oxidation was carried out as follows: Borane-THF complex (70 mL, 7.0x10$^{-2}$ mol) was charged to a 250 mL three-necked round-bottom flask equipped with mechanical stirrer, external ice/water bath, and nitrogen inlet/outlet. 5-Hydroxy-3,3,5-trimethylhexene (5.0 g, 3.5x10$^{-2}$ mol), dissolved in 22.5 mL THF (20 wt.% solution), was added dropwise via syringe to the reactor over 30 min. The reaction proceeded for 5 h. Aqueous NaOH solution (23.5 mL, 3 M solution) was added to the reactor via syringe at a rate such that the temperature of the reactor did not exceed 45°C (~45 min). Then 8 g H$_2$O$_2$ (30 wt% solution in water) was added quickly to the reactor, and the reaction was allowed to proceed for an additional 75 min. The aqueous phase was saturated with potassium carbonate, and the organic layer was separated and washed several times with DI H$_2$O and dried over magnesium sulfate. Solvent was removed by vacuum stripping, and the liquid product, 1,5-dihydroxy-3,3,5-trimethylhexane (80% yield, 4.5 g), was dried under vacuum at ambient temperature.

Chlorination of the hydroxyl groups was carried out as follows: To a 3-necked 250 mL round bottom flask equipped with a magnetic stirbar and condenser column fitted with a calcium chloride vent to a water trap was charged 10 g (6.25x10$^{-2}$ mol) 1,5-dihydroxy-3,3,5-trimethylhexane. The reactor was purged with N$_2$(g) and 3 mL (2.16x10$^{-2}$ mol) TEA was added via syringe. Then 30 mL (4.12x10$^{-1}$ mol) thionyl chloride was
added slowly via syringe, using N₂ to keep positive pressure in the reactor. The mixture was stirred at room temperature for 48 h, and 100 mL of methylene chloride was added to dissolve the product. The mixture was placed in a separatory funnel, and DI H₂O was added slowly until no more bubbles persisted. The organic layer was separated and dried over MgSO₄; the salts were then filtered off and excess solvent was removed by vacuum stripping to yield the final product 3,3,5-trimethyl-1,5-dichlorohexane (TMDCH) (82% yield).

Synthesis of PIB-PS Copolymers Using Quasiliving Cationic Polymerization with Sequential Monomer Addition Techniques

The following outlines the synthesis of PIB-PS copolymers initiated by TMDCH. The DiComp probe was inserted into a 250 mL 4-necked round bottom flask equipped with a platinum resistance thermometer, a stirring rod and bearing, and a Teflon paddle. The reactor was placed in the hexane/heptane bath and allowed to equilibrate to -70°C. Into the flask were charged 49 mL MCHex (-70°C), 32 mL MeCl (-70°C), 0.03 mL (2.6x10⁻⁴ mol) 2,4-lutidine, 0.02 mL (8.7x10⁻⁵ mol) DtBP, and 0.35 g (1.8x10⁻³ mol) TMDCH. This mixture was allowed to stir for 15 min, after which several background spectra were collected. Then 7.2 mL (8.9x10⁻² mol) IB (-70°C) was added to the flask. Several monomer baseline spectra were obtained, and .49 mL (4.5x10⁻³ mol) TiCl₄ (neat and at room temperature) was added to the flask. Once the IB achieved >99% conversion, a 1-2 mL aliquot was taken and added to 10 mL pre-chilled MeOH. The molar concentrations of the reagents were as follows: [IB]₀=1.0 M, [TMDCH]₀=2x10⁻² M, [DtBP]₀=1x10⁻⁴ M, [2,4-Lutidine]₀=3x10⁻³ M, [TiCl₄]₀=5x10⁻² M. The IB acquisition was then aborted, and the IR was set up for the styrene reaction. A new set of scans was
begun by acquiring several baseline spectra, followed by the addition of a pre-chilled solution of 12 mL (1.0x10^4 mol) styrene in 55 mL MCHex and 36 mL MeCl. When the reaction reached ~50% conversion, 60 mL pre-chilled MeOH was added to the reactor. The mixture was precipitated into 5x excess MeOH, and the solid product was filtered and dried in a vacuum oven at 25°C. The molar concentrations of styrene in the addition and in the total reaction were 2.0 M and 5.4x10^{-1} M, respectively.

*Site transformation of the Macroinitiator.*

The site transformation was carried out as follows: To eliminate the primary chloride at the initiator fragment and simultaneously dehydrochlorinate the PS chain end, a three-necked round bottom flask equipped with heating mantle, magnetic stirbar, and condenser column, was charged with PIB-PS (3 g, Mn=21,500 g/mol) dissolved in 50 mL distilled THF. The reactor was purged with N₂ and then equipped with a N₂ bubbler. Potassium tert-butoxide (0.07 g, 6.2x10^{-4} mol) dissolved in 5 mL THF was injected slowly via syringe. The reaction was refluxed overnight and cooled to room temperature, and the product was precipitated into excess MeOH. The solid product was filtered and dried in a vacuum oven at room temperature overnight (98% yield). The product was then spread in a thin layer in a heat-resistant container and placed in a preheated vacuum oven (130°C) for 48 h. The product was removed from the oven, cooled to room temperature, and collected to yield hydroxy-functional PIB-PS.

To incorporate a single bromine functionality onto the polymer chain end, the following procedure was employed: To a 250 mL three-necked round bottom flask equipped with magnetic stirbar, heating mantle, N₂ bubbler, and condenser column were charged hydroxy-functional PIB-PS (2.04 g, Mn=21,500 g/mol), 60 mL THF, 0.12 mL 2-
bromoisobutyryl bromide (9.7×10⁻⁴ mol), and 0.14 mL triethylamine (1.0×10⁻³ mol). The reaction was refluxed for 48 h (adding THF as needed to maintain constant reaction volume), and the mixture was precipitated into excess MeOH/DI H₂O (80/20 v/v). The solid product was dried overnight in a vacuum oven at room temperature to remove excess solvent (91% yield).

**Synthesis of PtBA-PIB-PS Linear Terpolymers via ATRP**

The following is an example of the synthesis of a PtBA-PIB-PS terpolymer: To a 100 mL Kjeldahl style schlenk flask, equipped with magnetic stirbar and contained within a dry box, were charged 6×10⁻³ g (4.2×10⁻⁵ mol) CuBr, 8.9×10⁻¹ g (4.2×10⁻⁵ mol, Mn=21,500) brominated PIB-PS, 10 mL toluene, 0.20 mL anisole, and 0.42 g (3.3×10⁻³ mol) tBA (sparged with N₂ for 30 min prior to use). The mixture was allowed to stir to solubilize the macroinitiator. The flask was then sealed with a rubber septum and cable tie and removed from the dry box. The flask was sparged with N₂ for 5 minutes. Then, 1.0×10⁻² mL (4.2×10⁻⁵ mol) PMDETA (sparged with N₂ prior to use) was added to the reactor via syringe. An initial aliquot (0.1 mL, t=0) was taken and quenched by freezing in liquid nitrogen (LN₂), and the reactor was submerged in an oil bath preheated to 90°C. Additional aliquots (0.1 mL) were taken at predetermined intervals via a N₂ purged syringe for kinetic analysis, and the reaction was quenched in LN₂ after 5.5 h. The polymer, dissolved in methylene chloride, was passed through a column consisting of a neutral alumina bottom layer and a DOWEX® MSC-1 ion-exchange resin top layer and precipitated into excess MeOH/DI H₂O (80/20 v/v). The solid product was collected by vacuum filtration and dried under vacuum at room temperature overnight (96% yield).
Monomer conversion for the polymerization was determined by $^1$H-NMR using anisole as an internal standard. Integration of the methoxy resonance in anisole (3.75 ppm) and the vinyl resonance in tBA (5.75-5.60 ppm) at predetermined time intervals allowed for the quantitative determination of tBA conversion.

Size Exclusion Chromatography (SEC)

Molecular weights and polydispersities (PDI) of the purified polymers were determined using a SEC system equipped with a Waters Alliance 2690 Separations Module, an on-line multi-angle laser light scattering (MALLS) detector operating at 690nm (MiniDAWN™, Wyatt Technology Inc.), an interferometric refractometer (Optilab DSP™, Wyatt Technology Inc.) operating at 35°C, and one set of PLgel™ (Polymer Laboratories Inc.) SEC columns connected in series. Tetrahydrofuran (THF), freshly distilled from CaH$_2$, was employed as the mobile phase and was delivered at a flow rate of 1.0 mL/min. Sample concentrations were approximately 7 mg/mL with an injection loop volume of 100μL. Detector signals were simultaneously recorded and absolute molecular weights and polydispersity indices (PDIs) were calculated using ASTRA™ software (Wyatt Technology Inc). The dn/dc value was calculated from the signal response of the Optilab DSP, assuming 100% mass recovery from the columns.

Proton Magnetic Resonance Spectroscopy ($^1$H NMR)

$^1$H were used for the structural elucidation of the copolymers and block copolymer composition. Solution $^1$H spectra were obtained on a Varian Unity 300 MHz spectrometer using 5 mm o.d. tubes with sample concentrations of 5-7% in deuterated chloroform (CDCl$_3$) (Aldrich Chemical Co.) containing 0.03% (v/v) tetramethylsilane as an internal reference. The spectra were the Fourier transformation of 32 transients. $^{13}$C
NMR was used to verify the incorporation of the PtBA segment. The samples for $^{13}$C NMR were run at 20% in a 90/10 (v/v) mixture of deuterated chloroform containing 0.03% (v/v) tetramethylsilane as an internal reference and deuterated methyl sulfoxide.

*Synthesis of 3,3,5-Trimethyl-1,5-dichlorohexane (TMDCH)*

The TMDCH initiator, which contains a cationic initiating site and a primary chloride functionality, was synthesized in three steps from methyl 3,3-dimethyl-4-pentenoate. In the $^1$H NMR spectrum of the starting material (Figure V.2), the methoxy protons of the ester functionality appear at 3.6 ppm. After the Grignard reaction, the peak is no longer present, and peaks associated with the newly formed hydroxyl functionality are present further upfield, near 2 ppm (Figure V.3).

The hydroboration-oxidation reaction was the most difficult stage of the synthesis. Addition of the NaOH solution had to be carried out very slowly (1 or 2 drops at a time) to avoid pressure due to uncontrolled exotherm. As the NaOH was introduced, a frothy white precipitate formed on the surface of the liquid, but disappeared as the reaction proceeded. As the reaction progressed, NaOH could be added more rapidly. The ice bath was maintained over the entire 7 h reaction time to keep the reactor below 45°C. Upon completion of hydroboration-oxidation, the peaks associated with the olefinic protons at 5-6 ppm in Figure V.3 shifted upfield to positions characteristic of methylene units (~1.7 and 3.7 ppm), and a broader peak appeared at ~2.5 ppm representing the two hydroxyl protons (Figure V.4).

The final step of the synthesis involved converting the hydroxyl groups to chloride functionalities. A large excess of SOCl$_2$ was added in order to carry the reaction to complete conversion. Neutralizing the excess solvent with water must be carried out
slowly in order to control the exotherm. Bubbles were generated in the separatory funnel as water contacted the \( \text{SOCl}_2 \). Water was added until no more bubbles were visible and gentle agitation of the funnel did not produce more gas. During separation of the aqueous and organic components, the bottom layer was noted as the organic layer due to the density of methylene chloride. The \(^1\text{H} \) NMR spectrum of the product is illustrated in Figure V.5. The signal associated with the methylene protons nearest the primary chloride has shifted to 3.5 ppm, and the broad peak associated with the hydroxyl groups has disappeared. Also, the peak representing the protons nearest the tertiary chloride has shifted to \(~1.6\) ppm. The starting material and all products of these reactions were liquid phase, with the final product being brown in color.

*Synthesis of PIB-PS Copolymers Using Quasiliving Cationic Polymerization with Sequential Monomer Addition Techniques*

ATRP macroinitiators containing a PIB block and a PS block were synthesized via quasiliving cationic polymerization using TMDCH as the initiator and TiCl\(_4\) as the coinitiator in a MCHex/MeCl (60/40 v/v) solvent system with DMP and DtBP as Lewis base additive and proton trap, respectively, at -70°C. At >99% conversion of the IB as determined by ATR-FTIR monitoring, an aliquot was removed for PIB block analysis by SEC, and then a 2.0 M charge of styrene in MCHex/MeCl was added to the reactor. The reaction was quenched at ~50% styrene conversion with prechilled methanol. The styrene polymerization was short-stopped in this manner to avoid side reactions that become important when the propagation reaction slows at high conversions. SEC analysis of the isolated polymers showed that there were no high molecular weight peaks
that would indicate chain coupling, and thus this side reaction was avoided. The polymers also had narrow PDIs.

Table V.1 lists molecular weight and compositional data for the PIB intermediate blocks and PIB-PS copolymers. Number average molecular weight of the PIB blocks by SEC (\(M_{n,\text{PIB(SEC)}}\)) was higher than theoretical, indicating low initiator efficiency. In fact, the efficiency was lower than that of TMCHA. This phenomenon is still poorly understood and requires further investigation.

Number average molecular weight of the PS block from SEC (\(M_{n,\text{PS(SEC)}}\)) was calculated as the difference in molecular weight between the overall block copolymer (\(M_{n,\text{PIB-PS(SEC)}}\)) and \(M_{n,\text{PIB(SEC)}}\). An alternative measurement, \(M_{n,\text{PS(nmr)}}\), was calculated from copolymer composition, as determined via \(^1\text{H}\) NMR spectroscopy. Figure V.6 illustrates the \(^1\text{H}\) NMR spectrum of the PIB-PS copolymer, with the inset being representative of the chain end region. The peak near 3.5 corresponds to the methylene protons nearest the primary chloride, as shown in the NMR spectrum of the initiator as well. The peak near 4.4 represents the styryl chloride end groups. Copolymer composition was determined by comparison of the relative intensities of the aromatic and aliphatic resonances, as described previously for PS-PIB-PS systems.\(^{42}\) \(M_{n,\text{PS(nmr)}}\) was calculated using a variation of a previously reported equation (Equation V.1,\(^{42}\)

\[
M_{n,\text{PS(nmr)}} = M_{n,\text{PIB(SEC)}} \cdot \frac{W_{\text{PS(nmr)}}}{(100 - W_{\text{PS(nmr)}})}
\]

where \(W_{\text{PS(nmr)}}\) is the weight percent of PS as determined by \(^1\text{H}\) NMR of the copolymer.

**Site Transformation of the Macroinitiator**

The end groups of the PIB-PS macroinitiators were transformed in two steps to allow for ATRP initiation. The first involved application of the strong base potassium
tert-butoxide to dehydrochlorinate each end group. The polymer was then heated under vacuum to remove any protective group that may have attached to the molecule in place of the primary chloride. Figure V.7 illustrates the $^1$H NMR spectrum. As shown in the end group region, the styryl chloride end groups have been dehydrochlorinated, but the primary hydroxyl remains intact.

The second step of site transformation involved the incorporation of an $\alpha$-bromo carbonyl species, such as 2-bromoisobutyryl bromide, for ATRP initiation. Because the primary chloride was still present in the sample instead of a hydroxyl functionality, the bromination of the sample was futile. $^1$H NMR indicated clear presence of the chloride group and no reaction of the compound with 2-bromoisobutyryl bromide.

*Synthesis of PtBA-PIB-PS Linear Terpolymers Using ATRP*

The ATRP of tBA was attempted, even though a primary chloride should not initiate the polymerization. Analysis of the final sample proved this hypothesis. There was no increase in molecular weight as determined by SEC, and $^{13}$C NMR did not illustrate incorporation of PtBA (there was no peak present at 28 ppm; Figure V.8).

Conclusions

The monofunctional cationic initiator 3,3,5-trimethyl-2,5-dichlorohexane (TMDCH) was synthesized in three steps and used for the successful initiation of PIB-PS copolymers. However, the initiation efficiency was not as good as that of TMCHA (30-39% at low molecular weights; 89% at high molecular weights). Also, the primary chloride proves difficult to remove in order to incorporate a functionality for ATRP initiation. Both SEC and $^{13}$C NMR illustrate the absence of a PtBA segment. Thus, new methods need to be examined if TMDCH is to be used as a multifunctional initiator.

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Table V.1  \( M_n \), Composition, and PDI data for PIB-PS copolymers.

<table>
<thead>
<tr>
<th>Entry</th>
<th>PIB ( M_n, \text{Th} ) (g/mol)</th>
<th>PIB ( M_n, \text{SEC} ) (g/mol)</th>
<th>PDI</th>
<th>PS ( M_n, \text{Th} ) (g/mol)</th>
<th>PS ( M_n, \text{SEC} ) (g/mol)</th>
<th>PS ( M_n, \text{NMR} ) (g/mol)</th>
<th>Copolymer ( M_n ) (g/mol)</th>
<th>PDI</th>
<th>Wt% PIB (NMR)</th>
<th>Wt% PS (NMR)</th>
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Figure V.1  Overall scheme for the synthesis of 3,3,5-trimethyl-2,5-dichlorohexane

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Figure V.2 $^1$H NMR spectrum of methyl-3,3-dimethyl-4-pentenoate
Figure V.3 $^1$H NMR spectrum of 5-hydroxy-3,3,5-trimethylhexene
Figure V.4 $^1$H NMR spectrum of 1,5-dihydroxy-3,3,5-trimethylhexane
Figure V.5 $^1$H NMR spectrum of 3,3,5-trimethyl-2,5-dichlorohexane
Figure V.6 $^1$H NMR spectrum of PIB-PS with expansion of the end group region (Table V.1, Entry A)
Figure V.7 $^1$H NMR spectrum of PIB-PS after dehydrochlorination. The primary chloride remains intact (Table V.1, Entry A)
Figure V.8 $^{13}$C NMR spectrum of polymer after ATRP. The absence of the small peak at 28 ppm indicates that no PtBA was incorporated into the polymer.
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