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In-situ High Resolution NMR Investigation on Polymerization Mechanism. II. Comparison between $BF_3 \cdot Bu_2O$ and $Cl\text{-}N_2PF_6$ as Catalysts in Homopolymerization of Trioxane and Copolymerization with Ethylene Oxide

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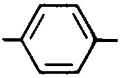
In-situ High Resolution NMR Investigation on Polymerization Mechanism. II. Comparison between $BF_3{\cdot}Bu_2O$ and Cl  N_2PF_6 as Catalysts in Homopolymerization of Trioxane and Copolymerization with Ethylene Oxide

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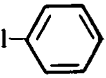
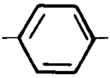
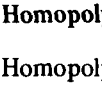
SUMMARY

A comparison of $BF_3{\cdot}Bu_2O$ and Cl  $-N_2PF_6$ as catalysts for cationic homopolymerization and copolymerization of trioxane has been made by employing high resolution nuclear magnetic resonance techniques. While no substantial difference was detected for the homopolymerization, two important differences were observed for the copolymerization with ethylene oxide; viz., 1) with Cl  $-N_2PF_6$ there is a lower build-up of formaldehyde concentration; 2) with Cl  $-N_2PF_6$, a lesser amount of cyclic compounds containing ethylene oxide units is formed (e.g., 1,3-dioxolane). Both observations suggest that depolymerization occurs to a lesser extent with the Cl  $-N_2PF_6$ catalyst.

INTRODUCTION

In our previous investigation [1] high resolution nuclear magnetic resonance spectroscopy was employed to elucidate the mechanism of $BF_3 \cdot Bu_2O$-initiated trioxane polymerization and copolymerization. Reactions involving changes in proton magnetic resonance which are not conveniently ascertained by other analytical means were shown. Based on results in polymerization kinetics, the molecular weight difference resulting from the catalyst was attributed primarily to less inherent chain transfer during propagation. It was the purpose of this investigation to elucidate, by high resolution NMR techniques, some other side reactions which might lead to a lower rate of polymerization and/or lower molecular weight of polymers. A comparison between $BF_3 \cdot Bu_2O$ and Cl––N_2PF_6-catalyzed polymerization of trioxane and its copolymerization with ethylene oxide is shown.

EXPERIMENTAL RESULTS AND DISCUSSION

The experimental procedures used in this study have been previously described [1]. p-Chlorophenyldiazonium hexafluorophosphate (Cl––N_2PF_6) was purchased from Ozark Mahoning Company as Phosfluorogen A and was recrystallized by a procedure described previously [2]. A mixture of water and methanol was used. White glistening plates were obtained; mp 152-154 (dec).

I. Homopolymerization

Homopolymerization of trioxane at 65 ± 1°C was investigated by employing four different Cl––N_2PF_6 concentrations (2.23×10^{-3}, 5.87×10^{-3}, 12.0×10^{-3}, and 16.5×10^{-3} mole %). Figure 1 shows representative NMR spectra as the polymerization proceeded. Similar to what was observed for the $BF_3 \cdot Bu_2O$ catalyzed homopolymerization [1], a new proton signal, attributed to the soluble, low molecular weight,

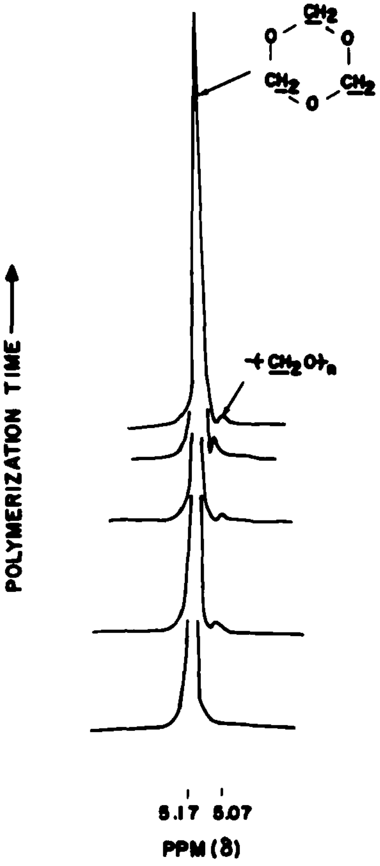
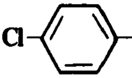
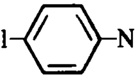


Fig. 1. Homopolymerization of trioxane in bulk at 65°C. Spectrum amp.: 0.16.

open chain polymers, appeared at 5.07 ppm (vs TMS) beside the sharp trioxane peak at 5.17 ppm. Again this signal reached a maximum concentration which remained relatively constant regardless of the catalyst concentration until the polymer precipitated from solution. An increase in catalyst concentration only increased the rate at which the steady-state concentration was attained. No formaldehyde was detected.

II. Copolymerization with Ethylene Oxide

1. Cl––N$_2$PF$_6$ as Catalyst. The effect of ethylene oxide comonomer concentration was investigated at 65 ± 1°C employing 6 X 10^{-3} mole % Cl––N_2PF_6. Figures 2-5 show the NMR spectra of copolymerization of trioxane with 1.3, 3.3, 7.2, and 10 mole % ethylene oxide, respectively. In the copolymerizations depicted in Figures 2-5 the following observations were noted: 1) Opening of the ethylene oxide ring occurred immediately upon addition of catalyst; 2) solidification occurred immediately after the disappearence of ethylene oxide; 3) "ingrowth" of new proton signals appeared. The new proton signals and their assignments are summarized in Table 1. The concentration of formaldehyde increased progressively, reaching a maximum immediately prior to precipitation of the polymer. The formaldehyde concentration was found to increase as the ethylene oxide comonomer concentration was increased. A relatively high formaldehyde build-up was observed at high ethylene oxide concentrations, viz., 13 and 18 mole % formaldehyde for 7.2 and 10 mole % ethylene oxide comonomer, respectively.

To gain more insight into the ethylene oxide distribution in the copolymers and to make more definite assignment of the proton resonance peak for

$$\left(CH_2-CH_2-O\right)_{1 \leqq n \leqq 3}$$

at 3.60-4.0 ppm (vs TMS), the resulting copolymers obtained subsequent to solidification were analyzed by a previously described method of acid hydrolysis [2]. Some results are presented in Table 2.

From these results it can be seen that the ethylene oxide is incorporated into the copolymer primarily as mono units, with lesser concentrations of dimer and trimer units. Based on these separate results and the NMR observations in Figs. 2-5, additional assignments were made; viz., the proton resonance of the monoethylene oxide unit in the linear chain occurs at 3.83 ppm (vs TMS). This peak becomes especially prominant immediately before formation of solid polymer, as shown in Figs. 2-5. The resonance peaks occuring at higher fields in this 3.6-4.0 ppm range can be assigned to dimer and trimer ethylene oxide units. It might be noted that the $C^{13}H$ resonance peak also appears in this chemical shift range as reported in our previous communication [1]. The resonance peak occurring at 3.90 ppm (vs TMS) has been assigned to ethylene oxide protons in nonstrained cyclic configurations; i.e., 1,3-dioxolane and/or larger member

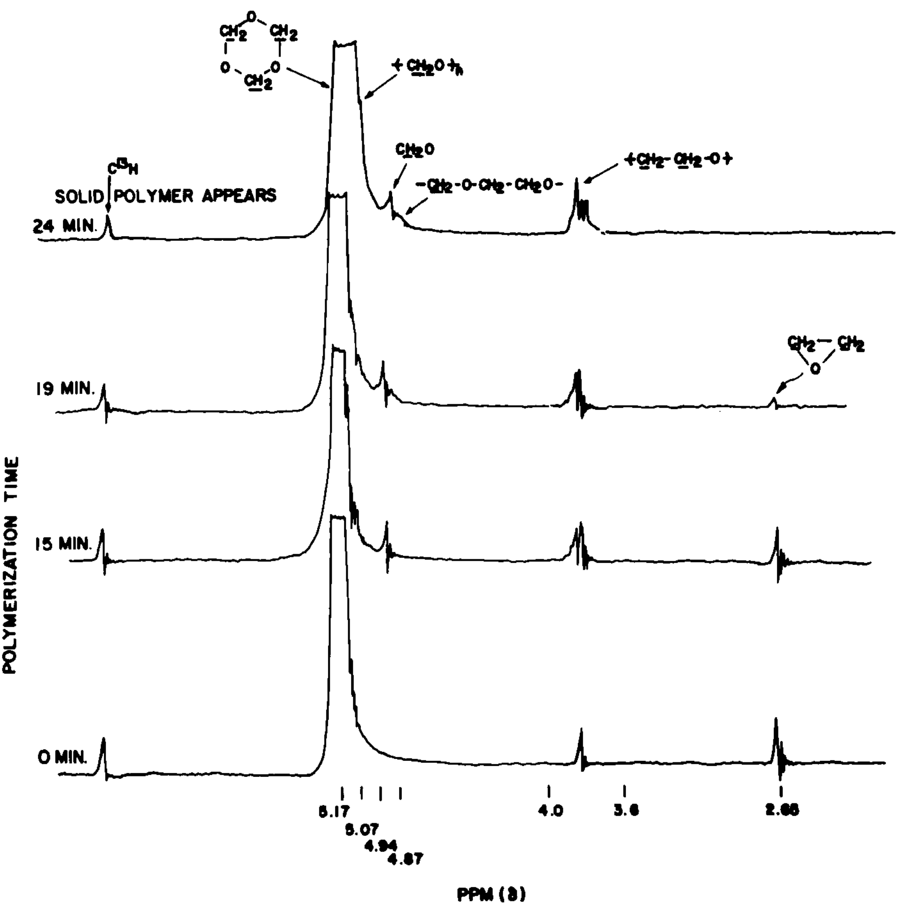
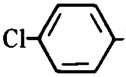


Fig. 2. Copolymerization of trioxane with 1.3 mole % ethylene oxide in bulk at 65°C.  $Cl-C_6H_4-N_2PF_6$: 6.0 X 10^{-3} mole %. Spectrum amp.: 2.0.

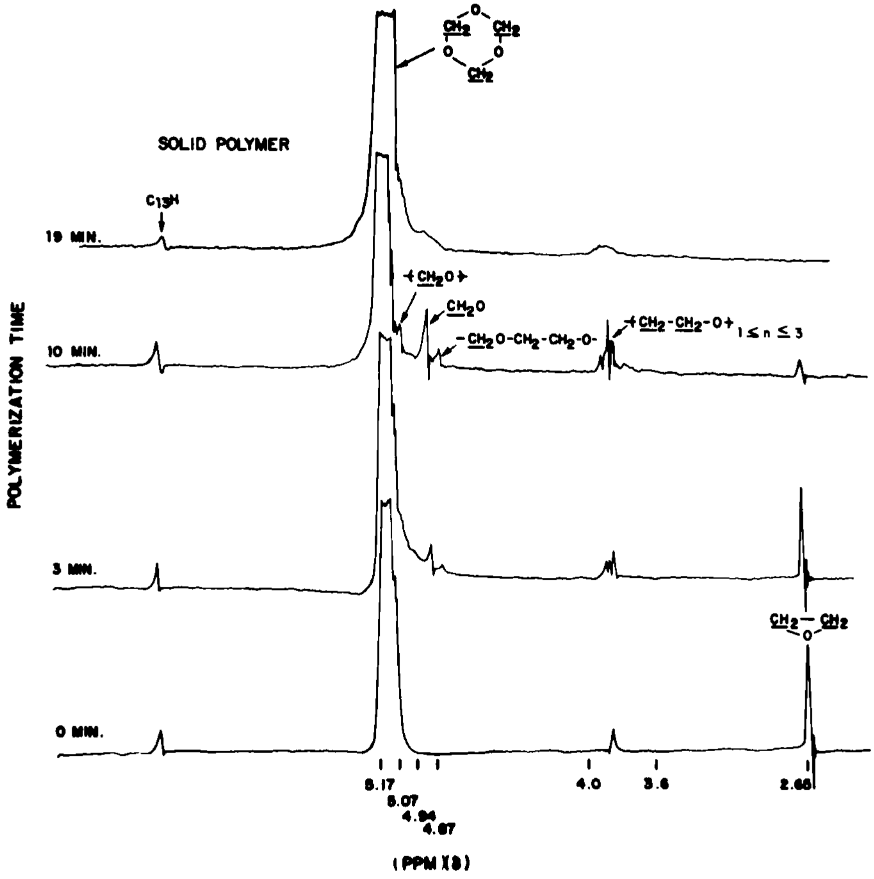
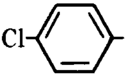


Fig. 3. Copolymerization of trioxane with 3.3 mole % ethylene oxide in bulk at 65°C. ClN_2PF_6: 6.0 X 10^{-3} mole %. Spectrum amp.: 2.0.

rings. It might be noted that the intensity of this resonance peak increases at higher ethelene oxide concentrations. The presence of cyclic compounds in this copplymerization system has been previously reported [3, 4].

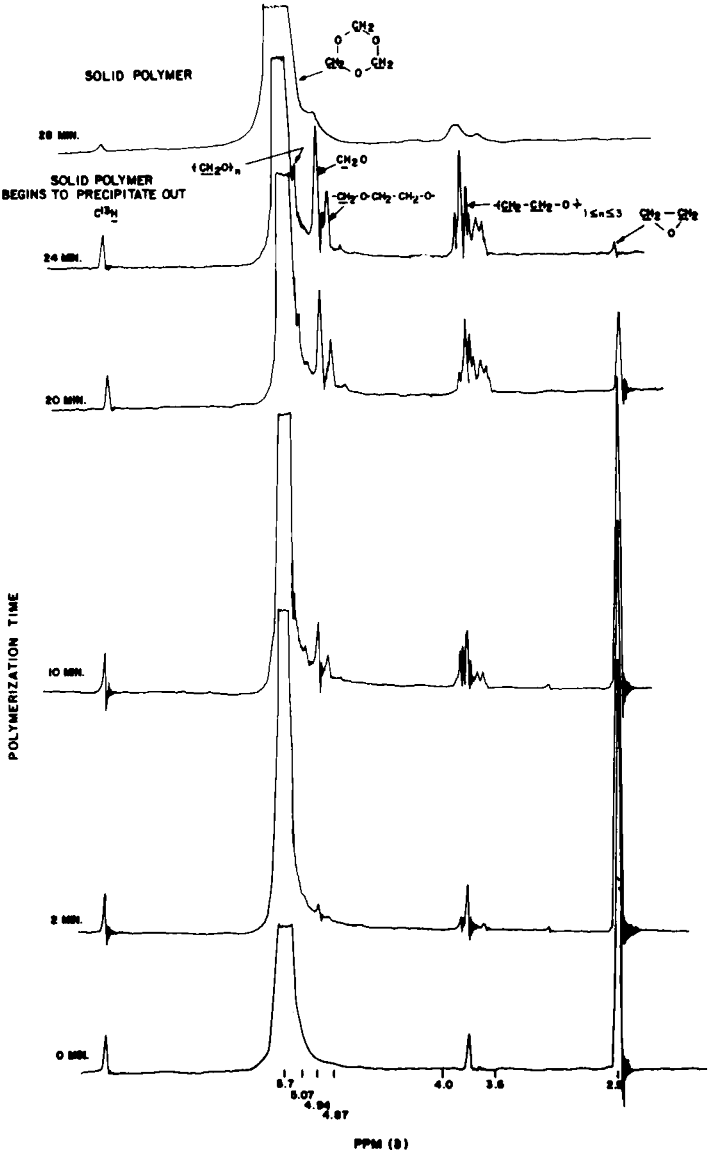
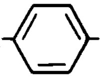


Fig. 4. Copolymerization of trioxane with 7.2 mole % ethylene oxide in bulk at 65°C. ClN_2PF_6: 6.0 X 10^{-3} mole %. Spectrum amp.: 4.0.

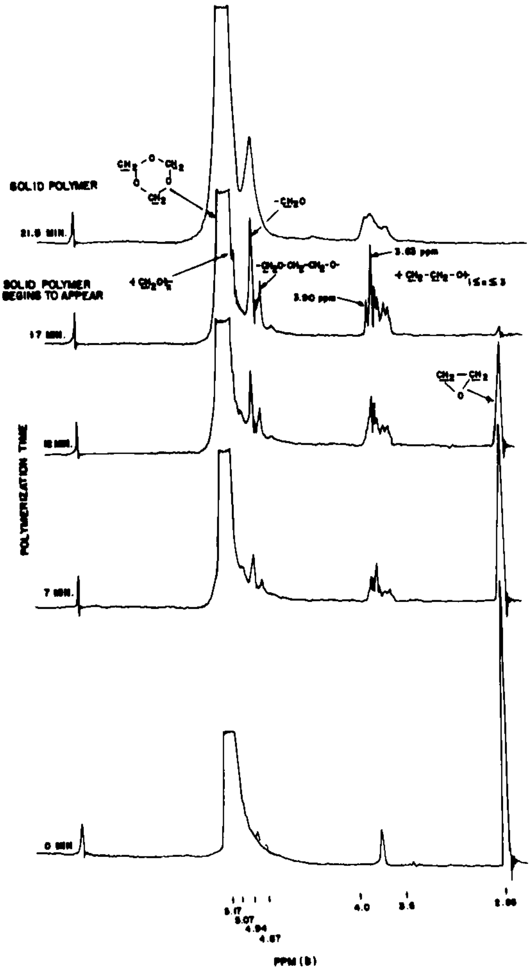


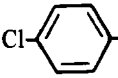
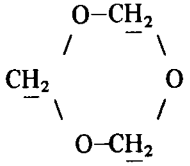
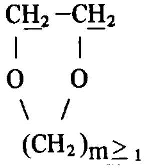
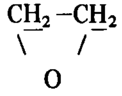
Fig. 5. Copolymerization of trioxane with 10 mole % ethylene oxide in bulk at 65°C. Cl--N_2PF_6: 6.0 × 10^{-3} mole %. Spectrum amp.: 4.0.

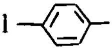
Table 1. Assignment of New Proton Signals During Copolymerization of Trioxane and Ethylene Oxide

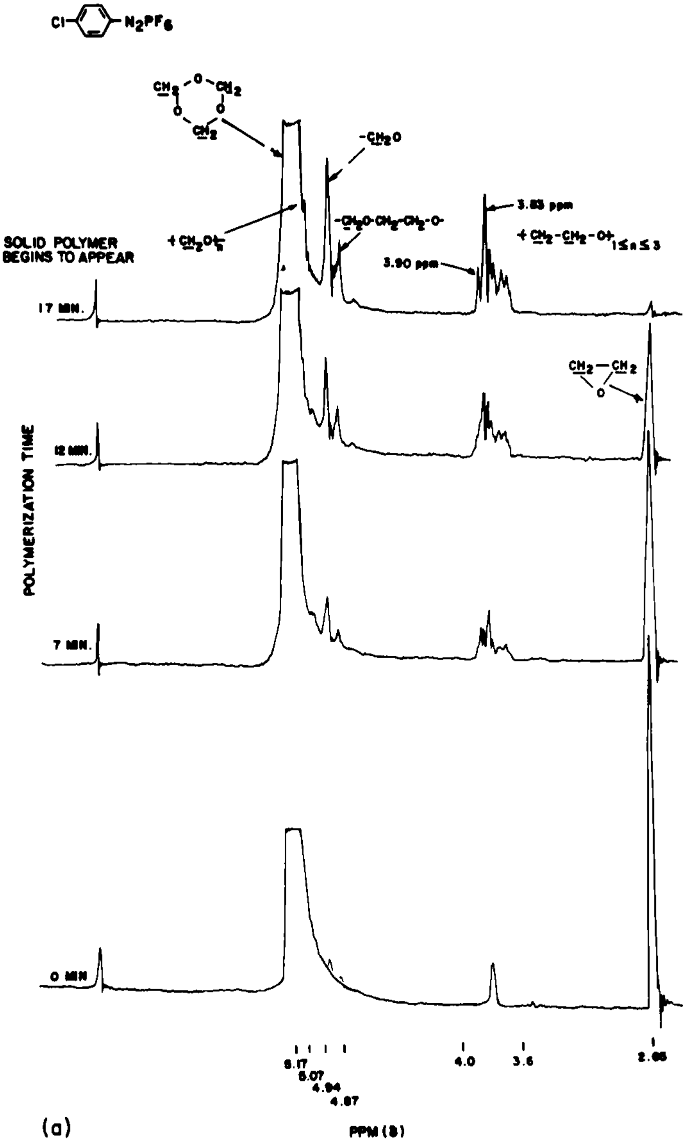
ppm vs TMS	Assignment
5.17	
5.07	$-\!(\underline{CH_2}-O)\!-_n$
4.94	$\underline{CH_2}O$
4.87	$-\underline{CH_2}-O-CH_2-CH_2-O-$
3.60-4.0[a]	$-\!(\underline{CH_2}-\underline{CH_2}-O)\!-_{1<n<3}$
3.90	
3.83	$-\!(\underline{CH_2}-\underline{CH_2}-O)\!-_{n=1}$
2.65	

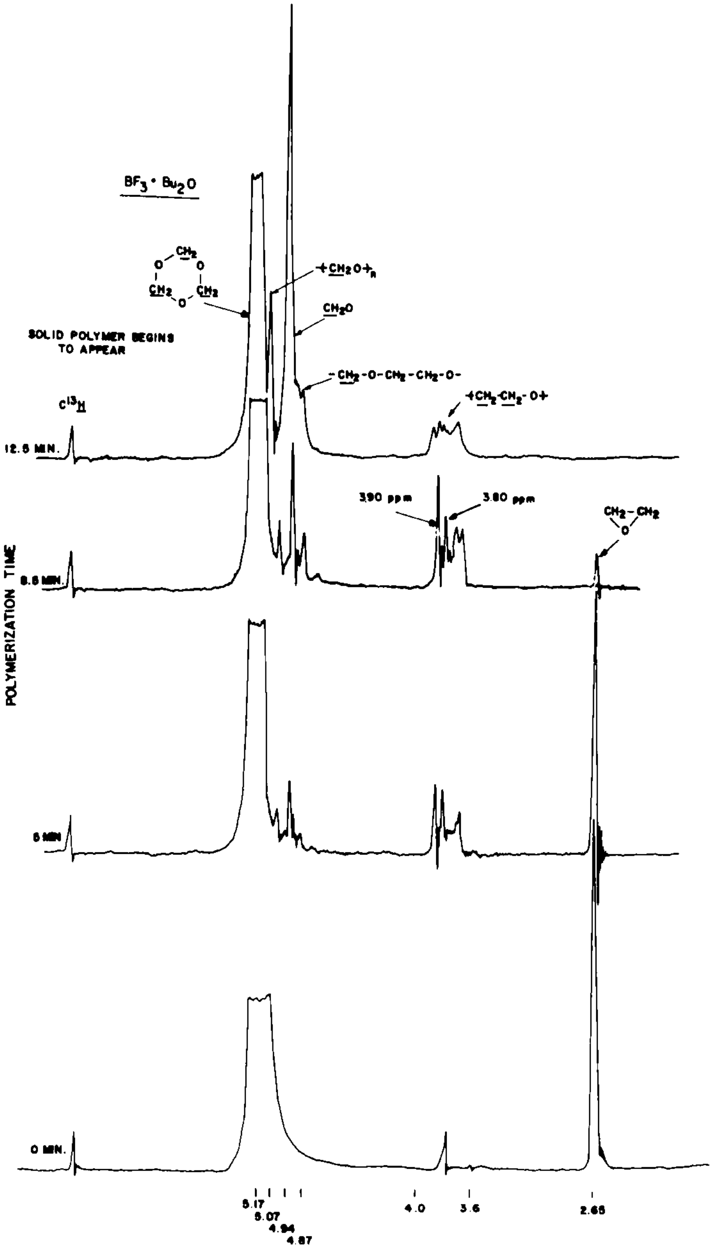
[a] A $C^{13}H$ peak symmetric to the one indicated on the left side of the trioxane peak also appears in this chemical shift range.

Table 2

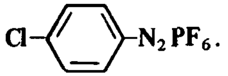
Initial concn. of ethylene oxide in monomers, mole % based on trioxane	$-\!(CH_2-CH_2-O)\!-_n$ in copolymer, mole % based on $-\!(CH_2-O)\!-_3$		
	n = 1	n = 2	n = 3
1.3	2.0	<0.2	<0.2
3.3	3.9	0.4	<0.2
7.2	6.2	1.3	0.6

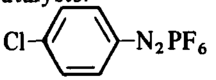
Fig. 6. Comparison between $BF_3 \cdot Bu_2O$ and Cl  N_2PF_6 as catalyst in copolymerization of trioxane and ethylene oxide. Ethylene oxide: 10 mole %. Catalyst: 6.0 X 10^{-3} mole %. Spectrum amp.: 4.0.

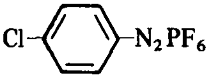



BF3 · Bu2O
+CH2O+n
CH2O
SOLID POLYMER BEGINS TO APPEAR
-CH2-O-CH2-CH2-O-
+CH2-CH2-O+
C13H
12.5 MIN.
3.90 ppm
3.80 ppm
CH2-CH2 O
POLYMERIZATION TIME
8.5 MIN.
5 MIN
0 MIN.
5.17
5.07
4.94
4.87
4.0
3.6
2.65
PPM (δ)

(b)

2. Comparison between $BF_3 \cdot Bu_2O$ and . Two significant differences were observed in the copolymerization reactions between these catalysts:

(1) In the  catalyst system, the formaldehyde concentration was found to be approximately half that found with the $BF_3 \cdot Bu_2O$ catalyst.

(2) In the  catalyst system, the formation of cyclic moities derived from the reaction of ethylene oxide subsequent to ring opening is less extensive (see Fig. 6).

The higher formaldehyde build-up along with the formation of greater concentrations of cyclic moities when $BF_3 \cdot Bu_2O$ is used as catalyst indicates that more extensive depolymerization occurs during this "induction" period. The higher stability of the propagating cation towards side reactions such as hydride ion transfer has been attributed to the PF_6^- gegenion. Here again, the effect of gegenion on another side reaction, viz., depolymerization, is demonstrated. Furthermore, it now can be concluded that in homopolymerization the lower molecular weight obtained with $BF_3 \cdot Bu_2O$ can be primarily attributed to the hydride ion transfer side reaction. In copolymerization with ethylene oxide, both hydride ion transfer and depolymerization side reactions are important factors in controlling the rate of polymerization and the molecular weight of polymers.

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[4] K. Weissermel, E. Fischer, K. Gutweiler, H. D. Hermann, and H. Cherdron, *Angew. Chem.*, **79**, 512 (1967).

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