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# Initiation of Cationic Polymerization with Alcohol/Lewis Acid Systems

## 3. Polymerization of Isobutylene

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## ABSTRACT

Alcohols in conjunction with $BCl_3$ have been found to be efficient initiating systems for the polymerization of isobutylene in $CH_2Cl_2$ solvent. The following alcohols exhibited high initiating activity: tert.-butanol, 1,1-diphenyl ethanol, 2-phenyl-2-propanol, benzhydrol. The organic moiety of the alcohol becomes the head-group of the polyisobutylene formed. The tail-group of the polymer is a tertiary chlorine most likely because termination is by chlorination by the $BCl_3OH^{\ominus}$ counter anion.

## INTRODUCTION

The discovery that tertiary alcohols $R^tOH$ in conjunction with $BCl_3$ are efficient cationic polymerization initiators prompted us to carry out systematic follow-up experimentation. The first parts of these studies have been described in the first two papers of this series[1,2] which concerned an examination of $R^tOH/BCl_3$ combinations in the absence of olefin, and model studies in which the "non-polymerizable monomer" 2,4,4-trimethyl-1-pentene was used in lieu of isobutylene. These prior investigations presented strong evidence that initiation with $R^tOH/BCl_3$ systems involves the following two events:

$$\underline{\text{ionization}}:\quad R^tOH + BCl_3 \rightleftharpoons R^{t\oplus}BCl_3OH^{\ominus}$$

$$\underline{\text{cationation}}:\quad R^{t\oplus} + C{=}C \longrightarrow R^t\text{-}C\text{-}C^{\oplus}$$

The present communication concerns polymerizations of isobutylene with various alcohols (i.e., 1,1-diphenyl ethanol $C\phi_2COH$, 2-phenyl-2-propanol $C_2\phi COH$, tert.-butanol $C_3COH$, and benzhydrol $H\phi_2COH$) $BCl_3$ combinations in $CH_2Cl_2$ solvent at -50°C under high vacuum conditions. According to spectroscopic ($^1H$ NMR and IR) and GPC analyses the head-group of polyisobutylenes produced by these initiating systems originates with the particular

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alcohol used, whereas the tail-group is a tertiary chlorine as expected for polyisobutylene produced by $BCl_3$[3].

## EXPERIMENTAL

Polymerizations were carried out under vacuum in an all glass (Pyrex) reactor with magnetic agitation. Chemicals were purified, dried and transferred under vacuum. Polymerizations were initiated by adding neat $BCl_3$ ($\sim$1 ml) to a mixture of isobutylene (11-12 ml), alcohol (7.5 m mole) and $CH_2Cl_2$ ($\sim$50 ml) at -50°C. The addition of neat $BCl_3$ to the charge results in very rapid polymerization accompanied by considerable heat generation. While the temperature profile has not been determined, we estimate from direct measurements in similar systems that the temperature maximum may not be far from 0°C. After 30 minutes prechilled methanol was introduced, then the polyisobutylene was precipitated in methanol and dried under vacuum. Control experiments in which $BCl_3$ was added to monomer/solvent charges (i.e., in the absence of alcohol) gave negligible polymer ($\sim$0.5%). Molecular weights and molecular weight distributions (MWD) were determined by GPC (THF solvent, Waters instrument, including a RI and UV detector and 5 Microstyragel columns; flow rate: 1 ml/min.). The calibration curve was prepared by narrow MWD polyisobutylenes. $^1H$ NMR (Varian T-60, $CCl_4$ solvent, TMS internal standard) and IR (Perkins-Elmer 521, $CC_4$ solutions) spectroscopy was used for end-group identification and quantitation.

## RESULTS AND DISCUSSION

Table 1 shows the conditions and results of isobutylene polymerizations initiated by alcohol/$BCl_3$ systems in $CH_2Cl_2$ at -50°C.

Figure 1 shows a representative GPC trace of a polyisobutylene (PIB) together with the Kennedy-Smith plot[4] obtained with the $C\phi_2COH/BCl_3$ system. The fact that the slope of the Kennedy-Smith plot is 1.05 indicates that the UV active aromatic groups are uniformly distributed over the whole PIB population.

Figure 2 shows $^1H$ NMR spectra of PIB's obtained in polymerization with various $ROH/BCl_3$ initiating systems. The resonance at 7.15 ppm indicates the presence of aromatic rings in the polymers. The spectrum obtained for the PIB prepared with $C_2\phi COH$ shows an additional resonance at 6.9 ppm which may be due to the presence of indane skelton formed in a side reaction[5,6]. Unsaturation or ether groups must be absent since resonances are absent in the 3-5 ppm range.

TABLE I

Polymerization of Isobutylene initiated by Different Alcohols in the Presence of $BCl_3$ in $CH_2Cl_2$ at -50°C.

| | Alcohol | M | i-$C_4H_8$ M | $BCl_3$ M | Conversion %(±5) | $\overline{M}_n$ | $\overline{M}_w$ | $\overline{M}_w/\overline{M}_n$ |
|---|---|---|---|---|---|---|---|---|
| 1 | $C_3$COH | 0.13 | 1.8 | 0.18 | 79 | 38,500 | 73,300 | 1.85 |
| 2 | $C_2$ØCOH | 0.15 | 1.8 | 0.18 | >90 | 3,650 | 6,300 | 1.74 |
| 3 | CØ$_2$COH | 0.13 | 1.9 | 0.19 | >90 | 3,600 | 6,750 | 1.87 |
| 3a | CØ$_2$COH<br>D<u>t</u>BP* | 0.12<br>0.9 | 1.9 | 0.17 | >90 | 2,600 | 4,350 | 1.67 |
| 4 | HØ$_2$COH | 1.13 | 2.0 | 0.22 | 43 | 4,000 | 6,800 | 1.70 |

*D<u>t</u>BP = 2,6-di-tert.-butylpyridine

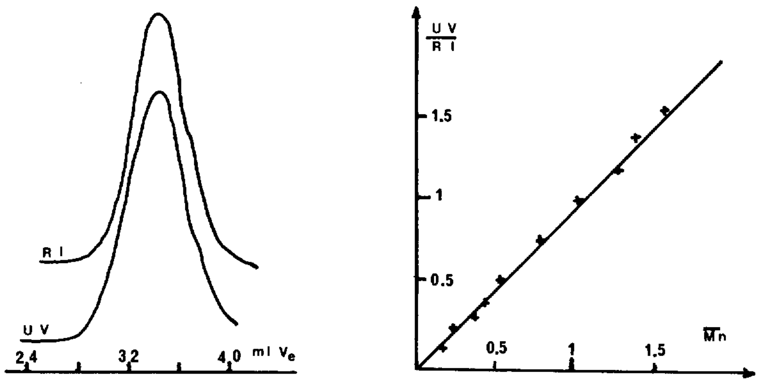


Figure 1:

a RI and UV traces of a polyisobutylene sample obtained with CØ$_2$COH/-$BCl_3$

b Kennedy-Smith plot for PIB obtained with CØ$_2$COH/$BCl_3$

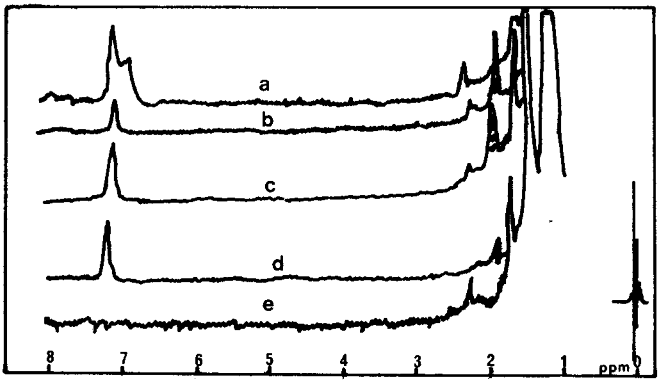


Figure 2: $^1$H NMR spectra of polyisobutylene samples obtained with ROH/BCl$_3$ initiating systems: ROH a) C$_2$ØCOH, b) CØ$_2$COH, c) CØ$_2$COH + DtBP, d) HØ$_2$COH, e) C$_3$COH

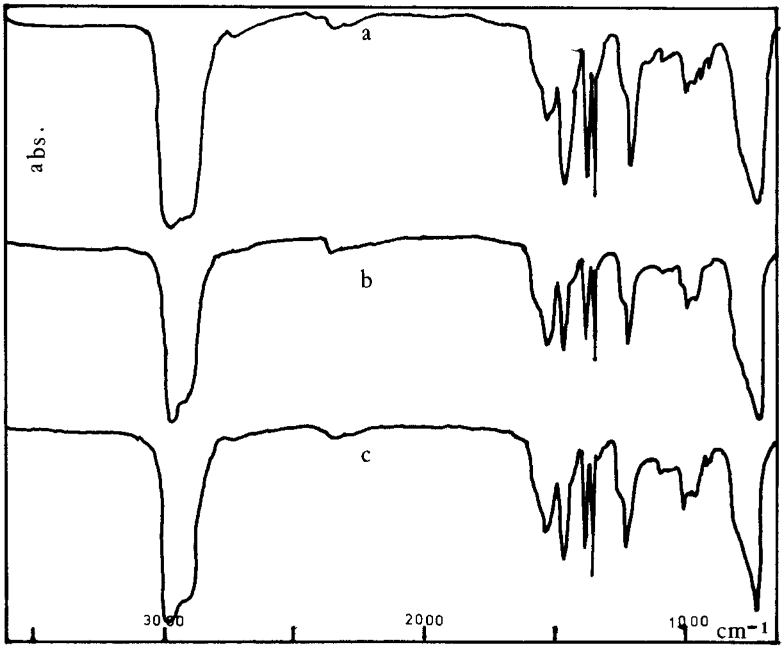
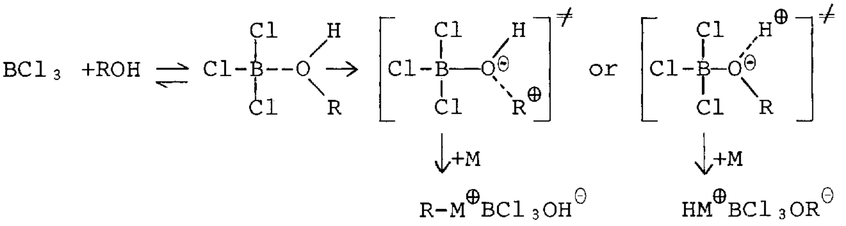


Figure 3: IR spectra of polyisobutylenes obtained by different ROH/BCl$_3$ systems: a) C$_2$ØCOH, b) C$_3$COH, c) CØ$_2$COH

According to IR spectra (Figures 3 a-c) PIB's produced by $ROH/BCl_3$ initiating systems do not contain OH groups (absence of peaks in the 3,300 - 3,700 $cm^{-1}$ region), double bonds (absence of peaks in the 1,600 - 1,700 $cm^{-1}$ region) or ether function (absence of peak at $\sim$1,100 $cm^{-1}$). The amount of aromatic groups is too low to appear in the characteristic 3,000-3,100 $cm^{-1}$ range.

Conversions are close to 100% with the tertiary aromatic alcohols $C_2\emptyset COH$ and $C\emptyset_2COH$ (in the presence or absence of DtBP); however, they reach $\sim$79% with the tertiary aliphatic alcohol $C_3COH$ and $\sim$43% with the secondary aromatic alcohol $H\emptyset_2COH$. These results may be accounted for by considering the transition states involved in initiation:



$ROH/BCl_3$ systems may produce $H^{\oplus}BCl_3OR^{\ominus}$ or $R^{\oplus}BCl_3OR^{\ominus}$. It is postulated that the nature of the R group will determine the direction of this process: In the presence of tertiary alcohols the O-R bond will prefeentially break (relatively weak O-R bond, stable carbenium ion); whereas with primary alcohols the O-H bond is expected to cleave (relatively strong O-R bond, unstable carbenium ion), although this latter process may be much less efficient than the former one (relatively strong O-H bond). Thus the character of the alcohol, i.e., whether it is aromatic or aliphatic, tertiary or secondary or primary, will determine the efficiency of the $ROH/BCl_3$ initiating system. According to our results the tertiary aromatic cation $C_2\emptyset C^{\oplus}$ and $C\emptyset_2C^{\oplus}$ are most effective, the tertiary aliphatic $C_3C^{\oplus}$ less so, and the secondary aromatic $H\emptyset_2C^{\oplus}$ even less.

The molecular weights obtained in these experiments have questionable significance, first because the exact temperature of polymerization is unknown (see experimental), second because of the very high conversions attained. The MWD data, however, are meaningful: It is of interest that $\overline{M}_w/\overline{M}_n$'s are invariably less than 2 indicating a transferless termination-controlled system[3].

An experiment has been carried out with the

$C\phi_2COH/BCl_3$ initiating system in the presence of an extremely large quantity (0.9 M) of the powerful proton trap 2,6-di-*tert*.-butylpyridine (D*t*BP). A comparison of the results of experiments 3 and 3a in Table I shows that D*t*BP does not affect the polymerizations involved which suggests that initiation by free proton cannot occur in these systems. D*t*BP would not interfere with initiation by tertiary carbenium ions. These experiments have been prompted by a large body of information collected on the effect of D*t*BP on cationic olefin polymerizations[3,5,6].

The presence of tertiary chlorine tail groups was demonstrated by a well established quantitative dehydrochlorination method.[7,8] Thus, we treated a PIB prepared by the $C\phi_2COH/BCl_3$ system with *t*-OBuK in refluxing THF solution for 24 hours. The $^1H$-NMR trace of the product shown in Figure 4 clearly indicates the presence of the external olefin-$C(CH_3)=CH_2$ (resonance at 4.7 and 4.9 ppm) and the internal olefin-$CH=C(CH_3)_2$ (resonance at 5.1 ppm). The internal olefin arose most likely because of moisture contamination during dehydrochlorination (moisture hydrolyses *t*OBuK, and the *t*-BuOH formed *in situ* gives rise to internal unsaturation; in the absence of this contaminant dehydrochlorination is regiospecific and exo olefin is formed exclusively).

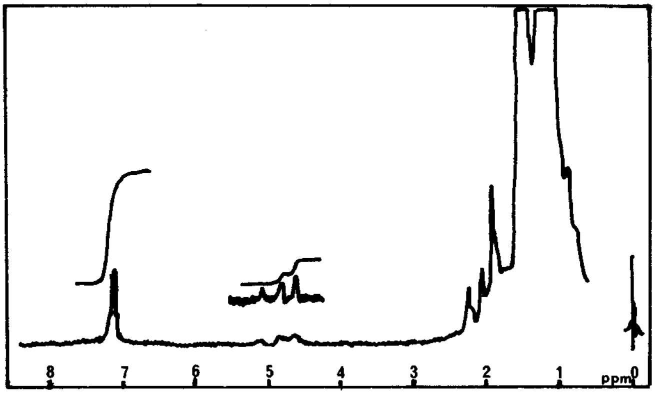


Figure 4: $^1H$ NMR spectrum of a polyisobutylene sample obtained with the $C\phi_2COH/BCl_3$ system, after dehydrochlorination by refluxing in a *t*-OBuK-THF solution.

The ratio of the number of phenyl protons over those of external olefinic protons, should give 10/2 = 5.

Integration of these resonances in Figure 4 yields 4.8, a datum which, considering that we have neglected the protons associated with the internal double bond, indicates quantitative dehydrochlorination. On the basis of these data the number of aromatic head groups and tert-chlorine tail groups is essentially identical.

Mechanistic considerations

In view of the above evidences and considerable previous experience with cationic polymerizations induced by $BCl_3$ coinitiator[3,6,7,8] we propose the following mechanism for isobutylene polymerizations with $R^tOH/BCl_3$ initiating system ($R^t$=tertiary group):

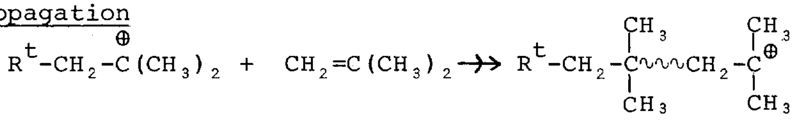
Ionization

$$R^tOH + BCl_3 \rightleftharpoons R^{t\oplus}BCl_3OH^{\ominus}$$

Cationation

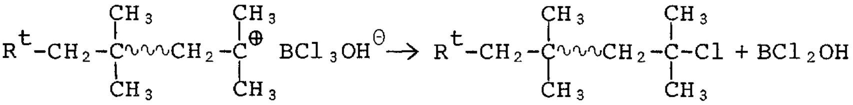
$$R^{t\oplus} + CH_2{=}C(CH_3)_2 \longrightarrow R^t{-}CH_2{-}\overset{\oplus}{C}(CH_3)_2$$

Propagation



$$R^t{-}CH_2{-}\overset{\oplus}{C}(CH_3)_2 + CH_2{=}C(CH_3)_2 \twoheadrightarrow R^t{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C}}{\sim\sim\sim}CH_2{-}\underset{CH_3}{\overset{CH_3}{C^{\oplus}}}$$

Termination



$$R^t{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C}}{\sim\sim\sim}CH_2{-}\underset{CH_3}{\overset{CH_3}{C^{\oplus}}}\ BCl_3OH^{\ominus} \longrightarrow R^t{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C}}{\sim\sim\sim}CH_2{-}\underset{CH_3}{\overset{CH_3}{C}}{-}Cl + BCl_2OH$$

The nature of $R^t$ strongly affects the polymerization: Relatively stable carbocations arising from the alcohol cationogen are most efficient polymerization initiators; however even tertiary aliphatic ($C_3COH$) or secondary aromatic ($H\phi_2COH$) alcohols are active.

Chain transfer to monomer is evidently unimportant in these systems. The absence of chain transfer to monomer in $BCl_3$ coinitiated isobutylene polymerizations has repeatedly been demonstrated[3,4,8].

The demonstration of cationic olefin polymerization by alcohols is a significant breakthrough in the field of cationic polymerizations. First of all, this discovery opens new avenues toward novel initiating systems operating by controlled initiation. Before this development, controlled initiation was possible only with active (allylic, benzylic, tertiary) halides and elementary halogen[3]. This discovery is also the starting point for the synthesis of new block and graft copolymers which are the subject of the next paper in this series of publications.

## ACKNOWLEDGEMENTS

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