

# Diblock and Triblock Copolymers of Styrene and Acetoxymethylstyrene by One-Pot ATRP

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**ABSTRACT:** We describe the synthesis of diblock and triblock copolymers by sequential atom transfer radical polymerization of styrene and acetoxymethylstyrene. Contrary to the usual block copolymerization involving isolation of the macroinitiator, a convenient one-pot procedure is developed. This is possible because of the preferential polymerization of acetoxymethylstyrene, even in the presence of residual styrene, as inferred from characterization of the intermediate polystyrenes and the block copolymers by size exclusion chromatography, <sup>1</sup>H NMR, Fourier transform infrared spectroscopy, differential scanning calorimetry, and GPEC techniques. The latent acetoxy functionalities in these block copolymers are shown to be easily unmasked to —OH and —Br functionalities, with the potential for block ionomers and dense graft architectures. © 2004 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 43: 575–583, 2005

**Keywords:** atom transfer radical polymerization; block copolymers; polystyrene; polyacetoxymethylstyrene

## INTRODUCTION

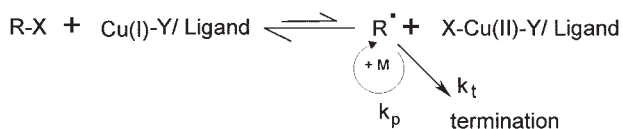
In the past, the majority of block copolymer synthesis involved living ionic polymerization techniques marked by stringent requirements for reaction conditions, as well as a restricted range of monomers and functionalities that could be used. The developments over the last decade in the controlled/living radical polymerization methods now offer the possibility of synthesis of a wider variety of materials with controlled molecular weights, under relatively less demanding reaction conditions because of the lower sensitivity to

moisture and other protic impurities. The following different controlled radical polymerization techniques have emerged: nitroxide-mediated polymerizations,<sup>1</sup> degenerative transfer with alkyl iodides,<sup>2–5</sup> reversible addition-fragmentation chain transfer polymerization,<sup>6</sup> and atom transfer radical polymerization (ATRP).<sup>7–10</sup> Of these techniques, ATRP is most often used, and involves the mechanism described in Scheme 1.

The radicals R<sup>•</sup> are generated from a dormant organic halide species R-X through the reversible redox process catalyzed by a transition metal complex [Cu (I)-Y/ligand] that undergoes a one electron oxidation by abstracting a halogen atom. The polymerization proceeds by the addition of monomers to the active radicals R<sup>•</sup>, in a manner similar to conventional radical polymerization. A good control during the reaction is obtained be-

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Scheme 1

cause the fast equilibrium of the reversible reaction maintains a small concentration of growing species ( $R^+$ ), resulting in negligible termination.<sup>7–10</sup>

ATRP has been used in the synthesis of several narrow polydispersity block, graft, and gradient copolymers.<sup>11</sup> Such structures have also been successfully synthesized by a combination of ATRP with living cationic,<sup>12,13</sup> anionic,<sup>14</sup> or ring-opening polymerization.<sup>15,16</sup> Almost all reported block copolymer synthesis involving ATRP relies on a two-pot synthesis, in which a homopolymer with a living chain-end is synthesized, isolated from the residual monomer, and then used as a macroinitiator for the synthesis of the subsequent blocks. A one-pot block copolymerization of *n*-butyl acrylate and methyl methacrylate (MMA) by the sequential addition of monomers was reported by Matyjaszewski et al.<sup>17</sup> We now report a one-pot synthesis of diblock and triblock copolymers of styrene and acetoxymethylstyrene. Starting with a mono or difunctional ATRP initiator, polymerization of styrene is first carried out. Subsequent addition of acetoxymethylstyrene to the reaction mixture leads to the desired block copolymers. Our choice of acetoxymethylstyrene is dictated by the acetoxy functionality, which provides potential for a variety of subsequent architectures. For example, the acetoxy groups are unmasked to reveal further initiating sites from which branches can be grown by similar ATRP.<sup>18</sup> On the other hand, hydrolysis and saponification of the acetoxy groups can lead to well defined ionomers.<sup>19</sup> We use a combination of characterization techniques to show that the chains continue to grow on addition of acetoxymethylstyrene, and acetoxymethylstyrene gets preferentially incorporated in the polymer even in the presence of residual styrene.

## EXPERIMENTAL

### Materials

Styrene (99.9%; Aldrich) and acetoxymethylstyrene (97%; Acros) were purified by passing

through a column of activated basic alumina to remove inhibitors, stored over  $\text{CaH}_2$ , and then vacuum-distilled before use.  $\text{CuBr}$  (98%; Aldrich) and  $\text{CuCl}$  (98%; Aldrich) were purified according to a literature procedure.<sup>20</sup> Diphenyl ether (98%; Merck) was purged with argon for 15 min before use. Other chemicals were used as received: *N,N,N',N',N''*-pentamethyldiethylene-triamine (PMDETA, 99%; Aldrich), 1,1,4,7,10,10-hexamethylene tetramine (HMTETA, 99%; Aldrich), ethyl 2-bromoisobutyrate (EBriB, 99%; Aldrich), dimethyldibromoheptanedioate (DMDBHD, 99.9%; Aldrich), potassium hydroxide solution in ethanol (0.1 N; Merck), chloroform- $d_1$  ( $\text{CDCl}_3$ , deuteration degree min 99.8% for NMR spectroscopy; Merck), tetrahydrofuran (THF, HPLC grade; Biosolve), THF- $d_8$  (*d*-THF, deuteration degree min 99.5% for NMR spectroscopy; Merck), dioxane (Biosolve), hydrochloric acid (37%; Aldrich), hydrogen bromide (30 wt % solution in acetic acid; Aldrich), methanol (AR stabilized; Biosolve) and heptane (AR stabilized; Biosolve).

### Measurements

$^1\text{H}$  NMR spectra (400 MHz) were recorded on a Varian Mercury Vx400 spectrometer with  $\text{CDCl}_3$  or *d*-THF as the solvent. Fourier transform infrared (FTIR) spectra were acquired with a Biorad FTS 6000 spectrometer with a Golden Gate Single Reflection High Temperature Diamond ATR (Specac).

Size exclusion chromatography (SEC) measurements were carried out with a Waters Model 510 pump and a Model 410 refractive index detector (at 40 °C). Injections were done by a Waters Model WISP 712 auto injector; the injection volume used was 50  $\mu\text{L}$ . The columns used were a PLgel guard (5  $\mu\text{m}$  particles) 50  $\times$  7.5 mm guard column followed by 2 PLgel mixed-C (5  $\mu\text{m}$  particles) 300  $\times$  7.5 mm columns (40 °C) in series. THF was used as an eluent at a flow rate of 1.0 mL/min. Calibration was done with polystyrene standards (Polymer Laboratories;  $M = 580$  to  $M = 7.1 \times 10^6$ ). Data acquisition and processing were performed with Waters Millennium32 (v3.2) software. Dilute solutions of the polymer samples in THF at concentrations of 1 mg/mL were filtered over a 13 mm  $\times$  0.2  $\mu\text{m}$  PTFE filter (Alltech) before injection.

A matrix assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF-MS) analysis was carried out on a Voyager DE-STR from Applied Biosystems. The matrix

**Table 1.** Linear Binary Gradient used for GPEC

Step	Time (min)	$\Phi_{\text{heptane}}^a$	$\Phi_{\text{THF}}^a$	Flow (mL/min)
1	0	1	0	0.5
2	50	0	1	0.5
3	60	0	1	1.5
4	65	1	0	1.5
5	70	1	0	0.5

<sup>a</sup> Represent the volume fraction of heptane and THF.

trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) (99%; Aldrich) was dissolved in THF (40 mg/mL). The salt silvertrifluoroacetate (98%; Aldrich) as a solution in THF (1 mg/mL) was used as the cationic ionization agent. The polymer sample was dissolved in THF (1 mg/mL). In a typical MALDI experiment, the matrix, salt, and polymer solutions were premixed in the ratio 5  $\mu\text{L}$  matrix:0.5  $\mu\text{L}$  salt:5  $\mu\text{L}$  sample. Approximately 0.5  $\mu\text{L}$  of this mixture was hand spotted on the target plate. All the spectra were acquired in a linear mode. For each spectrum, 1000 laser shots were accumulated.

Gradient polymer elution chromatography (GPEC) measurements were carried out on an Alliance Waters 2690 separation module with a Waters 2487 dual  $\lambda$  absorbance detector and a PL-EMD 960 ELSD detector ( $\text{N}_2$  flow 5.0 mL/min, temperature 70  $^\circ\text{C}$ ). A Zorbax silica 5  $\mu\text{m}$  column (4.6  $\times$  150 mm; Dupont Chromatography) was used at 30  $^\circ\text{C}$ . A Varian 9010 solvent delivery system was used to maintain a stable flow rate of the eluents. Chromatograms were analyzed with Millennium software version 3.05. A linear binary gradient starting from heptane to THF was used, as shown in Table 1. At the end of the gradient, the column was reset to the initial conditions between 60 and 70 min.

DSC measurements were done on a TA instruments Q1000 DSC equipped with an autosampler and refrigerated cooling system. The DSC cell was purged with a nitrogen flow of 50 mL/min. The temperature was calibrated with the onset of melting for indium (156.6  $^\circ\text{C}$ ) at a heating rate of 10  $^\circ\text{C}/\text{min}$ . The heat flow was calibrated with the heat of fusion of indium (28.45 J/g). Samples of 6–8 mg were prepared in aluminum pans and were first heated from 0 to 125  $^\circ\text{C}$ , kept isothermally for 3 min, cooled at 10  $^\circ\text{C}/\text{min}$  to 0  $^\circ\text{C}$ , and kept isothermally for 3 min. The subsequent heating scan at 10  $^\circ\text{C}/\text{min}$  was then recorded.

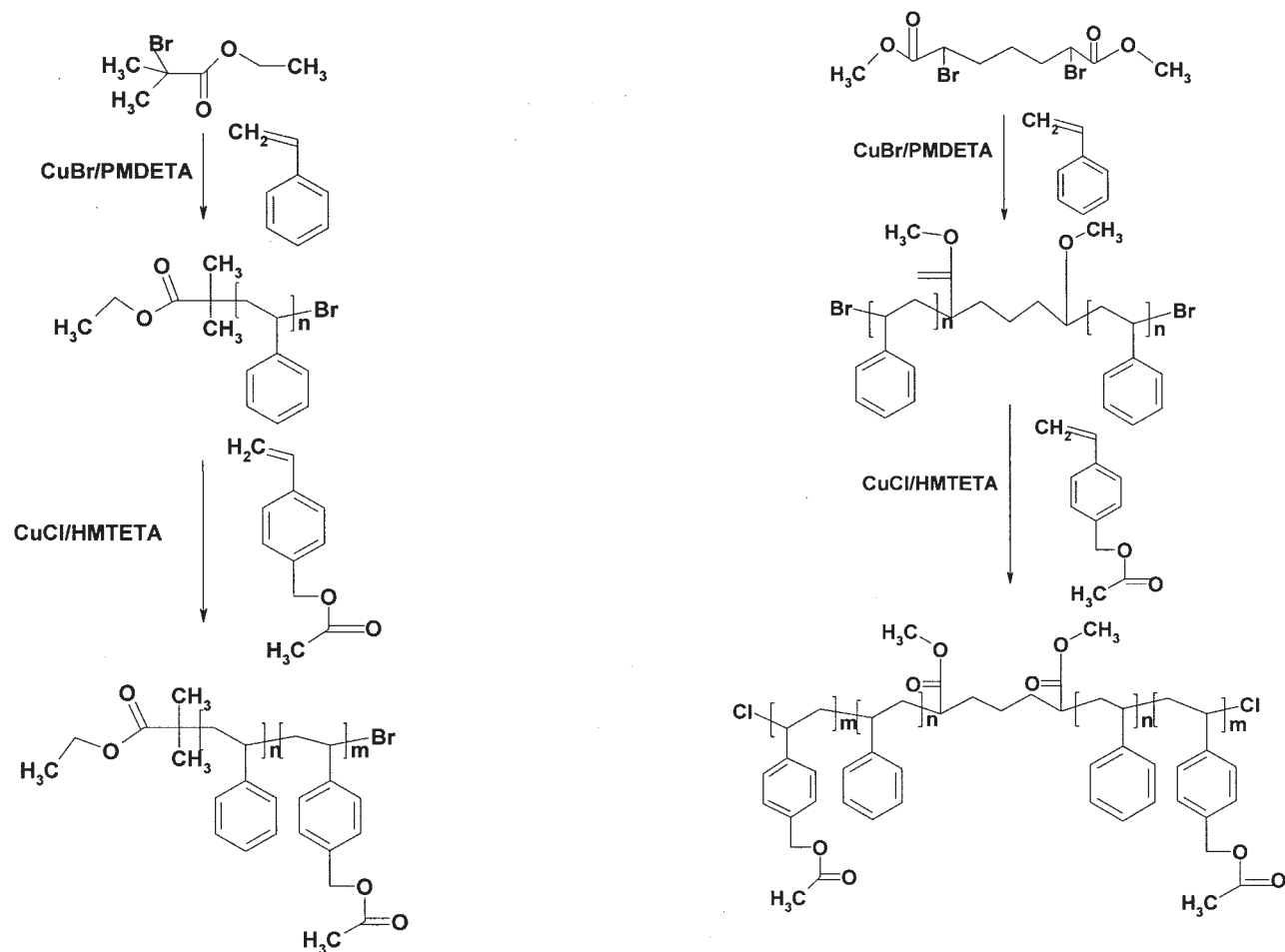
## Polymerization Procedures

### Synthesis of the Diblock Copolymer Poly(styrene-*b*-acetoxymethylstyrene) (PS-PAMS)

A 100 mL three-necked round-bottom flask was charged with styrene (5.2 g, 0.05 mol), CuBr (0.0143 g, 0.0001 mol), and PMDETA (0.0173 g, 0.0001 mol) and then purged with Ar for 30 min, with rapid stirring. In another flask, EBriB (0.0747 g, 0.0005 mol) and diphenyl ether (2.5 g) were added and degassed for 30 min. The mixture was then transferred to the monomer solution dropwise with a degassed syringe. The resulting mixture was placed in a thermostatically controlled oil bath at 100  $^\circ\text{C}$  and the reaction was left to proceed for 6 h at this temperature. A solution containing acetoxymethylstyrene (4.405 g, 0.025 mol), CuCl (0.00989 g, 0.0001 mol), and HMTETA (0.02304 g, 0.0001 mol), kept in a dropping funnel with Ar bubbling through it, was transferred to the reaction flask. The reaction was allowed to proceed for 14 h. The reaction mixture was diluted with THF and passed through a basic alumina column to remove the catalyst. The copolymer was precipitated from the resulting solution with heptane and dried *in vacuo*.

### Synthesis of the Triblock Copolymer Poly(acetoxymethylstyrene-*b*-styrene-*b*-acetoxymethylstyrene) (PAMS-PS-PAMS)

A 100 mL three-necked round-bottom flask was charged with styrene (5.2 g, 0.05 mol), CuBr (0.0286 g, 0.0002 mol), and PMDETA (0.0173 g, 0.0002 mol) and purged with Ar for 30 min, with rapid stirring. In another flask, DMDDBHD (0.173 g, 0.0005 mol) and diphenyl ether (5 g) were added and degassed for 30 min. The mixture was then transferred to the homogeneous monomer solution dropwise with a degassed syringe. The resulting mixture was placed in a thermostatically controlled oil bath at 100  $^\circ\text{C}$ . A solution containing acetoxymethylstyrene (8.81 g, 0.05 mol), CuCl (0.0197 g, 0.0002 mol) and HMTETA (0.0460 g, 0.0002 mol), kept in a dropping funnel with Ar bubbling through it, was transferred to the reaction flask after 3 h. The reaction was then allowed to proceed for 2 h. The reaction mixture was diluted with THF and passed through a basic alumina column to remove the catalyst. The copolymer was precipitated from the resulting solution with heptane and dried *in vacuo*.



**Scheme 2.** Diblock (PS-PAMS) and triblock (PAMS-PS-PAMS) copolymers by ATRP with CuBr/PMDETA in the first stage (styrene polymerization) and CuCl/HMTETA in the second stage (acetoxyethylstyrene polymerization).

#### Conversion to Poly(hydroxymethylstyrene-*b*-styrene-*b*-hydroxymethylstyrene) (PHMS-PS-PHMS)

The copolymer PAMS-PS-PAMS (1 g) was dissolved in 1,4-dioxane (60 mL). An alcoholic potassium hydroxide solution (60 mL) was added, and the reaction mixture was stirred for 24 h at 40 °C. The resulting polymer was precipitated from the reaction mixture with acidified water prepared from 7 mL of concentrated hydrochloric acid and 500 mL of distilled water, filtered, and dried *in vacuo* at 70 °C.

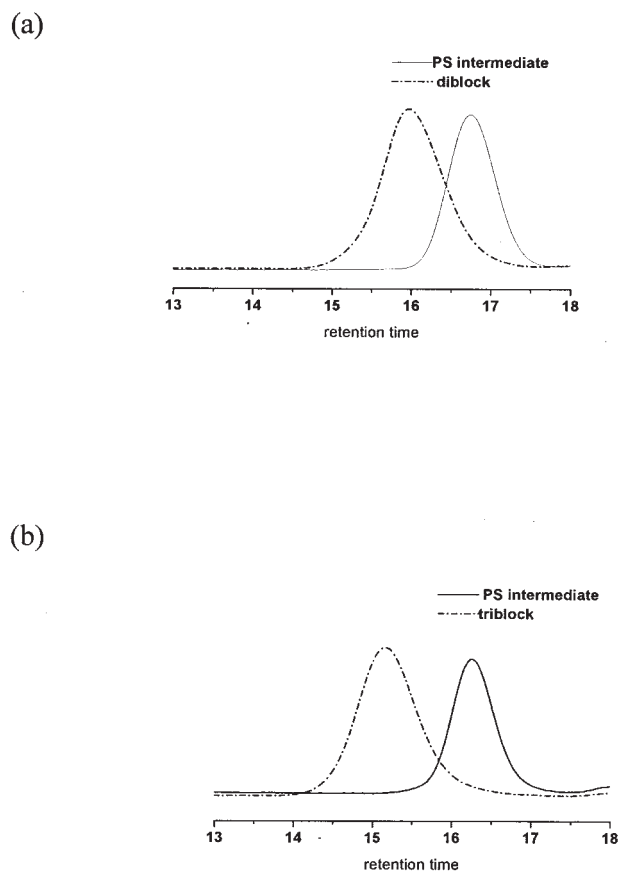
#### Conversion to Poly(bromomethylstyrene-*b*-styrene-*b*-bromomethylstyrene) (PBrMS-PS-PBrMS)

The copolymer PAMS-PS-PAMS (1 g) was dissolved in toluene (20 mL). Concentrated HBr (22.48 g) together with the phase-transfer cata-

lyst Aliquat 336 (0.3868 g) was added. The reaction was allowed to proceed for 24 h at 80 °C. The polymer was precipitated from the organic layer with methanol.

## RESULTS AND DISCUSSION

Scheme 2 shows the approach used for synthesis of the diblock copolymer PS-PAMS. Starting with the monofunctional initiator (EBriB), styrene was polymerized in the first stage with CuBr/PMDETA as the catalyst–ligand system. Acetoxyethylstyrene was added in the second stage, along with an additional catalyst–ligand system CuCl/HMTETA to invoke halogen exchange and to enhance initiation of intermediate polystyrene over the propagation of acetoxyethyl-



**Figure 1.** SEC traces of intermediate the polystyrene (—) and the copolymer (- - -) during synthesis of the (a) diblock PS-PAMS and (b) triblock (PS-PAMS-PS).

ylstyrene.<sup>17,21</sup> Synthesis of the triblock copolymer (Scheme 2) involved similar reactions but employed a difunctional initiator (DMDBHD).

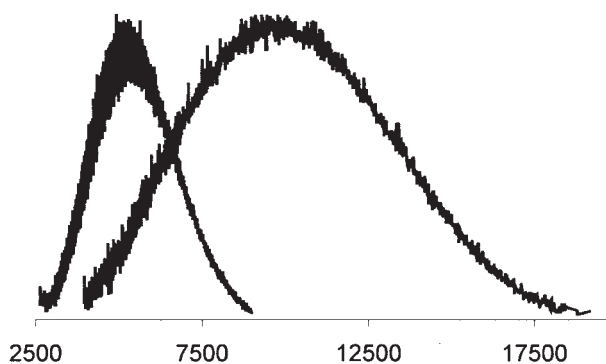
For the two cases, Figure 1 shows the SEC plots of the intermediate polystyrenes just before the addition of acetoxyethylstyrene, and the plots of the final copolymers. A decrease in the retention time after addition of the second monomer suggests that the polymerization continues after addition of acetoxyethylstyrene. The corresponding polydispersity index (PDI), as well as the number-average molecular weight ( $M_n$ ) as obtained by SEC, are shown in Table 2. The low PDI values of the intermediate polystyrenes indicate good control during the first stage of the polymerizations. However, the molar mass distributions of the copolymers from SEC are not reliable because the calibration of the SEC is based on polystyrene standards. In contrast, MALDI-TOF-MS can be used to determine absolute molecular weights.<sup>22</sup> We therefore used MALDI-TOF-MS in

**Table 2.** Molecular Weight Characteristics of the Intermediate and Final Block Copolymers as Determined by SEC and MALDI-TOF-MS

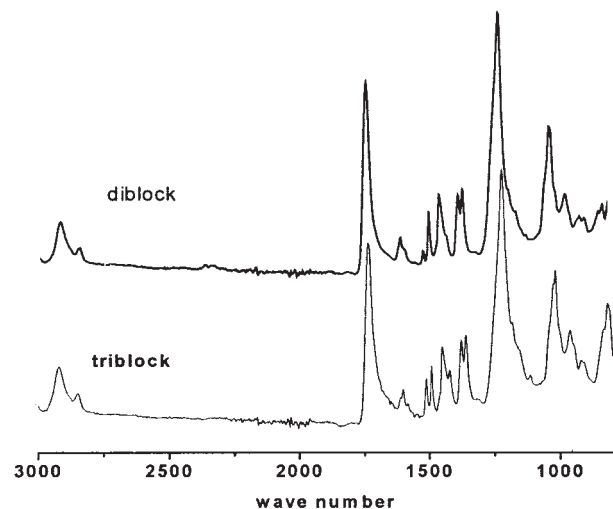
		SEC		MALDI-TOF	
		$M_n$	PDI	$M_n$	PDI
Diblock	Intermediate	2,260	1.19	—	—
	Final	4,780	1.23	5,369	1.05
Triblock	Intermediate	3,830	1.11	—	—
	Final	10,200	1.24	9,465	1.05

a linear mode to record the molar mass distribution of the two block copolymers (Fig. 2). The corresponding  $M_n$  values are included in Table 2, to compare with the corresponding SEC values. We find an acceptable match between the  $M_n$  determined by SEC and MALDI-TOF-MS. The low PDI values of the copolymers also indicate a possible good control during the second stage of the polymerizations. The lower PDI values obtained by MALDI-TOF-MS, as compared to the corresponding SEC values, could be related to the signal broadening in SEC because of axial dispersion,<sup>23</sup> and the mass discrimination in MALDI-TOF-MS because of detector saturation.<sup>24</sup>

Figure 3 shows the FTIR spectra of the copolymers. Signals at characteristic stretching frequencies for an acetate group at  $1734\text{ cm}^{-1}$  for both PS-PAMS and PAMS-PS-PAMS indicate the presence of acetoxyethyl groups in the polymer. However, FTIR is unable to distinguish between a copolymer and a blend of two homopolymers that can be formed by a chain transfer to acetoxyethylstyrene. Similarly, SEC involved monitoring the separation based on the hydrodynamic



**Figure 2.** MALDI-TOF-MS of the (left curve) diblock and (right curve) triblock copolymers.

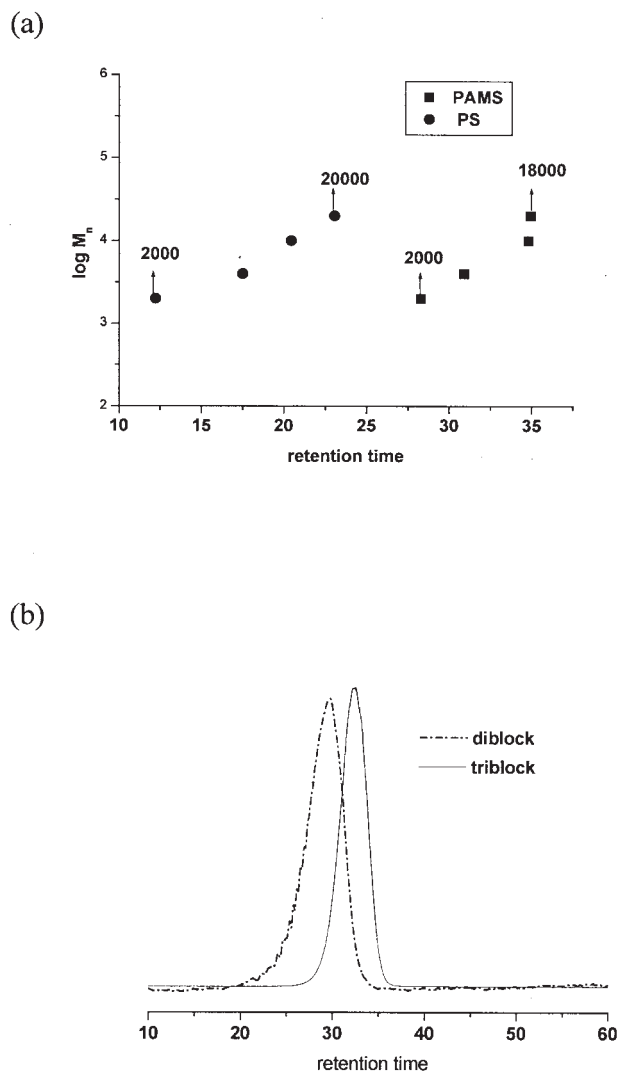


**Figure 3.** FTIR spectra of the diblock (PS-PAMS, upper curve) and the triblock (PS-PAMS-PS, lower curve) copolymers.

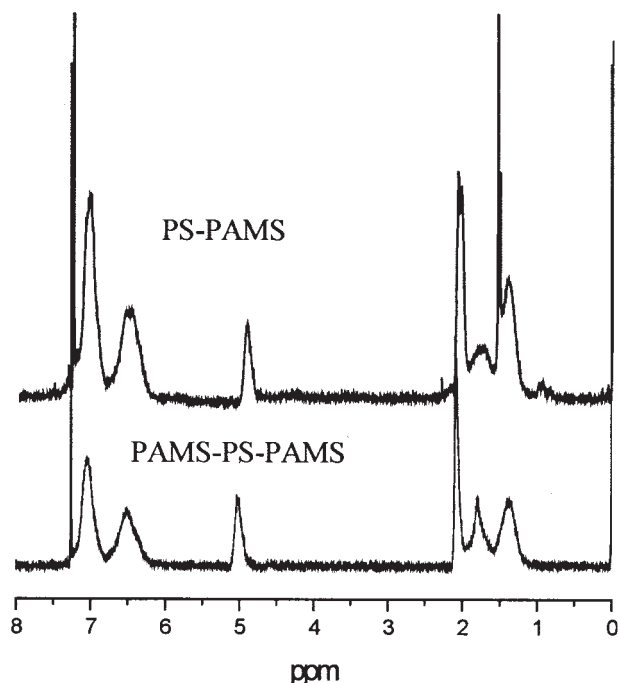
volume, and is unable to indicate possible incorporation of acetoxyethylstyrene in the block copolymers. We then characterized our copolymerization products by GPEC. It is a high performance liquid chromatographic method that uses a combination of precipitation, redissolution, and sorption mechanisms to separate polymer molecules according to their chemical compositions.<sup>25–27</sup> This makes it suitable for distinguishing between polymer blends and copolymers. We used reversed phase GPEC, where the polymer is first precipitated by injection of the polymer solution into a column running on a nonsolvent. Subsequently, the eluent character is gradually changed to favor dissolution and elution of the polymer, at retention times determined by their solubilities and sorption characteristics, which in turn are determined by the chemical compositions of the individual macromolecules. To ensure that there is a good separation in the chromatograms for polystyrene (PS) and polyacetoxyethylstyrene (PAMS), we first analyzed samples of the homopolymers PS and PAMS with different molecular weights. The  $M_n$  dependence of the retention time of the two homopolymers is shown in Figure 4(a). Although PS is eluted between 12 to 23 min, PAMS is eluted between 28 to 34 min. GPEC traces of our PS-PAMS and PAMS-PS-PAMS copolymers are shown in Figure 4(b). The absence of any signals in the PS homopolymer range (12–23 min) indicates that all the intermediate polystyrenes formed in the first step went

on to grow as copolymers with the incorporation of acetoxyethylstyrene.

The addition of acetoxyethylstyrene before complete conversion of styrene may be expected to result in competition between styrene and acetoxyethylstyrene for the propagating center, resulting in random incorporation of both styrene and acetoxyethylstyrene in the second block. We are now interested in evaluating the blocky nature of copolymers, that is, quantification of the



**Figure 4.** GPEC analysis with an eluent gradient as in Table 1. (a) Molar mass dependence of the retention times of the homopolymers polystyrene (PS) and polyacetoxyethylstyrene (PAMS) and (b) GPEC traces of the diblock (PS-PAMS, - - - -) and the triblock (PS-PAMS-PS, —) copolymers. The PS samples used were polymer standards obtained from Polymer Laboratories. The PAMS samples were synthesized by ATRP and characterized by SEC.

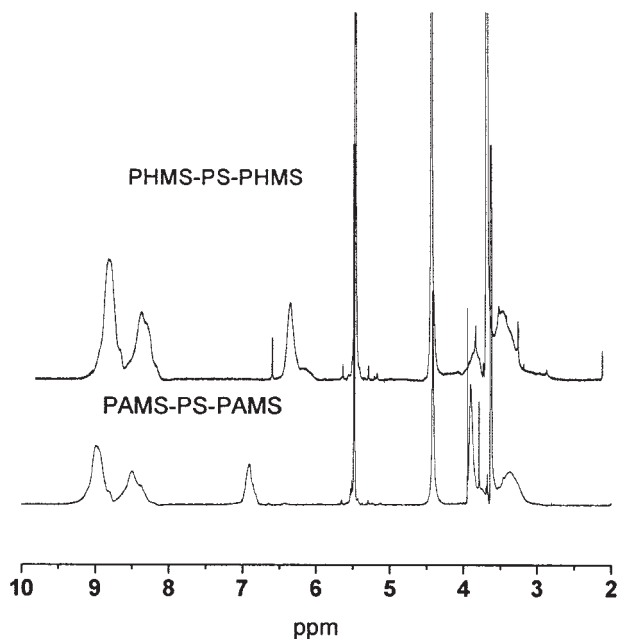


**Figure 5.**  $^1\text{H}$  NMR of the diblock (PS-PAMS, upper curve) and the triblock (PAMS-PS-PAMS, lower curve) copolymers in  $\text{CDCl}_3$ .

extent of incorporation of acetoxyethylstyrene during the second stage of the polymerizations.  $^1\text{H}$  NMR spectra (Fig. 5) of the copolymers show diagnostic signals at  $\delta = 5.0$  and  $2.1$  ppm, characteristic of the  $-\text{CH}_2-$  and the  $-\text{CH}_3$  of acetoxyethyl groups of copolymers. The areas of these peaks relative to the aromatic peaks allow us to calculate the molar fractions of acetoxyethylstyrene in the copolymers, and these values are shown in Table 3. The same table also shows the mole fractions of acetoxyethylstyrene calculated from the  $M_n$  of intermediate polystyrenes (SEC) and the  $M_n$  of copolymers (MALDI-TOF-MS) (Table 2), assuming incorporation of only acetoxyethylstyrene in the second step of the polymerizations. The excellent match indicates the acceptability of the assumption that it is

**Table 3.** Mole Fractions of Acetoxyethylstyrene in the Block Copolymers

	From $^1\text{H}$ NMR	From $M_n$ of intermediate and block copolymer
In diblock	0.480	0.45
In triblock	0.47	0.46

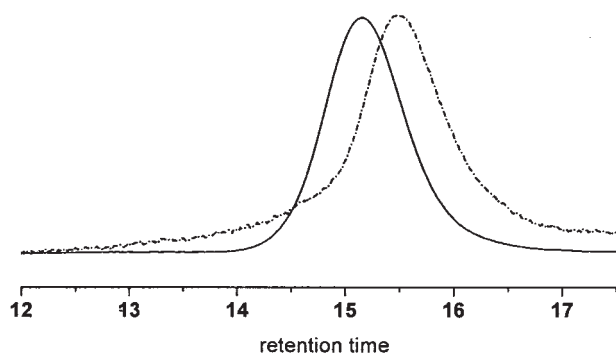


**Figure 6.**  $^1\text{H}$  NMR of the triblock copolymers PAMS-PS-PAMS (lower curve) and PHMS-PS-PHMS (upper curve) in  $d$ -THF.

predominantly acetoxyethylstyrene that gets incorporated in the second stage of the copolymerization reactions.

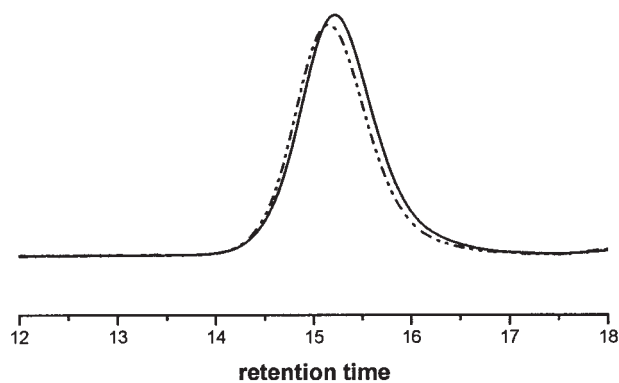
As a demonstration of the potential of these block copolymers for further modification, the acetoxy groups in the triblock copolymer PAMS-PS-PAMS were hydrolyzed with alcoholic KOH to yield the triblock copolymer PHMS-PS-PHMS. The  $^1\text{H}$  NMR (Fig. 6) in  $d$ -THF shows a clear shift from the pendant  $-\text{CH}_2-\text{O}-\text{CO}-\text{CH}_3$  peak ( $\delta = 7.0$  ppm) of PAMS-PS-PAMS to the  $-\text{CH}_2-\text{OH}$  peak ( $\delta = 6.3$  ppm) in PHMS-PS-PHMS. The SEC chromatogram (Fig. 7) shows a slight shift to a higher retention time, presumably because of its influence on the hydrodynamic volume and possible adsorption effects.

Another part of the triblock copolymer PAMS-PS-PAMS was converted to a triblock macroinitiator (PBrMS-PS-PBrMS). This was achieved by HBr treatment of the acetoxy groups to form bromomethyl groups. Although the SEC chromatogram (Fig. 8) shows a negligible shift, the  $^1\text{H}$  NMR in  $\text{CDCl}_3$  (Fig. 9) indicates the complete conversion of the  $-\text{CH}_2-\text{O}-\text{CO}-\text{CH}_3$  groups ( $\delta = 5.0$  ppm) of PAMS-PS-PAMS to  $-\text{CH}_2-\text{Br}$  ( $\delta = 4.5$  ppm) in PBrMS-PS-PBrMS. These bromomethyl groups can be considered useful as initiating sites for ATRP, leading to dense grafting on the two end-blocks of the triblock copolymer.

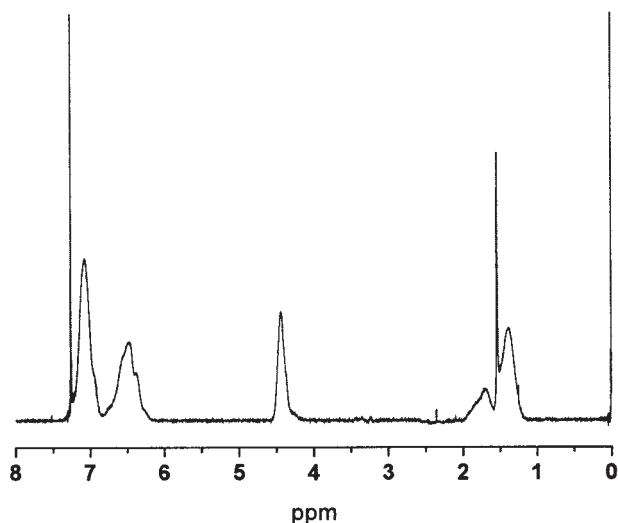


**Figure 7.** SEC traces of the triblock copolymers (—) PAMS-PS-PAMS and (---) PHMS-PS-PHMS. Based on polystyrene calibration, the  $M_n$  and the PDI of PHMS-PS-PHMS are 9058 and 1.25, respectively, as compared to 10,600 and 1.24 for the PAMS-PS-PAMS.

We also carried out DSC characterization of the diblock and triblock copolymers (Fig. 10). The diblock copolymer PS-PAMS shows a single glass-transition temperature ( $T_g \sim 47^\circ\text{C}$ ) and the triblock copolymer PS-PAMS-PS shows a single  $T_g \sim 70^\circ\text{C}$ . This can be compared with the  $T_g$ s of the homopolymers: the  $T_g \sim 105^\circ\text{C}$  for polystyrene ( $M_n = 8137$ ) and the  $T_g \sim 35^\circ\text{C}$  for polyacetoxymethylstyrene ( $M_n = 21700$ ), prepared under similar conditions. Thus, the diblock and the triblock copolymers each show single  $T_g$  values intermediate between the  $T_g$ s of the constituent homopolymers. Although the chemical composition (styrene:acetoxymethylstyrene) of the two block copolymers is similar (Table 3), the higher  $T_g$  of the triblock copolymer can be attributed to its higher  $M_n$  (Table 2). When the homopolymers polystyrene and polyacetoxymethylstyrene were solution blended (1:1 w:w) and precipitated, the subsequent differential scanning calorimetry



**Figure 8.** SEC traces of the triblock copolymers (—) PAMS-PS-PAMS and (---) PBrMS-PS-PBrMS.

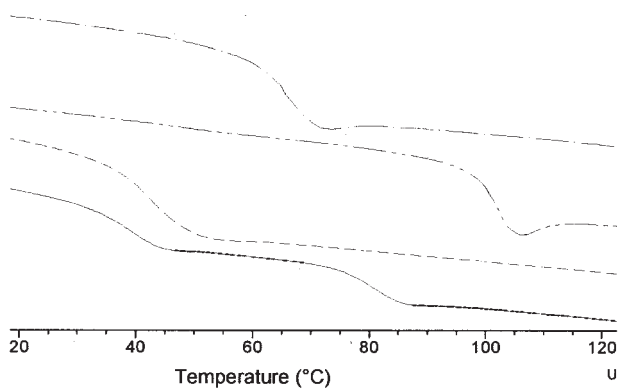


**Figure 9.**  $^1\text{H}$  NMR of PBrMS-PS-PBrMS in  $\text{CDCl}_3$ .

(DSC) shows two  $T_g$ s (Fig. 10), corresponding to each of the constituent homopolymers. Similarly, two  $T_g$ s of the corresponding blocks are expected in block copolymers that can undergo microphase separation.<sup>28</sup> As seen in Figure 10, we are unable to detect separate  $T_g$ s for the constituent blocks in our block copolymers PS-PAMS and PAMS-PS-PAMS. The modified triblock copolymer PBMS-PS-PBMS also displays a single  $T_g \sim 105^\circ\text{C}$ . It is well known that block copolymers are less prone to phase separation than the blends of the corresponding homopolymers.<sup>28</sup>

## CONCLUSIONS

We have described the synthesis of diblock (PS-PAMS) and triblock (PAMS-PS-PAMS) copoly-



**Figure 10.** DSC curves of (---) PS-PAMS, (-·-·-·) PAMS-PS-PAMS, (-·-·-·) PBrMS-PS-PBrMS, and a blend (—) of PS ( $M_n = 8137$ ) and PAMS ( $M_n = 21700$ ).



mers by a simple and convenient one-pot method. Sequential addition of styrene and acetoxyethylstyrene results in their sequential polymerization, even in the presence of styrene during the second stage of polymerization. The copolymer size and blockiness are characterized by a combination of SEC, MALDI-TOF-MS, FTIR, GPEC, and  $^1\text{H}$  NMR. The triblock copolymer PAMS-PS-PAMS is shown to be easily hydrolyzed to the triblock copolymer PHMS-PS-PHMS, providing potential for developing well-defined ionomers. Unmasking of the acetoxy groups of the triblock copolymer PAMS-PS-PAMS reveals bromomethyl groups that can be used as ATRP initiating sites for dense grafting on the end blocks.

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