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Cationic Modifications of Polychloroprene

5. A New Graft-Block Copolymer by Cationic Technique: Poly[Chloroprene-*g*)Isobutylene-*b*- *α*-Methylstyrene)]

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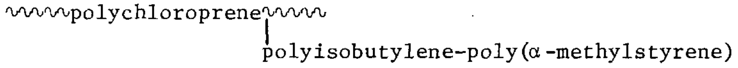
Summary

The synthesis of the novel graft-block copolymer poly[chloroprene-*g*-(isobutylene-*b*-α-methylstyrene)], i.e., a polychloroprene backbone carrying isobutylene/α-methylstyrene block copolymer branches, is described. The synthesis was accomplished by exploiting detailed insight into the mechanisms of initiation of isobutylene and α-methylstyrene polymerization, and termination of isobutylene polymerization.

Introduction

Recent advances in the understanding of elementary events in carbocationic polymerizations have led to macromolecular engineering by cationic techniques in general and to the synthesis of a large number and variety of novel graft, bigraft and block copolymers in particular (1). This paper concerns the synthesis and characterization of the first graft-block copolymer by carbocationic technique: poly[chloroprene-*g*-(isobutylene-*b*-α-methylstyrene)] CR-*g*-(PIB-*b*-PαMeSt), i.e., a polychloroprene rubber CR backbone to which are attached block copolymers of polyisobutylene PIB and poly(α-methylstyrene) PαMeSt:



CR-*g*-(PIB-*b*-PαMeSt)

As described in the previous papers of this series cationic grafting of PIB from CR can be effected by the use of BCl_3 (2,3). It has also been shown that termination in BCl_3-coinitiated isobutylene polymerization produces tertiary chlorine end groups (4). Further, tertiary chlorines in conjunction with Et_2AlCl are efficient initiators for the polymerization of αMeSt (5). Indeed, these facts have already been exploited in the synthesis of various di- and triblock copolymers, i.e., PIB-*b*-PαMeSt (6), PαMeSt-*b*-PIB-*b*-PαMeSt (7) and of the graft copolymer CR-*g*-PIB-$CH_2C(CH_3)_2Cl$ i.e., a CR backbone carrying PIB branches with tert. chlorine end groups (2).

Similarly poly(vinyl chloride), a resin that contains a sufficient quantity of active, most likely allylic, chlorines for graft copolymerization, has also been used in conjunction with BCl_3 to initiate the graft copolymerization of isobutylene and

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thus interesting new graft copolymers i.e., PVC-g-PIB, have been obtained (8,9). The tertiary chlorine end groups of the grafted PIB branches have been further derivatized, for example by the cyclopentadiene function (10).

Thus the synthesis of CR-g-(PIB-b-PαMeSt) was undertaken by exploiting our knowledge relative to the detailed structure of CR and elementary events of carbocationic polymerizations; specifically: 1. Knowing that CR contains a significant amount of active allylic chlorines (11), 2. Knowing that the allylic chlorines in CR in conjunction with BCl_3 coinitiator rapidly induce the graft copolymerization of isobutylene (2,8),3. Knowing that BCl_3-coinitiated isobutylene polymerizations proceed essentially in the absence of chain transfer (4),4. Knowing that BCl_3-coinitiated isobutylene polymerizations terminate by chlorination of the propagating $PIB^{\oplus}$ and give rise to $-CH_2-C(CH_3)_2Cl$ end groups (4), 5. Knowing that $-CH_2-C(CH_3)_2Cl$ groups in conjunction with certain alkylaluminum compounds, e.g., Et_2AlCl, readily initiate the polymerization of styrene derivatives (12), and 6. Knowing that direct proof of the mechanism of chain breaking in αMeSt polymerization in this particular system is lacking, however, anticipating that the PαMeSt chain ends will be indanyl structures that arise by intramolecular alkylation, or $-CH_2-CH(CH_3)(C_6H_5)$ groups that form by hydridation of the growing cation (13).

Scheme 1 summarizes this information and helps to visualize the synthesis route.

III. Experimental

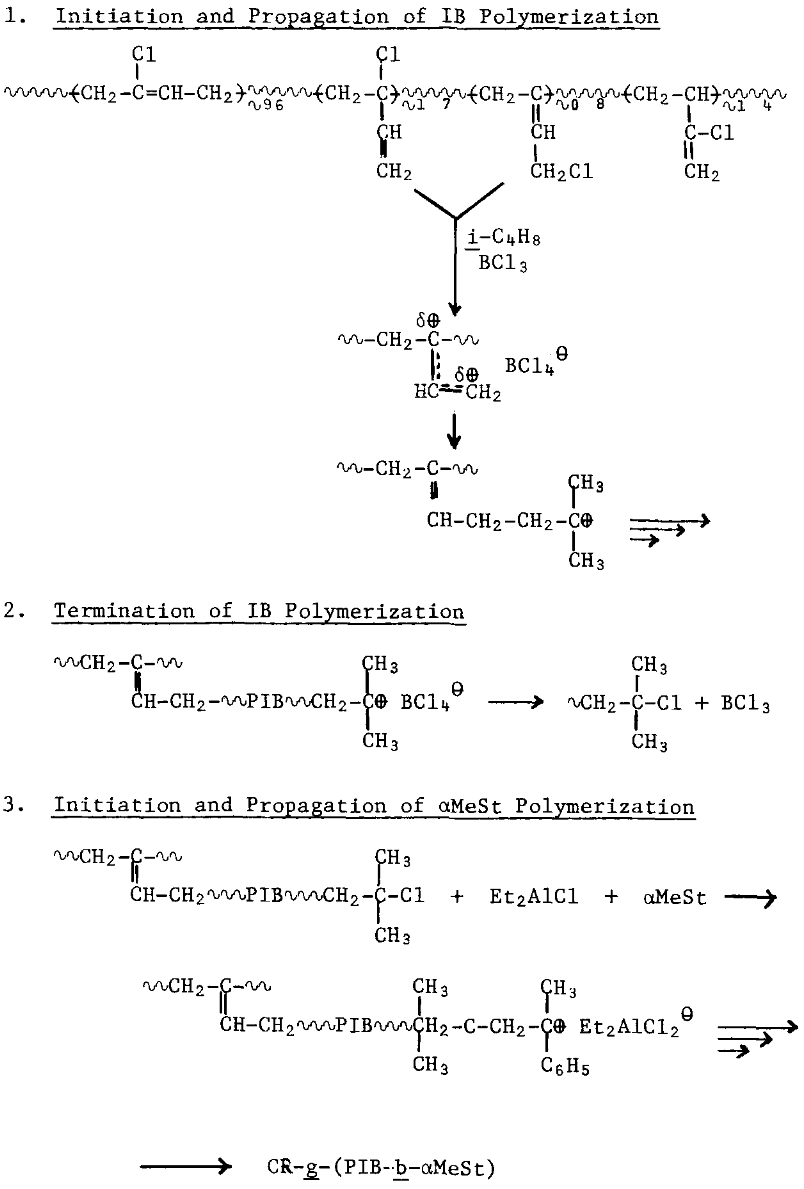
1. Materials

Polychloroprene (experimental samples 15894-79-1 and 15894-77-2, E. I. DuPont de Nemours and Co.) was purified by repeated precipitations 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. The purification of CR-g-$PIB-CH_2C(CH_3)_2Cl$ has been described (2). Methylene chloride and methylcyclohexane was stored over calcium hydride and then distilled from triethylaluminum. Isobutylene was dried by passing the gas through a column packed with barium oxide and molecular sieves (3Å). α-Methylstyrene was washed with dilute aqueous potassium hydroxide, repeatedly washed with water to neutral and stored over calcium chloride. Diethylaluminum chloride was distilled under reduced pressure from sodium chloride and stored at Dry Ice temperature until use.

2. Synthesis and Purifications

Polymerizations were carried out in a stainless steel safety enclosure under an atmosphere of nitrogen using 500 ml flasks equipped with mechanical stirrers. In one procedure, CR in methylene chloride and isobutylene were charged into the reactor with continuous stirring and thermoequilibrated. BCl_3 dissolved in methylene chloride was added and the polymerization was allowed to proceed for three hours. The temperature of the charge was raised by removing the flask from the heptane bath; the unreacted isobutylene and BCl_3 were stripped off under vacuum and the

Scheme 1. Synthesis of CR-g-(PIB-b-αMeSt)



1. Initiation and Propagation of IB Polymerization

2. Termination of IB Polymerization

3. Initiation and Propagation of αMeSt Polymerization

solvents were evaporated to dryness. The dry polymer was dissolved in methylene chloride/methylcyclohexane (75/25 v/v) and α-methylstyrene was added. The charge was cooled to -55°C and a chilled solution of Et_2AlCl in methylene chloride was added. The polymerization was quenched with chilled methanol.

In another procedure CR-g-PIB-$CH_2C(CH_3)_2Cl$, purified by selective solvent extraction, was dissolved in methylene chloride and α-methylstyrene was added. After thermoequilibrium, blocking was triggered by adding Et_2AlCl dissolved in methylene chloride. The polymerization was quenched with chilled methanol.

3. Characterization

Compositions of the extracted fractions were determined by ^{1}H-NMR spectroscopy using a Varian T-60 spectrometer. Sample solutions in CCl_4 (50 g/l) containing TMS internal standard were used.

Molecular weights were determined using a Mechrolab 503 high speed membrane osmometer at 37°C using toluene solutions.

Results and Discussion

The synthesis of CR-g-(PIB-b-PαMeSt) has been undertaken by keeping in mind the critical steps outlined in the Introduction.

Experimentally, CR-g-(PIB-b-PαMeSt) was synthesized by two different procedures: First, by preparing, isolating and characterizing the CR-g-PIB-$CH_2C(CH_3)_2Cl$ prepolymer (i.e., the pregraft copolymer with PIB branches carrying tertiary chlorine end groups) and second, by not separating this intermediate.

By the first route, the CR-g-PIB-$CH_2C(CH_3)_2Cl$ was synthesized (2) by inducing the graft copolymerization of isobutylene by the CR/BCl_3 initiating system, and purifying by selective solvent extraction. This intermediate was characterized by a battery of analytical techniques including ^{1}H NMR, GPC, osmometry, and thermal dehydrochlorination. Synthesis and characterization details of CR-g-PIB-$CH_2C(CH_3)_2Cl$ are collected in Table I.

The blocking of αMeSt from CR-g-PIB-$CH_2C(CH_3)_2Cl$ was carried out by the use of Et_2AlCl coinitiator in CH_2Cl_2 solvent. Details are given in the experimental part, Table II, and Figure 1 which also shows the selective solvent extraction procedure employed.

The crude product may contain PαMeSt, together with unreacted CR-g-PIB-$CH_2C(CH_3)_2Cl$ and aluminum-containing residues. The free PαMeSt was separated by precipitating a THF solution of the crude product into acetone, removing the soluble PαMeSt, redissolving the insoluble fraction in THF and reprecipitating into MEK. The acetone-and-MEK-insoluble fraction was regarded to be pure CR-g-(PIB-b-PαMeSt). Figure 1 shows a representative set of results.

Graft-blocks have also been synthesized without separating and characterizing the intermediate CR-g-PIB-$CH_2C(CH_3)_2Cl$. In these experiments the intermediate was obtained by inducing the polymerization of isobutylene by the CR/BCl_3 combination, the unreacted gases were removed under vacuum, and blocking of αMeSt was

TABLE I

Synthesis and Characterization of CR-*g*-PIB-$CH_2C(CH_3)_2Cl$

i-C_4H_8 (M)	BCl_3 (M)	Solvent	CR g/1	Temp. (°C)	Time hrs.	CR/PIB[c] Mole%	G.E.	CR-*g*-PIB[d] $M_n \cdot 10^{-5}$	$\overline{M}_{n\,\text{determined}}/\overline{M}_{n\,\text{theoretical}}$
3.4	0.20	CH_2Cl_2/ CH_3Cl	9.4	-78	1.5	82/18	48	1.69	1.08
2.3	0.13	CH_2Cl_2	22.2	-50	3.5	75/25	37	1.65	1.00
1.9[b]	0.10	"	20.0	-48	1.5	76/24	52	2.02	1.26
1.6	0.05	"	22.0	-40	1.0	79/21	30	1.60	1.00
1.7[a]	0.13	"	21.0	-40	1.0	90/10	-	-	-
2.6	0.20	"	22.2	-20	2.0	75/25	34	1.60	0.98
2.3	0.14	"	22.2[e]	-12	2.0	76/24	30	1.78	1.09
1.9[b]	0.10	"	22.2[e]	-55	3.0	50/50	60	1.90	0.96

a) plus 5 mole% i-C_4H_8

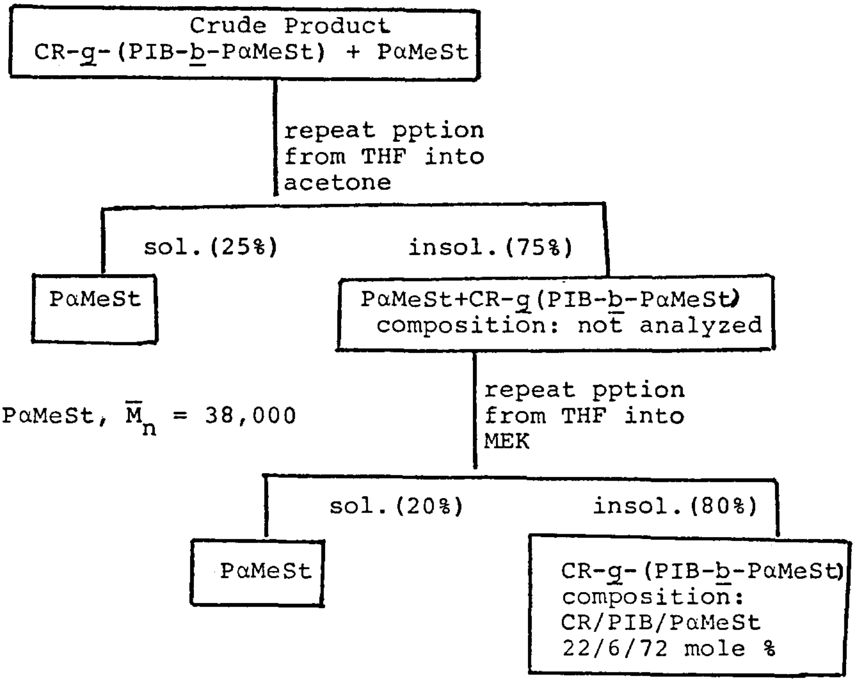
b) polymerization carried out under high vacuum conditions

c) H^1NMR

d) by osmometry

e) CR 15894-77-2

Figure 1. A Representative Synthesis and Purification of CR-g-(PIB-b-PαMeSt)



Reaction conditions: solvent: CH_2Cl_2, $[Et_2AlCl] = 3.2x10^{-2}M$
$[\alpha MeSt = 0.55M]$, [CR-g-PIB-Cl] = 1.2 g/l
Time = 30 min., Temperature = -52°C

TABLE II
Synthesis and Characterization of CR-g(PIB-b-PαMeSt)

CR g/l	CR-g-PIB g/l	CR/PIB mole %	αMeSt (M)	Et_2AlCl (M)	Time/Temp. min. °C	CR/PIB/PαMeSt mole %
-	12.0	75/25	0.55	0.03	30/-52	22/6/72
-	7.0	75/24	0.90	0.06	15/-52	16/5/79
2.6	-	-	1.57	0.02	5/-55	27/6/67

$\bar{M}_n$ of CR = 137,000; $\bar{M}_n$ of PIB branches ∿ 5,000

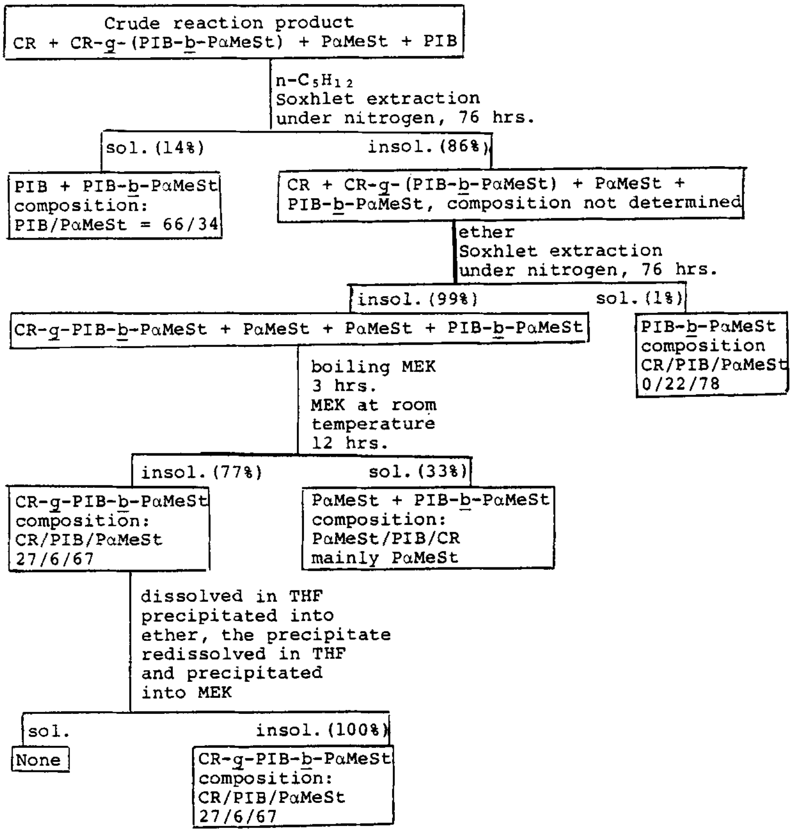


Figure 2. Selective Solvent Extraction for CR-g-(PIB-b-PαMeSt)

effected by adding the monomer and Et_2AlCl. In these experiments the crude product may contain unreacted CR in addition to PIB and PαMeSt. The selective solvent extraction procedure developed to obtain the pure graft-block is outlined in Figure 2. The figure also contains data relative to the quantities of the fractions obtained and their relative composition (mole % by ^1H NMR). According to the findings only a negligible amount of ungrafted CR survived and significant amounts of graft-blocking has occurred.

Acknowledgement

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