*Macromolecules* **1996,** *29,* 4605−4612

# Anionic Synthesis, Modification, and Characterization of ABC Triblock Copolymers

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*Received August 15, 1995; Revised Manuscript Received March 4, 1996*[⊗]

ABSTRACT: ABC triblock copolymers of poly(styrene)-*b*-poly(*tert*-butyl methacrylate)-*b*-poly(methyl methacrylate) (PS-P$^t$BMA-PMMA) were anionically synthesized by sequential addition of styrene, *tert*-butyl methacrylate, and methyl methacrylate, respectively. Characterization of these triblock copolymers was done using nuclear magnetic resonance spectroscopy (NMR), infrared spectroscopy (IR), differential scanning calorimetry (DSC), gel permeation chromatography (GPC), and transmission electron microscopy (TEM). The gel permeation chromatograms were found to be somewhat broad ($M_w/M_n \approx 1.2$) due to partial quenching of polystyryl anion upon switching to *tert*-butyl methacrylate. The actual polydispersity of these triblocks, not including PS homopolymer, was determined to be less than 1.1. TEM micrographs of these ABC triblocks indicated that the morphology is essentially lamellar. The long-range order of the microstructure, however, seems to decrease with decreasing spacer block length. The *tert*-butyl methacrylate middle block of these PS-P$^t$BuMA-PMMA triblocks could be selectively modified to anhydride and carboxylic acid functionalities in the presence of the PMMA block. Thermal treatment of these ABC triblocks (230 °C for 30 min) quantitatively transformed the P$^t$BMA middle block into poly(methacrylic anhydride) (PMAN). The PMAN block could then be quantitatively hydrolyzed to poly(methacrylic acid) (PMAA) under mild conditions ($NaHCO_3$, 70 °C, 1 h).

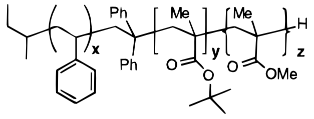
## Introduction

The compatibilization of polymer blends has recently been an area of great interest.[1,2] The blending of two polymers having markedly different physical properties can yield a new material having the properties of both components. Unfortunately, immiscible polymers often phase separate and coalesce during melt blending or processing. For this reason, the development of new compatibilizers for polymer blends is one of our primary research interests. Many groups have utilized diblock copolymers to compatibilize blends.[3−7] The interfacial presence of A-B diblock copolymers has been postulated to stabilize blend morphology by reducing the interfacial tension between the two immiscible bulk polymers in the blend, A and B.[8] However, studies have suggested that block copolymer micelle formation can decrease compatibilizer efficiency in some immiscible systems.[2,9] In these cases, increased compatibilization is achieved only when a large amount of diblock copolymer (above 5%) is used. Alternative concepts include reactive blending.[1,2,10] This method can be quite effective but requires the synthesis of polymers bearing the desired functional groups for a rapid interfacial reaction.

In an effort to improve compatibilization in polymer blends, we have synthesized and studied the use of ABC triblock copolymers as blend modifiers. Triblock copolymers also have many other potential applications in the areas of surface modification, lubrication, and adhesion.

Triblock copolymers have been shown to have higher critical micelle concentrations (CMC) than diblocks of similar molecular weight and composition.[11] If this is true, ABC triblocks may more efficiently compatibilize immiscible polymer blends than corresponding A-C diblocks. It has also been suggested that ionic groups attached to polymers most likely reside in the blend interface.[12] We hypothesize that an ABC triblock copolymer having a very polar B block might be an efficient immiscible blend compatibilizer.[13,14] In a forthcoming publication we will discuss the compatibilization efficiencies of three ABC triblocks and PS-PMMA diblocks of similar molecular weight and composition.[14]

In this work, we have synthesized poly(styrene)-*b*-poly(*tert*-butyl methacrylate)-*b*-poly(methyl methacrylate) (PS-P$^t$BMA-PMMA) triblock copolymers using anionic polymerization. Diblock copolymers of styrene and alkyl methacrylates have been well-studied.[15] It has also been shown that alkyl methacrylates can be introduced in any order during anionic synthesis.[16] The synthesis of PS-P$^t$BMA-PMMA triblocks (**1**) was then achieved by sequential addition of *sec*-butyllithium, styrene, 1,1-diphenylethylene, *tert*-butyl methacrylate ($^t$BMA), and methyl methacrylate. We also report procedures for the selective modification of the middle P$^t$BMA block of triblock **1** into poly(methacrylic anhydride) (PMAN, **2**) and poly(methacrylic acid) (PMAA, **3**) in the presence of the PMMA block.



**1**

## Experimental Section

**Materials.** Each monomer was initially purged with argon and stirred over $CaH_2$ (Aldrich) for 24 h ($^t$BMA was stirred for 72 h). Methyl methacrylate (MMA, Aldrich) was distilled (high-vacuum distillation using Schlenk techniques) into a flask containing 3−4 mL of 1 M $Et_3Al$ in hexanes (Aldrich) for each 50 mL of MMA. The bulk of the hexanes was removed from the receiving flask by distillation before MMA was

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[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1996.

S0024-9297(95)01193-4 CCC: $12.00

introduced. A pale yellow color formed after stirring for 2 h. The monomer was then distilled into an addition buret.[17] Styrene (Aldrich) was distilled into a flask containing 2−3 mL of 1 M $(nBu)_2Mg$ in hexanes (Aldrich). The bulk of the hexanes was removed by distillation before styrene was introduced. The monomer was stirred for 2 h and then distilled to an addition buret just prior to polymerization. *tert*-Butyl methacrylate ($^tBMA$, Polysciences) was distilled from $CaH_2$ three times, the final being to an addition buret just prior to polymerization. Tetrahydrofuran (THF; Omnisolv, unstabilized) was distilled from sodium−benzophenone ketyl. *sec*-Butyllithium ($^sBuLi$, Aldrich) was stored at −20 °C and was titrated as described by Gilman and Cartledge.[18] 1,1-Diphenylethylene (DPE, Aldrich) was purified by distillation from 2−3 mL of 1.3 M *sec*-butyllithium in hexanes (the bulk of the hexanes was removed before the introduction of DPE) and stored under argon at −20 °C.

**Polymer Synthesis.** All triblock copolymers and homopolymers were synthesized using the pressurized argon method.[19] The glassware was heated at 500 °C for 3 h before use. The magnetic stir bars and syringes were oven-dried and removed just prior to use. Each syringe was purged with argon before use. The reactor was baked at 280 °C for 3 h, and the addition burets were flame-dried under vacuum just before use. Oligomer synthesis was also performed using this method, but, in this case, the glassware was oven-dried at 110 °C and removed just before use. The reactor and burets in this case were flame-dried under vacuum just before the oligomerization.

The monomers were distilled to an addition buret and attached to the baked reactor (1 L for a batch of 25 g of copolymer). The reactor was then flushed five times with argon. The solvent was distilled directly into the reactor and cooled to −78 °C using a dry ice−isopropyl alcohol bath. For a typical batch of 25 g, about 750 mL of THF was introduced. The system was allowed to thermally equilibrate for 30 min. The synthesis of the 40K−20K−40K PS-P$^t$BMA-PMMA triblock is given as an example. The initiator (0.125 mL of 1.3 M $^sBuLi$ in hexanes) was then injected into the reactor through a septum. Styrene (6.76 g, 0.065 mol) was then added dropwise (0.5 mL/min). The polymerization was allowed to continue for 30 min after styrene addition was complete. 1,1-Diphenylethylene was then added by syringe to the polystyryl anion ($n$ 1,1-diphenylethylene = $1.2n$ $^sBuLi$) resulting in a characteristic deep red color. $^tBMA$ (3.20 g, 0.0225 mol) was then slowly added dropwise (0.25 mL/min) into the reactor, and the color immediately vanished. The polymerization was allowed to stir for 30 min after the addition of the last drop of $^tBMA$. MMA (6.70 g, 0.067 mol) was then slowly added dropwise at the same rate as $^tBMA$. The solution was then stirred for 30 min after the addition of the last drop of MMA. Degassed methanol was then injected through a septum to terminate the reaction. All of the above operations were performed at −78 °C using a dry ice−isopropyl alcohol bath. The block copolymers were precipitated with methanol, filtered, and freeze-dried from benzene.

**$^t$BMA Oligomer (5) Synthesis.** $^tBMA$ (8.80 g, 0.062 mol) was distilled into an addition buret and attached to a 1 L five-necked reactor. The reactor was flushed five times with argon and cooled to −78 °C. THF (300 mL) distilled directly into the reactor from sodium−benzophenone ketyl and was allowed to cool for 30 min. 1,1-Diphenylethylene (2.75 mL, 0.0155 mol) was added to the flask via syringe and initiated with a stoichiometric amount of 1.3 M $^sBuLi$ in hexanes (11.90 mL), resulting in a characteristic deep red color. $^tBMA$ was then added to the solution over a period of 5 min, causing the color to disappear. The polymerization was allowed to continue for 15 min at −78 °C and was quenched with degassed methanol. After warming, the oligomer was precipitated twice with hexanes (4 × the volume of THF) and dried under vacuum at room temperature for 24 h to yield 12.69 g (99 %) of **5**.

**Thermal Triblock Modification, Anhydride (2a−c) Synthesis. Procedure A.** Triblock **1c** (200 mg) was dissolved in 5 mL of THF and placed in a 25 mL Schlenk flask. The flask was purged with argon for 10 min, and the solvent was removed under high vacuum (30 min) to disperse a thin film (>1 mm) of the polymer on the flask wall. The flask was heated in an oil bath at 230 °C under vacuum for 30 min. Anhydride containing polymer **2c** was dissolved in a minimal amount of THF, precipitated with hexanes, filtered, and dried under vacuum at room temperature for 24 h. The overall mass recovery was typically around 80%.

**Procedure B.** Triblock **1c** (500 mg) was placed in a Mini-Max parallel plate mixer[20] and heated at 230 °C (shear rate $\approx 20\ s^{-1}$) for 20 min under a nitrogen atmosphere to give anhydride containing polymer **2c**. The overall mass recovery was typically around 80%.

**Anhydride Triblock Hydrolysis/Synthesis of 3a−c.** Anhydride containing triblock **2c** (150 mg) was placed in a 10 mL round bottomed flask fitted with magnetic stir bar and condenser. Aqueous $NaHCO_3$ (5 mL) and THF (15 mL) were added to the flask. The flask was heated to 70 °C for 1 h and allowed to cool to 25 °C. The resulting solution was treated with 10% HCl (1 mL) for 10 min and was poured into 50 mL of hexanes. The resulting polymer **3c** containing carboxylic acid was filtered and dried under vacuum at room temperature for 24 h. Polymer **3c** was typically isolated in 90% yield.

**Polymer Analysis.** Polymer molecular weights for **1a−c** were estimated using a Waters 150-C AlC GPC equipped with five Phenogel columns and UV and RI detectors. For these polymers, the UV detector was set at 256 nm and THF was used as the eluent. Five standard polystyrenes were used for the calibration: $97 \times 10^3$, $50 \times 10^3$, $35 \times 10^3$, $17 \times 10^3$, and $4 \times 10^3$ g/mol. The glass transition temperatures of the block copolymers were measured on a Perkin-Elmer DSC 7. Ramp rates between 10 and 40 °C/min were used. $^1H$ and $^{13}C$ NMR spectra were recorded on either a Varian 500 MHz or a Bruker 300 MHz spectrometer. IR spectra of thin polymer films were recorded on a Midac Prospect FT-IR.

**Transmission Electron Microscopy (TEM).** Ultra-thin sections (~400 Å) were cut with a diamond knife at room temperature from the block copolymer and floated on distilled water before picking them up on 400 mesh uncoated copper grids. The floated samples appeared silver-gray/gray in the reflection mode, confirming that the section thickness was less than 500 Å.[21] The sections were stained in the vapor phase of a 0.5% aqueous $RuO_4$ solution for 50 min and examined under bright field TEM using either a Jeol 100Cx or Jeol 1210 electron microscope operated at 100/120 kV accelerating voltage.

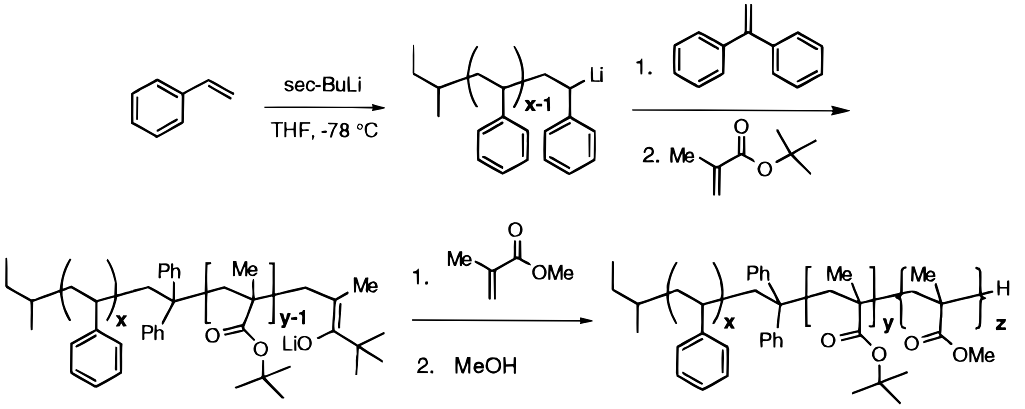
## Results and Discussion

**Polymer Synthesis.** The sequence of events used for synthesis of the PS-P$^t$BMA-PMMA triblocks are described in Scheme 1, and polymerization results are reported in Table 1. PMMA and P$^t$BMA homopolymerizations and a symmetrical diblock copolymerization of styrene and methyl methacrylate have been included also. Triblocks **1a−c** have 40K PS and PMMA segments but differ in the size of the middle P$^t$BMA block ($a$ = 5K, $b$ = 10K, and $c$ = 20K).

In this work, the PMMA homopolymer (Table 1, polymer **4**) and the block copolymers (polymers **6**, **1a−1c**) synthesized exhibited narrow molecular weight distributions. The homopolymer synthesis demonstrated excellent molecular weight control as the experimental molecular weight directly paralleled the predicted value. The molecular weight of the 85K PS-PMMA diblock copolymer **6** also agreed well with the calculated value. The polydispersity index of 1.05 for **6** was similar to that observed for the PMMA homopolymer **4** (1.09).

Syntheses of triblocks **1a−c** also yielded materials with narrow molecular weight distributions (polydispersity indexes ca. 1.15), but the experimental $M_n$'s did not coincide well with those predicted. Inherent differences in the hydrodynamic volumes of each copolymer block may be the cause of this disparity. Polystyrene standards were used for the GPC calibration. It is not

**Scheme 1. Stepwise Anionic Synthesis of PS-P$^t$BuMA-PMMA Triblock Copolymers**



| | x | y | z | |
|---|---|---|---|---|
| **1a** | 385 | 36 | 400 | = PS(40K)-P$^t$BMA(5K)-PMMA(40K) |
| **1b** | 385 | 72 | 400 | = PS(40K)-P$^t$BMA(10K)-PMMA(40K) |
| **1c** | 385 | 144 | 400 | = PS(40K)-P$^t$BMA(20K)-PMMA(40K) |
| **4** | - | 100 | - | = 10K PMMA |
| **5** | - | 4 | - | = P$^t$BMA oligomer |
| **6** | 380 | - | 400 | = 85K PS-PMMA diblock |

**Table 1. Conversion Results and GPC Characterization of Polymers Synthesized in THF at −78 °C**[a]

| polymer | styrene, mol | MMA, mol | $^t$BMA, mol | calcd spacer length (exptl NMR value), $10^3$ g·mol$^{-1}$ | $M_n$, $10^3$ g·mol$^{-1}$ calcd | $M_n$, $10^3$ g·mol$^{-1}$ obsd[b] (GPC) | $M_w/M_n$ | total conversion, wt % |
|---|---|---|---|---|---|---|---|---|
| **4** | | 0.1 | | | 10 | 11.1 | 1.09 | 97 |
| **5** | | | 0.062 | | 0.829 | 1.05 | 2.56 | 99 |
| **6** | 0.231 | 0.245 | | | 80 | 85 | 1.05 | 95 |
| **1a** | 0.062 | 0.066 | 0.008 | 5 (4.5) | 85 | 69 | 1.16 | 99 |
| **1b** | 0.072 | 0.076 | 0.014 | 10 (9.1) | 90 | 77 | 1.14 | 99 |
| **1c** | 0.065 | 0.067 | 0.0225 | 20 (19.1) | 100 | 86 | 1.23 | 98 |
| **1c**[c] | | | | 20 (22.9) | 100 | 103 | 1.10 | |

[a] $M_n$, number-average molecular weight; $M_w$, weight-average molecular weight. [b] Based on PS calibration. [c] PS homopolymer removed by fractionation with cyclohexane.

clear if this standard should permit an accurate extrapolation of the molecular weight of a PS-P$^t$BMA-PMMA block copolymer. For this reason, the GPC molecular weights obtained for the ABC triblocks should only be considered as estimates. Other experiments utilizing absolute methods for molecular weight determination were considered but were deemed unnecessary because **1a**−**c** had relatively narrow molecular weight distributions. The overall conversion to polymer based on mass recovery was also quantitative. Dispersity and conversion are more indicative of overall polymer composition than GPC molecular weight data for copolymers where standards are necessarily nonideal.

Figure 1 shows the GPC profile for triblock copolymer **1c**, which has a P$^t$BMA spacer length of 20 × $10^3$ g·mol$^{-1}$. A pronounced shoulder, more evident with UV than RI detection, appears on the low molecular weight side of the peak in the GPC trace of **1c**. This shoulder corresponds to PS homopolymer. This homopolymer was selectively extracted from the triblock copolymer **1c** using cyclohexane and was characterized using IR, NMR, and GPC. By GPC (see Figure 1), the mass percent of PS homopolymer in the triblock **1c** was determined to be 8.5. The number-average molecular weight and polydispersity index of the PS homopolymer isolated were 51K and 1.03, respectively. After the PS homopolymer was removed from triblock **1c**, $M_n$ increased from 86K to 103K, while the polydispersity index (PDI) decreased from 1.23 to 1.10. The purification of the $^t$BMA involved only multiple distillation from $CaH_2$.[22] We assume that adventitious impurities remained in either the monomer or diphenylethylene and terminated living polystyryl anions leading to the low molecular weight shoulder in the GPC trace. This shoulder was less pronounced in triblocks **1b** and **1a**. This result might be expected since fewer $^t$BMA groups were incorporated into each of these polymers relative to **1c** (**1c**, **1b**, **1a** = 20K, 10K, 5K, respectively); therefore, less impurities were present that were capable of quenching the living chain.

Figure 2 shows a $^1$H NMR spectrum of PS-P$^t$BMA-PMMA triblock copolymer **1c**. It shows that each monomer has been incorporated in the triblock copolymer. The peaks attributed to the phenyl ring of the styrene resonate at $\partial$ = 6.57 and 7.07 ppm. The resonance of the methyl ester of the PMMA at $\partial$ = 3.58

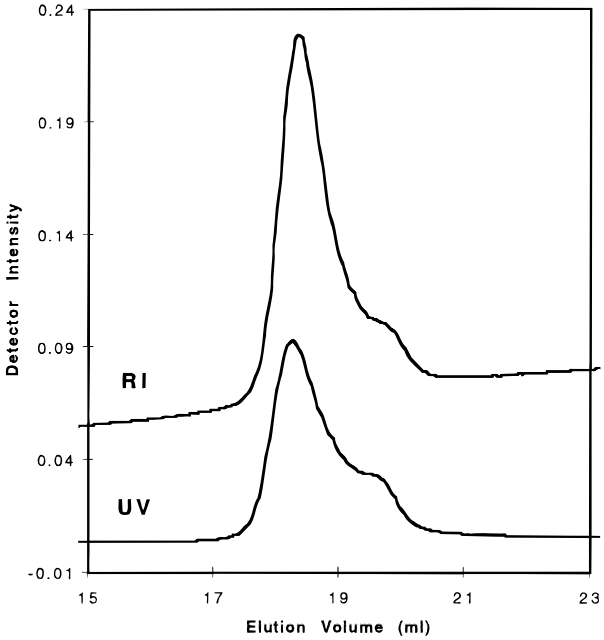


**Figure 1.** Gel permeation chromatogram for PS-P$^t$BMA-PMMA triblock copolymer **1c** (20K middle block). GPC legend: top trace = RI detector; bottom trace = UV detector.

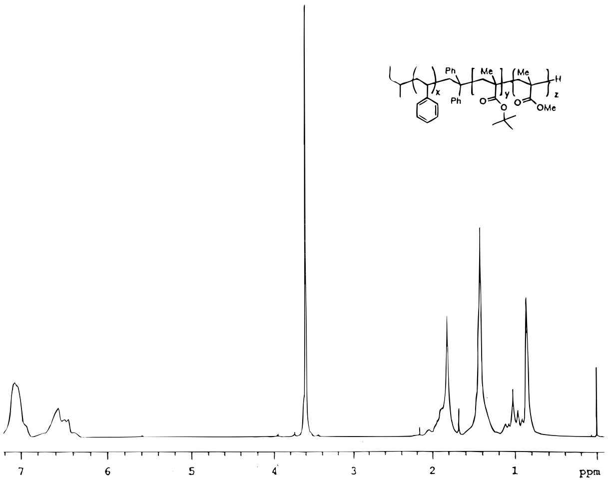


**Figure 2.** $^1$H NMR spectrum of PS-P$^t$BMA-PMMA (40K-20K-40K) triblock copolymer **1c**. Incorporation of all three monomers is supported by resonances at $\partial = 6.57$ ppm, $\partial = 7.07$ ppm (aromatic-PS), $\partial = 3.58$ ppm (methyl ester−PMMA), and $\partial = 1.41$ ppm (*tert*-butyl ester−P$^t$BMA).

ppm and the *tert*-butyl ester of P$^t$BMA at $\partial = 1.4$ ppm are easily identified. The integration ratio of the styrenic protons to the methyl ester resonance is approximately 5/3. This supports the conclusion that the PS and PMMA blocks are approximately equal in length. The *tert*-butyl ester appears at $\partial = 1.4$ ppm and overlaps the methylene resonance of the polystyrene backbone. Factoring this into the integral ratio for aromatic vs $CO_2Me$ vs $CO^tBu/CH_2$ (1.65/1.55/1, theory = 1.6/1.6/1) peaks leads to the conclusion that **1c** has a middle P$^t$BMA segment of 19.1 K. Similarly, the integrated ratio of aromatic to methyl and *tert*-butyl ester protons in triblocks **1a** and **1b** is 1.8/1/1.1 and 1.6/1.25/1; the theoretical ratios are 2/1/1.25 and 1.51/1.06/1, respectively. The calculated lengths of the P$^t$BMA blocks for **1a** and **1b** are 4.5K and 9.1K, respectively (see Table 1). These calculations do not take into account the amount of quenched PS homopolymer present (8.5 mass %). From our selective extraction results on **1c**, we estimate that no more than 20 mol % of the living PS chains were quenched by impurities. If 20 mol % of the chains were quenched, the middle block lengths for **1c**, **1b**, and **1a** would equal 22.9K, 10.9K, and 5.4K, respectively. Literature indicates that the tacticity of PMMA synthesized anionically in syndiotactic (s-PMMA); we assume the P$^t$BMA blocks to also be predominately syndiotactic.[23]

**Polymer Modification.** To investigate the effect of middle block polarity on the ability of ABC triblock copolymers to stabilize polymer blend interfaces, we designed these ABC triblocks to contain a chemically modifiable middle block. It was envisioned that the *tert*-butyl ester of P$^t$BMA could be transformed into carboxylic acid functionality under acidic conditions. Several procedures to carry out this transformation were investigated. Acid catalyzed *tert*-butyl ester removal in **1c** involving the use of catalytic tosic acid (TsOH) in toluene at 80 °C was found to competitively hydrolyze the methyl ester of PMMA on the basis of NMR integration ratios (≈50% $CO_2Me$ loss after 8 h).[24] Exposure of **1c** to trifluoroacetic acid in $CH_2Cl_2$ (RT of reflux) resulted only in recovery of intact **1c**.[25]

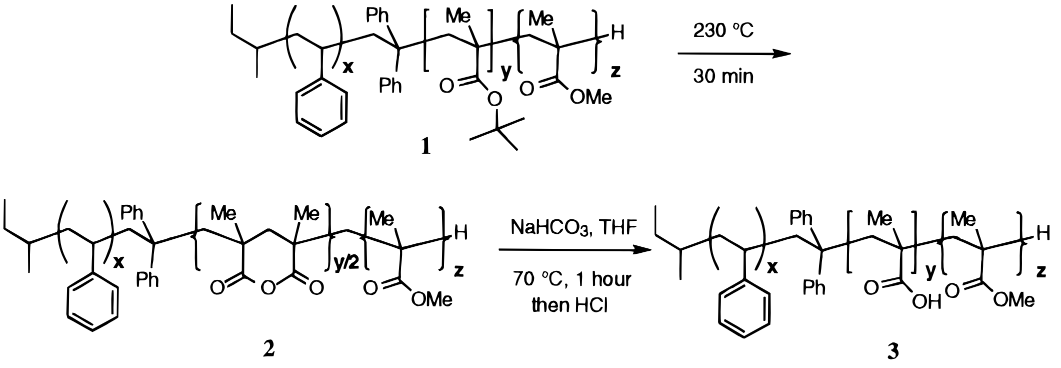
Trimethylsilyl iodide (TMS-I) has been reported to deesterify P$^t$BMA in the presence of PMMA. A procedure in which TMS-I is formed *in situ* was investigated.[26] Under these conditions the *tert*-butyl ester was consumed after treatment with TMS-I at room temperature for 10 min, but the methyl ester of PMMA was also partially removed (≈33%). Thus, we believe that TMS-I competitively deprotects the methyl ester of the PMMA block and results in the carboxylic acid functionality being present in both methacrylate blocks. This is not unreasonable when one considers that the ratio of *tert*-butyl methacrylate groups to methyl methacrylate groups in **1a**−**c** is 1/2.8, 1/5.6, and 1/11.2, respectively. The inherently higher concentration of methyl ester in these systems makes selective *tert*-butyl ester hydrolysis extremely difficult.

Pyrolysis of the *tert*-butyl ester in P$^t$BMA polymers has been reported to yield carboxylic acid functionality at temperatures above 200 °C.[27,28] It has also been reported that poly(methacrylic acid) (PMAA) can be converted to poly(methacrylic anhydride) (PMAN) under more forcing temperatures (220−240 °C).[29]

Application of this procedure to triblocks **1a**−**c** resulted in complete transformation of the *tert*-butyl ester of P$^t$BuMA to anhydride functionality in 30 min at temperatures between 225 and 230 °C.[30] This transformation was found to be highly selective for the P$^t$BMA block (see discussion of Figure 4). Neither modification nor significant chain degradation of PMMA was observed by either NMR spectroscopy (Figure 4) or GPC when this reaction was performed in the absence of oxygen.[31] Others have suggested that P$^t$BuMA is first converted to carboxylic acid at temperatures around 200 °C.[25,26] At these temperatures, no reaction of **1a**−**c** was detected after 30 min by either IR or NMR spectroscopy. P$^t$BMA homopolymers studied by others were atactic or isotactic in most cases. The predominantly syndiotactic backbone of the middle $^t$BMA block in **1a**−**c** may increase the kinetic barriers for deesterification and anhydride formation.

The relatively short segments of P$^t$BMA relative to the PS and PMMA blocks in **1a**−**c** made it difficult to detect intermediate carboxylic acid during pyrolysis by IR analysis. For this reason, the relative rate of

**Scheme 2. Selective Modification of ${}^{t}$BMA Block of PS-P${}^{t}$BMA-PMMA Copolymer**



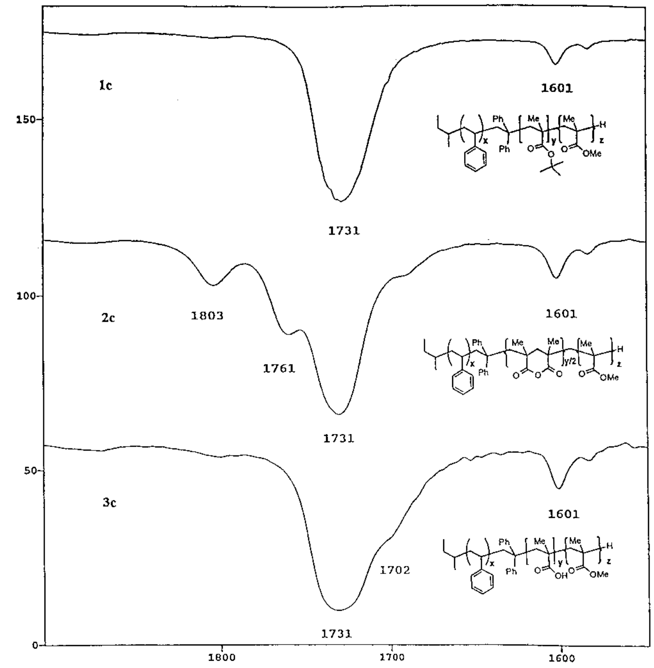


**Figure 3.** FT-IR spectra of modification of P${}^{t}$BMA block of triblock copolymer **1c** to anhydride (**2c**) and carboxylic acid (**3c**) functionalities (see Scheme 2). Spectra a (top): carbonyl region of triblock copolymer **1c** before modification. Spectra b (middle): carbonyl region of triblock copolymer **1c** after thermal modification to **2c** (230 °C, 30 min). Spectra **c** (bottom): carbonyl region of triblock copolymer **2c** after basic hydrolysis to **3c** (NaHCO$_3$, THF, 70 °C, 1 h).

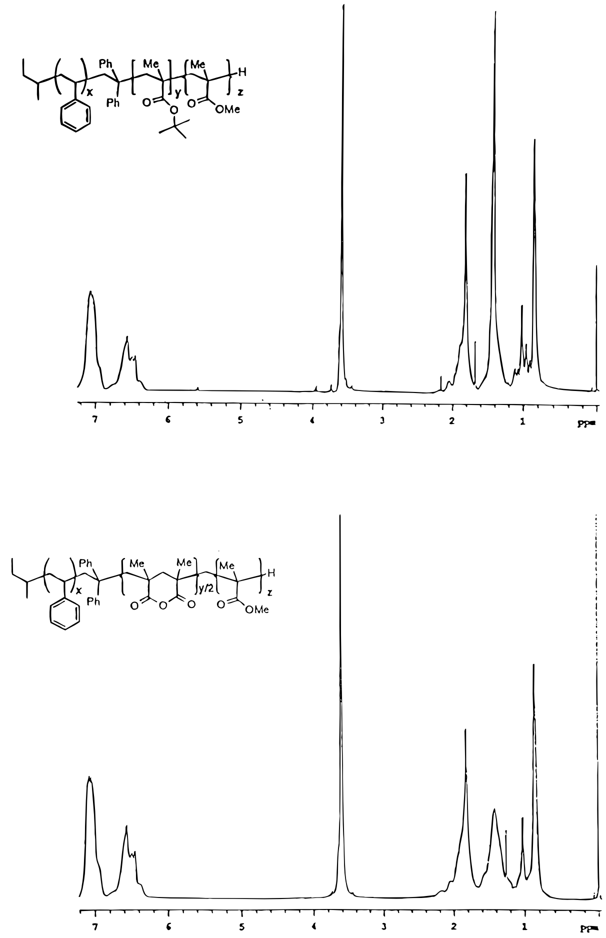


**Figure 4.** Proton NMR spectra of triblock copolymer **1c** before and after thermal modification to **2c**. Upon thermal treatment, the *tert*-butyl ester resonance of P${}^{t}$BMA at $\partial = 1.41$ ppm disappears. The remaining proton resonance corresponds to the PS methylene (CH$_2$).

deesterification to anhydride formation in the P${}^{t}$BMA segment of **1a**–**c** could not be determined.

The conditions for polymer modification are summarized in Scheme 2. Polyanhydrides **2a**–**c** could each be hydrolyzed to the corresponding polyacids **3a**–**c**. Treatment with aqueous sodium bicarbonate in THF at 70 °C followed by acidification with aqueous HCl provided **3a**–**c**. This functional group transformation was easily detected by IR spectroscopy (Figure 3).

Figure 3 contains the carbonyl stretching region of the FT-IR spectra of thin films of polymers **1c**, **2c**, and **3c**. Ester functionality is clearly converted to anhydride upon pyrolysis. In spectrum a, the stretches corresponding to methyl and *tert*-butyl esters of PMMA and P${}^{t}$BMA in **1c** overlap at 1731 cm$^{-1}$. The new IR stretches at 1803 and 1761 cm$^{-1}$ in spectrum b clearly show the conversion of *tert*-butyl ester functionality to anhydride upon pyrolysis. Spectra of aliquots at intermediate stages of pyrolytic conversion showed no detectable amounts of carboxylic acid functionality.

After hydrolysis of the anhydrides in **2**, the acid groups in **3** are indicated by the new carbonyl stretch at 1702 cm$^{-1}$, as well as a broad O–H absorption between 2500 and 3500 cm$^{-1}$.

The loss of the *tert*-butyl ester upon conversion to anhydride is apparent in the NMR spectra as well (Figure 4). The *tert*-butyl ester CH$_3$ protons, which resonate at $\partial = 1.4$ ppm, disappear after thermal modification. These protons happen to overlap with the methylene resonances in polystyrene, consistent with the resonance left at $\partial = 1.4$ ppm after thermal conversion of **1a** to **2a**. The integral ratio of the aromatic protons from the PS block to the methyl ester of the PMMA block was unchanged after thermal modification of the *tert*-butyl ester in **1a**–**c**. This also provides evidence that the PMMA blocks in **2a**–**c** have been neither thermally modified nor degraded.

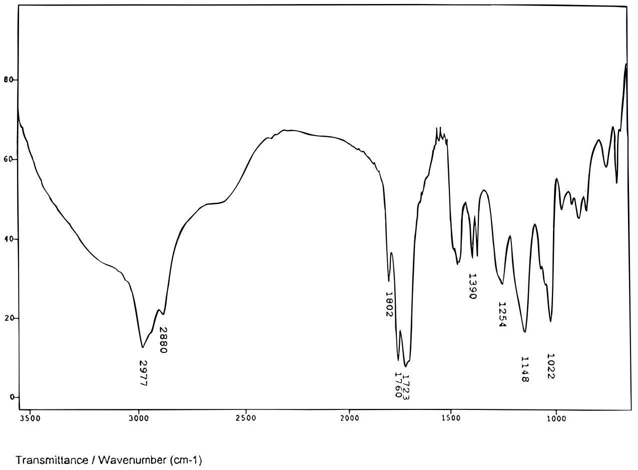
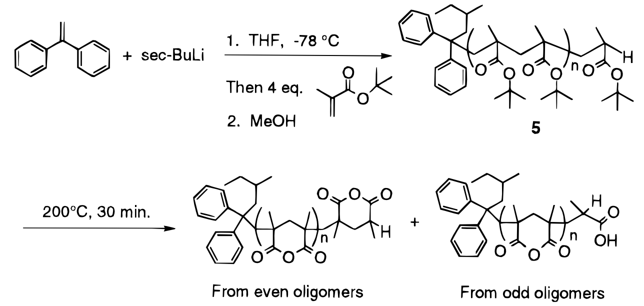


**Figure 5.** IR spectrum of $^{t}$BMA oligomer **5** after pyrolysis at 200 °C for 30 min.

**Scheme 3. $^{t}$BMA Oligomer Synthesis and Thermal Modification**



To further support the presence of anhydride functionality, an oligomeric version of P$^{t}$BMA (**5**) was synthesized using anionic techniques, detailed in Scheme 3. This oligomer was also subjected to the thermal modification conditions (200 °C, 30 min). The IR spectrum of **5** (Figure 5) contains characteristic stretches consistent with the presence of the six-membered ring anhydride (1802, 1760 cm$^{-1}$) and carboxylic acid (3500–2500 cm$^{-1}$) functionality. This is consistent with the fact that all odd length oligomers must contain at least one acid group.

**Thermal Analysis.** Differential scanning calorimetry was also used to characterize these materials. Heating triblock **1c** at 40 °C/min gave rise to an exotherm corresponding to thermal modification of this material, beginning at approximately 210 °C and continuing until 270 °C (Figure 6, trace A). $\Delta H_r$ of this modification was determined to be 54.9 J/g.

The glass transition temperatures for diblock **6** and triblock **2c** were also determined from DSC experiments (Figure 6, traces B and C, respectively). The literature values for the $T_g$'s PS, s-PMMA, i-P$^{t}$BMA, and PMAN are 105, 125, 118, and 159 °C, respectively.[32] In the case of the 85K symmetrical PS-PMMA diblock **6**, $T_g$'s of 107 and 132 °C were obtained for the PS and PMMA blocks, respectively (Figure 6, trace B). For triblock **2c**, three distinct $T_g$'s were hard to discern. Two $T_g$'s at approximately 110 and 140 °C were consistently witnessed (Figure 6, trace C). We hypothesize the first to be a result of the PS block and the second to possibly be the result of overlapping PMMA and PMAN peaks, resulting in a skewed $T_g$.

**TEM Results.** In the three triblocks **1a**–**c**, the length of the end (PS, PMMA) blocks was similar (40 kg/mol each). The length of the spacer (P$^{t}$BMA) block, however, varied (5, 10, and 20 kg/mol). In the limit of the 0 kg/mol spacer molecular weight, one retrieves the symmetrical 85 K diblock copolymer of PS-PMMA. Figure 7 shows the microstructure of the three triblocks **1a**–**c** and the 85K diblock **6** from solvent cast films at room temperature. The films (about 2 mm thick) were cast over 7 days from 5% toluene solutions. The samples were further dried and annealed under vacuum at 135 °C for 4 h. Sections for TEM analysis were cut in the direction orthogonal to the film surface (thickness = 40–60 nm).

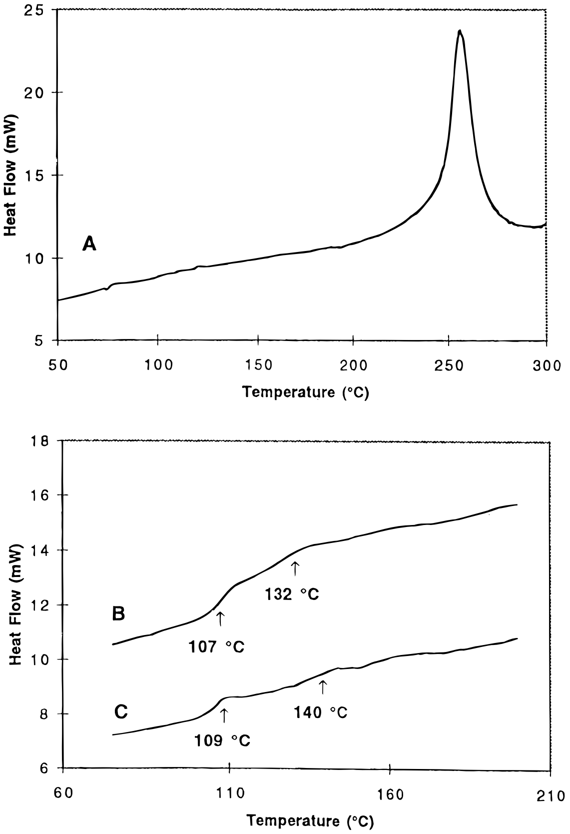


**Figure 6.** DSC traces showing thermal modification of PS-P$^{t}$BMA-PMMA triblock copolymer **1c** (A) and the glass transition temperatures of an symmetrical 85 K PS–PMMA diblock **6** (B) and an PS-P$^{t}$BMA-PMMA triblock copolymer **1c** (C). Arrows mark approximate $T_g$ points. (Note: heat flow data from trace C was multiplied by a common factor in order to display both traces on the same chart.)

As was expected, the morphology for triblocks **1a**–**c** is essentially lamellar. The triblock with the longest midblock shows the most order (Figure 7). To ensure that the PS homopolymer impurity in triblocks **1a**–**c** did not affect the morphology, TEM on **1c** after removal of homopolymer was performed. No change in the morphology of **1c** was witnessed after homopolymer removal, and the microphase separated lamellar structure with long-range ordering still persisted. The long-range order of the microstructure, however, seems to decrease with decreasing spacer block length. Auschra and Stadler have shown that interfacial tension effects can lead to significant modification of the ABC triblock microstructure when the length of the middle block is varied relative to the end blocks.[33,34] Even diblock **6**, containing the least impurity and having the most narrow polydispersity, showed a nearly disordered structure.[35] Since our annealing temperatures were close to the $T_g$ of PMMA, we annealed a second sample of diblock **6** at 195 °C for 24 h and repeated TEM

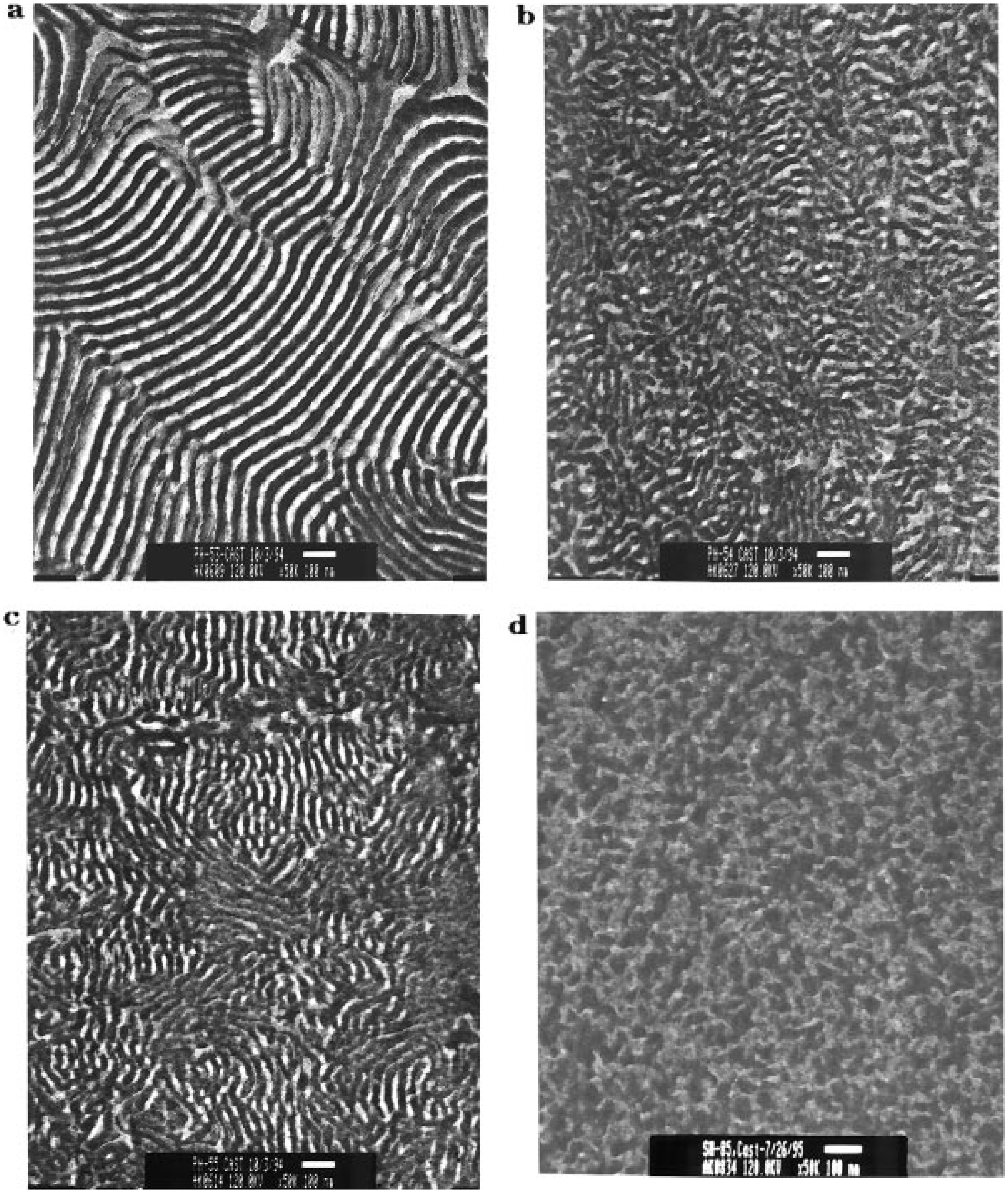


**Figure 7.** TEM micrographs showing the bulk microstructure of the triblocks (a) 20K spacer, **1c** (b) 10K spacer **1b**, and (c) 5K spacer **1a** relative to an 85K PS-PMMA diblock **6** (d). All three triblock copolymers assemble in a lamellar microstructure. Bar corresponds to 100 nm in each case.

analysis. A lamellar morphology resulted, but the long-range order was much less than that observed in triblock **1c**.

**Summary.** In this work PMMA homopolymers and block copolymers having narrow molecular weight distributions were synthesized using anionic polymerization techniques. PS-P$^t$BMA-PMMA triblock copolymers **1** were synthesized by sequential addition of styrene, *tert*-butyl methacrylate, and methyl methacrylate. GPC and NMR spectroscopy confirmed the length and composition of the triblock copolymers. Several techniques were investigated to selectively modify the middle P$^t$BMA block. Procedures using TsOH and TMS-I resulted in complete deesterification of the *tert*-butyl ester and partial deesterification of the methyl ester of PMMA (50 and 33% respectively). Thermal treatment of **1** (230 °C, 30 min) selectively modified the P$^t$BMA block to anhydride (PMAN, **2**). Basic hydrolysis of anhydride containing **2** yielded PS-PMAA-PMMA triblock copolymers **3**.

Thermal analysis of the PS-P$^t$BMA-PMMA triblock copolymers (**1**) indicated the presence of an exotherm between 210 and 280 °C corresponding to thermal modification to anhydride. Triblock copolymers **1** were found to possess $T_g$'s at 107 and 141 °C. The lack of three $T_g$'s is postulated to be a result of overlapping PMMA and PMAN exotherms. The $T_g$'s for a 85 K symmetrical PS-PMMA diblock (**6**) occurred at 107 and 132 °C.

TEM analysis of solvent cast films of triblocks **1a**−**c** indicated the morphology for all three triblocks is essentially lamellar at room temperature. The long-range order of the microstructure, however, seems to decrease with decreasing spacer block length.

The use of triblocks **1a**−**c** as compatibilizers for immiscible homopolymer blends has also been investigated and is described in a forthcoming article.[14]

**Acknowledgment.** This work was supported by grants from the National Science Foundation's Chemical Reaction Processes and Polymer Materials Programs, General Electric Corp., and the University of Minnesota Center for Interfacial Engineering. The authors also thank Thomas Gruenfelder for his work on the DSC measurements, Mark Schulz for his help in synthesizing polymer **6**, and the reviewers for several helpful suggestions that were incorporated into this manuscript.

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MA951193R