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The Synthesis, Characterization, and Copolymerization of the Macromonomer α-(*p*-Phenyl glycidyl ether)-ω-chloropolyisobutylene(PGE-PIB). 2.[†] The Synthesis of PGE-PIB and Its Copolymerization with Epichlorohydrin and Ethylene Oxide[‡]

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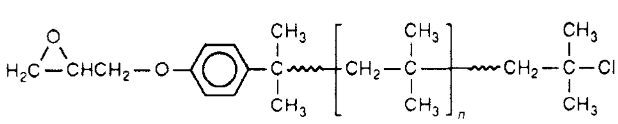
ABSTRACT: A convenient preparation for the new macromonomer α-(*p*-phenyl glycidyl ether)-ω-chloropolyisobutylene (PGE-PIB) has been developed. The synthesis involves a quantitative reaction between epichlorohydrin (ECH) and phenol-capped polyisobutylene (Ph-PIB). The reaction conditions were optimized by studying the epichlorohydrination of *p*-(1,1,3,3-tetramethylbutyl)phenol, a model compound that mimics the structure of Ph-PIB. The number-average phenyl glycidyl ether (PGE) functionality of PGE-PIB was analyzed independently by ^{1}H NMR spectroscopy and titration and was found to be $\bar{F}_n = 1.0 \pm 0.1$. The PGE-PIB macromonomers were copolymerized with ECH and ethylene oxide by the catalyst Et_3Al/H_2O. The graft copolymers were isolated by selective solvent extraction and characterized by ^{1}H NMR spectroscopy, GPC, and DSC.

A. Introduction

Ring-opening polymerization has in recent years become increasingly important and led to commercially significant polymers, e.g., poly(ethylene oxide) (PEO), polyepichlorohydrin (PECH), and poly(propylene oxide). There is a dearth of information in the area of macromonomers which bear functional head groups capable of ring-opening polymerization;[1–3] therefore it was thought worthwhile to investigate the synthesis of cyclic ether-functionalized polyisobutylene (PIB) macromonomers. After considering various synthetic routes to such a macromonomer, we have chosen to react phenol-capped PIB (Ph-PIB) with ECH to yield a phenyl glycidyl ether (PGE) capped macromonomer. The synthesis and characterization of Ph-PIB precursors have recently been described.[4]

This paper describes the reaction of ECH with the model compound *p*-(1,1,3,3-tetramethylbutyl)phenol (TMBP) and with Ph-PIB to yield *p*-(1,1,3,3-tetramethylbutyl)phenyl glycidyl ether (TMBPGE) and α-(*p*-phenyl glycidyl ether)-ω-chloropolyisobutylene (PGE-PIB), respectively. The copolymerization of the macromonomer with ECH and EO to form polyepichlorohydrin-*graft*-polyisobutylene (PECH-*g*-PIB) and poly(ethylene oxide)-*graft*-polyisobutylene (PEO-*g*-PIB), respectively, will also be described.



PGE-PIB

B. Experimental Section

Materials. TMBP (Pfaltz and Bauer) was recrystallized from *n*-hexane three times. *p*-(*tert*-Butyl)phenyl glycidyl ether (BPGE) (Aldrich) was distilled under nitrogen. ECH (Aldrich) was distilled under nitrogen. Tetra-*n*-butylammonium hydrogen sulfate (TBAHS) (Aldrich), ethylene oxide (EO) (Fluka, AG), and triethylaluminum (Et_3Al) (Ethyl Corp.) were used as received. Ph-PIB was synthesized and analyzed as described.[4]

Procedures. Macromonomer molecular weight measurements and model reaction analyses were carried out by GPC. The GPC was calibrated with standard PIBs of narrow molecular weight distribution prepared in our laboratories. The molecular weights of the standards were determined by light scattering.[5] The GPC system, a Waters Associates liquid chromatograph, was equipped with 10^6-, 10^5-, 10^4-, 10^3-, 500-, and 100-Å columns. The 500- and 100-Å columns were ultragel columns supplied by Analytical Services, Inc. Tetrahydrofuran (THF), at a flow rate of 1 mL/min, served as the carrier solvent.

Proton magnetic resonance spectra were recorded by using a Varian T-60 NMR spectrophotometer. Solvents were either carbon tetrachloride or deuterated chloroform. Tetramethylsilane was used as the internal reference.

In addition to ^{1}H NMR spectroscopy, the epoxide content of the macromonomer was determined by a standard titration.[6] Previous workers[7] have used dioxane as solvent for epoxide titration, but since PIB was insoluble in dioxane, we have used THF in the place of dioxane.

DSC thermograms were recorded at 10 °C/min with a Du Pont 1090 instrument.

1. Synthesis of the Model Compound *p*-(1,1,3,3-Tetramethylbutyl)phenyl Glycidyl Ether (TMBPGE). Into 100 mL of carbon tetrachloride were placed 0.06 g of TMBP (3×10^{-4} M), 6.3 mL of ECH (8×10^{-2} M), and 1.0 g of TBAHS (3×10^{-3} M). To this was added dropwise, while refluxing, 1.2 g of NaOH (3×10^{-2} M) in 15 mL of water. After a 12-h reaction, the mixture was washed with water until neutral. The solvent and excess ECH were removed by vacuum; the product was redissolved in *n*-hexane and dried for 12 h over magnesium sulfate. After filtration and evaporation of the *n*-hexane, the product was weighed and analyzed by GPC.

2. Synthesis of PGE-PIB. The macromonomer was synthesized under the same conditions as the model compound. Ph-PIB ($\bar{F}_n = 1.0$) was used in place of TMBP. After reaction, the bulk of the carbon tetrachloride was removed and the polymer was precipitated into methanol. The polymer was repeatedly dissolved in *n*-hexane and precipitated into methanol to ensure the complete removal of excess ECH. Finally, the polymer was redissolved in *n*-hexane, dried for 16 h over magnesium sulfate, and filtered and the hexane removed by vacuum to constant weight.

3. Copolymerization of the Macromonomer with ECH and EO. Copolymerizations of PGE-PIB with both ECH and

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[†] Part 1: Kennedy, J. P.; Carter, J. D. *Polym. Prepr.* **1986,** *27* (2), 29–30.

[‡] Considered part 8 in the series "Macromers by Carbocationic Polymerization". For paper 7 in this series, see: Kennedy, J. P.; Lo, C. Y. *Polym. Bull.* **1985,** *13,* 441.

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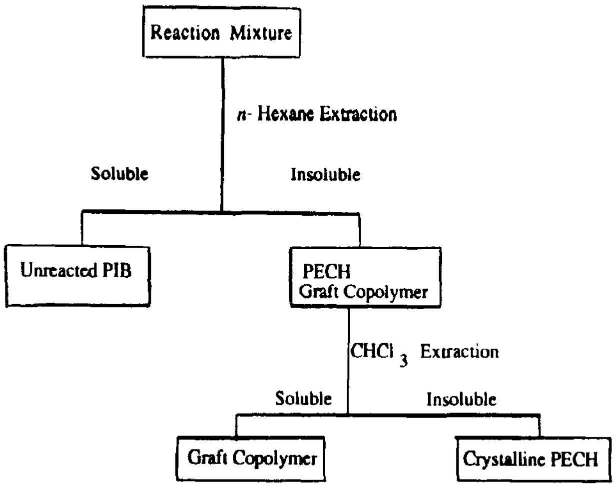


Figure 1. Separation scheme for the isolation of PECH-*g*-PIB.

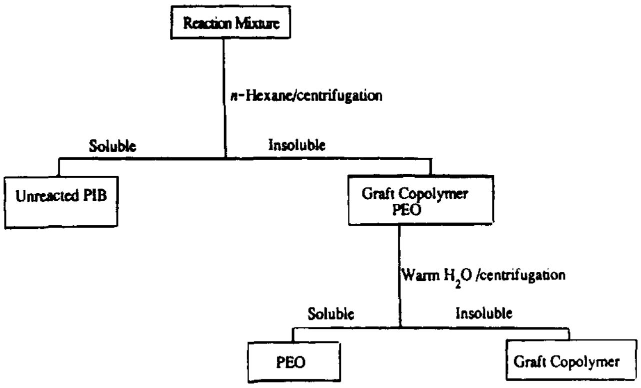
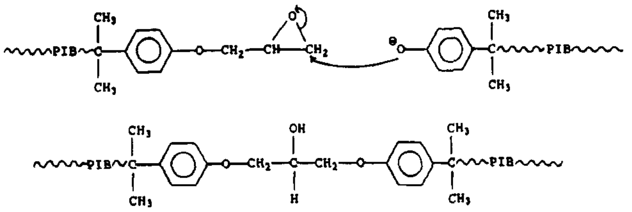


Figure 2. Separation scheme for the isolation of PEO-*g*-PIB.

Scheme I
Mechanism of Functionality Loss during the Synthesis of PGE-PIB



EO were carried out under nitrogen in carbon tetrachloride with stirring for approximately 19 h at room temperature. Polymerizations were induced by injecting Vandenberg catalyst solutions[8] ($[Et_3Al]/[H_2O] = 2$) into septum-sealed flasks. The catalyst concentration was 0.003 M. The reactions were terminated with a small amount of methanol.

The PECH-*g*-PIB was isolated by selective solvent extraction as outlined in Figure 1. The heterogeneous mixtures were washed with 5% aqueous HCl and then with water until neutral. The bulk of carbon tetrachloride was removed from the product by rotary evaporation and residual monomer by extraction with *n*-hexane. Finally, the reaction product was extracted exhaustively with chloroform and dried under vacuum at 40 °C and the percent conversion determined by weighing.

The PEO-*g*-PIB was isolated by selective solvent extraction and centrifugation as outlined in Figure 2. Carbon tetrachloride was removed by rotary evaporation. The product was then shaken with *n*-hexane, which caused the formation of a milky emulsion. This was centrifuged for 30 min at 4000 rpm and the *n*-hexane subsequently decanted. This process was repeated until the supernatant *n*-hexane was free of polymer. The same procedure was followed by using 50 °C distilled water until the supernatant was free of extract.

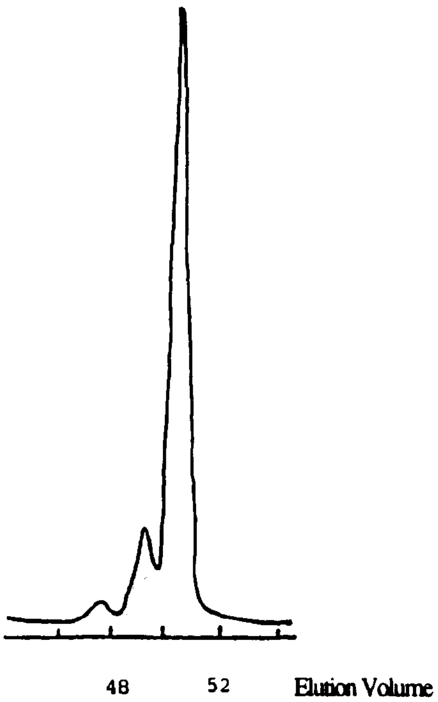


Figure 3. High-resolution GPC (Ultra Styragel) separation of the reaction mixture for the product of ECH and TMBP (ECH × 10 molar excess).

Table I
Optimization of the Reaction between TMBP and ECH[a]

exp	phenol, mol/L	ECH, mol/L	NaOH, mol/L	TBAHS, mol/L	yield, %
1	0.18	0.90	0.30	0.03	70
2	0.18	1.80	0.30	0.03	80
3	0.0070	0.14	0.15	0.0015	82
4[b]	0.0030	0.40	0.30	0.03	96
5	0.0030	0.80	0.30	0.03	93
6[b]	0.0030	0.80	0.30	0.03	98

[a] CCl_4, 77 °C, 15 h. [b] $NaOH/H_2O$ added last.

Table II
Epoxide End Group Analysis of the Model Compound and PGE-PIB (THF as Solvent)

sample	F_n	
	^1H NMR	titration
BPGE	-	0.995 ± 0.014
PGE-PIB		
$M_n = 16100$	1	0.97 ± 0.10
$M_n = 5600$	1	0.96 ± 0.11
$M_n = 4500$	1	0.96 ± 0.09

4. **Characterization of the Graft Copolymers.** The homogeneity of the graft copolymers was ascertained by GPC; a unimodal trace indicated acceptable homogeneity. Copolymer compositions were determined by ^1H NMR spectroscopy. Thermal properties were characterized by DSC.

C. Results and Discussion

1. **Model Studies.** The reaction between Ph-PIB and ECH to form the phenyl glycidyl ether functionality involves well-known epoxide chemistry. The phenoxy ion formed by aqueous NaOH attacks the ECH at the less substituted carbon and forms a halohydrin intermediate, which undergoes intramolecular nucleophilic displacement to form the epoxide and NaCl. If the phenoxide ion attacks an already formed phenyl glycidyl ether, chain extension occurs, which destroys functionality (see Scheme I). Therefore reaction conditions were sought that would minimize this functionality loss.

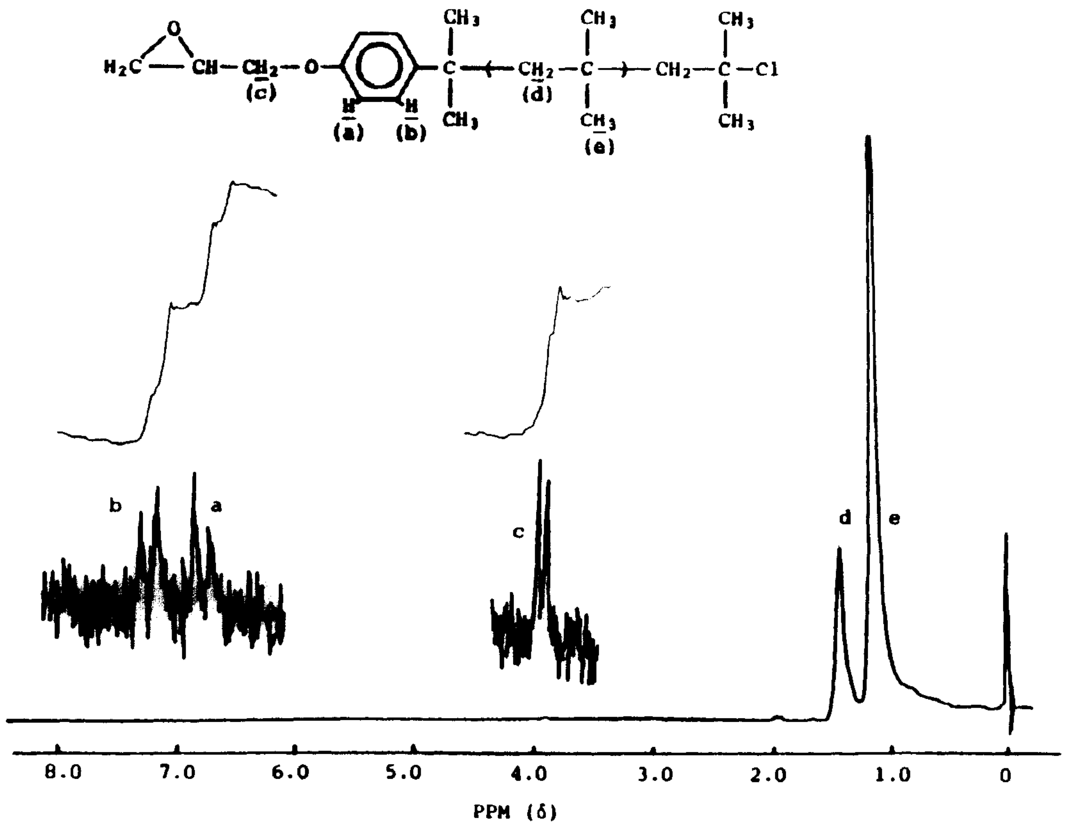


Figure 4. ^{1}H NMR spectrum of the reaction product of PGE-PIB and ECH (M_n = 4500).

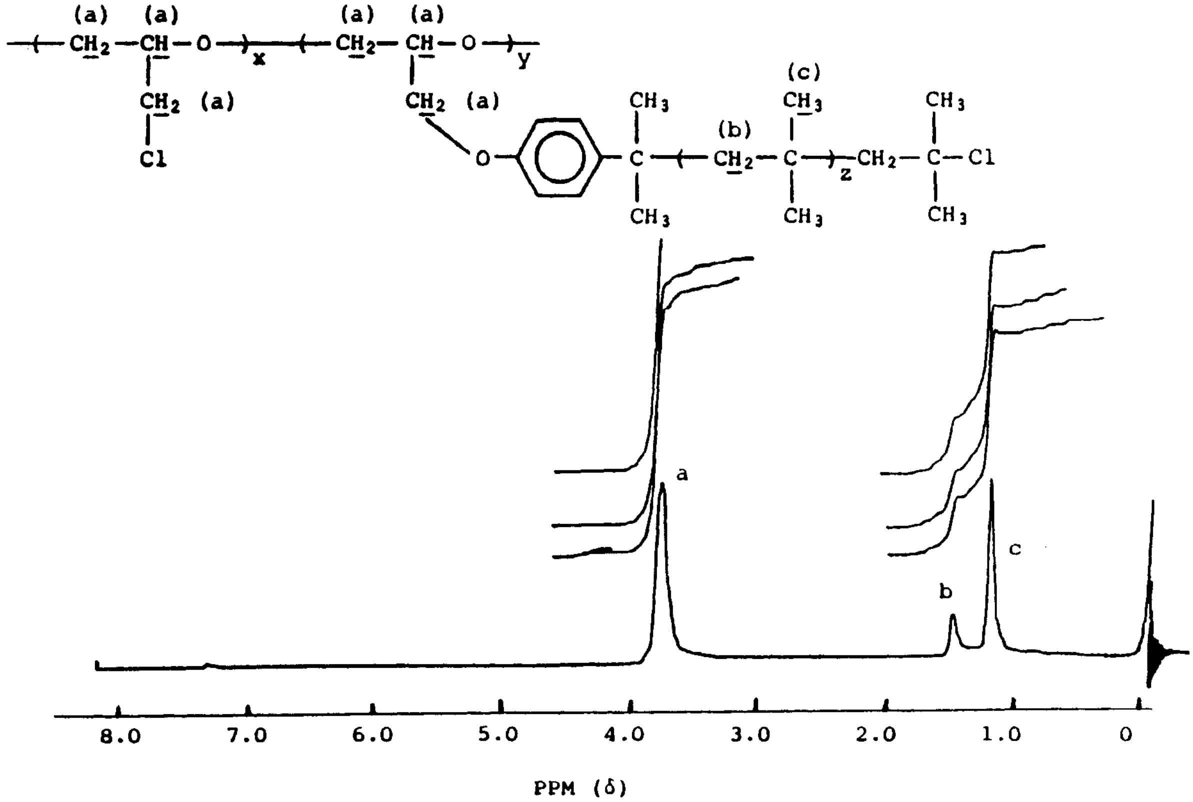


Figure 5. ^{1}H NMR spectrum of PECH-*g*-PIG (Table III, experiment 3).

Studies of the reaction between TMBP and ECH were carried out to optimize reaction conditions. Table I gives the conditions examined. In experiment 1, ECH is present in 5× molar excess. ^{1}H NMR spectroscopy of the product revealed an unexpected signal at 3.6 ppm, which was shown by fractional distillation to be present in the high boiling fraction. High-resolution GPC also showed the presence of two species other than the desired product. To verify the validity of the GPC analysis, a base-line separation of a 50/50 mixture of phenyl glycidyl ether and BPGE was obtained with the described GPC system.

Evidently, the phenoxy ion is attacking an already-formed PGE species, thereby reducing the yield of the PGE functionality. The presence of a smaller second extraneous peak in the GPC (see Figure 3) suggests that the

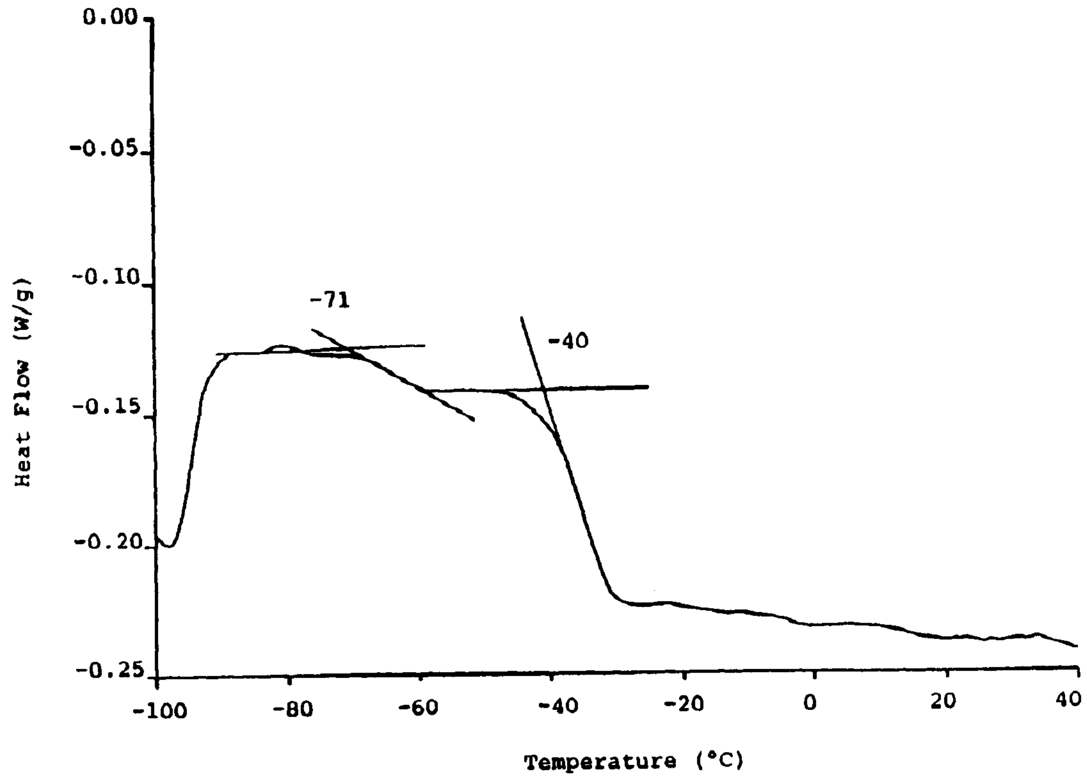


Figure 6. DSC scan of PECH-*g*-PIB (Table III, experiment 3).

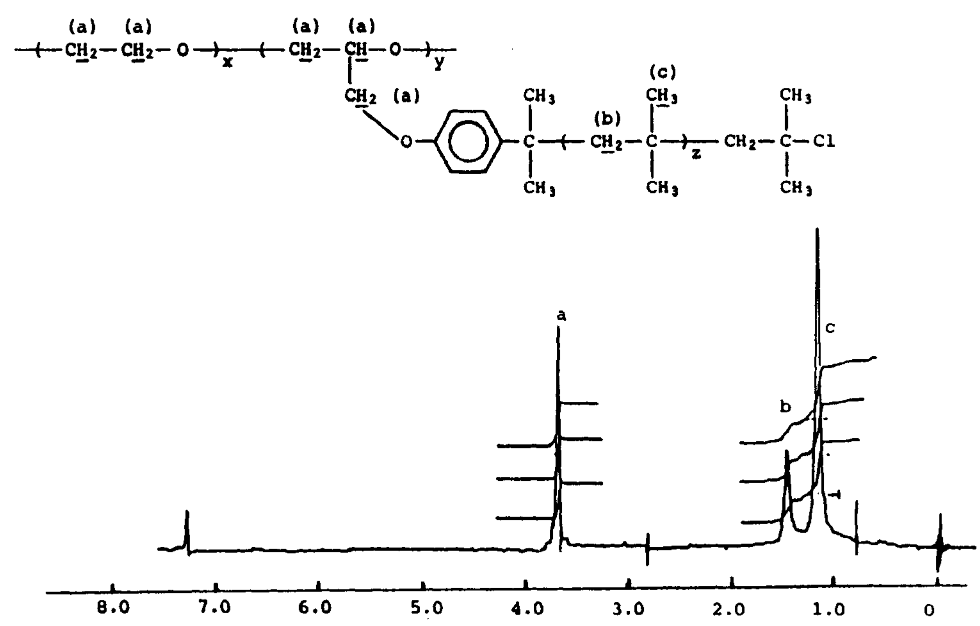


Figure 7. ^{1}H NMR spectrum of PEO-*g*-PIB (Table V, experiment 2).

product of the first attack may also undergo attack.

In experiments 2 and 3, a 10× and 20× molar excess of ECH was used, respectively. The yield of the desired product was still only 80% by GPC (see Figure 3).

In experiments 4 and 6 the ECH concentration was increased to 130× and 270× molar excess, respectively. Unlike in the previous experiments, however, the aqueous base was added dropwise to premixed phenol/ECH systems instead of adding the ECH dropwise to the phenol/aqueous base mixture. This resulted in a dramatic yield increase. Evidently, the higher molecular weight side products virtually do not form in the presence of a large excess of ECH and on addition of the aqueous NaOH to ECH/phenol mixtures.

The conditions of experiment 6 were used to react Ph-PIB with ECH. Table II lists the results of epoxide end group analysis of three different molecular weight macromonomers. Figure 4 shows a ^{1}H NMR spectrum of a representative product ($M_n = 4500$). The doublet (at 4.0 ppm) is associated with the methylene protons adjacent to the epoxide ring, indicating the presence of PGE functionality. Integration of this doublet against the aromatic proton signals gave the extent of the reaction: $\bar{F}_n$ = (2 × area of doublet at 4.0 ppm)/(area of the signal in the 6.5–7.5 ppm range). While ^{1}H NMR spectroscopy provided a rapid means to estimate the extent of the reaction, the PGE functionality was also determined by titration. As seen by the data in Table II, the results of titrations and those obtained by ^{1}H NMR spectroscopy are in satisfactory agreement.

2. Copolymerization of the PGE-PIB Macromonomer with ECH and EO. a. Epichlorohydrin (ECH).

Table III
Copolymerization Data for PGE-PIB (M_1) with ECH (M_2)

exp	$[M_1]$ in charge[a]	$[M_2]$ in charge	M_1, mol %	conv, % M_1	conv, % M_2	comp, mol % M_1	comp, mol % M_2	wt % PIB
1	3.9×10^{-3}	4.9	0.08	19.8	41.7	0.033	99.967	5.5
2	6.7×10^{-3}	6.7	0.10	21.6	45.6	0.041	99.959	6.9
3	1.2×10^{-2}	2.7	0.45	16.3	37.1	0.183	99.817	24.3

[a] M_n = 16 100.

Table IV
Glass Transitions of PECH-*g*-PIB

exp (Table III)	T_g, °C onset PIB	midpoint PIB	onset PECH	midpoint PECH
1	−68	−65	−17	−10
2	−73	−67	−29	−26
3	−71	−65	−40	−35

Table V
Copolymerization Data for PGE-PIB (M_1) with EO (M_2)

exp	$[M_1]$ in charge[a]	$[M_2]$ in charge	M_1, mol %	conv, % M_1	conv, % M_2	comp, mol % M_1	comp, mol % M_2	wt % PIB
1	4.0×10^{-3}	6.7	0.06	17.8	25.6	0.049	99.951	15.4
2	6.0×10^{-3}	1.5	0.40	14.0	19.0	0.317	99.683	53.0
3	8.0×10^{-3}	1.6	0.50	13.5	18.1	0.454	99.546	62.8

[a] M_n = 16 100.

The macromonomer ($\bar{M}_n$ = 16 100) was copolymerized with ECH. PECH grafted with PIB should be an ideal interfacial agent for the compatibilization of butyl and epichlorohydrin elastomers. Such blends should have outstanding properties where a high gas barrier is demanded.

Table III shows feed and copolymer compositions. Figure 5 shows a representative ^{1}H NMR spectrum of the graft copolymer, together with assignments. The mole percent macromonomer in the feed is higher than that in the copolymer. Similar deviations have previously been observed and attributed to microphase separation during synthesis.[9]

DSC studies have consistently shown two T_g's, the lower one corresponding to the PIB branches and the higher one corresponding to the PECH backbone. Figure 6 shows a representative DSC trace for a PECH-*g*-PIB containing 24% PIB by weight. Table IV gives the temperatures of the onset of T_g as well as the temperature at the transition midpoints for different graft copolymers. Both values are often used to specify T_g.

Unexpectedly, as the amount of PIB increased in the graft copolymer, the T_g of PECH decreased. Usually the T_g's of multiphase copolymers correspond to the T_g's of the homopolymers.[10] In agreement to our observations, Baccaredda et al.,[11] who studied the transitions of poly(1-butene-*graft*-styrene) and poly(butadiene-*co*-acrylonitrile-*graft*-styrene-*co*-acrylonitrile), found that as grafting onto the backbones occurred, the T_g of the backbones was reduced relative to the T_g of unreacted backbones. Baccaredda et al.[11] assume that the branches impede intermolecular interactions between the backbones, thereby allowing for greater backbone flexibility. Hence the T_g of the backbone is lowered.

b. Ethylene Oxide (EO). Copolymerization of PGE-PIB with EO was of interest because of the likelihood of obtaining amphiphilic graft copolymers, i.e., hydrophilic PEO backbones carrying hydrophobic PIB branches. The importance of such materials in emulsion technology is well-known.

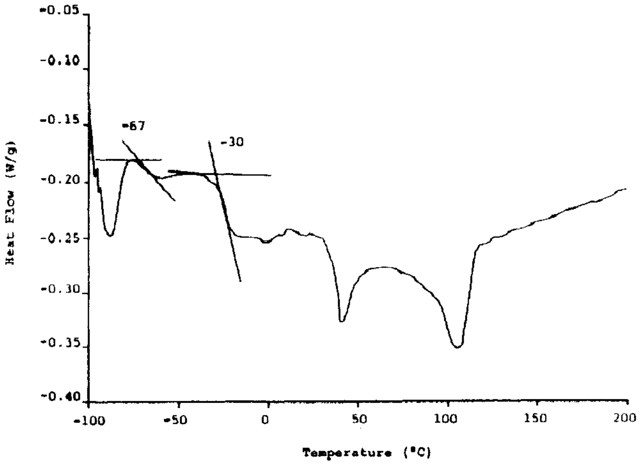


Figure 8. DSC scan of PEO-*g*-PIB (Table V, experiment 2).

Table V shows feed composition, conversion, and copolymer compositions. Figure 7 shows a representative ^{1}H NMR spectrum of a graft copolymer. While the graft copolymers were insoluble in water (good solvent for PEO, poor for PIB) and *n*-hexane (good solvent for PIB, poor for PEO), they formed emulsions in these solvents and were readily soluble in chloroform (good solvent for both PEO and PIB). The emulsions were destabilized by centrifugation, which permitted isolation of the graft copolymers (see Figure 2).

The reactivity of the macromonomer is slightly lower than expected from the modified copolymer composition equation.[12] The difference in feed and copolymer compositions might be due to phase separation during synthesis.[9]

Figure 8 shows the DSC scan of the graft copolymer containing 53% PIB. Evident at −30 °C is the T_g associated with the amorphous PEO segments. The T_g usually reported for PEO is −41 °C, although there is uncertainty in this measurement.[13] The highest T_g reported for PEO homopolymer is −40 °C, which is about 10 deg lower than that observed in the PEO-*g*-PIB graft copolymer.

We offer two possible explanations for this observed T_g shift. The first involves the effect of crystallinity on T_g. High molecular weight PEO, as prepared by organometallic catalysis, is highly crystalline. The degree of crystallinity in PEO has been measured as high as 95%.[14] The introduction of PIB grafts most probably impedes the degree of crystallization. It has been reported for poly(4-methyl-1-pentene)[15] that as percent crystallinity decreases T_g increases.

A problem with this argument is that it is unlikely that the crystallinity was reduced to levels never before observed in PEO. It is conceivable that the range of T_g's reported for PEO[13] is due to varying degrees of crystallinity within the samples. However, as previously mentioned, these values begin at −40 °C and decrease, suggesting that as crystallinity decreases, T_g decreases. This opposite effect of crystallinity on T_g has also been previously observed. The T_g of poly(vinyl chloride) was reported[16] to decrease with decreasing crystallinity.

Therefore perhaps a better explanation is that the PIB branches hinder the mobility of the PEO backbone and thereby increase the T_g. The opposite phenomenon observed for PECH-*g*-PIB may be due to the presence of polar CH_2Cl pendent groups on the PECH backbone, which contribute to higher intermolecular forces between the chains.

Also of interest are the melting endotherms of this graft copolymer. The high melting endotherm (ca. 100 °C) may be due to superheating. This effect occurs in high molecular weight semicrystalline polymers where chain entanglement in the amorphous phase reduces the rate of melting and thereby causes an increase in the crystalline T_m.[17] The lower endotherm (ca. 40 °C) is due to the T_m of the crystalline PEO phase; however, it is lower than that of conventional PEO (+65 °C). This behavior may be due to imperfect crystallization much the same way that impurities in a low molecular weight compound lower the melting point. In this system, the amorphous PIB branches may be the "impurities". A similar effect has been reported by Kargin in a nylon-*g*-PE system.[18]

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Registry No. TMBP, 140-66-9; TMBPGE, 5904-85-8; ECH, 106-89-8; (ECH)(IB) (graft copolymer), 124535-75-7; (EO)(IB) (graft copolymer), 124535-76-8.