

RAPID COMMUNICATION

Synthesis and Characterization of Block-Graft Copolymers Composed of Poly(styrene-*b*-ethylene-*co*-propylene) and Poly(ethyl methacrylate) by Atom Transfer Radical Polymerization

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INTRODUCTION

Block or graft copolymers with different macromolecular architectures are of great interests in both exploring theories of phase separation and morphologies and developing new polymeric materials based on the microphase structures. Since the early 90s "controlled/living" radical polymerization has attracted considerable attention, and rapidly developed due to its simplicity in practice and the controllability of the molecular parameters of the products.¹⁻⁸ Particularly, the studies of atom transfer radical polymerization (ATRP) have flourished since Wang et al.⁶ reported the living polymerization of styrene using a simple alkyl halide as an initiator and a transfer metal species complexed by suitable ligands as a catalyst. ATRP system is able to provide well-defined polymers with low polydispersity, and the degrees of polymerization can be simply predetermined by the ratio of the amount of monomer to that of the introduced initiator. Due to its versatility of monomers and controllability, ATRP has been successfully used to prepare homopolymers, block-graft copolymers, and highly branched polymers.⁹⁻¹¹ Quietly recently, Paik et al.¹² reported preparation of grafted polyvinyl chloride (PVC) with styrene and methacrylate via ATRP using modified PVC containing a small amount of vinyl chloroacetate units as a macroinitiator.

The scope of the present communication is to extend ATRP to a more complex architecture, i.e., block-graft copolymers,¹³ which containing an AB block backbone and C graft attached to B segments. Here, a commercial diblock product of poly(styrene-*b*-ethylene-*co*-propylene) (SEP) was used as the starting material. First, chloromethyl groups were introduced into the polystyrene (PS) block of SEP. The product (C1SEP) was then used as a macroinitiator to initiate "graft-form" copolymerization of ethyl methacrylate in the presence of CuCl and 2,2'-dipyridine (bpy). The copolymer products (SEPG) were characterized by FTIR, ¹H-NMR, SEC, and DSC. It was found that the polymerization follows the ATRP mechanism.

EXPERIMENTAL

Materials

Monodisperse SEP (Kraton147, Shell Co.) with $M_w = 130,000$, $M_w/M_n = 1.09$, and 29.0 wt % styrene units was used as the starting material. Ethyl methacrylate (EMA) was vacuum distilled over CaH₂ just before use. Bpy was recrystallized from acetone, and CuCl was purified by successively washing with acetic acid, ethanol, and ethyl ether followed by drying under vacuum at 60°C. SnCl₄, trioxane, and chlorotrimethylsilane were purified with routine methods.

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Table I. ATRP of EMA Initiated by C1SEP/CuCl/bpy

No.	Reaction Time (min)	$\ln[M]_0/[M]$	$M_n \times 10^{-5}$ (SEC)	$M_n \times 10^{-5}$ (theo)	M_w/M_n	${}^a W_{\text{EMA}}/W_{\text{SEP}}$
SEPG.1	40	0.09	2.94	2.96	1.14	0.77
SEPG.2	80	0.28	4.37	4.92	1.15	2.28
SEPG.3	130	0.56	5.34	7.06	1.23	3.93
SEPG.4	180	0.80	6.56	8.50	1.19	5.03
SEPG.5	240	1.04	7.32	9.68	1.22	5.95

^a Weight ratio of PEMA to that of C1SEP.

Chloromethylation

To avoid crosslinking and degradation of SEP in the processes of chloromethylation and graft copolymerization, saturation of the residue double bonds in the EP block was performed via successive brominating and hydrogenolysis according to the procedures reported previously.¹⁴ The chloromethylation procedure used was as follows.¹⁵ Typically, trioxane (0.9 g, 10 mmol) and chlorotrimethylsilane (3.8 mL, 30 mmol) were dissolved in chloroform (90 mL). The saturated SEP (1.5 g) was added to the above solution, and then 0.3 mL (2.58 mmol) of SnCl₄ was added after the reaction mixture was cooled to 0°C. The mixture was stirred at 0°C for 30 min and then for another 4 h at room temperature. The reaction was quenched by adding the 50/50 (v/v) methanol/water to the reaction mixture. The product was purified by repeat reprecipitation in THF/water, then was dried under vacuum.

Copolymerization

Typically, bulk copolymerization was carried out as follows: to a Schlenk flask 0.25 g of C1SEP with —CH₂Cl content of 6.4 mol % based on styrene units, 4.5 mg (0.045 mmol) of CuCl and 21.0 mg (0.14 mmol) of bpy were added, followed by adding 2.0 mL (0.016 mol) of EMA using a syringe. After completely dissolving by stirring for 30 min and degassing by three freeze-pump-thaw cycles, the flask was sealed under nitrogen. Then the flask was heated at 110°C in an oil bath. After a desired time, the reaction vessel was quenched in liquid nitrogen. The reaction mixture was then dissolved in about 20 mL of THF and followed by precipitation in 50/50 (v/v) methanol/water mixture containing a small amount of glacial acetic acid. Finally, the product SEPG was extracted in CH₃CN for 24 h, filtered, and dried under vacuum at 60°C to a constant weight. The kinetic and characterization data are shown in Table I.

Characterization

Proton nuclear magnetic resonance (¹H-NMR) spectra were measured on a Bruker MSL300 NMR spectrome-

ter using CDCl₃ as a solvent. FTIR spectra of thin polymer films on potassium bromide plates were obtained using a Perkin-Elmer 983G spectrophotometer. Size-exclusion chromatography (SEC) was performed using a Waters 510 pump, an ERMA ERC-7512 refractive index detector, and a set of polymer Standards Service columns with THF as the solvent at a 1.0-mL/min flow rate. Monodisperse polystyrene were used as standard samples for calibration. Glass transition temperatures were obtained at a heating rate 10°C/min and under dry nitrogen atmosphere, using a SHIMADZU DSC-50 differential scanning calorimeter (DSC).

RESULTS AND DISCUSSION

The structure of C1SEP was studied by FTIR and ¹H-NMR spectra. The FTIR spectrum of C1SEP in Figure 1 exhibits the characteristic bands of C—Cl stretch ($\nu = 1265 \text{ cm}^{-1}$), and the ¹H-NMR spectrum shown in Figure 2 displays the absorption at $\delta = 4.49 \text{ ppm}$, corresponding to the protons in —CH₂Cl. The extent of chloromethylation was determined from the ratio of the peak area of —CH₂Cl to that of the benzene ring from the ¹H-NMR spectra.

The formation of the block-graft copolymer SEPG was found by FTIR and ¹H-NMR spectra. As shown in Figure 1 for SEPG-3(b), besides the bands associated

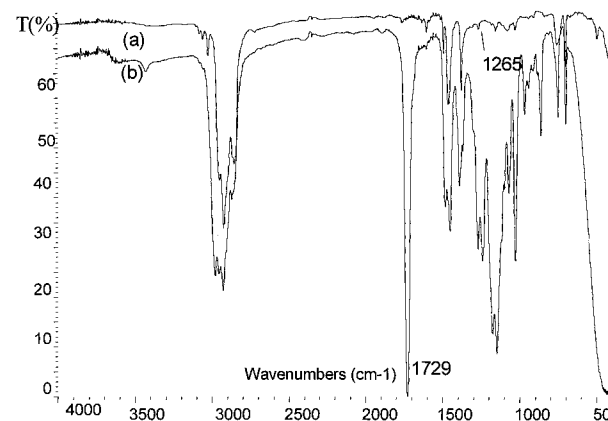


Figure 1. FTIR spectrum of (a) C1SEP (6.4 mol %), and (b) SEPG-1.

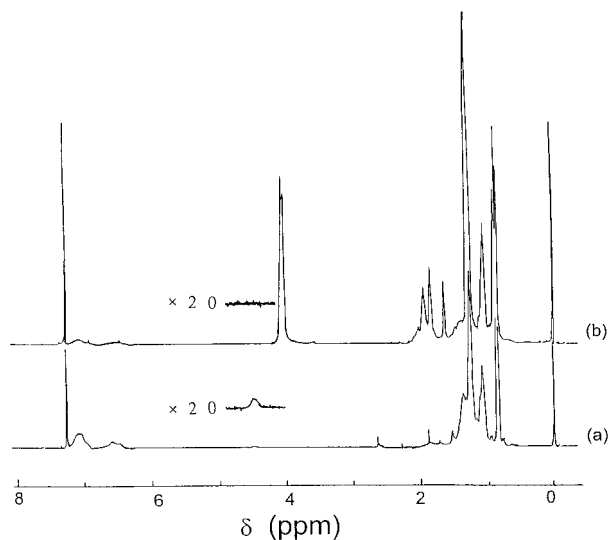


Figure 2. $^1\text{H-NMR}$ spectrum of (a) C1SEP (6.4 mol %), and (b) SEPG-3.

with both EP and PS blocks, a strong carbonyl peak was observed at $\nu = 1729\text{ cm}^{-1}$ corresponding to the carbonyl stretching of ethyl methylacrylate. In the $^1\text{H-NMR}$ spectrum (Fig. 2), a new peak $\delta = 4.0\text{ ppm}$, which comes from the methene (OCH_2) of the ether ester in EMA, also shows the existence of the grafts. The peak at 6.2–7.3 ppm is due to the absorbance of the benzene ring from the PS block in SEP and the peak at about 1.6 ppm to the resonance of the methyl group from the backbone of PEMA graft chains. These also corroborate the chemical structure of SEPG. At the same time, the complete disappearance of the resonance at $\delta = 4.49\text{ ppm}$ indicates that all the chloromethyl groups have participated in the grafting initiation of EMA. In addition, in a subsidiary experiment of polymerization of EMA, under the same conditions as above but without the macroinitiator, no detectable amount of PEMA homopolymer was produced after 6 h. Combining this fact and the narrow molecular weight distribution of the SEPG products, which is discussed below, it is clear that under the copolymerization conditions, almost no EMA homopolymer formed.

Figure 3 shows the DSC traces of C1SEP and SEPG. C1SEP presents two T_g 's, the low (-46°C) and high (103°C) ones are associated with the rubber EP block and glass PS block, respectively. Compared to C1SEP, the block-graft copolymer shows about the same T_g for the EP blocks. However, in SEPG, a new glass transition at 78°C emerges, which can no doubt be assigned to poly(ethyl methylacrylate) grafts. In addition, T_g associated with PS blocks in SEPG was found to shift to a higher temperature (123°C), which may be attributed to the multibranches attached to the PS blocks restricting mobility of the PS blocks.

Figure 4 presents the kinetics of the bulk graft polymerization of EMA at 110°C initiated by the macroinitiator in the presence of CuCl and bpy. The straight

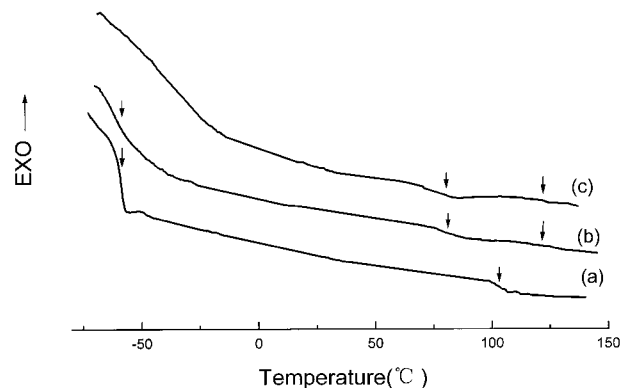


Figure 3. DSC curves of (a) C1SEP, (b) SEPG-1, and (c) SEPG-3.

semilogarithmic plot of $\ln([M]_0/[M])$, where $[M]_0$ is the initial monomer concentration and $[M]$ is that at time t , against time indicated that the concentration of the growing radicals is constant. A remarkable result that could be seen from the data in Table I is that the copolymerization of C1SEP with EMA only slightly alters the monodispersity of the starting block copolymer SEP. All the SEPG samples possess a low polydispersity index ranging 1.14–1.23. This serves as a clear indication of the controlled nature of the propagation radicals in the copolymerization. Moreover, the apparent molecular weight of SEPG measured by SEC increases with monomer conversion (Fig. 5).

The theoretical molecular weights, listed in Table I were calculated from eq. (1), where $\Delta[M]$, $[I]$, $(MW)_0$ represent the amounts of the consumed monomer EMA, the amount of macroinitiator C1SEP, and the molecular weight of C1SEP, respectively.

$$M_{n,\text{th}} = (\Delta[M]/[I]) + (MW)_0 \quad (1)$$

Figure 6 compares the theoretical and experimental molecular weights of the SEPG samples. It is clear that

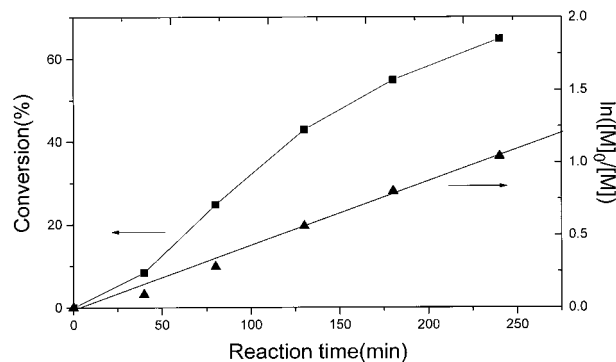


Figure 4. Conversion and $\ln([M]_0/[M])$ as functions of polymerization time at 110°C with $[-\text{CH}_2\text{Cl}] : [\text{CuCl}] : [\text{bpy}] = 1 : 1 : 3$.

they are close to each other when the conversion is very low. However, as the conversion increases, the deviation of the experimental value from the corresponding theoretical one becomes more substantial. This result is understandable because the experimental molecular weights were obtained by SEC using linear polystyrene as standard. It is well known that polymers with graft-like architecture always show a smaller hydrodynamic volume than the corresponding linear polymers, leading to a smaller apparent molecular weight.

The $W_{\text{EMA}}/W_{\text{SEP}}$ data in Table I show that the block-graft copolymers covering a very broad composition range, i.e., PEMA grafts being from a minor to a major component, were obtained just by changing the reaction time. Because microphase separation of a block or graft copolymer mainly depends on the composition, the flexibility of composition control in the present case may benefit our future morphology studies of the block-graft copolymer.

In addition, quite recently we found that this procedure can be used for the copolymerization of C1SEP with *t*-butyl acrylate as well. Further hydrolysis of the block-graft copolymer with poly(*t*-butyl acrylate) grafts is expected to produce amphiphiles having a hydrophobic SEP main chain and hydrophilic poly(acrylic acid) grafts, of which both number and length are controllable.

CONCLUSIONS

The well-defined block-graft copolymers with a narrow molecular distribution composed of poly(styrene-*b*-ethylene-*co*-propylene) (SEP) as a backbone and poly(ethyl methacrylate) as branches attached to PS blocks of SEP were prepared by atom transfer radical polymerization. The reaction was initiated by the macroinitiator SEP with a chloromethyl substituent, which was obtained by chemical modification of the commercial product SEP.

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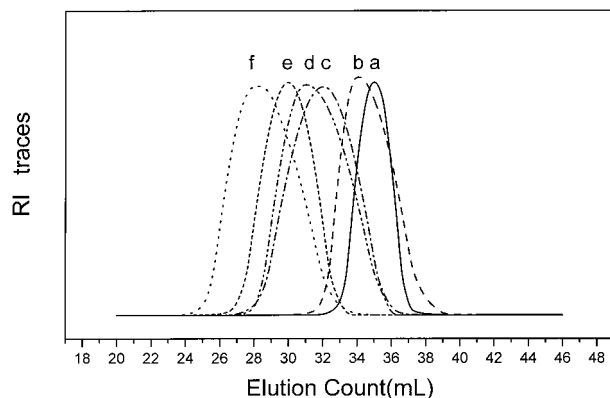


Figure 5. SEC traces of the bulk polymerization products obtained at different reaction time (a, b, c, d, e, f stand for C1SEP and SEPG-1, 2, 3, 4, 5, respectively).

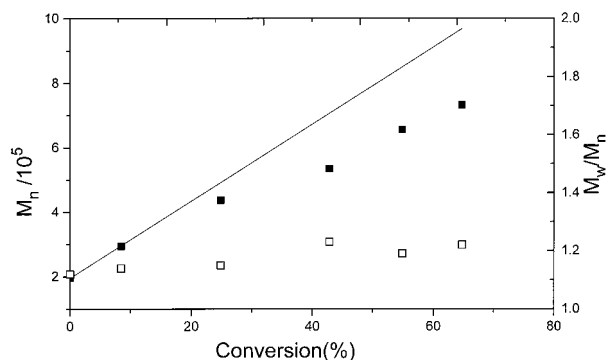


Figure 6. Dependence of the apparent M_n (■) and M_w/M_n (□) on conversion in bulk graft polymerization of EMA at 110°C with $[-\text{CH}_2\text{Cl}] : [\text{CuCl}] : [\text{bpy}] = 1 : 1 : 3$ (mol ratio); the straight line represents the change of theoretical molecular weight with conversion.

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