Preparation and Applicability of Functionalized Polyethylene with an Ethylene/1,7-Octadiene Copolymer

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ABSTRACT: The copolymerization of ethylene and 1,7-octadiene was carried out to synthesize polyethylene with unreacted vinyl groups. The prepared copolymer [poly(ethylene-*co*-1,7-octadiene) (PEOD)] was epoxidized with peracetic acid, *m*-chloroperbenzoic acid, or formic acid/H_2O_2. Of these, peracetic acid gave the best results. Epoxidized PEOD was subjected to a reaction with 2-mercaptobenzimidazole and poly(L-lactic acid). The bromination of PEOD was also performed in the presence of a Br_2/HBr solution at room temperature. The brominated poly(ethylene-*co*-1,7-octadiene) (PEOD-Br) was used as a macroinitiator for atom transfer radical polymerization. The polymerization of styrene, butyl methacrylate, and glycidyl methacrylate was performed in bulk or solution at 120°C with a PEOD-Br/CuBr/2,2′-dipyridyl initiator system. The thermal properties of the graft copolymers and the efficiency of the graft polymerization were investigated. These graft copolymers have potential applications as interfacial modifiers. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 3631–3638, 2008

Key words: graft copolymers; polyethylene (PE); polyolefins

INTRODUCTION

Polyolefins are macromolecular alkanes and include the most familiar and most commercially produced plastics. They have been used in various applications for daily human life. The low cost of these materials, combined with their diverse and desirable property profiles, drives such large-scale production. One property that renders polyolefins so attractive is their resistance to harsh chemical environments.[1] However, few polymers are compatible with polyolefins because of the absence of any interaction groups in polyolefins.[2]

The modification of polymers is a useful methodology for the generation of new materials with wide-ranging applications.[3] One example is the modification of polyolefins through the introduction of polar groups into the polymer chain. This results in modified polymers showing enhanced environmental stress cracking resistance, thermooxidative stability, good bonding to metals, and ion-exchange capacity. The literature suggests that there is great interest in finding suitable ways to combine these polymers into useful materials.[4–11]

Polyolefin modification is based on double-bond reactivity. The most common and explored reactions are epoxidation[12] and halogenation.[13] The introduction of halogen groups along the polymer backbone is one of the most promising methods of modifying polymers. Polymeric chains with halogen end groups that can be reactivated by an atom transfer radical polymerization (ATRP) catalyst system can be used as macroinitiators. In this respect, many block and graft copolymers have been synthesized with ATRP.[5] In the initiation step, the transition-metal complex abstracts the halogen from the organic halide (RX), creating a radical (R·) that adds to the vinyl monomer, and the resulting radical species further propagate. Inherent in the ATRP mechanism is the incorporation of the alkyl group (R) at one polymer chain end and the halogen at the other chain end.[5] Epoxidation is a well-established reaction for modifying polyolefins, and the formed epoxide can then be used for further reactions. An oxirane moiety can react readily with an amine and carboxyl moiety, thereby forming a covalent bond or linkage.

Saturated polyolefins, such as polyethylene (PE) and polypropylene, are inexpensive commodity polymers that find a wide array of uses because of their toughness, ease of processability, and resistance to degradation.[6] Despite these attractive properties, the absence of polar functional groups such as hydroxyl or carbonyl groups renders them ill suited for applications requiring miscibility with polar pigments, adhesion, or barrier properties.

In this study, poly(ethylene-*co*-1,7-octadiene) (PEOD) was polymerized with a bis(2-methyl idenyl) zirconium dichloride [(2-MeInd)$_2$ZrCl$_2$]/methylaluminoxane [MAO] catalyst system and functionalized by epoxidation and bromination. ATRP of styrene (ST), butyl methacrylate (BMA), and glycidyl

methacrylate (GMA) was performed in bulk or solution at 120°C with brominated poly(ethylene-*co*-1,7-octadiene) (PEOD-Br) as a macroinitiator. The thermal properties of the prepared graft copolymers and the efficiency of the PEOD-Br macroinitiator were evaluated. The applicability of the prepared functionalized PEOD was also investigated.

EXPERIMENTAL

Materials

(2-MeInd)$_2$ZrCl$_2$ was prepared and recrystallized by precipitation in CH$_2$Cl$_2$ after the reaction of a lithium salt of 2-methylrindene with ZrCl$_4$·tetrahydrofuran in a toluene medium. MAO (Akzo Chemical Co.; MMAO Type 3A, 8.4 wt % Al in toluene, Akzo Novel Polymer Chemicals LLC, Chicago, IL) was used without further purification.[9] Toluene was refluxed for over 8 h in the presence of sodium and benzophenone and was used after a second distillation. The purity of the ethylene gas (Samjung Gas, Co., Ltd., Incheon, Korea) was more than 99.5%, and traces of impurities were removed by the successive passage of the gas through CaCl$_2$ and CaSO$_4$. 1,7-Octadiene (1,7-OD; 98%), ST (99%), BMA (99%), and GMA (97%) were purchased from Aldrich Chemical Co., Inc. (Milwaukee, WI), and purified by vacuum distillation. CuBr, bromine, 2,2′-dipyridyl (bpy), peracetic acid, *m*-chloroperbenzoic acid (*m*-CPBA), and 2-mercaptobenzimidazole (MBI) were purchased from Aldrich Chemical and used as received.

Copolymerization of ethylene/1,7-OD

The copolymerization reaction was carried out in a 500-mL glass reactor with a magnetic stirrer. Toluene (100 mL) was used as a reaction medium. Ethylene gas was first introduced at 1 atm, and 5 mL of 1,7-OD was added to the glass reactor. The copolymerization was initiated by the addition of the (2-MeInd)$_2$ZrCl$_2$ catalyst (5.9×10^{-5} M) and MAO. The Al/Zr molar ratio was maintained at 2000. The reaction time was 2 h, and the reaction was terminated by the addition of methanolic HCl. The products were washed three times with plenty of methanol and were dried in a vacuum oven at 30°C until a constant weight was attained.

Instrumentation

^{1}H-NMR spectra of the samples were recorded at 130°C on a Fourier transform NMR spectrometer (AC-250 Fourier transform NMR, Bruker Instruments, Billerica, MA). NMR samples were prepared by the dissolution of 20 mg of the polymers in 0.3 mL of 1,3,5-trichlorobenzene-*d*$_3$.

The molecular weights and molecular weight distributions of the polymers were obtained by gel permeation chromatography (150C Plus, Waters Instruments, Rochester, MN) with a differential refractometer detector and a column composed of Styragel HT6E, HT5, and HT3 with 1,2,4-trichlorobenzene (1.0 mL/min) as an eluent at 135°C. Narrow molar mass polystyrene standards (SL-105, Showa Denko Co., Ltd., Tokyo, Japan) were used for the universal calibration.

The thermal properties of the polymers were determined by differential scanning calorimetry (DSC; DSC 7, PerkinElmer, Norwalk, CT). The thermal history of the samples was removed through scanning first to 200°C at a heating rate of 10°C/min and then to room temperature at a cooling rate of 5°C/min. Then, the crystallized samples were reheated at 10°C/min to 200°C, and the second-scan DSC thermogram was obtained.

Epoxidation of PEOD

The PEOD copolymer (2 g) was first dissolved in 1,2-dichloroethane/1,2,4-trichlorobenzene (50 mL, 5 : 1 vol %) at 100°C and kept under an N$_2$ blanket to prevent oxidation. After 30 min of stirring, the solution was cooled to room temperature. An oxidizer [peracetic acid (5 mL), formic acid/H$_2$O$_2$ (10 mL, 3 : 1 vol %), or *m*-CPBA (0.5 g)] was added to the reaction medium. This solution was stirred for 48 h at room temperature, precipitated into methanol, filtered, and dried in a vacuum oven at 40°C.

Bromination of PEOD

PEOD (2 g) was dissolved in 1,2,4-trichlorobenzene (20 mL) at 100°C and then cooled to 10°C. After 30 min of stirring, an HBr solution (5 mL) of bromine (0.2 mL) was added dropwise over 30 min. This solution was stirred for 48 h at room temperature and then precipitated into methanol, filtered, and dried in a vacuum oven at 40°C.

Synthesis of PEOD with thiobenzimidazoyl groups

Epoxidized PEOD (2 g) was dissolved in 1,2-dichloroethane (50 mL), and then MBI (0.5 g) was added. The solution was refluxed at 100°C for 48 h to complete the reaction. The product was precipitated into methanol, filtered, and dried in a vacuum oven; this was followed by Soxhlet extraction with boiling acetone for 1 day to remove unreacted MBI.

Reaction of epoxidized PEOD and poly(L-lactic acid) (PLLA)

Low-molecular-weight PLLA [weight-average molecular weight (M_w) = 10,700 kg/mol, M_w/number-
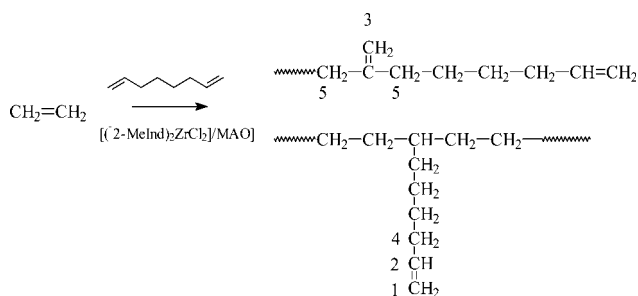
Scheme 1 Copolymerization of ethylene and 1,7-OD.

average molecular weight (M_n) = 1.68], obtained from the direct condensation polymerization of L-lactic acid in the bulk state,[11] was used for the reaction. Epoxidized PEOD (2 g) and PLLA (0.5 g) were dissolved in 1,2-dichloroethane (50 mL), and then triethylene amine (0.2 mL) was added. The solution was refluxed at 100°C for 6 h. The product was precipitated into chloroform, filtered, and dried in a vacuum oven; this was followed by Soxhlet extraction with boiling chloroform for 1 day to remove unreacted PLLA.

Solution polymerization of GMA

PEOD-Br (0.5 g) was dissolved in 1,2,4-trichlorobenzene (50 mL) at 120°C, and then GMA (10 mL) and CuBr (0.0304 g, 1.36×10^{-4} mol)/bpy (0.0424 g, 2.72×10^{-4} mol) in 1,2,4-trichlorobenzene (10 mL) solution were added. The polymerization was carried out at 120°C for 48 h. The product was precipitated into acetone, filtered, and dried in a vacuum oven; this was followed by Soxhlet extraction with boiling acetone for 1 day to remove poly(glycidyl methacrylate) during the graft copolymerization.

Bulk polymerization of ST and BMA

ST (or BMA; 10 mL) was bulk-polymerized in the presence of PEOD-Br (0.5 g)/CuBr (0.0304 g, 1.36×10^{-4} mol)/bpy (0.0424 g, 2.72×10^{-4} mol) at 120°C for 2 h. The product was precipitated in chloroform, filtered, and dried in a vacuum oven; this was followed by Soxhlet extraction with boiling chloroform for 1 day to remove the polystyrene [or poly(butyl methacrylate)] homopolymer.

Shake flask test

The antibacterial activity of the synthesized PEOD–MBI was tested against *Staphylococcus aureus* (ATCC 25923) and *Escherichia coli* (ATCC 25922) with the shake flask method (ASTM E 2149-01). The bacteria were subcultured in a nutrient broth and incubated overnight at 37°C. The cells were suspended in 50 mL of phosphate-buffered saline to yield a suspen-

sion of 1.2×10^{10} cfu/mL. The sample powder (20 mg) was weighed and shaken in 20 mL of a bacterial suspension for 24 h. The suspension was serially diluted in PBS and cultured in a nutrient broth at 37°C for 24 h. The number of viable organisms in the suspension was determined by multiplication of the number of colonies by the dilution factor, and the reduction percentage was calculated on the basis of the initial count.

RESULTS AND DISCUSSION

Polymerization and epoxidation of PEOD

Ethylene was copolymerized with 1,7-OD over (2-MeInd)$_2$ZrCl$_2$/MAO to synthesize PE with unreacted vinyl groups (Scheme 1). Figure 1(a) presents ^{1}H-NMR spectra of the PEOD copolymer. The methylene protons in 1,7-OD appeared in the region of 1.00–1.75 ppm. The methylene protons neighboring the vinyl linkages in PEOD appeared at 2.02 (H4), 2.13 (H4), and 1.75–2.02 ppm (H5). The peaks appearing at 4.75 (H3), 5.02 (H1), and 5.82 ppm (H2) corresponded to vinyl protons of the 1,7-OD unit. After polymerization at 80°C for 2 h, the vinyl content of the 2.7% ethylene/1,7-OD copolymer (PEOD)
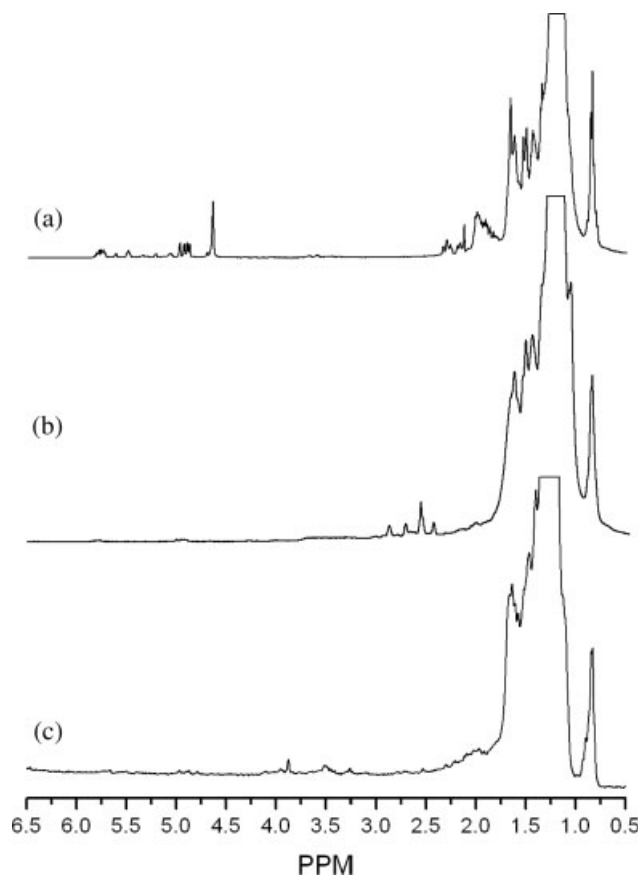

Figure 1 ^{1}H-NMR spectra of (a) PEOD, (b) epoxidized PEOD (PEODEP3), and (c) PEOD-Br.

TABLE I
Characteristics of the Epoxidized PEOD Copolymers

Sample code	Oxidizer	Yield (g)	Oxirane content (mol %)	T_m (°C)	T_c (°C)	ΔH_m (J/g)	M_w (kg/mol)	M_w/M_n
PEOD	—	—	—	108.7	93.3	33.6	19.4	7.17
PEODEP1	m-CPBA	1.85	0.54	110.8	95.2	23.5	22.3	8.69
PEODEP2	Formic acid/H_2O_2	1.71	1.30	112.0	98.0	10.9	22.5	9.03
PEODEP3	Peracetic acid	1.82	2.16	112.4	98.5	9.4	24.2	10.3

Reaction temperature = 27°C; reaction time = 48 h; PEOD = 2 g.

was obtained. The fraction of the vinyl units after the copolymerization was determined from the methine proton (H2) and methylene proton (H3) units. The prepared copolymer was soluble in 1,2-dichloroethane, 1,2,4-trichlorobenzene, ST, and BMA and did not have any insoluble fractions.

PEOD was epoxidized with three different oxidizers: peracetic acid, formic acid/H_2O_2, and m-CPBA. Figure 1(b) shows ^{1}H-NMR spectra of epoxidized PEOD. The methylene protons of the PE unit exhibited their peaks at 1.26 ppm. Epoxidized PEOD showed new peaks at 2.4–3.0 ppm, which were ascribed to the oxirane ring protons of 1,7-OD units. It is known that the epoxidation of unsaturated polymers can lead to various undesired byproducts in addition to the oxirane ring. The major byproducts are molecules containing hydroxyl, ester, carbonyl, and other groups.[14,15] The peak appearing at 2.5 ppm corresponded to the $\sim CH_2OH$ group due to a secondary addition reaction. The molar ratio of the oxirane ring was determined by ^{1}H-NMR measurements from the intensity ratio of the ethylene unit peak (ca. 0.8–2.3 ppm) to the oxirane group of 1,7-OD (2.42, 2.75, and 3.04 ppm).

The results of the epoxidation of PEOD are summarized in Table I. The melting temperature (T_m) and crystallization temperature (T_c) of epoxidized PEODEP increased as the oxirane content increased, whereas the enthalpy of melting (ΔH_m) of epoxidized PEOD decreased as the oxirane content increased. Even though the content of oxirane units in PEODEP1 was as low as 0.54 mol %, T_m and T_c of PEODEP1 were about 2°C higher than those of PEOD. Therefore, the introduction of polar oxirane groups promoted the intermolecular interaction between oxirane units and inhibited the crystallization of ethylene units. The molecular weights and molecular weight distributions of the polymers were obtained by gel permeation chromatography with 1,2,4-trichlorobenzene at 135°C. As the number of oxirane groups was increased, the molecular weight and its distribution were proportionally increased. Of the three approaches, the peracetic acid system was preferred on the basis of the yield and ease of purification.

Reaction of epoxidized PEOD with PLLA and MBI

The ability of an oxirane ring to react with a basic nucleophile is of great use in synthesis. The oxirane ring can react readily with an amine and carboxyl moiety, thereby forming a covalent bond or linkage. Epoxidized PEOD was reacted with MBI to give an imidazole polymer. The fraction of MBI units was determined from the intensity of the ^{1}H-NMR peaks at 7.6–7.8 ppm corresponding to the protons at the 4,5- and 3,6-positions of the benzimidazole ring and the peaks at 0.8–2.3 ppm corresponding to the methylene protons of PEOD units. The results shown in the NMR spectrum [Fig. 2(b)] demonstrate that more
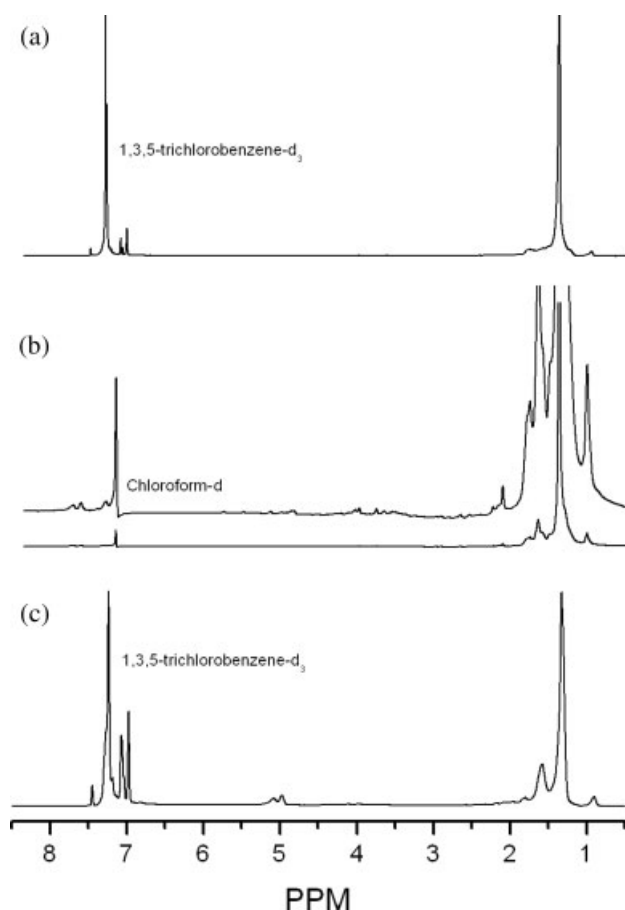

Figure 2 ^{1}H-NMR spectra of (a) epoxidized PEOD, (b) PEODEP3–MBI, and (c) PEOD-g-PLLA.

TABLE II
Antibacterial Activity of PEOD–MBI as Measured by the Shake Flask Test

Strain	Sample code	Concentration (w/v %)	cfu/mL (24-h contact)	Reduction rate (%)
S. aureus (Gram-positive)	Blank	0.0	1.2×10^{10}	—
	PEODEP3–MBI	5.0	1.8×10^{5}	99.9
E. coli (Gram-negative)	Blank	0.0	8.5×10^{8}	—
	PEODEP3–MBI	5.0	0	100

than 1.9 mol % MBI reacted with PEODEP3. Table II shows the antibacterial activity of the prepared imidazole polymer (PEODEP3–MBI), which was measured by the shake flask test against *S. aureus* and *E. coli* as test organisms because they represent Gram-positive and Gram-negative bacteria, respectively. The viable cell number after 24 h of incubation at 37°C after contact with PEODEP3–MBI was nil, indicating that this polymer was a very potent antibacterial material.

Epoxidized PEOD was also reacted with PLLA in the presence of triethylene amine at 100°C. Figure 2 shows ^{1}H-NMR spectra of the synthesized PEOD-*g*-PLLA. Methyl protons and methine protons of PLLA exhibited their peaks at 1.7 and 4.9 ppm, respectively. The methine protons of PLLA broadened to 4.8–5.1 ppm when PLLA was grafted onto PEOD. The peaks at 0.85 and 1.26 ppm corresponded to methyl and methylene protons of the PEOD units [Fig. 2(c)].

ATRP of ST, BMA, and GMA with the PEOD-Br macroinitiator

The bromination of PEOD was performed in the presence of HBr/Br$_2$ at room temperature. Figure 1(c) shows ^{1}H-NMR spectra of PEOD-Br. The vinyl protons of the 1,7-OD unit, which were expected to

appear at 4.5–5.8 ppm, shifted at 3.2–4.2 ppm as a result of the bromination. The bromination of PEOD for 48 h reached 95% conversion with M_w = 51,000 g/mol.

The polymerization of ST, BMA, and GMA was carried out in bulk or in solution at 120°C with the PEOD-Br/CuBr/bpy initiator system, and the results are summarized in Table III. The amount of GMA grafted to PEOD was much lower than that of ST and BMA. A substituent influences monomer reactivity because it increases or decreases the reactivity of the corresponding radical. The polymerization of GMA with a strong electron-donating substituent may not be successful under these conditions, presumably because of the oxidation of radicals to carbocations.[16]

Figure 3 shows the conversion percentage of ST, BMA, and GMA as a function of the polymerization time. After 8 h of polymerization, the conversion percentage of all monomers reached less than 50%. This poor conversion was simply due to the fact that the stiff PEOD-Br macroinitiator could not easily diffuse and match with other reactive groups during ATRP.

Figure 4 shows the molecular weight change of the PEOD-*g*-ST and PEOD-*g*-BMA copolymers as a function of the polymerization time and monomer conversion. The PEOD-*g*-GMA copolymer was

TABLE III
Characteristics of the PEOD-*g*-ST, PEOD-*g*-BMA, and PEOD-*g*-GMA Copolymers

Sample code	Reaction time (h)	[CuBr] (mol $\times 10^{-4}$)	Yield (g)[a]	Comonomer content (mol %)	T_m (°C)	T_c (°C)	ΔH_m (J/g)	χ_c (wt %)[b]	M_w (kg/mol)	M_w/M_n
PEOD-Br	—	—	—	0.0	113.5	102.0	47.0	16.2	51	15.0
PEOD-*g*-ST1	2	1.36	0.65	7.5	109.8	99.7	37.7	13.0	182	5.1
PEOD-*g*-ST2	4	1.36	2.60	39.4	108.3	98.5	12.4	4.3	221	4.8
PEOD-*g*-ST3	8	1.36	4.53	68.4	107.7	97.3	4.57	1.6	342	3.2
PEOD-*g*-BMA1	2	1.36	0.60	3.8	111.0	100.8	36.9	12.7	158	11.5
PEOD-*g*-BMA2	4	1.36	1.93	36.0	108.4	100.1	18.2	6.3	363	13.1
PEOD-*g*-BMA3	8	1.36	7.75	74.1	106.8	65.0	3.4	1.2	519	7.8
PEOD-*g*-GMA1	24	1.36	0.55	1.9	109.2	93.8	8.3	2.9	n.d.	n.d.
PEOD-*g*-GMA2	48	1.36	0.75	8.2	108.6	93.3	2.0	0.7	n.d.	n.d.
PEOD-*g*-GMA3	48	2.72	1.21	17.9	108.5	92.8	2.0	0.7	n.d.	n.d.
PEOD-*g*-GMA4	48	4.08	1.65	31.2	110.3	91.5	2.7	0.9	n.d.	n.d.

n.d. = not determined.
[a] Polymerization temperature = 120°C; macroinitiator = 0.5 g.
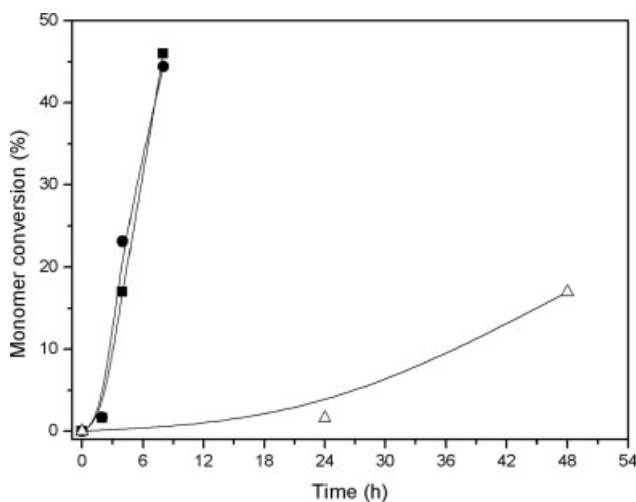[b] χ_c = crystallinity based on ΔH_m^o of orthorhombic PE (290 J/g).

Figure 3 Comonomer conversion as a function of the polymerization time for the ATRP of (●) ST, (■) BMA, and (△) GMA at 120°C with the PEOD-Br/CuBr/bpy initiator system.
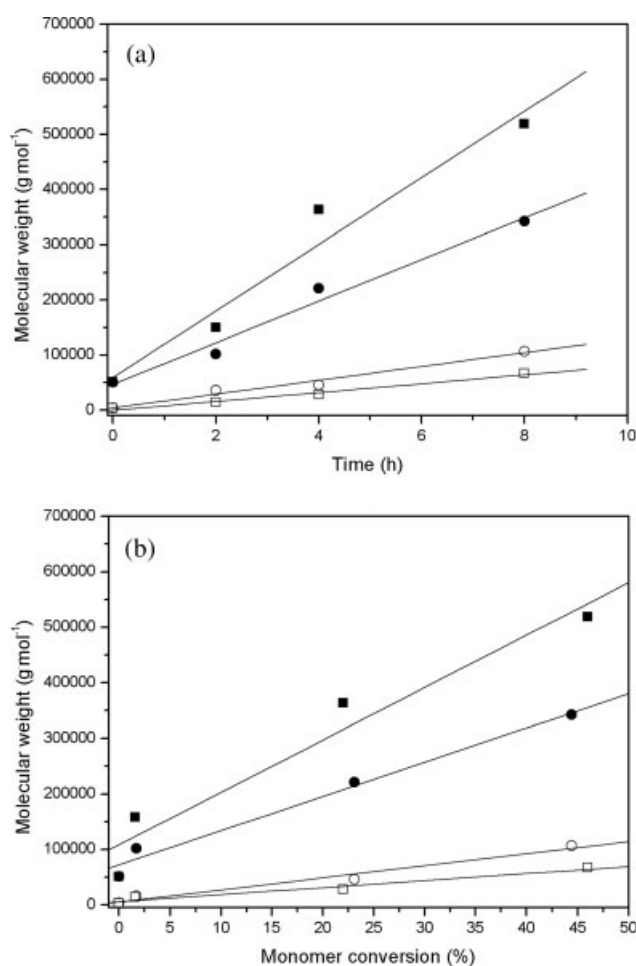
hardly soluble in solvents, and its molecular weight was not determined. As previously reported,[17,18] M_n and M_w of the ST and BMA copolymers followed a good linear relationship with respect to the polymerization time and monomer conversion.

The DSC thermograms of the PEOD-g-ST, PEOD-g-BMA, and PEOD-g-GMA copolymers are shown in Figure 5. PEOD-Br exhibited a broad range of T_m values because of its higher molecular weight distribution (M_w/M_n). As the comonomer content increased, T_m of the PE moiety in the graft copolymer decreased, and T_c appeared at a lower temperature; this indicated that the grafting branch reduced the crystallization rate of the PE phase. Typically, the melting peak of ethylene copolymers broadens
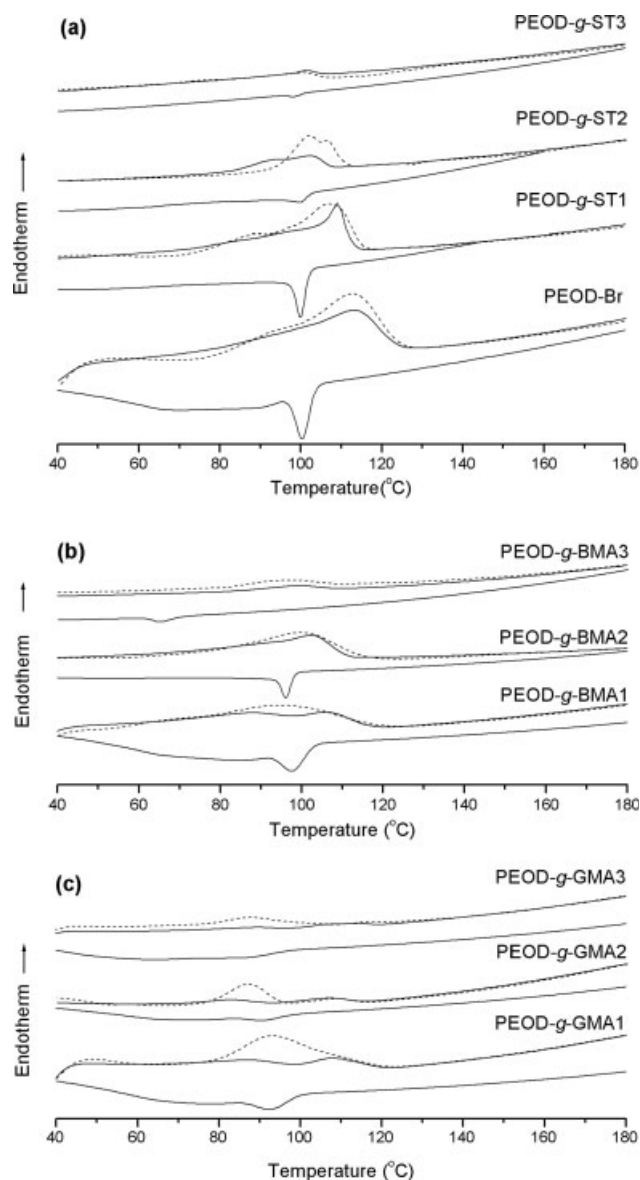

Figure 4 Molecular weight as a function of (a) polymerization time and (b) monomer conversion for the ATRP of ST [(●) M_w and (○) M_n] and BMA [(■) M_w and (□) M_n] at 120°C with the PEOD-Br/CuBr/bpy initiator system.

Figure 5 DSC thermograms of the (a) PEOD-g-ST, (b) PEOD-g-BMA, and (c) PEOD-g-GMA copolymers: (- - -) first and (—) second scans.
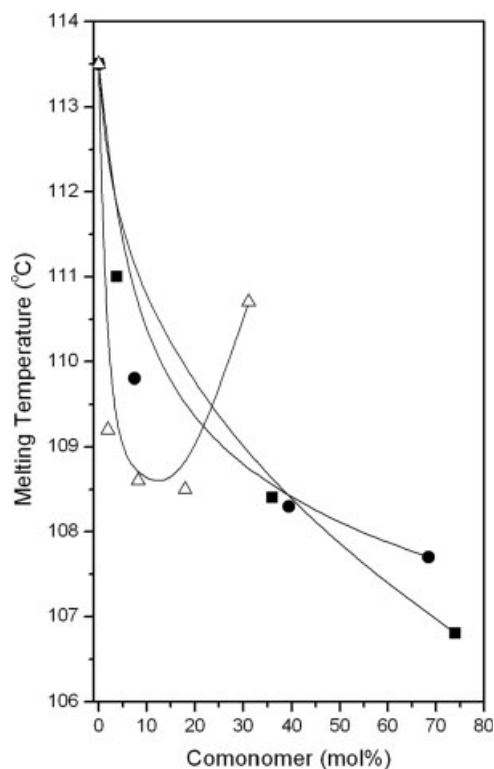
Figure 6 T_m values of the copolymers as a function of the molar percentages of (●) ST, (■) BMA, and (△) GMA.

as the comonomer content increases.[19] However, the melting peak of the copolymers with the highest comonomer contents, PEOD-*g*-ST3, PEOD-*g*-BMA3, and PEOD-*g*-GMA3, almost disappeared with only a slight change in the peak T_m value. This was ascribed to the fact that the amorphous grafting moieties seized hold of the crystallizable PEOD parts to effectively prevent the crystallization of the latter.

Figure 6 and 7 show the dependence of T_m and the crystallinity of the copolymer on the molar fraction of the comonomers, respectively. The crystallinity percentage was calculated with the following equation with a value of 290 J/g for the heat of fusion (ΔH_m^o) of 100% crystalline PE:[19]

$$\text{Crystallinity}(\%) = \frac{\Delta H_m}{\Delta H_m^o} \quad (1)$$

T_m of the copolymer with an equivalent molar content of GMA decreased more rapidly when ST and BMA were used (Fig. 6). This indicated that the graft branches of GMA more effectively prevented the crystallization of the PE moiety in the graft copolymer than those of ST or BMA. The unusual melting behavior of PEOD-*g*-GMA4 may be a result of a crosslinking reaction of oxirane groups in the polymer chain during the second DSC heating step. The dependence of the crystallinity on the comonomer

content (>15 mol %) was much less severe for the PEOD-*g*-GMA copolymer, as shown in Figure 7. Indeed, GMA copolymers with this level of comonomer content are virtually noncrystalline.

CONCLUSIONS

Ethylene was copolymerized with 1,7-OD, and the prepared copolymer was epoxidized with three different oxidizers. The shift of T_m to higher temperatures with an increase in the epoxidation percentage was due to the interaction of the oxirane groups in the polymer chains. Epoxidation is a well-established reaction for modifying diene polymers, and the formed epoxide can be used for further reactions. Epoxidized PEOD reacted with MBI to give an imidazole polymer. The resulting polymer showed excellent antibacterial activities against *S. aureus* and *E. coil*. Epoxidized PEOD was also reacted with PLLA in the presence of triethylene amine. PLLA is widely recognized as a biodegradable polymer. PEOD-*g*-PLLA is a potential additive for imparting an improved compatibilizing influence to polyolefin and biodegradable polyester blends.

The bromination of PEOD was performed in the presence of HBr/Br$_2$. The brominated polymer was polymerized in a controlled fashion with an ATRP
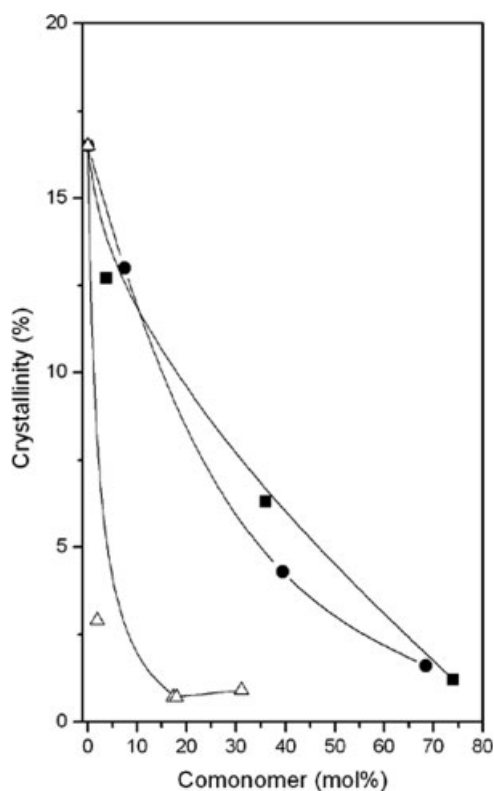

Figure 7 Crystallinity values of the copolymers as a function of the molar percentages of (●) ST, (■) BMA, and (△) GMA.

process. ST, BMA, and GMA were polymerized at 120°C with the PEOD-Br/CuBr/bpy initiator system. The efficiency of GMA grafted to PEOD was much lower than that of ST and BMA. However, polyethylene-*g*-poly(glycidyl methacrylate) is an interesting copolymer because its pendant oxirane rings can be opened and subsequent modifications are possible. The copolymers prepared in this study can be used as interfacial modifiers for blends of polyolefins with polar polymers.

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