Polymer Bulletin 6, 47–54 (1981)

Polymer Bulletin

Initiation of Cationic Polymerizations with Alcohol/Lewis Acid Systems

1. The Reaction Between Alcohols and Boron Trichloride

Hung Anh Nguyen* and Joseph P. Kennedy

Institute of Polymer Science, University of Akron, Akron, OH 44325, USA

Tertiary alcohols (both aromatic and aliphatic) in conjunction with BCl_3 have been found to be efficient initiating systems for the polymerization of isobutylene. The reactions between the tertiary alcohols triphenylmethanol, 1,1-diphenylethanol, 2-phenyl-2-propanol and tert.-butanol, and the secondary alcohol benzhydrol, with BCl_3 in CH_2Cl_2 at -50°C using high vacuum techniques have been studied. According to ^1H NMR and IR analyses, these alcohols yield the corresponding chlorides. The reaction most likely proceeds via: $ROH + BCl_3 \longrightarrow [R^{\oplus}\ BCl_3OH^{\ominus}] \longrightarrow RCl + BCl_2OH$. In the presence of excess BCl_3 a series of complex subsequent reactions ensue.

Introduction

Recently we have discovered that tertiary alcohols, both aromatic and aliphatic, in conjunction with BCl_3 are efficient initiating systems for the cationic polymerization of olefins, e.g., isobutylene. As a consequence of this discovery, we have started systematic experimentation, the aim of which is to determine the scope of possibilities offered by this new initiating principle and to elucidate the fundamentals of reactions between alcohols and Lewis acid in general, and BCl_3 in particular.

This paper, the first of a series of publications dealing with cationic polymerizations initiated by ROH/BCl_3 combinations, concerns reactions between the tertiary alcohols triphenyl methanol (ϕ_3COH), 1,1-diphenyl ethanol ($C\phi_2COH$), 2-phenyl-2-propanol ($C_2\phi COH$), and tert.-butanol (C_3COH), and the secondary alcohol benzhydrol ($H\phi_2COH$), with BCl_3 in CH_2Cl_2 at -50°C under high vacuum conditions. All the reactions seem to involve ionization of alcohols by BCl_3, followed by chlorination of the carbenium ion intermediate by the $BCl_3OH^{\ominus}$ counter anion.

Experimental

Chemicals were purified and dried by the use of high vacuum techniques[1]. Reactions were carried out under vacuum in an all glass (Pyrex) reactor and by the use of magnetic agitation. Alcohol solutions (0.1 M) in CH_2Cl_2 (50 ml) were cooled to -50°C and neat BCl_3 (0.6-0.75 ml, 0.15-0.18 M) was added. After one minute of reaction, CH_2Cl_2 and excess BCl_3 were removed by vacuum distillation (this operation did not exceed 25 minutes). CCl_4 was added to samples intended for ^1H NMR (Varian-T-60, TMS internal standard) and IR (Perkins-Elmer 521)

---

* Visiting Scientist; Permanent Address: Laboratoire de Synthese, Macromoleculaire Associe au CNRS, Universite Pierre et Marie Curie, 12 Rue Cuvier, 75005 Paris, France

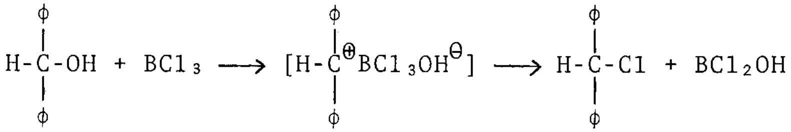
0170-0839/81/0006/0047/$01.60

analyses. The experiment with $C\phi_2COH$ was carried out by storing the system for three days at room temperature.

Results and Discussion

The reaction between BCl_3 and a series of tertiary alcohols and a secondary alcohol have been investigated by mixing these ingredients under conditions similar to those used in polymerization experiments, except in the absence of monomer, and determining ^1H NMR and IR spectra of the products.

Figure 1 shows the ^1H NMR spectra of $H\phi_2COH$ and the product of the $H\phi_2COH + BCl_3$ reaction together with the assignments (see also in Table I). According to this evidence, the reaction between $H\phi_2COH$ and BCl_3 leads exclusively to the chlorinated product and can be formulated as follows:



$$H-\overset{\phi}{\underset{\phi}{C}}-OH + BCl_3 \longrightarrow [H-\overset{\phi}{\underset{\phi}{C}}{}^{\oplus}BCl_3OH^{\ominus}] \longrightarrow H-\overset{\phi}{\underset{\phi}{C}}-Cl + BCl_2OH$$

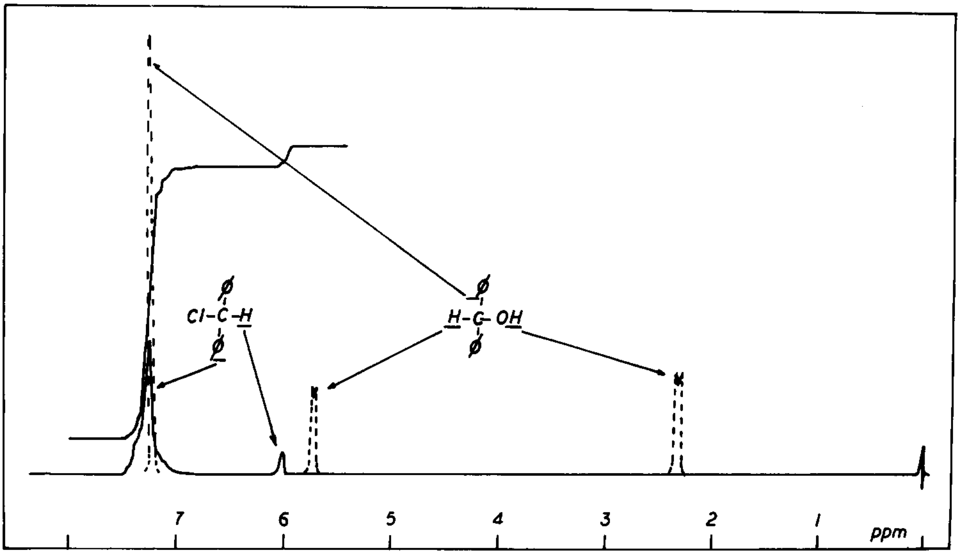


Figure 1: ^1H NMR spectrum of the benzhydrol + boron trichloride system [Spectrum of benhydrol (dashed line) is from (3)].

The reaction is quantitative and the final product is benzhydryl chloride or chlorodiphenylmethane. Comparison of IR spectra[2] of the starting material and that of the product helped to substantiate this conclusion (disappearance of ν_{Cl} at 700 cm^{-1}).

Figure 2 shows the ^1H NMR spectrum of the $C_2\phi COH + BCl_3$

TABLE I

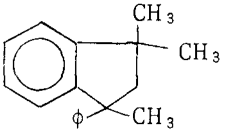
Experimental Conditions Used and Products Obtained Together With ^1H NMR Chemical Shifts for

$ROH + BCl_3$ Reactions in CH_2Cl_2 at -50°C

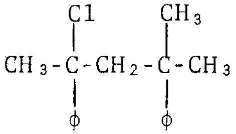
Alcohol		BCl_3	Time	^1H NMR*				Products	^1H NMR				YIELD		
Symbol	[C] M	[C] M	Min.	δ_H	δ_{CH_3}	δ_ϕ	δ_{OH}		δ_H	δ_{CH_2}	δ_{CH_3}	δ_ϕ	Overall %	Chlorination %	Others %
$H\phi_2COH$	0.1	0.16	1	5.7	-	7.2	2.4	benzhydryl chloride	6	-	-	7.35	100	100	-
C_3COH	0.1	0.17	1	-	1.3	-	1.15	tert-butyl chloride	-	-	1.6	-	100	100	-
$C_2\phi COH$	0.1	0.18	1	-	1.6	7.2 7.5	1.75	cumyl chloride	-	-	1.95	7.2	70	60	-
								2-chloro-2,4,diphenyl-4-methylpentane	-	2.2	1.05	7.2		8	-
								1-phenyl-1,3,3-tri-methylindane	-	2.8	1.3	7		-	1.9
								α-methylstyrene	-	5.1	2	7.2		-	0.1
$C\phi_2COH$	0.1	0.17	4320	-	1.9	7.1 7.4	3.45	1-methyl-1,3,3-tri-phenylindane	-	3.2	1.5	7.1 6.9	100	-	99.6
								1-chloro-1,1,3,3-tetraphenylbutane						0.4	
ϕ_3COH	0.1	0.18	1	-	-	7.3	4.8	triphenylmethyl chloride	-	-	-	7.2	100	100	-

*Data from ref. (3)

system. A mixture of several products is present. Comparison of this spectrum with spectra of authentic compounds[3] suggests the presence of the following products (see also in Table I):

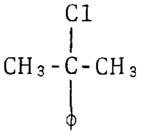


1-phenyl-1,3,3-trimethylindane



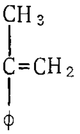
$CH_3-\overset{Cl}{\underset{\phi}{C}}-CH_2-\overset{CH_3}{\underset{\phi}{C}}-CH_3$

1-chloro-2,4-diphenyl-4-methylpentane



$CH_3-\overset{Cl}{\underset{\phi}{C}}-CH_3$

2-chloro-2-phenylpropane



$\phi-\overset{CH_3}{C}=CH_2$

α-methylstyrene

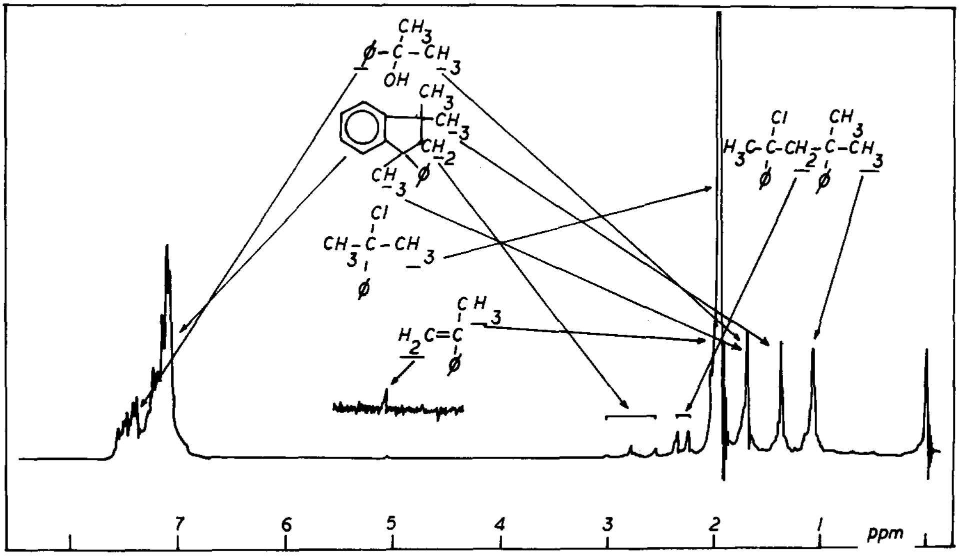
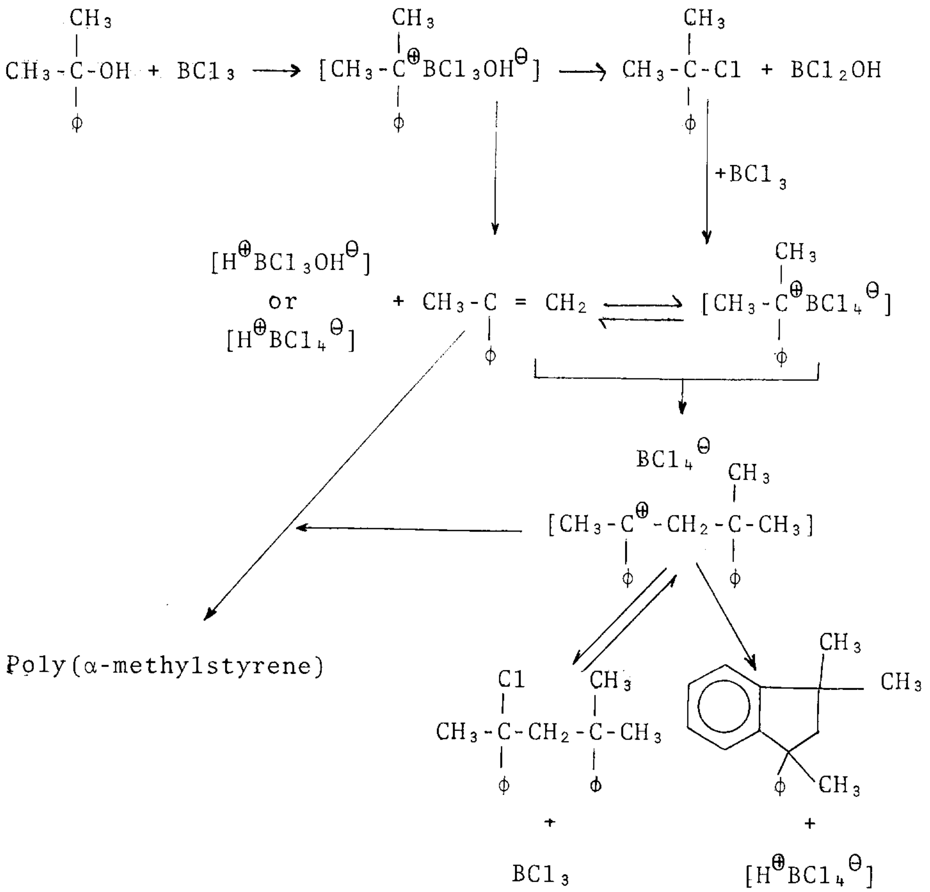


Figure 2: ^1H NMR spectrum of the 2-phenyl-2-propanol + boron trichloride system.

The presence of unreacted $C_2\phi COH$ shows that the $C_2\phi COH$ + BCl_3 reaction is not quantative; the overall conversion is ∿70%.

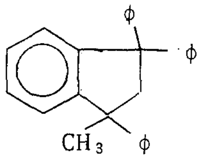
Scheme I outlines a possible mechanism that explains the formation of the four products:

Scheme I. Possible reactions between $C_2\phi COH$ + BCl_3.

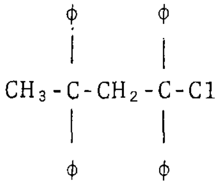


$C_2\phi COH$ is ionized by BCl_3 and the intermediate ion pair collapses to 2-chloro-2-phenylpropane (cumyl chloride) and BCl_2OH. In the presence of excess BCl_3, cumyl chloride readily produces the cumyl cation (+ $BCl_4^{\ominus}$) which may lose a proton and give rise to α-methylstyrene. The latter plus the cumyl cation may: a) collapse by chlorination (reversible) to 2-chloro-2,4-diphenyl-4-methylpentane, b) lead to 1-phenyl-1,3,3-trimethylindane by intramolecular cyclization, or c) lead to poly-(α-methylstyrene) with α-methylstyrene formed in situ. The lack of evidence for the presence of poly(α-methylstyrene) among reaction products indicate that the last alternative can be neglected.

Figure 3 shows the spectrum obtained for the $C\phi_2COH$ + BCl_3 reaction after one minute at -50°C and three days at room temperature. Comparison with authentic compounds indicates a mixture of two products:



1-methyl-1,3,3-
triphenylindane



$$CH_3\text{-}\underset{\phi}{\overset{\phi}{C}}\text{-}CH_2\text{-}\underset{\phi}{\overset{\phi}{C}}\text{-}Cl$$

1-chloro-1,1,3,3-
tetraphenylbutane

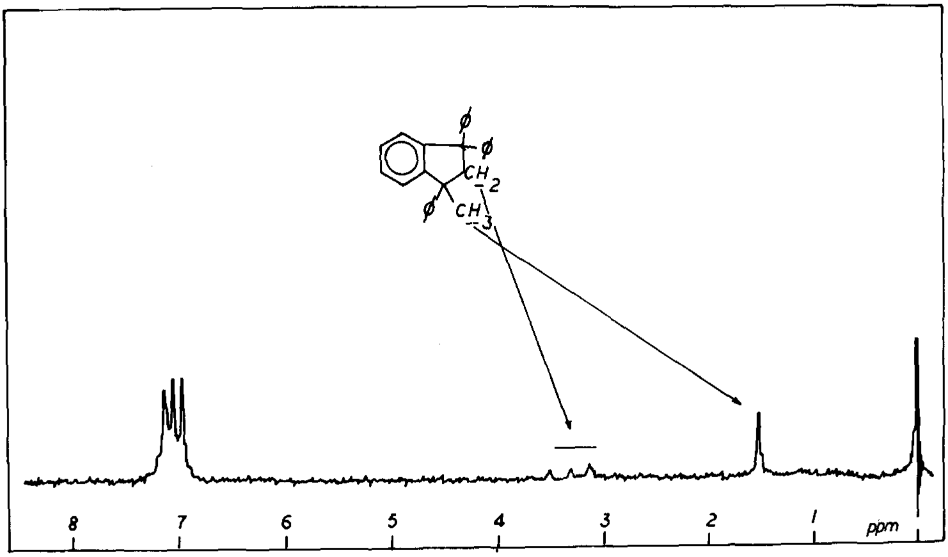


Figure 3: ^{1}H NMR spectrum of the 1,1-diphenylethanol + boron trichloride system.

The main product is the indane derivative and the presence of the linear product can only be detected by IR (presence of ν_{Cl} at 700 cm^{-1}). Intermediates, i.e., 1-chloro-1,1-diphenylethane or 1,1-diphenylethylene, are absent.

Figure 4 shows the ^{1}H NMR spectrum of the product obtained in the $\phi_3COH + BCl_3$ experiment. Evidently the only product is triphenylmethyl chloride:

$$\phi_3COH + BCl_3 \rightleftharpoons [\phi_3C^{\oplus}BCl_3OH^{\ominus}] \longrightarrow \phi_3CCl + BCl_2OH$$

In the absence of a β hydrogen atom in respect to the carbenium center side reactions due to proton elimination cannot occur. The carbenium ion is relatively stable even for three hours at room temperature and the yellow-brown color of the solution disappears only slowly indicating that the ion pair collapses to the corresponding chloride.

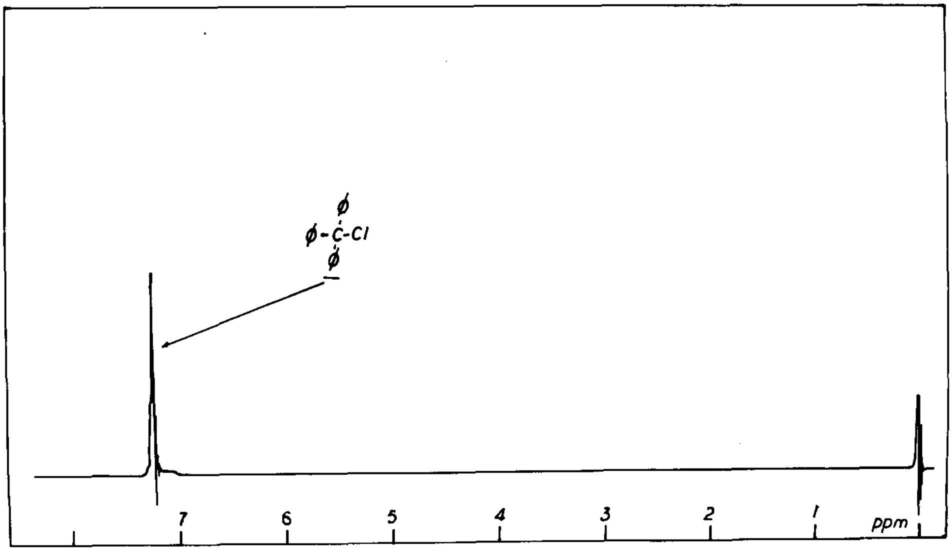


Figure 4: ^1H NMR spectrum of the triphenylmethanol + boron trichloride system.

Figure 5 shows the ^1H NMR spectrum obtained in the C_3COH + BCl_3 experiment. According to this evidence (singlet at 1.6 ppm characteristic of protons in tert.-butyl chloride), BCl_3 ionizes this aliphatic alcohol and the intermediate ion pair collapses before proton loss (absence of isobutylene) can occur:

$$C_3COH + BCl_3 \longrightarrow [C_3C^{\oplus}BCl_3OH^{\ominus}] \longrightarrow C_3CCl + BCl_2OH$$

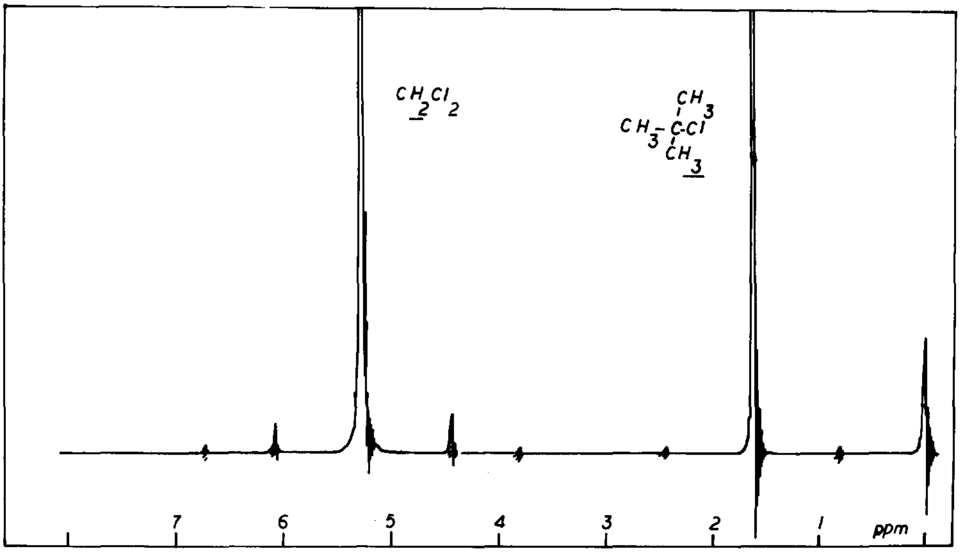


Figure 5: ^1H NMR spectrum of tert.-butanol + boron trichloride system.

These results are in agreement with earlier observations by others[4] according to which BCl_3 does not ionize C_3CCl or other tertiary aliphatic chlorides[5,6] and the C_3CCl/BCl_3 combination does not initiate the polymerization of olefins.

It is most surprising that BCl_3 readily ionizes tertiary aliphatic alcohols but is virtually inert in conjunction with tertiary aliphatic chlorides. Systematic research with tertiary aliphatic alcohol/BCl_3 systems has shown[7] that such combinations are efficient initiators of olefin polymerizations whereas tertiary aliphatic chlorine/BCl_3 systems are not[5,6].

Since the experiments reported in this paper have been carried out in the absence of moisture (high vacuum techniques), ionization of these alcohols cannot proceed via protonation (i.e., $R^tOH + "H^\oplus" \longrightarrow R^t\text{-}OH_2^\oplus \longrightarrow R^{t\oplus} + H_2O$) but must involve ionization via $R^tOH + BCl_3 \longrightarrow R^{t\oplus}BCL_3OH^\ominus \longrightarrow R^tCl + BCl_2OH$. The predominance of tertiary chlorides among the reaction products indicates that the collapse of the ion pair is extremely rapid. The reason for these unusual observations may be at least in part due to the very low nucleophylicity of the $BCl_3OH^\ominus$ counter anion (high Lewis acidity of BCl_3) combined with its surprisingly low stability.

Subsequent publications in this series will illustrate how this difference between tertiary alcohols and chlorides can be exploited for the synthesis of new polymers.

References

1. Cheradame, H.; Vairon, J. P. and Sigwalt, P., Europ. Polym. J., 4, 267 (1968).
2. The Aldrich Library of IR Spectra; Pouchert, Aldrich Chem. Co. (1975).
3. The Aldrich Library of NMR Spectra; Pouchert, C. J. and Campbell, J. C., Aldrich Chem. Co. (1974).
4. Cheradame, H. and Nguyen, H. A., unpublished results.
5. Kennedy, J. P.; Huang, S. Y. and Feinberg, S. C., J. Polym. Sci., Polym. Chem., Ed., 15, 2801 (1977).
6. Kennedy, J. P.; Hyang, S. Y. and Feinberg, S. C., J. Polym. Sci., Polym. Chem., Ed., 15, 2869 (1977).
7. Nguyen, H. A. and Kennedy, J. P., in press.

Accepted October 28, 1981