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Graft Copolymers from Linear Polyethylene via Atom Transfer Radical Polymerization

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ABSTRACT: Polyethylene-*graft*-poly(*n*-butyl acrylate) (PE-*g*-PBA) and polyethylene-*graft*-poly(methyl methacrylate) (PE-*g*-PMMA) were prepared through the combination of metallocene-catalyzed ethylene/10-undecen-1-ol copolymerization and conversion of the copolymer into a macroinitiator for atom transfer radical polymerization (ATRP). Well-defined acrylate and methacrylate graft copolymers were successfully prepared under dilute ATRP conditions. This was confirmed by analyses of the detached side chains. The molecular weights of both PBA and PMMA side chains agreed with predicted values, and molecular weight distributions were narrow. The PE-*g*-PMMA was evaluated as a compatibilizer for a blend of PE and PMMA and demonstrated the potential of such nonpolar/polar graft copolymers as a compatibilizing agent.

Introduction

The development of new technologies to incorporate polar segments into polyolefins, such as polyethylene and polypropylene, in controlled fashion is one of the long-term goals in polymer chemistry. The targeted materials would enable production of new polyolefin architectures with many desirable properties.[1,2] Indeed, this is a really attractive goal, not only in academia but also in industry, because polyolefins are the largest volume thermoplastics manufactured in the world, and new polymer materials based on polyolefins could strongly impact our life. So far, several polymerization systems have been reported to incorporate polar segments into polyolefins. They can be classified into two categories; one is direct copolymerization through transition-metal-catalyzed polymerization to yield random copolymers, and the other is the combination of different polymerization mechanisms to prepare block and graft copolymers. The former approach is based on either coordination or radical polymerization. The challenge for metallocene- and post-metallocene-catalyzed copolymerization is to increase the tolerance of the catalyst to polar groups, to increase activity, and to improve the ability of the catalyst to incorporate polar monomers.[3−5] In radical polymerization the challenge is to increase the rate of olefin incorporation.[6−10] On the other hand, block copolymers have already been synthesized using lanthanide or metallocene catalysts.[11−13] In these catalyst systems, block copolymers were synthesized by the combination of coordination olefin polymerization and enolate-mediated group transfer (meth)acrylate polymerization. Traditional graft polymerizations, for example, grafting maleic anhydride in the presence of styrene comonomer from polyethylene by radical polymerization, also provides an example of this approach to segmented copolymers.[14] However, the incorporation of maleic anhydride into the side chains is not controlled at all, since the polymerization proceeds by a conventional radical polymerization mechanism.

Controlled/“living” radical polymerization (CRP)[15−18] is one of the most noteworthy research areas developed in the past decade. CRP enables preparation of many new polymer architectures from commercially available monomers in a controlled fashion. CRP provides a versatile approach to new polymeric materials with desirable properties since polymer segments synthesized by other polymerization mechanisms including anionic, cationic, metathesis, and coordination polymerizations can be incorporated into the target material. A further advantage of CRP is the high tolerance of radical-based processes to polar groups so that designed polymer architectures based on polar polymers can be easily prepared. Among several CRP technologies developed in the past decade, atom transfer radical polymerization (ATRP)[19−30] could be the promising method due to its versatility. Several examples have been already reported combining ATRP with olefin polymerization, including block copolymer syntheses via chain extension polymerization,[31−35] graft copolymers syntheses via grafting through polymerization,[36,37] and graft copolymers syntheses via grafting from polymerization.[38−41] In a similar way, a graft copolymer was prepared by nitroxide-mediated polymerization.[42] Block copolymer synthesis, combining ring-opening metathesis polymerization (ROMP) and ATRP, was demonstrated for copper[43] and a ruthenium catalyst.[44] Direct copolymerization of α-olefins and polar monomers via ATRP was also reported.[6−10]

In this paper, we discuss the preparation and properties of polyethylene-*graft*-poly(*n*-butyl acrylate) and polyethylene-*graft*-poly(methyl methacrylate) copolymers. The copolymers were synthesized by a combination of metallocene-catalyzed ethylene/10-undecen-1-ol copolymerization with subsequent ATRP grafting of acrylate and methacrylate monomers. While there were several reports on the preparation of polyolefin/polar copolymers via CRP, as noted above, only a few examples involve copolymers with highly crystalline poly-

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olefin segments, i.e., linear polyethylene. This might be due to low solubility of crystalline polyolefins in CRP monomers/solvents, leading to limited conditions that can be employed for the ATRP. We focused on the preparation of graft copolymers from linear polyethylene segments because linear polyethylene produced by Ziegler−Natta or metallocene catalysts are continuing to gain market share compared to highly branched polyethylene produced by conventional radical process. In this paper, we will discuss the synthetic methodology developed for the preparation of polyethylene-*graft*-poly(*n*-butyl acrylate) and polyethylene-*graft*-poly(methyl methacrylate) copolymers through the combination of metallocene-catalyzed olefin copolymerization and subsequent grafting-from polymerization via ATRP. We will also discuss one potential application for the graft copolymer, as a compatibilizer for polar/nonpolar polymer blends.

Experimental Section

Materials. Ethylene was purchased from Sumitomo Seika Co. Ltd. Methylalminoxane (MAO) was purchased from Albemarle as a 20% toluene solution, and the remaining trimethylaluminum was removed under vacuum before use. Toluene was dried over Al_2O_3. Copper(I) chloride[45] and tris(2-(di(2-(*n*-butoxycarbonyl)ethyl)amino)ethyl)amine (BA_6TREN)[46] were purified and prepared as previously reported. *n*-Butyl acrylate (BA) and methyl methacrylate (MMA) were passed through a neutral alumina column to remove stabilizers, dried over calcium hydride, and distilled under reduced pressure before use. Polyethylene (M_w = 34 000, M_w/M_n = 2.27) and PMMA (M_w = 35 700, M_w/M_n = 1.52) samples for the polymer blend were prepared through ethylene polymerization catalyzed by metallocene/MAO and MMA polymerization catalyzed by CuBr/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine, respectively. All other reagents and solvents were used as received.

Synthesis of Linear Polyethylene Multifunctional Macroinitiator (PE Multifunctional Macroinitiator). The copolymerization of ethylene and 10-undecen-1-ol was conducted in the presence of dimethylsilylene (2-methylbenzo[*e*]-inden-3-yl) (2,7-di-*tert*-butyl-9-fluorenyl)zirconium dichloride, methylaluminoxane, and triethylaluminum as reported previously.[47,48]

Toluene (900 mL) was placed under nitrogen in a 1000 mL glass flask equipped with a mechanical stirrer, a thermometer, and a condenser. Toluene was heated to 80 °C, and ethylene gas feed (100L/h) was started. After 15 min, triethylaluminum (1.0 M toluene solution; 5.0 mL, 5.0 mmol) and 10-undecen-1-ol (0.80 mL, 4.0 mmol) were added to the flask. After 5 min, the zirconium−metallocene complex (0.025 mmol) activated by MAO (1.28 M toluene solution, 1.22 mL, 1.56 mmol) was added to the flask to start polymerization. The copolymerization was continued for 3.0 min under vigorous stirring (600 rpm). After 3.0 min, isobutyl alcohol (20 mL) was added to stop the reaction. The resulting mixture was added to an acidic methanol solution (2500 mL including 6 mL of concentrated HCl) to precipitate the copolymer. The resulting polymer was collected by filtration, washed with methanol (200 mL × 3), and dried at 80 °C under vacuum. Poly(ethylene-*co*-10-undecen-1-ol) was obtained as white powder. Yield was 10.1 g. According to ^{1}H NMR, 0.78 mol % of 10-undecen-1-ol was incorporated into the copolymer.

Poly(ethylene-*co*-10-undecen-1-ol) (8.0 g, 2.14 mmol of OH group), triethylamine (1.78 mL, 12.8 mmol), 2-bromoisobutyryl bromide (1.32 mL, 10.7 mmol), and toluene (300 mL) were added to a 500 mL glass flask equipped with a mechanical stirrer, a thermometer, and a condenser under nitrogen. The mixture was warmed to 80 °C and stirred for 2 h at this temperature. The reaction mixture was then cooled to room temperature to precipitate the polymer. The resulting polymer was collected by filtration, washed successively with methanol (20 mL × 3), 1 N HCl(aq) (10 mL × 2), and methanol (20 mL × 2), and dried at 50 °C overnight in a vacuum. PE multifunctional macroinitiator was obtained as white powder in quantitative yield. According to 400 MHz ^{1}H NMR in *o*-dichlorobenzene-d_4 at 120 °C, 0.90 mol % of the α-bromoisobutyrate group was incorporated in the resulting PE multifunctional macroinitiator, and no hydroxymethylene group was observed, indicating complete conversion of a hydroxy group to a haloester group. M_n = 36 000 and M_w/M_n = 3.09.

ATRP from PE Multifunctional Macroinitiator. A typical ATRP was performed as follows. Polymerization was conducted using standard Schlenk techniques. Solvents and monomers were degassed by bubbling with nitrogen for 30 min prior to use. CuCl (31.2 mg, 3.15×10^{-4} mol), $CuCl_2$ (2.1 mg, 1.56×10^{-5} mol), and BA_6TREN (301.8 mg, 3.30×10^{-4} mol) were dissolved in chlorobenzene (5 mL), and this solution was used as a stock catalyst solution. Separately, the PE multifunctional macroinitiator (119.1 mg, 3.49×10^{-5} mol of Br) was placed in a 25 mL Schlenk flask, and then BA (0.5 mL, 3.49×10^{-3} mol), chlorobenzene (1.8 mL), anisole (0.1 mL), and the stock catalyst solution (0.59 mL, 3.51×10^{-5} mol of CuCl/BA_6TREN, 1.74×10^{-6} mol of $CuCl_2/BA_6TREN$) were successively added to the flask. The resulting mixture was warmed to 100 °C to start the polymerization. The PE multifunctional macroinitiator dissolved in solvent/monomer mixture after a few minutes. After the desired polymerization time, the polymerization was stopped, and the resulting graft copolymer was precipitated in excess methanol. The graft copolymer was filtered, washed with methanol, and dried under vacuum at 60 °C.

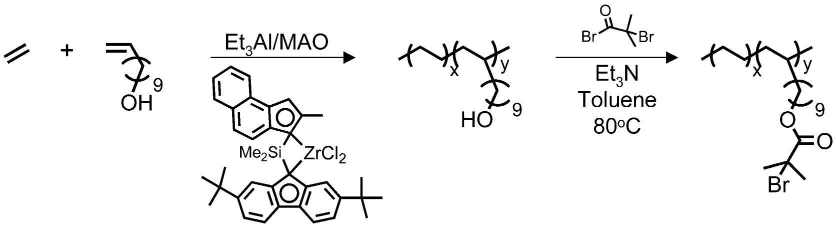
Side-Chain Cleavage and Analysis. Typical procedures for side-chain cleavage from the PE-*g*-PBA were as follows. The graft copolymer (30 mg) was dissolved in chlorobenzene (1 mL) at 100 °C, and butanol (4 mL) and H_2SO_4 (3 drops) were added to the solution. The resulting mixture was stirred at 100 °C for 3 days. After cooling, the anionic ion-exchange resin was added to neutralize the acid catalyst, and then the ion-exchange resin was removed by decantation. After evaporation of solvent, the remaining polymer was extracted with THF, and the molecular weight and molecular weight distribution of the cleaved side chain PBA were measured using THF GPC.

In the case of PE-*g*-PMMA, chlorobenzene (4 mL), methanol (1 mL), and 25% sodium methoxide in methanol (3 drops) were used for the cleavage reaction which was conducted under vigorous reflux at 90 °C for 3 days. H type cationic ion-exchange resin was used to neutralize base catalyst. After similar work-up procedures to the cleavage of PE-*g*-PBA, GPC of side-chain PMMA was taken using THF GPC.

Characterization. ^{1}H NMR spectra of PE multifunctional macroinitiator and graft copolymers were collected in *o*-dichlorobenezene-d_4 at 120 °C and in toluene-d_8 at 100 °C, using a 400 MHz JEOL JNM GSX400 and a Bruker 300 MHz, respectively. Conversion of monomer was determined by gas chromatography using a Shimadzu GC 14-A gas chromatograph equipped with a FID detector and J&W Scientific 30m DB WAX Megabore column. Molecular weight and molecular weight distribution of the graft copolymers were determined by high-temperature GPC using a Waters 150-C gel permeation chromatograph equipped with three Tosoh TSK-GEL columns (two sets of TSKgelGMH$_{HR}$-H(S)HT and one TSKgel-GMH$_6$-HTL) at 145 °C. GPC was performed using *o*-dichlorobenzene as eluent at the flow rate of 1 mL/min. The universal calibration technique was used to determine the molecular weight and molecular weight distribution of the PE multifunctional macroinitiator, and the same calibration technique was applied to the graft copolymers. The molecular weight and molecular weight distribution of the detached side chain poly(*n*-butyl acrylate) and poly(methyl methacrylate) were determined by GPC using PSS columns (styrogel 10^5, 10^3, 10^2 Å) with RI detector. GPC was performed using THF as an eluent at the flow rate of 1 mL/min. Linear polystyrene and poly(methyl methacrylate) standards were used for calibration of poly(*n*-butyl acrylate) and poly(methyl methacrylate), respectively.

TEM Analysis of Polymer Blend. The polymer mixture (total 1 g, PMMA/PE = 6/4 or PMMA/PE/PE-*g*-PMMA = 6/4/1

Scheme 1. Synthesis of PE Multifunctional Macroinitiator



by weight) was dissolved in *o*-xylene (50 mL) at 130 °C. After 1 h, the blended polymer mixture was precipitated into hexane (200 mL), filtered, and then dried under vacuum. After pressing the polymer mixture into a sheet, an ultrathin (ca. 100 nm) section was cut on a Reica Ultracut microtome equipped with a diamond knife at a low temperature and then stained with RuO$_4$. TEM was obtained using a Hitachi H-7000 transmission electron microscope at an acceleration voltage of 75 kV and at a magnification of 100 000×.

Results and Discussion

Synthesis of PE Multifunctional Macroinitiator. A synthetic route for the preparation of linear polyethylene multifunctional macroinitiator (PE multifunctional macroinitiator) is presented in Scheme 1. As reported earlier,[47,48] dimethylsilylene (2-methylbenzo[*e*]inden-3-yl) (2,7-di-*tert*-butyl-9-fluorenyl)zirconium dichloride is able to copolymerize ethylene and 10-undecen-1-ol in the presence of trialkylaluminum and activation with methylalminoxane (MAO) to give poly(ethylene-*co*-10-undecen-1-ol). The resulting polyethylene-based copolymer possesses a linear polyethylene backbone, according to ^{13}C NMR study, as reported previously.[47,48] In this catalyst system, the trialkylaluminum acts both as a protecting reagent for the polar group and as a chain transfer reagent so that both polar monomer incorporation and molecular weight of the resulting copolymer are strongly affected by the amount and the nature of the trialkylaluminum. For our purpose of graft copolymer preparation, the triethylaluminum was selected to obtain a copolymer with both the desired molecular weight and appropriate polar monomer content. After conducting the copolymerization of ethylene/10-undecen-1-ol, the hydroxyl functionality in the resulting copolymer was converted into an α-bromoisobutyrate functionality by reaction with excess of α-bromoisobutyryl bromide in the presence of triethylamine. The 400 MHz ^{1}H NMR spectra of both poly(ethylene-*co*-10-undecen-1-ol) and the resulting PE-multifunctional macroinitiator are presented in Figure 1 as spectra a and b, respectively. The spectra show the presence of triplet peaks characteristic of methylene protons being next to a hydroxy group ($-CH_2OH$, $\delta = 3.49$ ppm) and next to an ester group ($-CH_2OCOC(CH_3)_2Br$, $\delta = 4.07$ ppm) along with a singlet peak from the methyl protons in the ester groups ($-CH_2OCOC(CH_3)_2Br$, $\delta = 1.83$ ppm). After the esterification reaction no triplet assignable to hydroxy methylene protons was observed, indicating efficient conversion of the hydroxy group into the ester group. GPC measurement revealed that the PE multifunctional macroinitiator possessed high molecular weight ($M_n = 36\,000$) and relatively high polydispersity index ($M_w/M_n = 3.04$). According to ^{1}H NMR, 0.90 mol % haloester group was incorporated. These results suggest that this PE multifunctional macroinitiator possessed on average approximately 10 initiating groups per polymer chain. Thus, a linear PE multifunctional macroinitiator was successfully synthesized through ethylene/10-undecen-1-ol copolymerization and successive esterification.

Preparation of Polyethylene-*graft*-poly(*n*-butyl acrylate). Linear polyethylene is only soluble in hydrocarbons or halohydrocarbons at high temperatures. Because of this limited solubility, the polymerization conditions for an ATRP from above-mentioned PE multifunctional macroinitiator should be carefully selected. Since the initiating groups are concentrated along the polymer main chain, a copolymerization via grafting-from at high temperature is usually undesirable since radical−radical coupling termination could produce some cross-linking in contrast to small molecule initiators. Thus, low polymerization temperature is generally preferred for grafting-from polymerization to avoid undesired coupling termination. However, the linear PE multifunctional macroinitiator does not dissolve at low temperatures. To overcome this difficulty, the grafting-from copolymerization was conducted under very dilute monomer concentration conditions (17 vol % *n*-butyl acrylate in chlorobenzene), and the halogen

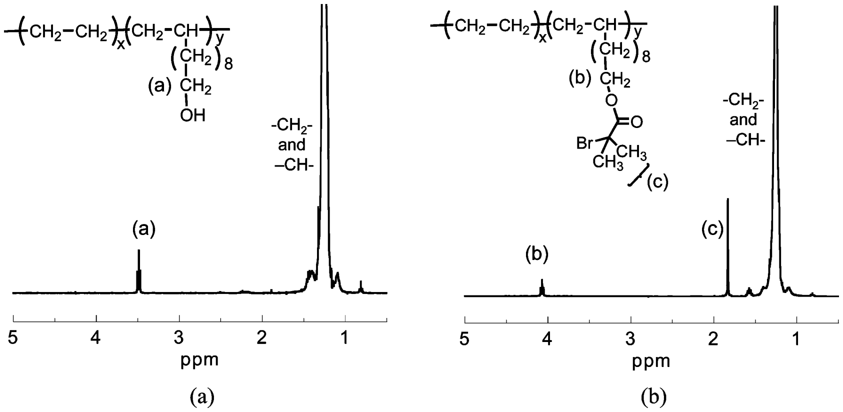


Figure 1. 400 MHz ^{1}H NMR spectra of (a) poly(ethylene-*co*-10-undecen-1-ol) and (b) PE multifunctional macroinitiator in *o*-dichlorobenzene-d_4 at 120 °C.

Table 1. ATRP of BA from PE Multifunctional Macroinitiator[a]

no.	t (h)	conv (%)	M_{n}[b]	$M_{\mathrm{n,theo}}$[b]	M_{w}[b]	$M_{\mathrm{w}}/M_{\mathrm{n}}$[b]	M_{n}[c] ($\times 10^{-4}$)	$M_{\mathrm{n,theo}}$[c] ($\times 10^{-4}$)	M_{w}[c] ($\times 10^{-4}$)	$M_{\mathrm{w}}/M_{\mathrm{n}}$[c]
macroinitiator							3.60		10.9	3.04
1	1	13.0	2410	1670	3180	1.32	3.01	5.35	11.7	3.89
2	3	38.8	5180	4970	6690	1.29	2.90	8.83	15.3	5.28
3	6	52.8	6040	6760	7730	1.28	3.12	10.7	14.4	4.54

[a] Polymerization conditions: $[\mathrm{BA}]_0/[\mathrm{PE\text{-}M}]_0/[\mathrm{CuCl}]_0/[\mathrm{CuCl_2}]_0/[\mathrm{BA_6TREN}]_0 = 100/1/1/0.05/1.05$; $[\mathrm{BA}]_0 = 1.16$ mol/L; solvent = chlorobenzene; initiator = PE multifunctional macroinitiator (2.34 wt % Br, $M_{\mathrm{n}} = 36\,000$, $M_{\mathrm{w}}/M_{\mathrm{n}} = 3.09$); $T = 100$ °C. [b] PBA side chain after detachment from main chain. [c] High-temperature GPC of graft copolymer.

Table 2. ATRP of MMA from PE Multifunctional Macroinitiator[a]

no.	t (h)	conv (%)	M_{n}[b]	$M_{\mathrm{n,theo}}$[b]	M_{w}[b]	$M_{\mathrm{w}}/M_{\mathrm{n}}$[b]	M_{n}[c] ($\times 10^{-4}$)	$M_{\mathrm{n,theo}}$[c] ($\times 10^{-4}$)	M_{w}[c] ($\times 10^{-4}$)	$M_{\mathrm{w}}/M_{\mathrm{n}}$[c]
macroinitiator							3.60		10.9	3.04
1	2	35.5	4770	3740	6390	1.34	5.49	7.15	21.2	3.86
2	4	49.0	5350	5120	7120	1.33	5.55	8.53	25.6	4.61

[a] Polymerization conditions: $[\mathrm{MMA}]_0/[\mathrm{PE\text{-}M}]_0/[\mathrm{CuCl}]_0/[\mathrm{CuCl_2}]_0/[\mathrm{BA_6TREN}]_0 = 100/1/1/0.05/1.05$, $[\mathrm{MMA}]_0 = 0.58$ mol/L; solvent = chlorobenzene; initiator = PE multifunctional macroinitiator (2.34 wt % Br, $M_{\mathrm{n}} = 36\,000$, $M_{\mathrm{w}}/M_{\mathrm{n}} = 3.09$); $T = 100$ °C. [b] PMMA side chain after detachment from main chain. [c] High-temperature GPC of graft copolymer.

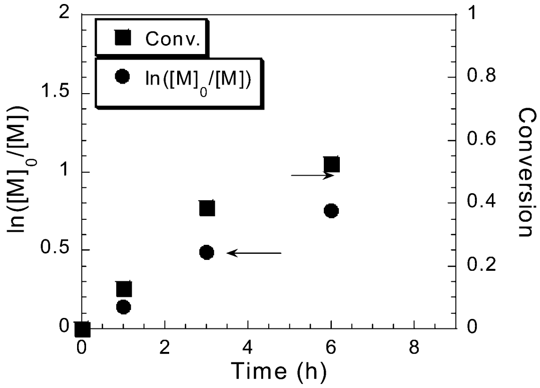


Figure 2. Kinetic plots for the polymerization of BA from PE multifunctional macroinitiator. See Table 1 for polymerization conditions.

exchange technique was applied to reduce radical concentrations.[49] $\mathrm{CuCl_2}$ was also added at the beginning of polymerization (5 mol % vs CuCl) to increase deactivator concentration. To attain a satisfactory high polymerization rate even under dilute monomer conditions, $\mathrm{BA_6TREN}$ was selected as ATRP ligand. This ligand forms a catalyst complex which possesses high activity in ATRP and has relatively good solubility, as reported before.[46] Thus, grafting from the PE multifunctional macroinitiator was conducted with $[\mathrm{BA}]_0/[\mathrm{I}]_0/[\mathrm{CuCl}]_0/[\mathrm{CuCl_2}]_0/[\mathrm{BA_6TREN}]_0 = 100/1/1/0.05/1.05$ in chlorobenzene at 100 °C. Under these conditions, polymerization proceeded successfully up to >50% monomer conversion (Table 1). A semilogarithmic plot of monomer conversion showed an almost linear relationship vs polymerization time, indicating constant radical concentration during polymerization (Figure 2). However, when polymerization was continued further, an insoluble polymer gel formed, plausibly due to cross-coupling termination. Thus, conditions that result in much lower radical concentrations might be necessary to achieve higher degrees of polymerization. Several graft copolymers having different side chain lengths were prepared by changing polymerization time. Solubility of the resulting graft copolymers was still limited, and the copolymers were only soluble in organic solvents at elevated temperature.

To confirm that well-controlled grafting-from occurred, the PBA side chains were cleaved from the polyethylene main chain and analyzed by GPC. PBA side chains were detached from the PE main chain through an ester exchange reaction in 1-butanol/chlorobenzene mixed solvent in the presence of $\mathrm{H_2SO_4}$ as catalyst. Under these conditions the 1-butanol cleaves the ester bond between PE main chain and PBA side chain but does not cause any change in the overall composition of PBA side chain. Therefore, after the cleavage reaction the resulting polymer mixture would consist of poly(ethylene-*co*-10-undecen-1-ol) and homo-PBA. PBA was easily extracted from the mixture by dissolution in THF and used for GPC analysis. GPC traces of the resulting PBA shifted with monomer conversion to the higher molecular weight region (Figure 3). The molecular weight of side-chain PBA increased linearly with conversion and agreed with predicted molecular weight, up to >50% monomer conversion. The polydispersity index decreased with conversion and eventually reached 1.28 (Figure 4). These facts indicate that the polymerization of BA from the PE multifunctional macroinitiator was well controlled by the $\mathrm{CuCl/CuCl_2/BA_6TREN}$ catalyst complex, and approximately 10 PBA side chains with $M_{\mathrm{n}} = 2400$, 5200, and 6000 were incorporated in each linear polyethylene backbone chain with $M_{\mathrm{n}} = 36\,000$. In this manner the weight proportion of the PBA segments in the copolymer was varied from 33 to 66 wt %.

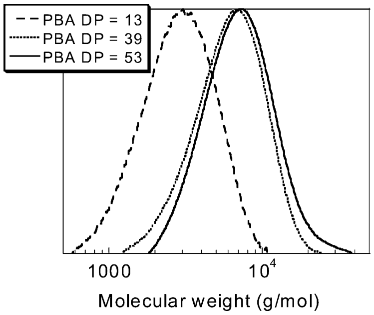


Figure 3. GPC traces of detached PBA side chain in THF. See Table 1 for polymerization conditions.

The graft copolymers, before detachment of the grafts, were analyzed by high-temperature GPC in *o*-dichlorobenzene at 145 °C. As shown in Figure 5, all GPC traces of graft copolymers were monomodal, indicating negligible homopolymerization of *n*-butyl acrylate. However, interestingly, the GPC traces of the graft copolymers essentially did not shift to higher molecular weight region with monomer conversion, and peak maxima remained almost at the same position. When molecular weight and polydispersity index were plotted vs conver-

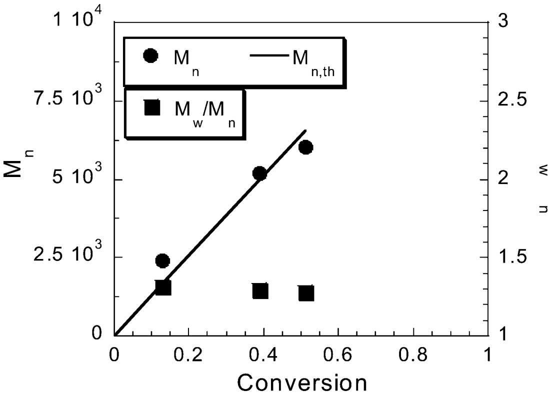


Figure 4. Evolution of M_n and M_w/M_n vs conversion of detached PBA side chain from the polymerization of BA from PE multifunctional macroinitiator. See Table 1 for polymerization conditions.

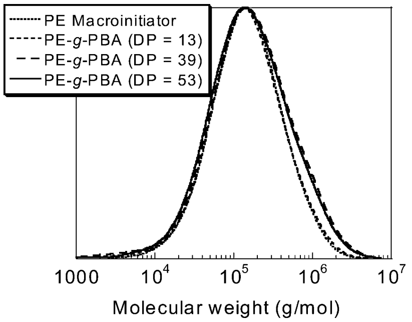


Figure 5. GPC traces of PE multifunctional macroinitiator and PE-*g*-PBA in *o*-dichlorobenzene at 145 °C. See Table 1 for polymerization conditions.

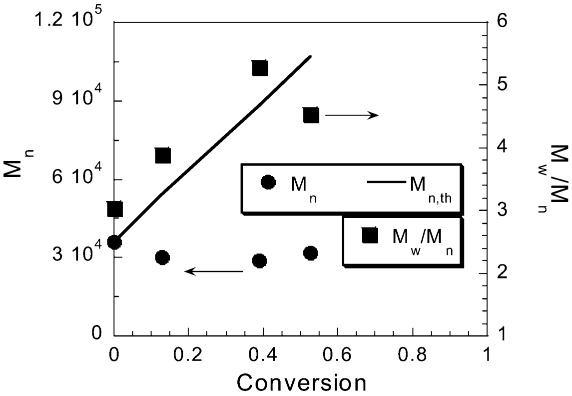


Figure 6. Evolution of M_n and M_w/M_n vs conversion for the polymerization of BA from PE multifunctional macroinitiator. See Table 1 for polymerization conditions.

sion, molecular weight did not increase with conversion but molecular weight distributions were getting broader with conversion (Figure 6). Since well-controlled polymerization was confirmed by analysis of the cleaved PBA side chains, these observations might indicate that the hydrodynamic volumes of the graft copolymer, polyethylene-*graft*-poly(*n*-butyl acrylate), in *o*-dichlorobenzene do not correlate with real molecular weights. Under these conditions the PBA side chains might aggregate intramolecularly[50] to form more compact structures as compared to original PE multifunctional macroinitiator.

^{1}H NMR spectra support formation of graft copolymers. The 300 MHz ^{1}H NMR spectrum of PE-*g*-PBA with DP = 53 in toluene-d_8 at 100 °C is presented in Figure 7. A broad singlet arising from PE segment was observed at δ = 1.38 ppm, and a set of peaks from PBA segments were also detected. From comparison of values from integration of these signals the molar ratio of ethylene monomer units to *n*-butyl acrylate monomer units was 1/0.39, close to the value 1/0.41 expected from monomer conversion data. Thus, ^{1}H NMR also supports the formation of poly(*n*-butyl acrylate) graft copolymer with polyethylene backbone.

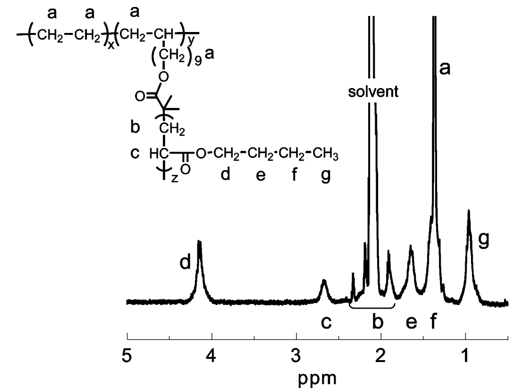


Figure 7. 300 MHz ^{1}H NMR spectra of PE-*g*-PBA (DP = 53) in toluene-d_8 at 100 °C.

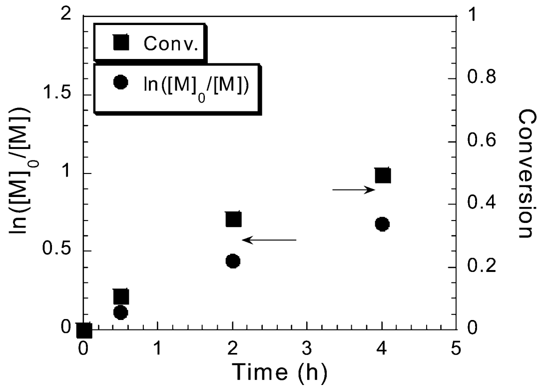


Figure 8. Kinetic plots for the polymerization of MMA from PE multifunctional macroinitiator. See Table 2 for polymerization conditions.

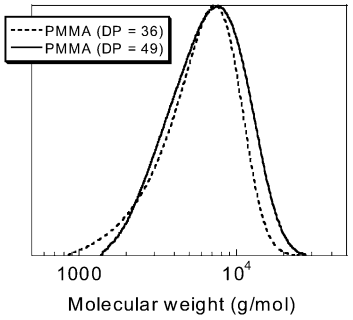


Figure 9. GPC traces of detached PMMA side chain in THF. See Table 2 for polymerization conditions.

Morphology and thermal properties of these graft copolymers will be discussed separately.

Preparation of Polyethylene-*graft*-poly(methyl methacrylate). ATRP of methyl methacrylate from the PE multifunctional macroinitiator was also investigated. First, MMA polymerization was conducted under the same conditions as BA polymerization; however, an insoluble polymer gel formed under comparable conditions after 2 h, though monomer conversion was only 44%. The concentration of growing radicals is higher in the ATRP of methacrylates than with acrylates under similar conditions. Since high polymerization temper-

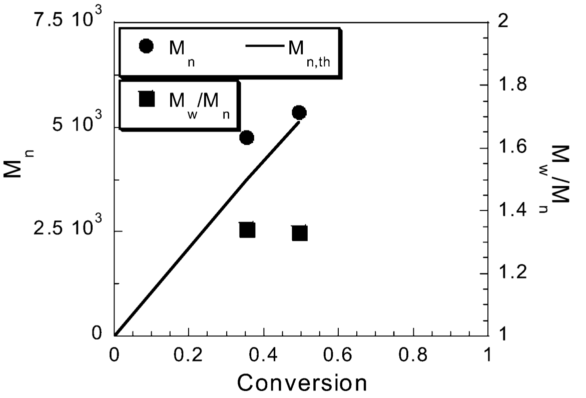


Figure 10. Evolution of M_n and M_w/M_n vs conversion of detached PMMA side chains. See Table 2 for polymerization conditions.

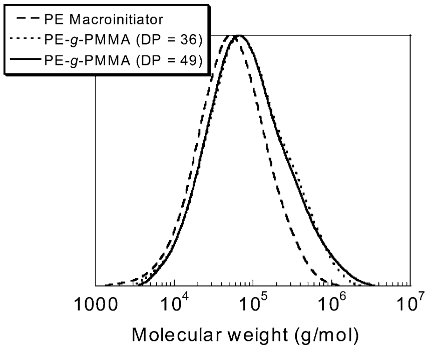


Figure 11. GPC traces of PE multifunctional macroinitiator and PE-*g*-PMMA in *o*-dichlorobenzene at 145 °C. See Table 2 for polymerization conditions.

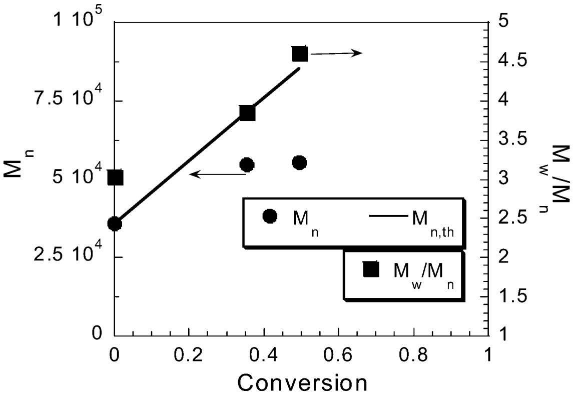


Figure 12. Evolution of M_n and M_w/M_n vs conversion for the polymerization of BA from PE multifunctional macroinitiator. See Table 2 for polymerization conditions.

ature is required to dissolve the PE multifunctional macroinitiator, polymerization was conducted under even more dilute conditions to decrease radical concentration. MMA monomer was diluted to 6 vol % in chlorobenzene solvent. However, polymerization still proceeded faster than for BA, and monomer conversion reached 49% in 4 h. First-order kinetic plots of monomer conversion vs polymerization time showed some curvature only at high monomer conversion (Figure 8). The resulting graft copolymers were soluble in hydrocarbons at high temperature. Polymer gel was formed when polymerization was continued beyond 4 h.

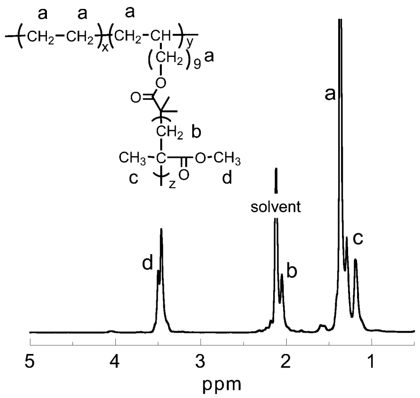


Figure 13. 300 MHz ^{1}H NMR spectra of PE-*g*-PMMA (DP = 49) in toluene-d_8 at 100 °C.

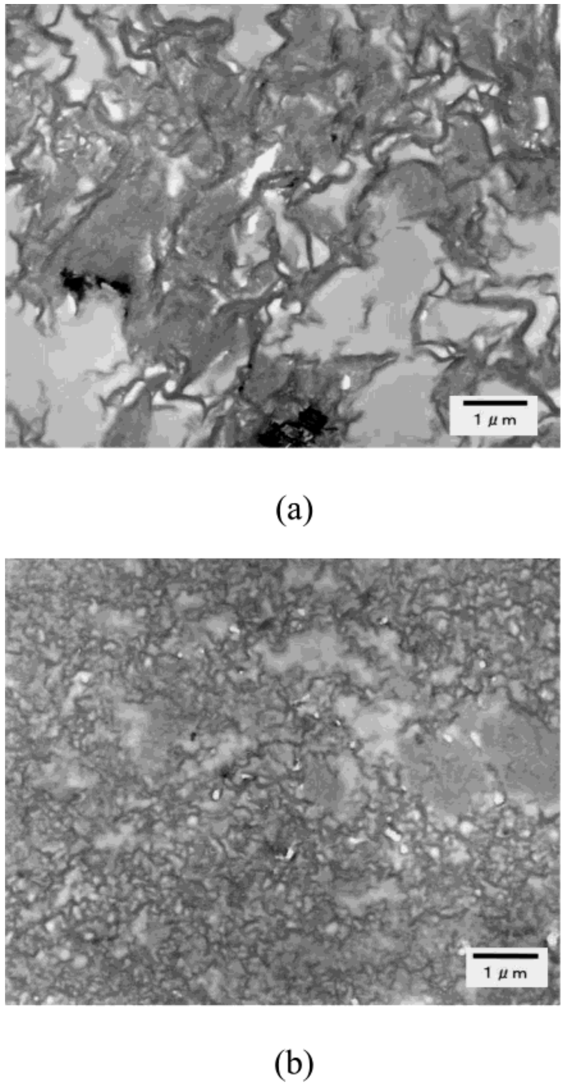


Figure 14. TEM micrographs of polymer blends: (a) PE/PMMA (4/6 weight ratio) and (b) PE/PMMA/PE-*g*-PMMA (4/6/1 weight ratio).

Side-chain PMMA analysis was also performed to confirm the well-controlled nature of the grafting-from by a procedure similar to that described for PE-*g*-PBA analysis. The detached PMMA side chains were analyzed by GPC after their cleavage from the graft copolymers using methanol, catalyzed by sodium methoxide. Molecular weights were close to predicted values (Figures 9 and 10). In contrast to the PE-*g*-PBA, high-temperature GPC traces of PE-*g*-PMMA shifted to high molecular weight region in comparison with the PE multifunctional macroinitiator. However, the molecular weight of the graft copolymers still did not agree with predicted values, perhaps due to calibration with polyethylene standards (Figures 11 and 12).

The 300 MHz ^{1}H NMR spectra of the PE-*g*-PMMA (DP = 49) in toluene-d_8 at 100 °C in Figure 13 shows the presence of both a PE segment and a PMMA segment. The broad singlet at $\delta = 1.38$ ppm was assigned to the methylene protons of PE segments, and a set of peaks from PMMA segments was also observed. The molar ratio of ethylene monomer units to methyl methacrylate monomer units was 1/0.36, in agreement with a ratio of 1/0.38 expected from monomer conversion data.

Although the polymerization was less controlled than for BA, a PE-*g*-PMMA was successfully synthesized through grafting-from polymerization of MMA via ATRP using a linear PE multifunctional macroinitiator.

Polyethylene-*graft*-poly(methyl methacrylate) as a Compatibilizer in a Polymer Blend. One of the possible applications for a graft copolymer having both nonpolar and polar segments is a compatibilizer for immiscible polymers. The PE-*g*-PMMA (DP = 49) was evaluated as compatibilizer for a blend of PE (M_n = 15 000, M_w/M_n = 2.27) and PMMA (M_n = 23 500, M_w/M_n = 1.52). PE and PMMA were blended at 4/6 weight ratio, and 10 wt % of PE-*g*-PMMA was added as a compatibilizer. Phase separation was observed using transmission electron microscopy (TEM). Parts a and b of Figure 14 show the TEM images of PE/PMMA polymer blends in the absence and presence of PE-*g*-PMMA, respectively. A comparison of the images shows that the sizes of both PE and PMMA domains were reduced by the addition of PE-*g*-PMMA. Although further optimization of the microstructure of the graft copolymer could be necessary,[37] these results indicate the potential of these graft copolymers for compatibilizer applications.

Conclusions

Polyethylene-*graft*-poly(*n*-butyl acrylate) and polyethylene-*graft*-poly(methyl methacrylate) were successfully synthesized by the combination of metallocene-catalyzed olefin copolymerization and ATRP of (meth)-acrylate. Poly(ethylene-*co*-10-undecen-1-ol) was a suitable building block for preparation of graft copolymers having a linear polyethylene backbone. The key for success in the controlled ATRP of acrylate and methacrylate monomers from the PE multifunctional macroinitiator was a combination of low monomer concentration and halogen exchange. The PE-*g*-PMMA acts as a compatibilizer for immiscible PE/PMMA polymer blends. These nonpolar/polar hybrid polymers are promising materials heralding a new generation of polyolefin-based copolymers.

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