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Synthesis of Block Copolymers of Styrene and Methyl Methacrylate by Conventional Free Radical Polymerization in Room Temperature Ionic Liquids

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Introduction. Well-defined block copolymers from conventional free radical polymerizations evince great interest because of the robust, economical processes and wide selections of monomers.¹ There exist several reports of block copolymer preparation through macro-radical approaches.^{2–5} These include the syntheses of polystyrene-*b*-poly(ethylene oxide) (PS-*b*-PEO),² polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA),^{3,4} and poly(acrylonitrile)-*b*-poly(ethylene glycol)-*b*-poly(acrylonitrile) (PAN-*b*-PEG-*b*-PAN).⁵ All these processes require post-polymerization reactions to activate the “protected” radical initiator. Seymour et al. reported high levels of block copolymer formation when macro-radicals were produced in viscous poor solvents, e.g., silicone oils.^{6–8} More recently, Hadjichristidis et al. prepared block terpolymers of *N*-methyl methacrylamide (NMeMA) with styrene and isoprene (PNMeMA-*b*-PS-*b*-PI and PNMeMA-*b*-PI-*b*-PS) by heterogeneous radical polymerization in benzene.⁹ They took advantage of the poor solubility of PNMeMA in benzene, where precipitation of growing polymer chains prolongs the lifetime of the radical propagation centers. However, Gilbert and co-workers have argued against the trapped radical mechanism, suggesting that residual primary radicals could result in a mixture of graft and statistical copolymers being formed.¹⁰

Free radical polymerizations are typically done in volatile organic solvents, which have been blamed for the increasing air pollution. Room-temperature ionic liquids (RTILs) have emerged as potential replacements for volatile organic solvents, and over the past several years the number of studies on RTILs as reaction media has increased markedly.¹¹ The use of RTILs as polymerization solvents has also started to be explored. Carlin and co-workers¹² found the combination of TiCl₄ and AlEtCl₂ in AlCl₃–ImCl to be catalytically active for ethylene polymerization in an AlCl₃–1-ethyl-3-methylimidazolium chloride (ImCl) melt. Using Cp₂TiCl₂ instead of TiCl₄, higher yields of polyethylene were achieved.¹³ Those authors also produced a new electroactive material by electrochemical oxidation of triphenylsilyl chloride (Ph₃SiCl) in the acidic ionic liquid (AlCl₃–ImCl).¹⁴ Polymerization of benzene electrochemically in ionic liquids to prepare poly(*p*-phenylene) has also been reported.^{15–19} In all these studies, ionic liquids were used mainly as convenient electrolytes. However, one of the major drawbacks of chloroaluminate(III)

based ionic liquids is that they are water-sensitive. Quite recently, Haddleton et al.²⁰ used 1-butyl-3-methylimidazolium hexafluorophosphate ([C₄mim]PF₆), an air and water-stable RTIL, as solvent for the copper(I) *N*-propyl-2-pyridylmethanimine mediated “living” radical polymerization of methyl methacrylate (MMA). They found that the rate of polymerization was enhanced in comparison to other polar/coordinating solvents. Moreover, the polymerization product was made copper free by a simple solvent wash, which avoids the contamination of the polymer product by the catalyst. Other atom transfer radical polymerizations in RTILs have recently been reported.^{21,22}

In this paper, we report the synthesis of PS-*b*-PMMA via conventional free radical polymerization using benzoyl peroxide (BPO) and sequential monomer addition in [C₄mim]PF₆. The polymerizations were monitored by size exclusion chromatography (SEC). The raw products of the copolymerization were freed of homopolymer by extraction using selective solvents for PS and PMMA. The purified block copolymers were characterized by NMR spectroscopy, differential scanning calorimetry (DSC) and fractional precipitation.

Experimental Section. Materials. Styrene (Aldrich, 99%), MMA (Aldrich, 99%) were distilled to remove inhibitors and stored in calibrated ampules. [C₄mim]PF₆ (provided by Sachem Inc. or made at the University of Alabama) was washed with pure water five times. Toluene (Fisher, ≥99.5%) and methanol (Fisher, ≥99.8%) were used as received. BPO (Aldrich, 97%) was recrystallized from methanol and dried under vacuum.

Instrumentation. SEC was used to measure molecular weights and molecular weight distributions, M_w/M_n , with respect to polystyrene (PS) standards (Pressure Chemical Co.). The SEC experiments were carried out at 30 °C in THF using a Waters 510 pump and a Waters 410 differential refractometer as detector (flow rate: 1 mL/min, columns: Polymer Standards Service; one 100 Å and one 5 μm linear column in series).

¹H NMR spectra of the polymers were obtained on a Bruker ARX-400 spectrometer at room temperature. Sample concentrations were about 10–25% (w/v) in CDCl₃. TMS (0 ppm) was used as an internal reference. DSC (Mettler-Toledo model: DSC 30) was used to determine the glass transition temperatures (*T*_g) at a heating rate of 10 °C/min. Fractional precipitations were done using toluene as solvent and methanol as nonsolvent according to the literature.⁴

Polymerization. All polymerizations were done under high vacuum (<10^{–6} mmHg) to ensure that the systems were oxygen free. After charging the desired amounts of initiator (BPO) and solvent ([C₄mim]PF₆) into a round-bottom flask with a constriction, the system was degassed by pumping on the vacuum line for 2 h and a predetermined quantity of monomer (styrene, MMA) was then distilled into the reactor. The flask was removed from the vacuum line by heat-sealing at the constriction and placed in a preheated water bath at 70 °C. The polymerization was allowed to continue for about 4 h. After taking about 5 mL of solution for sampling, the unreacted monomer was pumped away on the vacuum line at room temperature. A predetermined quantity of the second monomer (MMA) was then distilled into the system, and the reaction was kept at

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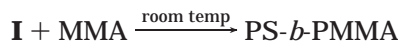
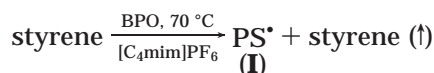
Table 1. Characteristics of Preparation of PS-*b*-PMMA from BPO at 70 °C in [C₄mim]PF₆

polymer	PS block		block copolymer		composition (St mol %) ^b		yield ^d (%)
	$M_w^a \times 10^{-3}$	M_w/M_n^a	$M_w^a \times 10^{-3}$	M_w/M_n^a	found	expected	
S3M1	38.9	3.67	211.3	2.52	59.9	73.4	51.1
S1M1	55.7	2.52	808.9	2.38	38.4	48.3	50.3
S1M3	43.4	2.67	677.1	2.49	11.4 ^c	23.4	47.4

^a From SEC (calibrated with PS standards). ^b Composition of extracted block copolymers, obtained from ¹H NMR. ^c From SEC with dual detectors (RI, UV). ^d Obtained from the total monomers (styrene and MMA) feeding and the extracted block copolymers.

room temperature for 4 to 6 days. The polymers were isolated by washing with methanol ([C₄mim]PF₆ is soluble in methanol) and drying under vacuum.

Results and Discussion. The basic approach to preparing PS-*b*-PMMA is as follows:



Styrene was polymerized first in [C₄mim]PF₆ at 70 °C with BPO as the initiator for about 4 h. The polymerization was cooled to room temperature and unreacted monomer (styrene) was pumped away under high vacuum (<10⁻⁶ mmHg). A small aliquot (~5 mL) was taken to characterize the PS block. When the elimination of the styrene was completed, as indicated by the recovery of the initial vacuum, the desired amount of purified MMA (the second monomer) was then introduced by distillation through the vacuum line. The reactor was sealed off and kept at room temperature for 4 days. The use of a longer reaction time and lower temperature was chosen to minimize the effect of residual BPO, whose existence cannot be overlooked after 4 h at 70 °C, on the products. Even though radical generation by thermal decomposition of residual BPO would be expected to be negligible (see below), it is still possible for polymeric radicals to transfer to initiator, which in turn would yield homopolymer of the second monomer. The polymerization of MMA was diffusion-controlled and very fast.^{23,24} The crude block copolymer was then extracted with cyclohexane to remove PS and with acetonitrile to remove PMMA homopolymers, and the results are summarized in Table 1.

The success of this approach depends on the poor solubility of PS in [C₄mim]PF₆. The precipitation of PS from the medium hinders diffusion of the propagating radical centers, which must find one another to terminate, and thus increases their lifetimes.^{9,25} When a second monomer that is miscible with the polymer dispersion is added, it diffuses to radical sites, polymerization continues, and block copolymer is formed. The appropriate choice of temperatures and reaction times during polymerization of the two blocks is very important. Typically one should utilize higher temperatures and shorter times for polymerization of the first block relative to the second block. The higher temperature during formation of the first block promotes relatively rapid radical formation with initiators like BPO. The use of a much lower temperature during polymerization of the second monomer minimizes generation of new free radicals that would lead to homopolymer contaminants derived from homopolymeri-

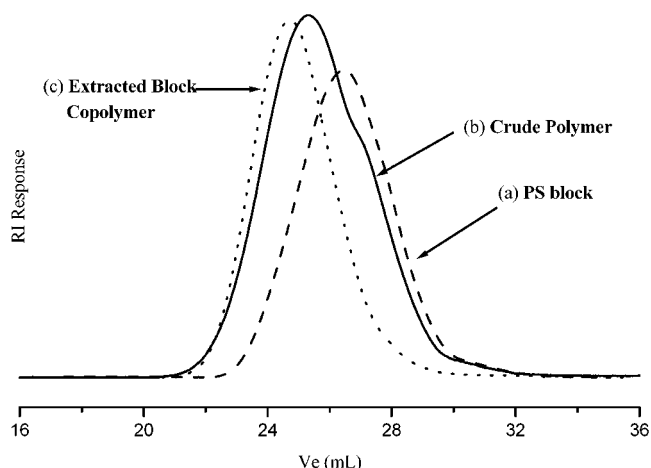


Figure 1. SEC traces of (a) PS block from BPO in [C₄mim]PF₆, (b) PS-*b*-PMMA before extraction, and (c) PS-*b*-PMMA (S3M1 in Table 1) after extracting with cyclohexane and acetonitrile.

zation of the second monomer by newly created radicals. Although Gilbert and co-workers' controlled experiments raised doubts about the trapped macroradical mechanism,¹⁰ our results indicate, as will be discussed in the next section, that PS-*b*-PMMA is the major product. However, we cannot exclude the possibility of formation of PS with grafted PMMA side chains (PS-*g*-PMMA) via a chain transfer to polymer mechanism. The attempts to make PMMA-*b*-PS copolymers under the same condition were less successful because PMMA has better solubility in [C₄mim]PF₆.²⁶

Figure 1 shows the SEC traces for the block copolymerization of styrene and MMA (styrene was polymerized first). Although there is unavoidably PS homopolymer present in the un-extracted ("raw") block copolymers, the product is mostly block copolymer. It should be noted that the actual amount of PS homopolymer by mass (SEC is a mass detector, i.e., the RI response is proportional to molecular weight) is exaggerated in Figure 1 because the $d n/d c$ value for PS in THF ($d n/d c_{\text{PS}} = 0.189$) is higher than that for PMMA ($d n/d c_{\text{PMMA}} = 0.089$).²⁷ Cyclohexane (solvent for PS and nonsolvent for PMMA) was used to remove PS homopolymer and the results are summarized in Table 1. Attempts to extract the block copolymers using acetonitrile (solvent for PMMA and nonsolvent for PS) failed to recover any polymer, which indicates that there is negligible PMMA homopolymer present. This is not surprising since the rate of decomposition of any residual BPO to generate free radicals is essentially zero at room temperature. The half-life of BPO ($t_{1/2}$) at 25 °C is more than 45 000 h as calculated from the Arrhenius equation ($K_d = A \exp(-E_a/RT)$) and the initiation rate equation ($t_{1/2} = \ln 2/K_d$), with $E_a = 139.0 \text{ kJ mol}^{-1}$, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, and $A = 9.34 \times 10^{15} \text{ s}^{-1}$.²⁸ When the feed ratio of styrene to MMA is 1:3 (S1 M3 in Table 1), a small low molecular weight peak ($M_n \sim 4 \text{ kg/mol}$) appeared in the SEC traces of raw copolymer and the cyclohexanes-extracted product. This peak is not present after extraction with acetonitrile, which indicates that it is PMMA homopolymer from thermoinduced polymerization or induced decomposition of BPO. The monomodal nature of the SEC trace of extracted crude polymer indicates, to a certain extent, the homogeneity of the final block copolymers. The polymers were further characterized by using DSC and fractional precipitation.

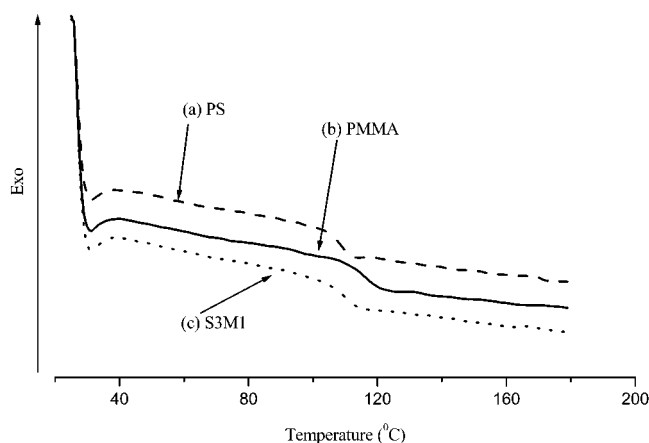


Figure 2. DSC traces of (A) PS from BPO in $[C_4mim]PF_6$, (b) PMMA from BPO in $[C_4mim]PF_6$, and (c) PS-*b*-PMMA after extracting with cyclohexane and acetonitrile.

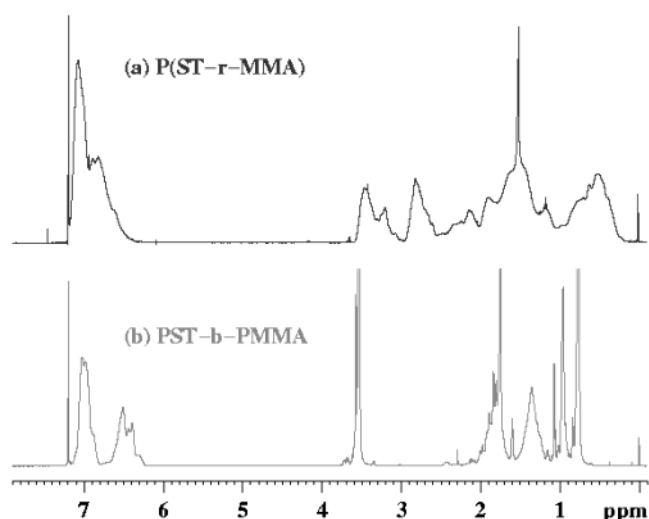


Figure 3. 1H NMR spectra of (a) P(ST-*r*-MMA) and (b) PST-*b*-PMMA made from BPO in $[C_4mim]PF_6$.

Figure 2 shows the DSC traces for a PS-*b*-PMMA along with PS and PMMA homopolymers (all the three polymers have similar molecular weights). It is expected that there should be two distinct glass transitions (T_g) corresponding to PS and PMMA blocks, whereas a random copolymer should exhibit a single intermediate T_g . Unfortunately, the T_g s for PS and PMMA blocks are too close to be separated. 1H NMR spectra, as shown in Figure 3, clearly demonstrate that the polymers are not of a random nature since resonances that would indicate a styrene unit next to a methyl methacrylate unit are not detected. Fractional precipitation was used to further verify the formation of the block copolymers, since it provides definite evidence for the formation of block copolymers.⁴ Figure 4 shows the fractional precipitation curves, obtained using the toluene/methanol system, for S1M1 (polymer 2 in Table 1) and PMMA and PS homopolymers. Even though toluene is a good solvent and methanol is a nonsolvent for both PS and PMMA, their different solubility parameters result in different precipitation behavior as indicated in the positions of the precipitation curves. It is very important to notice that many factors, such as molecular weight, molecular weight distributions, microstructures, and temperature, control the precipitation behavior of a polymer.²⁹ Nevertheless, Figure 4 clearly shows that the

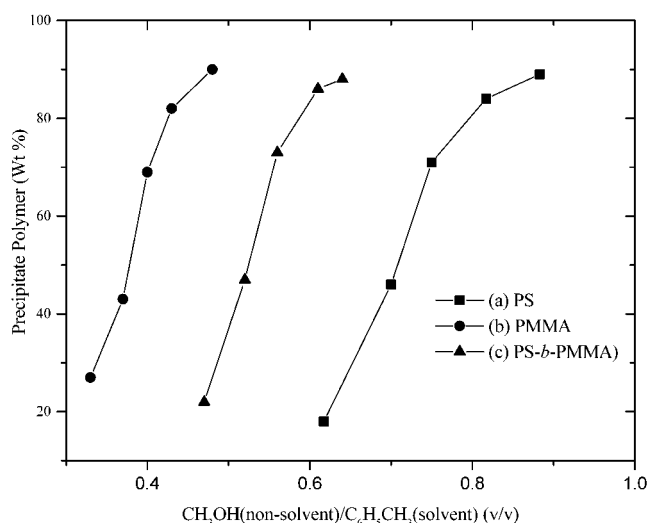


Figure 4. Fractional precipitations of (a) PS, (b) PMMA, and (c) PS-*b*-PMMA (S1M1 in Table 1). Solvent: toluene. Nonsolvent: methanol.

precipitation curve for the extracted polymer is located between those of PS and PMMA, which further demonstrates the successful synthesis of block styrene and MMA copolymers. As mentioned early, it also is possible to produce PS-*g*-PMMA during this process. The final product could be PS-*b*-PMMA or PS-*g*-PMMA or their mixtures. Unfortunately, the characterization methods used above could not distinguish between PS-*b*-PMMA and PS-*g*-PMMA. A detailed study of these polymers using SEC equipped with a multiangle laser light scattering detector (SEC-MALLS), which will shed light on the architecture of the products, is in progress, and the results will be reported separately.

Conclusions. Block copolymers of styrene and MMA have been made by sequential addition of the monomers in the room-temperature ionic liquid $[C_4mim]PF_6$ using BPO as the initiator. The polymers could be easily separated from the reaction medium gravimetrically, followed by washing with methanol, because of their poor solubility in $[C_4mim]PF_6$. The polymerization products were characterized by SEC, NMR, and DSC. Fractional precipitation experiments provide definite evidence of the formation of PS-*b*-PMMA block copolymers.

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