Synthesis of a Linear Polyethylene Macromonomer and Preparation of Polystyrene-*graft*-Polyethylene Copolymers via Grafting-Through Atom Transfer Radical Polymerization

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ABSTRACT: A vinyl-terminated linear polyethylene (number-average molecular weight = 1800, weight-average molecular weight/number-average molecular weight = 1.7, functionality = 92%) prepared by ethylene coordination polymerization was transformed into a monohydroxy-terminated linear polyethylene by hydroalumination of the vinyl group with diisobutylaluminum hydride and subsequent oxidation and hydrolysis. This monohydroxy-terminated linear polyethylene was quantitatively converted into a linear polyethylene macromonomer with a terminal α-methacrylate group through esterification followed by dehydrobromination. A grafting-through atom transfer radical polymerization of the α-methacrylate-terminated polyethylene and styrene was performed to yield a well-defined polystyrene-*graft*-polyethylene copolymer. The number-average molecular weight of the graft copolymers, measured by gel permeation chromatography, was lower than the predetermined number-average molecular weight, presumably because of the intramolecular aggregation of polyethylene side chains. The α-methacrylate-terminated polyethylene content and number-average molecular weight of polystyrene-*graft*-polyethylene were determined by ^{1}H-NMR.
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Key words: atom transfer radical polymerization (ATRP); graft copolymers; macromonomers; polyethylene (PE)

INTRODUCTION

Polyolefins, such as polyethylene (PE) and polypropylene, are the largest volume commodity polymers in the marketplace and are indispensable to our lifestyle because of the combination of low cost and excellent properties. Despite the commercial success of PE, its poor compatibility with other polymers limits its utilization, mainly because of the high crystallinity and low surface energy of the linear homopolymer. A compatibilizing agent could overcome this deficiency in the PE properties and expand its utility to higher value applications. So far, the most promising compatibilizer candidates are PE segmented copolymers, such as block or graft copolymers. Generally, segmented copolymers migrate to the surface of the PE domains and act as surfactants to improve the miscibility between the two separate phases.[1–9] The efficiency of a segmented copolymer to act as a surfactant, and not undergo self-aggregation, ultimately depends on the composition and topology of the segmented copolymers. Currently, the effect of the molecular structure on the miscibility is still unclear. Therefore, the preparation of PE segmented copolymers with precisely controlled structures will advance our understanding of the parameters contributing to miscibility. However, the synthesis of well-defined segmented copolymers is challenging in terms of the multiple synthetic procedures that have to be employed.[10–15]

Presently, the combination of coordination polymerization and controlled radical polymerization (CRP) is the best approach for preparing PE segmented copolymers in a controlled fashion. Recent advances in coordination polymerization catalysts have allowed the production of PEs with well-defined structures.[16–20] Therefore, the first step is basically the synthesis of PE segments with functional groups that are available for CRP. The role of CRP is the incorporation of the desired properties, which is accomplished through changes in the monomer type and molecular weight of the second segment. Atom transfer radical polymerization (ATRP) is among the most versatile CRP techniques developed.[21–38] It has been successfully used to prepare various block and graft copolymers.[11,39–53] Strategies for the synthesis of PE segmented copolymers can be organized into

This article is dedicated to the memory of Professor Marian Kryszewski

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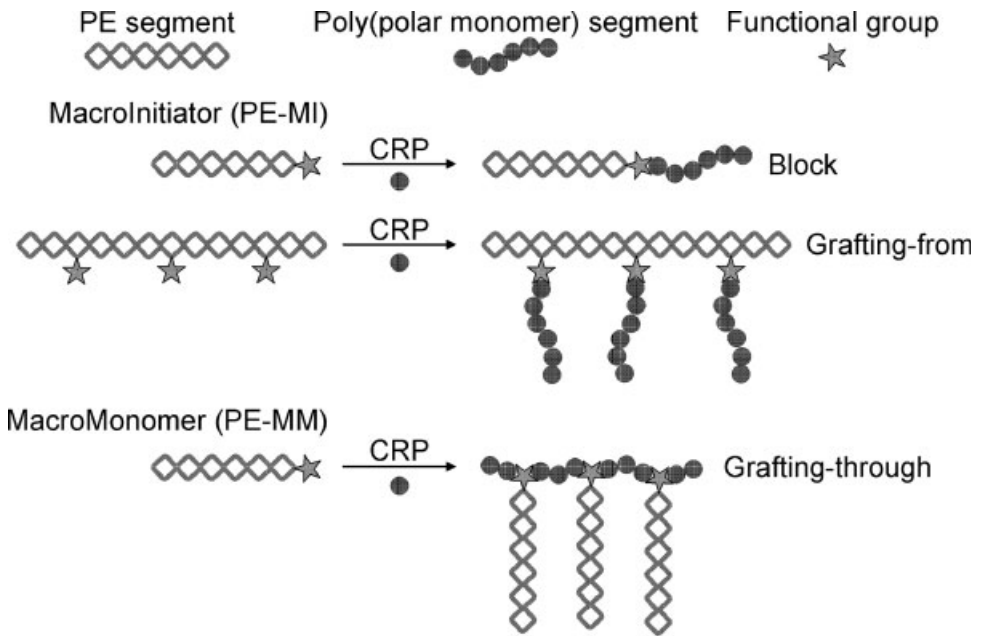


Scheme 1 Three strategies for the synthesis of PE segmented copolymers.

three categories (Scheme 1). The first method involves the synthesis of block copolymers via chain extension.[4,6,54,55] The second is the preparation of graft copolymers through the grafting-from polymerization of a PE backbone.[3,46,56,57] The third approach is directed toward the synthesis of graft copolymers with PE side chains via a grafting-through polymerization.[55,58] There are only a few reports concerning this third strategy, most likely because of the difficulty of efficiently synthesizing a PE macromonomer. As a result, the chemical and physical properties of graft copolymers with PE side chains are rarely explored. Therefore, the efficient synthesis of PE macromonomers is a crucial step for investigating the properties of graft copolymers with PE side chains.

The direct synthesis of an α-methacrylate-terminated polyethylene (PE–MM) with high chain-end functionality (~ 100%) was accomplished with living coordination polymerization.[58] A palladium complex bearing a methacryloyl fragment was employed as the catalyst for a living polymerization of ethylene, resulting in the preparation of PE–MM [number-average molecular weight (M_n) = 10,000–15,000, weight-average molecular weight/number-average molecular weight (M_w/M_n) < 1.05] with a branched PE topology. However, the critical deficiency of this method was the low productivity because the synthesis of PE–MM required one catalyst unit per PE–MM on account of the nature of the living polymerization. To overcome this deficiency, efficient syntheses of chain-end-functionalized PEs with the degenerative-transfer ethylene polymerization technique was developed.[55] An iron complex was used as a catalyst for ethylene polymerization in the presence of excess diethyl zinc as a chain-transfer agent. The advantage of this technique was the preparation of thousands of samples of zinc-terminated linear polyethylene (PE–Zn) with a low polydispersity (M_w/M_n = 1.3) from each iron complex. Moreover, PE–Zn was easily and efficiently converted into a monohydroxy-terminated linear polyethylene (PE–OH). However, the poor solubility of PE–Zn in the polymerization medium limited the molecular weight of the PE fragment (M_n ~ 700). This was the primary deficiency of this technique because an M_n value lower than 1000 will be too short to form a robust linkage with a PE domain in a polymer blend.

It is known that a bis(salicylaldiminato)zirconium complex activated with methylaluminoxane can selectively produce a vinyl-terminated linear polyethylene (PE–Vinyl) with high functionality (>90%) and high activity (>100 kg of PE/mmol of Zr h).[59] Moreover, the careful selection of the ligand structure for the complex enables the production of PE–Vinyl with a wide range of viscosity-average molecular weight (M_v) values (1000–1,000,000). Therefore, PE–Vinyl is a good candidate for preparing PE segmented copolymers. Indeed, the synthesis of the α-bromoisobutyrate-terminated polyethylene [i.e., polyethylenyl α-bromoisobutyrate (PE–MI)] was achieved by the reaction of PE–Vinyl and 2-bromoisobutyric acid in the presence of trifluoromethanesulfonic acid.[6] Accordingly, the synthesis of PE–MM from PE–Vinyl is a prospective pathway for the efficient formation of graft copolymers with PE side chains. In this article, we report the successful synthesis of PE–MM from PE–Vinyl with conventional organic

reagents and the subsequent preparation of a graft copolymer composed of a polystyrene (PSt) backbone and PE side chains via grafting-through ATRP.

EXPERIMENTAL

Characterization

^{1}H-NMR spectra of the linear PE derivatives (PE–Vinyl, PE–OH, PE–MI, and PE–MM) were obtained in tetrachloroethane-d_2 at 110°C with a Bruker 300-MHz spectrometer with a delay time of 2 s. The ^{1}H-NMR spectrum of the graft copolymers was examined in chloroform-*d* at 30°C with a Bruker (Billerica, MA) 300-MHz spectrometer with a delay time of 2 s. The monomer conversion of styrene (St) was determined by gas chromatography (GC) with a Shimadzu (Kyoto, Japan) GC 14-A gas chromatograph equipped with a flame ionization detector and a ValcoBond 30-m VB-WAX megabore column. Anisole was used as an internal standard for GC. The molecular weights and molecular weight distributions of the PSt samples and the graft polymers were measured by gel permeation chromatography (GPC) with poly(styrene sulfonate) columns (10^5-, 10^3-, and 10^2-Å Styragel columns) and a refractive-index detector. GPC was performed with tetrahydrofuran (THF) as an eluent at a flow rate of 1 mL/min at 35°C. The molar masses of the PSt samples and the graft polymers were determined with respect to linear PSt calibration standards.

Materials

PE–Vinyl (M_n = 1800, M_w/M_n = 1.7, functionality = 92%) was prepared by Mitsui Chemicals, Inc., (Tokyo, Japan) with bis[*N*-(3-*tert*-butylsalicylidene) methylaminato]zirconium(IV) dichloride as a postmetallocene catalyst supported on methylaluminoxane/silica particles under a constant ethylene atmosphere (0.9 MPa) in heptane.[59] Toluene (Fisher Scientific; >99%) (Waltham, MA) was distilled over sodium/benzophenone and degassed with nitrogen. Tris[(*N*,*N*-dimethylamino)ethyl]amine (Me_6TREN) was synthesized according to the procedure reported previously.[60] Copper(I) bromide (Acros; 98%) (Morris Plains, NJ), was purified by the method in the previous report.[23] St (Aldrich; 99%) (St. Louis, MD) were passed through a basic alumina column to remove the stabilizer, dried over calcium hydride, distilled under reduced pressure, and degassed with nitrogen. Anisole (Aldrich; 99%) was dried over molecular sieves and degassed with nitrogen. All other reagents were used as received.

Synthesis of PE–OH from PE–Vinyl

PE–Vinyl (3.01 g, functionality = 92%, 1.54×10^{-3} mol) was placed in a Schlenk flask (250 mL) equipped with a magnetic stirring bar, and then the flask was evacuated and backfilled with nitrogen three times. *o*-Xylene (anhydrous-grade, 120 mL) and a toluene solution of diisobutylaluminum hydride (DIBAL–H; 1.0 mol/L, 15 mL, 1.50×10^{-2} mol) were added to the flask under a nitrogen atmosphere. The resulting mixture was heated at 100°C with stirring for 18 h. Then, dry air, passed through a dry-ice/acetone trap and calcined molecular sieves, was bubbled into the resulting slurry for 5 h at this temperature. After the oxidation reaction was complete, concentrated aqueous HCl (3 mL) was added to the flask, and the reaction was stirred for 10 min at 100°C. The resulting pale yellow slurry was poured into methanol (1 L) to precipitate PE–OH. The white powder was filtered, washed with methanol, and then dried *in vacuo* at 80°C. The yield was 2.85 g.

Transformation of PE–OH into PE–MM

PE–OH (2.80 g, 1.56×10^{-3} mol) was placed in a Schlenk flask (500 mL) equipped with a magnetic stirring bar, and then the flask was evacuated and backfilled with nitrogen three times. Toluene (200 mL) was added to this flask, and the mixture stirred for 20 min at 100°C. Triethylamine (1.0 mL, 7.17×10^{-3} mol) was added to the solution and was followed by 2-bromo-2-methylpropionyl bromide (0.8 mL, 6.47×10^{-3} mol); the reaction was reheated to 100°C for 2 h. The reaction mixture was cooled to room temperature and then poured into methanol (1.5 L). The white, powdery precipitate was collected through filtration, washed with THF and methanol, and dried *in vacuo* at 80°C. PE–MI was obtained as a white solid. The yield was 2.86 g (96%).

PE–MI (2.76 g, 1.40×10^{-3} mol) was placed in a Schlenk flask (500 mL) equipped with a magnetic stirring bar, and then the flask was evacuated and backfilled with nitrogen three times. Toluene (120 mL) was added to this flask, and this mixture was allowed to warm to 80°C with stirring. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU; 16 mL, 1.07×10^{-1} mol) was added to this mixture, and stirring was continued for 20 h at 80°C. After the reaction mixture was cooled to room temperature, it was poured into methanol (1.2 L). The white, powdery precipitate was filtered, washed with THF and methanol, and dried at 80°C under reduced pressure. PE–MM was obtained as a white solid. The yield was 2.59 g (97%).

Grafting-through ATRP of PE–MM with St

A typical ATRP (run 2 in Table I) was conducted with standard Schlenk techniques. The solvent, internal standard, and monomer were degassed via bubbling with nitrogen for 30 min before use. Me_6TREN (3.3×10^{-3} mL, 1.26×10^{-6} mol) was placed in a

TABLE I
Conditions and Results for the ATRP of St in the Presence or Absence of PE–MM

No.	PE–MM (mg)	$[St]_0/[PE–MM]_0/[CuBr]_0/[L]_0/[I]_0$ (molar ratio)	Time (h)	St conversion (%)[a]	$M_{n,th} \times 10^{-4}$[b]	$M_{n,NMR} \times 10^{-4}$[c]	$M_{n,GPC} \times 10^{-4}$[d]	M_w/M_n[d]
1	0	900/0/1/1/1	1	11.4	1.09	—	1.05	1.08
			2	17.9	1.69	—	1.95	1.08
			4	32.8	3.09	—	3.50	1.09
			8	59.2	5.57	—	5.92	1.21
2	497	900/12.5/1/1/1	1	22.1	2.86	3.20	0.83	1.18
			3	47.2	5.92	5.89	2.47	1.14
			6	66.8	8.21	7.22	3.76	1.17

The (co)polymerization conditions were as follows:
$[St]_0/[PE–MM]_0/[CuBr]_0/[Me_6TREN]_0/[MBP]_0 = 900/0$ (or 12.5)/1/1/1; monomer = St (1.3 mL); mass of PE–MM = 497 mg ($M_n = 1890$, functionality = 60%); solvent = anisole (0.39 mL); initiator = MBP; and temperature = 115°C.

[a] The conversion of St was measured by GC.

[b] $M_{n,th}$ of PSt was calculated with the following equation: $M_{n,th} = 167.0 + \text{Conversion} \times 900$. $M_{n,th}$ of the graft copolymers was calculated on the basis of the initial feed of both monomers and the monomer reactivity ratios of St (0.57) and lauryl methacrylate (0.45).

[c] $M_{n,NMR}$ was evaluated on the basis of an ^{1}H-NMR study (see Table II for details).

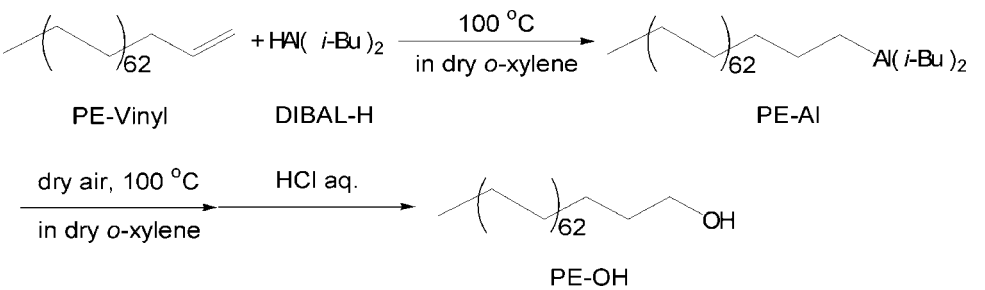
[d] The GPC data were based on PSt standard calibration, and M_n and M_w/M_n of the copolymers were determined after the elimination of the remaining PE–MM peak from the whole GPC traces.

Schlenk flask equipped with a magnetic stirring bar and cooled in a liquid-nitrogen bath. CuBr (1.8 mg, 1.26×10^{-6} mol) and PE–MM (497 mg, 1.58×10^{-5} mol) were added to this flask, and the flask was evacuated and backfilled with nitrogen three times. St (1.3 mL, 1.13×10^{-2} mol) and anisole (0.39 mL) were added in sequence to this mixture, and then the resulting mixture was stirred at 115°C for 15 min. After the mixture cooled to room temperature, methyl 2-bromopropionate (MBP; 1.4×10^{-3} mL, 1.26×10^{-6} mol) was added to the flask. The flask was reheated to 115°C to start the copolymerization. Samples were taken periodically, via a syringe, to follow the kinetics of the polymerization process. The samples were diluted with THF and filtered through a neutral alumina column and a Gelman Acrodisc 0.2-μm poly(tetrafluoroethylene) filter before analysis by GC and GPC. After 6 h, the polymerization mixture was poured into methanol (200 mL), and the precipitate was filtered off and washed with methanol. The resulting solid was extracted with THF (300 mL) to remove any unreacted PE–MM from the graft copolymer. After the evaporation of the solvent, the residual solid was dried at 80°C *in vacuo*. A polystyrene-*graft*-polyethylene (PSt-*graft*-PE) copolymer was obtained as a brown solid. The yield was 235 mg.

RESULTS AND DISCUSSION

Synthesis of PE–OH from PE–Vinyl

The synthesis of PE–MI through the reaction of PE–Vinyl with 2-bromoisobytyric acid in the presence of trifluoromethanesulfonic acid was reported previously.[6] This method provides the direct synthesis of PE–MI with a couple of side products such as γ-substituted PE–MI and PE with an internal double bond. The reason for the formation of side products is most likely the harsh reaction conditions. The hydroalumination of a vinyl group with DIBAL–H can provide the selective formation of an α-aluminated compound with a high regioselectivity and a high yield under mild reaction conditions.[61] Accordingly, this reaction is applicable to the preparation of an aluminum-terminated polyethylene (PE–Al). In addition, PE–Al is a good intermediate for the production of PE–OH because the terminal aluminum–polymer bond can be easily oxidized by dry air. Therefore, the reaction procedure illustrated in Scheme 2 can be continuously carried out *in situ* in one flask. PE–Vinyl ($M_n = 1800$, $M_w/M_n = 1.7$, functionality = 92%) was reacted with excess DIBAL–H



Scheme 2 Procedure for the preparation of PE–OH from PE–Vinyl with DIBAL–H.

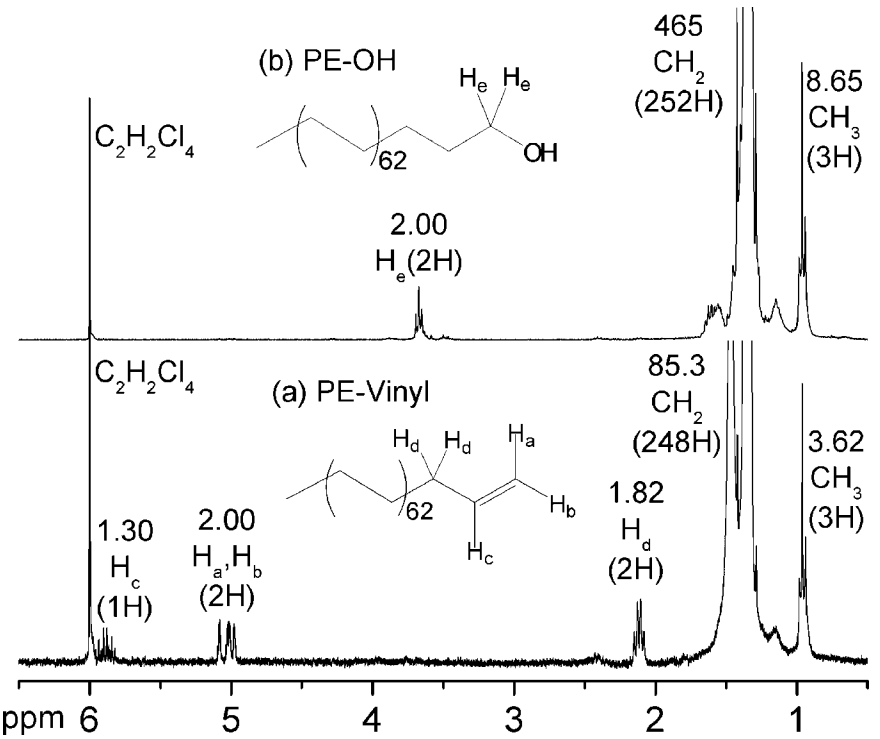


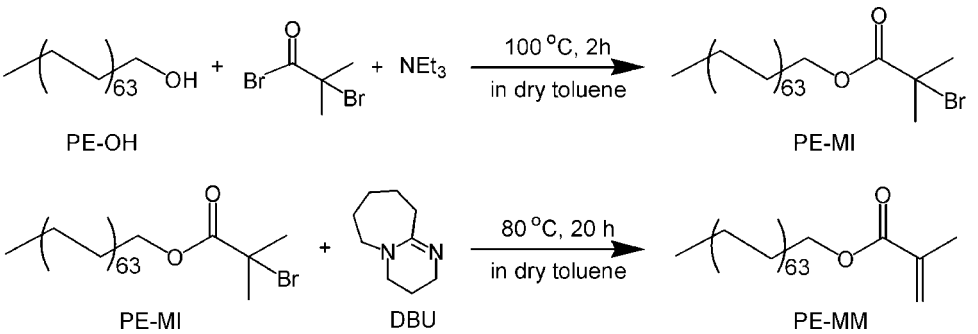
Figure 1 ^{1}H-NMR spectra (300 MHz) of (a) PE–Vinyl and (b) PE–OH in tetrachloroethane-d_2 at 110°C.

at 100°C to form PE–Al. A high temperature was required to achieve the homogeneous reaction because of the poor solubility of PE–Vinyl. The resulting aluminum–polymer bond in PE–Al was oxidized at 100°C via the bubbling of dry air through the reaction mixture to prepare the polyethylenoxyaluminum species. After the oxidation reaction was complete, hydrolysis to PE–OH was conducted *in situ* with an aqueous solution of hydrochloric acid. Consequently, PE–Vinyl was transformed into PE–OH in a one-pot reaction.

The molecular structure of PE–OH was investigated by ^{1}H-NMR with tetrachloroethane-d_2 as a solvent. Figure 1 shows the spectra of PE–OH and PE–Vinyl. No peaks attributable to protons in a terminal vinyl group were observed at 2.1, 5.0, and 5.9 ppm in Figure 1(b), and this suggested the quantitative conversion of the terminal vinyl group. The presence of a triplet peak (—CH_2OH, δ = 3.7 ppm, peak H_e), which was assignable to methylene protons next to an oxygen atom, indicated that the oxidation proceeded successfully. However, it is possible to form linear PE as a side product through the reaction of PE–Al with any residual moisture in the dry air during the oxidation.[55] Therefore, the purity of the chain-end functionality of PE–OH was evaluated through a comparison of the integrals of signals in Figure 1(b). Unfortunately, there was a limitation to quantifying the chain-end functionality with ^{1}H-NMR. The integral ratio of the methylene groups against peak H_e in PE–OH [233 = 465/2.00; Fig. 1(b)] was much higher than the ratio of methylene groups to the vinyl group in PE–Vinyl [85 = 85.3/1.00; Fig. 1(a)], even though the polymers had almost the same number of methylene groups. This implied lower sensitivity of a methylenoxy group in PE–OH, plausibly because of the aggregation of hydroxyl chain ends in tetrachloroethane-d_2.[62] Therefore, the chain-end functionality was quantified after the preparation of PE–MM.

Transformation of PE–OH into PE–MM

The direct synthesis of PE–MM from PE–OH with methacryloyl chloride was not considered to be a suitable pathway because of the formation of side products even under mild reaction conditions.[55] Therefore, PE–OH was transformed into the desired PE–MM via PE–MI with conventional organic chemistry (Scheme 3). First, the hydroxyl group on PE–OH was converted into the α-bromoisobutyrate group by a reaction with excess 2-bromo-2-methylpropionyl bromide in the presence of triethylamine in toluene at 100°C. As shown in Figure 2(a), the ^{1}H-NMR spectrum of the product revealed the presence of a triplet peak for the methylene protons bonding to an oxygen atom (—CH_2O—, δ = 4.2 ppm, peak H_a) and a singlet peak for methyl protons in the ester group [—(CH_3)$_2$Br, δ = 2.0 ppm]. The integral of the singlet (I_{CH_3} = 6.00) was 3 times larger than



Scheme 3 Synthetic pathway for the preparation of PE–MM from PE–OH.

that of the triplet ($I_{CH_2O} = 2.00$), indicating the quantitative conversion of the OH functionality. Moreover, the chemical shift of a triplet peak from 3.7 to 4.2 ppm also supported complete esterification of the terminal —OH in PE–OH. Next, dehydrobromination of the α-bromoisobutyrate group to the α-methacryloyl ester functionality was accomplished with excess DBU in toluene at 80°C for 20 h. The ^{1}H-NMR spectrum of the resulting compound showed the appearance of two new multiple peaks (=CH_2, δ = 5.6 and 6.1 ppm, peaks H_c and H_d), which were characteristic of the vinylidene protons in a methacrylate group, suggesting the production of an α-methacryloyl functionality [Fig. 2(b)]. A triplet peak for methylenoxy protons (—CH_2O—, δ = 4.2 ppm, peak H_a) was shifted slightly upfield compared with those in the parent PE–MI, whereas no shift was observed for the singlet peak from the methyl protons in the methacrylate group [—C(=CH_2)CH_3, δ = 1.8 ppm]. The ratio of the integrals of H_c, H_d, H_a, and CH_3 peaks (1.04, 1.05, 2.00, and 2.65) was in relatively good agreement with the ideal ratio (1/1/2/3), supporting the quantitative dehydrobromination of PE–MI.

Because the esterification of PE–OH and subsequent dehydrobromination of PE–MI were carried out quantitatively, the resulting PE–MM contained only the linear PE as a side product. Therefore, the chain-end functionality of PE–MM was evaluated from the integral of the chain-end methyl group

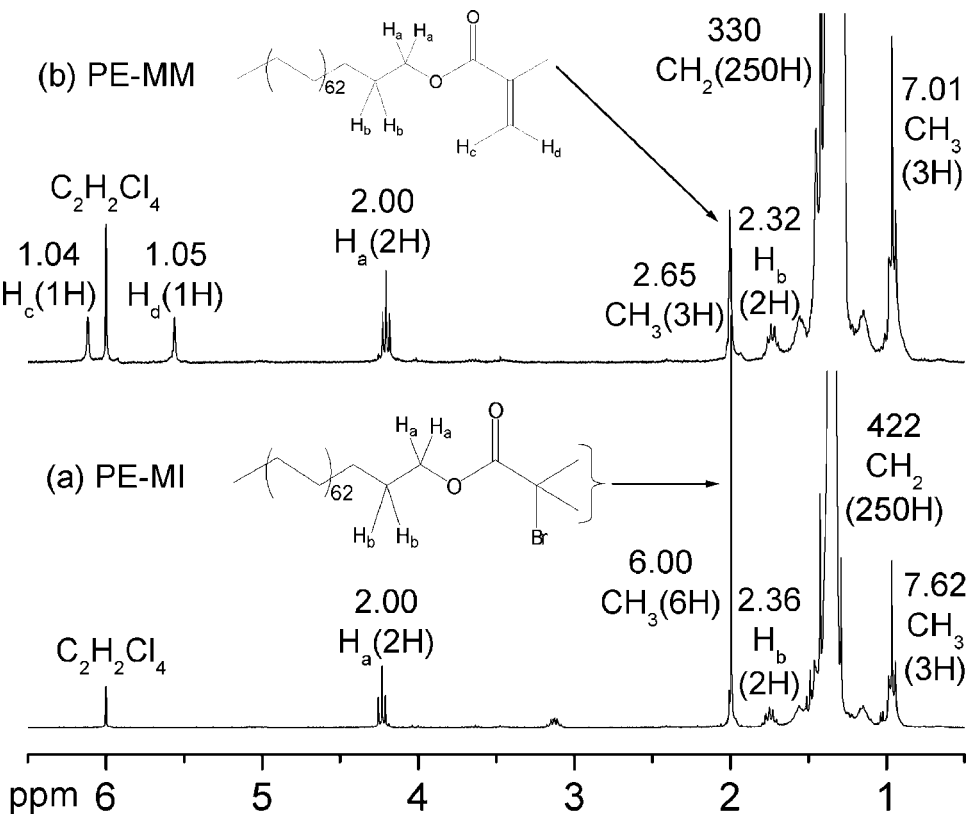


Figure 2 ^{1}H-NMR spectra (300 MHz) spectra of (a) PE–MI and (b) PE–MM in tetrachloroethane-d_2 at 110°C.

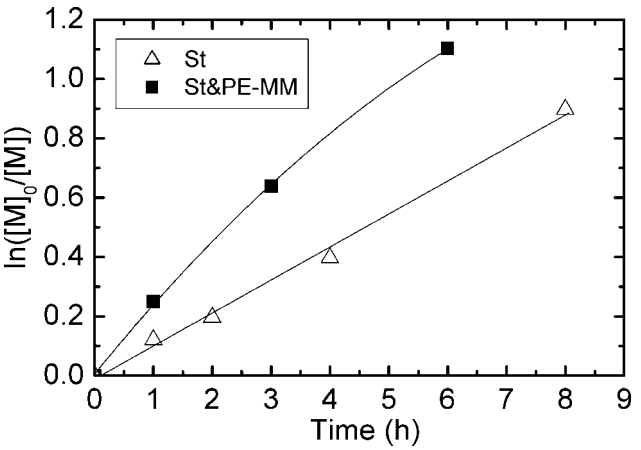


Figure 3 Kinetic plots for the ATRP of St in the presence or absence of PE–MM at 115°C: (△) the polymerization of St and (■) the copolymerization of St and PE–MM [see Table I for the (co)polymerization conditions].

[I_{CH_3} = 7.01, δ = 0.9 ppm; Fig. 2(b)]. This integral was composed of signals from one chain-end methyl group originating from PE–MM ($I_{CH_3–MM}$) and both terminal methyl groups arising from the linear PE ($I_{CH_3} = I_{CH_3–MM} + 2I_{CH_3–PE}$). Theoretically, $I_{CH_3–MM}$ should be 3.00 when the integral of —CH_2O— group in PE–MM is 2.00. Accordingly, the integral of one chain-end methyl group derived from the linear PE was 2.01 [$I_{CH_3–PE}$ = (7.01–3.00)/2]. Thus, the chain-end functionality of PE–MM was determined to be 60% [= 3.00/(3.00 + 2.01)], and the molecular weight of PE–MM was 1890. As a result of the esterification and subsequent dehydrobromination, the chain-end functionality was reduced from 92% in PE–Vinyl to 60% in PE–MM. As mentioned previously, the formation of linear PE is mainly due to the reaction of PE–Al with any residual moisture in the dry air during the oxidation. Therefore, the use of other oxidation reagents such as hydrogen peroxide or benzoic peroxide may provide better conversions.

Preparation and characterization of PSt-*graft*-PE

The grafting-through ATRP of PE–MM with St was conducted to provide a graft copolymer with a predominately PSt backbone and linear PE side chains. An ATRP of pure St was also performed under the same conditions used for the reference. Me_6TREN was selected as a ligand for a copper catalyst to achieve a high-molecular-weight PSt backbone. Anisole (30 vol %) was used as the solvent to dissolve the copper catalyst, PE–MM, and the resulting graft copolymer. The copolymerization was carried out at 115°C because this temperature was above the melting point of PE–MM. The ATRP conditions and results are summarized in Table I.

The polymerization medium remained homogeneous during the ATRP of St, whereas the reaction system became cloudy and slurry after 1.5 h, despite the addition of anisole, in the case of the copolymerization. As shown in Figure 3, the rate of the ATRP of St homopolymerization was first-order with time, and the conversion of St increased up to 59% for 8 h. In the case of the copolymerization of St and PE–MM, the rate of polymerization was faster than that of St homopolymerization, and the St conver-

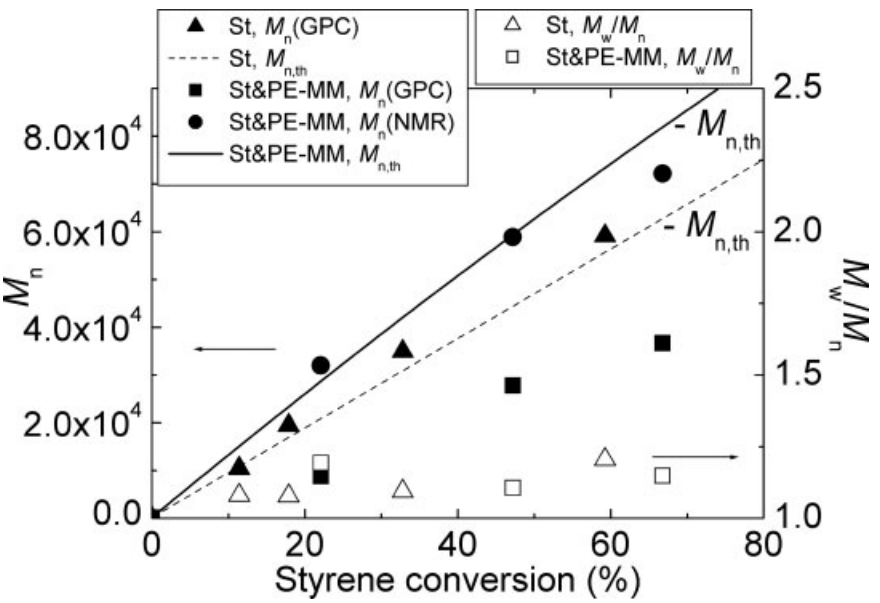


Figure 4 Evolution of M_n and M_w/M_n as a function of the St conversion for the ATRP of St in the presence or absence of PE–MM at 115°C: (▲,△) the polymerization of St and (●, ■, □) the copolymerization of St and PE–MM [see Table I for the (co)polymerization conditions].

sion reached 67% after only 6 h. This acceleration of the rate of copolymerization was presumably due to the contribution of the larger propagation rate coefficient (k_p) for methacrylates (k_p = 650–1000 at 50°C) in comparison with that of St (k_p = 160 at 40°C), suggesting the successful incorporation of PE–MM.[63]

The evolution of M_n for PSt was investigated by GPC (Fig. 4). The theoretical molecular weight ($M_{n,\mathrm{th}}$) was calculated on the basis of the assumption of a living polymerization process and quantitative initiation. Accordingly, $M_{n,\mathrm{th}}$ consists of the sum of the molecular weights of the initiator and PSt evaluated from the St conversion measured by GC. M_n of pure PSt increased with the conversion along the theoretical line, suggesting almost no thermal initiation of St for 8 h. Furthermore, the polydispersity indices of PSt remained below 1.2, and GPC traces for PSt showed monomodal shapes, indicating good control over the polymerization. In the case of copolymerization, the GPC traces for the samples displayed bimodal peaks [Fig. 5(a)]. The peak area of the lower M_n polymer progressively decreased with the St conversion. This peak stayed at the same position, as expected for PE–MM [0% conversion in Fig. 5(a)]. The higher molecular weight peak, corresponding to a graft copolymer, continuously shifted toward the higher M_n region. The evolution of M_n for the graft copolymer was examined after the elimination of the PE–MM peaks by deconvolution of the GPC traces [Fig. 5(b)], and the results are plotted in Figure 4. M_n of the graft copolymer increased monotonously with the St conversion. However, the overall M_n value of the graft copolymer was lower than $M_{n,\mathrm{th}}$ of pure PSt. The observation of a lower M_n value is plausibly due to a smaller hydrodynamic volume for the graft copolymer with respect to pure PSt. This contraction may be caused by the intramolecular aggregation of PE side chains because of their poor solubility in THF. Similar behavior was previously observed for poly(butyl acrylate)-*graft*-polyethylene.[55] The polydispersities of the graft copolymers after deconvolution were less than 1.2, suggesting that the copolymerization was well controlled.

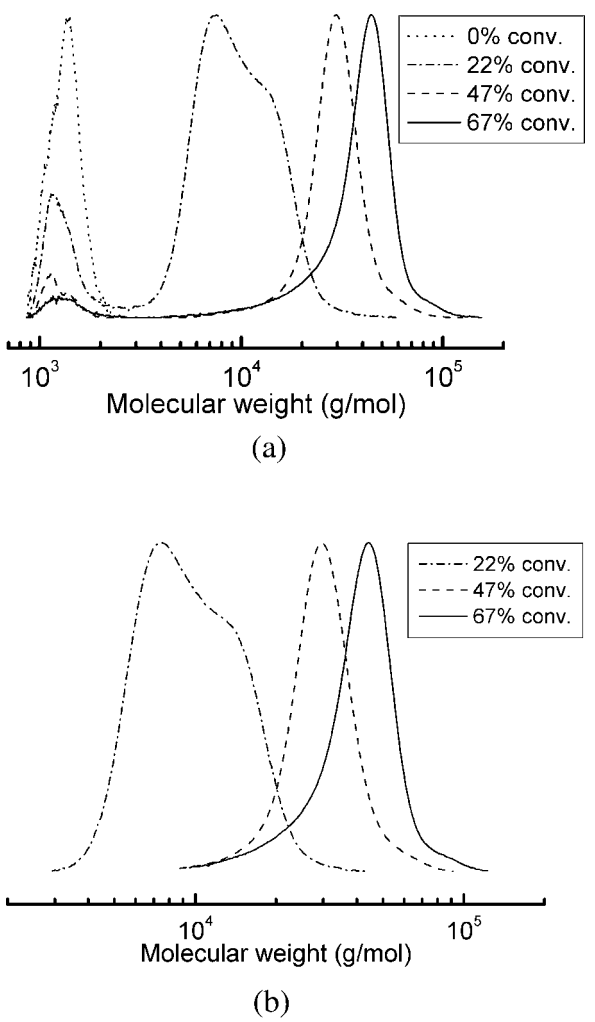


Figure 5 GPC traces from the ATRP copolymerization of PE–MM with St: (a) complete GPC traces and (b) traces after the elimination of PE–MM signals from the whole traces (see Table I for the copolymerization conditions).

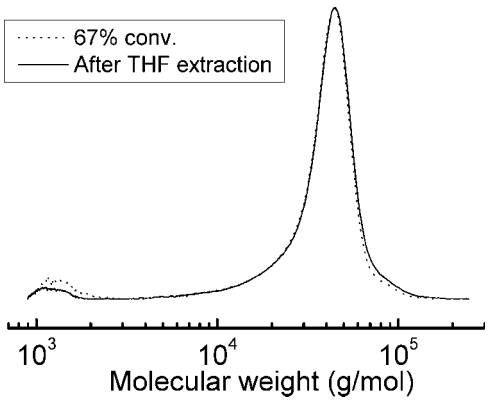


Figure 6 GPC traces before and after the fractionation of the final sample of PSt-*graft*-PE (see Table I for the copolymerization conditions).

To determine the accurate M_n value of the graft copolymer, the remaining unreacted PE–MM in a sample was removed from the polymer sample by fractionation with THF. After the fractionation, the M_n value of the graft copolymer, exemplified by the case of the copolymer formed at a 67% St conversion in Figure 6, was analyzed by GPC. The peak area of the unreacted PE–MM decreased slightly after fractionation. This fractionation process was also performed for the purification of the other samples.

After fractionation, the molecular structure of the graft copolymers was characterized with ^{1}H-NMR spectroscopy. Figure 7 shows the spectrum of the graft copolymer formed at a 67% St conversion. The

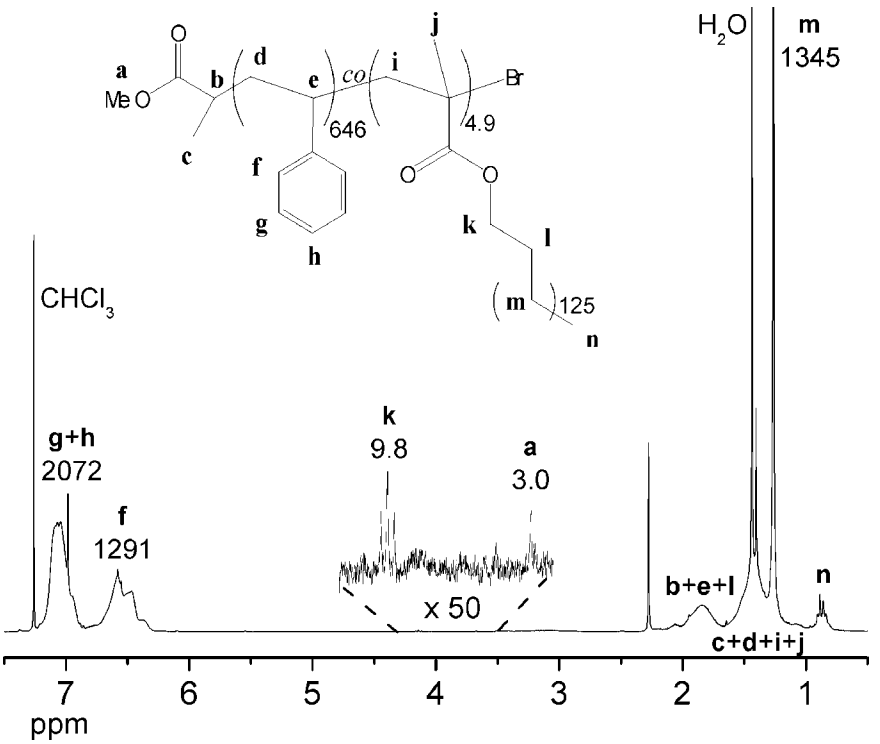


Figure 7 ^{1}H-NMR spectrum of PSt-*graft*-PE after fractionation (at 6 h) in $CDCl_3$ at 30°C (300 MHz).

characteristic singlet of the methylene protons (δ = 1.25 ppm, peak *m*) and triplet peak derived from —C*H*$_2$O— (δ = 4.15 ppm, peak *k*) in the PE–MM units could be observed, suggesting the successful incorporation of PE–MM into the copolymer. The degree of polymerization (DP) of PE–MM was estimated by a comparison of the integral for the methoxy protons in the initiator (I_{CH_3O} = 3.0, δ = 3.65 ppm, peak *a*) with the integral for —C*H*$_2$O— protons in PE–MM (I_{CH_2O} = 9.8, peak *k*). When the integral for the initiator (I_{CH_3O} = 3.0) was taken as corresponding to one end group, the integral from —C*H*$_2$O— protons in PE–MM (I_{CH_2O} = 9.8) corresponded to multiples of two protons. Thus, the ratio of the PE–MM signals to the initiator signal corresponded to 4.9 grafts per chain (DP_{PE-MM} = 9.8/2). The value of DP_{PE-MM} was also calculated on the basis of the comparison of the integral for the initiator (I_{CH_3O} = 3.0) with the integral for the methylene protons in PE–MM (I_{CH_2} = 1345, δ = 1.25 ppm, peak *m*), and the value was determined to be DP_{PE-MM} = 5.4 (= 1345/250). The small difference between these two numbers was most likely due to the overlap of another peak (peak *c* + peak *d* + peak *i* + peak *j*) at 1.25 ppm. The DP of St was also evaluated by the comparison of the integral for the methoxy protons in the initiator (I_{CH_3O} = 3.0, peak *a*) with the integral for the *ortho*-phenyl protons in PSt (I_H = 1291, δ = 6.3–6.8 ppm, peak *f*). The integral for the *ortho*-phenyl protons (I_H = 1291) corresponded to 646 units of methylene groups (DP_{St} = 1291/2) when the integral of the initiator corresponded to 1 unit. Accordingly, the average numbers of St units and PE–MM units in the graft copolymer at a 67% St conversion were 646 and 4.9, respectively.

The M_n values of the other PSt-*graft*-PE copolymers were also calculated with the same methodology with ^{1}H-NMR (Fig. 8). Because the chain-end methoxy protons were not clearly visible on the chart, presumably on account of the small amounts

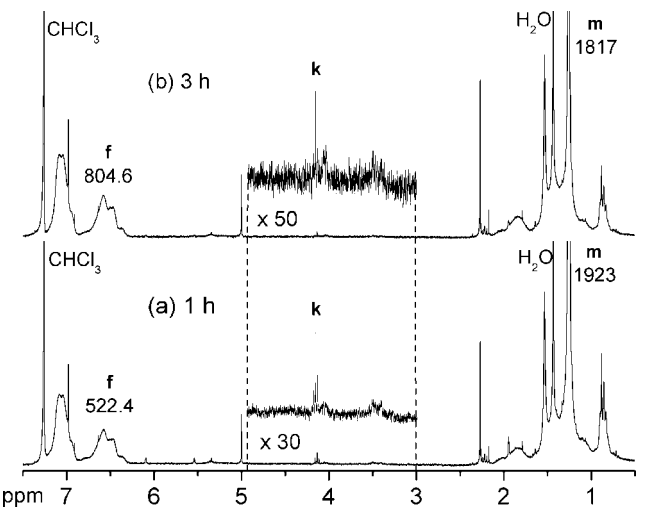


Figure 8 ^{1}H-NMR spectra of PSt-*graft*-PE (a) at 1 h and (b) at 3 h in $CDCl_3$ at 30°C (300 MHz).

TABLE II
Determination of the Molar Mass of PSt-*graft*-PE by ^{1}H-NMR in $CDCl_3$ at 30°C

Time (h)	PE–MM/St (mol %)[a]	St Conversion (%)[b]	DP_{PE-MM}[c]	$M_{n,NMR} \times 10^{-4}$ [d]	$M_{n,th} \times 10^{-4}$ [e]
1	2.95	22.1	5.87	3.20	2.86
3	1.81	47.2	7.69	5.89	5.92
6	0.83	66.8	4.99	7.22	8.21

[a] PE–MM/St (mol %) = $(I_{peak\ m}/250)/(I_{peak\ f}/2)$, where $I_{peak\ m}$ is the integral of peak *m* and $I_{peak\ f}$ is the integral of peak *f*.
[b] The conversion of St was measured by GC.
[c] $DP_{PE-MM} = 900 \times$ St conversion $\times$ (PE–MM/St).
[d] $M_{n,NMR} = 167.01 + 104.15 \times 900 \times$ St conversion $+ 1890 \times DP_{PE-MM}$.
[e] $M_{n,th}$ was calculated on the basis of the initial feed of both monomers and the monomer reactivity ratios of St (0.57) and lauryl methacrylate (0.45).

of the copolymers, DP_{PE-MM} was estimated by the comparison of the integral for the phenyl protons in PSt (δ = 6.3–6.8 ppm, peak *f*) with the integral for the methylene protons in PE–MM (δ = 1.25 ppm, peak *m*). The calculated results are summarized in Table II. The molar fraction of PE–MM with respect to St in the copolymer decreased with increasing St conversion, suggesting a gradient sequence in the copolymer. DP_{PE-MM} was determined by the combination of the PE–MM/St molar ratio and St conversion measured by GC. Theoretically, DP_{PE-MM} should increase with time, whereas DP_{PE-MM} at 6 h was lower than that at 3 h. PSt-*graft*-PE with high PE–MM contents at 6 h could be removed from resulting graft copolymers by fractionation with THF because of the relatively poor solubility. The M_n values of PSt-*graft*-PEs were calculated with DP_{PE-MM} and the St conversion measured by GC (Table II), and the values are plotted in Figure 4. Because it was difficult to determine the monomer reactivity ratios of St and PE–MM, the monomer reactivity ratios of St (0.57) and lauryl methacrylate (0.45)[64] reported previously were used to estimate $M_{n,th}$ of the graft copolymer (Table II). In addition, $M_{n,th}$ of the graft copolymer was calculated on the basis of the assumption of quantitative initiation and a living polymerization process. As shown in Figure 4, M_n calculated from NMR increased monotonously with the conversion along the $M_{n,th}$ line. Because the GPC traces for the graft copolymers retained low polydispersities, these results indicated good control over the polymerization. Because segmented copolymers are often successfully used as compatibilizers for polymer blends, the resulting PSt-*graft*-PE copolymers with well-controlled structures also have potential as compatibilizers for blends of PE and PSt.

CONCLUSIONS

PE–Vinyl was converted into PE–OH with hydroalumination and subsequent oxidation and hydrolysis in a one-pot reaction. PE–OH was successfully and efficiently transformed into PE–MM by esterification and dehydrobromination. PE–MM was used for the preparation of a well-defined graft copolymer via a grafting-through ATRP with St. The resulting PSt-*graft*-PE has potential as a compatibilizer for blends of PE and PSt, which would find utility in recycling operations. The production of graft copolymers via the ATRP of PE–MM with other functional monomers will further expand the range of applications for PE segmented copolymers.

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