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Initiation of Cationic Polymerization with Alcohol/Lewis Acid Systems

4. Synthesis of Poly(Styrene-*g*-Isobutylene), Poly(Isobutylene-*g*-Indene) and Poly(Isobutylene-*b*-Indene) from Polymers Carrying Hydroxyl Groups

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Summary

The discovery that tertiary alcohols in conjunction with BCl_3 are efficient cationic polymerization systems was exploited for the synthesis of new graft and block copolymer, i.e., poly(styrene-g-isobutylene), poly(isobutylene-g-indene) and poly(isobutylene-b-indene). Syntheses involved the initiation of isobutylene and indene polymerizations by polymeric alcohols (i.e., randomly hydroxylated polystyrene, and randomly terminally hydroxylated polyisobutylene) in the presence of BCl_3. The starting prepolymers, i.e., hydroxylated polystyrene and polyisobutylene, were synthesized by conventional techniques. The syntheses of these sequential copolymers prove that the mechanism proposed for initiation with ROH/BCl_3 systems is fundamentally correct.

Introduction

Earlier papers in this series (1,2,3) concerned the polymerization of isobutylene by ROH/BCl_3 initiating systems and supporting model experiments. The most efficient initiating systems are tertiary alcohols R^tOH in conjunction with BCl_3. In the course of this work, we postulated that R^tOH/BCl_3 combinations could be exploited for the synthesis of novel graft and block copolymers by the use of polymers containing tertiary OH groups randomly distributed along a chain or as end groups. Thus we have prepared -OH containing polystyrenes (i.e., polystyrenes carrying $-CH_2-C-(C_6H_5)OH$-units) and polyisobutylenes (i.e., polyisobutylenes carrying $-CH_2-C(CH_3)OH$-units) and used these polymers in the presence of BCl_3 to initiate the grafting of isobutylene and indene, respectively. Similarly, we prepared polyisobutylenes carrying tert -OH end groups (i.e., $PIB-CH_2-C-(CH_3)_2OH$) and used these prepolymers to block indene from it.

The demonstration of the syntheses of these block and graft copolymers not only opens new avenues towards the preparation of new materials but also proves that our basic postulate, namely the R^t-OH/BCl_3 combinations initiate cationic polymerizations by direct cationation, is fundamentally correct.

Experimental

All manipulations and polymerizations were carried out in all glass (Pyrex) assembly under high vacuum. Polystyrene PSt (Polysciences Inc.) was purified by dissolving it in benzene, precipitating into methanol and drying under vacuum. The poly-

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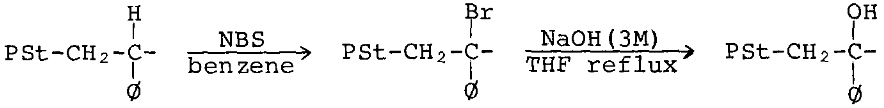
isobutylene PIB was in fact a copolymer of isobutylene and $\sim$ 5% isoprene (Enjay Chemical Co.). The viscous product was purified by dissolving in n-hexane, precipitating in acetone, and drying under vacuum. Polymerizations were carried out by charging a reactor (50 ml) with monomer, solvent (CH_2Cl_2 for experiments with PSt, or CH_2Cl_2/n-hexane mixtures for experiments with PIB) and prepolymer. The charge was agitated magnetically and cooled to -50°C. Polymerizations were induced by adding neat BCl_3 by shattering the breakseal of a vial. Polymerizations occurred instantaneously with considerable heat evolution. The temperature profile of the reactions is unknown and the maximum may be near 0°C. After 30 minutes of stirring the homogeneous solutions, reactions were terminated by prechilled methanol. The polymers were precipitated in methanol and dried under vacuum. Molecular weights were determined by osmometry (Mechrolab-503 instrument, toluene solutions) and the distribution of the sequential copolymers was examined by inspection of GPC traces (Waters instrument, THF solutions). Structures and compositions were analyzed by ^1H NMR (Varian T-60 instrument, TMS internal standard), ^{13}C NMR (Varian CFT-20 instrument and IR (Perkins-Elmer 521 instrument) spectroscopies.

Results and Discussion

1. Synthesis of Polystyrene Carrying -OH Groups

Since 2-phenyl-2-propanol in the presence of BCl_3 is an efficient initiator for the polymerization of isobutylene (3), we reasoned that PSt carrying -OH groups would also initiate the polymerization of this olefin and thus would lead to grafts with PIB branches.

Prepolymers were prepared by brominating PSt with N-bromosuccimide (NBS) and substituting the bromines by hydroxyl groups:



$$\mathrm{PSt{-}CH_2{-}}\overset{\mathrm{H}}{\underset{\phi}{\mathrm{C}}}{-}\ \xrightarrow[\text{benzene}]{\text{NBS}}\ \mathrm{PSt{-}CH_2{-}}\overset{\mathrm{Br}}{\underset{\phi}{\mathrm{C}}}{-}\ \xrightarrow[\text{THF reflux}]{\text{NaOH(3M)}}\ \mathrm{PSt{-}CH_2{-}}\overset{\mathrm{OH}}{\underset{\phi}{\mathrm{C}}}{-}$$

Tertiary halides readily lose hydrogen halide upon treatment with base and yield a mixture of elimination and substitution products; indeed, elimination is the predominate (4). We also found elimination to predominate when 1-chloro-2,4,4-trimethylpentane was treated with NaOH(3M) (i.e., 90% 2,4,4-trimethyl-1-pentene and 10% 1,4,4-trimethylpentanol). Interestingly, however, NaOH treatment of brominated PSt gave insignificant elimination (absence of resonances in the 4-5.5 ppm region by ^1H NMR, or absorptions at 1600-1700 and 980 cm^{-1} by IR indicating unsaturation). The presence of -OH groups ($\sim$ 5%) in PSt was demonstrated by IR spectroscopy (absorption at 3650 cm^{-1} Figure 1b).

2. Synthesis of Poly(styrene-g-isobutylene)

The grafting of isobutylene from PSt containing OH groups occurred readily. Neat BCl_3 (0.22 ml) was added to a charge of $PSt{-}CH_2{-}C(C_6H_5)OH{-}$ (2g) and isobutylene (0.76 ml) in CH_2Cl_2 (50 ml) at -50°C. After 30 minutes of stirring the reaction was terminated by prechilled methanol, the charge was poured into an excess of methanol, the precipitate was filtered and dried under vacuum.

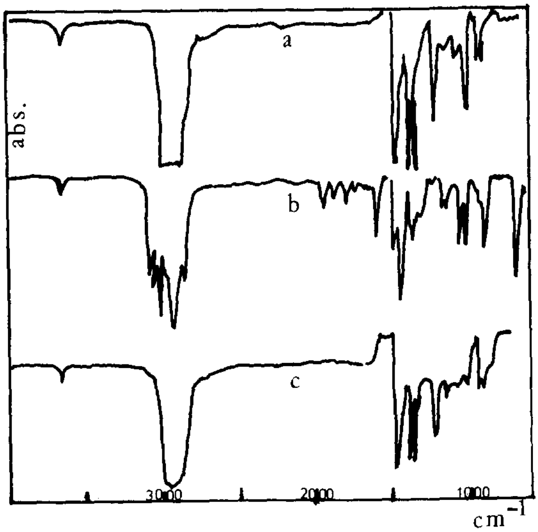
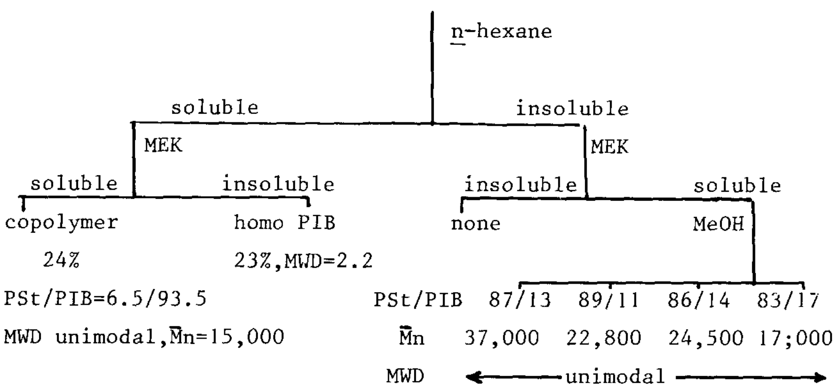


Figure 1. IR spectra of prepolymers carrying OH groups. a) Polyisobutylene, b) Polystyrene, and c) Polyisobutylene having OH end groups.

Yield = 3.1g, isobutylene conversion $\simeq$ 50%. The crude product was selectively fractionated coupled with turbidimetry, as outlined in Scheme I. The amount and composition of the fractions are included in Scheme I. Since PSt is soluble in MEK (methylethyl ketone) and PIB is insoluble in this solvent, and since

Scheme I. Fractionation Scheme for Poly(styrene-g-isobutylene)

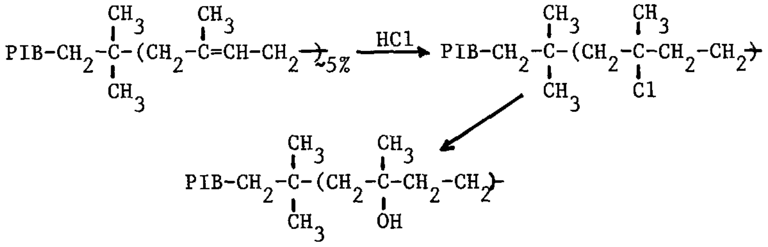


PSt is insoluble in *n*-hexane, whereas PIB is soluble in it, the *n*-hexane-soluble-MEK-soluble fractions must contain graft copolymers. The relative composition of PSt-*g*-PIB can be readily determined by ^1H NMR spectroscopy and these data are also shown in Scheme I.

We estimate our grafting efficiency ($G_{eff}=W_gPIB/(W_gPIB + W_hPIB)$ where W_gPIB = weight of PIB in the graft and W_hPIB = weight of PIB extracted) to be 80%, and the percent PIB grafted (W_gPIB/W_g where W_g = weight of graft copolymer) to be 23%. The absence of polymer in the *n*-hexane-insoluble-MEK-insoluble fraction indicates the absence of unreacted PSt.

3. Synthesis of Polyisobutylene Carrying OH Groups

Tert.-butanol in conjunction with BCl_3 readily initiates the polymerization of isobutylene (3); thus, we expected to grow branches from polymers containing similar tertiary alcohol functions. We introduced OH groups into a copolymer of isobutylene containing ∿ 5% isoprene by hydrochlorinating the starting material and then substituting the tertiary chlorines by OH.



The starting material was dissolved in a CH_2Cl_2/*n*-hexane mixture and HCl was bubbled through the system (0°C, 1 hour). The solvent was removed and the polymer was refluxed in NaOH-THF solution. After decanting and washing with water the product was precipitated and dried under vacuum. The presence of OH groups was demonstrated by IR spectroscopy (Figure 1a).

4. Synthesis of Poly(isobutylene-*g*-indene)

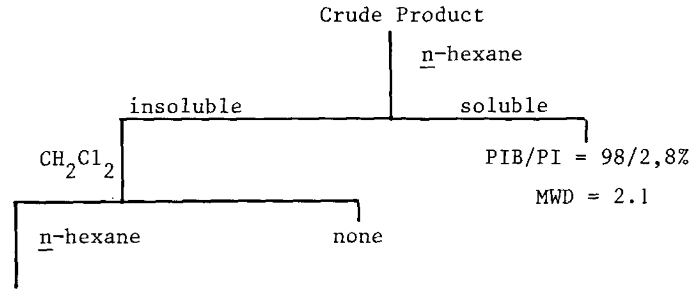
We decided to grow polyindene (PI) branches from a PIB backbone and thus to produce a thermoplastic elastomer.

We dissolved hydroxylated polyisobutylene (1g, MWD = 2.2 $\bar{M}_n$=27,000) in a mixture of CH_2Cl_2/*n*-hexane (75/25, 60 ml) and indene (0.56 ml, 4g), and cooled the system to -50°C. Grafting was initiated by the addition of BCl_3 (neat, 0.8 ml). After 30 minutes of stirring, prechilled methanol was added, the product precipitated in excess methanol, filtered and dried under vacuum. Yield = 3.62 g, indene conversion = 65%. The crude product was selectively fractionated coupled with turbidimetry as outlined in Scheme II.

This scheme shows also the composition of fractions and their relative amounts as determined by ^1H NMR. G_{eff} was 93% and PI grafted was 78%.

n-Hexane is a good solvent for PIB and a nonsolvent for PI whereas CH_2Cl_2 is a bad solvent for PIB and a good solvent for PI. The fact that the *n*-hexane-insoluble-CH_2Cl_2-soluble fraction contained PIB indicates that this PIB is chemically

Scheme II. Fractionation of Poly(isobutylene-g-indene)

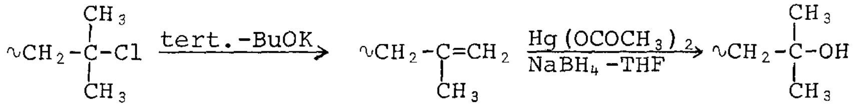


PIB/PI	96/4	37/63	25/75	29/71	30/70	0/100
%	6.3	63.4	5.5	3.3	6.9	6.5
$Mn\times10^{-3}$	63.7	49	36.1	29.7	24	38

attached to PI segments, i.e., graft copolymers have formed. The n-hexane-soluble fraction contains $\sim$ 2% PI, i.e., this fraction was regarded to be pure PIB.

5. Synthesis of -OH Terminated Polyisobutylene

After having demonstrated grafting from a PIB carrying many OH groups, we proceeded to block cationically polymerizable monomers from PIB's carrying a terminal tertiary OH function. The starting material was prepared by first synthesizing a PIB using the benzhydrol/BCl_3 initiating system described in ref. (3). This PIB carries the $HØ_2C$- head group and the $-CH_2-C-(CH_3)_2-Cl$ tail group (3). The latter was dehydrochlorinated with t-BuOK to the exo-olefin terminus $-CH_2-C-(CH_3)=CH_2$, which in turn was converted by treatment with $Hg(OCOCH_3)_2$ and $NaBH_4$ to the tert.-alcohol (5):



$$\sim CH_2-\overset{CH_3}{\underset{CH_3}{C}}-Cl \xrightarrow{\text{tert.-BuOK}} \sim CH_2-\underset{CH_3}{C}=CH_2 \xrightarrow[NaBH_4\text{-THF}]{Hg(OCOCH_3)_2} \sim CH_2-\overset{CH_3}{\underset{CH_3}{C}}-OH$$

The presence of the terminal tert-OH group was demonstrated by IR spectroscopy (absorption band at 3,650 cm^{-1}, Figure 1c).

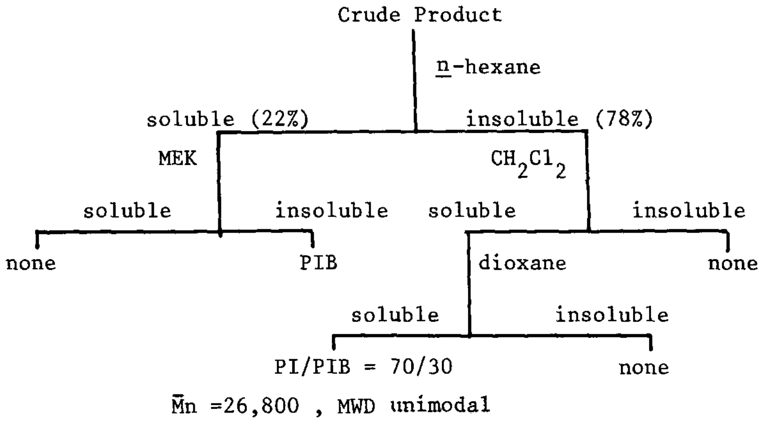
6. Synthesis of Poly(isobutylene-b-indene)

A charge of PIB-OH (0.55 g, $\overline{M}_n$=4,000, MWD = 1.87), indene (1 g) and CH_2Cl_2 (55 ml) was cooled to -50°C, and neat BCl_3 (0.1 ml) was introduced. After 30 minutes of stirring, prechilled methanol was added and the solution was poured in excess methanol. The product was filtered and dried under vacuum. Yield = 0.64 g, conversion of indene = 23%. The crude product was fractionated as outlined in Scheme III.

The n-hexane-soluble-MEK-insoluble fraction is PIB. The n-hexane-insoluble-CH_2Cl_2-soluble-dioxane-soluble fraction must be the block copolymer (CH_2Cl_2 is a solvent for PI, a bad solvent for PIB, whereas dioxane is a nonsolvent for PI and PIB is soluble in it). The fact that we did not find a fraction insoluble in dioxane indicates the absence of homopolyindene and thus quantitative blocking efficiency. The composition and

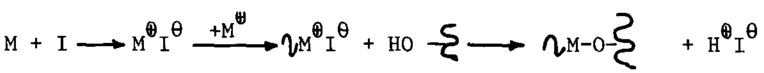
and molecular weight of block copolymer are indicated in Scheme III. The MWD of poly(isobutylene-b-indene) was unimodal and very narrow by GPC.

Scheme III. Fractionation of Poly(isobutylene-b-indene)

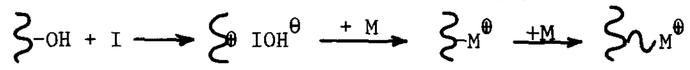


7. Mechanistic Considerations

Grafting may involve either a grafting-onto or grafting-from process. However, the data indicate predominant grafting-from. Thus grafting-onto would start with initiation and propagation characteristic of a homopolymerization; the growing chain would react with a nucleophilic OH group on the polymer and thus an ether bridge would arise:



In contrast, grafting-from would involve direct cationation of monomer by a macroion followed by propagation:



GPC studies of poly(isobutylene-g-indene), poly(styrene-g-isobutylene) and poly(isobutylene-b-indene) show monomodal distributions and ^{1}H and ^{13}C NMR spectra demonstrate the presence of both components. The ^{13}C NMR spectra of poly(isobutylene-g-indene) and poly(isobutylene-b-indene) shown in Figure 2 exhibit sharp peals at 32, 38.5 and 60 ppm corresponding to the three kinds of carbons (methyl, quaternary and methylene) in polyisobutylene, and diffuse peaks at about 35, 45, 53, 124, 128, 144-146 ppm corresponding to the carbons in the indanyl skeleton (methylene, methine and phenyl carbons).

IR analysis (Figure 3) did not show sharp absorption bands at ∿ 1,100 cm^{-1} characteristic of the ether group. According to these results, the reactions occurred by grafting and blocking from processes. These findings directly prove that ROH/BCl_3 combinations may function as efficient cationic initiating systems.

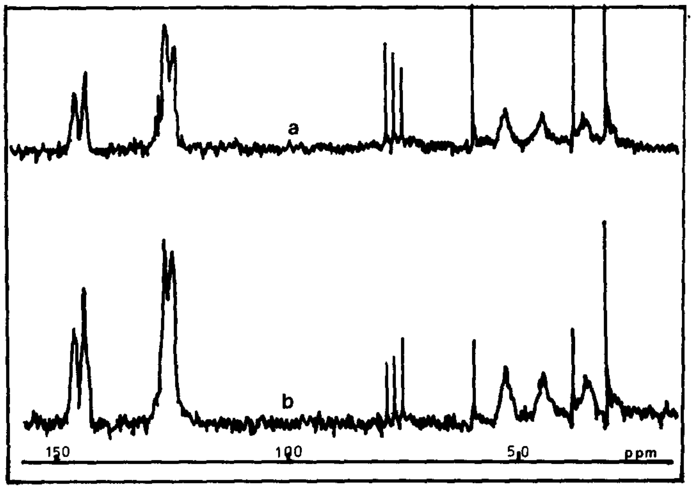


Figure 2: ^{13}C NMR Spectra of a) poly(isobutylene-g-indene) and b) poly(isobutylene-b-indene)

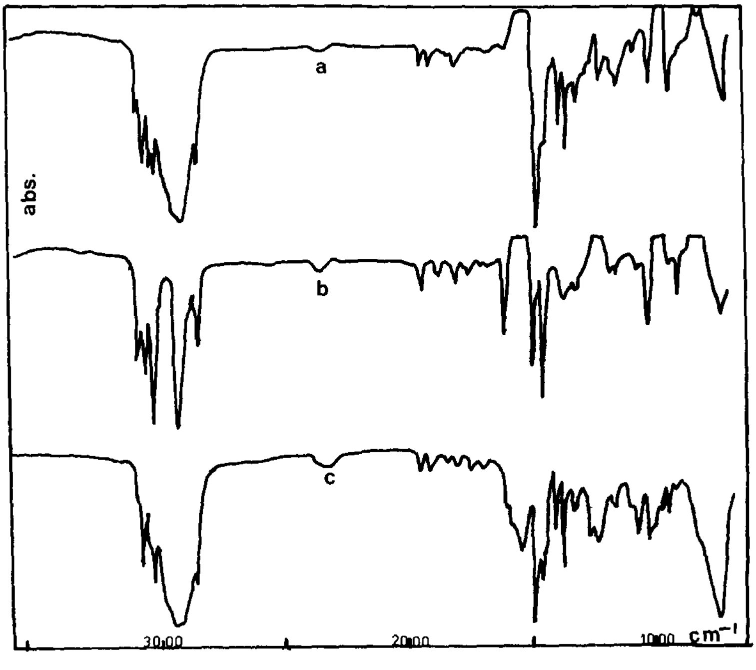


Figure 3: IR Spectra of a) poly(isobutylene-g-indene) b) poly(styrene-g-indene) and poly(isobutylene-b-indene)

Acknowledgement

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