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Poly(*tert*-butyl acrylate-*b*-isobutylene-*b*-styrene) terpolymer from a carbocationic initiator containing a latent radical initiating site

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Abstract

A poly(isobutylene-*b*-styrene) (PIB-PS) copolymer was synthesized via quasi-living carbocationic polymerization from an initiator containing a latent site for atom transfer radical polymerization (ATRP) initiation. The initiator, 3,3,5-trimethyl-5-chlorohexyl acetate (TMCHA), was synthesized in four steps from methyl 3,3-dimethyl-4-pentenoate. The PIB block was created at −70 °C in a methylcyclohexane/methyl chloride (60:40) cosolvent system, using $TiCl_4$ as the catalyst, followed by sequential addition of styrene. The acetate head group of the resulting block copolymer was converted to a hydroxyl group using a strong base and subsequently esterified with 2-bromopropionyl bromide to create an initiating site for ATRP of *tert*-butyl acrylate, which was carried out using a Cu(I)Br/1,1,4,7,7,-pentamethyl-diethylenetriamine (PMDETA) catalyst system. The final terpolymers had compositions that were very close to theoretical.

Keywords: Carbocationic polymerization; Block terpolymer; Atom transfer radical polymerization

1. Introduction

Controlled polymerizations (CP) offer an effective way to create block copolymers with well-defined structures and polydispersities, with the primary advantage being the broad selection of monomers that may be employed. CPs are characterized by an equilibrium between active and reversibly terminated (dormant) chain ends. The equilibrium constant is usually very small, indicating that most of the chains are in the dormant state at any given time. These methods also enable the synthesis of a variety of polymer architectures, such as stars. Termination of the polymers results in predictable end group functionalities, which can be modified to create polymers with various block connectivities.

The combination of controlled/living polymerization techniques allows the creation of block copolymers that could not otherwise be synthesized. This becomes possible if the end groups of the first block can be transformed to create an effective initiator for the subsequent polymerization or if the polymer is already functionalized for initiation. Quasi-living cationic polymerization (QCP) is a chain reaction that has been shown to successfully create well-defined block copolymers [1–3]. However, the utility of QCP is limited to nucleophilic monomers such as isobutylene and styrene. Electrophilic monomers such as acrylates require different methods. Thus it is attractive to combine QCP with other types of CPs in order to create new materials and architectures [4–13]. Particularly, attractive in this regard is atom transfer radical polymerization (ATRP), which involves a reversible radical formation catalyzed by a transition metal complex. The latter is usually a copper halide species, such as Cu(I)Cl or Cu(I)Br, and the polymerization employs a halogenated initiator to polymerize the monomers in a controlled manner. Because ATRP is a radical polymerization, a variety of monomers, including acrylates and methacrylates, can be used in this method [14].

Our group is interested in creating materials that are permselective towards water but also have barrier properties similar to butyl rubber. Poly(styrene-*b*-isobutylene-*b*-styrene) triblock copolymers [15] have been studied in comparison to crosslinked butyl rubber because the isobutylene segments provide similar barrier properties. However, as phase-separated thermoplastic elastomers, the triblock copolymers can be easily processed, and the phenyl rings can be modified by sulfonation and sol–gel reactions to confer hydrophilicity and enhanced water transmission [16]. While this approach has proven successful [17], it is believed that the presence of the hydrophilic phase within the crosslinking phase could adversely affect the physical properties of the final polymer.

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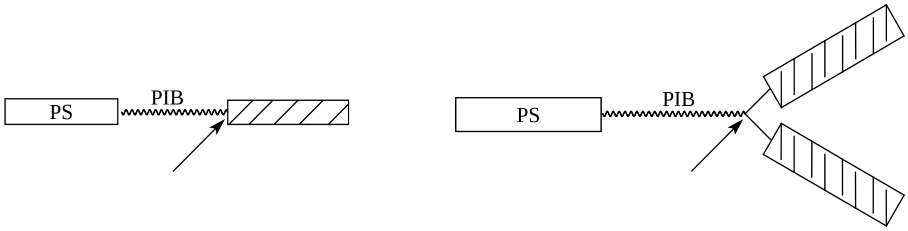


Scheme 1. Linear triblock and three-armed star terpolymer architectures that may be created using a cationic polymerization initiator containing a latent site for initiation of atom transfer radical polymerization. The arrows indicate the position of the initiator.

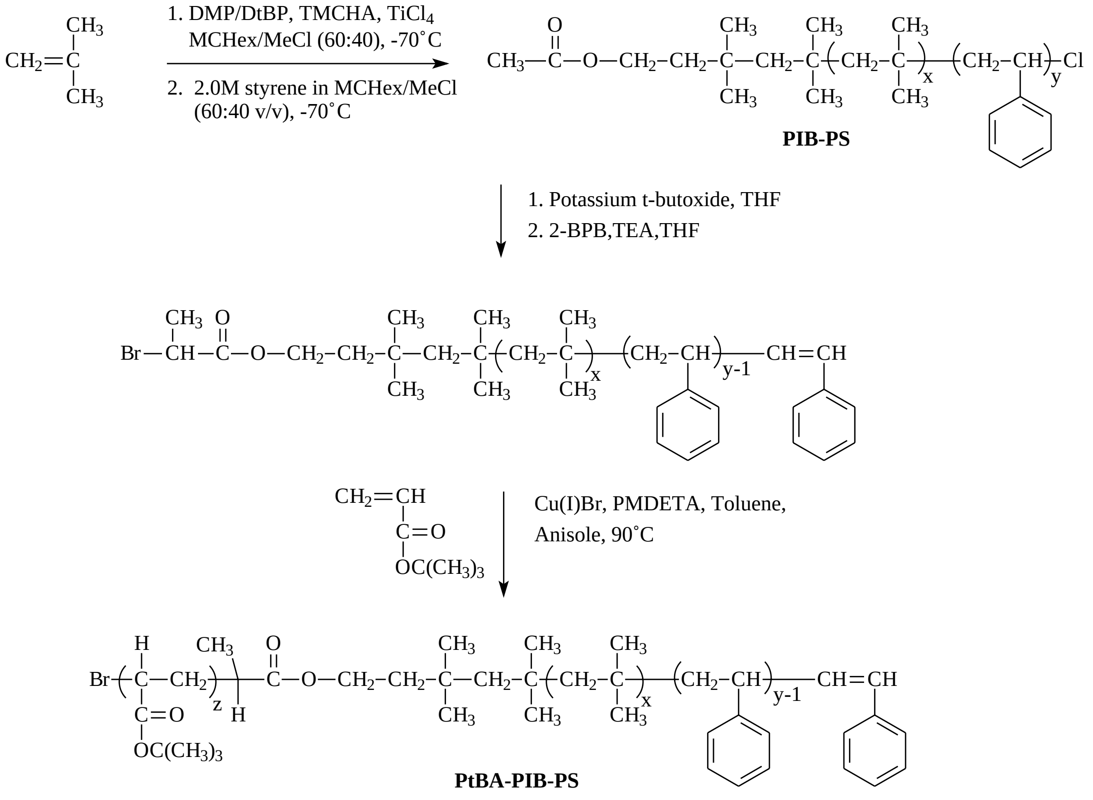
Thus, we seek to incorporate functional initiators into poly(isobutylene-*b*-styrene) (PIB-PS) copolymers, followed by ATRP site creation and polymerization, which would allow the formation of tri-phasic materials of various architectures, as shown in Scheme 1. These model structures will then be used in morphological studies to determine structure–property relationships as a function of block connectivity in tri-phasic polymer systems.

In this paper, we discuss the synthesis of the initiator used to create these architectures and the synthesis of the linear triblock terpolymer. The overall reaction is illustrated in Scheme 2 and begins with the quasi-living cationic polymerization of isobutylene from a monofunctional cationic initiator that contains a blocked hydroxyl group, followed by sequential monomer addition of styrene. The latent hydroxyl functionality of the initiator is then deblocked and used for ATRP of *tert*-butyl acrylate (tBA). The final materials contain sites for further modification to impart both hydrophobic and hydrophilic segments.

2. Experimental

2.1. 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+%), 2,6-lutidine (DMP, 99+%), $TiCl_4$ (99.9%, packaged under N_2 in Sure-Seal bottles), potassium *t*-butoxide (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_3Cl (MeCl) (both BOC, 99.5%) were dried through columns packed with $CaSO_4$ and $CaSO_4$/4 Å molecular sieves,



Scheme 2. Synthesis of triblock terpolymer.

respectively. Ammonium chloride was used as received from Fisher Chemical Co. Styrene, 2,6-di-*tert*-butylpyridine, *tert*-butyl acrylate, 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.

2.2. Instrumentation

Molecular weights and molecular weight distributions (or polydispersity, PDI) of polymers were determined using a GPC system consisting of a Waters Alliance 2695 Separations Module, an on-line multi-angle laser light scattering (MALLS) detector (MiniDAWN™, Wyatt Technology, Inc.) fitted with a Gallium arsenide laser (20 mW) operating at 690 nm, and an interferometric refractometer (Optilab DSP™, Wyatt Technology, Inc.) operating at 35 °C and 690 nm, and two mixed D PL gel (Polymer Laboratories, Inc.) GPC columns (pore size range 50–10^4 Å, 5 μm bead size) connected in series. Freshly distilled THF served as the mobile phase and was delivered at a flow rate of 1.0 mL/min. Sample concentrations were 7 mg/mL in freshly distilled THF, and the injection volume was 100 μL. The detector signals were simultaneously recorded using ASTRA software (Wyatt Technology, Inc.). PIB samples (recovered from aliquots removed prior to addition of styrene) were analyzed using a known d*n*/d*c* value of 0.103 mL/g. PIB-PS blocks and final P*t*BA–PIB–PS terpolymers were analyzed using a d*n*/d*c* calculated from the refractive index detector response and assuming 100% mass recovery from the columns.

Solution ^1H NMR spectra were obtained on a Varian 300 MHz spectrometer using 5 mm o.d. tubes with sample concentrations of 5–7% (w/v) in deuterated chloroform ($CDCl_3$) (Aldrich Chemical Co.) containing tetramethylsilane as an internal reference.

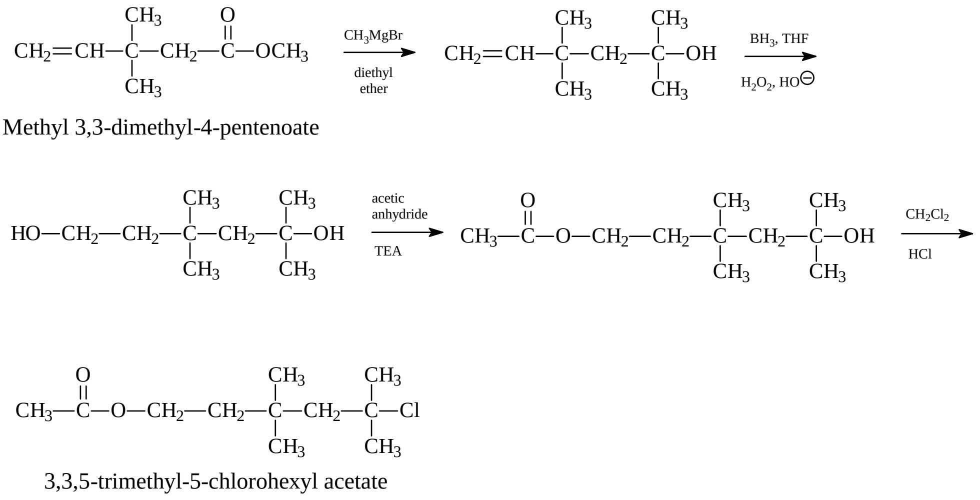
A ReactIR 1000 reaction analysis system (light conduit type) (ASI Applied Systems, Millersville, MD), equipped with a DiComp (diamond composite) insertion probe, a general purpose type PR-11 platinum resistance thermometer, and CN76000 series temperature controller (Omega Engineering, Stamford, CT) was used to collect spectra of the polymerization components and monitor reaction temperature in real time as previously described [18]. The light conduit and probe were contained within a glove box (MBraun Labmaster 130) equipped with a hexane/heptane cold bath.

IR spectra were obtained from films cast from freshly distilled THF onto a NaCl plate using a Bruker Equinox 55 FTIR spectrometer.

2.3. TMCHA synthesis

The initiator, 3,3,5-trimethyl-5-chlorohexyl acetate (TMCHA), was synthesized using a variation of a previously reported procedure [19]. The overall reaction sequence is illustrated in Scheme 3. First, methyl 3,3-dimethyl-4-pentenoate was converted to a tertiary alcohol intermediate by a Grignard reaction using methyl magnesium bromide, followed by hydroboration–oxidation to form a primary hydroxyl group at the other end of the molecule. 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 3 M solution in diethyl ether). Methyl 3,3-dimethyl-4-pentenoate (15 mL, 9.4×10^{-2} mol) was added dropwise via syringe over 30 min. The reaction was stirred for 1.5 h 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_2O 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, 7.0×10^{-2} mol) was charged to a 250 mL three-necked round-bottom flask equipped with mechanical stirrer, external ice/water bath, and nitrogen



Scheme 3. Synthesis of TMCHA initiator.

inlet/outlet. 5-Hydroxy-3,3,5-trimethylhexene (5.0 g, 3.5×10^{-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_2O_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_2O 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 (6×10^{-2} mol) 1,5-dihydroxy-3,3,5-trimethylhexane dissolved in 30 mL triethylamine and 6 g (6×10^{-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).

2.4. PIB–PS copolymer synthesis

The DiComp probe was inserted into a 1 L three-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 220 mL MCHex (−70 °C), 146 mL MeCl (−70 °C), 0.14 mL (1.2×10^{-3} mol) 2,6-lutidine, 0.08 mL (3×10^{-4} mol) D*t*BP, and 0.2 g (9×10^{-4} mol) TMCHA. This mixture was allowed to stir for 15 min, after which several background spectra were collected. Then 32 mL (4×10^{-1} mol) IB (−70 °C) was added to the flask. Several monomer baseline spectra were obtained, and 1.5 mL (1.4×10^{-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: $[IB]_o=1.0$ M, $[TMCHA]_o=2\times10^{-3}$ M, $[DtBP]_o=1\times10^{-3}$ M, $[2,6\text{-Lutidine}]_o=3\times10^{-3}$ M, $[TiCl_4]_o=3.5\times10^{-2}$ M. A new set of scans was begun by acquiring several baseline spectra, followed by the addition of a pre-chilled solution of 48 mL (4.2×10^{-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 5× 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 and 6.9×10^{-1} M, respectively.

2.5. Site transformation of macroinitiator

The two-step site transformation reaction was carried out using a variation of a previously reported procedure [20]. 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 condenser column, was charged with PIB–PS (5 g, $M_n=14{,}450$ g/mol) dissolved in 50 mL distilled THF. The reactor was purged with N_2 and then equipped with a N_2 bubbler. Potassium *tert*-butoxide (0.16 g, 1.4×10^{-3} 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_2O. The solid product was filtered and dried in a vacuum oven at room temperature overnight (98% yield).

To incorporate a 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_2 bubbler, and condenser column were charged hydroxy-functional PIB–PS (2.5 g, $M_n=14{,}450$ g/mol), 20 mL THF, 0.3 mL 2-bromopropionyl bromide (2.8×10^{-3} mol), and 0.3 mL triethylamine (2.2×10^{-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 H_2O (80/20, v/v). The solid product was dried overnight in a vacuum oven at room temperature to remove excess solvent (93% yield).

2.6. Synthesis of PtBA–PIB–PS triblock terpolymers by ATRP

A typical procedure for ATRP was as follows. To a 100 mL Schlenk-type flask, equipped with magnetic stirbar and contained within a dry box, were charged 4.1×10^{-2} g (2.87×10^{-4} mol) CuBr, 2.3 g (1.6×10^{-4} mol) brominated PIB–PS, 15 mL toluene, 0.30 mL anisole, and 1.03 g (8.0×10^{-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. Then, 6.0×10^{-2} mL (2.87×10^{-4} mol) PMDETA (sparged with N_2 prior to use) was added to the reactor via syringe. An initial aliquot was taken and quenched by freezing in liquid nitrogen (LN_2), and the reactor was submerged in an oil bath preheated to 90 °C. Aliquots were taken at predetermined intervals, and the reaction was

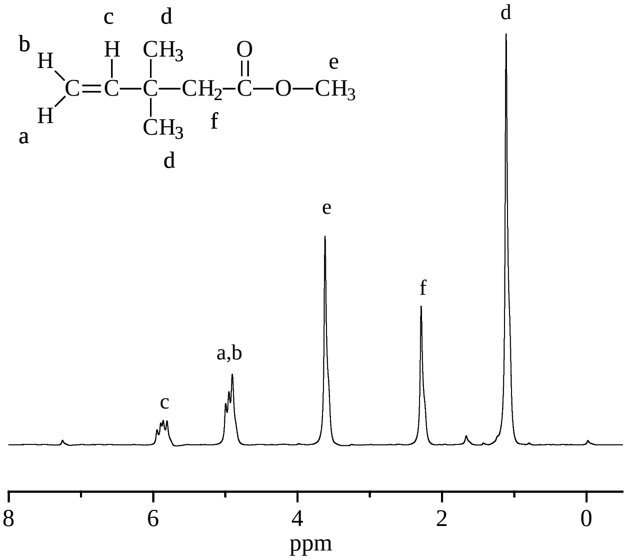


Fig. 1. ^{1}H NMR spectrum of methyl-3,3-dimethyl-4-pentenoate.

quenched in LN_2 after 5.5 h. The polymer, dissolved in methylene chloride, was passed through a column consisting of an alumina bottom layer and a DOWEX® MSC-1 ion-exchange resin top layer and precipitated into excess MeOH. The solid product was collected by vacuum filtration and dried under vacuum at room temperature overnight (96% yield).

3. Results and discussion

3.1. TMCHA synthesis

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 (Fig. 1), 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 (Fig. 2).

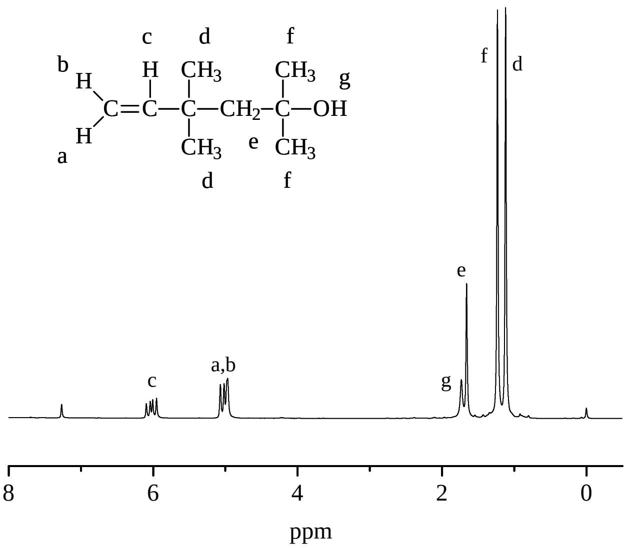


Fig. 2. ^{1}H NMR spectrum of 5-hydroxy-3,3,5-trimethylhexene.

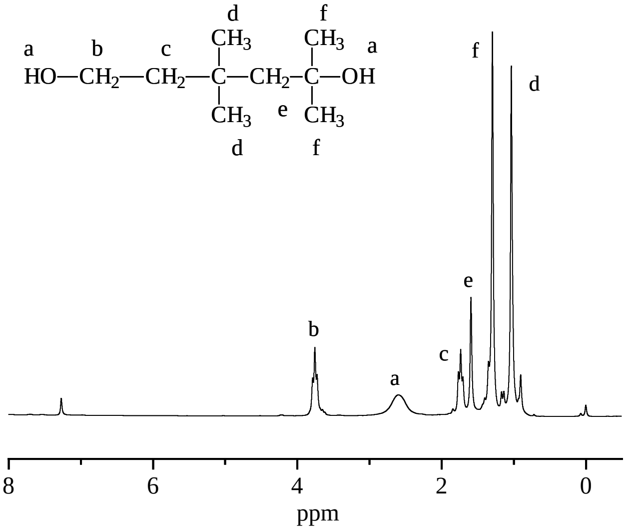


Fig. 3. ^{1}H NMR spectrum of 1,5-dihydroxy-3,3,5-trimethylhexane.

The hydroboration–oxidation reaction was the most difficult stage of the synthesis. Addition of the NaOH solution had to be carried out very slowly (one or two 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 (Fig. 2) 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 (Fig. 3).

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

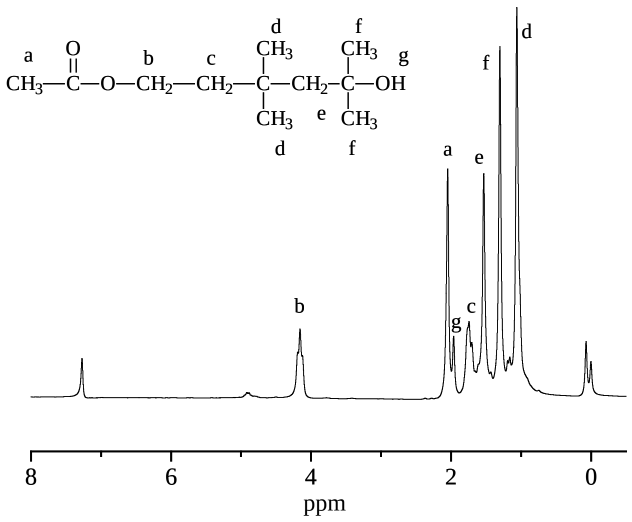


Fig. 4. ^{1}H NMR spectrum of 5-hydroxy-3,3,5-trimethylhexyl acetate.

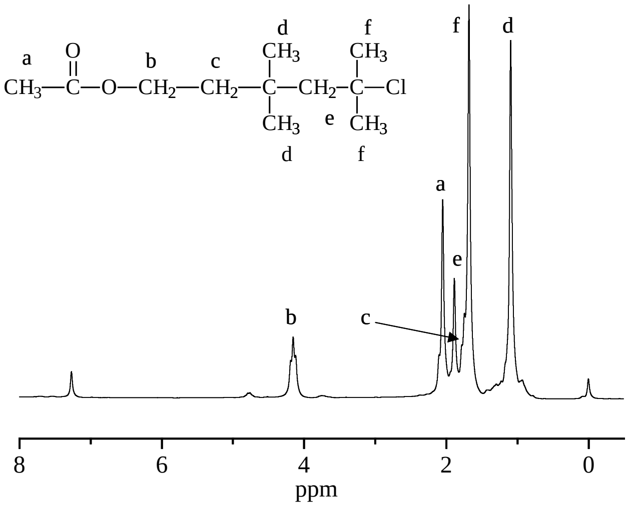


Fig. 5. ^{1}H NMR spectrum of 3,3,5-trimethyl-5-chlorohexyl acetate.

shifted slightly downfield (Fig. 4). 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 (Fig. 5). The starting material, three intermediates, and final product were all liquids at room temperature.

3.2. Synthesis of PIB–PS copolymer

ATRP macroinitiators containing a PIB block and a PS block were synthesized via quasi-living cationic polymerization using TMCHA 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 $\sim 50\%$ styrene conversion with cold 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 occurance 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, which are characteristic of CPs.

Table 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 ($M_{n,PIB(SEC)}$) was higher than theoretical, indicating low initiator efficiency ($I_{eff}=0.56$–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 ($\sim$4 h). Experiments that employed [$TiCl_4$] at 0.8 and 1.2×[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. Although the cause of low I_{eff} with TMCHA is poorly understood and currently under investigation, it was observed that initiation of styrene by quasi-living PIB was quantitative; thus by adjusting the [IB]/[TMCHA] ratio to compensate for the low I_{eff} of TMCHA, the targeted compositions of the copolymers were achieved, and the initiator was successfully used to create the diblock system.

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 $M_{n,PIB(SEC)}$. An alternative measurement, $M_{n,PS(nmr)}$, was calculated from copolymer composition, as determined via ^{1}H NMR spectroscopy. Fig. 6 shows the ^{1}H NMR spectrum of the copolymer; composition was determined by comparison of the relative intensities of the aromatic and aliphatic resonances, as described previously for PS–PIB–PS systems [15]. $M_{n,PS(nmr)}$ was calculated using a variation of a previously reported equation (Eq. (1)) [15]

$$M_{n,PS(nmr)} = M_{n,PIB(SEC)} \frac{W_{PS(nmr)}}{100 - W_{PS(nmr)}} \tag{1}$$

where $W_{PS(nmr)}$ is the weight percent of PS as determined by ^{1}H NMR. As shown in Table 1, the two measures of PS block molecular weight were in excellent agreement.

3.3. Site transformation

The end groups of the PIB–PS macroinitiator 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

Table 1
Molecular weight (g/mol) and composition data for PIB–PS copolymers

Sample ID	$M_{n,PIB(Th)}$	$M_{n,PIB(SEC)}$	PDI_{PIB}	$M_{n,PS(Th)}$	$M_{n,PS(SEC)}$	$M_{n,PS(NMR)}$	$M_{n,PIB-PS(SEC)}$	PDI_{PIB-PS}	wt% PIB (NMR)	wt% PS (NMR)
1[a]	5,000	6,900	1.1	5,000	7,500	7,600	14,400	1.3	47.5	52.5
2[b]	3,500	6,300	1.3	3,500	7,300	7,500	13,600	1.3	45.8	54.2

[a] $[TiCl_4]_o$, 3.48×10^{-2} M; $[TMCHA]_o$, 1.12×10^{-2} M.

[b] $[TiCl_4]_o$, 4.50×10^{-2} M; $[TMCHA]_o$, 1.63×10^{-2} M.

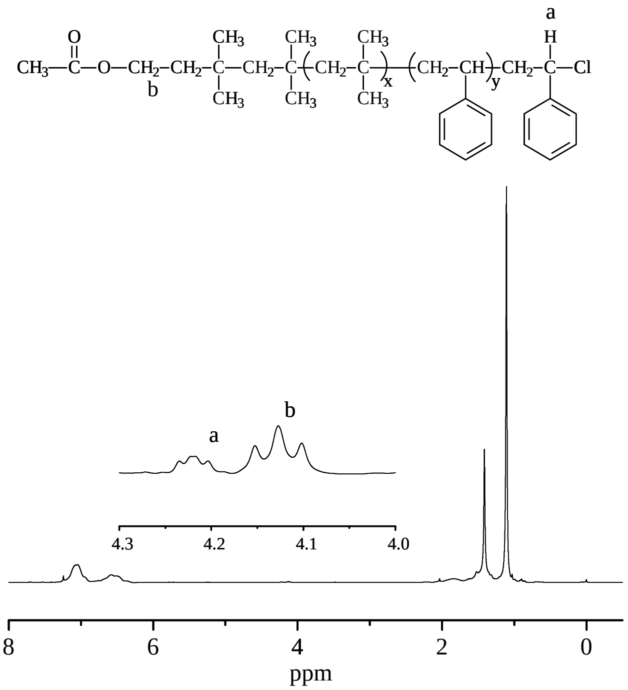


Fig. 6. ^{1}H NMR spectrum of PIB–PS copolymer with expansion of the chain ends (Table 1, Entry 1).

simultaneously dehydrochlorinate the tail group of the PS segment. Fig. 6 (inset) shows the resonances associated with the methylene protons nearest the protected hydroxyl group (b) and the proton nearest to the terminal chlorine atom (a). The integrated areas of these two resonances were found to be in a ratio of approximately two to one, as predicted based upon the structure of the copolymer. 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 (Fig. 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 ~3.7 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 (Fig. 3).

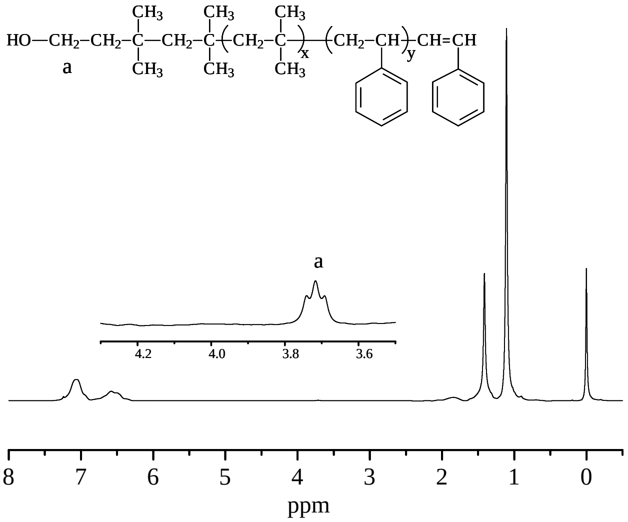


Fig. 7. ^{1}H NMR spectrum of deprotected PIB–PS, with inset illustrating the hydroxyl head group (Table 1, Entry 1).

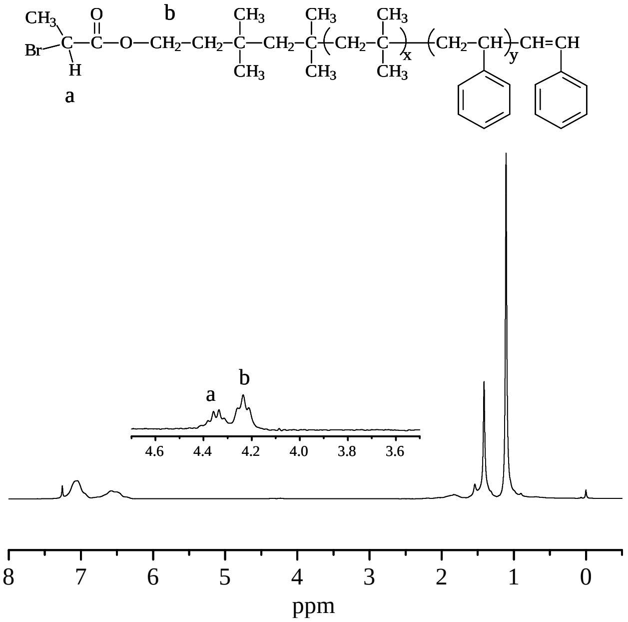


Fig. 8. ^{1}H NMR spectrum of brominated PIB–PS, with expansion of the head group region (Table 1, Entry 1).

The second step of site transformation involved the incorporation of an α-bromo carbonyl species, such as 2-bromopropionyl bromide, for ATRP initiation. This reaction was facile but slow; 48 h were needed for complete conversion. The ^{1}H NMR spectrum of the product is shown in Fig. 8.

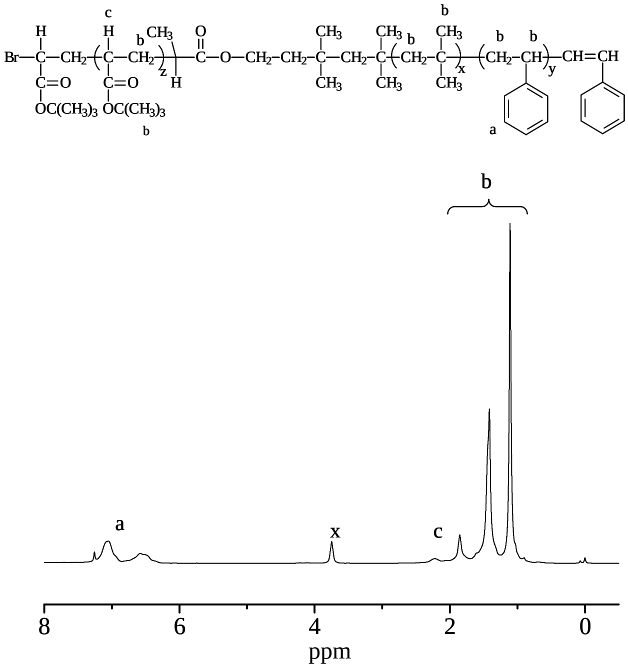


Fig. 9. ^{1}H NMR spectrum of P*t*BA–PIB–PS triblock terpolymer (Table 2, Entry 3).

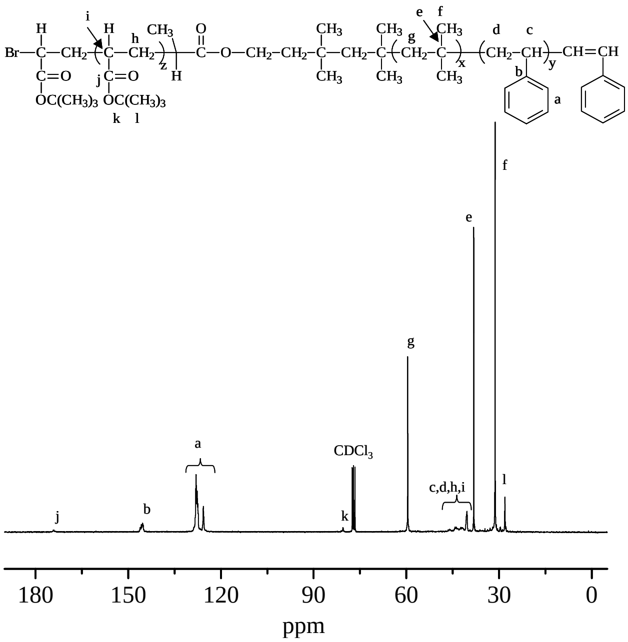


Fig. 10. ^{13}C NMR spectrum of P*t*BA–PIB–PS triblock terpolymer (Table 2, Entry 3).

The inset of this plot 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. This species has been shown to be an effective initiator for ATRP.

3.4. Synthesis of *Pt*BA–PIB–PS terpolymers

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 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.

Figs. 9 and 10 show the ^{1}H and ^{13}C NMR spectra, respectively, of a representative triblock terpolymer. The resonances between 6.2–7.3 and 0.5–2.0 ppm of the ^{1}H NMR spectrum 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 P*t*BA 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 P*t*BA 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 anisole (peak x) 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

Table 2
Molecular weight (g/mol) and composition data for P*t*BA–PIB–PS terpolymers

Sample ID	$[L]_o$:[-Cu]$_o$:$[CE]_o$[a]	Pzn. time (min)	Conv. (%)	$M_{n,PIB\text{–}PS(SEC)}$	$PDI_{PIB\text{–}PS}$	$M_{n(SEC)}$	PDI	wt% PIB (NMR)	wt% PS (NMR)	wt% PtBA (NMR)
3	1:1:1	300	85.6	14,400	1.3	23,000	1.4	28.7	35.1	36.2
4	2:2:1	330	41.9	14,400	1.3	21,600	1.3	33.6	36.6	29.7
5	1:1:1	275	54.0	13,600	1.3	18,100	1.3	37.6	44.7	17.7

[a] $[Ligand]_o$:$[Cu(I)Br]_o$:$[CE]_o$.

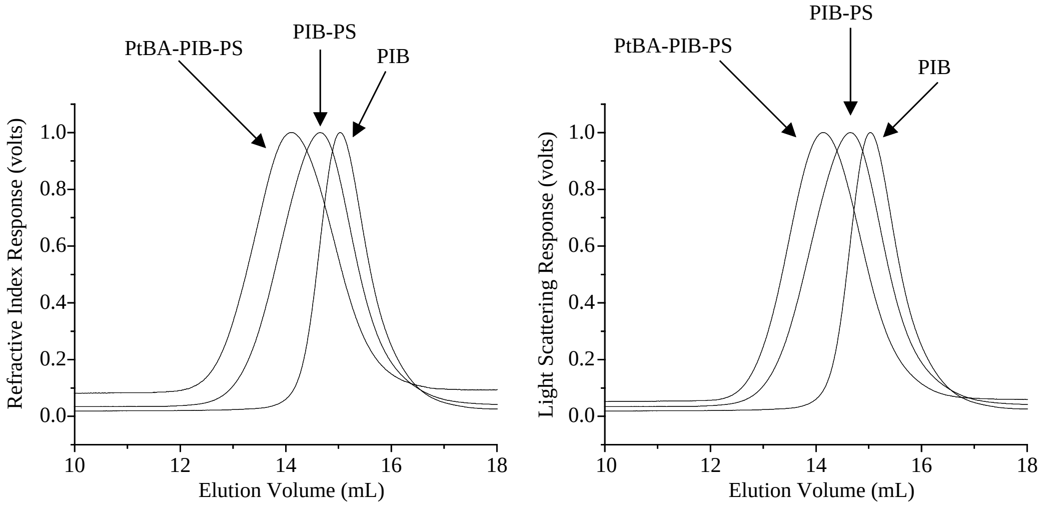


Fig. 11. SEC traces of PIB, PIB–PS, and P*t*BA–PIB–PS (Table 2, Entries 4 [left] and 5 [right]).

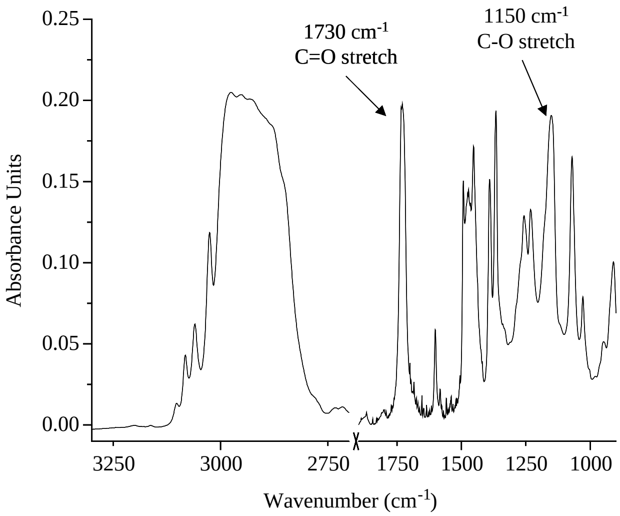


Fig. 12. FTIR spectrum of P*t*BA–PIB–PS triblock terpolymer (Table 2, Entry 3).

of PS (125–128 and 146 ppm), and the carbonyl (174 ppm) and *t*-butyl groups (28 and 80 ppm) of P*t*BA.

Table 2 illustrates the results of the ATRP reactions. Terpolymer composition was calculated from ^{1}H NMR data as described previously [12]. Number average molecular weight of the terpolymer, $M_{n,\mathrm{P}t\mathrm{BA-PIB-PS}}$, was determined by SEC-MALLS. Molecular weight and compositional data were in excellent agreement.

SEC traces (normalized intensity) representing each stage of the terpolymer synthesis sequence, i.e. PIB, PIB–PS, and final P*t*BA–PIB–PS, are shown for two different samples in Fig. 11. For both samples, elution volume decreases, and molecular weight as determined by MALLS increases, with the addition of each block segment.

An FTIR spectrum (Fig. 12) of the P*t*BA–PIB–PS triblock was obtained to confirm the incorporation of the P*t*BA segment and establish that side-chain thermolysis did not occur during the drying process. As illustrated, the C=O and C–O stretches appear near 1730 and 1150 cm^{-1}, respectively, which are characteristic of P*t*BA. If the *tert*-butyl groups had been lost, 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 have been observed [12].

4. Conclusions

P*t*BA–PIB–PS triblock copolymers were synthesized from TMCHA, an initiator containing a cationic initiating site and a latent hydroxyl functionality. PIB–PS macroinitiators were prepared from this initiator using quasi-living cationic polymerization. After isolating the block copolymers, the hydroxyl functionality of the initiator was de-blocked and esterified with 2-bromopropionyl bromide, an ATRP initiator. P*t*BA blocks were then created via ATRP using a Cu(I)Br/PMDETA catalyst/ligand system. ^{1}H NMR analysis of each step of the synthesis demonstrated the overall composition of the systems could be controlled. Molecular weights of the PIB and PS blocks were slightly higher than targeted, and this was attributed to interactions between the TMCHA carbonyl group and $TiCl_4$. Further physical characterization of the materials is anticipated as the subject of a future publication.

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