Cationic Modifications of Polychloroprene. IV. Synthesis and Characterization of Poly(chloroprene-g-isobutylene) Carrying tert-Chloride Branch Termini

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Cationic Modifications of Polychloroprene. IV. Synthesis and Characterization of Poly(chloroprene-g-isobutylene) Carrying tert-Chloride Branch Termini

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ABSTRACT

This paper concerns the preparation and characterization of a new graft copolymer comprising polychloroprene backbone and polyisobutylene branches which carry tertiary chlorine termini. Synthesis involved the grafting of isobutylene from polychloroprene by the use of BCl_3 coinitiator in methylene chloride solvent in the -12 to -78°C range. Conditions have been defined for efficient and convenient graft copolymerizations. Carefully purified grafts (selective solvent extraction) were characterized by a battery of analytical techniques including ^{1}H-NMR spectroscopy and GPC. Agreement between calculated and experimental graft $\overline{M}_n$'s indicate absence of disturbing side reactions, i.e., backbone degradation and cross-linking, during synthesis. The presence of tertiary chlorine

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endgroups has been demonstrated by thermal dehydrochlorination studies. Branch molecular weight, molecular weight distribution, and frequency have been obtained by selective oxidative destruction of the polychloroprene backbone followed by surviving branch analysis. A graft prepared at -20° carried ~5 polyisobutylene branches of $\overline{M}_n$ = 5000 each.


INTRODUCTION

Numerous patents [1-10] and publications [11, 12] concern the synthesis of various graft copolymers of polychloroprene by anionic and free radical techniques. However, none of them mention grafts containing polyisobutylene (PIB) branches. The discovery [13] that certain polymer halides in conjunction with select organoaluminum compounds are excellent carbenium ion precursors for the polymerization of cationically polymerizable olefins led to the efficient synthesis of many graft copolymers containing PIB branches.

Recent investigations on the detailed mechanism of elementary events in BCl_3-coinitiated isobutylene polymerizations [14] opened new avenues for the synthesis of novel telechelic [15] and block [16] copolymers exhibiting useful properties. We have recently discovered that graft copolymers comprising a polychloroprene (CR) backbone carrying PIB branches with tertiary chlorine endgroups,

$$
\begin{array}{c}
C \\
| \\
CR\text{-}g\text{-}PIB \sim\!\sim C\text{-}C\text{-}Cl \\
| \\
C
\end{array}
$$
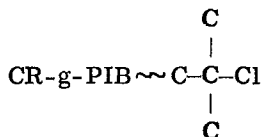
can be synthesized using the CR/BCl_3/isobutylene system. This paper concerns a discussion of experimental conditions for the efficient synthesis of

$$
\begin{array}{c}
C \\
| \\
CR\text{-}g\text{-}PIB \sim\!\sim C\text{-}C\text{-}Cl \\
| \\
C
\end{array}
$$
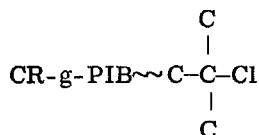
and detailed graft characterization studies. Selective solvent extraction of the graft coupled with ^{1}H-NMR, molecular weight determination, selective destructive oxidation of the CR backbone followed by surviving PIB branch analysis, and quantitative thermal dehydrochlorination were used to characterize the detailed structure of

$$\text{CR-g-PIB} \sim\sim \underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-\text{Cl}$$
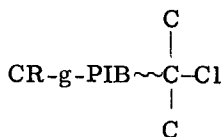
EXPERIMENTAL

Materials

Polychloroprene (15894-79-1 and 15894-79-2, experimental sam-
ples, E. I. duPont de Nemours and Co.) was purified by repeated pre-
cipitations from toluene solutions into methanol and then once into
n-pentane. The polymer was dried in vacuum, sealed under nitrogen,
and stored at Dry Ice temperature protected from light. Methylene
chloride used in the dry box experiments was stored over calcium
hydride and distilled under nitrogen first from calcium hydride and
then from triethylaluminum. For high vacuum experiments methyl-
ene chloride was further dried over baked barium oxide and sodium
mirrors. Isobutylene was dried by passing the gas through a column
packed with a mixture of barium oxide and molecular sieves (3 Å),
then condensed and dried in the vacuum line over sodium mirrors.
BCl_3 was dried over sodium mirrors before distilling into vials with
break seals.

Synthesis and Purifications

Polymerizations were carried out in a stainless steel safety en-
closure under an atmosphere of N_2 using 500 mL flasks equipped with
mechanical stirrers. CR solution and isobutylene were charged into
the reactor and thermoequilibrated. Polymerizations were triggered
by adding BCl_3 dissolved in methylene chloride and terminated by
chilled methanol. A copolymerization experiment of isobutylene with
isoprene (5 mol% i-C_5H_8 on i-C_4H_8) has been carried out; work-up
procedures were the same as in homopolymerizations. Select polym-
erizations were carried out in an all-glass assembly under high
vacuum conditions using the apparatus as shown in Fig. 1. Graft
copolymers were purified by selective solvent extractions with n-
pentane to remove PIB, and THF-ethyl acetate mixtures to remove
ungrafted CR. The separation scheme is shown in Fig. 2.

Characterization

^{1}H-NMR spectra were taken using a Varian T-60 NMR instrument.
Sample solutions in CCl_4 (50 g/L) containing TMS internal standard
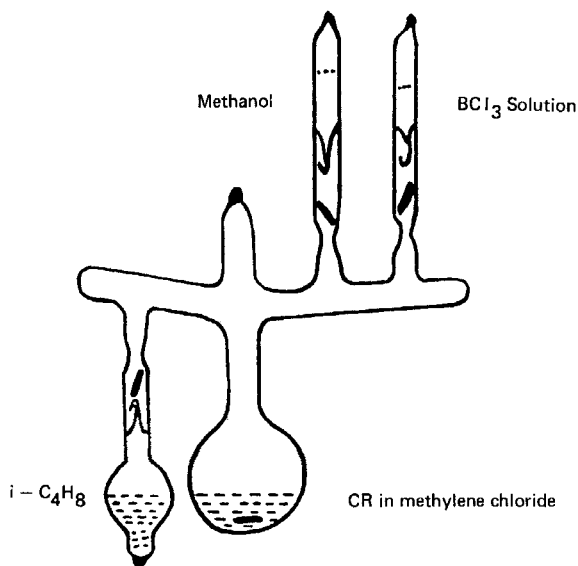were used.

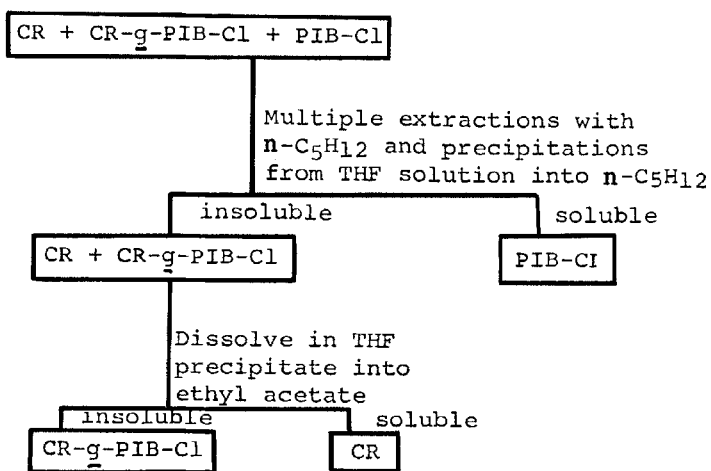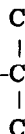FIG. 1. Polymerization apparatus for high vacuum experiments.

FIG. 2. Separation scheme for CR-g-PIB~C–C–Cl.

Molecular weights were determined using a Hewlett-Packard Mechrolab high speed membrane osmometer Model 503 at 37°C and toluene solvent.

Molecular size distributions were obtained using a Waters Ana Prep GPC with a differential refractive index detector.

The PIB branches were obtained by exhaustive selective oxidative degradation of the backbone with m-chloroperbenzoic acid in chloroform at room temperature for 24 h followed by cleavage of the epoxide using excess periodic acid at 60°C in aqueous THF for 4 h.

Thermal dehydrochlorination was carried out under nitrogen at 190°C. The HCl evolved from 20-40 mg samples in the form of thin films was determined by conductivity measurements. The method has been described in detail [17, 18].
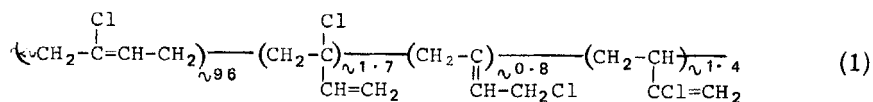
RESULTS AND DISCUSSION

Synthesis Principle

It has been established [19, 20] that CR contains ~ 97.5% relatively stable vinylic chlorines and ~2.5 allylic chlorines. It has also been demonstrated [13] that allylic chlorines are efficient carbenium ion precursors and that they initiate the polymerization of olefins in the presence of certain alkylaluminum compounds. These facts have already been exploited [21] for the synthesis of CR-g-PIB by the use of $CR/Et_2AlCl/$isobutylene systems.

Recent insight into the mechanism of BCl_3-coinitiated isobutylene polymerizations open new leads for the synthesis of grafts comprising CR backbone carrying PIB branches with $\sim C(CH_3)_2Cl$ termini. Thus Kennedy et al. [14] found that substituted allylic chlorines in conjunction with BCl_3 efficiently initiate isobutylene polymerization and that the terminus of the polymer is $-C(CH_3)_2Cl$. The latter arises by the chlorination of the propagating carbenium ion by the $BCl_4^{\ominus}$ counteranion.

Consideration of this information led to the postulate that CR grafts carrying PIB branches with $\sim C(CH_3)_2Cl$ termini could be prepared by grafting isobutylene from CR by the use of BCl_3 coinitiator. Equation (1) helps to visualize the anticipated reaction.

Graft Copolymerization

Representative results of graft copolymerization are compiled in Table 1. The temperature range from -12 to -78°C was dictated by the boiling point of isobutylene and the precipitation point of CR in the solvent systems used. Several solvent systems including methylene chloride, methylene chloride/methyl chloride, ethyl chloride, and ethyl chloride/methyl chloride combinations have been examined.

$$\{CH_2-\underset{\underset{CH=CH-CH_2}{|}}{\overset{\overset{Cl}{|}}{C}}=CH-CH_2)_{\sim 96}\!\!\!-\!\!\!(CH_2-\underset{\underset{CH=CH_2}{|}}{\overset{\overset{Cl}{|}}{C}})_{\sim 1.7}\!\!\!-\!\!\!(CH_2-\underset{\underset{CH-CH_2Cl}{\|}}{C})_{\sim 0.8}\!\!\!-\!\!\!(CH_2-\underset{\underset{CCl=CH_2}{|}}{CH})_{\sim 1.4} \qquad (1)$$

$$\quad I \qquad\qquad\qquad II \qquad\qquad III \qquad\qquad IV$$

$$\overbrace{} \quad \xrightleftharpoons{BCl_3}$$

$$\sim\!\!\sim CH_2-\overset{\overset{\delta\oplus}{|}}{\underset{\underset{CH \;=\!=\!= \;CH_2BCl_4^{\;\delta\oplus}}{\|}}{C}}-\!\!\sim\!\!\sim \;^\Theta \xrightarrow{CH_2=C(CH_3)_2} \sim\!\!\sim CH_2-\overset{\|}{\underset{\underset{CH-CH_2}{}}{C}}-\!\!\sim\!\!\sim$$

$$\underset{\qquad\qquad\qquad\qquad\qquad\qquad\qquad CH_2-\underset{\underset{CH_3}{}}{\overset{\overset{CH_3}{}}{C}}\;^\oplus \; BCl_3^{\;\Theta}}{}$$

$$V$$

$$V \;+\; nCH_2=C(CH_3)_2 \longrightarrow \sim\!\!\sim CH_2-\overset{\|}{\underset{\underset{CH-CH_2}{}}{C}}-\!\!\sim\!\!\sim$$

$$\underset{(CH_2-C\underset{CH_3}{\overset{CH_3}{<}}\rightarrow)_n \; CH_2-C\underset{CH_3}{\overset{CH_3}{<}}\oplus BCl_4^{\;\Theta}}{}$$

$$\sim\!\!\sim CH_2-\overset{\|}{\underset{\underset{CH-CH_2}{}}{C}}-\!\!\sim\!\!\sim$$

$$(CH_2-C\underset{CH_3}{\overset{CH}{<}}\rightarrow)_n\!-\!CH_2-C\underset{CH_3}{\overset{CH_3}{<}}Cl \;+\; BCl_3$$

$$CR\text{-}\underline{g}\text{-}PIB\sim\!\!\sim C\text{-}C\underset{C}{\overset{C}{<}}Cl$$
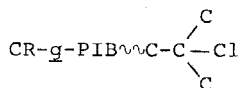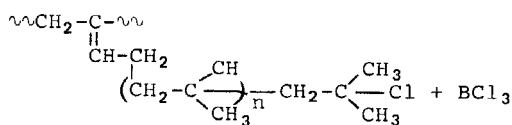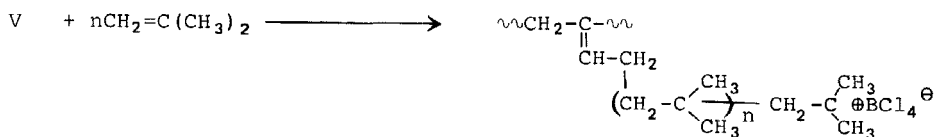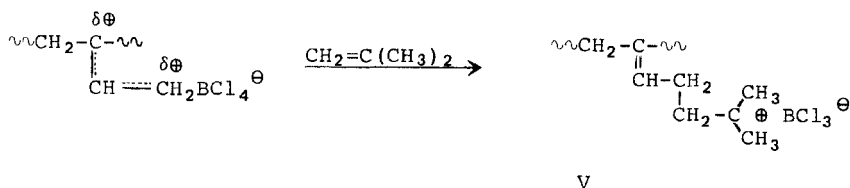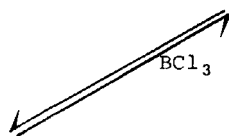
Graft copolymerization carried out by the use of ethyl chloride and ethyl chloride/methyl chloride combinations gave insignificant PIB yield and low molecular weight PIB. For example, grafting carried out by the use of 0.04 M isobutylene and 0.04 M BCl₃ in ethyl chloride solvent at -44°C yielded 6% PIB after 15 min. ¹H-NMR of the purified product indicated negligible PIB in the graft. Similarly, grafting did not occur in methyl chloride/ethyl chloride combinations at -50°C for 3 h.

TABLE 1. Synthesis and Characterization of Poly(chloroprene-g-isobutylene)

Conditions						Results			
							CR-g-PIB[d]		
i-C_4H_8 (M)	BCl_3 (M)	Solvent	CR (g/L)	Temperature (°C)	Time (h)	G_{eff} (%)	Mol%[c]	$M_n \times 10^{-5}$	$\overline{M}_{nexp.}/\overline{M}_{ntheor.}$
3.4	0.20	CH_2Cl_2/CH_3Cl	9.4	-78	1.5	48	82/18	1.69	1.08
2.3	0.13	CH_2Cl_2	22.2	-50	3.5	37	75/25	1.65	1.00
1.9[a]	0.10	"	20.0	-48	1.5	52	76/24	2.02	1.26
1.6	0.05	"	22.0	-40	1.0	30	79/21	1.60	1.00
1.7[b]	0.13	"	21.0	-40	1.0	-	90/10	-	-
2.6	0.20	"	22.2	-20	2.0	34	75/25	1.60	0.98
2.3	0.14	"	"	-12	2.0	30	76/24	1.78	1.09
1.9[b]	0.10	"	"	-55	3.0	60	50/50	1.90	0.96

[a] Polymerization carried out under high vacuum.
[b] Plus 5 mol% i-C_5H_8.
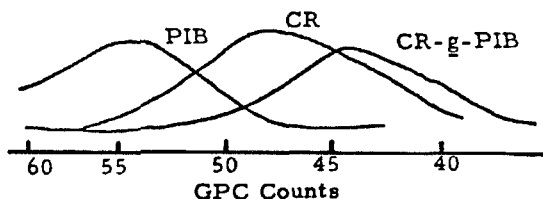[c] By ^1H-NMR.
[d] By osmometry.

FIG. 3. GPC of polychloroprene, polyisobutylene, and poly(chloro-prene-g-isobutylene).
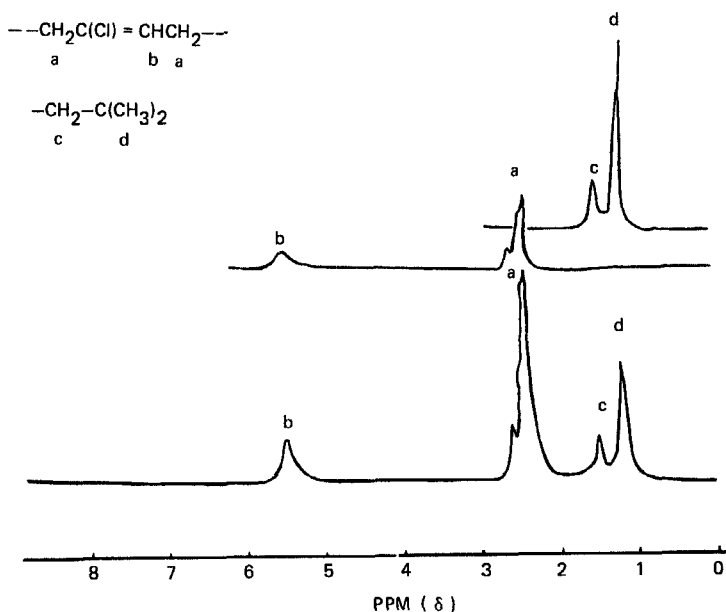

FIG. 4. ^{1}H-NMR spectra of polyisobutylene, polychloroprene, and poly(chloroprene-g-isobutylene).

Grafting occurred in methylene chloride and methylene chloride/methyl chloride combinations. The grafting efficiency should be close to 100% since graft initiation can occur only at the backbone and the polymerization of isobutylene by BCl₃ proceeds in the absence of chain transfer. The observed lower grafting efficiencies are presumably due to trace amounts of unscavengable protic impurities which may initiate isobutylene polymerization in conjunction with BCl₃.

The crude reaction product obtained in grafting experiments have been purified by selective extraction (Fig. 2). Figure 3 shows GPC traces of fractions obtained in a representative extraction study. According to these data, the n-pentane-soluble fraction (PIB) is well separated from the THF/ethyl acetate-soluble fraction (CR) and the insoluble fraction

$$CR\text{-}g\text{-}PIB \sim C\text{-}\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}\text{-}Cl$$
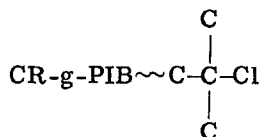
This separation method is suitable for quantitative characterization studies.

The composition of the various fractions have been determined by ^{1}H-NMR spectroscopy. Figure 4 shows representative spectra and pertinent assignments. The spectra of PIB and CR obtained by n-pentane and THF/ethyl acetate extractions, respectively, are identical to the spectra of authentic PIB and CR samples. The spectrum of the n-pentane-and-THF/ethyl acetate-insoluble fraction shows elements of PIB and CR and hence should be the desired graft. The amount of ungrafted CR was negligible (~5%).

Graft Characterization

The number average molecular weight of

$$CR\text{-}g\text{-}PIB \sim C\text{-}\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}\text{-}Cl$$
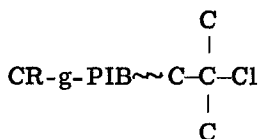
can be calculated from the number-average molecular weight of the CR backbone (M_B) and the overall graft composition ($X_b\%$):

$$\overline{M}_{n_{theor.}} = M_B/(1 - X_b/100)$$

Agreement between $\overline{M}_{n_{theor.}}$ and $\overline{M}_{n_{exp.}}$ ($\overline{M}_n$ determined by osmometry) is strong indication for the proposed grafting and proof of the absence of disturbing side reactions, i.e., backbone scission and cross-linking, during grafting. Thus $\overline{M}_{n_{theor.}} > M_{n_{exp.}}$ would indicate backbone scission, while $\overline{M}_{n_{theor.}} < \overline{M}_{n_{exp.}}$ would suggest

cross-linking. The excellent agreement between $M_{n_{theor.}}$ and $M_{n_{exp.}}$ shown by the data in Table 1 indicate "clean" grafting and satisfactory graft purification. This is in contrast to the findings with the CR/ Et_2AlCl/isobutylene system [18] in which significant degradation of the CR backbone occurs at higher polymerization temperatures.

Branch Characterization: Branch Molecular Weight, Molecular Weight Distribution, and Frequency

Molecular weight and molecular weight distribution of the grafted branches and average number of branches per backbone (b/B) were determined by selective oxidative degradation of the CR backbone followed by surviving PIB fragment analysis. This method has already been used for the characterization of branches in poly(chloroprene-g-isobutylene) [21], poly(chloroprene-g-styrene) [19], and ABS [20] graft copolymers.

Exhaustive controlled oxidation of the CR backbone by m-chloro-perbenzoic acid in chloroform followed by cleavage, separation, and purification yielded pure PIB. Equation (2) summarizes the reactions involved:
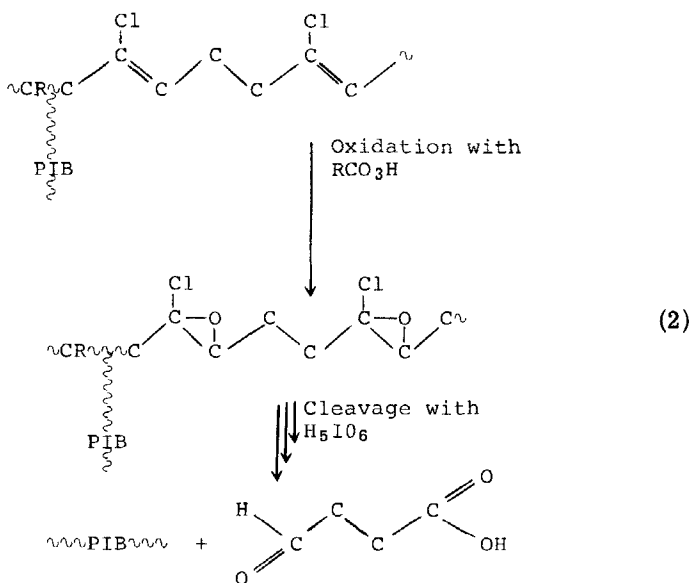

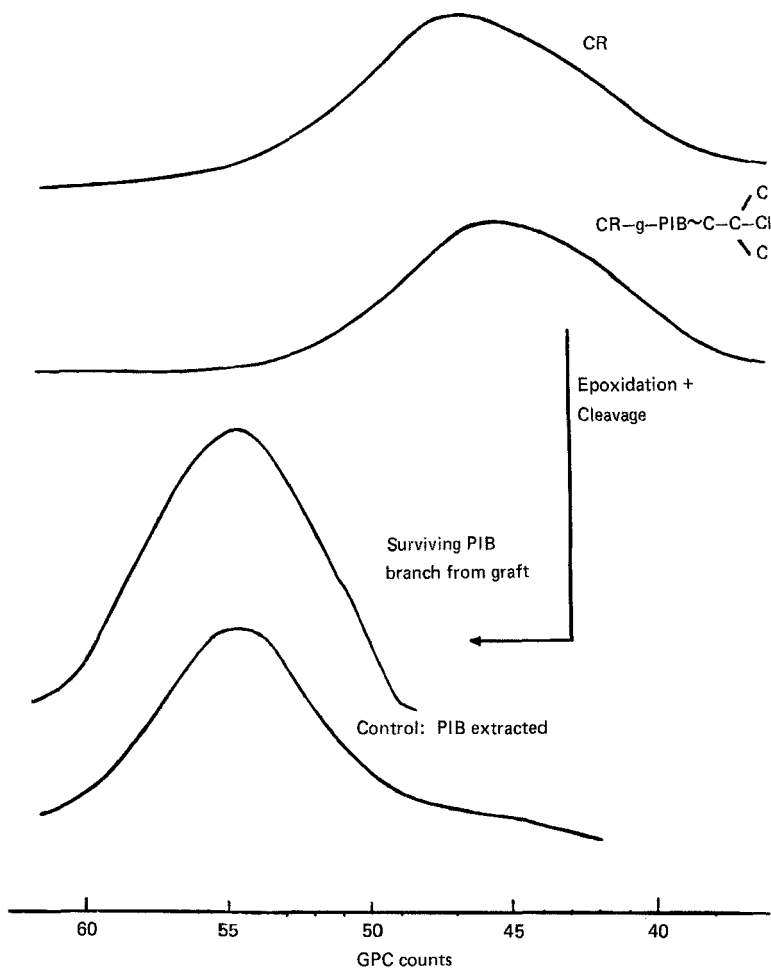$$(2)$$

Figure 5 shows representative GPC traces of ungrafted CR and

CR

CR–g–PIB~C–C–Cl

Epoxidation +
Cleavage

Surviving PIB
branch from graft

Control: PIB extracted

60   55   50   45   40

GPC counts

FIG. 5. GPC traces of polychloroprene, poly(chloroprene-g-isobutylene), grafted polyisobutylene, and extracted polyisobutylene.

$$CR\text{-}g\text{-}PIB \sim C\text{-}C\text{-}Cl,$$

(with C substituents above and below the central C)
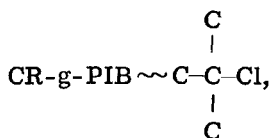
together with those of surviving PIB branches and a PIB control obtained by n-pentane extraction of the crude product of a grafting experiment. According to the data the molecular weight and molecular

TABLE 2. Branch Characterization: Molecular Weight, Molecular Weight Distribution, and Branch Frequency of Polyisobutylene Branches in Poly(chloroprene-g-isobutylene)

Polymerization temperature (°C)	CR/PIB (mol%)	Surviving PIB branch ($\overline{M}_n \times 10^{-3}$)[a]	Branch $\overline{M}_w/\overline{M}_n$ [a]	b/B [b]
-20	75/25	5.0	3.0	5
-48	75/24	15.4	2.0	2
-40	90/10	6.2[c]	3.8	2
-55	50/50	17.0	2.0	4

[a] By GPC.
[b] Average number of branches per backbone.
[c] From extracted IIR from graft.

weight distribution of the branches and extractable PIB are very similar if not identical. This suggests that the backbone has little effect on the course of the polymerization after initiation. This also suggests that branch frequency could be calculated from the molecular weight of the extracted PIB from the graft. Indeed, previous workers [18] have used this approach to calculate branch frequency where direct characterization of the branches could not be carried out because of the saturated backbones used in these studies. Also, direct characterization of the branches could not be carried out with the CR backbone carrying butyl rubber (IIR) branches. Molecular weight determination of the extracted IIR indicated significantly lower molecular weight and negligible amount of IIR in the graft (10 mol% IIR in the graft at -40°C). The number of branches per backbone (b/B) and the molecular weight of the branches for grafts prepared at -20 to -55°C are shown in Table 2. The branch molecular weight increases with a decrease in temperature, presumably because of the freezing out of termination at lower temperatures relative to propagation.

Characterization of Branch Functionality by Thermal Dehydrochlorination

Endgroup formation in BCl_3-coinitiated isobutylene polymerization is well documented, and unequivocal experimental evidence indicates the presence of $-C(CH_3)_2-Cl$ endgroups [14]. The rapid, sensitive, and quantitative dehydrochlorination method [18] developed for the characterization of structures of chlorinated polymers has been used to define the $-C(CH_3)_2-Cl$ terminus of PIB in
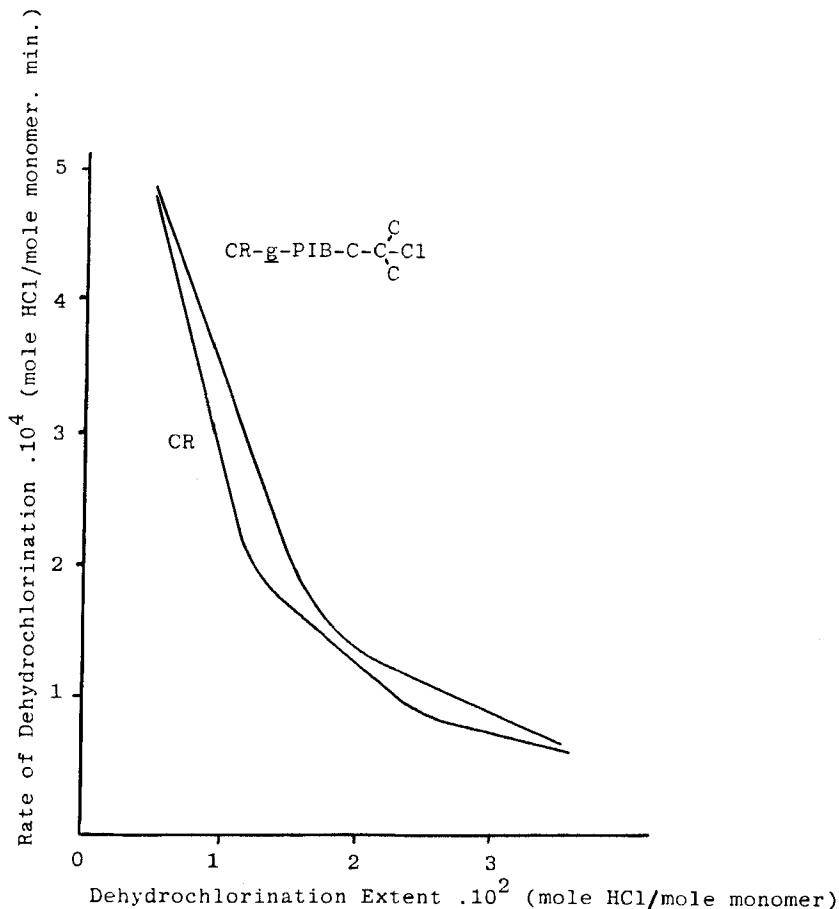
FIG. 6. The dehydrochlorination rate as a function of conversion for polychloroprene and poly(chloroprene-g-isobutylene).
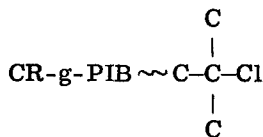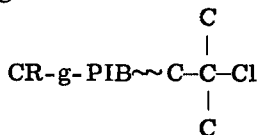
$$\text{CR-g-PIB} \sim \overset{\displaystyle C}{\underset{\displaystyle C}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}}\text{--C--Cl}$$

Figure 6 shows the rate of HCl loss of CR and

$$\text{CR-g-PIB} \sim \overset{\displaystyle C}{\underset{\displaystyle C}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}}\text{--C--Cl}$$

versus the extent of HCl loss. The diagnostic value of the rate versus the extent of HCl loss curves has been discussed in detail [18].

The rate versus extent of dehydrochlorination plot traverses three distinct phases in the case of CR. The rate of dehydrochlorination diminishes rapidly during the first dehydrochlorination phase. Subsequently, the rate traverses a relatively long transition phase after which it decreases very slowly. These findings were explained in terms of three dehydrochlorination regimes associated with the four contributing structures in polychloroprenes. The first rapid phase of dehydrochlorination is mainly due to Units II and III in CR (see Eq. 1); this is followed by a slower rate attributed to Units I, III, and IV. The very slow dehydrochlirination phase is thought to be due to the presence of relatively stable vinylic structures I and IV.

Cationic modification [18] of CR using organoaluminum compounds or $AgPF_6$ results in the complete disappearance of allylic chlorines II and III. The rate versus extent of dehydrochlorination of

$$
\text{CR-g-PIB} \leadsto \text{C}-\overset{\displaystyle \text{C}}{\underset{\displaystyle \text{C}}{\overset{|}{\underset{|}{\text{C}}}}}-\text{Cl}
$$
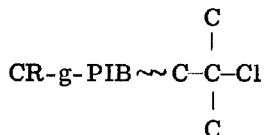
shows only two distinct phases: the initial fast rate is visualized to be due to $\sim C(CH_3)_2$ Cl termini whereas the subsequent slow rate reflects the presence of relatively stable vinylic chlorines.

ACKNOWLEDGMENTS

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