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Cationic Polymerization with Boron Halides. VIII. Synthesis of $(CH_3)_2C=CHCH_2$-Polyisobutylene-Cl Prepolymer and Subsequent Preparation of $(CH_3)_2C=CHCH_2$-Poly(isobutylene-b-styrene) and $(CH_3)_2C=CHCH_2$-Poly(isobutylene-b-α-methylstyrene)

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ABSTRACT

Asymmetric telechelic polyisobutylene, α-PIB-ω, carrying the olefinic head group $\alpha = (CH_3)_2C{=}CHCH_2{-}$ and tertiary chlorine endgroup $\omega = {-}C(CH_3)_2Cl$ has been synthesized by the use of the $(CH_3)_2C{=}CHCH_2Cl/BCl_3$ initiating system. Highest yields were obtained by using methylene chloride diluent at about -50°C. The presence and position of the olefinic head-group was proven by epoxidation/titration and epoxidation/cleavage. The presence and position of a tertiary chlorine endgroup was proven by initiating block polymerization of a second monomer, such as styrene or α-methylstyrene, by using the asymmetric telechelic polyisobutylene prepolymer in conjunction with Et_2AlCl coinitiator. According to $1/DP$ versus $1/[M]$ plots obtained in model block copolymerization experiments, with the

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use of the tert-BuCl/Et_2AlCl initiating system at -30°C, significant chain transfer to monomer occurs during blocking of styrene; however, monomer transfer is negligible during blocking of α-methylstyrene. Thus, under suitable conditions head-functionalized block copolymers $(CH_3)_2C{=}CHCH_2{-}PIB{-}\underline{b}{-}P\alpha MeSt$ virtually free of homopolymer contaminants can be obtained.

INTRODUCTION

New avenues for the synthesis of novel block polyolefins have been opened by the use of BCl_3-based initiator systems [1-6]. This paper concerns the synthesis and characterization of $(CH_3)_2C{=}CHCH_2{-}$poly(isobutylene-b-styrene), $(CH_3)_2C{=}CHCH_2{-}PIB{-}\underline{b}{-}PSt$, and $(CH_3)_2C{=}CHCH_2{-}$poly(isobutylene-b-α-methylstyrene) $(CH_3)_2C{=}CHCH_2{-}$PIB-b-PαMeSt, i. e., saturated block-copolymers carrying an unsaturated head-group. These syntheses also necessitated the preparation and characterization of a valuable new intermediate, an asymmetric telechelic isobutylene prepolymer: $(CH_3)_2C{=}CHCH_2{-}$poly-isobutylene$-CH_2{-}C(CH_3)_2Cl$, abbreviated $(CH_3)_2C{=}CHCH_2{-}PIB{-}Cl$. The steps involved in the syntheses are as follows.

1. Initiating cation formation:

$$(CH_3)_2C{=}CHCH_2Cl + BCl_3 \rightleftharpoons (CH_3)_2C{=}CH\overset{\oplus}{C}H_2BCl_4^{\ominus}$$

2. Initiation of isobutylene polymerization:

$$(CH_3)_2C{=}CH\overset{\oplus}{C}H_2 + CH_2{=}C(CH_3)_2 \longrightarrow (CH_3)_2C{=}CHCH_2CH_2\overset{\oplus}{C}(CH_3)_2$$

3. Propagation of isobutylene polymerization:

$$(CH_3)_2C{=}CHCH_2CH_2\overset{\oplus}{C}(CH_3)_2 + CH_2{=}C(CH_3)_2 \longrightarrow (CH_3)_2C{=}CHCH_2{\sim}PIB{\sim}CH_2\overset{\oplus}{C}(CH_3)_2$$

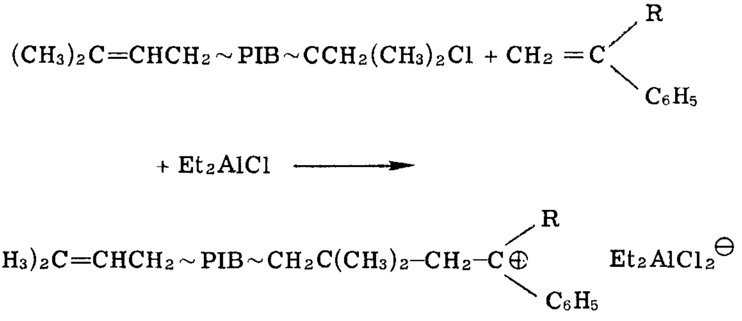
4. Termination of isobutylene polymerization:

$$(CH_3)_2C{=}CHCH_2{\sim}PIB{\sim}CH_2\overset{\oplus}{C}(CH_3)_2\ BCl_4^{\ominus} \longrightarrow (CH_3)_2C{=}CHCH_2{\sim}PIB{\sim}CH_2C(CH_3)_2Cl + BCl_3$$

Chain transfer to monomer is absent.

5. Removal of unreacted isobutylene and BCl_3 by evaporating under vacuum and washing with inert solvent.

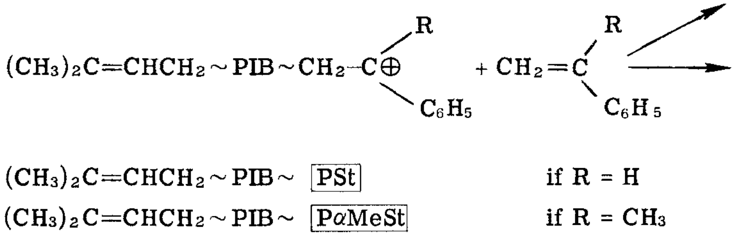
6. Initiation of styrene or α-methylstyrene polymerization by telechelic polyisobutylene prepolymer in presence of Et_2AlCl:



$$\mathrm{(CH_3)_2C{=}CHCH_2{\sim}PIB{\sim}CCH_2(CH_3)_2Cl + CH_2{=}C(R)(C_6H_5) + Et_2AlCl \longrightarrow (CH_3)_2C{=}CHCH_2{\sim}PIB{\sim}CH_2C(CH_3)_2{-}CH_2{-}C^{\oplus}(R)(C_6H_5)\quad Et_2AlCl_2^{\ominus}}$$

where R = H or CH_3.

Propagation and termination of styrene or α-methylstyrene polymerization:



$$\mathrm{(CH_3)_2C{=}CHCH_2{\sim}PIB{\sim}CH_2{-}C^{\oplus}(R)(C_6H_5) + CH_2{=}C(R)(C_6H_5) \longrightarrow}$$

$$\mathrm{(CH_3)_2C{=}CHCH_2{\sim}PIB{\sim}}\boxed{\mathrm{PSt}}\quad \text{if } R = H$$

$$\mathrm{(CH_3)_2C{=}CHCH_2{\sim}PIB{\sim}}\boxed{\mathrm{P\alpha MeSt}}\quad \text{if } R = CH_3$$

EXPERIMENTAL

Materials

Initially boron trichloride was distilled under high vacuum. However, later experience showed the high vacuum distillation was unnecessary, and thereafter BCl_3 was used as received. 1-Chloro-3-methyl-2-butene was dried with calcium hydride and distilled under high vacuum. Diethylaluminum chloride was refluxed over NaCl for 2 hr and then distilled under reduced nitrogen atmosphere. The distilled material was stored at -78°C over NaCl. Heptane and methylcyclohexane were dried by refluxing for 2 hr over calcium hydride and then distilled under nitrogen into septum-capped bottles. Isobutylene was dried by passing the gas through drying towers containing BaO and molecular sieves (4 Å). Methylene chloride was refluxed overnight with triethylaluminum and distilled under nitrogen atmosphere into septum-capped bottles. Styrene was dried with calcium hydride and distilled under vacuum. α-Methylstyrene was dried over calcium hydride and distilled under nitrogen. n-Pentane, dioxane, and acetone used in selective solvent extractions were used as received.

Synthesis of $(CH_3)_2C{=}CHCH_2{-}PIB{-}Cl$

In a nitrogen-filled dry box, methylene chloride, 1-chloro-3-methyl-2-butene, and isobutylene were pipetted into a tube, capped, and cooled. Reactions were started by addition of a solution of BCl_3 in CH_2Cl_2. Polymerizations were stopped after desired reaction times by the addition of a few milliliters of methanol. Telechelic polyisobutylenes for use in subsequent blocking reactions were prepared in "baked out" flasks. Polyisobutylene precipitated as the reaction proceeded and was recovered either by quickly filtering and washing the reaction mixture with CH_2Cl_2 at room temperature, or by quickly connecting the flask to a vacuum manifold and rapidly distilling off unreacted isobutylene, boron trichloride, and 1-chloro-3-methyl-2-butene.

Syntheses of $(CH_3)_2C{=}CHCH_2{-}PIB{-}\underline{b}{-}PSt$ or $(CH_3)_2C{=}CHCH_2{-}PIB{-}\underline{b}{-}P\alpha MeSt$

Telechelic PIB prepolymer obtained by the preceding syntheses was dissolved in n-heptane or methylcyclohexane, and methylene chloride (> 30 vol %) was added to increase medium polarity. Styrene or α-methylstyrene was added, and the stirred mixture was cooled to the desired temperature while carefully watching for signs of inhomogeneity. If insoluble polymer appeared (haziness), nonpolar solvent was added to achieve homogeneity. Blocking was initiated by adding to the homogeneous charge a solution of Et_2AlCl in methylene chloride. Blocking was allowed to proceed for 30 min and terminated by the addition of ~5 ml methanol.

Experimental techniques used for the syntheses of $(CH_3)_2C{=}CHCH_2{-}PIB{-}\underline{b}{-}PSt$ and $-P\alpha MeSt$ were quite similar, except that in the latter syntheses unreacted BCl_3, $(CH_3)_2C{=}CHCH_2Cl$, $i{-}C_4H_8$, and solvent were removed from the prepolymer $(CH_3)_2C{=}CHCH_2{-}PIB{-}Cl$ by evaporating under reduced pressure.

Selective Solvent Extraction of $(CH_3)_2C{=}CHCH_2{-}PIB{-}\underline{b}{-}PSt$ and $(CH_3)_2C{=}CHCH_2{-}PIB{-}\underline{b}{-}P\alpha MeSt$

Unreacted $(CH_3)_2C{=}CHCH_2{-}PIB{-}Cl$ prepolymer was removed by n-pentane extraction. In the case of $(CH_3)_2C{=}CHCH_2{-}PIB{-}\underline{b}{-}PSt$, polystyrene is removed by Soxhlet extraction with acetone.

In the case of $(CH_3)_2C{=}CHCH_2$–PIB-b–PαMeSt, a more elaborate selective dissolution method had to be employed. After n-pentane extraction, 1.0 g of n-pentane-insoluble polymer was placed in 100 ml acetone and stirred at room temperature for several hours. The suspension was allowed to settle for several hours; 10 ml of the supernatant was withdrawn and placed into a preweighed aluminum dish; the volume of the suspension diminished by withdrawing an aliquot was replenished with an equal volume of dioxane. The weight and composition of soluble polymer in the aliquot was determined by evaporating the solvent and weighing and by NMR spectroscopy, respectively. This procedure was repeated until the medium consisted predominantly of dioxane. The amount of polymer dissolved versus solvent composition was plotted.

Epoxidation/Titration of $(CH_3)_2C{=}CHCH_2$–PIB–Cl

This analysis was performed according to Dreyfuss and Kennedy [7]. Unsaturation data used to calculate unsaturations per molecule shown in the last column of Table 1 have been obtained by this method.

Cleavage of Olefinic Bond

Cleavage of terminal unsaturation was performed following Kennedy and Metzler's [8] method.

Determination of Chain Transfer to Monomer in α-Methylstyrene Polymerization Induced by tert-BuCl/Et_2AlCl Initiating System

These experiments were carried out by using a medium of n-heptane and 10 vol % methylene chloride at -30°C. Monomer concentration was varied by replacing various volumes of the n-heptane by α-methylstyrene. On handling in this manner, the polarity of the system remained unchanged. Polymerizations were initiated by introducing tert-BuCl (1×10^{-3} M) to quiescent α-methylstyrene Et_2AlCl (2×10^{-2} M) charges. Conversions were < 5%. Molecular weights were determined by osmometry.

Gel Permeation Chromatography

GPC analyses were performed by using either a Waters Associates Ana-Prep or a Waters 6000A high pressure GPC instrument. Calibration curves for PIB were obtained using carefully fractionated standards. Sample concentrations were 0.2-0.4 wt % PIB in THF.

Membrane Osmometry

A Hewlett-Packard 503 high speed membrane osmometer and 0.3-1.0 wt % samples in toluene solvent at 37°C were used.

Vapor Pressure Osmometry

A Hitachi/Perkin-Elmer 115 instrument and 19.7-218 g/kg sample solutions in toluene were used.

RESULTS AND DISCUSSION

Synthesis and Characterization of $(CH_3)_2C{=}CHCH_2-$PIB-Cl Prepolymer

It was first established that $(CH_3)_2{=}CHCH_2Cl$ in conjunction with BCl_3 initiates the polymerization of isobutylene. Representative data are shown in Table 1. Synthetically useful amounts of PIB have been obtained by using CH_2Cl_2 diluent at -52°C. Increasing $(CH_3)_2C{=}CHCH_2Cl$ initiator concentration increases isobutylene conversion; however, PIB molecular weights remain unchanged.

Provided side reactions including chain transfer to monomer are absent, initiation by $(CH_3)_2C{=}CHCH_2Cl$ will give rise to a $(CH_3)_2C{=}CHCH_2-$ or $(CH_3)_2\overset{|}{C}CH{=}CH_2$ head-group. Previous work has shown [2-5] that isobutylene polymerization coinitiated with BCl_3 proceeds in the absence of chain transfer to monomer and terminates by chlorination to produce a tertiary chlorine endgroup. Since side reactions other than cationation of isobutylene by the $(CH_3)_2\,{}^{\delta\oplus}C-CH-{}^{\delta\oplus}CH_2$ carbenium ion are possible, it was necessary to prove not only the presence but also the position of unsaturation in the polymer.

The presence of approximately one (1.3-0.8) unsaturation per polymer chain has been determined by epoxidation/titration [7]. Results are shown in the last column of Table 1. While the data are considered to be only of qualitative significance, since isobutylene conversions were too high for meaningful molecular weight determination, they seem to indicate the presence of stoichiometrically equivalent amounts of olefin and polyisobutylene.

Isoprene formation by proton elimination from the 3-methyl-2-butenyl cation is possible, i. e.,

$$(CH_3)_2C{=}CH\overset{\oplus}{C}H_2 \longrightarrow CH_2{=}C(CH_3){-}CH{=}CH_2 + H^{\oplus}$$

followed by copolymerization of isobutylene with isoprene. In this

TABLE 1. Polymerization of Isobutylene by $(CH_3)_2C{=}CHCH_2Cl/BCl_3$ Initiating System and Demonstration of Head-Groups in Polyisobutylenes by Epoxidation Titration Analysis[a]

Sample	BCl_3 (M)	[IN][a] (M)	[Isobutylene] (M)	$\frac{[\text{Isobutylene}]}{[\text{IN}]}$	Conv. (%)	$\overline{M}_n$	No. unsat. per molecule[b]
1A	0.043	0.041	1.81	44	68	12,500[c]	1.3
1B	0.043	0.041	1.81	44	81	11,800	1.3
2A	0.087	0.082	1.81	22	88	12,400	1.3
2B	0.087	0.082	1.81	22	66	14,300	1.4
3A	0.130	0.130	1.81	14	83	9,320	1.2
3B	0.130	0.130	1.81	14	80	11,200	2.0
56a	0.076	0.075	1.50	23	79	9,100	0.8
56b	0.075	0.075	1.50	23	79	10,000	0.8

[a] [IN] = 1-chloro-3-methyl-2-butene. Temp: -52°C. Reagent introduction sequence: $i\text{-}C_4H_8 + BCl_3 + IN$. Total volumes in Expts. 1A-3B: 13.08 ml, in Expt. 56a and b: 14.0 ml. Dry box runs but BCl_3 and IN purified on vacuum line. Molecular weights by GPC.

[b] For analytical method see Experimental.

[c] $\overline{M}n$ = 14,000 by VPO.

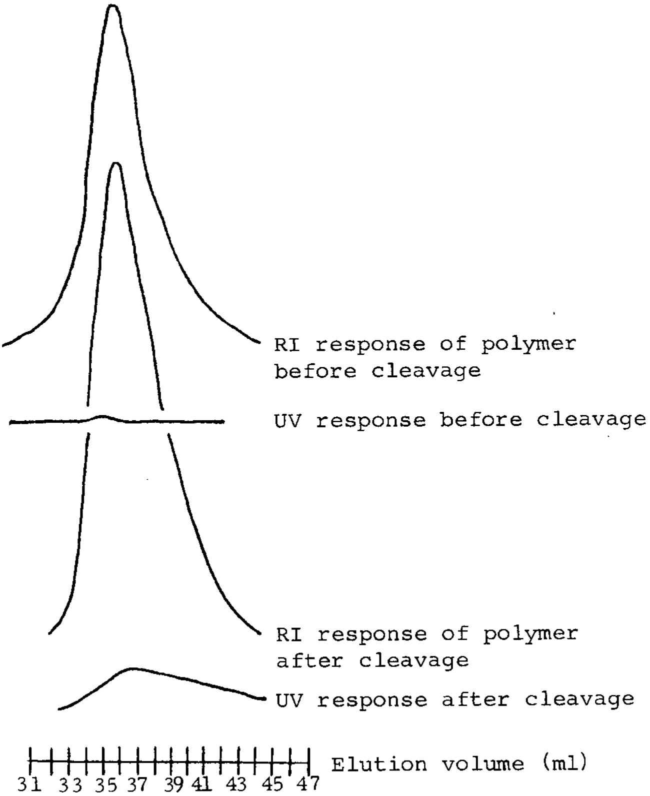


FIG. 1. GPC of $(CH_3)_2C{=}CHCH_2{-}PIB{-}Cl$ before and after olefin cleavages (curves not normalized).

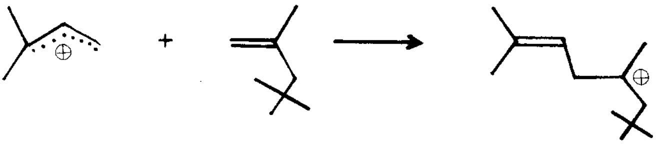
event unsaturation due to isoprene incorporation would arise in the "interior" rather than at the α-terminus of the chain. This possibility was examined by oxidatively degrading the product [8] and determining the $\overline{M}_n$ of the surviving fragments. If, however, double bonds are in the interior of the chain, the molecular weight of surviving polyisobutylenes will be substantially reduced by cleavage.

An efficient quantitative method to cleave double bonds in polymer chains consists of epoxidizing olefinic groups with m-chloroperbenzoic acid, hydrolyzing the epoxide with aqueous acid to form the glycol, and cleaving the glycol with periodate [8]. According to GPC analysis of samples obtained before and after oxidative degradation (shown in Fig. 1) the molecular weights remain virtually unchanged, indicating that olefinic unsaturation was at the α-position of the PIB chain. The source of the UV absorption (at 254 nm) noticeable after cleavage is obscure (m-chloroperbenzoic acid impurity?).

The initiating allylic carbocation contains a tertiary and a primary allylic carbenium ion center and cationation of monomer could occur at either position [Eq. (8)]

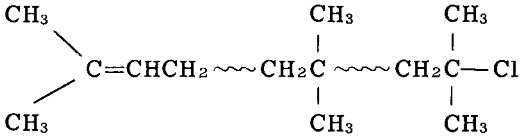
$$(CH_3)_2\overset{\oplus}{C}{-}CH{=}CH_2 \longleftrightarrow (CH_3)C{=}CH{-}\overset{\oplus}{C}H_2$$

According to model experiments [4], the reaction between this carbocation and 2,4,4-trimethyl-1-pentene predominantly involves the primary allylic site:



On this basis we believe that initiation of isobutylene polymerization by the $(CH_3)_2C{=}CHCH_2Cl/BCl_3$ system mainly leads to $(CH_3)_2C{=}CH{-}CH_2$ head-groups in PIB.

Proof positive for the presence and position of the terminal tertiary chlorine in the prepolymer was provided by blocking experiments described below. Combination of these evidences substantiate our proposition that PIB's produced by the $(CH_3)_2C{=}CHCH_2Cl/BCl_3$ initiating system in CH_2Cl_2 at or below -50°C have the following structure:



$$(CH_3)_2C{=}CHCH_2{\sim\sim\sim}CH_2\overset{CH_3}{\underset{CH_3}{C}}{\sim\sim\sim}CH_2\overset{CH_3}{\underset{CH_3}{C}}{-}Cl$$

These molecules may be of interest for a variety of applications. We have used the terminal tertiary chlorine to initiate block copolymerizations of styrene and α-methylstyrene.

Synthesis of $(CH_3)_2C{=}CHCH_2{-}PIB{-}\underline{b}{-}PSt$

The asymmetric telechelic prepolymer $(CH_3)_2C{=}CHCH_2{-}PIB{-}Cl$ in conjunction with Et_2AlCl has been used to initiate the block copolymerization of styrene St and α-methylstyrene αMeSt. These experiments led to the synthesis of head-functionalized isobutylene-styrene and isobutylene-α-methylstyrene block copolymers $(CH_3)_2C{=}CHCH_2{-}PIB{-}\underline{b}{-}PSt$ and $(CH_3)_2C{=}CHCH_2{-}PIB{-}\underline{b}{-}P\alpha MeSt$.

TABLE 2. Synthesis of $(CH_3)_2C{=}CHCH_2$–PIB–b–PSt, Step 1: Synthesis of $(CH_3)_2C{=}CHCH_2$–PIB–Cl

Expt.	i-C_4H (M)	[IN] × 10^2 (M)	[BCl_3] × 10^3 (M)	Temp. (°C)	Time (min)	Conv. (%)	$\overline{M}_n$ × 10^3 g/mole
A	1.7	7.5	7.5	-50	20	60	-
B	1.7	7.5	7.5	-52	30	60	15.5
C	2.0	8.2	8.7	-52	30	76	24.5
D	2.0	7.5	7.5	-54	30	76	26.5

Tables 2 and 3 show details of the synthesis of $(CH_3)_2C{=}CHCH_2$–PIB–b–PSt and Fig. 2 the extraction sequence used. Extraction of the crude reaction product, presumed to contain the desired $(CH_3)_2C{=}CHCH_2$–PIB–b–PSt, together with unreacted PIB prepolymer and PSt formed as a consequence of cationogenic impurities in the system and/or chain transfer to styrene during blocking, with methyl ethyl ketone (MEK) usually yielded 76-90% soluble and 10-24% insoluble material. The MEK-insoluble fraction (fraction B) must contain PIB prepolymer and PIB-rich block copolymer. Indeed, most (> 90%) of fraction B was found to be soluble in n-pentane, a good solvent for PIB. The n-pentane-insoluble fraction was aluminum-containing residues due to the quenching of Et_2AlCl with methanol.

Extraction with n-pentane of the MEK-soluble fraction (fraction A) yielded insignificant amounts (< 10%) of soluble material (fraction C). Further extraction of the MEK-soluble, n-pentane-insoluble fraction (fraction D) with acetone, a selective solvent for PSt up to $\overline{M}_n \sim 50{,}000$, produced the desired pure $(CH_3)_2C{=}CHCH_2$–PIB–b–PSt (fraction H) together with PSt (fraction G). The results of several experiments have shown that 20-30% of the crude reaction mixture was PSt.

These experiments demonstrate that $(CH_3)_2C{=}CHCH_2$–PIB–b–PSt can be obtained by using the $(CH_3)_2C{=}CCH_2$–PIB–Cl/Et_2AlCl/styrene/CH_2Cl_2/-50°C system. Under the synthesis conditions employed (Tables 2 and 3) the block copolymer product was contaminated by 20-30% PSt and perhaps by some unreacted PIB prepolymer. The PSt is likely due to initiation of styrene polymerization by some cationogenic impurity or more likely by chain transfer during blocking. We are confident that much purer product could be obtained under optimum conditions, however, process development has been discontinued in favor of blocking research with α-MeSt. This monomer not only promised to lead in preliminary experiments to pure block copolymer, but also to better overall properties than PSt.

TABLE 3. Synthesis of $(CH_3)_2C{=}CHCH_2$–PIB–b–PSt, Step 2: Blocking Styrene from $(CH_3)_2C{=}CHCH_2$–PIB–Cl Prepolymer

Expt.	St (M)	Pre-polymer (g)	$[Et_2AlCl] \times 10^3$ (M)	Temp. (°C)	Time (min)	Solv. comp. (vol %) CH_2Cl_2/n-C_7H_{16}	Vol (ml)
A'	0.79	1.0	15	-50	50	50/50	89
B'	0.47	0.86	5	-50	50	50/50	75
C'	0.47	0.95	2.7	-50	50	50/50	85
D'[a]	0.47	1.5	1.3	-54	50	44/56	85
E'[a]	0.47	0.73	1.3	-54	50	44/56	75

[a] The product of D in Table 2 was divided and used in two subsequent experiments, D' and E'.

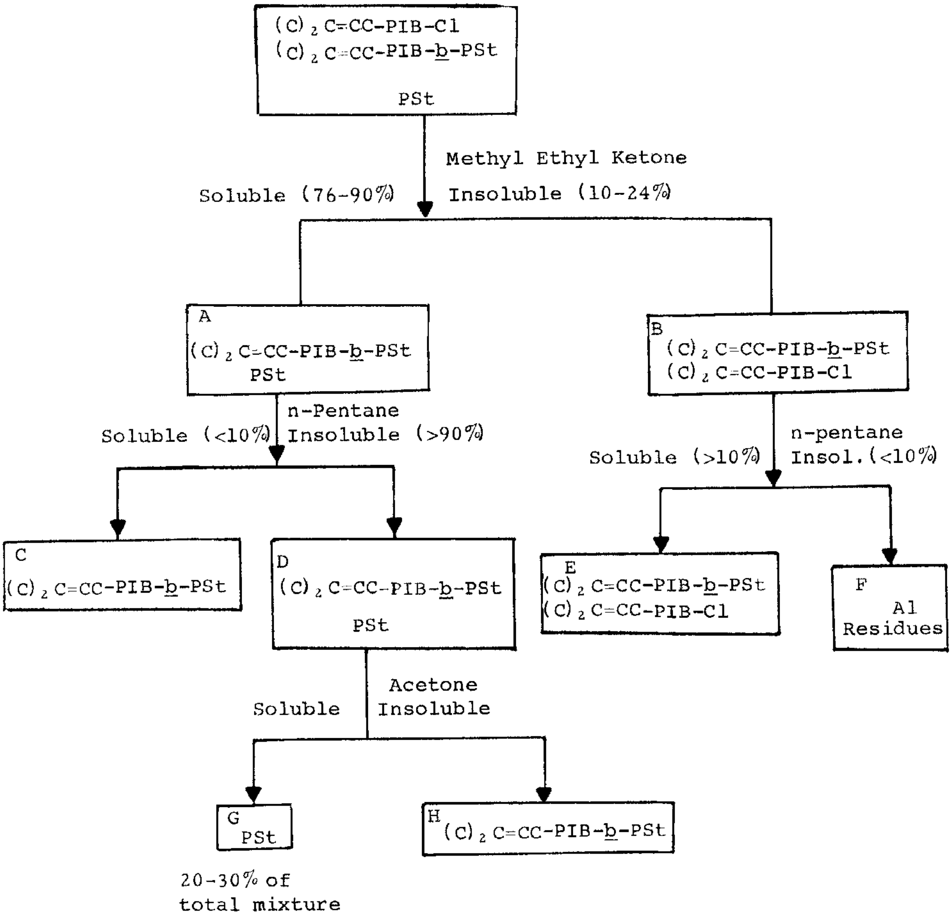


FIG. 2. Extraction scheme for $(CH_3)_2C{=}CHCH_2$–PIB–b–PSt.

Synthesis of $(CH_3)_2C{=}CHCH_2$–PIB–b–PαMeSt

The growing $PSt^{\oplus}$ is believed to undergo facile chain transfer to monomer by intramolecular penultimate alkylation [9, 10]. It was theorized that this process will be less bothersome with the growing $P\alpha MeSt^{\oplus}$ because molecular models showed that the transition state leading to terminal indenyl unit by penultimate alkylation would require two methyl groups to occupy unfavorable 1,3 axial positions. Also $P\alpha MeSt^{\oplus}$ is more stable than $PSt^{\oplus}$ and therefore was expected to be more selective toward propagation.

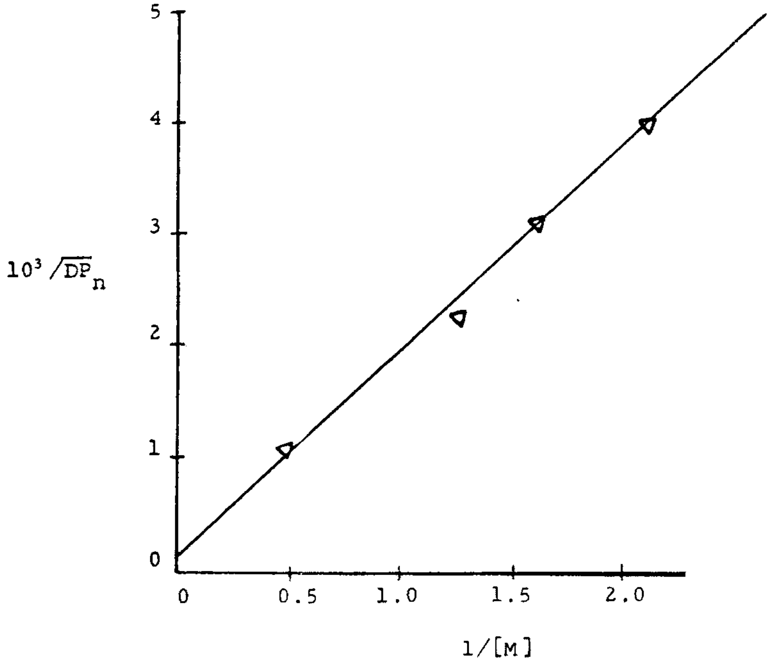


FIG. 3. Plot of $1/DP_n$ vs. 1/[M] for α-methylstyrene polymerization. [Et_2AlCl] = 0.02 M; [t-BuCl] = 0.001 M; CH_2Cl_2/heptane = 10/90; -30°C.

Chain transfer to α-MeSt was quantitatively assessed by $1/\overline{DP}_n$ versus 1/[M] plots and model experiments in which blocking of α-MeSt from the tertiary chlorine endgroup in $(CH_3)_2C{=}CHCH_2$–PIB–Cl was mimicked by the use of tert-BuCl. The intercept and slope of the $1/\overline{DP}_n$ versus 1/[M] plot gives $k_{tr,M}/k_p$ and k_t/k_p, respectively, and the ratio of the slope to the intercept provides $k_t/k_{tr,M}$. According to the data obtained with the tert-BuCl/Et_2AlCl/α-methylstyrene system at -30°C shown in Fig. 3, $k_{tr,M}/k_p = 0.2 \times 10^{-3}$ and $k_t/k_{tr,M} > 10$ suggesting that termination (probably by hydridation) [12] is at least 10 times faster than chain transfer to monomer at -30°C. Since decreasing temperatures usually decrease the rate of monomer transfer more than that of termination [11], α-MeSt polymerization with Et_2AlCl coinitiator should proceed in the virtual absence of chain transfer to monomer below -30°C.

TABLE 4. Synthesis of $(CH_3)_2C{=}CHCH_2$–PIB–b–PαMeSt, Step 1: Synthesis of $(CH_3)_2C{=}CHCH_2$–PIB–Cl Prepolymer

Expt.	i-C_4H_8 (M)	$(CH_3)_2CCHCH_2Cl$ × 10^2 (M)	BCl_3 × 10^2 (M)	Temp. (°C)	Conv. (%)	$\overline{M}_n$ (g/mole)
1	2.0	3.0	4.0	-52	25	16,000
2	2.0	3.0	4.0	-52	23	14,000
3	1.0	3.0	4.0	-50	34	33,000
4	1.0	3.0	4.0	-50	20	8,000

On hand of this information, blocking of α-MeSt from $(CH_3)_2C{=}CHCH_2$–PIB–Cl in the presence of Et_2AlCl was carried out at or somewhat below -50°C. Results of syntheses of $(CH_3)_2C{=}CHCH_2$–PIB–b–PαMeSt together with experimental details are collected in Tables 4 and 5. Prepolymers 1-4 have been employed in subsequent blocking experiments 1B-4B. Analysis of these results indicate that the target block copolymer can readily be obtained and under select conditions essentially pure product is formed.

Considerable effort was devoted to develop a satisfactory purification procedure and estimate the amount of homopolymer contamination in $(CH_3)_2C{=}CHCH_2$–PIB–b–PαMeSt. Selective solvents to remove both PIB and PαMeSt could not be found. While n-pentane can be used to dissolve PIB selectively from diblock copolymers high in PαMeSt, no selective solvent for PαMeSt could be found.

The first two diblock copolymers in Table 5, 1B and 2B, were designed to contain quite different amounts of PαMeSt, with 1B containing much more PαMeSt than 2B.

Since diblock mixture 1B is much higher in PαMeSt than 2B, PIB contamination should be selectively removable by n-pentane extraction of 1B. n-Pentane extraction (Soxhlet, 48 hr) of reaction mixture 1B produced less than 3% soluble material identified by NMR to be PIB. According to these results the reaction mixture 1B and similar diblock reaction mixtures (i. e., 2B) contain very small amounts (3%) of PIB.

The pentane-insoluble portion of 1B contains diblock copolymer and possibly PαMeSt. Unfortunately we could not find a selective solvent for PαMeSt; acetone ($\delta = 10.0$), a selective solvent for PSt is suitable only for PαMeSt below $\overline{M}_n \sim 10{,}000$. Dioxane ($\delta = 9.9$) dissolves PαMeSt and diblock copolymer rich in PαMeSt.

The amount of PαMeSt in this mixture may be determined by selective dissolution with acetone-dioxane mixtures. The amount of soluble polymer was determined at various solvent compositions while the medium is gradually changed from nonsolvent (acetone) to solvent (dioxane) for PαMeSt. The first component to dissolve

TABLE 5. Synthesis of $(CH_3)_2C{=}CHCH_2{-}PIB{-}\underline{b}{-}P\alpha MeSt$, Step 2: Blocking α-Methylstyrene from Prepolymer

Expt.	α-MeSt ($\underline{M}$)	Solv. comp. (vol %) $CH_2Cl_2/n\text{-}C_7H_{16}$	Prepolymer (g)	$Et_2AlCl \times 10^3$ ($\underline{M}$)	Vol. (ml)	Temp. (°C)	Conv. (%)	$\overline{M}_n$ (g/mole)	PIB/PαMeSt (wt %) (NMR)
1B	0.85	40/60	3.2	7.0	285	-52	62	47,000	13/87
2B	0.81	38/62	2.4	2.2	90	-52	55	31,000	48/52
3B	0.44	58/42	3.7	2.3	175	-50	40	-	92/8
4B	0.70	47/53	2.1	14.0	114	-50	57	-	70/30

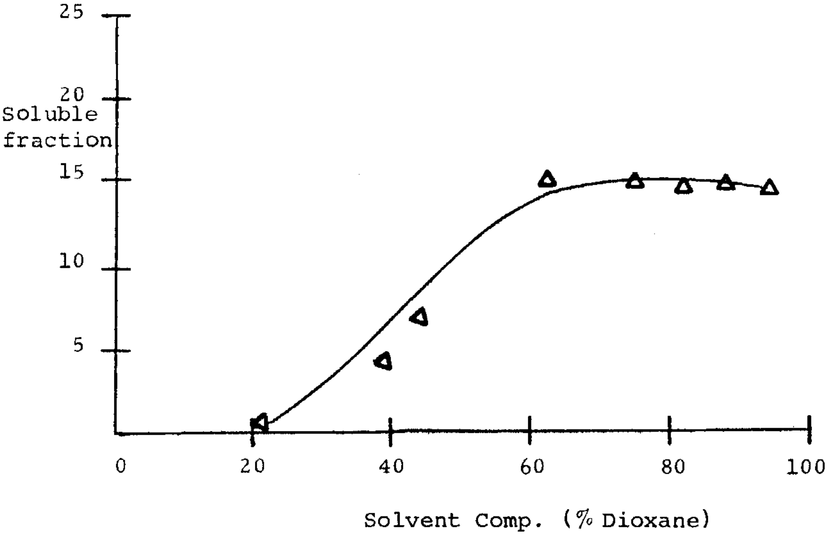


FIG. 4. Soluble fraction vs. solvent composition for pentane-insoluble portion of 1B.

should be PαMeSt, since PIB in the diblock should render it insoluble in polar solvents (acetone/dioxane mixtures). A plot of weight percent soluble material versus solvent composition for the n-pentane-insoluble fraction of 1B is shown in Fig. 4. The amount of dissolved material increases with increasing dioxane concentration up to about 60 vol % of dioxane. Above 60 vol % dioxane, the soluble fraction remains constant. The soluble component is PαMeSt (greater than 98 wt % by NMR). The height of the plateau in Fig. 4 suggests the material to contain about 16 wt % PαMeSt.

Since the $1/\mathrm{DP}_n$ vs. $1/[\mathrm{M}]$ plot indicates chain transfer to monomer is negligible, the PαMeSt in 1B is probably due to initiation by impurity during blocking.

The reaction mixture of 2B was extracted with n-pentane. After several days of Soxhlet extraction more than 85% of the sample was found to be n-pentane-soluble. This fact, together with those obtained from analysis of reaction mixture 1B suggest that reaction mixture 2B contains less than 15 wt % PαMeSt and that the n-pentane-soluble fraction is predominantly diblock copolymer (since < 3% PIB was found in reaction mixture 1B).

That the n-pentane-soluble fraction is essentially pure diblock is further demonstrated by correlating pertinent molecular weight and composition data. According to the data in Table 5 the theoretical $\overline{M}_n$ of diblock 2B is 29,200:

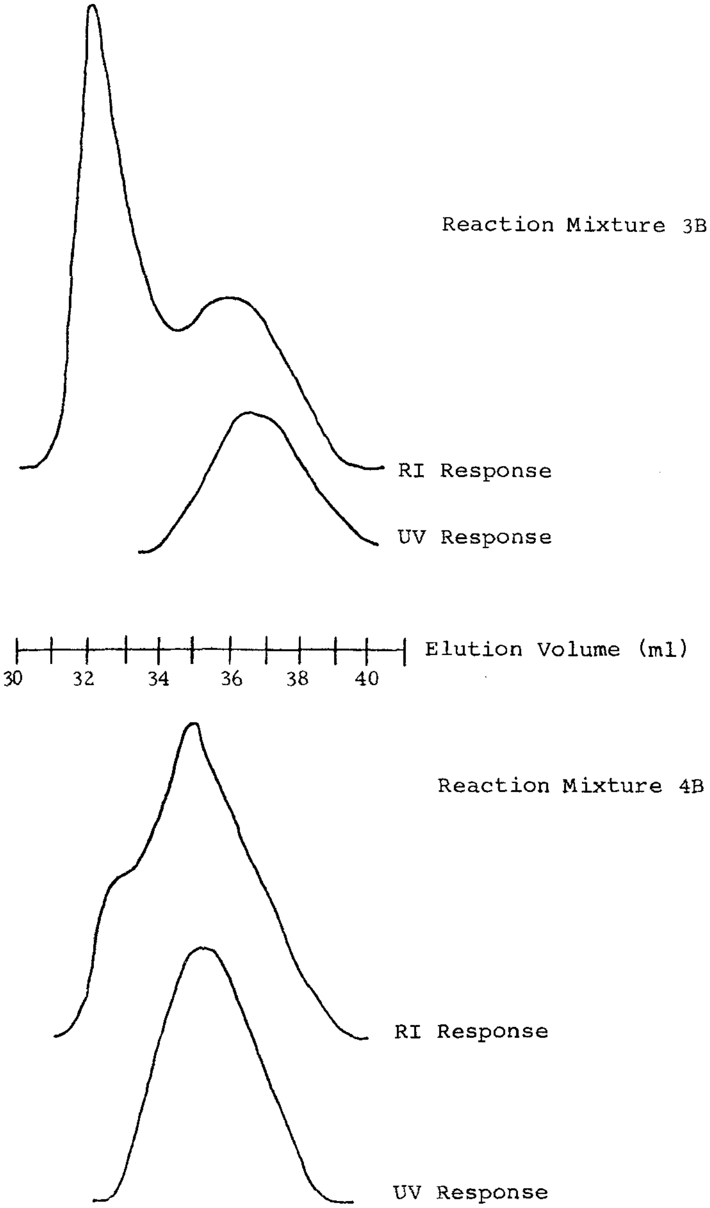


FIG. 5. GPC of diblock reaction mixtures 3B and 4B (curves not normalized).

$$\text{Theoretical } \overline{M}_n = \frac{\overline{M}_n \text{ of prepolymer/2}}{\text{PIB content of n-pentane soluble 2B}}$$

$$= \frac{14{,}000}{0.48} = 29{,}200$$

This value is within experimental error of the experimental (osmotic) $\overline{M}_n$ of the n-pentane-soluble portion of 2B (31,000). This agreement demonstrates the absence of appreciable amounts of PIB in the n-pentane-soluble fraction, since if PIB were present the theoretical $\overline{M}_n$ would be much less than the actual $\overline{M}_n$.

High pressure GPC analyses of prepolymers 1 and 2, and reaction mixtures 1B and 2B showed smooth monomodal distributions. Homopolymer contaminants would be indicated by multimodal molecular weight distribution, shoulder, or skewing, UV and/or RI responses; however, no such evidence was found by GPC in the crude reaction mixtures of 1B or 2B.

In experiments leading to diblocks 3B and 4B, lower concentrations of α-MeSt were used in the blocking step in the hope of producing a diblock copolymer higher in PIB content than 2B. However, according to GPC analysis of 3B and 4B (Fig. 5), after 30 min of blocking, considerable amounts of PIB were still present. Evidently virtually complete incorporation of the telechelic PIB prepolymer into the diblock is achieved only when [α-MeSt > 0.8 M in the blocking step.

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