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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

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**To cite this Article** Kennedy, J. P. and Plamthottam, S. S.(1980) 'Cationic Modification of Polychloroprene. II. Homopolymerization of Isobutyl Vinyl Ether and Synthesis and Characterization of Poly(chloroprene-g-Isobutyl Vinyl Ether)', *Journal of Macromolecular Science, Part A*, 14: 5, 729 – 738

**To link to this Article:** DOI: 10.1080/00222338008066644

**URL:** <http://dx.doi.org/10.1080/00222338008066644>

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## Cationic Modification of Polychloroprene. II. Homopolymerization of Isobutyl Vinyl Ether and Synthesis and Characterization of Poly(chloroprene-g-Isobutyl Vinyl Ether)\*

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### ABSTRACT

It was discovered that allylic chlorines [ $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{Cl}$ ,  $\text{CH}_2=\text{CHCH}(\text{Cl})\text{CH}_3$ ] in the presence of  $\text{AgPF}_6$  are efficient initiators of isobutyl vinyl ether polymerization. The transitory allyl cation formed during the precipitation of  $\text{AgCl}$  is presumed to be the initiating entity. This knowledge was exploited in the subsequent synthesis of the graft copolymer poly(chloroprene-g-isobutyl vinyl ether). In this synthesis, allylic chlorines in polychloroprene function as graft initiating sites in conjunction with  $\text{AgPF}_6$ . Grafting efficiencies are low due to the great propensity for chain transfer of isobutyl vinyl ether polymerization. Pure grafts have been obtained by selective solvent extractions and were characterized by gravimetry, osmometry,  $^1\text{H-NMR}$  and DSC. Poly(isobutyl vinyl ether) branch frequency was 7-12 in graft copolymerization carried out at 15 to  $0^\circ\text{C}$ .

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\*Paper I in this series: J. P. Kennedy and D. K. Metzler, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, 30, 141 (1977).

## INTRODUCTION

A detailed fundamental understanding of elementary events in carbocationic polymerization has led to the synthesis of a series of novel telechelic [1] and sequential [2, 3] copolymers exhibiting unique physical and chemical properties. Although most of these materials were synthesized by using organoaluminum or boron trichloride co-initiators, sequential [4-6] copolymers of heterocyclic monomers and olefins [7] have also been synthesized by the use of certain metal salt coinitiators  $\text{AgPF}_6$ ,  $\text{AgClO}_4$ ,  $\text{AgOSO}_2\text{CF}_3$ ,  $\text{AgBF}_4$ ,  $\text{AgSbF}_6$ ,  $\text{LiPF}_6$ .

Recently we have discovered that isobutyl vinyl ether (IBVE) polymerization can readily be initiated by allylic chloride/ $\text{AgPF}_6$  initiator systems. Subsequently this lead has been exploited in the synthesis of a new graft copolymer comprising a polychloroprene CR backbone with PIBVE branches: CR-g-PIBVE. This paper concerns preliminary studies that establish experimental parameters for efficient IBVE polymerization under simulated grafting conditions, grafting syntheses resulting in the preparation of new CR-g-PIBVE, and graft characterization studies aimed at the elucidation of select molecular parameters, e. g., branch frequency, of these novel materials.

## EXPERIMENTAL

Materials

Polychloroprene (CR) (15894-79-2, an experimental sample provided by the E. I. du Pont de Nemours and Co.) was purified by repeated precipitations from toluene into methanol and then once from boiling ethyl chloride into n-pentane. The polymer was dried under vacuum, sealed under nitrogen, and stored at Dry Ice temperature protected from light. Isobutyl vinyl ether was distilled from sodium dispersion. Methylene chloride was stored over calcium hydride and distilled once from calcium hydride and then from triethylaluminum. 3-Chloro-1-butene and 1-chloro-3-methyl-2-butene were dried over calcium hydride and distilled under reduced pressure.  $\text{AgPF}_6$  was used as received.

Synthesis

Polymerizations were carried out in dry nitrogen atmosphere in a stainless steel enclosure using baked glassware cooled under a blanket of dry nitrogen. Graft copolymerizations were carried out in stirred glass reactors. CR dissolved in methylene chloride and IBVE were

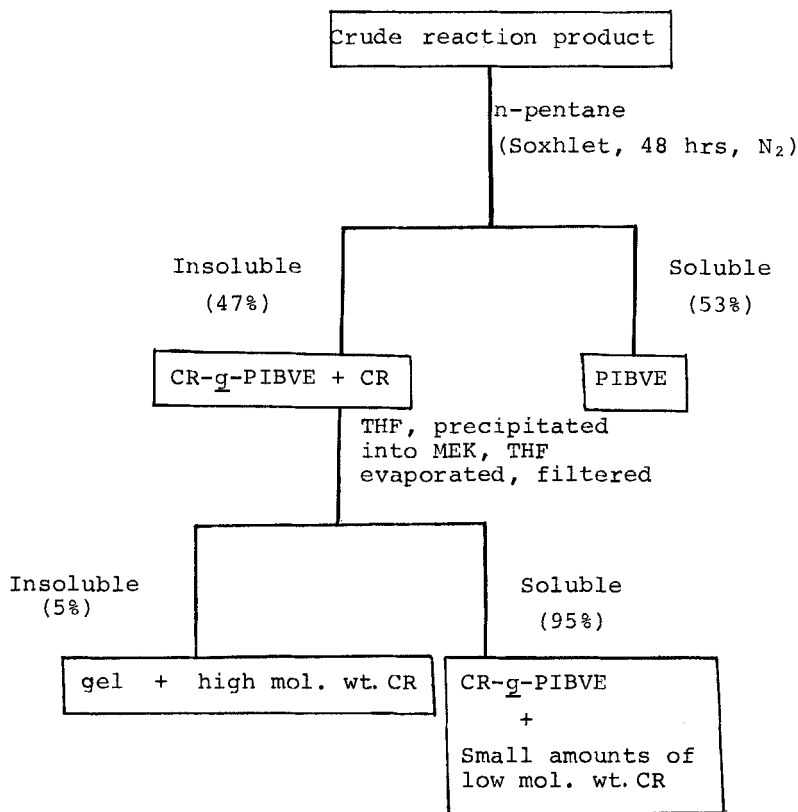


FIG. 1. Graft separation scheme. Numbers in parentheses are percent materials obtained in experiment at 0°C.

thermoequilibrated, and the polymerization was triggered by adding chilled AgPF<sub>6</sub> solution in methylene chloride. The charge slowly assumed a blue and later a violet color during polymerization. Reactions were terminated by the introduction of prechilled methanol which immediately discharged the color of the charge. The polymer was dissolved, filtered, precipitated into methanol and dried under vacuum. To remove ungrafted homopolymer, polymers were selectively extracted under nitrogen with n-pentane and THF/MEK as shown in Fig. 1.

### Characterization

Graft copolymer compositions were determined by <sup>1</sup>H-NMR spectroscopy with a Varian T-60 spectrometer from the instrument

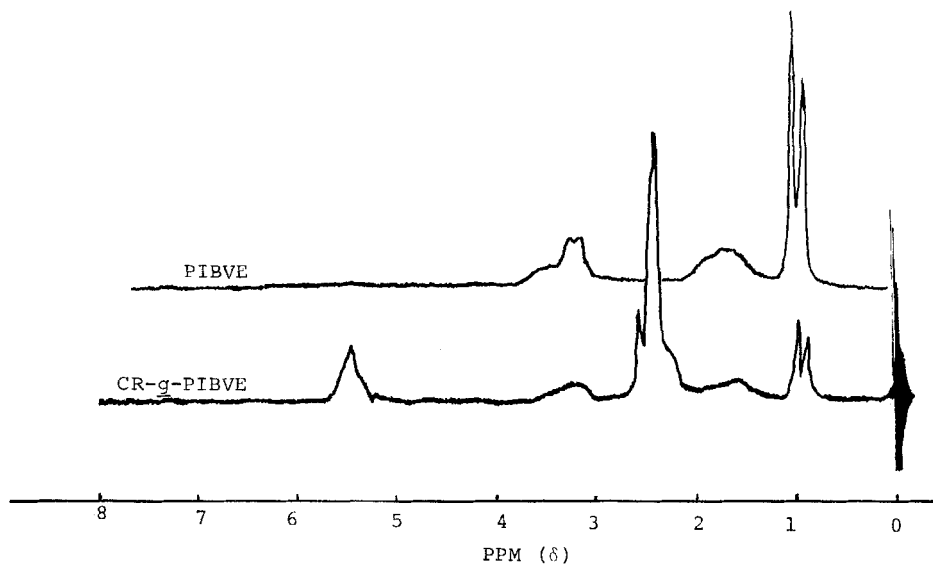


FIG. 2.  $^1\text{H}$ -NMR spectroscopy of poly(chloroprene-*g*-isobutyl vinyl ether).

integrated areas of the methylene multiplet of CR at 2.7 ppm and the methyl doublet at 0.9 ppm of PIBVE. A typical graft copolymer spectrum is shown in Fig. 2. Number-average molecular weights were determined by vapor-pressure osmometry and high-speed membrane osmometry. Glass transition temperatures  $T_g$  were determined by a du Pont Thermal Analyzer 990 on 15-20 mg samples at a  $20^\circ\text{C}/\text{min}$  heating rate. Grafting efficiency GE was calculated as

$$\text{GE (\%)} = 100 W_b / (W_b + W_h)$$

where  $W_b$  is the weight of grafted branches and  $W_h$  is the weight of PIBVE homopolymer formed. Branch frequency is calculated by

$$b/B = \frac{M_B X_b / 100}{M_b (1 - X_b / 100)}$$

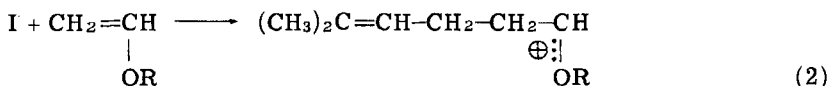
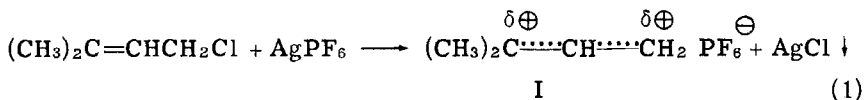
where  $M_B$  is the backbone molecular weight and  $M_b$  that of the branches,  $X_b$  is the weight percent of PIBVE in the graft, and  $b/B$  is characteristic of the grafting process independent of side reactions.

## RESULTS AND DISCUSSION

IBVE Polymerizations with  $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{Cl}$  and  $\text{CH}_2=\text{CHCH}(\text{Cl})\text{CH}_3/\text{AgPF}_6$  Initiating System

It was postulated and subsequently proven that under well designed experimental conditions, allyl cations presumably arising during  $\text{AgCl}$  precipitation formed upon mixing an active allylic chlorine and  $\text{AgPF}_6$  initiate the polymerization of IBVE. Thus in a series of orienting experiments it has been established that the addition of  $\text{AgPF}_6$  to thoroughly dried charge of  $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{Cl}$  or  $\text{CH}_2=\text{CH}-\text{CH}(\text{Cl})\text{CH}_3$ /IBVE in  $\text{CH}_2\text{Cl}_2$  rapidly induces polymerization and yields reasonably high molecular weight product in the +15 to  $-35^\circ\text{C}$  range. Below this temperature, polymerization is too slow for practical experimentation. Table 1 shows representative results.

Polymerization is visualized to occur as a consequence of transitory allyl cations [ Eqs. (1) and (2)].



Direct cationation appears to be reasonable; however, it has not been proven by independent experiments. Further, in line with model experiments with  $(\text{CH}_3)_2\text{C}=\text{CH}-\text{CH}_2\text{Cl}/\text{BCl}_3$ /isobutylene [ 8 ], we theorize that initiation would occur preferentially at the less hindered primary cation of the allyl system. Rapid cationation is expected because of the relatively high thermodynamic stability of the propagating carboxonium ion. Although polymerization is rapid above  $0^\circ\text{C}$ , induction times of several minutes are observed below this temperature if the IBVE and  $\text{AgPF}_6$  are premixed. Induction disappears if initiator/coinitiator are premixed a few seconds before monomer addition. Since silver salts form [ 9, 10 ] complexes with  $\pi$  electron donors, induction may be due to the competitive formation of rapid argention of IBVE at low temperatures.

Synthesis of CR-g-PIBVE

On the basis of experiments described in the first section, transitory allylic cations in conjunction with  $\text{PF}_6^\ominus$  initiate polymerization of IBVE. This knowledge was subsequently exploited in the synthesis of graft copolymers from CR backbones. According to the latest

TABLE 1. Orienting Experiments: Polymerization of Isobutyl Vinyl Ether Using Allylic Chlorine/AgPF<sub>6</sub> Initiating Systems

Initiator	Initiator × 10 <sup>3</sup> (M)	AgPF <sub>6</sub> × 10 <sup>3</sup> (M)	IBVE (M)	Temp (°C)	Time (min)	Conver- sion (%)	$\bar{M}_n$	Observation
-	-	4.9	0.83	15 to -48	10-135	0	-	No polymeri- zation
(CH <sub>3</sub> ) <sub>2</sub> C=CHCH <sub>2</sub> Cl	3.4	"	-	15 to -48	-	-	-	Rapid AgCl precipitation
"	"	"	0.83	15	10	90	3500 <sup>a</sup>	Rapid polym- erization
"	"	"	"	0	10	96	4000 <sup>a</sup>	"
"	"	"	"	-24	35	99	6000 <sup>a</sup>	Slow polymeri- zation
"	"	"	"	-48	135	0	-	No polymeri- zation
CH <sub>2</sub> =CHCHCH <sub>3</sub>   Cl	7.6	7.6	3.8	-25	75	65	96,000 <sup>b</sup>	Slow polym- erization
"	8.6	8.6	2.3	-35	130	24	164,000 <sup>b</sup>	"
"	"	"	"	-50	140	0	-	No polymeriza- tion

<sup>a</sup> By vapor pressure osmometry.

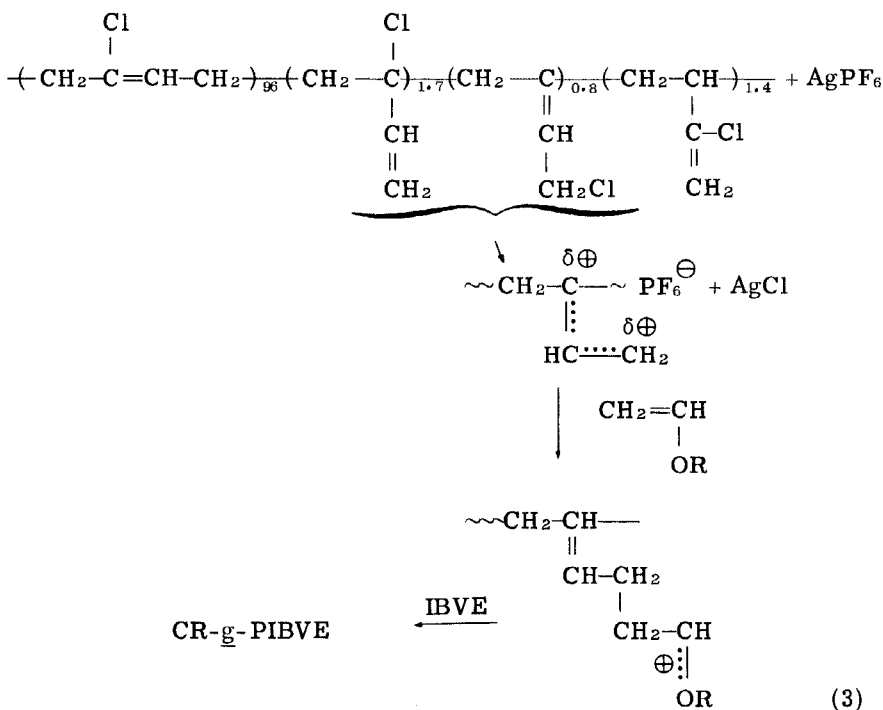
<sup>b</sup> By membrane osmometry.

TABLE 2. Synthesis and Characterization of Poly(chloroprene-g-isobutyl Vinyl Ether)

IBVE M	CR (g/100 ml)	AgPF <sub>6</sub> × 10 <sup>3</sup> (M)	Temp (°C)	Time (min)	PIBVE (%)	CR/PIBVE (wt %)	GE (%)	PIBVE branch $\bar{M}_n$	b/B Average apparent branch frequency
0.83	3.15	4.9	15	10	59	84/16	9.2	2700	7
0.62	2.86	3.67	4	4	23	87.3/12.7	29.1	-	-
0.83	3.15	4.9	0	10	76	77/23	10.2	-	-
0.62	2.23	5.6	0	10	81	64/36	18.9	5000	12
0.83	3.15	4.9	-24	35	77	89/11	5.0	14,400	~1
0.83	3.15	4.9	-48	135	92	90.5/9.5	3.5	24,000	-



information [11, 12] concerning the microstructure of CR, this rubber contains, in addition to ca. 97.5% relatively stable vinylic chlorines, two kinds of allylic chlorines suitable for graft copolymerization initiation in the presence of silver salts. In line with these considerations experiments have been carried out to examine the possibility of grafting IBVE from CR by the use of  $\text{AgPF}_6$ . Equations (3) summarize our synthesis concept, and Table 2 shows results of representative experiments.



These experiments were carried out by introducing various amounts of  $\text{AgPF}_6$  in  $\text{CH}_2\text{Cl}_2$  into stirred charges of CR and IBVE in  $\text{CH}_2\text{Cl}_2$ . Homopolymer of IBVE was removed by selective solvent extractions.

A typical grafting experiment carried out at  $0^\circ\text{C}$  produced graft copolymer containing 36 wt % of PIBVE, with an apparent branch frequency of 12 and branch molecular weight 5000. Decreasing polymerization temperatures decreases branch frequency; for example, grafting at  $-24^\circ\text{C}$  produced b/B  $\sim 1.0$ ; however, branch molecular weights were higher ( $M_n$  of branch  $\sim 14,400$ ). That grafting efficiencies are low compared with similar CR-g-polyisobutylene grafts [13] is not surprising, since monomer transfer is known to dominate in isobutyl vinyl ether polymerization [14].

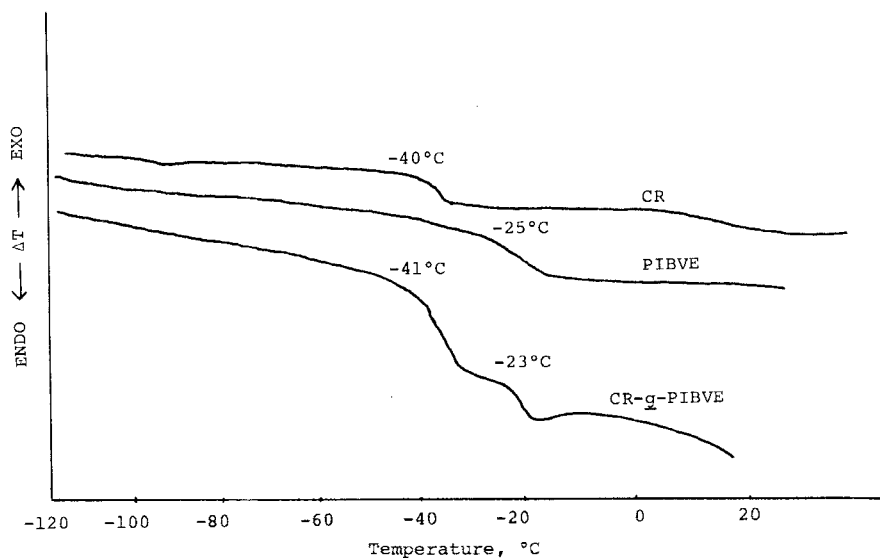


FIG. 3. DSC trace of poly(chloroprene-g-isobutyl vinyl ether). Synthesis and purification procedures are given in Fig. 1.

Figure 3 shows the DSC trace of purified CR-g-PIBVE. The material exhibits two  $T_g$ 's, one at  $-41^\circ\text{C}$  and the other at  $-23^\circ\text{C}$ , corresponding to the transitions of the backbone CR and the PIBVE branches, respectively.

#### ACKNOWLEDGMENTS

The authors are grateful to Drs. R. Pariser and A. L. Barney of the E. I. du Pont de Nemours and Co., for polychloroprene samples and to the National Science Foundation (DMR-77-27618) for financial assistance.

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Accepted by editor April 17, 1979

Received for publication May 15, 1979