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Butyl rubber graft copolymers: synthesis and characterization

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This paper discusses four closely related themes. (a) First, we present the synthesis of new butyl rubber graft copolymers that have a polyisobutylene backbone and several free-radical polymerized polymers, such as poly(methyl methacrylate), in the side chains. The chemistry involves commercial butyl rubber, poly(isobutylene-*co*-isoprene) and free-radical graft-from reaction using a borane reagent. (b) The selective autoxidation reaction of secondary alkyl-9-borabicyclononane offers the conditions for producing desirable polymeric radicals in graft-from polymerization with high grafting efficiency and controllable copolymer compositions. (c) The structure of graft copolymers is characterized. Several techniques, especially gel permeation chromatography measurement with on-line refractive index, photodiode-array and light scattering detectors, were used to provide detailed microstructural information. (d) Finally, compatibility is studied using graft copolymers as the compatibilizers in polyisobutylene blends.

(Keywords: butyl rubber graft copolymers; synthesis; characterization)

INTRODUCTION

Butyl rubber (polyisobutylene-*co*-isoprene) is a very important commercial elastomer with many desirable physical properties[1], such as low air permeability and broad damping properties. The principal uses of this material are in the tyre industry for the preparation of inner tubes and inner liners of passenger car tyres. Despite these unique properties, there are some deficiencies associated with this polymer, mainly poor compatibility with other materials, including elastomers, plastics and carbon black. This poor compatibility greatly limits the application of butyl rubber in many application areas. In fact, the improvement of interfacial adhesion among butyl rubber, general-purpose rubbers and carbon black has been an intense research area for some time.

The use of graft and block copolymers as emulsifiers and interfacial compatibilizers[2–4] is an established technique to improve polymer interaction and morphology in polymer blends. Unfortunately, only very few butyl rubber graft and block copolymers[5] have been reported, most of which were made by sequential cationic polymerization[6,7]. The cationic process provides well defined block copolymers with predictable molecular weights and narrow molecular-weight distribution in each block. However, this process is 'living' only under very inconvenient conditions and involves high concentration of initiator, co-initiator and electron donor (proton trap). In addition, only few monomers undergo living cationic propagation. On the other hand, the preparation of butyl rubber graft copolymers usually resulted in inconclusive products, both by cationic methods[8] involving halogenated butyl rubber and by a free-radical process[9,10] by grafting onto polyisobutylene.

Recently, we have discovered a new method[11–13] for the preparation of graft copolymers using borane. The borane groups in a polymer can be selectively oxidized to form polymeric radicals, which then initiate graft-from polymerization. Several graft copolymers, such as polypropylene-*g*-poly(methyl methacrylate) (PP-*g*-PMMA), polyoctene-*g*-PMMA and polyethylene-*co*-propylene-*g*-PMMA, have been reported. Under certain oxidation reaction conditions, high graft efficiency and a broad composition of graft copolymers were obtained.

RESULTS AND DISCUSSION

In this paper, we report the extension of this new grafting reaction to prepare butyl rubber graft copolymers that have a polyisobutylene (PIB) backbone and several free-radical polymerized polymers, such as poly(methyl methacrylate) (PMMA), in the side chains. This polymer could be a very interesting material, not only providing a saturated elastic backbone with multiple phase properties but also offering low air permeability and broad damping properties in polymer blends and composites. *Scheme 1* illustrates the synthesis.

The chemistry starts from the hydroboration reaction of commercial butyl rubber, poly(isobutylene-*co*-isoprene) (**I**). The borane groups in butyl rubber (**II**)

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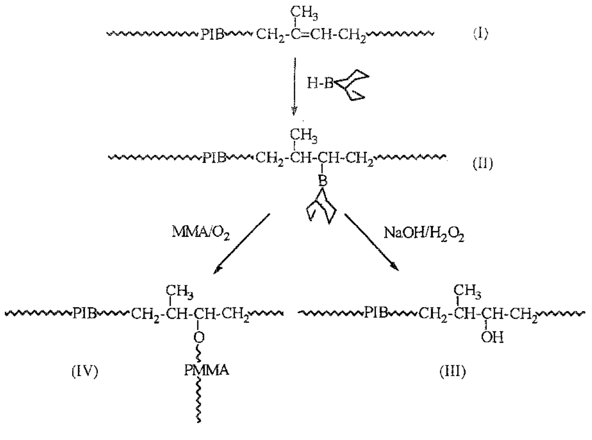


Scheme 1

are used as the reactive sites to create the desirable polymeric radicals for graft-from reactions. To achieve high grafting efficiency and controllable composition of graft copolymers, the determining step is the selective oxidation of the B–C bond in the linear alkyl group of secondary alkyl-9-borabicyclononane (alkyl-9-BBN) in polymer **II**. A control reaction involving secondary alkyl-9-BBN and oxygen was studied to determine the appropriate oxidation conditions. Many desirable graft copolymers have been obtained from this reaction scheme. In general, it is very difficult to determine the molecular structure (graft density and chain length and composition distribution) of graft copolymers. In this study, we adopted a combination of several techniques, viz. g.p.c. measurement with on-line refractive index, photodiode-array and light scattering detectors, which offers detailed microstructure information. The compatibility study of butyl rubber graft copolymers in polymer blends will also be discussed.

Hydroboration reaction of butyl rubber

Commercial poly(isobutylene-*co*-isoprene) (**I**), containing 1.5 mol% of isoprene, was used as the starting material. Hydroboration was carried out by adding 9-borabicyclononane (9-BBN) into polymer/tetrahydrofuran (THF) solution. Owing to the good 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 complete hydroboration of the internal double bonds, the reaction was run for 5 h at 65°C. A small portion of hydroborated product, such as compound **II**, was sampled and oxidized to hydroxylated polymer (**III**) by reacting with NaOH/H_2O_2 at 40°C for 3 h. *Figure 1* compares the ^1H n.m.r. spectra of isobutylene-*co*-isoprene before and after hydroboration, and subsequent oxidation reaction.

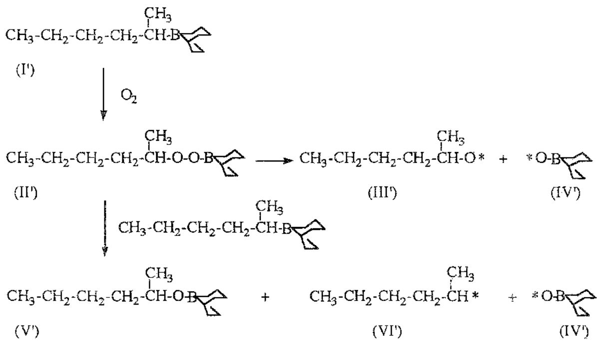
The triplet chemical shift at 5.35 ppm, corresponding to the olefinic (=CH) units in compound **I**, disappears with the appearance of new chemical shifts between 1.8 and 2.0 ppm, corresponding to the (CH_2) units in the bicyclic structure of 9-BBN in compound **II**. After the oxidation reaction, a new chemical shift at 3.3 ppm appears in *Figure 1c*, indicating the existence of secondary alcohol groups in compound **III**. Apparently, the hydroboration reaction was quite effective. The concentration of borane groups in the polymer can be controlled by the quantity of borane reagents used during the reaction. Only a slight excess of 9-BBN was needed to hydroborate most of the double bonds in the polymer to the limit of n.m.r. sensitivity. In g.p.c. studies, both polymers **I** and **III** show similar molecular weight and molecular-weight distribution. The hydroboration and oxidation reactions do not involve detectable side reactions.

Selective autoxidation of 2-(B-9-BBN)hexane

The borane group located along the polyisobutylene chain is an asymmetric trialkylborane with one linear secondary alkyl group joined to the polymer and two secondary alkyl groups that are part of the bicyclononane structure. The B–C bonds are readily oxidized by oxygen at ambient temperature. To generate the desirable polymeric radical in graft-from polymerization, it is essential to control the oxidation reaction so that it occurs at the linear C–B bond joined to the polymer. A control oxidation reaction using 2-(B-9-BBN) hexane was studied to determine the desirable reaction conditions that can offer selective autoxidation reaction. *Scheme 2* illustrates the possible reaction mechanism.

It is logical to predict that oxygen insertion into 2-(B-9-BBN) hexane starts at the linear alkyl group, instead of the bicyclic ring. The stable double chain structure can prevent the unfavourable insertion of peroxyl group into the chair form of six-membered ring, which increases the ring strain. The peroxyl group in compound **II′** will further decompose at room temperature because of a weakening of the O–O bond caused by the electron-withdrawing effect from the neighbouring borane moiety. The peroxyl borane may proceed through a free-radical homolytic chain mechanism[14] to yield an alkoxyl radical (**III′**) and a B–O$^\cdot$ radical (**IV′**). Alternatively, the peroxide (**II′**) can react with another 2-(B-9-BBN) hexane, especially at the early stage of oxidation. This bimolecular reaction[15] generates an alkyl radical (**VI′**), a B–O$^\cdot$ radical and a borinate product. Both alkoxyl radical (**III′**) and alkyl radical (**VI′**) are known to initiate free-radical polymerization of methacrylates, styrene, acrylamide, vinyl acetate, acrylonitrile, etc., at room temperature. The B–O$^\cdot$ radical (**IV′**) may be too stable, owing to the unpaired electron back-donating electron density to the empty orbital on boron, to initiate polymerization.

Figure 2 compares the ^{13}C n.m.r. (DEPT-135) spectra of B-(2-hexyl)-9-BBN and the oxidation adducts. In *Figure 2a*, the chemical shifts at 33.4 and 23.2 ppm are



Scheme 2

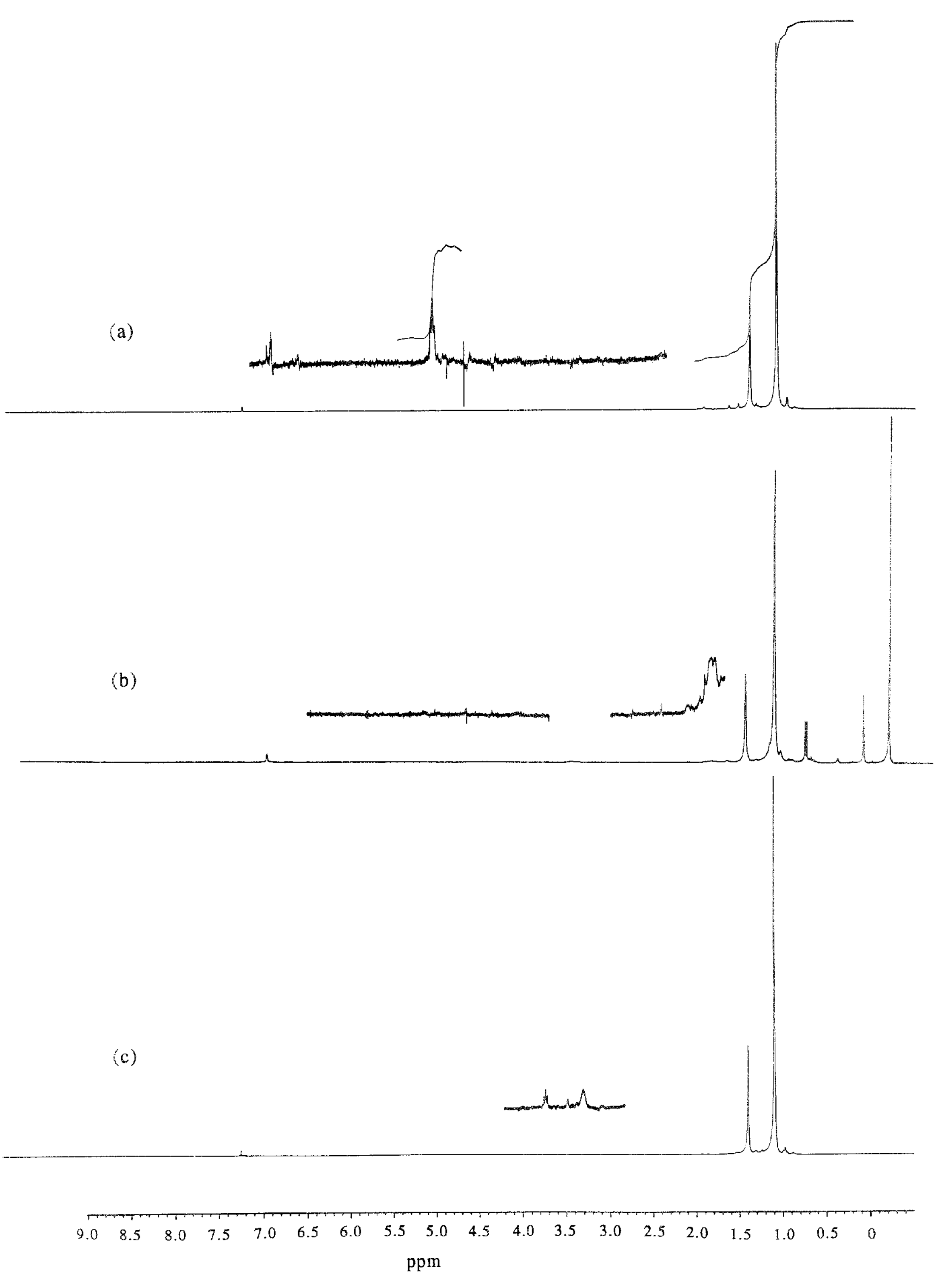
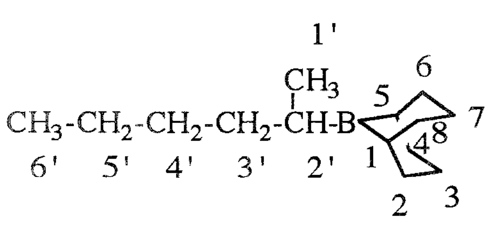


Figure 1 The ^{1}H n.m.r. spectra of (a) butyl rubber, poly(isobutylene-*co*-isoprene), (b) the hydroborated and (c) the hydroxylated products

assigned to C2,C4,C6,C8 and C3,C7 in the bicyclononane structure[16], respectively, as shown below:



It is difficult to see the chemical shifts corresponding to the bridge heads (C1 and C5) and C2′ due to peak broadening by coupling with boron. The peaks near 14 ppm are assigned to C1′ and C6′ in the linear alkyl group. A clear indication of the occurrence of autoxidation reaction in B-(2-hexyl)-9-BBN was seen after exposure to 50 mol% (vs. borane) of oxygen. *Figure 2b* shows a new major peak at 71.5 ppm, accompanied by several minor peaks between 67 and 76 ppm. The positive intensities indicate the alkoxide products CH–O, which are the oxidation adducts of the methine CH–B bond in the linear hexyl group. In the upfield region, the similar

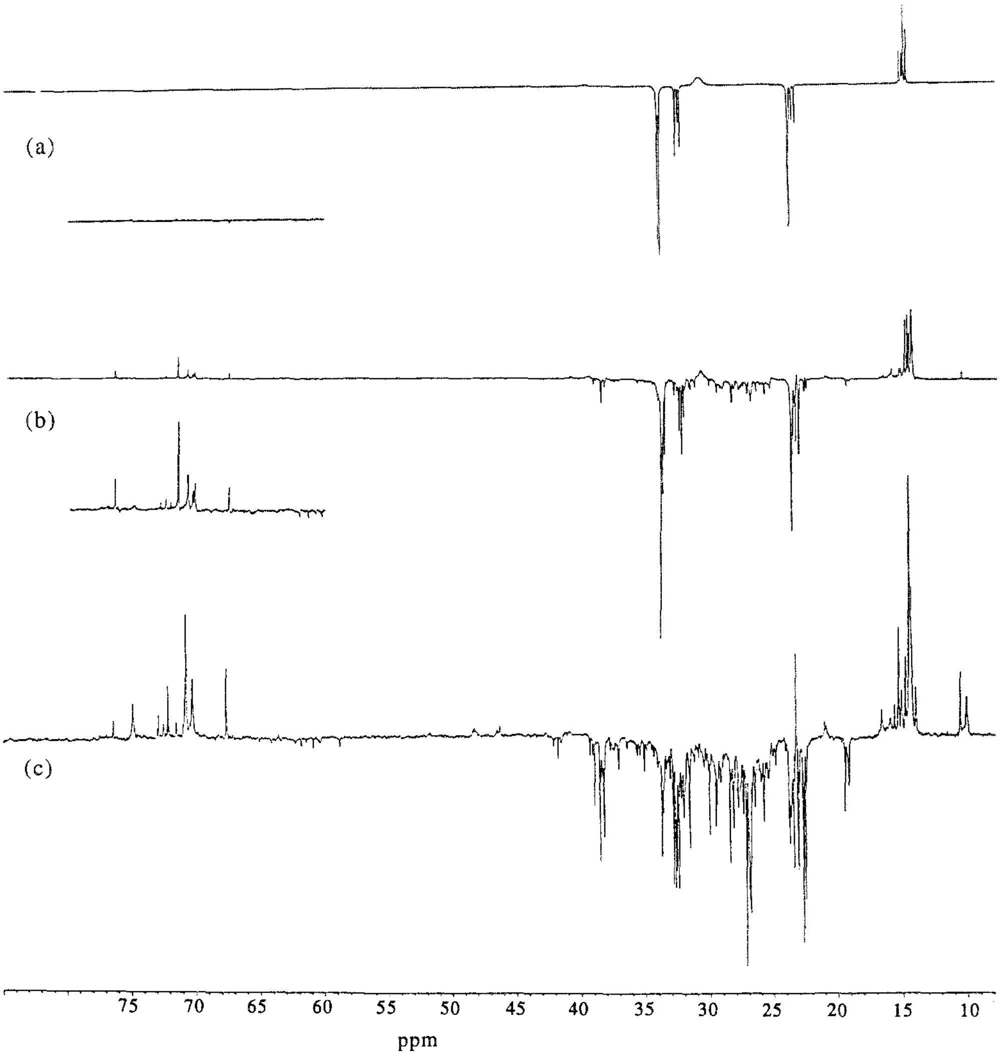


Figure 2 The ^{13}C n.m.r. (DEPT-135) spectra of (a) B-(2-hexyl)-9-BBN and its oxidation adducts with various mole ratios of oxygen: (b) 50% and (c) 100%

chemical shifts for CH_2 groups as for B-(2-hexyl)-9-BBN indicate no significant changes in the bicyclononane structure. As seen in *Figure 2c*, a much more complex spectrum was observed when 100 mol% of oxygen (vs. borane) was used. Many new peaks in the upfield region imply severe breakage of bicyclic structures due to the oxidation reaction of two B–CH bonds in bicyclononane. In fact, several new peaks around 73 and 76 ppm correspond to the oxidation adducts (CH–O species) from the bicyclic structure, which are the same chemical shifts as seen in the oxidation of B-(1-octyl)-9-BBN[13] under similar reaction conditions. Considering the heterogeneous reaction, the 1/1 oxygen/borane ratio creates an excess of oxygen for the borane molecules located on the surface of solution. To maintain the selectivity of oxidative reaction at the linear hexyl group, a control quantity of oxygen (below half the amount of borane groups) is essential.

PIB-g-PMMA copolymers

The control reaction provides the conditions for the selective oxidation reaction of alkyl-9-BBN groups in polyisobutylene. The resulting polymeric radicals are essential for graft-from polymerization. The hydroborated butyl rubber (**II**) was usually mixed with methyl methacrylate in THF solution. The oxygen was then 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 concentration would lead not only to loss of selectivity but also to over-oxidation to borinates, 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. The reaction was terminated by precipitating polymer in MeOH. Some unreacted B–C bonds were further oxidized by $NaOH/H_2O_2$. The product, isolated by filtration and washed with boiling MeOH, was then extracted with hexane and acetone in a Soxhlet apparatus for 24 h respectively. *Figure 3* compares the ^1H n.m.r. spectra of three fractions.

The peak at 3.58 ppm corresponds to methoxyl groups (CH_3O) in PMMA. The peaks at 1.09 and 1.39 ppm respectively are due to CH_3 and CH_2 protons in PIB. The hexane-soluble fraction shown in *Figure 3a* is basically ungrafted butyl rubber, which is usually only a small portion. On the other hand, the acetone-soluble fraction shown in *Figure 3b* contains both butyl rubber and PMMA structures, which indicates the fraction containing some acetone-soluble graft copolymer with high

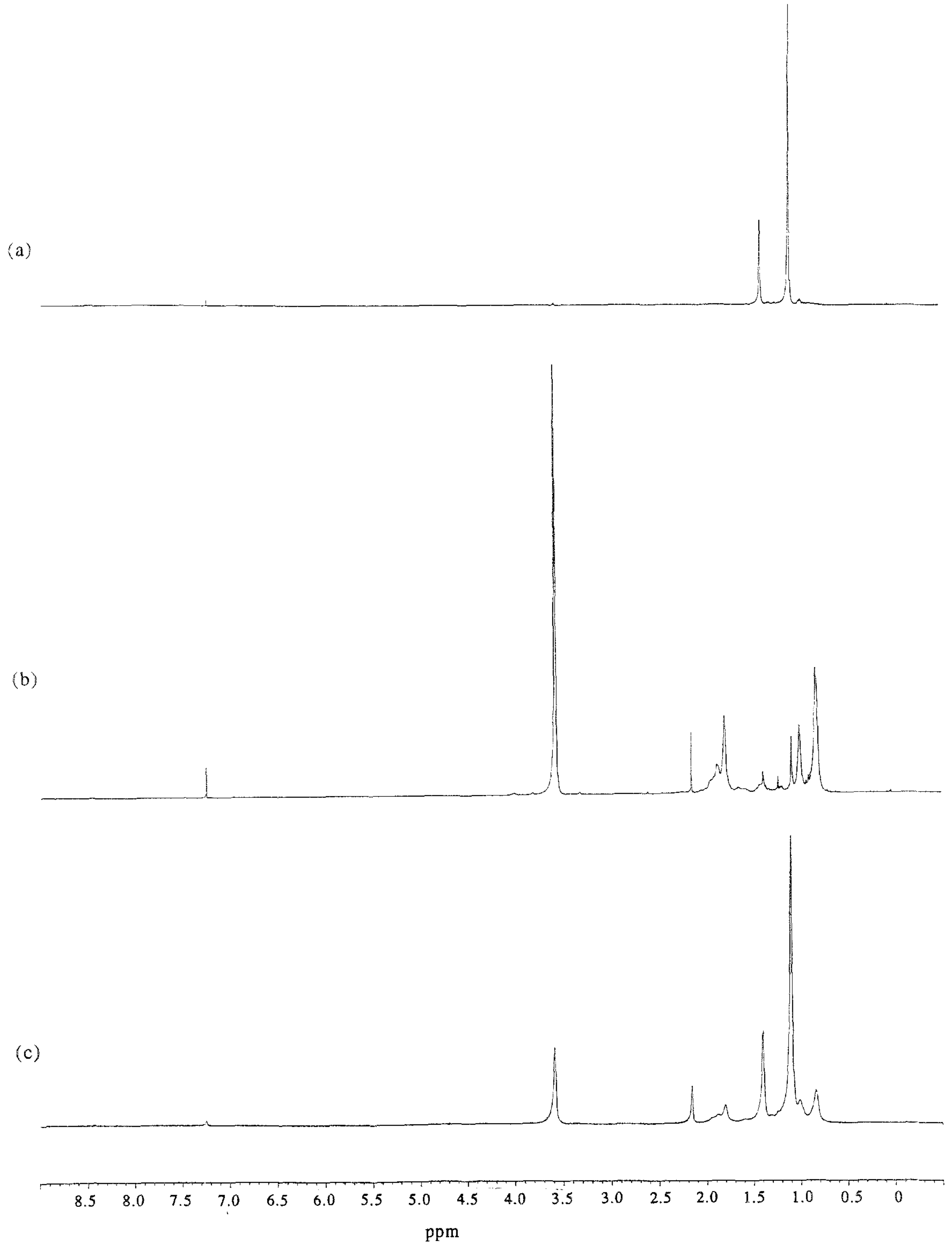


Figure 3 The comparison of ^{1}H n.m.r. spectra of three fractionation products: (a) hexane-soluble, (b) acetone-soluble and (c) hexane- and acetone-insoluble but soluble in THF

concentration of PMMA. It is interesting to note that the butyl rubber graft copolymers exhibit relatively better solubility in acetone than the EP rubber graft copolymers of similar compositions. This phenomenon may be related to the slight crystallinity in EP rubber. Despite many attempts, further fractionation of the acetone-soluble fraction to remove PMMA homopolymer was unsuccessful due to the microemulsion formed in many solutions. Only the graft copolymers shown in *Figure 3c* with concentration below ~ 60 mol% of PMMA are insoluble in acetone but soluble in THF and chloroform.

Figure 4 compares the i.r. spectra of several PIB-*g*-PMMA copolymers that are insoluble in hexane and acetone but soluble in THF. The absorption peak at 1730 cm^{-1} is due to the carbonyl group in PMMA segments. The peak intensity increases with the increase of PMMA concentration in the copolymer. The quantitative analysis of copolymer composition was calculated from the corresponding ^{1}H n.m.r. spectra, using the ratio of the two integrated intensities between 3.58 and 1.39 ppm and the number of protons both chemical shifts represent. *Figures 4a*, *4b* and *4c* indicate 8,

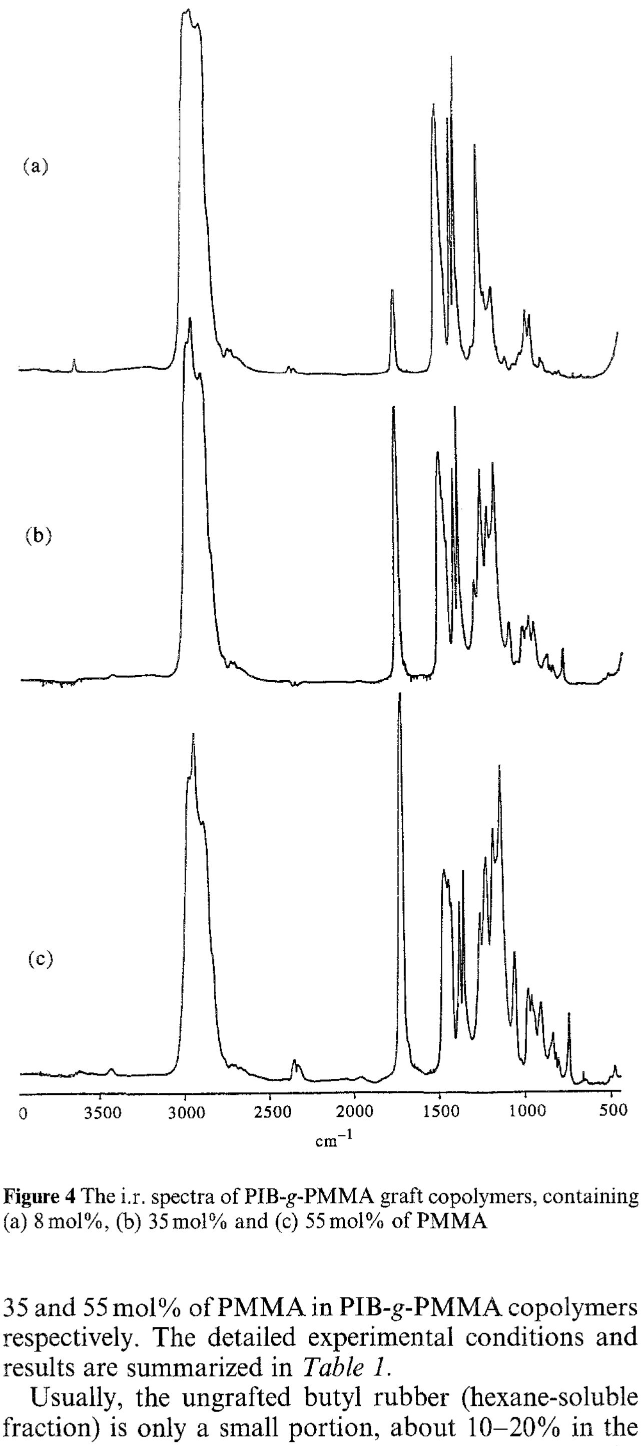


Figure 4 The i.r. spectra of PIB-*g*-PMMA graft copolymers, containing (a) 8 mol%, (b) 35 mol% and (c) 55 mol% of PMMA

35 and 55 mol% of PMMA in PIB-*g*-PMMA copolymers respectively. The detailed experimental conditions and results are summarized in *Table 1*.

Usually, the ungrafted butyl rubber (hexane-soluble fraction) is only a small portion, about 10–20% in the total product. Among runs 1–3, a clear trend shows the significant decrease in ungrafted PIB with an increase in MMA concentration. High monomer concentration seems important to ensure effective initiation. The acetone-soluble fraction is relatively large, in some cases more than 30%. The graft copolymers mainly exist in the insoluble fraction, and some in the acetone-soluble fraction. Comparing runs 2, 5 and 6, there is only a small difference in the graft-from reaction by using stoichiometric or excess amounts of 9-BBN reagent. The hydroboration reactions must be quite effective; there is only a slight difference in borane concentration in the hydroborated butyl rubbers.

G.p.c. studies

On-line g.p.c. measurement with r.i., p.d.a. and light scattering detectors was used to gain an insight into the structures of graft copolymers. *Figure 5* compares the r.i. curves of the starting butyl rubber and the PIB-*g*-PMMA copolymer (sample 2 in *Table 1*). The graft copolymer shows a bimodal molecular-weight distribution, and each peak has similar polydispersity to that of starting butyl rubber. It is very surprising to see the elution volume (or time) of the graft copolymer with one peak above and the other below that of the starting butyl rubber. This result implies that some of the graft copolymers have smaller hydrodynamic volume than the starting butyl rubber. Obviously, the g.p.c.-r.i. measurement by simply comparing elution volume (or time) between branched and linear structures alone cannot offer the accurate molecular weight of graft polymer.

It is very important to determine the molecular weight of graft copolymer by light scattering technique. On-line g.p.c.-r.i. and light scattering measurement offers the true molecular weight of each fraction in the g.p.c. curve. As shown in *Figure 6*, the same two curves in *Figure 5* are now plotted with intensity vs. molecular weight obtained from light scattering on-line measurement.

Overall, the graft copolymer has much higher molecular weight than the starting butyl rubber. The peak average molecular weights, 1.6×10^6 and 2.0×10^6 respectively, of graft copolymer are about 4–5 times the starting value for butyl rubber, which has a weight-average molecular weight of 4×10^5. Assuming the weight-average molecular weight of PMMA side chain in PIB-*g*-PMMA copolymer is about 2.0×10^5, which is the weight-average molecular weight of PMMA homopolymer obtained from a control reaction under similar reaction conditions, the PIB-*g*-PMMA copolymer with 2.0×10^6 molecular weight may have about eight PMMA side chains located along the butyl rubber backbone.

Table 1 A summary of PIB-*g*-PMMA copolymers

	Reaction conditions[a]				Products (g)			
Run	9-BBN/olefin	MMA (g)	O_2 (ml)	MMA conversion (%)	Hexane-soluble	Acetone-soluble	Insoluble fraction[b]	PMMA in insoluble fraction (wt%)
1	1/1	5	12	60	2.72	0.50	1.58	29
2	1/1	10	12	74	0.94	3.49	5.17	51
3	1/1	20	12	44	0.52	4.45	5.18	48
4	1/1	30	12	28	1.07	2.67	5.33	60
5	2/1	10	14	82	0.85	4.23	5.52	53
6	4/1	10	18	85	1.29	3.63	6.09	55

[a] All graft-from reactions were run by using 3 g of poly(isobutylene-*co*-isoprene) in 120 ml of THF solvent. The oxygen was slowly introduced to the reaction solution, 1 ml of oxygen hourly, at ambient temperature

[b] Insoluble in hexane and acetone, but completely soluble in THF

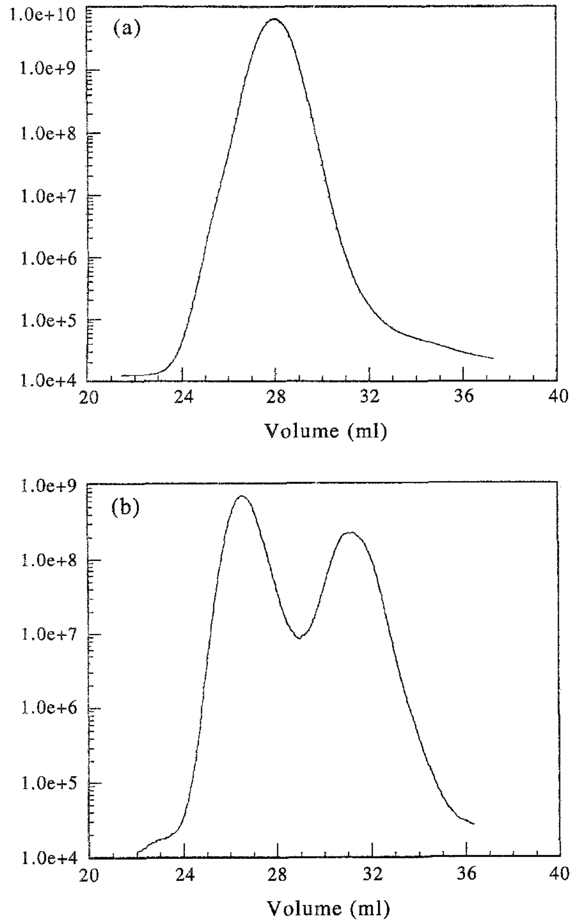


Figure 5 The g.p.c.-r.i. curves of (a) the starting butyl rubber and (b) the PIB-*g*-PMMA copolymer

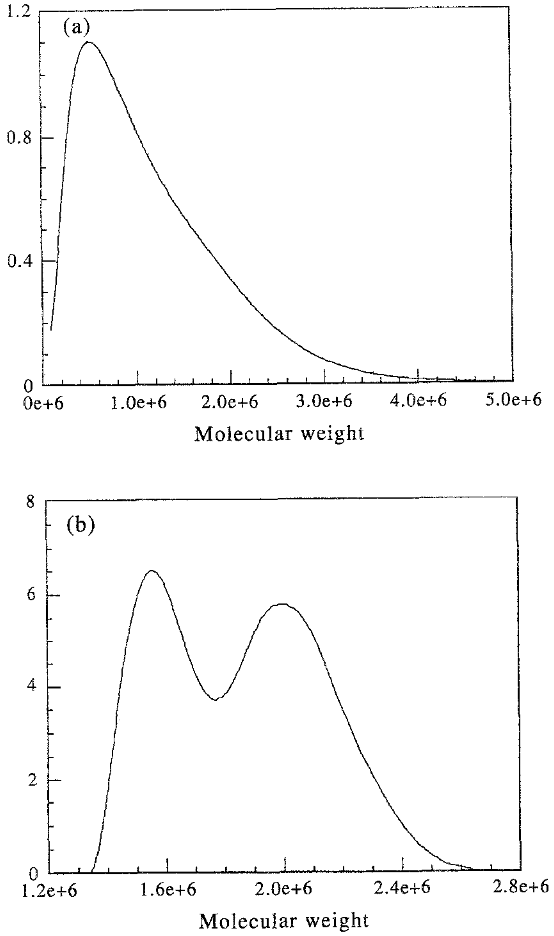


Figure 6 The g.p.c.-light scattering curves of (a) the starting butyl rubber and (b) the PIB-*g*-PMMA copolymer

In addition to g.p.c. with r.i. and light scattering measurements, a p.d.a. detector was also installed on-line, which provide composition information of the graft copolymer. *Figure 7* compares r.i. and u.v. ($\lambda = 235\,\text{nm}$) curves. At the wavelength of 235 nm, only PMMA absorbs light, with no response from PIB. The high-molecular-weight peak in the u.v. curve matches well with the corresponding r.i. peak, which indicates a homogeneous distribution of PMMA in the high-molecular-weight fraction of the graft copolymer. However, the low-molecular-weight peak with only low u.v. response indicates quite low concentration of PMMA in the low-molecular-weight fraction. The reasons for the two types of reaction modes during the graft-from reaction are under investigation.

Thermal properties

The thermal properties of the copolymer were determined by d.s.c. measurement. The samples were first heated to 170°C and then rapidly cooled to −150°C. The curves shown in *Figure 8* are heating curves obtained from these quenched samples at a heating rate of $20^{\circ}\text{C}\,\text{min}^{-1}$. To give better interpretation, the PIB-*g*-PMMA copolymer is compared with butyl rubber and PMMA homopolymer ($M_w = 200\,000$ g mol^{-1}, $M_w/M_n = 2.3$), which was prepared by a control reaction using 2-hexenyl-9-BBN/O_2 initiator and similar reaction conditions. As shown in *Figure 8*, two glass transition temperatures (T_g), −61 and +130°C, exist in butyl rubber-*g*-PMMA copolymer with 65/35 composition. Both T_g values are almost identical to those of the two corresponding homopolymers, butyl rubber and PMMA. This result indicates clear phase separation between the butyl rubber backbone and the PMMA side chains. The copolymer backbone must have sufficient successive sequences of isobutylene units to form separate domains, and the side chain must be high-molecular-weight polymer with a microstructure similar to PMMA homopolymer. The clear phase separation with hard (polar) and soft (non-polar) domains is a very interesting molecular structure. In fact, the copolymer behaves like a thermoplastic elastomer. The detailed mechanical properties of the graft copolymer and its blends are currently under investigation.

Morphology studies

Scanning electron microscopy (SEM) was used to examine the morphology of graft copolymer and polymer blends. The samples were prepared by solution casting before vapour deposition of a thin gold film on the surface. *Figure 9* compares the SEM micrographs of three polymer blends. *Figure 9a* presents the two-homopolymer blend A, which contains butyl rubber ($M_w = 400\,000$) and PMMA homopolymer ($M_w = 200\,000$) with 30/70 wt% ratio. The magnification of the original is 100×. The two distinct and irregular phases indicate the incompatibility between the two polymers. In fact, gross phase separation and inhomogeneity can be observed by simple visual inspection.

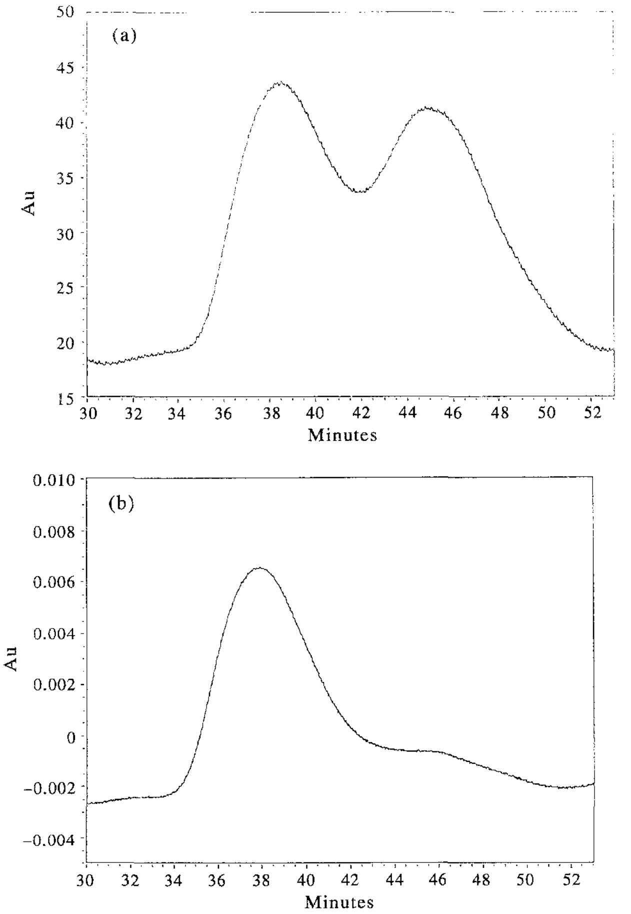


Figure 7 The comparison g.p.c. curves of PIB-*g*-PMMA copolymer using (a) r.i. and (b) u.v. ($\lambda = 235$ nm) detectors

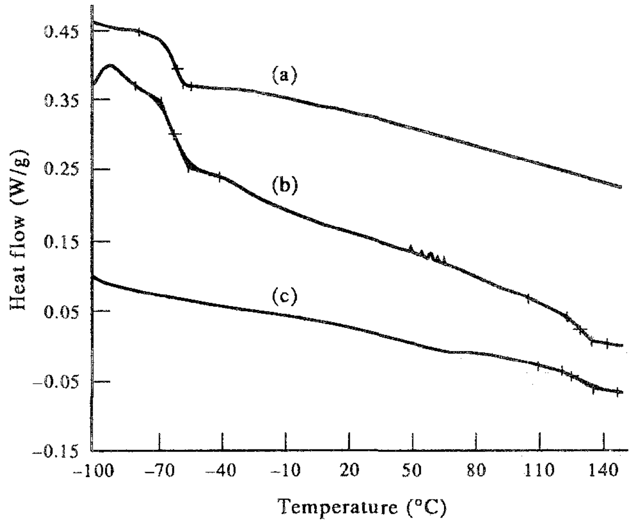


Figure 8 D.s.c. curves comparison between (a) butyl rubber and (b) PIB-*g*-PMMA copolymers containing 52 mol% of PMMA and (c) PMMA homopolymer

Figure 9b is the micrograph of the PIB-*g*-PMMA graft copolymer with an original magnification of 1000×. In this graft copolymer, the weight ratio between PIB and PMMA is 33/67 and the molecular weights of PIB and PMMA segments are similar to the corresponding homopolymers in polymer blend A. The domain sizes are significantly reduced, with spherical rubber particles homogeneously distributed in PMMA matrix. The film is clear with strong mechanical properties. *Figure 9c* presents the polymer blend obtained by mixing 10 wt% of graft copolymer into homopolymer blend A. As can be seen, solubilization of the homopolymer into the corresponding segment domains in the graft copolymer takes place. The formation of micro-heterogeneous domain structure of two incompatible components by solvent casting of the three polymer solutions suggests the emulsifying effect of the graft copolymer. Moreover, the uniformity of the domain size as well as the regularity of the domain shape in the cast films indicates that a high degree of emulsification[13] is achieved and the graft copolymer serves as a compatibilizer between two incompatible polymers.

EXPERIMENTAL

Instrumentation and materials

All ^{1}H n.m.r. and ^{13}C n.m.r. spectra were recorded on a Bruker WP-200 or a Bruker AM-300 spectrometer with the DISNMR software. The molecular weight of polymer was determined using a Waters GPC 600E (with Millenium-2 software) and on-line multiple detectors, Waters Photodiode Array Detector (PDA), Wyatt Dawn DSP-F Laser Photometer (with Astra and Easi softwares) and Waters 410 Differential Refractometer. The columns used were Waters Ultrastyragel of 10^5, 10^4, 10^3 and 500 Å. A flow rate of 0.7 ml min^{-1} was used, and the mobile phase was THF. The d*n*/d*c* values were determined by Wyatt Optilab 903 Interferometric Refractometer, with values of 0.1, 0.08 and 0.09 for butyl rubber, PMMA and PIB-*g*-PMMA copolymer respectively. Differential scanning calorimetry (d.s.c.) was measured on a Du Pont 2000 instrument. The d.s.c. measurements were taken from −120 to 160°C with a heating rate of 20°C min^{-1}. All O_2 and moisture-sensitive manipulations were performed inside an argon-filled Vacuum Atmosphere dry-box equipped with a MO-40-1 dry-train.

The commercial butyl rubber, Butyl 365, was obtained from Exxon Chemical Co. The polymers were purified by the solution–dissolution process using THF as solvent and methyl ethyl ketone (MEK) as non-solvent. The 9-borabicyclononane (9-BBN) was used as received from Aldrich. H.p.l.c.-grade THF was distilled from sodium anthracenide. Methyl methacrylate, styrene and 2-hexene were dried with CaH_2 and distilled under N_2.

*Hydroboration of poly(isobutylene-*co*-isoprene)*

Under inert atmosphere, 3 g of commercial butyl rubber, poly(isobutylene-*co*-isoprene) containing 1.6 mol% of isoprene, was dissolved in 150 ml of THF solvent. The

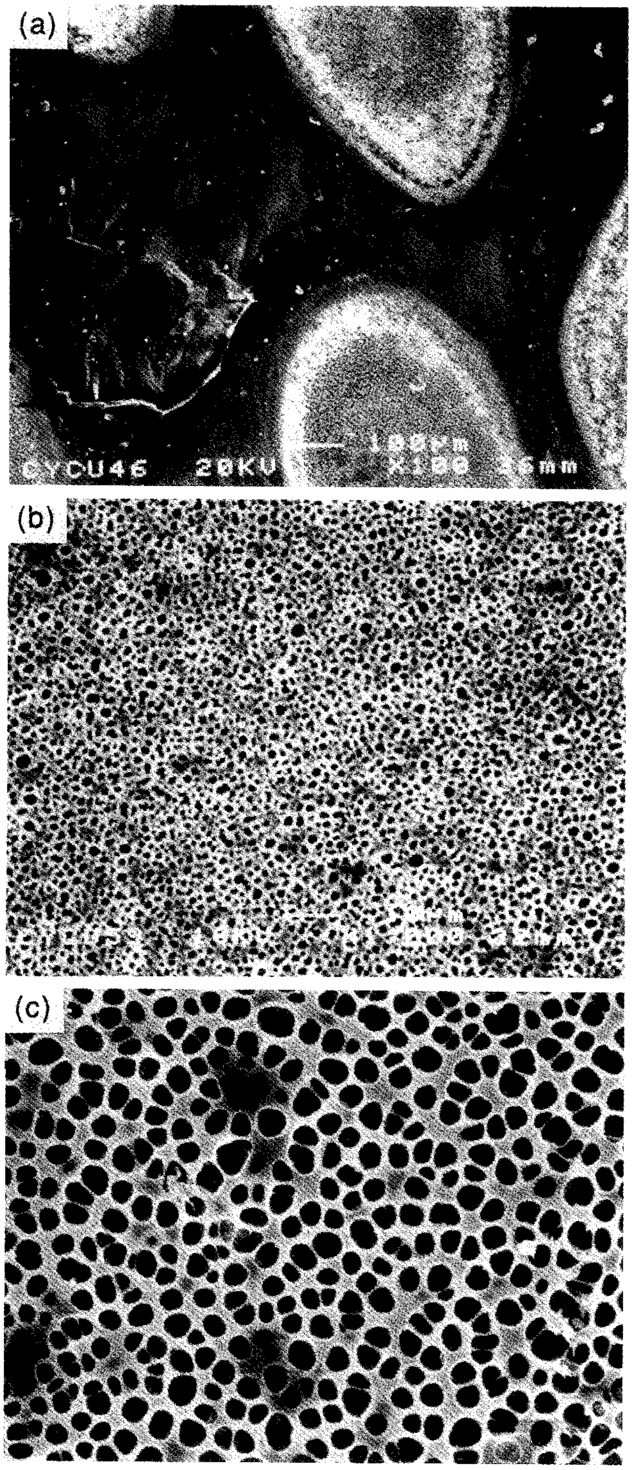


Figure 9 SEM micrographs of (a) two-homopolymer blend with butyl rubber/PMMA = 30/70 (100×), (b) PIB-*g*-PMMA copolymer (1000×) and (c) two-homopolymer blend with PIB-*g*-PMMA compatibilizer, butyl rubber/PIB-*g*-PMMA/PMMA = 30/10/70 (1000×)

hydroboration reaction was completed by adding 0.065 g of 9-BBN crystals to the solution, then refluxing at 68°C for 10 h. In most cases, the resulting hydroborated butyl rubber in THF solution was used directly for graft-from reaction to prepare butyl rubber 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), then 110 mg of H_2O_2 (30% in water). Both reagents were deoxygenated with argon before addition. The reaction took place at ambient temperature for 3 h before precipitating 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 ^{1}H n.m.r. spectrum indicates 94% of double bonds have been converted to hydroxy groups.

*Synthesis of polyisobutylene-*g*-PMMA*

In a typical example, 3 g of hydroborated butyl rubber was dissolved in 120 ml THF solution in an argon-filled dry-box, and then was mixed with 10 g of methyl methacrylate. After stirring for 0.5 h in the dry-box, the septa-equipped flask was taken out of the box. Immediately 1 ml of O_2 was injected into the reaction flask. After every hour of stirring, another 1 ml of O_2 was added until a total of 12 ml of oxygen had been injected. The solution was stirred at room temperature for an additional 2 h before termination by the addition of 5 ml (6 N) NaOH solution, then 10 ml of 30% H_2O_2. Both reagents were deoxygenated with argon before adding. After 2 h stirring at room temperature, the polymer was isolated by precipitation into methanol, then washed with methanol several times before drying in a vacuum oven. The product (~ 10 g) was fractionated by solvent extraction using hexane and acetone solvents. The hexane- and acetone-soluble fractions yielded 0.94 and 3.49 g respectively, and the insoluble fraction (soluble in THF) was 5.17 g.

Control reaction

In a 100 ml flask, 11 ml of 9-BBN in THF solution (5.5 mmol of 9-BBN) was allowed to react with 1 ml of 2-hexene (excess) at room temperature for 3 h. After the reaction, the excess 2-hexene and THF were removed by vacuum distillation at room temperature. The product was further distilled at 90°C to obtain 1 g of the 2-hexenyl-9-BBN.

In a 250 ml flask fitted with an air-tight septum, 20 ml of purified methyl methacrylate (0.187 mol) was dissolved in 100 ml THF. The initiator, 2-hexenyl-9-BBN (3.6 g, 0.0187 mol), was transferred into the flask under argon. The polymerization was initiated by reacting with O_2 (air), which diffused into the flask through air-tight septum. The reaction was allowed to progress at room temperature for 2 days. The reaction mixture was then exposed to air for another 2 h. The homopolymer of poly(methyl methacrylate) was then precipitated with isopropanol. After vacuum drying overnight, 6.6 g of PMMA (35% yield) was obtained with a weight-average molecular weight of about 200 000 g mol^{-1}.

CONCLUSION

The commercial importance of improving the compatibility between butyl rubber and other polymers led us to develop a compatibilizer to control the morphology of polymer blends. The development of graft-from reaction using borane offers a convenient process to prepare graft copolymers with controllable molecular compositions. The difficult goal of analysing the detailed molecular structure can be achieved by the combination of experimental techniques, especially on-line analysis of g.p.c. with r.i., u.v. and light scattering detectors. Based on the colloidal concept, the graft copolymer of two homopolymers can serve as emulsifier located at the interface between two polymer domains. The synthetic approaches for the preparation of various graft polymers is discussed in detail in this paper.

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