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Synthesis of Polyethylene-*g*-polystyrene and Polyethylene-*g*-poly(*p*-methylstyrene) Graft Copolymers

T. C. Chung,* H. L. Lu, and R. D. Ding

Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802

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ABSTRACT: This paper describes a new method to prepare polyethylene graft copolymers, such as polyethylene-*g*-polystyrene and polyethylene-*g*-poly(*p*-methylstyrene), with a relatively well-controlled reaction mechanism. The chemistry involves a transformation process from the metallocene copolymerization of ethylene and *p*-methylstyrene to the anionic living polymerization of styrene or *p*-methylstyrene. The metallocene catalysis produces poly(ethylene-*co*-*p*-methylstyrene) random copolymers with molecular weight distribution ($\bar{M}_w/\bar{M}_n$) of about 2.5. The following selective metalation reaction of *p*-methylstyrene units in the copolymer and the subsequent anionic "living" graft-from polymerization were effective to produce polymeric side chains with well-defined structure. Both graft density and graft length can be controlled by *p*-methylstyrene content in the PE backbone, metalation reagent, and the quantity of monomer used in the graft-from reaction. In the bulk, the individual PE and PS segments in the graft copolymers are phases-seperated to form crystalline PE domains and amorphous PS domains. The microscopy studies reveal the effectiveness of PE-*g*-PS in the polymer blends by reducing the phase sizes, improving the dispersion, and increasing interfacial interaction between domains.

Introduction

Despite their commercial importance, the lack of reactive groups in high density polyethylene (HDPE) and linear low density polyethylene (LLDPE) has limited some of their end uses, particularly where interaction with other materials is paramount. The use of graft and block copolymers as emulsifiers and interfacial compatibilizers[1,2] is an established technique to improve polymer interaction and morphology in polymer blends. In general, the chemistry to prepare polyolefin graft copolymers is very limited both in the direct and post-polymerization processes. Some considerable efforts have been devoted to the preparation of polyethylene-*g*-polystyrene (PE-*g*-PS) copolymers by radiation[3−6] of PE films in the presence of styrene monomers. In most cases, the products were not well-characterized, especially the microstructure of the resulting graft copolymer. As can be expected, this free radical process produced considerable amounts of ungrafted homopolymers and potentially some cross-linking products. Both graft density and graft length were very difficult to control. On the other hand, the direct copolymerization[7] of ethylene and PS macromonomer (α-olefin-terminated polystyrene) by Ziegler−Natta catalyst also encountered some problems, such as the large difference in the reactivity ratios between ethylene and macromonomer, the diffusion limitation of macromonomer, and the purity of macromonomer (i.e. α-olefin-terminated polystyrene). In general, the incorporation of polystyrene (graft efficiency) is inversely proportional to the molecular weight of the polymer.

It has also been reported that the diblock copolymer of polyethylene-*b*-polystyrene[8] was prepared by a transformation reaction from anionic to Ziegler−Natta polymerization mechanisms. The living anionic polystryrene (capped with several butadiene units) was used as the alkylating agent in the production of a Ziegler−Natta catalyst which was then used to synthesize polyethylene block. Usually, less than 33% of the diblock copolymers were formed in this process.

In our general approach to the preparation of polyolefin graft copolymers, we have adopted the transformation process via the reactive polyolefins.[9−11] In other words, the process involves the transition metal (metallocene and Ziegler−Natta) copolymerization to produce polyolefin copolymer containing reactive comonomer units which can be transformed to initiators for graft-from polymerization. To be successful, the transformation reaction must be effective and selective to produce the initiation sites only in the comonomer units of the polyolefin backbone. In addition, the resulting polymeric initiators must be sufficiently stable (or "living") for the following graft-from polymerization which is essential to prevent side reactions, such as cross-linking and homopolymerization.

In our previous papers, we have described a novel method[9] to prepare polyolefin graft copolymers by using borane-containing polyolefins and the borane/O_2 free radical graft-from reaction. The "stable" radical polymerization[12] was very effective for the functional monomers containing oxygen and nitrogen atoms, such as methyl methacrylate, vinyl acetate, and acrylonitrile, and produced graft copolymers with minimum side reactions. However, this chemistry is inefficient in the graft-from reaction of pure hydrocarbon monomers, such as styrene and its derivatives. The B/O and B/N coordinations may play an important role during the propagation reaction. In this paper, we will introduce a complementary method to prepare polyolefin graft copolymers, i.e., polyethylene-*g*-polystyrene and polyethylene-*g*-poly(*p*-methylstyrene).

Results and Discussion

The chemistry to prepare polyethylene graft copolymers involves three steps as shown in eq 1. First, the backbone polymer (**I**), i.e. poly(ethylene-*co*-*p*-methylstyrene), was prepared by metallocene catalysts. The use of catalysts with constrained ligand geometry, such as $[C_5Me_4(SiMe_2N\text{-}t\text{-}Bu)]TiCl_2$ and $Et(Ind)_2ZrCl_2$, produced the random copolymer with molecular weight distribution ($\bar{M}_w/\bar{M}_n$) of about 2.5. Secondly, the transformation

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* Author to whom all correspondence should be addressed.

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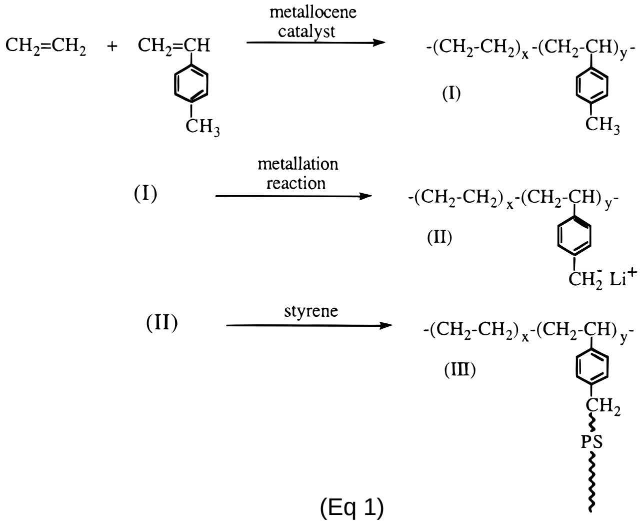


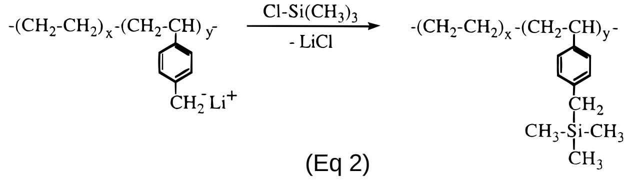
(Eq 1)

reaction from metallocene to anionic processes was carried out by a metalation reaction of *p*-methylstyrene units with *s*-butyllithium/TMEDA (tetramethylethylenediamine) complex. Despite the heterogeneous condition, the reaction was selective and effective to achieve more than 65% conversion. In fact, the heterogeneous reaction condition provides the advantage of convenient removal of the unreacted reagents from the metalated polymer (**II**). Finally, the addition of styrene or *p*-methylstyrene to the suspended metalated polymer started the “living” anionic graft-from polymerization to form graft copolymer (**III**) with well-defined side chains, i.e. designed graft density and graft length with narrow molecular weight distribution.

Synthesis of Poly(ethylene-*co*-*p*-methylstyrene) (P[E-*co*-(*p*-MS)]). In the copolymerization reaction, p-methylstyrene comonomer exhibits excellent incorporation[13] with ethylene by using metallocene catalyst, i.e. $[C_5Me_4(SiMe_2N\text{-}t\text{-}Bu)]TiCl_2$ and $Et(Ind)_2ZrCl_2$, with constrained ligand geometry. The spatial opening at the active site and the cationic coordination mechanism provide favorable conditions for the copolymerization reactions. Usually, more than 80% of p-methylstyrene was converted to copolymer within 1 h. Both DSC and ^{13}C NMR results showed the random distribution[14] of *p*-methylstyrene units in the copolymer structure. A complete range of copolymer compositions can be prepared by controlling the comonomer ratio. However, in the preparation of graft copolymers, the P[E-*co*-(*p*-MS)] with very low (<1 mol %) *p*-methylstyrene content was preferred as the starting material, because it will produce the graft copolymer with a long consecutive sequence of ethylene units in the backbone. It is very desirable to preserve the PE backbone with high melting point and high crystallinity, similar to those of HDPE, to assure the effective cocrystallization in polymer blends (will be discussed later). In this study, a P[E-*co*-(*p*-MS)] copolymer containing 0.9 mol % of *p*-methylstyrene was used in the preparation of all graft copolymers. This P[E-*co*-(*p*-MS)] copolymer has molecular weight and molecular weight distribution ($\bar{M}_w/\bar{M}_n$), determinated by high temperature GPC measurements, of about 100 000 g/mol and 2.5, respectively.

Metalation Reaction. One major advantage of the *p*-methylstyrene-containing copolymers is the versatility[15,16] of the benzylic protons in the *p*-alkylstyrene unit, which can be converted to various functional groups under mild reaction conditions. The lithiation reaction[17,18] took place by mixing poly(ethylene-*co*-*p*-methylstyrene) powder with excess alkyllithium, such as *s*- and *n*-BuLi/TMEDA, at 60 °C for a few hours. The unreacted reagents can be easily removed by filtration and washing the lithiated PE powders with hexane a few times. It is interesting to note that the heterogeneous condition allows the easy removal of excess reagent, which was impossible under the homogeneous conditions, such as in the case of poly(isobutylene-*co*-*p*-methylstyrene).[19] The unreacted alkyllithium complex is much more reactive than benzylic lithium and can produce a lot of undesirable ungrafted homopolymers during the graft-from reaction.

To study the efficiency of the lithiation reaction, some of the lithiated polymer was converted to organosilane-containing polymer by reacting with chlorotrimethylsilane as shown in eq 2.



(Eq 2)

A slight molar excess of chlorotrimethylsilane was used to assure the complete reaction. Figure 1 compares the ^1H NMR spectra of the starting P[E-*co*-(*p*-MS)], containing 0.9 mol % of *p*-methylstyrene, and the resulting trimethylsilane-containing PE copolymers, which had been metalated by either *s*- or *n*-BuLi/TMEDA, respectively, under the same reaction conditions.

In Figure 1a, in addition to the major chemical shift at 1.35 ppm, corresponding to CH_2, there are three minor chemical shifts around 2.35, 2.5, and 7.0−7.3 ppm, corresponding to CH_3, CH, and aromatic protons in *p*-MS units, respectively. After the functionalization reaction, Figure 1b,c show the reduction of peak intensity at 2.35 ppm and no detectable intensity change at both 2.5 and 7.0−7.3 ppm chemical shifts. In addition, two new peaks at 0.05 and 2.1 ppm, corresponding to $Si\text{-}(CH_3)_3$ and $\phi\text{-}CH_2\text{-}Si$, are observed. Overall, the results indicate a “clean” and selective metalation reaction at the *p*-methyl group. The integrated intensity ratio between the chemical shift at 0.05 ppm and the chemical shifts between 7.0 and 7.3 ppm and the number of protons both chemical shifts represent determines the efficiency of the metalation reaction. The *n*-butyllithium/TMEDA converted only 24 mol % of *p*-methylstyrene to benzyllithium. On the other hand, the *s*-butyllithium/TMEDA was much more effective, achieving 67 mol % conversion. Apparently, the metalation reaction was not inhibited by the insolubility of polyethylene; most of the *p*-MS units must be located in the amorphous phases which are swellable by the appropriate solvent during the reaction. Both DSC and GPC studies, by comparing copolymer samples before and after functionalization reaction, indicate no significant change in the melting point and the molecular weight, respectively.

Anionic “Living” Graft-from Polymerization. Most of the lithiated PE powder was suspended in cyclohexane before addition of styrene or *p*-methylstyrene. The living anionic polymerization took place at room temperature, similar to the well-known solution anionic polymerization.[20] To assure sufficient time for monomer diffusion in the heterogeneous condition, the reaction continued for 1 h before terminating by the addition of methanol. The conversion of monomers

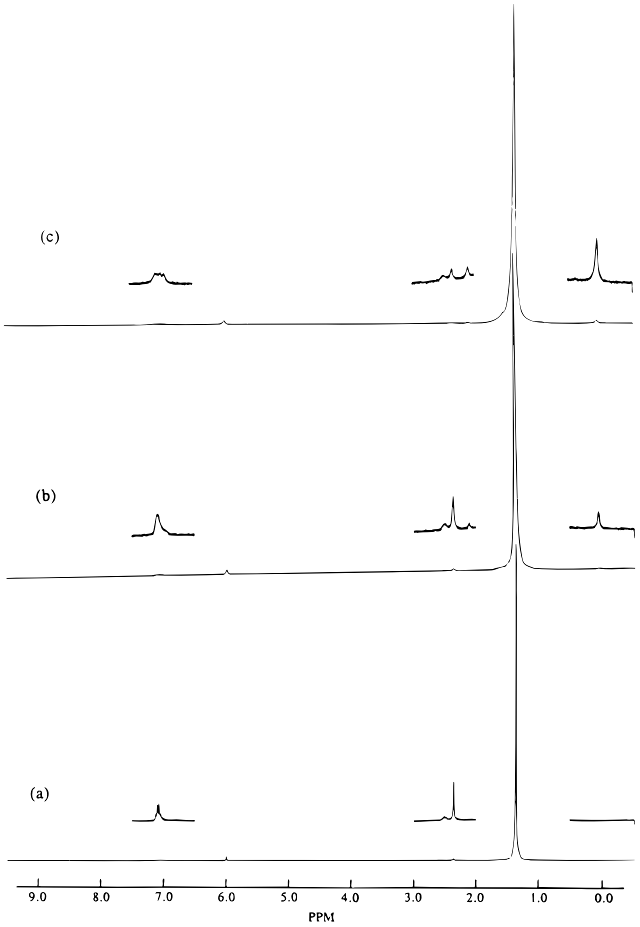


Figure 1. The comparison of ^{1}H NMR spectra of (a) poly(ethylene-*co*-*p*-methylstyrene) with 0.9 mol % of *p*-methylstyrene and two corresponding trimethylsilyl derivatives prepared via lithiation reactions using (b) *n*-BuLi/TMEDA and (c) *s*-BuLi/TMEDA reagents.

(estimated from the yield of graft copolymer) was almost quantitative (>90%) in 1 h. The reaction mixture was usually subjected to a vigorous extraction process, by refluxing THF through the sample in a Soxhlet extractor for 24 h, to remove any polystyrene or poly(*p*-methylstyrene) homopolymers. In all cases, only a small amount (<10%) of the THF-soluble fraction was obtained. The THF-insoluble fraction is mainly PE graft copolymer and is completely soluble in xylene at elevated temperature. Figure 2 shows the ^{1}H NMR spectra of three PE-*g*-PS copolymers.

Compared with the ^{1}H NMR spectrum of the starting P[E-*co*-(*p*-MS)] shown in Figure 1a, three additional chemical shifts arise at 1.55, 2.0, and 6.4−7.3 ppm, corresponding to CH_2, CH, and aromatic protons in polystyrene. The quantitative analysis of copolymer composition was calculated by the ratio of two integrated intensities between aromatic protons ($\delta = 6.4-7.3$ ppm) in PS side chains and methylene protons ($\delta = 1.35-1.55$ ppm) and the number of protons both chemical shifts represent. Parts a, b, and c of Figure 2 indicate 25.6, 38.1 and 43.8 mol % of PS, respectively, in PE-*g*-PS copolymers. On the other hand, the ^{1}H NMR spectra of three polyethylene-*g*-poly(*p*-methylstyrene) (PE-*g*-PMS) copolymers are shown in Figure 3.

Four new chemical shifts around 1.55, 1.95, 2.35, and 6.4−7.0 ppm, corresponding to CH_2, CH, CH_3, and aromatic protons in PMS side chains, are observed in all three PE-*g*-PMS copolymers. The concentration of PMS was determined by the intensity ratio of two chemical shifts, $\delta = 1.35-1.55$ ppm for methylene protons and $\delta = 6.4-7.0$ ppm for aromatic protons in the side chains, and the number of protons both chemical shifts represent. Parts a, b, and c of Figure 3 indicate three PE-*g*-PMS copolymers containing 13.8, 27.9, and 37.2 mol % of PMS, respectively.

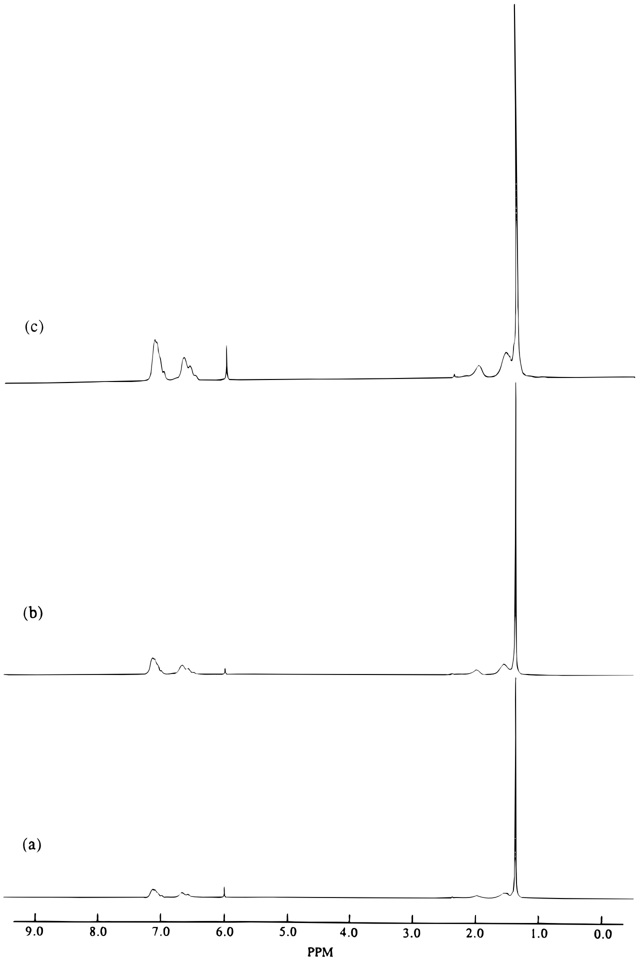


Figure 2. The ^{1}H NMR spectra of PE-*g*-PS copolymers, containing (a) 25.6, (b) 38.1, and (c) 43.8 mol % of polystyrene.

Table 1 summarizes the experimental conditions and results of three sets of comparative graft-from reactions, all of them were started from the same P[E-*co*-(*p*-MS)] copolymer, containing 0.9 mol % of *p*-MS. The runs A1−3 are the same three graft copolymers shown in Figure 2 and the runs C1−3 are the same graft copolymers shown in Figure 3.

Both yield and graft composition (PS or PMS content) of the graft copolymer are basically proportional to the quantity of monomers used in the graft-from reaction. The good control of graft copolymer formation is obviously due to the living anionic polymerization which effectively converts monomers to the grafted side chains. The graft density is defined as the number of grafted side chains per 1000 repeating methylene units of the polyethylene backbone. Since this process involves living anionic polymerization and fast initiation, it is reasonable to assume that each benzylic lithium produces one PS side chain and that the side chains have a narrow molecular weight distribution. Therefore, the graft density is the same as the density of benzylic anions and can be calculated by a simple equation shown below:

Table 1. A Summary of PE-*g*-PS and PE-*g*-PMS Graft Copolymers

run no.	reaction conditions [a]		graft copolymers						
	PE$^-$-Li$^+$,[b] g	ST/*p*-MS, g	yield, g	graft composition PS or PMS, mol % (wt.%)	graft density, # of graft/1000 C of backbone	graft length, 10^3 g/mol	T_g, °C	T_m, °C	ΔH_f, J/g of graft (J/g of PE)
	starting material [c]			0	0	0		127.8	199.0 (199.0)
A1	1.0	ST/1.7	2.30	25.6 (56.1)	0.8	23.4	103.6	121.9	60.6 (138.0)
A2	1.0	ST/2.9	3.30	38.1 (69.6)	0.8	41.4	103.8	120.3	41.7 (137.2)
A3	1.0	ST/4.0	3.90	43.8 (74.3)	0.8	52.2	103.0	120.9	31.1 (121.0)
B1	1.0	ST/1.4	2.00	20.5 (48.9)	2.0	6.99	84.6	126.6	99.6 (195.0)
B2	1.0	ST/2.3	2.50	27.4 (58.4)	2.0	10.5	91.9	123.2	80.4 (193.1)
B3	1.0	ST/4.2	4.42	47.8 (77.3)	2.0	23.9	103.7	120.3	25.4 (111.9)
C1	0.58	*p*-MS/0.50	0.92	13.8 (40.3)	2.0	4.10			
C2	0.60	*p*-MS/1.43	1.60	27.9 (62.0)	2.0	11.6	80.0	121.4	70.7 (186.0)
C3	0.60	*p*-MS/2.60	2.10	37.2 (71.4)	2.0	17.5	102.0	121.4	34.2 (119.6)

[a] Solvent, anhydrous cyclohexane (30 mL/g PE); reaction time, 1 h; reaction temperature, 25 °C. [b] PE$^-$-Li$^+$ = lithiated polyethylene. In A1−A3, *n*-BuLi/TMEDA was used as the lithiation reagent; the efficiency[21] of lithiation was 17.8%, as confirmed by ^{1}H NMR after converted into a $Si(CH_3)_3$ group. In B1−B3 and C1−C3, *s*-BuLi/TMEDA was used as the lithiation reagent; the efficiency[21] of lithiation was 45.8%, as confirmed by ^{1}H NMR after converted into a $Si(CH_3)_3$ group. [c] The starting material was poly(ethylene-*co*-*p*-methylstyrene) with 0.90 mol % of *p*-MS, $\bar{M}_w$ = 100 000 g/mol, $\bar{M}_w/\bar{M}_n$ = 2.5.

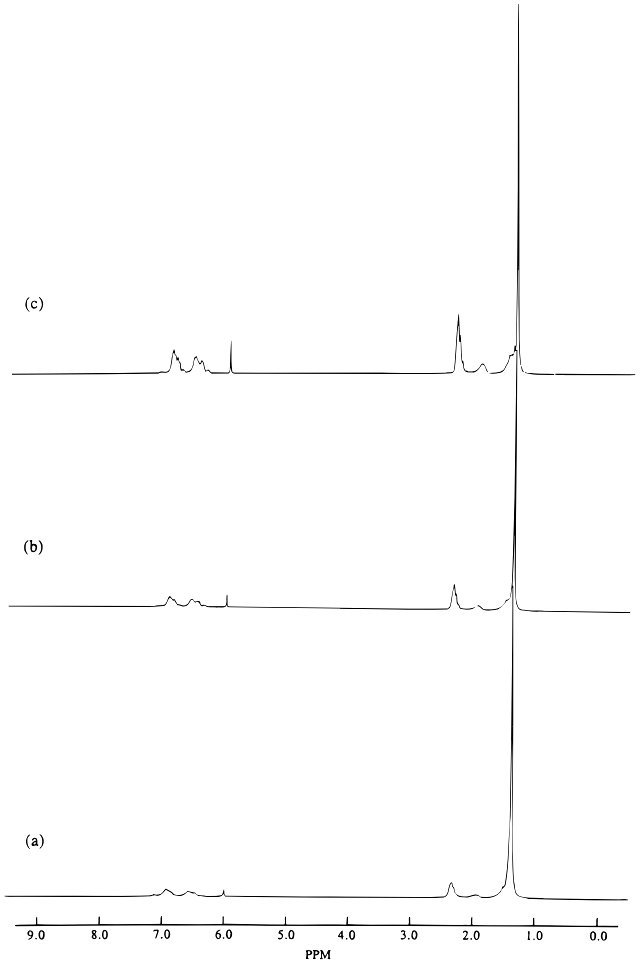


Figure 3. The ^{1}H NMR spectra of polyethylene-*g*-poly(*p*-methylstyrene) copolymers, containing (a) 13.8, (b) 27.9, and (c) 37.2 mol % of poly(*p*-methylstyrene).

$$\text{graft density} = \frac{(\text{mol of } p\text{-MS}) \times (\text{efficiency of metalation})}{2} \times 10$$

In sets A, B and C, the graft densities are about 0.8, 2 and 2, which in average correspond to about 2.5, 6 and 6 side chains per PE backbone, respectively. Under the same assumption of living anionic graft-from polymerization, the graft length (defined as the average molecular weight of the side chain) can be estimated by the following equation.

$$\text{graft length (g/mol)} = \frac{(\text{wt of graft copolymer}) - [\text{wt of starting P(E-}co\text{-}p\text{-MS)}]}{\text{mol of benzylic lithium}}$$

The molecular weight of side chain is inversely proportional to the degree of metalation and proportional to the quantity of monomer used in the graft-from polymerization.

Overall, this chemistry provides a very useful route to prepare PE-*g*-PS and PE-*g*-PMS copolymers with relatively well-defined molecular structures, i.e. relatively narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 2.5) of backbone and well-defined side chains. All important factors in a graft copolymer, including graft density, graft length, and copolymer composition, can be controlled during the reaction processes.

Thermal Properties. The graft copolymers were analyzed by DSC thermogram to study their thermal properties. Figure 4 compares the DSC curves of the starting P[E-*co*-(*p*-MS)] and three PE-*g*-PS copolymers (runs B1−3 in Table 1), which have the same graft density and different graft length. All samples were measured with the same weight and were given the same thermal treatment by heating at 20 °C/minute.

In Figure 4a, the endotherm peak at 127.8 °C is clearly due to the melting point (mp) of crystalline PE. It is interesting to note that as the PS graft length increases, the mp of PE only slightly decreases. The sample B3, containing 47.8 mol % (77.3 wt %) of PS, still shows the mp at 120.3 °C. On the other hand, the heat of fusion (ΔH_f = J/g of graft copolymer) is very dependent on the PS or PMS graft chain length as shown in Table 1. In samples B1, B2, and C1, with the graft chain length $< 12 \times 10^3$ g/mol, the heat of fusion after normalizing with the content of PE (ΔH_f = J/g of PE) in each case is very similar to that of pure PE sample despite relatively high PS or PMS contents (48.9, 58.4, and 62.0 wt %, respectively). The simple dilution effect seems to govern the heat of fusion in the graft copolymers. However, in samples A1−3, B3, and C3, with the graft length $> 17 \times 10^3$ g/mol, the additional disorder associated with long grafted side chains becomes significant. So far, there is no theoretical explanation for the graft chain length effect to the crystallinity of the PE backbone. The glass transition temperature (T_g) of PS was also observed in Figures 4

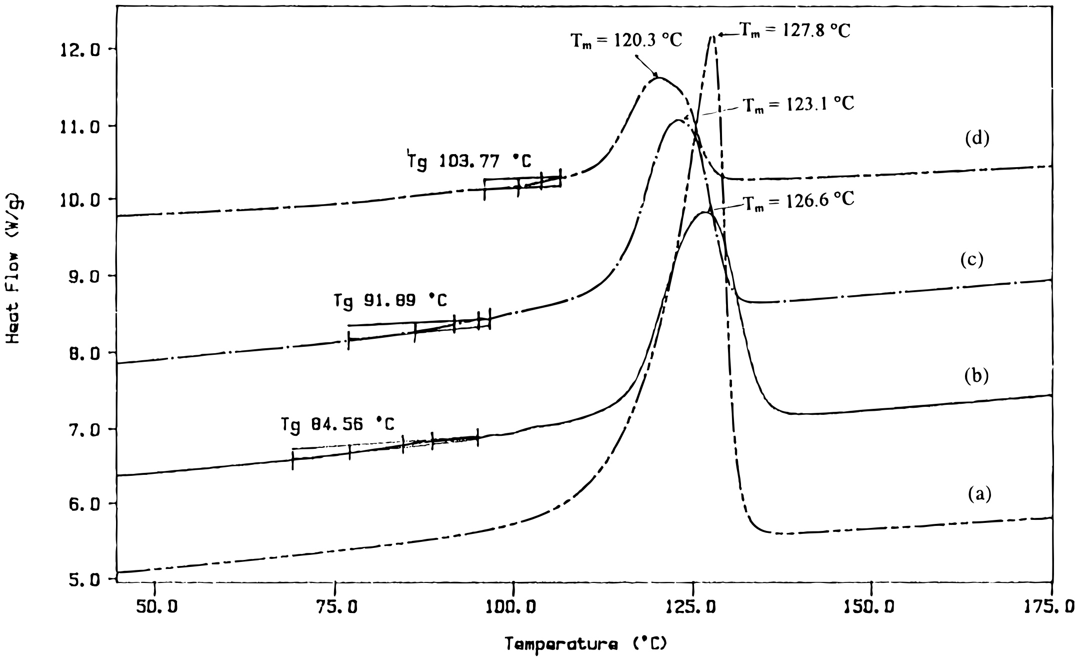


Figure 4. DSC curves comparison between (a) starting poly(ethylene-*co*-*p*-methylstyrene) and three PE-*g*-PS copolymers, containing (b) 20.5, (c) 27.4, and (d) 47.8 mol % of polystyrene.

(b), (c) and (d). As the molecular weight of PS in the graft copolymer increases, so does the T_g. The T_g becomes constant when the graft length exceeds 15 × 10^3 g/mol. Overall, the results indicate that both the PE and PS domains are phase-separated.

PE/PS Polymer Blends. It is interesting to study the compatibility of PE-*g*-PS copolymer in HDPE and PS blends. Polarized optical microscope and the SEM were used to examine the surfaces and bulk morphologies, respectively. Two blends comprised of overall 50/50 weight ratio of PE and PS, one is a simple mixture of 50/50 between HDPE and PS and the other is 45/45/10 weight ratio of HDPE, PS, and PE-*g*-PS (containing 50 mol % of PS). Figure 5 compares the polarized optical micrographs of two blends which were prepared by casting chlorobenzene solutions of the polymer mixtures on glass slides.

The optical patterns are very different. A gross phase separation in Figure 5a shows the spherulitic PE and the amorphous PS phases. The PS phases vary widely in both size and shape due to the lack of interaction with the PE matrix. On the other hand, the continuous crystalline phase in Figure 5b shows the compatibilized blend. Basically, the large phase-separated PS domains are now dispersed into the interspherulite regions and cannot be resolved by the resolution of the optical microscope. The graft copolymer behaving as a polymeric emulsifier increases the interfacial interaction between the PE crystalline and the PS amorphous regions to reduce the domain sizes.

Figure 6 shows the SEM micrographs, operating with secondary electron imaging, which show the surface topography of cold-fractured film edges. The films were cryofractured in liquid N_2 to obtain an undistorted view representative of the bulk material.

In the homopolymer blend, the polymers are grossly phase-separated, as can be seen by the PS component which exhibits nonuniform, poorly dispersed domains and voids at the fracture surface, as shown in Figure 6a. This "ball and socket" topography is indicative of poor interfacial adhesion between the PE and PS domains and represents PS domains that are pulled out of the PE matrix. Such pull out indicates that limited stress transfer takes place between phases during fracture. The similar blend containing graft copolymer shows a totally different morphology in Figure 6b. The material exhibits flat mesa-like regions similar to pure PE. No distinct PS phases are observable, indicating that fracture occurred through both phases or that the PS phase domains are too small to be observed. The PE-*g*-PS is clearly proven to be an effective compatibilizer in PE/PS blends.

Experimental Details

Instrumentation and Materials. All ^{1}H NMR spectra were recorded on a Bruker AM 300 instrument in 1,1,2,2-tetrachloroethane-d_2 at 110°C. DSC analysis were carried out by using a Perkin-Elmer DSC-7 instrument. The measurements were run from 30 to 180 °C with the heating rate of 20 °C/min. In the optical microscopy studies, the samples were observed and photographed with an Olympus BH2 microscope under cross polarizers mounted with a 35-mm C-35A-4 camera and an Olympus AD Systems exposure control unit. The samples were prepared by casting thin films onto glass microscope slides and covering with a cover slip. The PE-based polymers were usually cast from dilute solution of hot xylene or chlorobenzene. Scanning electron microscopy was used to view some of the polymer films with a Topcon International Scientific Instruments ISI-SX-40 using secondary electron imaging. SEM samples were prepared from films cryofractured in liquid N_2. Samples were mounted on an aluminum stub and carbon coated to form a conductive coating.

All O_2 and moisture sensitive manipulations were carried out inside of an argon-filled Vacuum Atmosphere drybox. Hexane and toluene were distilled over CaH_2 under argon. Anhydrous cyclohexane (Aldrich) was used as received. All three solvents were stored in the drybox. Both catalysts, $[C_5Me_4(SiMe_2N\text{-}t\text{-}Bu)]TiCl_2$ and $Et(Ind)_2ZrCl_2$, were prepared by the published procedures.[22,23] Methylaluminoxane (MAO) (Ethyl) and *n*- and *s*-BuLi (Aldrich) were purchased and used as received.

Copolymerization of Ethylene and *p*-Methylstyrene. In a typical ethylene copolymerization condition, the comonomer (i.e. *p*-methylstyrene) was mixed with solvent (toluene or hexane) and the methylaluminoxane (MAO) (30 wt % in toluene) needed in a Parr 450 mL stainless autoclave equipped

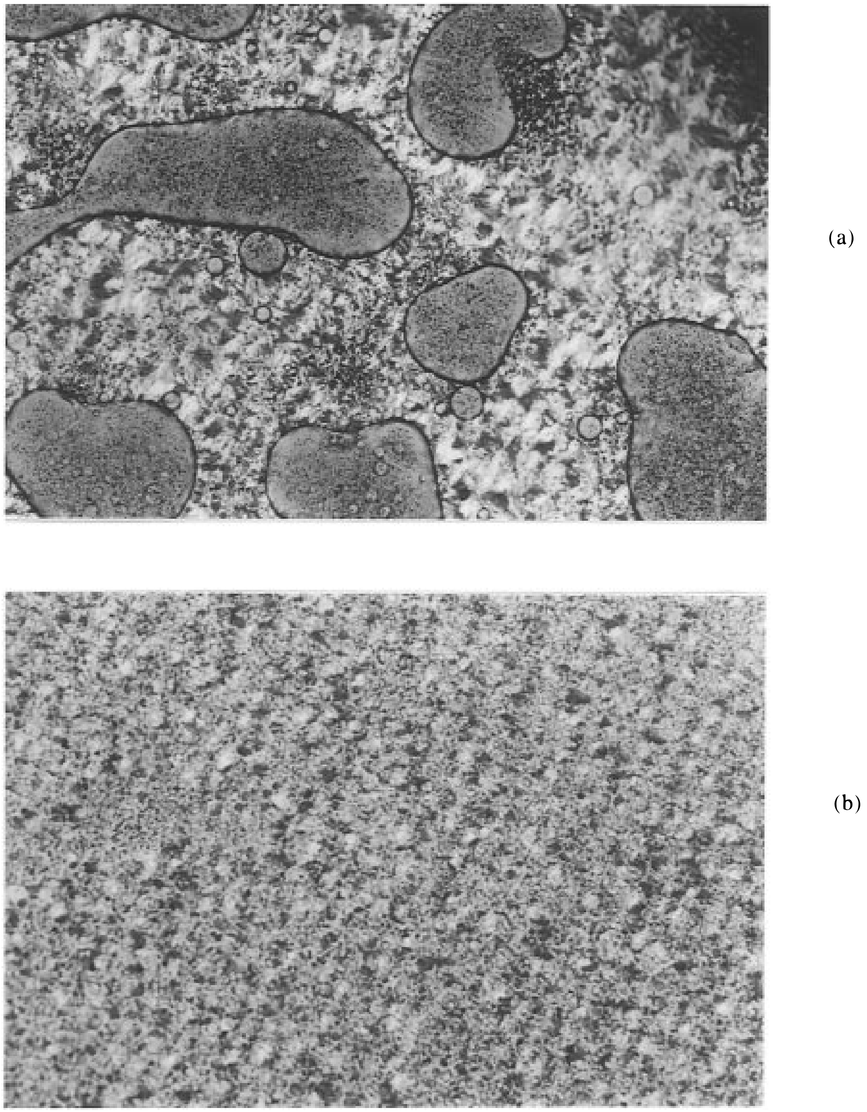


Figure 5. Polarized optical micrographs of polymer blends: (a) two homopolymers with PE/PS = 50/50 (100×) and (b) two homopolymers and PE-*g*-PS copolymer with PE/PE-*g*-PS/PS = 45/10/45 (100×).

with a mechanical stirrer. The sealed reactor was then saturated with 3.1×10^5 Pa (45 psi) ethylene gas at 50 °C before adding catalyst solution, $Et(Ind)_2ZrCl_2$ in toluene, to initiate the polymerization. Additional ethylene was fed continuously into the reactor by maintaining a constant pressure of about 3.1×10^5 Pa during the whole course of the polymerization. After 60 min, the reaction was terminated by adding 100 mL of dilute HCl solution in MeOH. The polymer was isolated by filtering and washed completely with MeOH and dried under vacuum at 50 °C for 8 h.

Lithiation and Silylation Reactions of Poly(ethylene-*co*-*p*-methylstyrene). In an argon filled drybox, 5 g of poly(ethylene-*co*-*p*-methylstyrene) with 0.9 mol % of *p*-methylstyrene (1.56 mmol) was suspended in 80 mL of cyclohexane in a 250 mL air-free flask with a magnetic stirer bar, 6 mL (7.8 mmol) of 1.3 M *s*-BuLi solution and 2 mL (13.0 mmol) of TMEDA were added to the flask, the flask was then brought out of the drybox and heated up to 60 °C for 4 h under N_2, the reaction was then cooled down to room temperature and moved back to the drybox. The resulting polymer was filtered and washed with cycohexane a few times. A yellow lithiated polymer powder was obtained. To study the degree of metalation reaction, some (~1 g) of the lithiated polymer was suspended in 20 mL of dry THF, 0.5 g of Me_3SiCl was added, and the mixture was stirred at room temperature for 2 h. The resulting polymer was then filtered and washed with THF, methanol, water, and methanol, then was dried under vacuum. The ^1H NMR spectrum shows a strong peak at 0.05 ppm corresponding to the methyl proton next to Si.

Graft-from Reaction. Before the graft-from reaction, the lithiated polyethylene copolymer was washed repeatedly with anhydrous cyclohexane (in an argon-filled drybox) until decoloration of filtrate and then was dried under vacuum. Such a purification process assures the complete removal of the unreacted BuLi, which could produce homopolymer. Typically, about 1 g of yellow polymer powder was then suspended in 100 mL of anhydrous cyclohexane, and the graft-from reactions were carried out at ambient temperature in slurry solution by reacting the lithiated polyethylene copolymer with anionic polymerizable monomers, such as styrene and *p*-methylstyrene, with various quantities as shown in Table 1. After 1 h, 10 mL of methanol was added to terminate the graft-from reaction. The precipitated polymer was filtered and then subjected to fractionation. A good solvent (THF) for PS side chain polymers was used during the fractionation, using a Soxhlet apparatus under N_2 for 24 h. The soluble fractions were isolated by vacuum-removal of solvent. Usually, the total soluble fractions were less than 10% of the product. The major insoluble fraction was PE graft copolymer, which was completely soluble in xylene or 1,1,2,2-tetrachloroethane at elevated temperatures.

Polymer Blending. All the blends were prepared in solution to obtain molecular level mixing. The PE was first dissolved in refluxing chlorobenzene inhibited with butylated hydroxytoluene (BHT) and kept under a N_2 blanket to prevent oxidation. The PE-*g*-PS and PS were then slowly added to the hot solution. After the polymer mixture had formed a clear, homogeneous solution, the blend was precipitated into

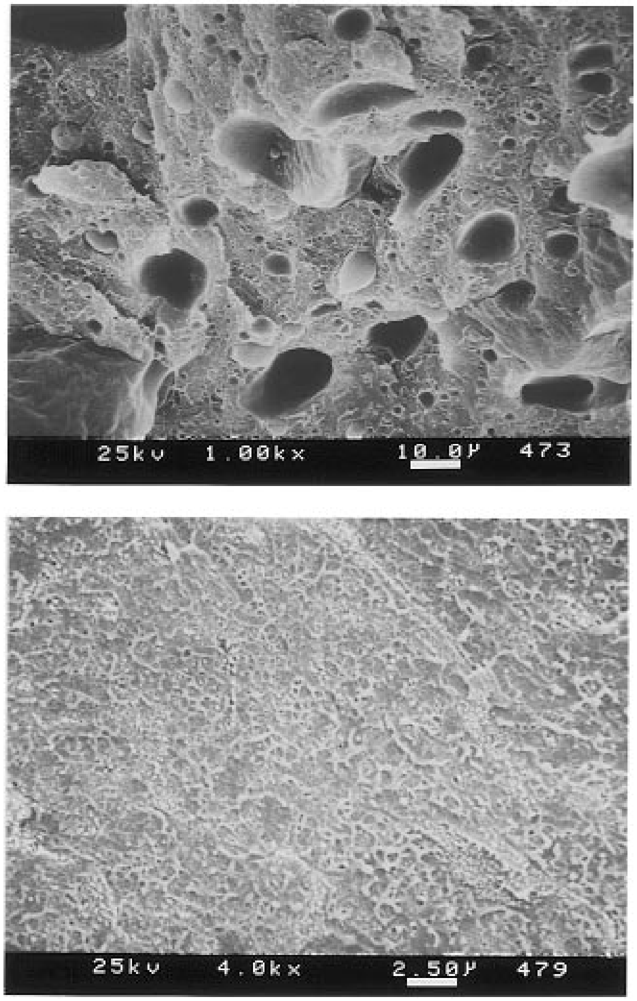


Figure 6. SEM micrographs of the cross-section of two polymer blends: (a) two homopolymers with PE/PS = 50/50 (1000×) and (b) two homopolymers and PE-*g*-PS copolymer blend with PE/PE-*g*-PS/PS = 45/10/45 (4,000×).

cold hexane. The blend was dried under vacuum before being melt pressed to form a film.

Conclusion

This research is part of our continuous efforts to develop new routes to prepare polyolefin graft copolymers which can serve as the effective compatibilizers in polyolefin blends. The combination of the metallocene catalyst and *p*-methystyrene comonomer shows a new approach to prepare polyethylene graft copolymers with relatively well-defined molecular structures. The chemistry allows the good control of copolymer composition and microstructure, such as graft density and graft length. In polymer blends, the PE-*g*-PS copolymer have been shown to be a good compatibilizer in PE/PS blends, as evidenced by the improved dispersion of PS in the PE matrix and the strong interfacial interactions.

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