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Synthesis of Ethylene–Propylene Rubber Graft Copolymers by Borane Approach

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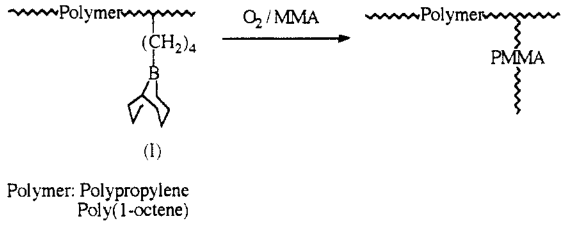
ABSTRACT: This paper describes a new method to prepare graft copolymers which have an EP rubber backbone and several free radical polymerized polymers grafted thereto. The process involves hydroboration of commercial EPDM rubbers, such as poly(ethylene-*co*-propylene-*co*-1,4-hexadiene) and poly(ethylene-*co*-propylene-*co*-5-ethylidene-2-norbornene), with 9-borabicyclononane (9-BBN). The resulting secondary alkyl–9-BBN moieties in the EPDM copolymers were then exposed to oxygen in the presence of free radical polymerizable monomers. Under certain conditions, the selective autoxidation reaction of secondary alkyl–9-BBN took place to create desirable polymeric radicals which can in situ initiate free radical polymerization. High graft efficiency was observed with controllable copolymer compositions. The graft copolymer of EP-*g*-PMMA is used to show the chemistry as well as some of the physical properties.

Introduction

The polymers with multiple phases, such as block and graft copolymers, present a unique combination of physical properties.[1-3] The commercial success in thermoplastic elastomers, such as poly(styrene-*b*-isoprene-*b*-styrene) and poly(styrene-*b*-butadiene-*b*-styrene),[4] clearly show the advantages in this type of multiphase systems. In addition, block and graft copolymers can be used as compatibilizers[5] in polymer blends and composites. By adding a suitable compatibilizer, the incompatible polymer blends alter their morphology as well as physical properties by reducing the domain sizes and increasing the interaction between domains.

The extension of block and graft copolymer composition to polyolefins is scientifically challenging and commercially important. The low surface energy of polyolefins significantly limits their end uses, particularly those in which adhesion and compatibility with other materials is paramount. It is especially desirable to prepare polyolefin graft copolymers with the second polymer containing functional groups, such as PMMA, which could dramatically increase the interaction of polyolefin to a broad range of materials. In general, polyolefins have been the most difficult materials in chemical modifications. Numerous methods have been employed in forming graft copolymers with polyolefins. Ionizing radiation (X-ray, γ-rays, and e-beams) in the presence of air, ozone, UV with accelerators, and free radical initiators have all been used to form polymeric peroxides.[6,7] When heated in the presence of monomers, the polymeric peroxides can initiate graft polymerizations. However, these high energy reactions lead to side reactions such as cross-linking and chain cleavage, resulting in diminished mechanical properties. In most cases, the structure and composition of copolymers are difficult to control with the considerable amounts of ungrafted homopolymers.

In the previous papers, we have discussed a new route to prepare poly(1-octene)[8] and polypropylene[9] graft copolymers using borane containing polymers which were obtained from direct Ziegler–Natta copolymerization using α-olefin and borane monomer.[10,11] Both cases involve primary alkyl–9-BBN groups located along the polymer backbone, as shown in eq 1. The graft-from reactions offered high graft efficiency and a broad composition of graft copolymers under certain oxidation reaction conditions.



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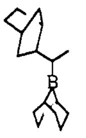
Results and Discussion

It is very interesting to explore the scope and limitations of this new graft reaction. In this paper, the graft-from reaction is extended to secondary alkyl–9-BBN groups, such as structures II and III, which are the hydroboration adducts of the commercial EPDM rubbers, such as poly(ethylene-*co*-propylene-*co*-1,4-hexadiene) and poly(ethylene-*co*-propylene-*co*-5-ethylidene-2-norbornene).[12] It is both of scientific and technologic interest to use EP rubber as the polymer backbone in the graft copolymers. In addition to the commercial availability, EP polymer offers a saturated main chain structure which has a better environmental stability than those of diene-based elastomers.



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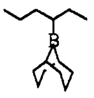

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Hydroboration Reaction of EP Rubbers. The commercial EPDM rubbers, containing 1–2 mol % of 1,4-hexadiene (I′) or 5-ethylidene-2-norbornene (I″) adducts, were used as the starting materials. On average, each has about 30–60 internal double bonds homogeneously distributed along the polymer chain. The hydroboration was carried out by adding 9-borabicyclononane (9-BBN) into the polymer/THF solution. Due to the excellent solubility of borane reagents and borane containing polymers, the hydroboration reaction of the polymer is very similar to those of small organic compounds. However, to ensure

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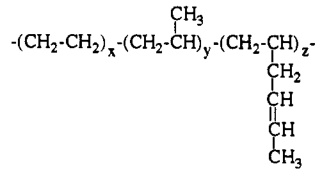
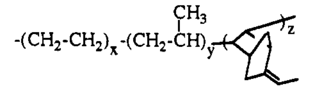


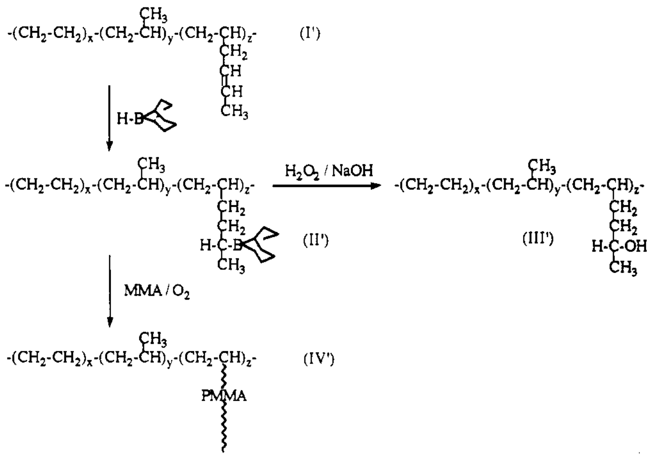
$-(CH_2-CH_2)_x-(CH_2-\underset{}{\overset{CH_3}{CH}})_y-(CH_2-CH)_z-$ with side chain $CH_2-CH=CH-CH_3$

(I')



(II")

complete hydroboration of the internal double bonds, the reaction was run at 65 °C for 12 h in an argon atmosphere. Usually, a small portion of hydroborated product was sampled and oxidized to hydroxylated polymer(III') by reacting with NaOH/H_2O_2 reagents at ambient temperature for 3 h, as shown in eq 2. On the basis of GPC results, both polymeras I' and III' have similar molecular weights and molecular weight distributions. The hydroboration and oxidation reactions do not involve detective side reactions. Figure 1 compares the ^1H NMR spectra of poly(ethylene-*co*-propylene-*co*-1,4-hexadiene) before and after hydroxylation. The intensity of the chemical shift at 5.37 ppm, corresponding to the olefin units, decreases with the increase of the intensity of the chemical shifts at 3.75 and 3.54 ppm, corresponding to the methine groups in the secondary alcohols at the 4 and 5 positions of hexadiene. Apparently, the hydroboration reaction was quite effective. The concentration of the borane groups in the polymer can be controlled by the quantity of borane reagents used during the hydroboration reaction. Only a slightly excess of 9-BBN was needed to hydroborate most of the double bonds in the polymer in the limit of NMR sensitivity.



(2)

Selective Autoxidation of Secondary Alkyl-9-BBN. The borane group located along the polymer chain is an asymmetric trialkylborane with one linear secondary alkyl group joined to the polymer and two secondary alkyl groups which are part of the borabicyclononane structure. The B–C bonds are readily oxidized by oxygen at ambient temperature. To get the polymeric radical for graft-from polymerization, it is essential to control the oxidation reaction at the needed C–B bond which is joined to polymer. Equation 3 illustrates the possible reaction mechanism. It is logical to predict that the oxygen insertion into alkyl-9-BBN starts at the linear alkyl group, instead of the bicyclic ring. The stable double chair form structure can prevent the unfavorable ring strain increase in the insertion of a peroxyl group into the chair form of the six-membered ring. The peroxyl group in compound IV will further decompose at room temperature. The electron-withdrawing from the neighboring borane moiety weakens the O–O bond. The peroxyl borane (IV) may proceed through a free radical homolytic chain mechanism[13] to yield an alkoxyl radical (V) and a B–O• radical (VI). Alternatively, the peroxide (IV) can react with another alkyl-9-BBN, especially at the early stage of oxidation. This bimolecular reaction[14] generates an alkyl radical (VIII), a B–O• radical (VI), and a borinate product (VII). Both the alkoxyl radical (V) and alkyl radical (VIII) are known to initiate free radical polymerization of methacrylates, vinyl acetate, acrylonitrile, styrene, acrylamide, etc., at room temperature. The B–O• radical (VI) may be too stable to initiate polymerization due to the electron back-donating to the empty p-orbital in boron.

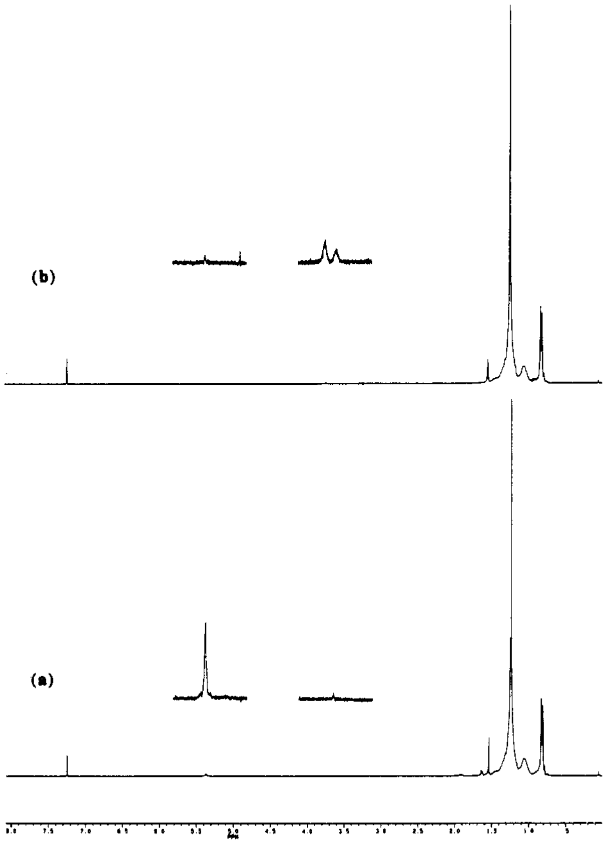
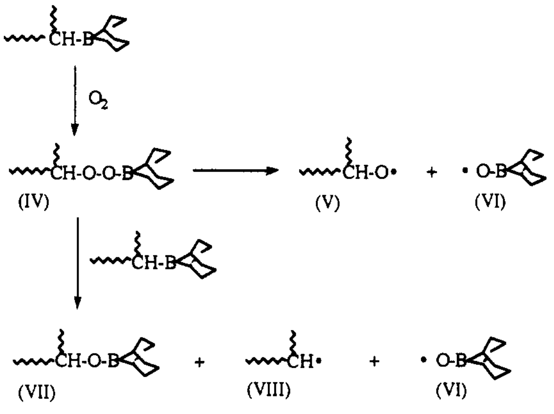


Figure 1. ^1H NMR spectra of (a) EPDM, poly(ethylene-*co*-propylene-*co*-1,4-hexadiene), and (b) the hydroxylated product.



(3)

To provide some experimental evidence for the selective oxidation, a controlled reaction was studied by exposing B–(1-octyl)–9-BBN to various quantities of oxygen at room temperature. The use of the primary octyl group, instead of a secondary alkyl group, in the borane compound is for simplifying the ^{13}C NMR (DEPT-135) interpretation so as to allow us to distinguish the oxidation products

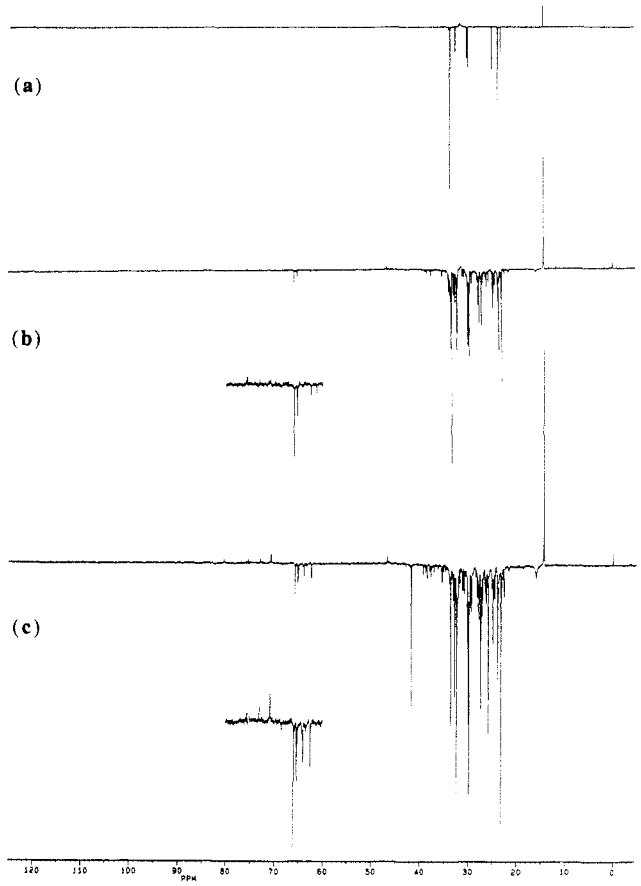
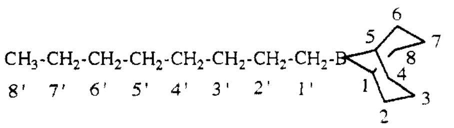


Figure 2. ^{13}C NMR (DEPT-135) spectra of (a) octyl-9-BBN and its oxidation adducts with various mole ratio of oxygen, (b) 50% and (c) 100%.

involving the primary alkyl C-B bond and secondary borabicyclononyl C-B bonds. In addition, the tendency of oxidation[15] in symmetrical trialkylborane compounds is known to be tertiary > secondary > primary. Therefore, the results of the B-(1-octyl)-9-BBN study can be logically translated to the secondary alkyl-9-BBN cases. In this study, it is expected that the radicals formed in the oxidation reaction will couple with each other to produce several oxygen-containing species and even pure alkanes. Figure 2 compares the ^{13}C NMR (DEPT-135) spectra of octyl-9-BBN and the oxidation adducts. In Figure 2a, the chemical shifts at 33.2 and 23.4 ppm are assigned to C-2,4,6,8 and C-3,7 in the bicyclononane structure[16] as shown here.



It is difficult to see the chemical shifts corresponding to the bridgeheads (C-1 and C-5) and C-1′ due to the rapid relaxation associated with the J' coupling with boron. The peaks at 14.3 and 22.9 ppm are assigned to C-8′ and C-2′, respectively, in the linear alkyl group. A clear indication of an autoxidation reaction took place in octyl-9-BBN after exposing it to 50 mol % (vs borane) of oxygen at ambient temperature. Figure 2b shows a new major peak at 65.9 ppm, accompanied by several minor peaks between 66 and 60 ppm. The negative intensities indicate several *methylenes with adjacent oxygen* due to *oxidation* occurring between the boron and the adjacent CH_2 of the octyl group. The selectivity diminished with increasing oxygen addition. As shown in Figure 2c, several additional new peaks with positive intensity appear between 70 and 75 ppm, which correspond to the oxidation occurring between the methine and the boron in the borabicyclononane group.

EP-*g*-PMMA Copolymers. The control reaction provides the conditions for the selective oxidation reaction of alkyl-9-BBN groups to obtain the polymeric radicals which are essential for graft-from polymerization. The hydroborated EPDM rubbers were usually mixed with methyl methacrylate in THF solution. Upon exposure to oxygen, the graft-from reaction took place at room temperatures as shown in eq 2. The reaction was terminated by precipitating the polymer in MeOH. Some unreacted B-C bonds were further oxidized by NaOH/H_2O_2. The product, isolated by filtration and washed with MeOH, was then extracted with hexane and acetone for 24 h, respectively. This process proved to be effective for removal of EPDM and PMMA homopolymers from their blends. The hexane soluble fraction is usually a very small quantity and is almost identical with pure EPDM rubber by ^1H NMR and GPC studies. On the other hand, the acetone soluble fraction contains both PMMA and EP with significantly high PMMA concentration. These results imply that the acetone soluble fraction contains either the EP-*g*-PMMA copolymer with a high concentration of PMMA or a mixture of graft copolymer and some PMMA homopolymer. The major portion is insoluble in both hexane and acetone but soluble in THF, which is EP-*g*-PMMA copolymer with PMMA concentration less than 60 mol %.

Figure 3 compares the ^1H NMR spectra of the resulting EP-*g*-PMMA copolymers and the starting EPDM rubber (I′), poly(ethylene-*co*-propylene-*co*-1,4-hexadiene). The chemical shift at 3.6 ppm in Figure 3b,c corresponds to methyl groups (CH_3O) in PMMA. The chemical shifts between 2.1 and 0.7 ppm include all protons in EP and five protons in the methyl group located on the PMMA backbone. The copolymer composition was calculated by the ratio of the two integrated intensities at 3.6 and 2.1-0.7 ppm and the number of protons both chemical shifts represent. Parts b and c of Figures 3 indicate 28 and 52 mol % of PMMA in EP-*g*-PMMA copolymers, respectively. The detailed experimental conditions and results are summerized in Table 1. Considering the mixing difficulties between polymer solution and oxygen gas, the oxygen was introduced slowly into the reactor so that $[O] \ll [B]$ at any time. Excess O_2 is a poison for free radical polymerizations. Also, high O_2 concentrations lead not only to losing selectivity but also to overoxidation to boronates and borates which are poor free radical initiators at room temperature. The total oxygen used was only 50% (vs borane groups) to ensure the selective oxidation reaction, as discussed in the previous section. In most cases, the overall graft efficiencies are very high with less than 10% unreacted EPDM rubber remaining. The graft copolymers mainly exist in the insoluble fraction, and some in the acetone soluble fraction. Comparing runs 3 and 4, there is no significant difference in the graft-from reaction by using a moderately higher temperature (55 °C). The temperature insensitivity implies the ready decomposition of C-O-O-B at room temperature, which is very different from the tranditional thermal initiators, such as benzoyl peroxide, which are usually used above 65 °C. It is also interesting to note that the use the BH_3 in run 6 offers a poor graft efficiency. No selective oxidation reaction is expected in this case.

Another commercially important EPDM rubber (I″), poly(ethylene-*co*-propylene-*co*-5-ethylidene-2-nor-

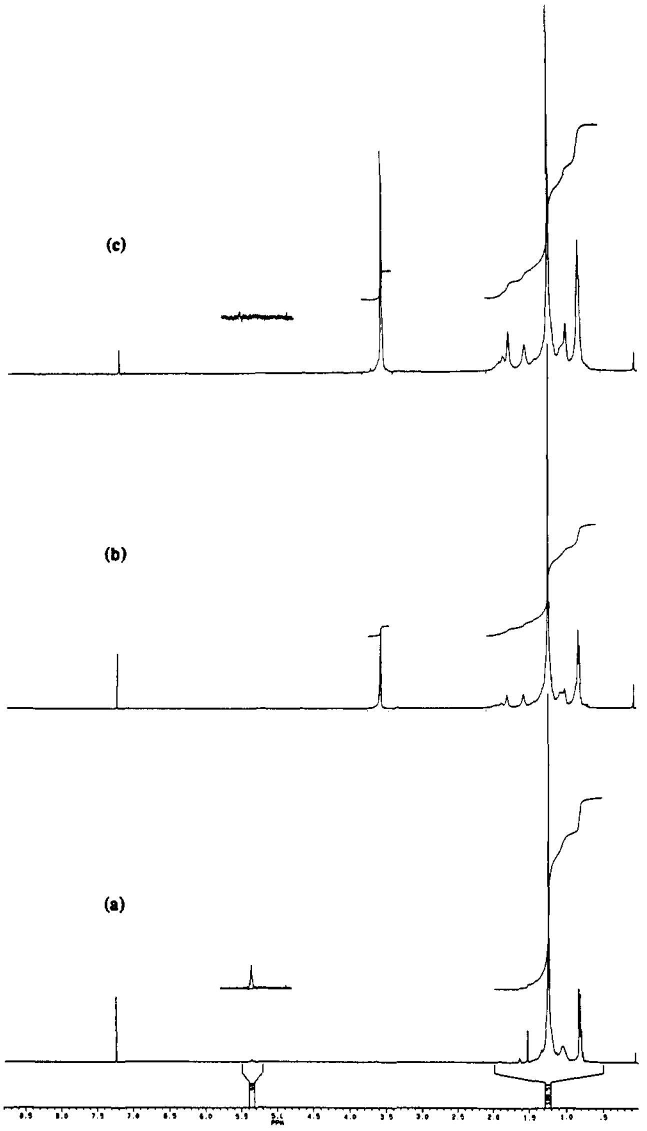


Figure 3. Comparison of ^{1}H NMR spectra of EP-*g*-PMMA graft copolymers, containing (a) 0 mol %, (b) 28 mol %, and (c) 52 mol % of PMMA in EPDM I′.

bornene) was also studied under similar reaction conditions. The difference in the secondary alkyl group in the borane moiety is not expected to alter significantly the reaction mechanism during both hydroboration and graft-from reactions. A broad composition range of graft copolymers was also obtained under various reaction conditions. Figure 4 shows the IR spectra of two EP-*g*-PMMA copolymers, with 51 and 28 mol % of PMMA, which are compared with that of starting EPDM rubber. A new absorption peak ($\nu_{C=O}$ = 1710 cm^{-1}), corresponding to the carbonyl group in PMMA, clearly shows the existence of PMMA in the graft copolymers. The quantitative compositions were determined by ^{1}H NMR spectra. Table 2 summarizes the detailed results. In runs 1 and 2, the reactions were carried out under identical conditions except for the quantity of MMA monomer. The increase in MMA concentration results in the higher concentration of PMMA in the graft copolymer, which may be due to the increase of PMMA molecular weight in the side chain. Comparing runs 2 and 4, there is no significant difference in the use of stoichiometric or double amounts of 9-BBN reagent. The hydroboration reactions must be quite effective: there is only a slight difference in borane concentration in both EP polymers. In run 3, the use of more than 50% oxygen does increase both hexane and acetone soluble fractions, indicating the loss of some oxidative selectivity.

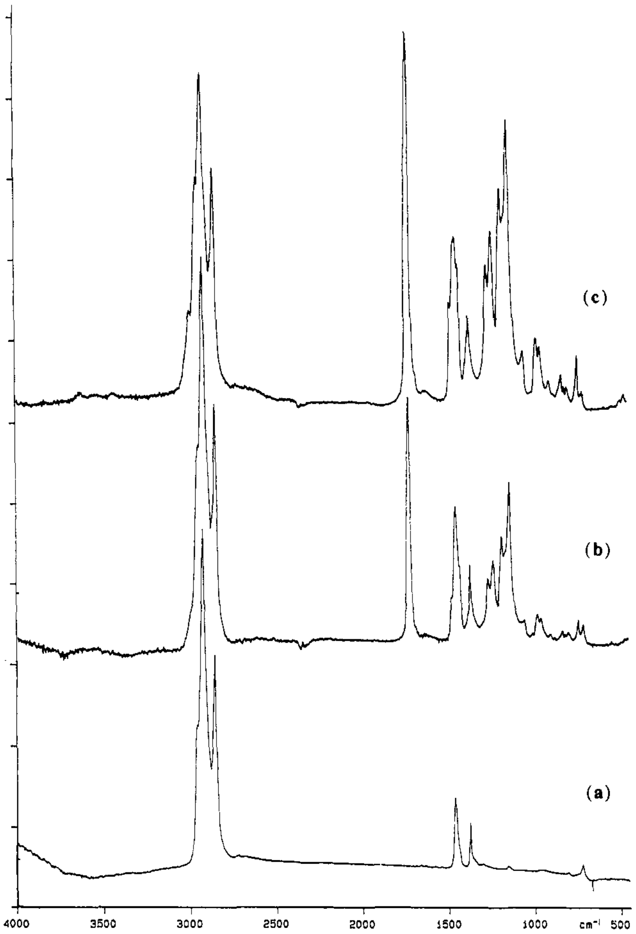


Figure 4. Comparison of IR spectra of EP-*g*-PMMA graft copolymers, containing (a) 0 mol %, (b) 28 mol %, and (c) 51 mol % of PMMA in EPDM I″.

Thermal Properties. The thermal properties of the graft copolymers were determined by DSC measurement. The samples were first heated to 160 °C and then rapidly cooled to −120 °C. The curves shown in Figure 5 are heating curves obtained from these quenched samples at a heating rate of 20 °C/min. To give a better interpretation, the EP-*g*-PMMA copolymer is compared with EPDM rubber and PMMA homopolymer (M_w = 80 000, M_w/M_n = 2.8) which was prepared by a control reaction using 2-hexyl-9-BBN/O_2 initiator under similar reaction conditions. Two glass transition temperatures (T_g), −47 and +130 °C, exist in EP rubber-*g*-PMMA copolymer with 50/50 composition. The uneven baselines between 0 and 100 °C in both graft copolymer and EPDM rubber are reproducible in all samples. They may be due to some small crystalline domains[17] existing in the EPDM rubber, which are the result of the inhomogeneous distribution of ethylene and propylene monomers in the polymer backbone. Basically, the two T_g's are very close to those of the two corresponding homopolymers. This result indicates clear phase separation between the EP backbone and the PMMA side chains. The copolymer backbone must have enough consecutive sequences of EP backbone units to form separate domains. The side chain must be of high molecular weight polymer with a microstructure similar to that of the PMMA homopolymer. Unfortunately, it is very difficult to determine the exact molecular structure of the graft copolymer by conventional methods.

The clear phase separation with hard (polar) and soft (nonpolar) domains is a very interesting molecular struc-

Table 1. Summary of EP-*g*-PMMA Copolymers Prepared by EP Rubber I′

reactn no.	reactn conditions[a]			fractionation products (g)			PMMA in EP-*g*-PMMA (mol %)
	9-BBN/olefin	MMA (g)	O_2/9-BBN	hexane sol	acetone sol	insoluble fraction[b]	
1	2/1	14	1/2	0.038	0.473	2.001	52
2	2/1	7	1/2	0.041	0.142	1.229	35
3	1/1	7	1/2	0.112	0.243	0.992	28
4	1/1	7	1/2[c]	0.060	0.487	0.993	32
5	0.5/1	7	1/2	0.119	0.246	0.889	28
6	2/1[d]	14	1/1	0.601	0.442	0.161	32

[a] All graft-from reactions were run by using 0.75 g of poly(ethylene-*co*-propylene-*co*-1,4-hexadiene) in 80 g of THF solvent. The oxygen was slowly introduced to the reaction solution, 10% of oxygen hourly, at ambient temperature. [b] Samples are soluble in THF. [c] The graft-from reactions were carried out at 55 °C. [d] BH_3 was used in the hydroboration reaction.

Table 2. Summary of EP-*g*-PMMA Copolymers Prepared by EP Rubber II′

reactn no.	reactn conditions[a]			fractionation products (g)			PMMA in EP-*g*-PMMA (mol %)
	9-BBN/olefin	MMA (g)	O_2/9-BBN	hexane sol	acetone sol	insoluble fraction[b]	
1	2/1	14	1/2	0.138	1.194	1.259	51
2	2/1	7	1/2	0.083	0.118	1.016	28
3	2/1	7	1/1	0.155	0.327	0.949	34
4	1/1	7	1/2	0.092	0.216	0.957	25

[a] All graft-from reactions were run by using 0.75 g of poly(ethylene-*co*-propylene-*co*-ethylenenorbornene) in 80 g of THF. The oxygen was slowly introduced to the reaction solution, 10% of oxygen hourly, at ambient temperature. [b] Samples are soluble in THF.

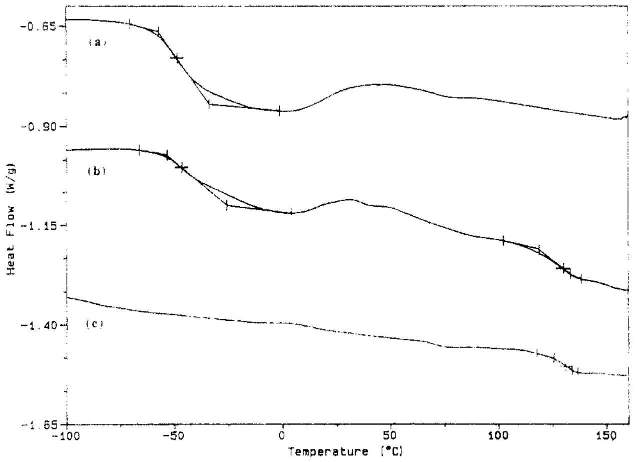


Figure 5. DSC curves comparison between (a) EPDM and (b) EP-*g*-PMMA copolymers containing 52 mol % of PMMA and (c) PMMA homopolymer.

ture. In fact, some of the graft copolymers behave like thermoplastic elastomers. The detailed morphology and mechanical properties of the graft copolymer and its blends are currently under investigation.

Experimental Details

Instrumentation and Materials. All ^1H NMR and ^{13}C NMR were recorded on a Bruker WP-200 or a Bruker AM-300 spectrometer with the DISNMR software. The molecular weight of the polymer was determined using a Waters GPC. The columns used were Phenomenex Phenogel of 10^5, 10^4, 10^3, and 500 Å. A flow rate of 0.7 mL/min was used, and the mobile phase was THF. Narrow molecular weight polystyrene standards were used to estimate the molecular weight. Differential scanning calorimetry (DSC) was measured on a DuPont 2000 instrument. The DSC's were measured from −120 to +160 °C with a heating rate of 20 °C/min. All O_2 and moisture sensitive manipulations were performed inside an argon filled Vacuum Atmospheres drybox equipped with a MO-40-1 dry-train.

Both commercial EPDM rubbers, Nordel 1660 and Vistolon 2504, were obtained from Exxon Chemical Co. The polymers were purified by the solution–dissolution process using THF as solvent and methanol as nonsolvent. The 9-borabicyclononane (9-BBN) was used as received from Aldrich. HPLC grade THF was distilled from sodium anthracenide. Methyl methacrylate, 2-hexene, and 1-octene were dried with CaH_2 and distilled under N_2.

Hydroboration and Oxidation Reactions. In a typical hydroboration reaction, 3 g of EP rubber containing 1.6 mol % of diene adducts was dissolved in 140 mL of THF solvent. The hydroboration reaction took place by adding 0.16 g of 9-BBN crystal to the solution under inert atmosphere. After refluxing at 65 °C for 5 h, the hydroborated polymer was precipitated by adding 150 mL of 2-propanol and then isolated by filtration. In some cases, especially when less than the stoichiometric amount of 9-BBN (vs double bonds) was added, the resulting hydroborated polymer in THF solution was used directly for graft-from reaction to prepare EP graft copolymers.

To measure the concentration of 9-BBN in the polymer, 0.75 g of the hydroborated product was dissolved in 30 mL of THF and then was oxidized by adding 25 mg of NaOH dissolved in the mixed solvent (water/methanol/THF = 1:1:2) followed by 110 mg of H_2O_2 (30% in water). Both reagents were deoxygenated with argon before adding. The reaction took place at ambient temperature for 3 h before precipitation in 30 mL of methanol. The hydroxylated polymer was purified by redissolving in THF and reprecipitated in methanol twice before drying in a vacuum oven at 40 °C for 24 h. The ^1H NMR spectrum indicates 94% of the double bonds have been converted to hydroxy groups.

Graft-from Reaction. In an argon filled drybox, 0.75 g of borane containing EP rubber in THF solution, directly obtained from the previous example, was mixed with 7 g of methyl methacrylate in a reaction flask equipped with a high vacuum stopcock. After stirring for $^1/_2$ h in the drybox, the flask was taken out and connected to a vacuum line. About 0.8 mL of O_2 was introduced into the reaction flask through the vacuum line. After 1 h of stirring, another 0.8 mL of O_2 was added. The same procedure was repeated five times. The solution was stirred at room temperature for 24 h before pumping out unreacted oxygen and then precipitating the resulting polymer in 30 mL of 2-propanol. For the complete removal of borane groups, the polymer was redissolved in 30 mL of THF and reacted with 25 mg of NaOH which was dissolved in the mixed solvent (water/methanol/THF = 1:1:2) and 110 mg of H_2O_2 (30% in water). After reacting at ambient temperature for 3 h, the polymer was precipitated into 30 mL of 2-propanol. The extraction processes were carried out by stirring polymer in hexane and acetone solvents for 24 h, respectively. After solvent removal, three fractions were dried in a vacuum oven at 40 °C for 24 h. The hexane and acetone insoluble fractions (but soluble in THF) yielded 1.229 g of graft copolymer with a 35:65 mole ratio between PMMA and EP by ^1H NMR measurement.

Synthesis of PMMA Homopolymer by 2-Hexyl-9-BBN. In a 100-mL flask, 6 g of 9-BBN in 20 mL of THF was reacted with 4.3 g of 2-hexane (excess) at ambient temperature for 12 h. After the reaction, the excess 2-hexene and THF were removed by vacuum distillation at room temperature. The product was then distilled at 90 °C under 30 μm of pressure to obtain 8.7 g of 2-hexyl-9-BBN. The chemical structure was confirmed by ^{1}H NMR measurement.

In a 250-mL flask equipped with a high vacuum stopcock, 7 g of purified methyl methacrylate was dissolved in 25 mL of THF. The initiator of 2-hexyl-9-BBN (42 mg) was transferred into the flask in a drybox. The polymerization took place by reacting with 5 mL of O_2, which was introduced into the flask through the vacuum line, in the same manner described in the graft reaction. The reaction was held at room temperature for 24 h. The homopolymer of poly(methyl methacrylate) was then precipitated in 30 mL of 2-propanol. After vacuum-drying overnight, 1.95 g of PMMA was obtained with the average molecular weight of M_w = 80 000 and M_w/M_n = 2.8.

Conclusion

The combination of selective oxidation of alkyl-9-BBN and free radical graft-from reaction offers a new method for the preparation of graft copolymers. Both primary and secondary alkyl groups in borane moieties are found to be useful with high graft efficiencies and controllable copolymer compositions. The new chemistry allows us to overcome the difficulties usually associated with the functionalization and grafting of polyolefins. With the commercial EP polymer as the polymer backbone and the functional (polar) polymers as the side chains, the new graft copolymer is a very interesting material. Many applications, such as thermoplastic elastomers, adhesives, rubber toughened thermoplastics, viscosity improvers, and compatibilizers in blends and composites, are currently under investigation.

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References and Notes

(1) Aggarwal, S. L. *Block Polymers*; Plenum Press: New York, 1970.

(2) Riess, G.; Periard, J.; Banderet, A. *Colloidal and Morphogical Behavior of Block and Graft Copolymers*; Plenum Press: New York, 1971.

(3) Lohse, D. J.; Datta, S.; Kresge, E. N. *Macromolecules* **1991**, *24*, 561.

(4) Holden, G.; Milkovich, R. U.S. Pat. 3,265,765, 1966.

(5) Epstein, B. N. U.S. Pat. 4,174,358, 1979.

(6) Natta, G.; Beati, E.; Severine, F. *J. Polym. Sci.* **1959**, *34*, 548.

(7) Ranby, B.; Feng, Z. G. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31*, 446.

(8) Chung, T. C.; Jiang, G. J. *Macromolecules* **1992**, *25*, 4816.

(9) Chung, T. C.; Rhubright, D. *Macromolecules* **1993**, *26*, 3467.

(10) Ramakrishnan, S.; Berluche, E.; Chung, T. C. *Macromolecules* **1990**, *23*, 378.

(11) Chung, T. C.; Rhubright, D. *Macromolecules* **1991**, *24*, 970.

(12) VerStrate, G. *Encycl. Polym. Sci. Eng.* **1986**, *6*, 522.

(13) Mikhailov, B.; Bubnov, Y. *Organoboron Compounds in Organic Synthesis*; Harwood Academic Publishers: Chur, Switzerland, 1984.

(14) Milovskaya, E. B.; Zamoiskaya, L. V.; Kopp, E. L. *Russ. Chem. Rev. (Engl. Transl.)* **1969**, *38*, 420.

(15) Brown, H. C.; Midland, M. M.; Kabalka, G. W. *J. Am. Chem. Soc.* **1971**, *93*, 1024.

(16) Brown, H. C.; Soderquist, J. A. *J. Org. Chem.* **1980**, *45*, 846.

(17) Baldwin, F. P.; VerStrate, G. *Rubber Chem. Technol.* **1972**, *45*, 709.