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Synthesis of Novel Linear Polyethene-Based Graft Copolymers by Atom Transfer Radical Polymerization[†]

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Introduction

Polyethene (PE) is by far the most important commercial polymer. However, the lack of reactive groups on the saturated organic backbone has restricted some end uses, especially where adhesion and interaction with other materials are required. This problem can be solved by using graft or block compatibilizers that incorporate polyethene and a second functional polymeric component.[1] Because of the general inability of a single initiator to polymerize both ethene and functional monomers, graft or block copolymers have only been prepared by post-polymerization processes which include a borane/O_2 free radical initiator,[2] "living" anionic polymerization,[3] and alkoxyamine "living" free radical chemistry.[4]

Recently, much effort has been devoted to atom transfer radical polymerization (ATRP).[5,6] In this polymerization, a dormant polymer halide, R−(monomer)$_n$−X, is repeatedly activated by a transition metal compound, M_t^{n+}, to produce the growing radical, R−(monomer)$_n^{\bullet}$, and an oxidized transition metal species M_t^{n+1}. The equilibrium between dormant and growing species is fast and reversible. The low concentration of radicals minimizes termination relative to propagation, and a controlled/living polymerization is achieved.

In an earlier paper,[7] we demonstrated that syndiotactic polystyrene (*s*PS) could be partially brominated at the benzylic positions using *N*-bromosuccinimide (NBS) to form a "poly" benzyl bromide. Syndiotactic polystyrene graft copolymers were synthesized by atom transfer radical polymerization using the brominated syndiotactic polystyrene as initiator and CuBr combined with pentamethyldiethylenetriamine as catalyst. In this paper, we use this method to prepare novel linear polyethene-based graft copolymers, including poly(ethene-*co*-styrene)-*g*-poly(methyl methacrylate), poly(ethene-*co*-styrene)-*g*-polystyrene, poly(ethene-*co*-styrene)-*g*-(poly(methyl methacrylate)-*b*-polymethyl acrylate), poly(ethene-*co*-styrene)-*g*-(poly(methyl methacrylate)-*b*-polystyrene), and poly(ethene-*co*-styrene)-*g*-(poly(methyl methacrylate)-*b*-poly(2-hydroxyethyl methacrylate)). To our knowledge, the latter materials constitute the first examples of linear polyethene-based copolymers with diblock grafts.

Experimental Section

Materials. Styrene (St, 99%), methyl acrylate (MA, 99%), 2-hydroxyethyl methacrylate (HEMA, 98%), and methyl methacrylate (MMA, 99%) were vacuum-distilled and stored under N_2. CCl_4 (99+%), anisole (99%), CuBr (98%), pentamethyldiethylenetriamine (PMDETA, 99%), and 1,4,8,11-tetraazacyclotetradecane (Me_4Cyclam, 98%) were obtained from Aldrich and used without further purification. $[C_5Me_4(SiMe_2N^tBu)]TiCl_2$ was purchased from Boulder Scientific Co. Poly(ethene-*co*-styrene) (PE/St) was prepared by a published procedure using the $[C_5Me_4(SiMe_2N^tBu)]TiCl_2$/MAO system.[8] The styrene content of the polymer was 2.74 mol %. ^{1}H NMR (1,1,2,2-$C_2D_2Cl_4$), ppm: 1.3 (br, $-CH_2-CH_2-$, $-CH_2-$), 2.5 ($-CH-$), 7.0−7.5 (Ph) (Figure 1a). M_n: 66 500; M_w/M_n: 2.7.

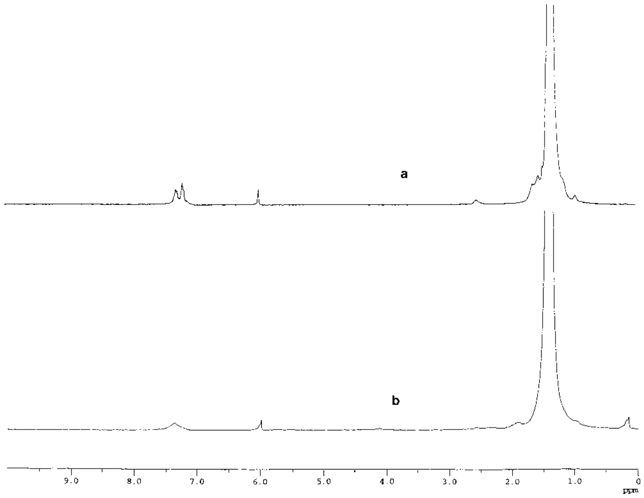

Figure 1. ^{1}H NMR spectra of (a) poly(ethene-*co*-styrene) and (b) brominated poly(ethene-*co*-styrene).

Characterization. NMR spectra were recorded at 130 °C on a Bruker FX-300 spectrometer using 1,1,2,2-tetrachloroethane-d_2 as the solvent. The chemical shifts are referenced to the solvent. Molecular weights and molecular weight distributions were determined at 135 °C on a Waters 150C high-temperature gel permeation chromatograph using standard polystyrene as reference and 1,2,4-trichlorobenzene as eluent. Thermal analyses of polymers were conducted on a Perkin-Elmer DSC-7 operating from 25 to 300 °C with a heating rate of 20 °C/min. Thermal history differences were erased by reheating samples and recording a second DSC scan. Scanning electron microscopy (SEM) images were viewed on a Topcon International Scientific Instruments ISI-SX-40 system. Samples were prepared from melt-pressed films which were cryofractured in liquid N_2.

Bromination of Poly(ethene-*co*-styrene) To Form PE/St−Br. In a typical experiment, *N*-bromosuccinimide (NBS, 2.05 g, 11.5 mmol) and AIBN (0.28 g, 1.71 mmol) were added to a suspension of poly(ethene-*co*-styrene) (6 g, styrene: 2.74 mol %) in CCl_4 (200 mL) in a 500 mL round-bottomed flask with a magnetic stirring bar. After refluxing at 90 °C for 5 h, the reaction mixture was filtered and washed well with acetone and then dried overnight under vacuum at ambient temperature. Yield: 6.35 g. M_n: 62 800; M_w/M_n: 2.9. The bromine content of the product, determined through elementary analysis by Galbraith Laboratories, was 2.60 mol %. The bromination efficiency for the conversion of −CH(Ph)− to −CBr(Ph)− was 95%. ^{1}H NMR (1,1,2,2-$C_2D_2Cl_4$, ppm): 1.3 (br, $-CH_2-CH_2-$, $-CH_2-$), 7.0−7.5 (Ph).

Synthesis of PE/St-*g*-PMMA (Table 1, Run 4). In a typical experiment, a dry round-bottomed flask was charged with anisole (10 mL), CuBr (0.043 g, 0.3 mmol), PMDETA (0.051 g, 0.3 mmol), MMA (3 g, 30 mmol), and PE/St−Br (0.25 g, 0.23 mmol of Br). The flask was sealed, and O_2 was removed by two cycles of freeze−pump−thaw. Then the flask was filled with purified N_2. After the mixture was allowed to stir at ambient temperature for 5 min, the flask was placed in an oil bath at 95 °C for 4.5 h. The reaction was terminated by pouring the contents of the flask into a large amount of acidic methanol. The precipitated polymer was washed and dried

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[†] S.L. dedicates this paper to Professor Baotong Huang on the occasion of his 80th birthday.

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Table 1. Syntheses of Poly(ethene-*co*-styrene) with Monoblock Grafts^{a}

run	PE/St−Br (mmol)	monomer (mmol)	time (h)	yield (conv %)^{d}	composition (graft mol %)^{e}	T_m (°C)
1					0	128.6
2	0.25 g (0.23)^{b}	MMA, 3.0 g (30)	1	1.05 g (26.7)	55.9	123.7
3	0.25 g (0.23)^{b}	MMA, 3.0 g (30)	3	1.35 g (36.7)	61.7	125.2
4	0.25 g (0.23)^{b}	MMA, 3.0 g (30)	4.5	2.51 g (75.3)	75.5	122.8
5	0.25 (0.09)^{c}	MMA, 3.0 g (30)	3	1.52 g (42.3)	58.8	122.5
6	0.50 g (0.18)^{c}	MMA, 2.0 g (20)	5	2.07 g (78.5)	49.3	123.1
7	0.25 g (0.09)^{c}	MMA, 5.0 g (50)	8	2.72 g (49.4)	72.3	121.5
8	0.25 g (0.09)^{c}	MMA, 1.0 g (10)	2.5	0.56 g (31.0)	42.1	123.4
9	0.25 g (0.09)^{c}	St, 3.0 g (29)	8	0.80 g (18.3)	47.3	121.3
10	0.25 g (0.23)^{b}	St, 3.0 g (29)	8	1.45 g (40.0)	58.9	124.3

^{a} Conditions: 10 mL of anisole; 0.3 mmol of CuBr; 0.3 mmol of PMDETA; 95 °C (MMA); 125 °C (St). ^{b} Br content: 2.60 mol %. ^{c} Br content: 0.85 mol %. ^{d} Based on monomer used. ^{e} Based on ^{1}H NMR spectra.

Table 2. Syntheses of Poly(ethene-*co*-styrene) with Diblock Grafts^{a}

run	CuBr (mmol)	ligand (mmol)	R−Br (mmol Br)	monomer (mmol)	time (h)	yield (conv %)^{d}	composition^{e} (mol %)
11	0.3	PMDETA (0.3)	0.25 g (0.09)^{b}	(a) MMA, 1.0 g (10) (b) St, 4.0 g (38)	2.5 1.0	0.66 g (8.2)	PE/PMMA/PS 74.2/21.3/4.5
12	0.3	PMDETA (0.3)	0.25 g (0.09)^{b}	(a) MMA, 1.0 g (10) (b) St, 4.0 g (38)	2.5 2.5	0.72 g (9.4)	PE/PMMA/PS 57.3/32.2/10.5
13	0.3	PMDETA (0.3)	0.25 g (0.06)^{c}	St, 4.0 g (38)	2.0	0.61 g (9.0)	PE/PMMA/PS 24.1:30.4:45.5
14	0.3	PMDETA (0.3)	0.40 g (0.08)^{c}	HEMA, 2.5 g (19)	19	0.50 g (4.0)	PE/PMMA/PHEMA^{f} 39.6:49.9:10.5
15	0.1	Me_4cyclam (0.1)	0.15 g (0.04)^{c}	HEMA, 3.0 g (23)	19	0.24 g (3.0)	PE/PMMA/PHEMA^{f} 28.7:46.3:25.0
16	0.1	PMDETA (0.1)	0.40 g (0.04)^{c}	MA, 3.0 g (35)	22	0.76 g (12)	PE/PMMA/PMA 12.6:38.7:48.7
17	0.1	PMDETA, (0.1)	0.40 g (0.04)^{c}	MA, 0.5 g (6)	22	0.45 g (10)	PE/PMMA/PMA 48.2:46.8:5.0

^{a} Conditions: 10 mL of anisole; 95 °C (MMA), 125 °C (St), 90 °C (MA, HEMA). ^{b} PE/St−Br. ^{c} PE/St-*g*-PMMA−Br. ^{d} Based on monomer used. ^{e} Based on ^{1}H NMR spectra. ^{f} Based on yield due to insolubility of the product.

under vacuum. Yield: 2.51 g. Conversion: 75.3%. Composition: 75.5 mol % PMMA. ^{1}H NMR (1,1,2,2-$C_2D_2Cl_4$), ppm: 0.98, 1.12 ($-CH_3$), 1.3 (br, $-CH_2-CH_2-$), 1.92, 2.01 ($-CH_2$), 3.68 ($-COOCH_3$). ^{13}NMR (1,1,2,2-$C_2D_2Cl_4$), ppm: 17.9, 19.7 ($-CH_3$), 29.8 ($-CH_2-CH_2-$), 45.4, 45.7 ($-C-$), 51.5 ($-OCH_3$), 54.5 ($-CH_2$), 176−178 ($C{=}O$).

Synthesis of PE/St-*g*-PS (Table 1, Run 9). A dry round-bottomed flask was charged with anisole (10 mL), CuBr (0.043 g, 0.3 mmol), PMDETA (0.051 g, 0.3 mmol), St (3 g, 29 mmol), and PE/St−Br (0.25 g, 0.09 mmol of Br). The flask was sealed, and O_2 was removed by two cycles of freeze−pump−thaw. Then the flask was filled with purified N_2. After the mixture was allowed to stir at ambient temperature for 5 min, the flask was placed in an oil bath at 125 °C for 8 h. The reaction was terminated by pouring the contents of the flask into a large amount of acidic methanol. The precipitated polymer was washed and dried under vacuum. Yield: 0.80 g. Conversion: 18.3%. Composition: 47.3 mol % PS. ^{1}H NMR (1,1,2,2-$C_2D_2Cl_4$), ppm: 1.3 (br, $-CH_2-CH_2-$), 1.48 ($-CH_2-$), 1.92 ($-CH-$), 6.3−7.4 (Ph).

Synthesis of PE/St-*g*-(PMMA-*b*-PS) (Table 2, Run 12). A dry round-bottomed flask was charged with anisole (10 mL), CuBr (0.043 g, 0.3 mmol), PMDETA (0.051 g, 0.3 mmol), MMA (1.0 g, 10 mmol), and PE/St−Br (0.25 g, 0.09 mmol of Br). The flask was sealed, and O_2 was removed by two cycles of freeze−pump−thaw. Then the flask was filled with purified N_2. After the mixture was allowed to stir at ambient temperature for 5 min, the flask was placed in an oil bath at 95 °C for 2.5 h. After cooling to room temperature, the unreacted MMA was removed in a vacuum and St (4.0 g, 38 mmol) was added to the flask. O_2 was removed by another two cycles of freeze−pump−thaw. Then the flask was filled with purified N_2 and placed in an oil bath at 125 °C for 2.5 h. The reaction was terminated by pouring the contents of the flask into a large amount of acidic methanol. The precipitated polymer was washed and dried under vacuum. Yield: 0.72 g. Conversion: 10%. Composition (mol %): PE/PMMA/PS = 57.3/32.2/10.5. ^{1}H NMR (1,1,2,2-$C_2D_2Cl_4$), ppm: 0.98, 1.12 ($-CH_3$, MMA), 1.3 (br, $-CH_2-CH_2-$), 1.48 ($-CH_2-$, St), 1.92, 2.01 ($-CH_2-$, MMA; $-CH-$, St), 3.68 ($-COOCH_3$, MMA), 6.3−7.4 (Ph, St).

Synthesis of PE/St-*g*-(PMMA-*b*-PMA) (Table 2, Run 16). A dry round-bottomed flask was charged with anisole (10 mL), CuBr (0.014 g, 0.1 mmol), PMDETA (0.017 g, 0.1 mmol), MA (3 g, 35 mmol), and PE/St-*g*-PMMA−Br (0.40 g, 0.04 mmol of Br). The flask was sealed and O_2 was removed by two cycles of freeze−pump−thaw. Then the flask was filled with purified N_2. After the mixture was allowed to stir at ambient temperature for 5 min, the flask was placed in an oil bath at 90 °C for 22 h. The reaction was terminated by pouring the contents of the flask into a large amount of acidic methanol. The precipitated polymer was washed and dried under vacuum. Yield: 0.76 g. Conversion: 12%. Composition (mol %): PE/PMMA/PMA = 12.6/38.7/48.7. ^{1}H NMR (1,1,2,2-$C_2D_2Cl_4$) ppm: 0.98, 1.12 ($-CH_3$, MMA), 1.3 (br, $-CH_2-CH_2-$), 1.55, 1.77 ($-CH_2-$, MA), 1.92, 2.01 ($-CH_2$, MMA), 2.45 (CH, MA), 3.68 ($-COOCH_3$, MMA), 3.74 ($COOCH_3$, MA). ^{13}NMR (1,1,2,2-$C_2D_2Cl_4$) ppm: 17.9, 19.7 ($-CH_3$, MMA), 29.8 ($-CH_2-CH_2-$), 35.5 ($-CH_2$, MA), 41.8, 42.0 (CH, MA), 45.4, 45.7 ($-C-$, MMA), 51.5 ($-OCH_3$, MMA, MA), 53.8−54.9 ($-CH_2$, MMA), 176−178 ($C{=}O$, MMA), 174.8 ($C{=}O$, MA).

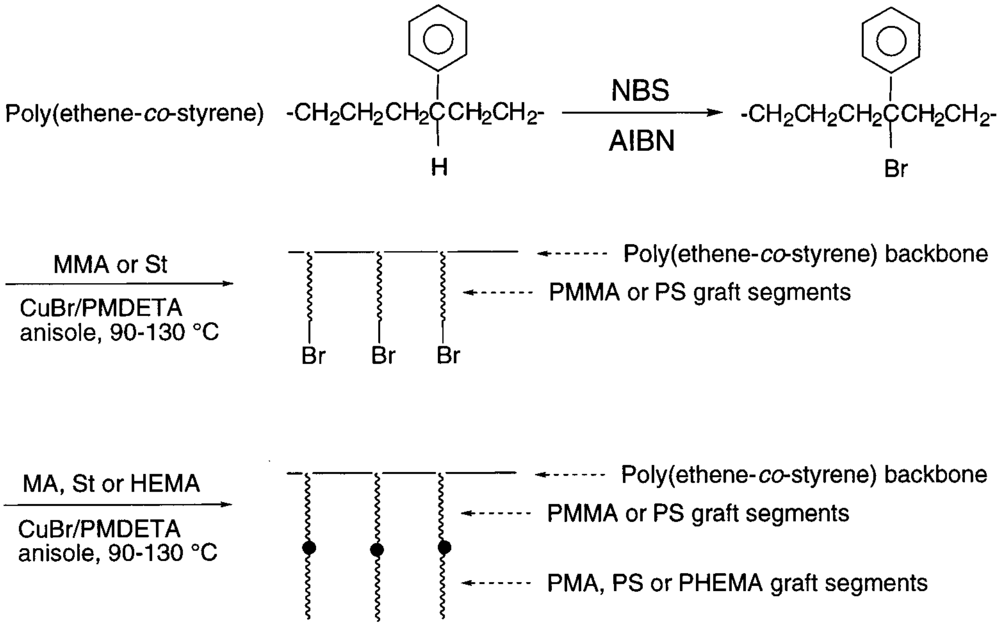
Synthesis of PE/St-*g*-(PMMA-*b*-PHEMA) (Table 2, Run 15). A dry round-bottomed flask was charged with anisole (10 mL), CuBr (0.014 g, 0.1 mmol), Me_4cyclam (0.023 g, 0.1 mmol), HEMA (3.0 g, 23 mmol), and PE/St−*g*-PMMA−Br (0.15 g, 0.04 mmol of Br). The flask was sealed, and O_2 was removed by two cycles of freeze−pump−thaw. Then the flask was filled with purified N_2. After the mixture was allowed to stir at ambient temperature for 5 min, the flask was placed in an oil bath at 90 °C for 19 h. The reaction was terminated by pouring the contents of the flask into a large amount of acidic methanol. The precipitated polymer was washed and dried under vacuum. Yield: 0.24 g. Conversion: 3.0%. Composition (mol %): PE/PMMA/PHEMA = 28.7/46.3/25.0.

Polymer Blending. PE−PMMA and PE−PMMA−PE/St-*g*-PMMA blends were prepared by the solution/precipitation method. The blending components were dissolved in chlorobenzene by refluxing under N_2 until a homogeneous solution formed. The blend was then quantitatively precipitated out by adding the solution to a large amount of hexanes. The solid blend was collected and dried under vacuum.

Results and Discussion

Bromination Reaction. Bromination was carried out using a suspension of poly(ethene-*co*-styrene), PE/

Scheme 1



St, in CCl_4 in the presence of NBS and AIBN (Scheme 1). Figure 1 shows the ^1H NMR spectra of the starting poly(ethene-*co*-styrene) and the brominated product, PE/St−Br. The resonances at 2.5 and 7.0−7.5 ppm are assigned to the C*H* and aromatic protons in the styrene units of poly(ethene-*co*-styrene). After bromination the intensity of the C*H* resonance decreased significantly due to benzylic bromination. The bromine content of this product, as determined through elementary analysis, was 2.60 mol %.

Grafting Reaction. Scheme 1 shows the synthetic route to the graft copolymers. The reaction conditions and the results obtained for the synthesis of mono- and diblock grafts are summarized in Tables 1 and 2, respectively.

Unlike the usual ATRP processes in which the organic halide initiator is soluble in the reaction medium, the brominated poly(ethene-*co*-styrene), PE/St−Br, is completely insoluble. Nevertheless, as shown in Tables 1 and 2, the grafting was quite efficient. Because of the "living" nature of ATRP, copolymers containing longer grafts were easily obtained by simply prolonging the reaction time.

The thermal properties of PE/St-*g*-PMMA and PE-*g*-PS copolymers were analyzed by DSC (Table 1). The starting PE/St had a melting point (T_m) of 128.6 °C. Unlike the PE-based random copolymers where the T_m value is significantly affected by incorporation of a second monomer, the T_m values for our graft copolymers are only slightly lower than that of the starting polymer. This is true even for copolymers with very high graft contents (up to 75 mol %). Our observation of only a very modest change in T_m upon grafting is consistent with previous reports.[3]

One of the interesting features of ATRP is that each molecule of the product is capped with a halogen atom and, therefore, can serve as a new initiator for the next ATRP cycle to yield well-controlled block copolymers. This unique technology could provide an efficient route to the synthesis of polyethene with multifunctional grafts, which is usually difficult to achieve by other methods.

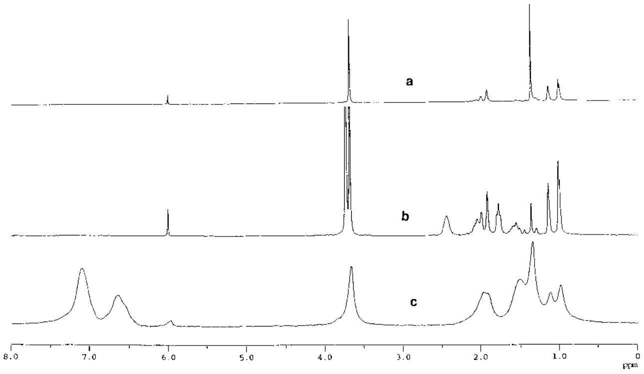


Figure 2. ^1H NMR spectra of (a) PE/St-*g*-PMMA, (b) PE/St-*g*-(PMMA-*b*-PMA), and (c) PE/St-*g*-(PMMA-*b*-PS).

Two different ways were employed to prepare diblock grafts, such as PE/St-*g*-(PMMA-*b*-PS). The intermediate, PE/St-*g*-PMMA−Br, which serves as the initiator for the next block, can either be isolated after the first ATRP step or used directly in the second ATRP cycle after the removal of unreacted MMA. The second route is simpler and more economical since it is not necessary to add any catalyst for the next ATRP cycle.

It is possible to convert one initiator to a different one through the ATRP process, thereby increasing the versatility of the procedure. For example, the synthesis of PE/St-*g*-PMA by ATRP is quite difficult due to the inefficiency of the initiator $-CH_2C(Br)(Ph)-$. However, as shown in Table 2, run 16, $-CH_2C(Br)(Ph)-$ is converted to $-CH_2C(Br)(CH_3)(COOCH_3)$ following the ATRP of MMA, and the latter initiator is very effective for the ATRP of MA, with the MA content in the copolymer reaching 48.7 mol %.

The^1H NMR spectra of typical graft copolymers are shown in Figure 2. In the spectrum of PE/St-*g*-PMMA (Figure 2a), in addition to the chemical shift at 1.3 ppm corresponding to CH_2 units of PE, PMMA resonances were observed at 0.98, 1.12 (both CH_3), 1.92, 2.01 (both CH_2), and 3.68 ($COOCH_3$) ppm. The ^1H NMR spectrum of PE/St-*g*-(PMMA-*b*-PMA) (Figure 2b) contained additional peaks due to the PMA segments at 1.77, 1.55 (both CH_2), 2.45 (CH), and 3.74 ($COOCH_3$) ppm. The

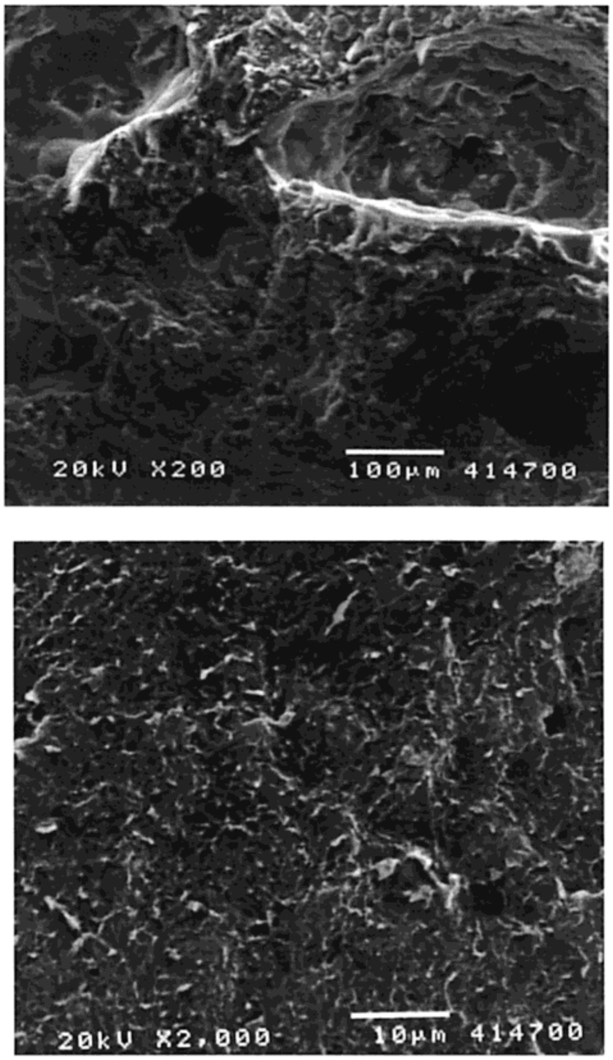


Figure 3. SEM micrographs of (a, top) PE−PMMA blend (70/30 molar ratio) and (b, bottom) PE−PMMA−PE/St-*g*-PMMA blend (70/25/5 molar ratio).

resonances at 6.30−7.40 ppm in the spectrum of PE/St-*g*-(PMMA-*b*-PS) (Figure 2c) are attributable to the aromatic protons of the polystyrene segments.

Effect of PE-*g*-PMMA on PE−PMMA Blends. SEM was used to study the effect of adding PE/St-*g*-PMMA to blends of PE and PMMA. In the homopolymer blend (PE−PMMA: 70/30 molar ratio) the fractured surface indicates nonuniform dispersion of the PMMA phase in the PE matrix (Figure 3a). The large "holes" demonstrate that PMMA was pulled out without deformation, a typical feature of poor interfacial adhesion. On the other hand, when a small amount of the graft copolymer, PE/St-*g*-PMMA (composition: MMA 58.8 mol %), was added, the morphology of the blend (PE−PMMA−PE/St-*g*-PMMA: 70/25/5 molar ratio) was markedly improved as shown by the presence of small and evenly dispersed PMMA phases and the rough interface between the PMMA and PE domains.

Conclusion

We have described the efficient synthesis of a range of new polyethene-based graft copolymers through atom transfer radical polymerization. This includes the first examples of linear polyethene-based copolymers with diblock grafts. The method of preparation is attractive because of the relatively wide scope of monomers that can be employed, the stability of the initiator, the simple polymerization procedure, and good control of graft structure. The PE/St-*g*-PMMA was an efficient compatibilizer for blends of polyethene and poly(methyl methacrylate).

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