A Method To Synthesize Multiblock Copolymers of Methyl Methacrylate and Styrene Regardless of Monomer Sequence

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ABSTRACT: Multiblock copolymers of methyl methacrylate and styrene were created using atom transfer radical polymerization. The syntheses of poly(styrene-*b*-methyl methacrylate-*b*-styrene) (S-M-S) and poly(methyl methacrylate-*b*-styrene-*b*-methyl methacrylate) (M-S-M) triblock copolymers and poly(methyl methacrylate-*b*-styrene-*b*-methyl methacrylate-*b*-styrene-*b*-methyl methacrylate) (M-S-M-S-M) and poly(styrene-*b*-methyl methacrylate-*b*-styrene-*b*-methyl methacrylate-*b*-styrene) (S-M-S-M-S) pentablock copolymers are reported. This method is novel in that the resultant copolymers are very blocky in nature and yet can be synthesized regardless of the direction of cross-propagation; a styrene end can initiate the polymerization of methyl methacrylate, and methyl methacrylate ends can initiate the polymerization of styrene. This is contrary to anionic polymerization, which is commonly used to prepare block copolymers of styrene and methyl methacrylate. SEC analysis shows the kinetics of the homopolymerizations and the copolymerizations, while NMR analysis confirms the blocky nature of the copolymers.

Introduction

Copolymers are unique materials whose characteristics may be a hybrid of the individual homopolymers. The properties of the copolymer, such as thermal behavior, dielectric properties, and solubility, can be controlled through its composition.[1] One use of copolymers is as a compatibilizer in immiscible polymer blends.[2,3] Copolymers that are composed of monomers that are miscible with the polymers being blended will often be soluble in both phases of an incompatible polymer blend. This solubility allows the copolymer to act as an interfacial modifier and couple the two phases together, which leads to improved mechanical properties, phase behavior, and interfacial adhesion in the blend.[2−8] Copolymer architecture and sequence distribution can be important parameters that impact the solubility and thus the ability of a copolymer to compatibilize a polymer blend. For example, random,[4,5] block,[6,7] multiblock,[3,8] alternating,[9] and graft[3,10] copolymers behave differently when mixed in immiscible polymer blends. Experimental[4−7,10] and theoretical[11,12] data indicate that blocky or multiblock copolymers rather than random-like copolymers are better interfacial modifiers in biphasic polymer blends. Unfortunately, it is currently very difficult to reproducibly synthesize multiblock copolymers in a cost-effective manner. Additionally, the most common method to synthesize block and multiblock copolymers, via anionic conditions, is expensive and limits the types of copolymers that can be produced.[1,13,14]

Atom transfer radical polymerization (ATRP), however, is a synthetic technique that may be useful for producing multiblock copolymers that cannot be prepared by conventional (anionic) methods. We expect to find a set of conditions where a multiblock copolymer can be formed by sequentially polymerizing monomer A, then monomer B, then monomer A, then monomer B... using atom transfer radical polymerization techniques. ATRP is a process that synthesizes polymers with fairly narrow molecular weight distributions via a "living" radical mechanism.[15−22] A number of different initiating systems have been used to yield polymers synthesized by these methods. Nitroxide-based initiators[18] effectively polymerize styrenic monomers by a living free radical mechanism, while acrylates are polymerized efficiently by organocobalt complexes.[19] In addition, copper halides complexed with either 2,2′-bipyridine or a 4,4′-disubstituted 2,2′-bipyridine catalyze the polymerization of both styrenes and acrylates with a suitable initiator.[15−17] Of particular interest for our study is Percec and Barboiu's controlled polymerization of both methyl methacrylate and styrene using arenesulfonyl chlorides with a copper halide/2,2′-bipyridine complex.[20−22] Low polydispersities ranging from 1.1 to 1.5 have been achieved using this technique.

A few multiblock, mainly triblock, copolymers have been synthesized using ATRP techniques. Triblocks of poly(styrene-*b*-isobutylene-*b*-styrene) (S-I-S)[23] and poly(styrene-*b*-vinylidene fluoride-*b*-styrene) (S-V-S)[24] have been prepared by combining the ATRP method with site transformation techniques. Matyjaszewski and co-workers have demonstrated the ability of ATRP to synthesize multiblock copolymers without site transformation methods.[25−27] A-B-A triblock copolymers of poly(methyl methacrylate-*b*-butyl acrylate-*b*-methyl methacrylate)[25] and poly(*tert*-butyl acrylate-*b*-styrene-*b*-*tert*-butyl acrylate)[27] have been reported. An A-B-C triblock and an A-B-C-D tetrablock, poly(*tert*-butyl acrylate-*b*-styrene-*b*-methyl acrylate)[27] and poly(*tert*-butyl acrylate-*b*-styrene-*b*-methyl acrylate-*b*-methyl methacrylate),[26] respectively, have also been prepared by Matyjaszewski's group using ATRP methods. These results suggest that it is difficult to repeatedly alternate between two monomers to create multiblock copolymers larger than triblocks and to accurately control the sequence distribution of the copolymer. We are interested in developing just such a technique so that copolymers with varying blockiness can be reproducibly synthesized and examined as interfacial modifiers. In particular, we seek to develop an ATRP method by which multiblock copolymers of styrene and methyl methacrylate can be repro-

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Table 1. Reaction Conditions for Homopolymer and Copolymer Polymerizations

polymer prepared	synthetic method	$[MMA]_0/[I]_0$	$[styrene]_0/[I]_0$	[CuCl]/[I]	[Bipy]/[I]	*p*-xylene (mL)
PS	bulk		400	0.074	0.351	0.7
PS	solution		400	0.050	0.234	11.5
PMMA	bulk	400		0.074	0.351	0.7
PMMA	solution	400		0.050	0.234	10.7
SMS	bulk		600	0.017	0.08	0.7
SMS	solution		600	0.025	0.12	8.0
MSM	bulk	600		0.027	0.129	0.7
MSM	solution	600		0.025	0.117	8.0
SMSMS	bulk		500	0.010	0.045	0.0
MSMSM	bulk	600		0.008	0.036	0.0

ducibly synthesized regardless of monomer sequence. Assuming the chains can cross-propagate regardless of monomer sequence, larger multiblock copolymers (penta, hepta, etc.) with reproducible control of the block structure can be synthesized.

In this paper, we examine the feasibility of using phenoxybenzene-4,4′-disulfonyl chloride (PDSC), a difunctional arenesulfonyl chloride, as the initiator and a copper chloride/2,2′-bipyridine complex as the catalyst[21] in the polymerization of styrene and methyl methacrylate monomers to homopolymers, triblock copolymers, and pentablock copolymers, with both styrene and methyl methacrylate center blocks. The requirement that this technique works when either styrene or methyl methacrylate is the center block can only be met if one monomer can cross-propagate to another regardless of monomer sequence. The effect of the amount of solvent on the polymerization process for the homopolymers and triblock copolymers is also examined. The kinetics of the block lengths were monitored throughout the polymerization using size exclusion chromatography (SEC), and the structures of the homopolymers, triblock copolymers, and pentablock copolymers were characterized by both ^{13}C and ^{1}H NMR.

Experimental Section

Materials. Methyl methacrylate (99%) and *p*-xylene (99%) were purchased from Aldrich and used without further purification. Styrene (99%), copper(I) chloride (99%), and 2,2′-bipyridine (99%) were purchased from Acros and also used as acquired. Phenoxybenzene-4,4′ disulfonyl chloride (PDSC) was synthesized by the dropwise addition of chlorosulfonic acid (Acros, 98%) to diphenyl ether (Aldrich, 99%) by a literature procedure.[21]

Size Exclusion Chromatography. SEC analysis was performed at room temperature (25 °C) using a Waters 600E system equipped with three Waters Styragel columns [HR-1 (100 Å), HR-3 (10^3 Å), HR-5E (mixed bed)] or two Polymer Laboratories PLgel 5 μm mixed-D columns and a Waters 410 differential refractometer as a detector. Samples were 0.2 wt % solution, and tetrahydrofuran (THF) was the eluent at a flow rate of 1.0 mL/min. The SEC curves were calibrated using narrow molecular weight distribution polystyrene standards.

Nuclear Magnetic Resonance Spectroscopy. ^{1}H and ^{13}C NMR spectra of the homopolymers and copolymers were recorded on a Bruker AC250 MHz NMR spectrometer. Solutions were prepared with deuterated chloroform as the lock solvent with an internal standard of trimethylsilane. ^{1}H NMR was utilized to determine the composition of the synthesized copolymers,[28] while ^{13}C NMR was utilized to provide details of the sequence distribution of the copolymer.[28−33]

Homopolymer Procedures. In a typical polymerization of styrene by bulk methods, styrene (17.2 mL, 0.150 mol), PDSC (0.138 g, 3.76×10^{-4} mol), copper(I) chloride (74 mg, 7.52×10^{-3} mol), 2,2′-bipyridine (0.351 g, 2.26×10^{-3} mol), and *p*-xylene (0.7 mL) were added to a three-necked round-bottom flask under inert atmosphere. The contents of the flask were then immediately subjected to freeze−thaw techniques to remove trace impurities. The flask was then heated by an oil bath to 125 °C under a positive argon flow to allow the polymerization to proceed. Yield: 13.9 g (89%). ^{1}H NMR ($CDCl_3$): δ 7.3−6.3 (broad Ar **H**), 2.2−1.1 (broad, −C**H**$_2$−C**H** (Ar)−). SEC: $M_n = 27\,000$, $M_w/M_n = 1.36$.

Similar procedures were completed for the polymerization of styrene by solution methods and of MMA by solution and bulk methods with the specific contents of the reaction flask given in Table 1. We use the terms "solution" and "bulk" to denote the processes with significant (ca. 50 wt %) amount of solvent present and with very little solvent (<10 wt %) present, respectively. Additionally, methyl methacrylate was polymerized at 95 °C.

Multiblock Copolymer Procedure. The outer blocks of the multiblock copolymers were polymerized by techniques similar to the homopolymer procedure, except the reaction occurred in the presence of the end-capped homopolymer. While specific descriptive examples are given below, the amount of each reagent added to the reaction flask is given in Table 1 for each copolymer synthesized.

A. Triblock Copolymer Example. In the synthesis of the SMS triblock by bulk methods, PMMA homopolymer (3.0 g, 8.53×10^{-5} mol), styrene monomer (5.9 mL, 0.0512 mol), copper(I) chloride (17 mg, 1.72×10^{-4} mol), 2,2′-bipyridine (80 mg, 5.15×10^{-4} mol), and *p*-xylene (0.7 mL) were placed in a three-necked flask under inert atmosphere. The system was then subjected to the freeze−thaw process, and the polymerization was allowed to proceed by heating the system to 125 °C under a positive argon pressure. Yield: 7.7 g (92%). ^{1}H NMR ($CDCl_3$): δ 7.3−6.3 (broad Ar **H**), 2.2−1.1 (broad, −C**H**$_2$−, −C**H**−), 3.7−3.5 (−OC**H**$_3$), 1.1−0.7 (broad, −C**H**$_3$). SEC: $M_n = 51\,300$, $M_w/M_n = 1.78$.

B. Pentablock Copolymer Example For the synthesis of the MSMSM pentablock copolymer, the SMS triblock (2.0 g, 3.89×10^{-5} mol), methyl methacrylate monomer (2.5 mL, 0.0233 mol), copper(I) chloride (7.7 mg, 7.78×10^{-5} mol), and 2,2′-bibyridine (36.5 mg, 2.33×10^{-4} mol) were added to a three-necked round-bottom flask under inert atmosphere. Freeze−thaw techniques were executed to remove trace impurities, and the flask was heated to 95 °C under a positive argon flow to polymerize the outer blocks. Yield: 3.65 g (84%). ^{1}H NMR ($CDCl_3$): δ 7.3−6.3 (broad Ar **H**), 2.2−1.1 (broad, −C**H**$_2$−, −C**H**−), 3.7−3.5 (−OC**H**$_3$), 1.1−0.7 (broad, −C**H**$_3$). SEC: $M_n = 76\,200$, $M_w/M_n = 1.80$.

Precipitating in methanol and drying in a vacuum oven initially isolated all homopolymers and multiblock copolymers. The final product was then further purified by redissolving in THF or toluene and reprecipitating in methanol multiple times, followed by drying in a vacuum oven.

Results

Polymerization Kinetics. To monitor the kinetics of the polymerization, samples were periodically removed under positive argon pressure, purified, and evaluated by size exclusion chromatography (SEC). The kinetics of the polymerization of the homopolymer and triblock copolymers are shown in Figures 1 and 2, which show the number-average molecular weight (M_n) of the growing species as a function of time for polystyrene-

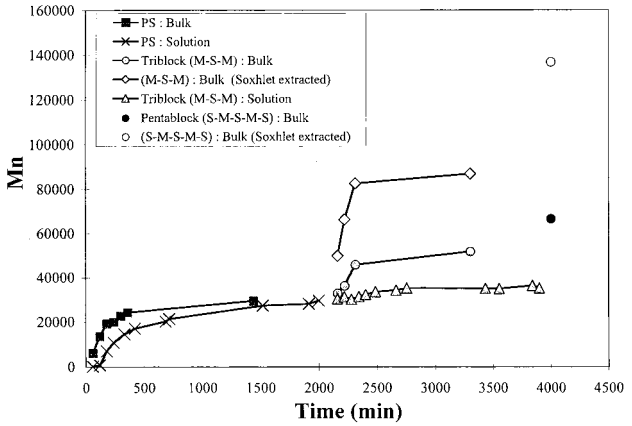

Figure 1. Time evolution of the molecular weight of the polystyrene homopolymers and styrene-centered multiblock copolymers.

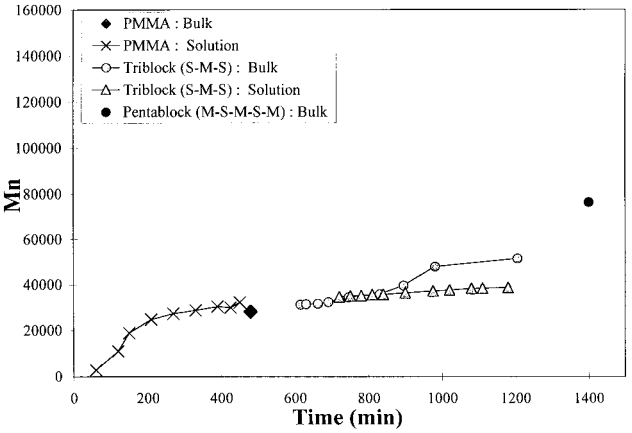

Figure 2. Time evolution of the molecular weight of the poly(methyl methacrylate) homopolymers and MMA-centered multiblock copolymers.

centered polymers and poly(methyl methacrylate)-centered polymers, respectively. The polystyrene homopolymer synthesized by either bulk or solution methods increases substantially in molecular weight (Figure 1). The PS synthesized by bulk methods has a much greater initial growth rate than the solution polymerization. In addition, the bulk-PS achieves its final molecular weight after only 6 h whereas the solution-PS requires about 33 h to approach a similar molecular weight. Both PS homopolymers approach the target molecular weight of 4.0×10^4 but fall slightly short. Failing to fully achieve the target molecular weight is in part due to the periodic removal of SEC samples, and thus monomer, to monitor the kinetics. However, typical conversions for PS homopolymers without the periodic removal of samples completed in our lab usually fall in the range of 80−95%.

Data showing the kinetics of the growth of the PMMA homopolymer are only available for the solution polymerization of MMA. However, bulk polymerization produced PMMA on the same time scale as solution techniques. Figure 2 shows that both the bulk and solution methods produce PMMA that approaches the target molecular weight of 4.0×10^4 within 8 h. Therefore, the slower growth of the solution polymerization observed during the PS synthesis is apparently not duplicated for the PMMA.

Table 2 provides the polydispersities and molecular weight data of the final products for all synthesized

Table 2. Molecular Weight Characteristics of Homopolymers and Copolymers

polymers	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	poly-dispersity
PS bulk	2.70	3.67	1.36
PS solution	3.20	4.00	1.25
PMMA bulk	2.80	3.52	1.26
PMMA solution	3.52	3.80	1.08
M-S-M triblock bulk	5.16	10.3	1.99
M-S-M triblock bulk (after Soxhlet extraction)	86.9	13.7	1.58
M-S-M triblock solution	3.62	4.92	1.36
S-M-S triblock bulk	5.13	9.15	1.78
S-M-S triblock solution	3.85	5.27	1.37
S-M-S-M-S pentablock bulk	6.65	13.4	2.01
S-M-S-M-S pentablock bulk (after Soxhlet extraction)	13.7	22.1	1.62
M-S-M-S-M pentablock bulk	7.62	13.7	1.80

homopolymers and copolymers. The advantage of the solution technique is that it produces a polymer with a lower polydispersity. For instance, the solution polymerization of PMMA (PDI = 1.08) results in a lower polydispersity than the bulk method (PDI = 1.26). Recent bulk polymerizations of PMMA completed in our lab, however, indicate that PMMA can also be synthesized by bulk methods, resulting in low polydispersities. More specifically, samples with approximate M_w of 3.0×10^4 and 5.0×10^4 have been created with polydispersities of 1.10 ($M_w = 3.2 \times 10^4$, $M_n = 2.9 \times 10^4$ and $M_w = 5.4 \times 10^4$, $M_n = 4.9 \times 10^4$, respectively).

Both bulk and solution methods were then attempted to produce triblock copolymers. The homopolymers obtained from the solution methods were used as the starting materials in all triblock reactions, as they have narrower molecular weight distributions. Figures 1 and 2 show that there is an increase in the molecular weight of both triblock copolymers (S-M-S and M-S-M) as a function of time, indicating that either monomer can cross-propagate onto the other. However, there exists considerable differences between the solution and bulk syntheses of the triblock copolymers. Both copolymers synthesized using the bulk method exhibit a substantial increase in molecular weight. However, the solution technique fails to give higher molecular weights for either triblock copolymer in the time scales examined in this study. Comparison of the kinetics of the bulk polymerization of the outer blocks in the S-M-S to the kinetics of M-S-M demonstrates that the addition of styrene to methyl methacrylate is slower than the addition of methyl methacrylate to styrene. This is consistent with the PS homopolymers requiring much longer reaction times than the PMMA polymers.

Figures 3 and 4 show the evolution of the polydispersity index for the styrene-centered triblocks and the methyl methacrylate-centered triblocks, respectively. The polydispersity of the PS homopolymers develops as expected for ATRP polymerizations, steadily decreasing with conversion to a limiting value. However, the polydispersity of the triblocks is quite different. Both bulk polymerizations show an increase in the polydispersity with conversion, while the solution polymerizations do not show much change from the polydispersity of the initial macroinitiators. This low polydispersity of the solution process is not very useful, however, as there is very little chain growth, and the propagation is therefore not efficient.

Possible reasons for the increase in the polydispersity of the triblock copolymers include slow and/or incom-

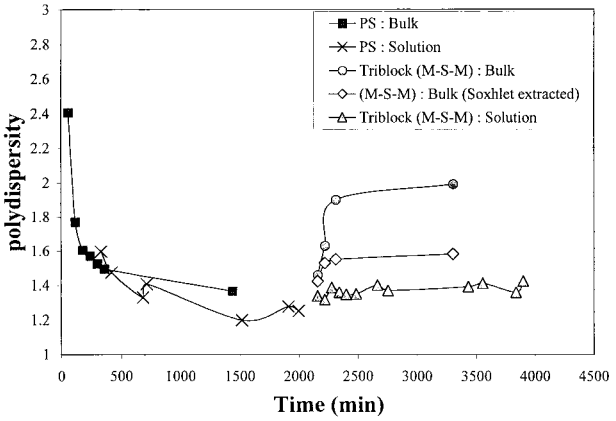

Figure 3. Polydispersity of the styrene-centered polymers as a function of reaction time.

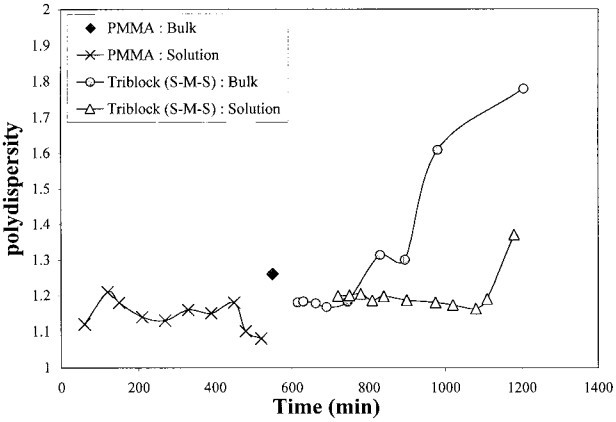

Figure 4. Polydispersity of the methyl methacrylate-centered polymers as a function of reaction time.

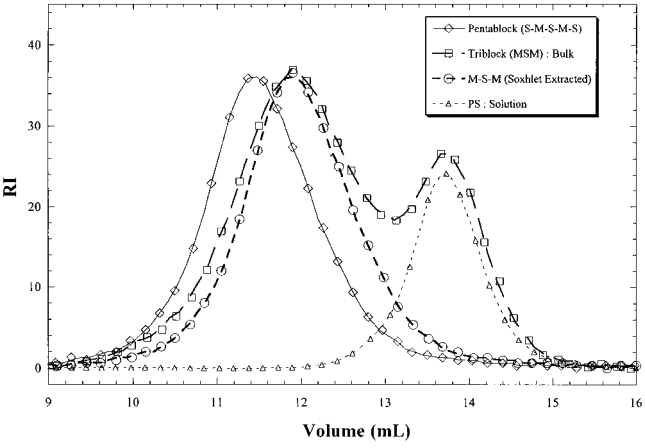

Figure 5. SEC curves of the polystyrene homopolymer, unpurified M-S-M triblock copolymer (73 mol % styrene), the M-S-M triblock after Soxhlet extraction (23 mol % styrene), and S-M-S-M-S pentablock copolymer (71 mol % styrene).

plete initiation of the monomer by the macroinitiator, the presence of chain transfer reactions, and heterogeneity in the reaction mixture. Figure 5 provides some insight, showing the SEC curves for the synthesized polystyrene homopolymers and polystyrene-centered copolymers. The bulk triblock (M-S-M) SEC curve is bimodal, and the position of the higher elution time peak is at the same position as the peak for the homopolymer starting material. This suggests that a primary reason for the increase in the polydispersity of the triblock with conversion is unreacted homopolymer. Matyjaszewski's group reported similar difficulties attempting to synthesize block copolymers of PMMA from a chloride end-capped polyacrylate macroinitiator via ATRP techniques.[25] They attributed the slow or incomplete initiation of the PMMA by the polyacrylate to the ineffectiveness of secondary halides at initiating methyl methacrylate.[25,34] The macroinitiator, chloride-capped styrene, used to prepare the M-S-M triblocks is a secondary halide, and therefore initiation of MMA may be slow compared to propagation, resulting in residual unreacted homopolymer. Matyjaszewski overcame this obstacle by utilizing a halide exchange system, which uses a Br initiator and CuBr catalyst to form the macroinitiator followed by block extension with CuCl as the catalyst.[25,34] The use of a halide exchange system in the preparation of M-S-M triblock to lower the polydispersity will be investigated in our lab in the future.

The presence of unreacted polystyrene was verified by Soxhlet extraction of the bulk-synthesized M-S-M triblock using cyclohexane as a solvent to remove the polystyrene homopolymer. The extraction recovered approximately 70% of the material, indicating that the dead chains are the minor component of the product. The SEC curve of the extracted M-S-M triblock is also shown in Figure 5 and exhibits one peak that occurs at a higher molecular weight than the starting homopolymer. The purified M-S-M triblock has an M_n of 8.69×10^4 and a polydispersity of 1.58. Comparison of this copolymer to the homopolymer and the unpurified M-S-M illustrates that the addition of the methyl methacrylate to the styrene end, while not perfect, is efficient enough to produce at least 70% conversion of the macroinitiator. Additionally, the low molecular weight tail of the SEC curves in Figure 5 shows that there is little M-S-M copolymer chains in the purified sample with the same molecular weight as the pure homopolymer.

The importance of the unreacted polystyrene on the kinetics of the polymerization of the M-S-M triblock is also shown in Figures 1 and 3. Figure 1 demonstrates that, f*or the chains that are growing*, there is significant chain growth within the first few hours and that the chains more than double in size. Figure 3 illustrates that there is only a moderate increase in the polydispersity of triblocks from the starting homopolymers.

Figure 6 shows the SEC curves of the poly(methyl methacrylate) and the poly(methyl methacrylate)-centered copolymers. The bulk triblock (S-M-S) does not exhibit a shoulder or bimodal distribution as was observed in the M-S-M triblock, suggesting that unreacted PMMA homopolymer is not present in this sample. To verify this, the S-M-S triblock was Soxhlet extracted with glacial acetic acid. There was no change in molecular weight or polydispersity after extraction, and thus, the PMMA macroinitiator efficiently initiates the styrene monomer.

Another possible source for the increase in the polydispersity of the triblock copolymers may occur during removal of the SEC samples during polymerization. During sample abstraction, the reaction vessel was opened to the atmosphere. Samples were removed under positive argon pressure to minimize oxygen contamination, yet oxygen may still enter. The presence of oxygen can lead to chain transfer or termination reactions, which will increase the polydispersity of the triblocks. The S-M-S bulk triblock which had nine SEC samples removed had a final polydispersity of 1.78, compared

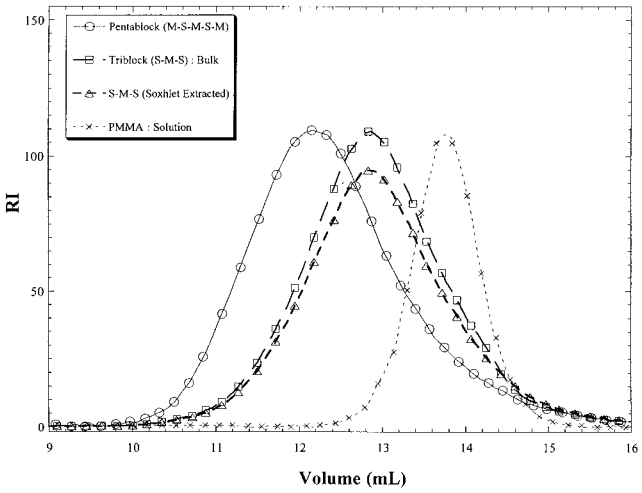

Figure 6. SEC curves of the poly(methyl methacrylate) homopolymer, unpurified S-M-S triblock copolymer (43 mol % MMA), S-M-S after Soxhlet extraction (43 mol % MMA), and M-S-M-S-M pentablock copolymer (56 mol % MMA).

to the M-S-M Soxhlet extracted triblock in which only four samples were taken and had a final polydispersity of 1.58. Triblock copolymers (both S-M-S and M-S-M) synthesized without sampling demonstrated lower polydispersities ranging from 1.4 to 1.5. For example, a S-M-S triblock synthesized without sampling had a final M_w equal to 11.5×10^4 and M_n equal to 7.7×10^4 (PDI = 1.5), and an MSM triblock was synthesized with a final M_w equal to 15.3×10^4 and M_n equal to 10.9×10^4 (PDI = 1.4).

While kinetic sampling contributes to the increase in polydispersity, it is certainly not the only important effect. In any radical chain polymerization, there is a finite probability that two radicals will come together and terminate the chain reaction by combination or disproportionation. While the ATRP mechanism minimizes the encounters between growing radicals by keeping their concentration low, combination and disproportionation will not be entirely eliminated, and thus there must exist some chains in the reaction mixture that are not active to further chain growth. This, in turn, increases the polydispersity of the final product.

Finally, to illustrate that the triblocks can be extended further, both styrene-centered and methyl methacrylate-centered pentablock copolymers were also prepared. Both pentablocks were synthesized by further addition of the opposite monomer to the corresponding triblock. Given that only the bulk methods exhibited sufficient growth of the outer blocks in the synthesis of the triblock copolymers, only bulk polymerization techniques were used to prepare pentablock copolymers. The triblock copolymers used as starting material for the pentablocks were used without Soxhlet extraction, and the styrene-centered pentablock (S-M-S-M-S) therefore still had unreacted PS homopolymer present. Kinetic data were not obtained for the synthesis of the pentablock copolymers. The final molecular weights of the pentablock copolymers are shown as the last points in Figures 1 and 2 and are greater than the molecular weight of the triblock copolymers, indicating that the formation of a pentablock copolymer was successful.

To determine the effect of the presence of the unreacted PS chains on the pentablock growth, residual homopolymer PS was removed by Soxhlet extraction with cyclohexane from the S-M-S-M-S pentablock. The

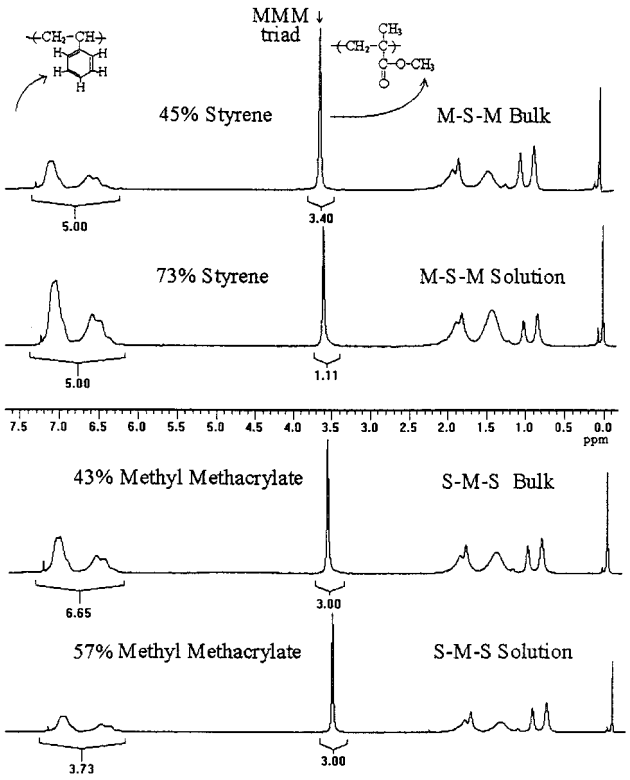

Figure 7. Proton NMR curves of the triblock copolymers. These curves are utilized to determine the composition of the copolymers, which are denoted in the figure.

extracted S-M-S-M-S pentablock produced a polymer with $M_n = 1.36 \times 10^5$ and a polydispersity of 1.62. Although the polydispersities of the unpurified triblock and pentablock copolymers were similar, the molecular weight of the pentablock was much higher after Soxhlet extraction, indicating that the styrene monomer adds to both the triblock and the unreacted homopolymer at similar rates.

Table 2 shows that the polydispersities of the pentablock copolymers are similar to those of the corresponding starting triblock (1.78 for S-M-S vs 1.80 for M-S-M-S-M and 1.99 for M-S-M vs 2.01 for S-M-S-M-S). One explanation for this may be that the limited miscibility of the homopolymer and the second monomer affects the cross-propagation reaction in the triblock synthesis. The triblock will be more miscible with the second monomer than the homopolymer, and thus this factor is eliminated in the creation of pentablock copolymer. This possibility will be examined in future studies.

Therefore, the results from the kinetics analysis of the synthesis of the triblock and pentablock copolymers demonstrate that ATRP techniques can be successfully utilized to synthesize multiblock copolymers of styrene and methyl methacrylate, though care must be taken to remove unreacted starting material on each successive step.

Structure

Copolymer Composition. The composition of the multiblock copolymers was determined by ^{1}H NMR spectroscopy[28] for both the unpurified and Soxhlet extracted samples. The ^{1}H NMR spectra of the unpurified M-S-M and S-M-S triblock for both bulk and solution polymerizations are given in Figure 7. Analysis of these spectra[29−32] shows that the bulk polymerized triblocks include substantial amounts of both mono-

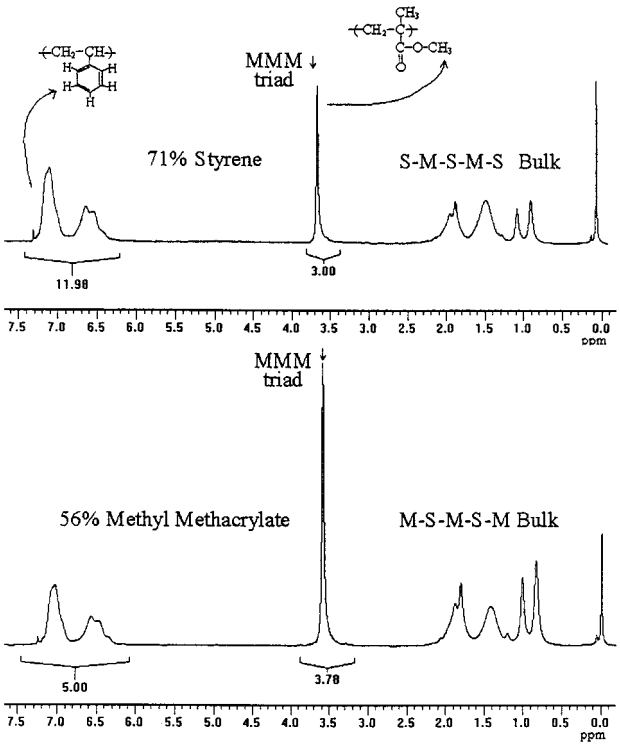

Figure 8. Proton NMR curves of the pentablock copolyemrs. These curves are utilized to determine the composition of the copolymers, which are denoted in the figure.

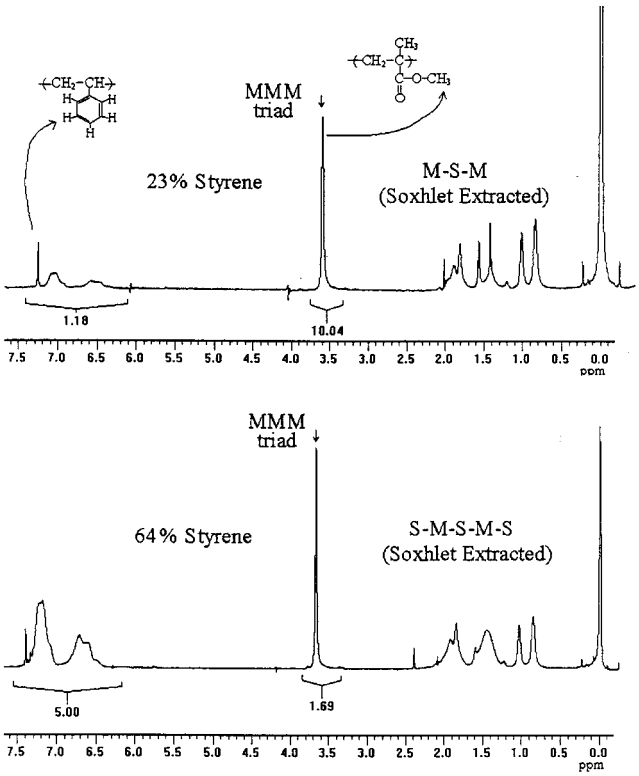

Figure 9. Proton NMR curves of the Soxhlet-extracted styrene-centered multiblock copolymers. These curves are utilized to determine the composition of the copolymrs, which are denoted in the figure.

mers. However, the spectra also show that the solution polymerizations failed to efficiently cross-propagate the other monomer, in agreement with the SEC data.

Quantitative composition analysis of the ^{1}H NMR spectra for the unpurified pentablock copolymers (Figure 8) also agree with the results obtained by SEC. For example, the percent of methyl methacrylate in the M-S-M-S-M copolymer increases to 56% from 43% in the S-M-S triblock. This corroborates the data from the SEC analysis, which shows that the molecular weight increases from 5.14×10^4 g/mol for the S-M-S triblock to 7.62×10^4 g/mol for the pentablock. Similar results are found for the S-M-S-M-S pentablock copolymer.

The ^{1}H NMR data for the Soxhlet-extracted styrene-centered copolymers, shown in Figure 9, confirms that the percent styrene present increases after Soxhlet extraction of the M-S-M triblock and the S-M-S-M-S pentablock copolymers. The Soxhlet-extracted bulk M-S-M triblock contains 23% styrene, while the unpurified triblock is 45%. Similarly, the purified pentablock is 64% styrene, compared to the unpurified pentablock, which contains 71% styrene.

Copolymer Sequence Distribution. NMR spectroscopy is also used to determine the sequence distribution of the copolymers to ensure that there exists no chain transfer or other scrambling reactions to randomize the monomer sequence distribution. The order of monomers throughout the copolymer structure is determined by the presence of peaks in the NMR spectra that correspond to distinct monomer triad arrangements.[33] For example, the presence of MMM, MMS, and SMS triads can be examined through the presence of unique peaks attributed to the methoxy (OCH_3) protons in a ^{1}H NMR spectra, as described by San Roman et al.[32] and Aerdts et al.[31]

The proton NMR spectra of the unpurified triblock and pentablock copolymers (Figures 7 and 8, respectively) both exhibit a sharp peak at 3.6 ppm, which corresponds to the methoxy proton in an MMM triad.[29,31,32] The proton NMR spectra for the Soxhlet-extracted styrene-centered triblock and pentablock copolymers (Figure 9) also display this sharp methoxy proton peak at 3.6 ppm. Therefore, the methyl methacrylate monomers are in long consecutive runs of methyl methacrylate in the synthesized copolymers. ^{13}C NMR spectroscopy can also be used to determine the structure of methyl methacrylate centered triads by examination of the carbonyl resonance at 175−179 ppm.[29,30] The results from this analysis agree with those presented from the ^{1}H NMR investigation.

Examination of the styrene-centered triads by ^{13}C NMR also confirms the lack of randomization. The presence of each styrene-centered triad is determined by analysis of the C_1 region of styrene (142−148 ppm) in the ^{13}C NMR spectra.[29,30] The SSS triad exhibits three main peaks present at approximately 145.4, 145.8, and 146.2 ppm due to different tacticities, as exemplified by the spectra of the polystyrene homopolymer. Other peaks present in copolymers are assigned to MSM or SSM triads by correlating their presence in the spectra of alternating and random copolymers. Utilizing this correlation between ^{13}C peaks and triad presence, the ^{13}C NMR spectra of the unpurified bulk polymerized triblock copolymers reveal the presence of primarily SSS triads. Similarly, the spectra for the purified styrene-centered multiblock copolymers given in Figure 10 also indicate primarily the SSS triad. This confirms the results of the analysis of the methyl methacrylate-centered triads, indicating no randomization of the copolymers as prepared by ATRP methods. Examination of the methyl methacrylate-centered pentablock reveals

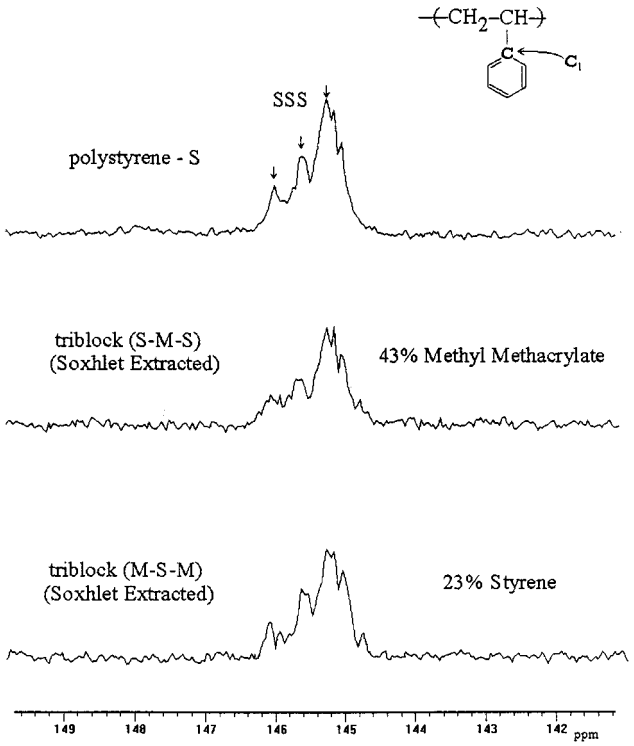

Figure 10. ^{13}C NMR curves of Soxhlet-extracted triblocks. These curves verify the prevalence of SSS triads in the synthesized triblock copolymers. Copolymer compositions are denoted in the figure.

similar spectra, verifying that further chain growth retains the blocky nature of the copolymer.

It can be argued that a blend of two homopolymers would also provide the behavior described in the NMR results presented above. To investigate this possibility, thin films of the copolymers were made by melt pressing and found to be transparent. As a blend of PS and PMMA would be immiscible and thus opaque, this result further supports the conclusion that blocky copolymers are the results of this synthetic procedure.

Discussion

The goal of this project is to find a synthetic method by which multiblock copolymers of styrene and methyl methacrylate can be synthesized. It must be emphasized that we are not trying to create narrow molecular weight, well-defined triblock and pentablock copolymers that can microphase separate. While this would be a valuable result, the ATRP techniques that we have utilized are not sufficiently selective to be useful in this endeavor. We are, more broadly, interested in developing a synthetic routine whereby copolymers of styrene and methyl methacrylate that are very blocky in nature can be created. The results presented above indicate that we have been successful: SEC results demonstrate that chain growth does occur regardless of cross-propagation direction, while optical and NMR results show that the resultant copolymers are very blocky in nature.

The procedure is not perfect, however. Purification and SEC results show that for some of the copolymer growth reactions there exist a significant amount of dead chains that do not grow, as would be expected with most radical chain reactions. These dead chains contribute to an increase in the polydispersity of the resultant copolymer. However, it was also shown that Soxhlet extraction is very efficient at removing these chains. The final purified copolymer exhibits the characteristics of the desired multiblock copolymer, with molecular weight polydispersity indices around 1.5. Fortunately, for the application that is of most interest to us, interfacial modification, this lack of monodispersity is advantageous as it will minimize the propensity of the copolymer to microphase separate.

Conclusions

This article presents a technique by which multiblock copolymers of styrene and methyl methacrylate can be synthesized using atom transfer radical polymerization methods. The syntheses of triblock copolymers of poly(styrene-*b*-methyl methacrylate-*b*-styrene) (S-M-S) and poly(methyl methacrylate-*b*-styrene-*b*-methyl methacrylate) (M-S-M) were shown to be successful. In addition, these triblock copolymers were extended further to produce poly(methyl methacrylate-*b*-styrene-*b*-methyl methacrylate-*b*-styrene-*b*-methyl methacrylate) (M-S-M-S-M) and poly(styrene-*b*-methyl methacrylate-*b*-styrene-*b*-methyl methacrylate-*b*-styrene) (S-M-S-M-S) pentablock copolymers. This technique is, to our knowledge, the first where styrene and methyl methacrylate will cross-propagate in block copolymer synthesis regardless of monomer sequence. Thus, this method provides a mechanism by which the sequence distribution of styrene and methyl methacrylate copolymers can be carefully regulated by controlling the number and length of each block.

Specifically, the ATRP technique described is successful in preparing multiblock copolymers with these two monomers by bulk polymerization techniques. There is an increase in the polydispersity of the sample during the synthesis of the triblock, and further experiments are underway to understand and limit this problem. However, Soxhlet extraction of the multiblock copolymer is successful at improving the polydispersity by removing unreacted homopolymer.

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