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Polymer 49 (2008) 1154–1163

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Polyisobutylene-based miktoarm star polymers via a combination of carbocationic and atom transfer radical polymerizations

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Received 24 July 2007; received in revised form 7 January 2008; accepted 8 January 2008
Available online 12 January 2008

Abstract

Poly(isobutylene-*b*-styrene) (PIB–PS) copolymers and polyisobutylene (PIB) homopolymers were synthesized via quasiliving carbocationic polymerization from the initiator 3,3,5-trimethyl-5-chlorohexyl acetate, which contains a protected hydroxyl group. The PIB block was created at −70 °C in a methylcyclohexane/methyl chloride (60:40) cosolvent system, using $TiCl_4$ as co-initiator, followed optionally by sequential addition of styrene. Using a strong base, the acetate head group of the resulting block copolymer was cleaved to yield a hydroxyl group, which was subsequently esterified with the branching agent 2,2-bis((2-bromo-2-methyl)propionatomethyl)propionyl chloride (BPPC) to create dual initiating sites for atom transfer radical polymerization (ATRP). ATRP of *tert*-butyl acrylate was carried out using a Cu(I)Br/1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA) catalyst system. In some cases, the ester side chains of the poly(*tert*-butyl acrylate) (P*t*BA) blocks were cleaved to create poly(acrylic acid) (PAA) blocks. The final miktoarm star polymers had compositions that were very close to theoretical.

Keywords: Polyisobutylene; Poly(isobutylene-*b*-styrene); Poly(*tert*-butyl acrylate)

1. Introduction

A star polymer is defined as a macromolecule possessing branches (arms) radiating from a central core [1–3]. Star polymers may be synthesized in several ways. The *arm-first* method joins preformed arms together using a linking agent, and the *core-first* method utilizes a multi-functional initiator to grow the arms outward [4]. Hybrid methods also exist; for example, preformed arms are linked to the core and then a second polymerization of a different monomer is carried out using the core as a macroinitiator [5,6]. This type of star polymer synthesis has become known as the ''in–out'' method [6]. The arms of a star polymer may be uniform with regard to molecular weight and chemical composition or they may be heterogeneous in either/or both of these characteristics. For star polymers with uniform arms, the arms may be composed of the same homopolymer or they may be similar to block copolymers, with connected segments. Star polymers within the latter group are often referred to as star-block copolymers [7,8]. Star polymers, and especially star-block copolymers, can offer several advantages in physical properties over their linear counterparts [8,9]. These include added stability provided by the central core of the molecule and easier processability, which results from a lower viscosity provided by shorter segments for a given molecular weight.

Star polymers that possess two or more chemically different arm types are termed miktoarm star polymers [1]. There are a variety of ways in which the arms may be arranged, as shown in Scheme 1. Although the first synthesis of a miktoarm star polymer was reported by Eschwey and Burchard in 1975 [10], the majority of work in this area has been done much more recently. The most common method of synthesis involves living anionic polymerization and the linking of one or more preformed arms of the first type to a core molecule. Arms of the second type may be subsequently linked to the core or they may be polymerized from the core using the *in–out* method. These

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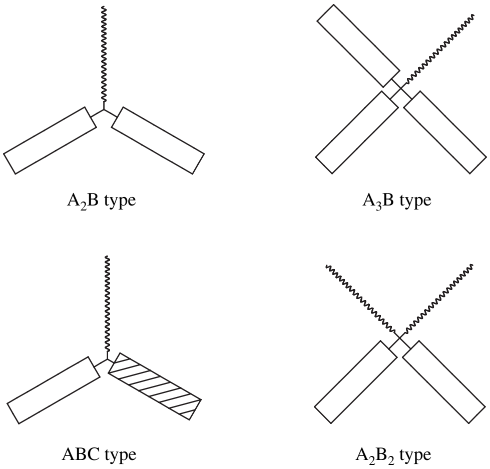
doi:10.1016/j.polymer.2008.01.012

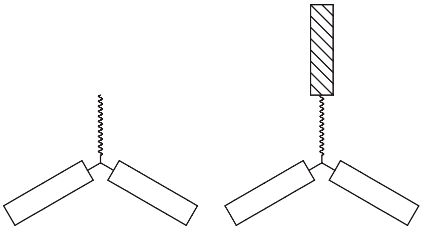


Scheme 1. Possible miktoarm star configurations.

methods have been used to successfully create polymers of the A_nB_n [10–12], A_2B_2 [13,14], and A_2B and A_3B types [1,15,16]. Using similar methods, miktoarm star polymers have also been created via quasiliving cationic polymerization by linking arms with a divinylether compound [17] and by controlled radical polymerization [18].

A drawback to any method involving the linking of preformed arms is the elimination of unlinked arms from the final star polymer. Core-first methods involving a multi-functional initiator typically avoid this problem, and in general, quasiliving cationic and controlled radical polymerizations are more amenable to this approach than living anionic polymerization, due to poor solubility of most polyanionic initiators. Thus, the core-first method is commonly used to create star polymers via cationic polymerization. For example, Storey and coworkers reported the synthesis of three-armed star radial block copolymers using tricumyl chloride as an initiator [19]. Multi-functional cationic initiators have also been used to synthesize four-armed [20,21], six-armed [22] and eight-armed [23] stars, although in all of these cases, only star polymers with uniform arms were reported.

Multi-functional initiators can provide synthetic routes to miktoarm stars by combining initiation sites for two or more polymerization techniques, e.g., cationic, radical, etc. [24]. In this paper, we discuss the synthesis of A_2B miktoarm star polymers that are an extension of a linear terpolymer structure previously reported by us [25]. The targeted polymer architectures and reaction sequence are illustrated in Schemes 2 and 3. The synthesis involved quasiliving cationic polymerization of isobutylene from a monofunctional cationic initiator that also contains a blocked hydroxyl group, followed optionally by sequential addition of styrene. The latent hydroxyl functionality of the initiator was then de-blocked, functionalized with a branching agent, and used for atom transfer radical polymerization (ATRP) of *tert*-butyl acrylate (*t*BA). This resulted in $(\mathrm{P}t\mathrm{BA})_2$–PIB and $(\mathrm{P}t\mathrm{BA})_2$–PIB–PS miktoarm star copolymers and star-block terpolymers. In some cases, the ester side chains of the P*t*BA blocks were cleaved to create poly(acrylic acid) (PAA) blocks, thereby yielding $(\mathrm{PAA})_2$–PIB and $(\mathrm{PAA})_2$–PIB–PS miktoarm star co- and terpolymers.



Scheme 2. Miktoarm star polymer architectures created using a cationic polymerization initiator containing latent sites for dual initiation of atom transfer radical polymerization.

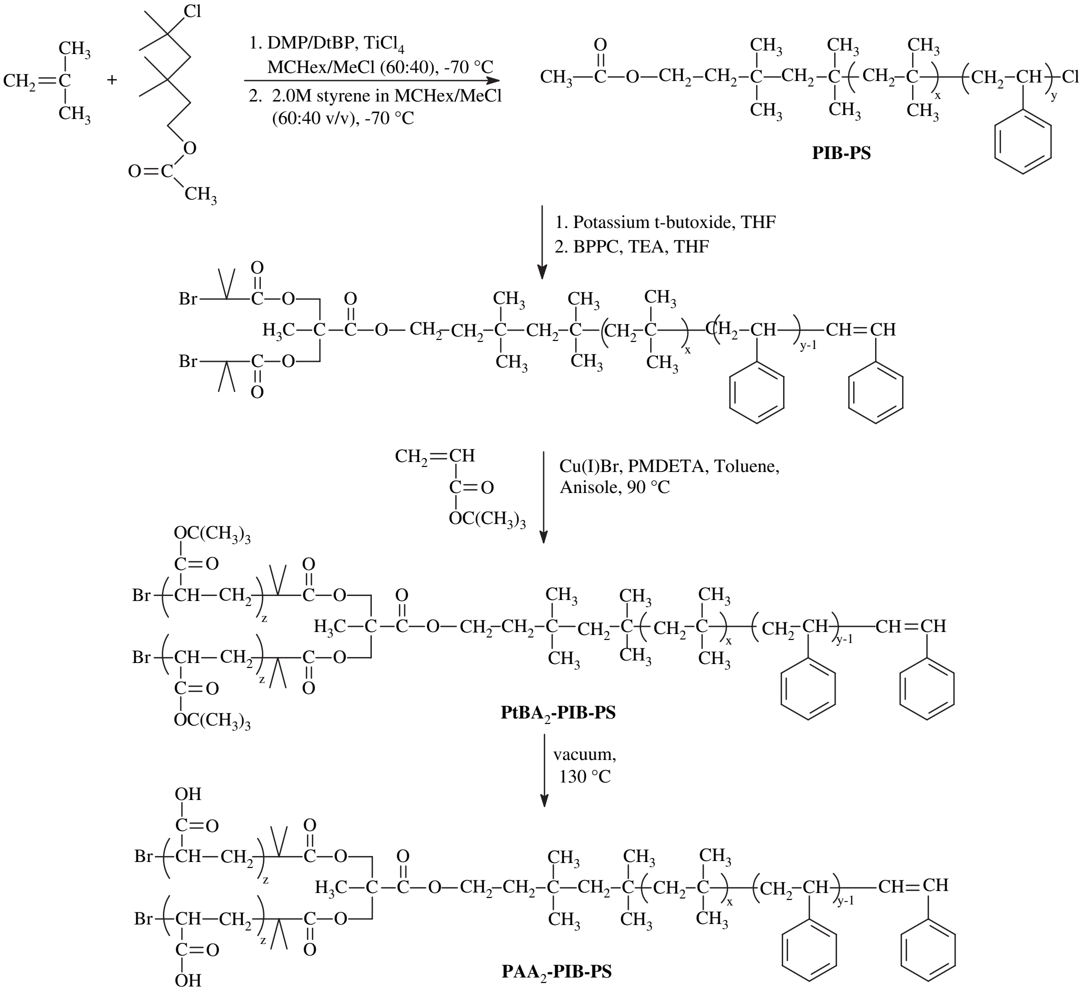
2. Experimental

2.1. Materials

2-Bromoisobutyryl bromide (98%), 2,2-bis(hydroxymethyl)propionic acid (98%), benzene (99.9%), phosphorus pentachloride (95%), triethylamine (99.5%), hexane (anhydrous, 95%), methylcyclohexane (MCHex, anhydrous, 99+%), 2,4-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, respectively. Styrene, 2,6-di-*tert*-butylpyridine, *tert*-butyl acrylate, and THF (all from Sigma–Aldrich) were distilled from CaH_2 under reduced pressure. 1,1,4,7,7-Pentamethyldiethylenetriamine (PMDETA) (99%) from Sigma–Aldrich and distilled *tert*-butyl acrylate (*t*BA) were sparged with dry $N_{2(g)}$ for 20 min before use. 3,3,5-Trimethyl-5-chlorohexyl acetate (TMCHA) was synthesized as previously described [25].

2.2. Instrumentation

Molecular weights and polydispersity index (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, 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 the addition of styrene) were analyzed using a known d*n*/d*c* value of 0.103 mL/g. PIB–PS blocks and final $(\mathrm{P}t\mathrm{BA})_2$–PIB–PS terpolymers were analyzed using a d*n*/d*c* value calculated from



Scheme 3. Overall synthesis of miktoarm star polymers.

the refractive index detector response and assuming 100% mass recovery from the columns.

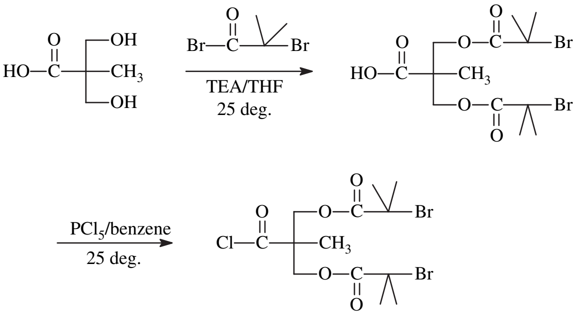
Solution ^1H and ^{13}C NMR spectra were obtained on a Varian 300 MHz spectrometer using 5 mm o.d. tubes with sample concentrations of 5–7 and 20% (*m*/*v*) for ^1H and ^{13}C NMR, respectively, in deuterated chloroform ($CDCl_3$) (Aldrich Chemical Co.) containing tetramethylsilane as an internal reference. ^{13}C NMR spectra of the polymers containing PAA were obtained using sample concentrations of 20% (*m*/*v*) in deuterated methyl sulfoxide/deuterated chloroform (10/90 v/v) (Aldrich Chemical Co.) containing 0.03% (v/v) 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 a 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 [26]. The $=CH_2$ wags of IB and styrene, which occur at 887 and 911 cm^{-1}, respectively, were monitored to determine monomer conversion. The light conduit and probe were contained within a glove box (MBraun Labmaster 130) equipped with a hexane/heptane cold bath.

FTIR spectra of polymers were obtained using a Bruker Equinox 55 FTIR spectrometer from films cast from freshly distilled THF directly onto KBr slides.

2.3. Branching agent synthesis

The overall reaction scheme for the synthesis of the branching agent 2,2-bis((2-bromo-2-methyl)propionatomethyl)propionyl chloride (BPPC) is illustrated in Scheme 4. To a 250 mL



Scheme 4. Synthesis of the branching agent 2,2-bis((2-bromo-2-methyl)-propionatomethyl)propionyl chloride.

three-necked round bottom flask equipped with a magnetic stir bar and ice bath were charged 5.0 g (3.7×10^{-2} mol) 2,2-bis-(hydroxymethyl)propionic acid and 80 mL THF. Then 10.4 mL (7.5×10^{-2} mol) triethylamine was added via syringe. The solution became homogeneous upon TEA addition. A solution of 9.3 mL (7.4×10^{-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. Salts were removed by filtration and the bulk of the solvent was removed by rotary evaporation. The resulting concentrated solution was filtered to remove residual salts and the product was further dried under vacuum at room temperature until the soft white solid, 2,2-bis(2-bromo-2-methyl)propionatomethyl)propionic acid (BPPA) was formed. The product was used without further purification (90% yield).

BPPA was converted to the acid chloride as follows: to a 250 mL three-necked round bottom flask equipped with magnetic stir bar was charged 11 g (2.5×10^{-2} mol) BPPA dissolved in 50 mL benzene. Then 6.7 g (3.2×10^{-2} mol) phosphorus pentachloride was added quickly to the reactor to minimize exposure to the atmosphere. The reaction was allowed to proceed overnight with stirring at room temperature. The resulting mixture was filtered and benzene was removed by vacuum stripping. The liquid product was washed with hexanes to remove excess PCl_5. Additional salts were removed by filtration and the brown liquid product 2,2-bis((2-bromo-2-methyl)propionatomethyl)propionyl chloride was recovered by removing hexane under vacuum (75% yield).

2.4. Synthesis of PIB and PIB–PS copolymers

A representative procedure for the synthesis of PIB containing a blocked hydroxyl head group was as follows: the DiComp probe was inserted into a 250 mL four-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 (5.2×10^{-4} mol) 2,4-lutidine, 0.04 mL (1.8×10^{-4} mol) D*t*BP, and 0.074 g (3.4×10^{-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 (1.8×10^{-1} mol) IB (−70 °C) was added to the flask. Several monomer baseline spectra were obtained and 1.2 mL (1.1×10^{-2} mol) $TiCl_4$ (neat and at room temperature) was added to the flask. Once 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, $[TMCHA]_0 = 1.9 \times 10^{-3}$ M, $[DtBP]_0 = 9.8 \times 10^{-4}$ M, $[2,4\text{-lutidine}]_0 = 2.9 \times 10^{-3}$ M, $[TiCl_4]_0 = 6.0 \times 10^{-2}$ M. The IB spectral data acquisition was then discontinued 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 four-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) 2,4-lutidine, 0.08 mL (3×10^{-4} mol) D*t*BP, and 0.21 g (9.5×10^{-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 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, $[TMCHA]_0 = 2.4 \times 10^{-3}$ M, $[DtBP]_0 = 1 \times 10^{-3}$ M, $[2,4\text{-lutidine}]_0 = 3.0 \times 10^{-3}$ M, $[TiCl_4]_0 = 3.5 \times 10^{-2}$ M. The IB spectral data acquisition was then discontinued 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 (4.2×10^{-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 the macroinitiator

The two-step site transformation was carried out using a variation of a previously reported procedure [27]. A representative procedure, using PIB as the macroinitiator, was as follows: to deblock the hydroxyl group at the initiator fragment and simultaneously dehydrochlorinate the chain end, a three-necked round bottom flask, equipped with heating mantle, magnetic stir bar, and condensing column, was charged with PIB (10.3 g, $M_n = 31{,}600$ g/mol) dissolved in 110 mL distilled THF. The reactor was purged with N_2 and then equipped with a N_2 bubbler. Potassium *tert*-butoxide (0.15 g, 1.3×10^{-3} mol) dissolved in 20 mL THF was injected slowly via syringe. The reaction mixture was refluxed for 48 h and cooled to room temperature. Hexanes (75 mL) were added to extract the polymer. The product was washed with 80/20 (v/v) MeOH/DI H_2O and then with DI H_2O to remove THF. The hexane layer was dried over magnesium sulfate, filtered, and vacuum stripped to remove the solvent. The product was dried in a vacuum oven at room temperature overnight (98% yield).

A representative procedure to incorporate dual ATRP initiating sites was as follows: to a 250 mL three-necked round bottom flask equipped with magnetic stir bar, heating mantle, N_2 bubbler, and condenser column were charged hydroxy-functional PIB (6.1 g, $M_n = 31{,}600$ g/mol), 150 mL THF, 0.98 g (2.1×10^{-3} mol) BPPC, and 0.36 mL triethylamine (2.6×10^{-3} mol). The reaction mixture 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. The same procedures were used for PIB−PS macroinitiators except that the reaction products were precipitated into 80/20 (v/v) MeOH/DI H_2O rather than washed with MeOH and water. The solid products were then collected by filtration and dried in a vacuum oven.

2.6. ATRP of tert-butyl acrylate

A representative procedure for ATRP polymerization was as follows: to a 100 mL Kjeldahl-style Schlenk flask, equipped with magnetic stir bar and contained within a dry box, were charged 3.0×10^{-2} g (2.2×10^{-4} mol) CuBr, 1.0 g (1.1×10^{-4} mol; 2.2×10^{-4} mol ATRP initiating sites) PIB, 8 mL toluene, 0.16 mL anisole, and 1.39 g (1.1×10^{-2} mol) *t*BA (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 min. Then, 4.5×10^{-2} mL (2.2×10^{-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 (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 N_2 purged syringe for kinetic analysis, and the reaction was quenched in LN_2 after 4.5 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_2O (80/20 v/v). The product was collected and dried under vacuum at room temperature overnight (96% yield).

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

2.7. Cleavage of tert-butyl acrylate side chains

The poly(*tert*-butyl acrylate) segments were converted to poly(acrylic acid) by thermolysis, with volatilization of isobutylene. A monolayer of $(PtBA)_2$−PIB (small crumbs) or $(PtBA)_2$−PIB−PS (powder) was spread onto a heat-resistant dish and placed in a vacuum oven that was preheated to 130 °C. After 48 h, the dish was removed, and the polymer was cooled to room temperature to be collected.

3. Results and discussion

3.1. Branching agent synthesis

In the synthesis of the branching agent intermediate, BPPA, the solid white starting material, (2,2-bis(hydroxymethyl)propionic acid), was observed to go into the solution upon addition of TEA. After stirring the reaction mixture overnight, and again after initial removal of the solvent, solid TEA−HBr was observed in the reactor and removed by filtration. Upon removing the residual solvent with a vacuum pump, the product was revealed as a soft, white solid with ~90% yield. Fig. 1 illustrates the ^1H NMR spectrum of the product. The methylene protons are 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. The peak near 1.3 ppm represents the methyl group nearest to the acid functionality. The unlabeled peaks between 3 and 4 ppm are due to residual 2,2-bis(hydroxymethyl)propionic acid and THF. Steps for further purification were not taken because the impurities do not carry through to the final product.

When the acid was converted to an acid chloride, the methylene peak near 4.3 shifted slightly to ~4.4 ppm, and the methyl peak near 1.3 shifted to 1.45 ppm, as illustrated in the ^1H NMR spectrum in Fig. 2. Because these changes were subtle, the primary indication of conversion to the final product was the disappearance of the peak associated with the acid functionality. The color of the mixture changed from yellow to orange as the reaction proceeded, and the final product, BPPC, was a brown liquid obtained with ~75% yield.

3.2. Synthesis of PIB and PIB−PS copolymers

ATRP macroinitiators, either PIB homopolymer or in some instances PIB−PS, were synthesized via quasiliving cationic polymerization using TMCHA as the initiator and $TiCl_4$ as

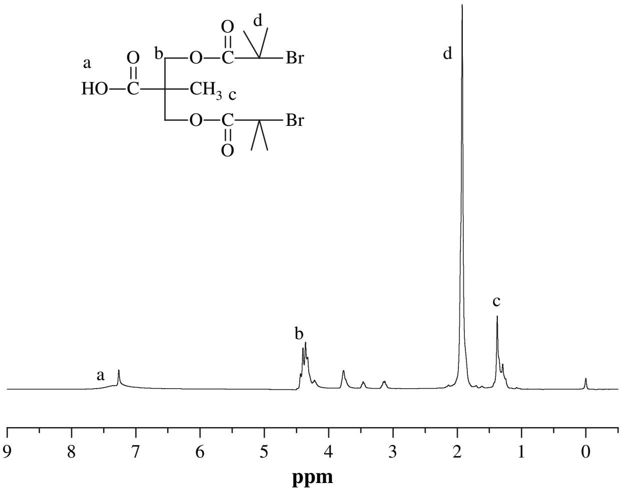


Fig. 1. ^1H NMR spectrum of 2,2-bis((2-bromo-2-methyl)propionatomethyl)-propionic acid. The acid proton appears as a broad peak (a) underneath the sharp chloroform signal at 7.3 ppm.

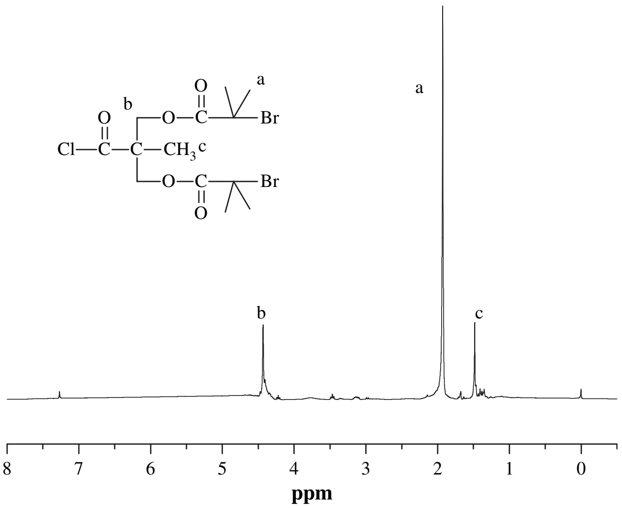


Fig. 2. ^{1}H NMR spectrum of 2,2-bis((2-bromo-2-methyl)propionatomethyl)-propionyl chloride.

the co-initiator in a hydrocarbon/MeCl (60/40 v/v) solvent system with DMP and D*t*BP as Lewis base additive and proton trap, respectively, at −70 °C. At >99% conversion of IB as determined by ATR-FTIR monitoring, PIB homopolymerizations were terminated with pre-chilled methanol; for PIB−PS block copolymers 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 then quenched at ~50% styrene conversion with pre-chilled methanol. The styrene polymerization was short-stopped in this manner to avoid electrophilic aromatic substitution reactions [28] 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.

Table 1 lists molecular weight and compositional data for the PIB intermediate blocks and PIB−PS macroinitiators as well as PIB macroinitiators that were not blocked to PS segments. Number average molecular weights of the PIB blocks determined by SEC ($M_{n,PIB(SEC)}$) were higher than theoretical, indicating low initiator efficiency ($I_{eff} = 0.72-0.95$). This phenomenon is apparently related to complexation of $TiCl_4$ with the carbonyl group in the initiator and has been discussed by other authors [29,30] as well as by us [25]. Number average molecular weight of the PS block from SEC ($M_{n,PS(SEC)}$) was calculated as the difference between the molecular weight of the overall block copolymer determined by SEC ($M_{n,PIB-PS(SEC)}$) and $M_{n,PIB(SEC)}$. For comparison, $M_{n,PS(NMR)}$ was calculated from copolymer composition using Eq. (1) [28],

$$M_{n,PS(NMR)} = M_{n,PIB(SEC)} \times \frac{W_{PS(NMR)}}{\left(100 - W_{PS(NMR)}\right)} \tag{1}$$

where $W_{PS(NMR)}$ is the weight percent of PS as determined by ^{1}H NMR spectroscopy of the copolymer. $W_{PS(NMR)}$ was calculated using the ratio of the areas of the aromatic and aliphatic regions of the NMR spectrum of PIB−PS (Fig. 3), according to Eq. (2) [28],

$$W_{PS(NMR)} = \frac{M_{St} \times A_{Ar}}{(M_{St} \times A_{Ar}) + M_{IB}(5 \times A_{Al} - 3 \times A_{Ar})/8} \times 100\% \tag{2}$$

where M_{St} and M_{IB} are the molecular weights of styrene and isobutylene monomer units, respectively, A_{Ar} is the area of the aromatic region, and A_{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. Polydispersity index (PDI) for PIB homopolymers was uniformly low (<1.1), which is typical for quasiliving polymerization of IB under these conditions. PDI for PIB−PS was considerably broader and is caused by high run number for styrene quasiliving cationic

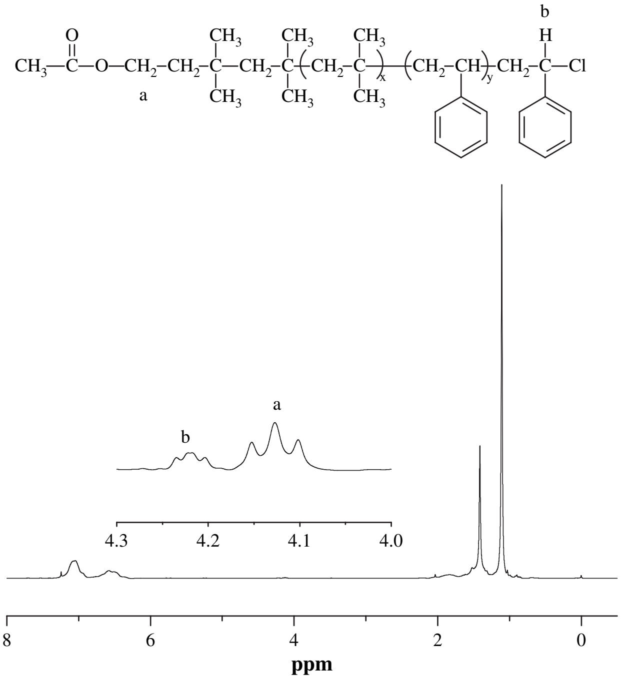


Fig. 3. ^{1}H NMR spectrum of PIB−PS copolymer (Table 1, Entry A) with expansion of the chain end resonances.

Table 1
M_n, PDI, and composition data for PIB−PS and PIB macroinitiators

Entry	PIB block			PS block			PIB−PS copolymer			
	$M_{n,PIB(Theo)}$ (g/mol)	$M_{n,PIB(SEC)}$ (g/mol)	PDI	$M_{n,PS(Theo)}$ (g/mol)	$M_{n,PS(SEC)}$ (g/mol)	$M_{n,PS(NMR)}$ (g/mol)	$M_{n,SEC}$ (g/mol)	PDI	Wt% PIB ($W_{PIB,NMR}$)	Wt% PS ($W_{PS,NMR}$)
A	5000	6900	1.08	5000	7500	7500	14,400	1.36	47.8	52.2
B	30,000	31,600	1.06	–	–	–	–	–	–	–
C	7500	9200	1.07	–	–	–	–	–	–	–

polymerization under these conditions [31,32], coupled with relatively short PS block length.

3.3. Site transformation of the macroinitiator

The head groups of the PIB and PIB−PS macroinitiators were transformed in two steps to allow for ATRP initiation. The first involved application of potassium *tert*-butoxide to de-protect the hydroxyl functionality of the initiator fragment. A secondary consequence of this treatment was the simultaneous dehydrochlorination of the tail group of the polymer to form an olefin. The latter, derived either from the *tert*-chloride group of PIB or from the *sec*-benzylic chloride group of PS is more thermally stable than chloride and appears to be inert toward the subsequent radical polymerization [25]. The base was introduced into the copolymer as a slurry in THF and the mixture became homogeneous as the reaction proceeded. Fig. 3 illustrates the resonances associated with the methylene protons nearest to the protected hydroxyl group (peak (a)) and the proton nearest to the terminal chlorine atom (peak (b)) in the PIB−PS samples prior to reaction. In the PIB homopolymers (Fig. 4), peak (b) is not present and the protons near the terminal chlorine are located at 1.68 and 1.96 ppm. After reaction, peaks (a) and (b) are no longer present in the ^{1}H NMR spectrum of PIB−PS (Fig. 5) and a new peak at $\sim$3.7 ppm has appeared. This peak is associated with the methylene protons of the initiator fragment nearest to the hydroxyl group. The same peak is present in the PIB sample (not shown).

The second step of site transformation involved the incorporation of a bromine-functionalized branching agent for ATRP initiation. This reaction was facile but slow; 48 h were needed for complete conversion. Fig. 6 shows the ^{1}H NMR spectrum of the site-transformed PIB homopolymers, 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 (b) and 4.35 ppm (a), which represent the methylene protons of the branching agent and of the original initiator fragment, respectively. 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.

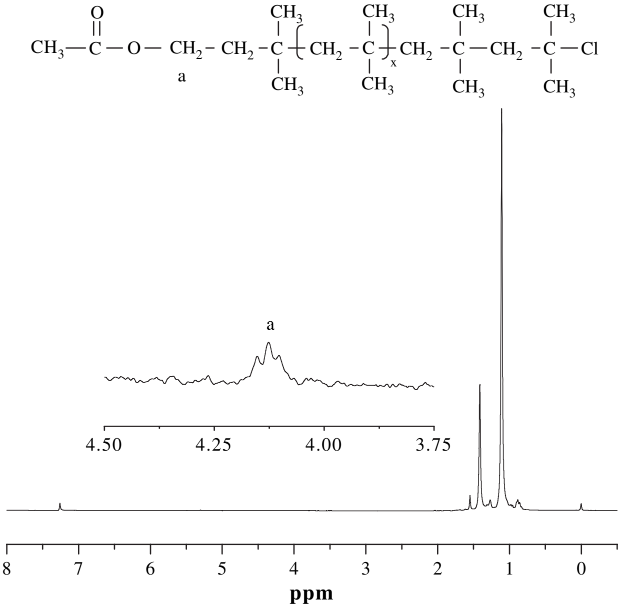


Fig. 4. ^{1}H NMR spectrum of PIB (Table 1, Entry B) with expansion of the chain end resonance.

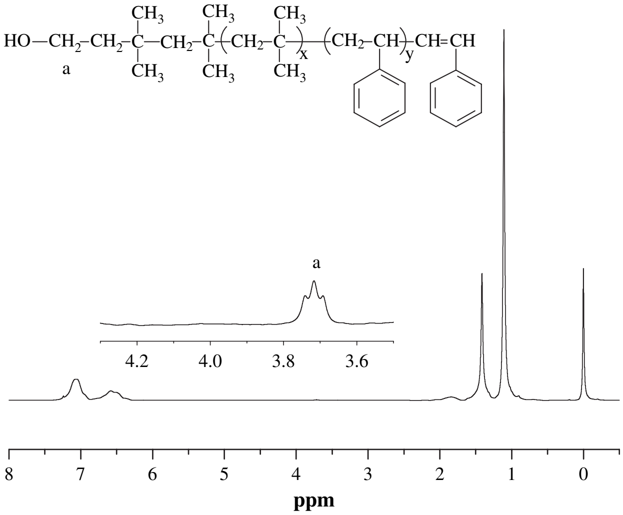


Fig. 5. ^{1}H NMR spectrum of de-protected PIB−PS (Table 1, Entry A) with expansion illustrating the hydroxyl head group.

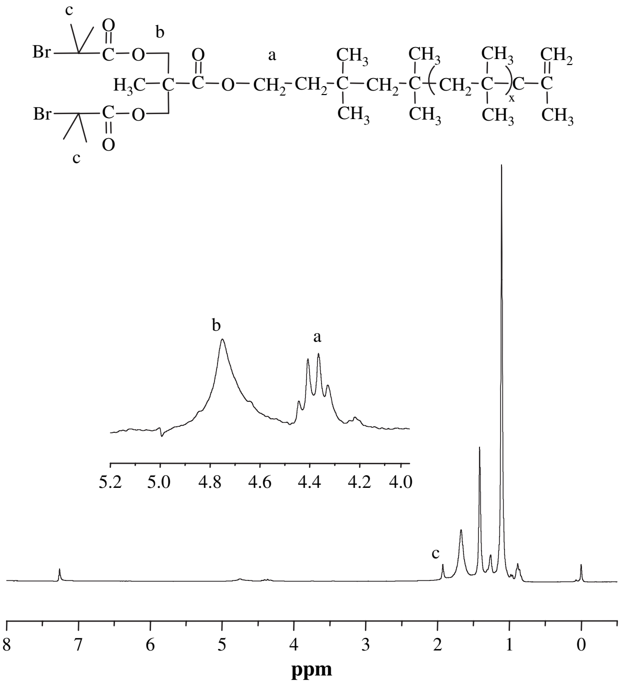


Fig. 6. ^{1}H NMR spectrum of branched PIB (Table 1, Entry B) with expansion of the end group region.

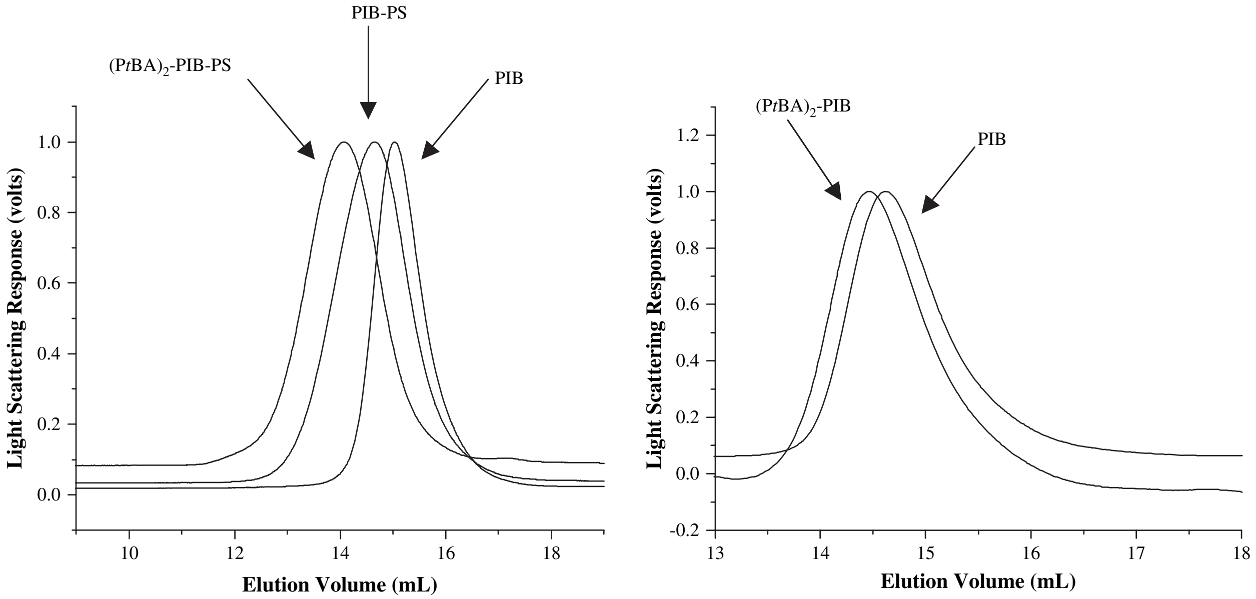


Fig. 7. SEC traces representing each stage of star polymer synthesis: $(PtBA)_2$–PIB–PS (Table 2, Entry D) (left) and $(PtBA)_2$–PIB (Table 2, Entry G) (right).

3.4. ATRP of tert-butyl acrylate

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. In all cases, $[\text{ligand}]_0{:}[\text{Cu(I)Br}]_0{:}[\text{CE}]_0 = 1{:}1{:}1$. 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 mixture turned light green. As higher conversion was obtained, a darker green color developed.

SEC traces (normalized intensity) representing each stage of the terpolymer synthesis sequence for a $(PtBA)_2$–PIB–PS star and a $(PtBA)_2$–PIB star are shown in Fig. 7. For both samples, molecular weight as determined by MALLS increased with the addition of each block segment, as expected.

Figs. 8 and 9 show the ^1H and ^{13}C NMR spectra, respectively, of a representative miktoarm star copolymer, $(PtBA)_2$–

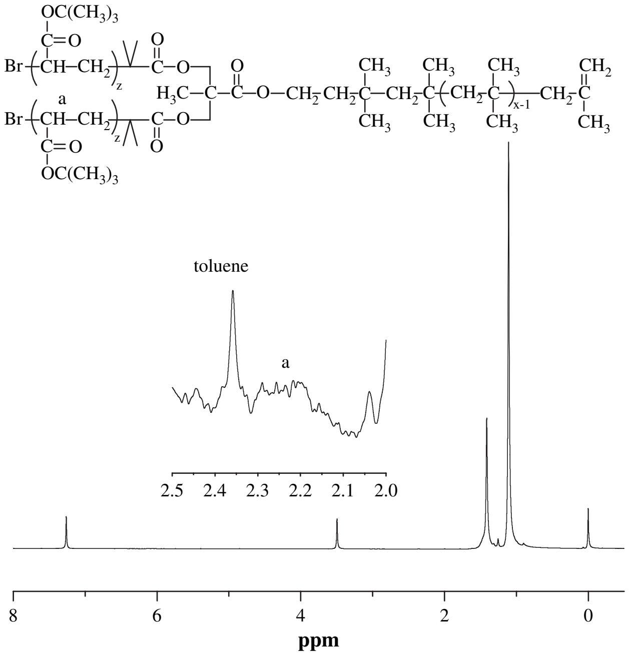


Fig. 8. ^1H NMR spectrum of $(PtBA)_2$–PIB (Table 2, Entry F) with the inset illustrating the methine proton of PtBA.

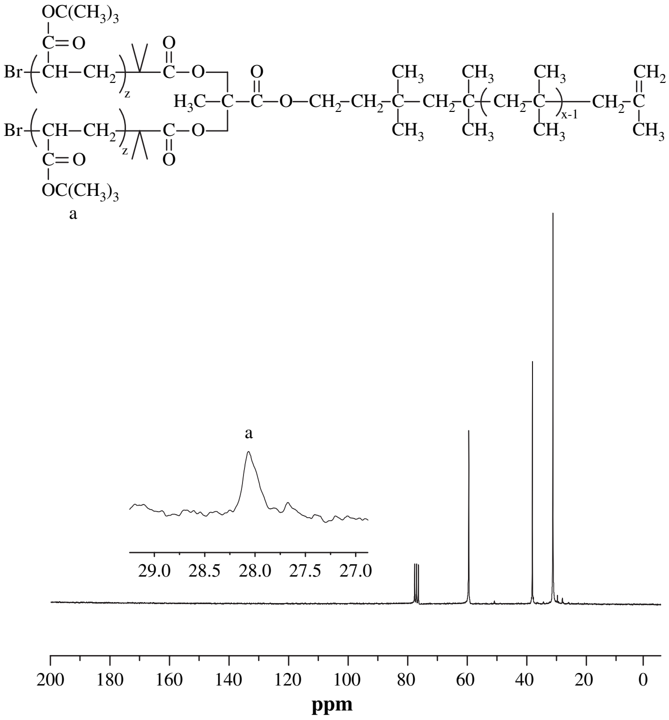


Fig. 9. ^{13}C NMR spectrum of $(PtBA)_2$–PIB (Table 2, Entry F) with expansion of the 28 ppm region.

Table 2
M_n, PDI, and composition data[a] for $(PtBA)_2$–PIB–PS and $(PtBA)_2$–PIB miktoarm star polymers

Entry	Macroinitiator		PtBA blocks[b]				$(PtBA)_2$–PIB–PS or $(PtBA)_2$–PIB				
	Type	$M_{n,SEC}$ (g/mol)	ATRP time (min)	ATRP conv. (%)	$M_{n,PtBA(Theo)}$ (g/mol)	$M_{n,PtBA(SEC)}$ (g/mol)	$M_{n,SEC}$ (g/mol)	PDI	Wt% PIB	Wt% PS	Wt% PtBA
D	PIB–PS	14,400	276	26.4	6900	7500	21,900	1.37	30.2	33.1	36.7
E	PIB–PS	14,400	282	81.7	5200	4500	18,900	1.38	36.8	40.4	22.8
F	PIB	31,600	308	–	–	19,300	50,900	1.37	62.1	–	37.9
G	PIB	9200	275	14.5	4300	5600	14,800	1.54	62.2	–	37.8

[a] Composition of $(PtBA)_2$–PIB–PS determined by NMR; composition of $(PtBA)_2$–PIB determined by SEC.

[b] Data refer to both PtBA blocks combined.

PIB. Addition of the acrylate block was indicated by the appearance of a new resonance at ~2.2 ppm (a), 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. Because the methine proton peak (a) was very weak, ^{13}C NMR (Fig. 9) was the primary method of verification. Of note is the peak associated with the *t*-butyl groups of PtBA at 28 ppm (methyl, peak (a)), which is the largest peak attributed to the acrylate segment. The same resonance can be seen in $(PtBA)_2$–PIB–PS terpolymers.

Table 2 illustrates the results of the ATRP reactions. Number average molecular weights of the final co- and terpolymer stars were determined by SEC-MALLS. These values were in good agreement with the theoretical molecular weights calculated from the molecular weights of the macroinitiator and the ATRP monomer conversions. PDI after ATRP was in the range 1.4–1.5; these values are similar to those obtained earlier by us [25]. For most of the samples, the conversion was low due to low chain end concentration, [CE]. For example, Sample D shows a lower conversion than Sample E because the chain end concentration was lower for the reaction ($[CE] = 2.8 \times 10^{-2}$ M for Sample D as compared to 5.1×10^{-2} M for Sample E). The terpolymer molecular weight for Sample D is higher than that of Sample E because a higher PtBA molecular weight was targeted in this system to achieve a larger acrylate composition, and thus, a larger hydrophilic segment. Terpolymer composition of the $(PtBA)_2$–PIB–PS stars was calculated from ^1H NMR data by comparing the peak areas from two different spectra as described previously [33]. In these calculations, the aromatic region of the spectrum, due only to the PS

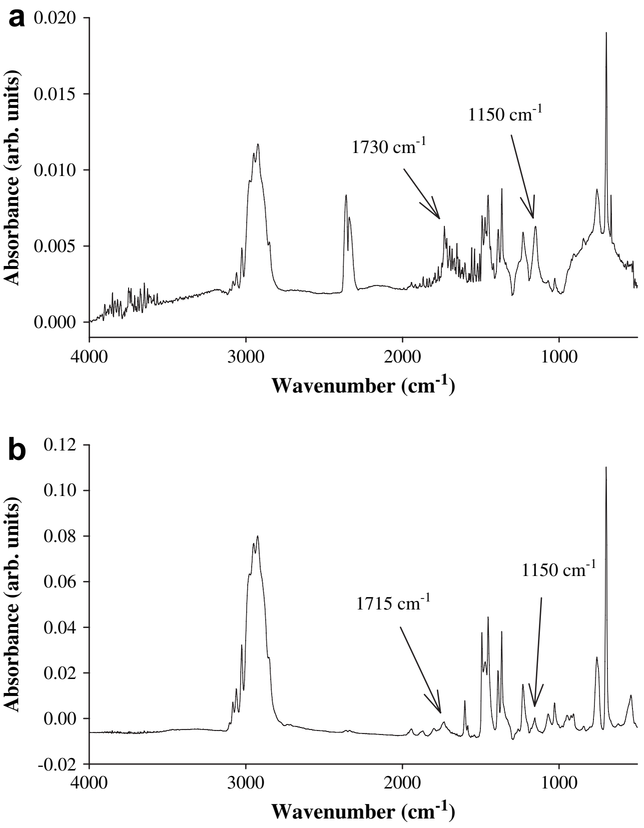


Fig. 10. FTIR spectra of $(PtBA)_2$–PIB–PS (a) and $(PAA)_2$–PIB–PS (b) (Table 2, Entry D).

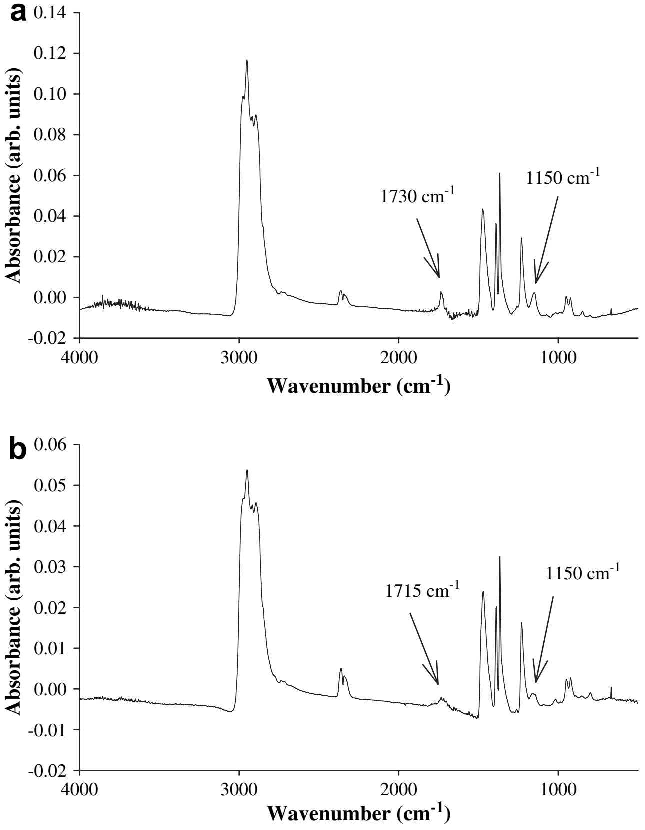


Fig. 11. FTIR spectra of $(PtBA)_2$–PIB (a) and $(PAA)_2$–PIB (b) (Table 2, Entry F).

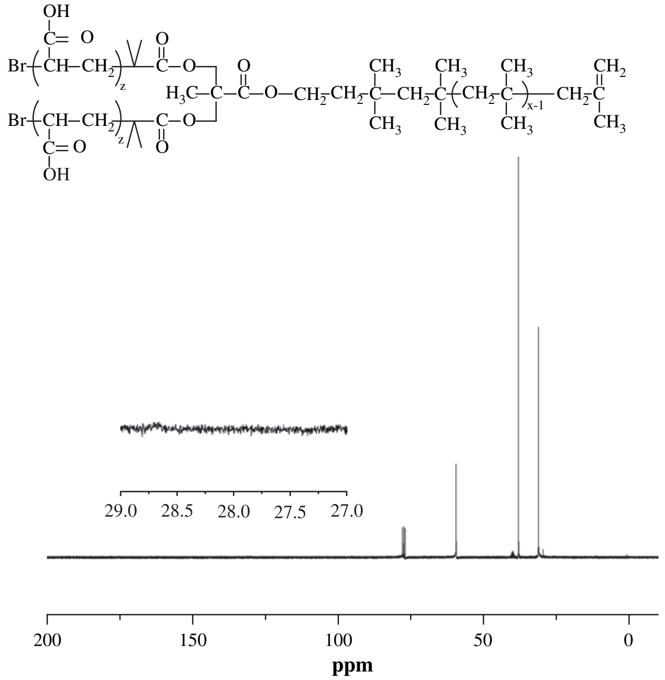


Fig. 12. ^{13}C NMR spectrum of $(PAA)_2$–PIB (Table 2, Entry F) with expansion of the 28 ppm region.

block, was used as an internal reference, which allowed for a direct comparison in the two spectra. Molecular weight and compositional data were in excellent agreement for the terpolymers. Because the peaks of P*t*BA and PIB overlap in the ^{1}H NMR spectrum and there is no aromatic region that may be used as a reference for integration, the compositions of those copolymers cannot be calculated by NMR. Thus, compositions listed in Table 2 for $(\text{P}t\text{BA})_2$–PIB stars are based on SEC values.

3.5. Cleavage of tert-butyl acrylate side chains

FTIR spectra (Fig. 10) of a $(\text{P}t\text{BA})_2$–PIB–PS star (Table 2, Entry D) were obtained before (a) and after hydrolysis (b) to confirm first the incorporation of the P*t*BA segment, then the cleavage of the *t*-butyl groups. Similar spectra are shown in Fig. 11 for a $(\text{P}t\text{BA})_2$–PIB star (Table 2, Entry F). As illustrated, C=O and C–O stretches, which are characteristic of P*t*BA, appear near 1730 and 1150 cm^{-1}, respectively, in Figs. 10(a) and 11(a). The spectra of the hydrolyzed materials illustrate the cleavage of the P*t*BA side chains to create the hydrophilic poly(acrylic acid). The hydrolyzed polymers are characterized by a slight shift in the 1730 cm^{-1} stretch to about 1715 cm^{-1} and strong decrease in intensity of the 1150 cm^{-1} peak. It was difficult to obtain well resolved FTIR spectra of the hydrolyzed samples due to widely differing solvation characteristics of the various blocks; thus, the conversion to PAA was verified by ^{13}C NMR spectroscopy. The small peak representing the *t*-butyl groups that formerly was present at 28 ppm (Fig. 8, copolymer) completely disappeared, as illustrated in Fig. 12.

4. Conclusions

PAA_2–PIB–PS and PAA_2–PIB miktoarm star polymers were synthesized from TMCHA, an initiator containing a cationic initiating site and a latent hydroxyl functionality. Macroinitiators were prepared from this initiator using quasiliving cationic polymerization. After isolating the PIB or PIB–PS copolymers, the hydroxyl functionality of the initiator was de-blocked and esterified with the branching agent 2,2-bis-((2-bromo-2-methyl)propionatomethyl)propionyl chloride, a difunctional 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 that the overall composition of the systems could be controlled.

Acknowledgements

The Robert M. Hearin Support Foundation and the National Science Foundation Materials Research Science and Engineering Center (DMR 0213883) are gratefully acknowledged for fellowship support to L. Krystin Breland.

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