structures and molecular weights are very similar to each other. Therefore, the three catalysts seem to be different only in the feasibility of producing the same propagating end. From these considerations, the following scheme is assumed:

$$\begin{tikzcd}
 & \text{complex I} \arrow[dr, "PA"] & & \\
WCl_6 \arrow[ur, "Ph_4Sn"] \arrow[dr, "PA"'] & & \text{propagating species} \arrow[r, "PA"] & \text{polymer} \\
 & \text{complex II} \arrow[ur, "PA"'] & &
\end{tikzcd}$$

The structures of complexes I and II are not known yet. However, the results on the tungsten oxidation state suggest that the complexes and the propagating end consist of species less oxidized than W(VI). It is presumed that complex I is $WCl_4 \cdot 2Ph$ or simply WCl_4, and complex II is $WCl_4 \cdot nPA$ (a σ complex, π complex, or metal-carben complex). The propagating species may be a metal–carben complex or a four-membered metalocycle on the basis of the polymerization behavior.[1,2,8]

In conclusion, it is found that Ph_4Sn accelerates remarkably the polymerization of phenylacetylene and that oxygen decelerates the polymerization. The reaction mechanism of initiation is proposed. However, the structures of the active complexes are not identified. Further investigation is being performed to determine the structures of complexes I and II.

References and Notes

(1) T. Masuda, K. Hasegawa, and T. Higashimura, *Macromolecules*, **7**, 728 (1974).
(2) K. Hasegawa, T. Masuda, and T. Higashimura, *Macromolecules*, **8**, 255 (1975).
(3) K. Hasegawa, T. Masuda, and T. Higashimura, *J. Polym. Sci., Polym. Chem. Ed.*, in press.
(4) E.g., as a recent review, G. Dall'Asta, *IUPAC Additional Publication*, **1**, 133 (1974).
(5) L. A. Rothman and E. I. Becker, *J. Org. Chem.*, **24**, 294 (1959).
(6) E. J. Arlman and J. R. De Jong, *Recl. Trav. Chim. Pays-Bas*, **79**, 910 (1960).
(7) T. Masuda, T. Miura, M. Mizuno, and T. Higashiumra, unpublished data.
(8) T. Masuda, N. Sasaki, and T. Higashimura, *Macromolecules*, **8**, 717 (1975).
(9) G. Lehnert, D. Maertens, G. Pampus, and M. Zimmermann, *Makromol. Chem.*, **175**, 2617 (1974).
(10) J. L. Wang and H. R. Menapace, *J. Org. Chem.*, **33**, 3794 (1968).

Polymerization of Phenylacetylenes. 5. Polymerization of Phenylpropyne Catalyzed by Tungsten Hexachloride–Tetraphenyltin

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ABSTRACT: *Phenylpropyne was found to polymerize easily with an equimolar mixture of* WCl_6 *and tetraphenyltin* as catalyst. Polymers having a molecular weight of 3000–6000 were produced in hydrocarbons and halogenated hydrocarbons as solvents. At temperatures higher than 60 °C the polymerization proceeded at a high initial rate but stopped before all monomer was consumed. On the other hand, in a range of 0–30 °C no saturation phenomenon was observed. The poly(phenylpropyne) formed was a white powder and soluble in aromatic and chlorinated hydrocarbons. The softening point was in a range of 230–240 °C. Ir, ^1H NMR, ^{13}C NMR, and uv spectroscopies showed that the polymer possesses a polyene structure having phenyl and methyl side groups. The phenomenon that the polymer is white in spite of having a polyene structure was explained in terms that the polyene does not take a planar conformation due to the steric effect of the two bulky groups.

We found that phenylacetylene was polymerized easily by WCl_6 at room temperature and formed a polymer having a molecular weight of 10 000–15 000.[1] Further, we reported in the preceding paper[2] that a catalytic amount of tetraphenyltin (Ph_4Sn) accelerates the polymerization of phenylacetylene by WCl_6 to a great extent without changing the molecular weight of the polymer. Therefore, it will be interesting to see if this catalyst system, which is very effective in the polymerization of phenylacetylene, is effective also in the polymerization of other acetylenic compounds.

In general, α,β-disubstituted olefins and acetylenes are expected to be less reactive than monosubstituted ones in polymerization. This is probably due to the steric effect. Although there are many studies on the cyclic trimerization of internal acetylenes,[3,4] very few have been reported with regard to the polymerization of internal acetylenes. To our knowledge, there has been only one report on the polymerization of phenylpropyne; recently Woon and Farona have reported that phenylpropyne is polymerized by Mo complexes to a polymer with a molecular weight of ca. 1500.[5]

The present paper describes the reactivity of phenylpropyne in the polymerization by $WCl_6 \cdot Ph_4Sn$ and the structure of poly(phenylpropyne) produced. The $WCl_6 \cdot Ph_4Sn$ catalyst was found to be very effective for polymerization of phenylpropyne. No cyclic trimer was observed during polymerization. The polymer was white due to little conjugation of the main chain.

Experimental Section

Materials. phenylpropyne was synthesized from α-methylcinnamic acid by reported methods.[6] α-Methylcinnamic acid was prepared by the Perkin reaction.[7] The purity of the phenylpropyne was greater than 99% according to gas chromatography. Solvents, WCl_6, and Ph_4Sn were purified by the same methods as described in previous papers.[1,2]

Procedures. Polymerization was carried out under the same conditions as the polymerization of phenylacetylene.[2] An equivalent amount of Ph_4Sn was added to a WCl_6 solution and this catalyst solution was aged at 60 °C for 15 min just before polymerization. Polymerization was started by adding the catalyst solution to the monomer solution. Monomer consumption was determined by measuring residual monomer concentration by gas chromatography. The number-average molecular weight of the polymer was measured by use of a Hitachi 117 vapor pressure osmometer. Ir spectra of the polymers were measured with KBr disks. ^1H NMR spectra of the polymers were measured in a 20% carbon tetrachloride solution (JEOL MH60). ^{13}C

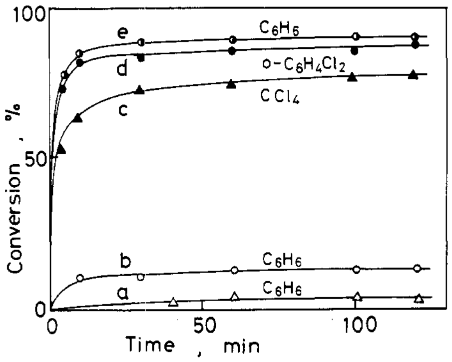

Figure 1. Effect of additives and solvents on the polymerization of phenylpropyne by WCl_6 at 60 °C: $[M]_0 = 1.0$ M, $[WCl_6] = 30$ mM, Additive: (a) none; (b) $[H_2O] = 15$ mM; (c, d, and e) $[Ph_4Sn] = 30$ mM.

Table I
Molecular Weight of Poly(phenylpropyne)[a]

Solv	Temp, °C	Conv, %	Polymer yield,[b] %	$\bar{M}_n$
CCl_4	60	77	69	5200
C_6H_6	60	90	68	4500
$C_6H_5CH_3$	60	85	67	3900
o-$C_6H_4Cl_2$	60	89	62	3900
$(CH_2Cl)_2$	60	81	71	3800
$C_6H_5NO_2$	60	0[c]	0	
$C_6H_5CH_3$	90	62	54	3900
	60	85	67	3900
	30	95	72	5000
	0	92[c]	65	6100

[a] Polymerized at $[M]_0 = 1.0$ M, $[WCl_6 \cdot Ph_4Sn] = 30$ mM, 2 h. [b] Methanol-insoluble part in the product. [c] Polymerization time: 24 h.

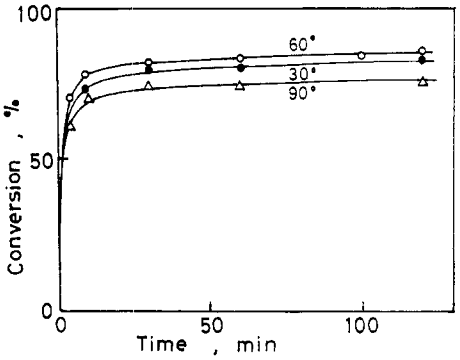

Figure 2. Effect of aging temperature on the polymerization of phenylpropyne by $WCl_6 \cdot Ph_4Sn$ in toluene at 60 °C: $[M]_0 = 1.0$ M; $[C]_0 = 30$ mM; aging time, 15 min.

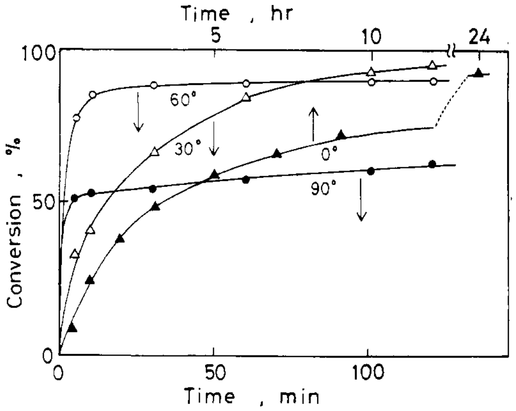

Figure 3. Effect of polymerization temperature on the polymerization of phenylpropyne by $WCl_6 \cdot Ph_4Sn$ in toluene: $[M]_0 = 1.0$ M, $[C]_0 = 30$ mM; aging of catalyst, 60 °C, 15 min.

NMR spectra were observed after the accumulation of 200 scans in a 20% $CDCl_3$ solution (JEOL PFT100). Uv spectra were measured in ethylene dichloride solutions (0.20 mM).

Results and Discussion

Polymerization of Phenylpropyne by Tungsten Hexachloride–Tetraphenyltin. Phenylpropyne was polymerized with an initial monomer concentration of 1.0 M and a catalyst concentration of 30 mM under a dry nitrogen atmosphere. Figure 1 shows the effect of H_2O and Ph_4Sn for the polymerization of phenylpropyne by WCl_6 at 60 °C. It was previously shown that both H_2O and Ph_4Sn were effective catalyst components for the polymerization of phenylacetylene by WCl_6.[1,2] On the other hand, Ph_4Sn was much more effective in the polymerization of phenylpropyne than H_2O as shown in Figure 1 (see curves b and e). Ph_4Sn remarkably increased not only the polymerization rate but also the final conversion.

The products obtained by WCl_6 alone and by $WCl_6 \cdot H_2O$ were soluble in methanol, but when an equimolar amount of Ph_4Sn was used as a catalyst component, about 70% of the monomer consumed was a methanol-insoluble polymer. The methanol-soluble product was found to be a linear oligomer. The methanol-insoluble polymer was a white powder and soluble in benzene. As will be described below, the polymer possessed a molecular weight of several thousand. To our knowledge, this presents the first example of the synthesis of poly(phenylpropyne) with a molecular weight as high as several thousand.

In the polymerization of phenylacetylene by $WCl_6 \cdot Ph_4Sn$, as reported in the previous paper,[2] time and temperature for aging the catalyst greatly affected the polymerization.[2] However, as shown in Figure 2 the aging temperature was found not to influence very much the activity of the catalyst in a range of 30–90 °C in the polymerization of phenylpropyne. In all the later experiments the catalyst was aged at 60 °C, and an aging time of 15 min was adopted on the basis of results for the polymerization of phenylacetylene.[2]

The effects of solvents on the polymerization of phenylpropyne were also investigated. Aromatic hydrocarbons and halogenated hydrocarbons were used as solvents. As seen in Figure 1, the time–conversion curves for the polymerization in these solvents were similar to that in benzene. As Table I shows, the final conversions and the portions of the methanol-insoluble polymer were almost constant regardless of the solvents. The molecular weight of methanol-insoluble polymer, however, decreased as the polarity of solvent increased. Phenylpropyne was not polymerized in nitrobenzene, which is also the case for phenylacetylene.[1,2]

Phenylpropyne was polymerized by a 1:1 mixture of WCl_6 and Ph_4Sn in toluene at several temperatures between 90 and 0 °C. As shown in Figure 3, when the polymerization was carried out at 90 or 60 °C, the reaction was very rapid but within a few minutes stopped before all monomer was consumed. On the other hand, the reaction proceeded slowly at 30 or 0 °C, but conversions increased with time. Even at 0 °C the polymerization proceeded to high conversion though it took long hours. This result indicates that as the polymerization temperature is raised, a termination reaction or a reaction inactivating catalyst takes place. The portion of methanol-insoluble product was low at 90 °C. Further, the molecular weight of the methanol-insoluble polymer increased as the polymerization temperature was lowered, and at 0 °C

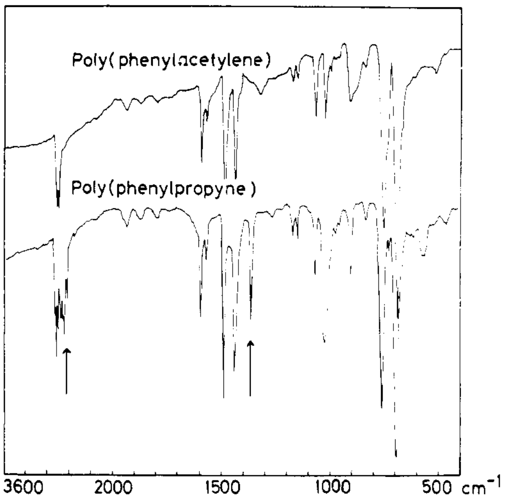

Figure 4. Ir spectra of poly(phenylpropyne) and poly(phenylacetylene) produced by $\mathrm{WCl_6{\cdot}Ph_4Sn}$ in benzene; polymerization conditions: $[M]_0 = 1.0$ M, $[C]_0 = 30$ mM, 60 °C for poly(phenylpropyne); $[C]_0 = 10$ mM, 30 °C for poly(phenylacetylene).

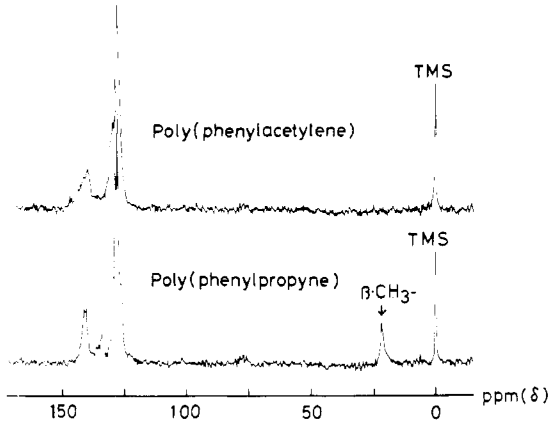

Figure 5. ^{13}C NMR spectra of poly(phenylpropyne) and poly(phenylacetylene) produced by $\mathrm{WCl_6{\cdot}Ph_4Sn}$ in benzene; polymerization conditions are the same as in Figure 4.

a polymer whose molecular weight was as high as 6000 was obtained.

Structure of Poly(phenylpropyne). In contrast to poly(phenylacetylene), poly(phenylpropyne) (the methanol-insoluble part of the product) was a white powder. The polymer was soluble in aromatic hydrocarbons and chlorinated hydrocarbons. In the present paper the structure of the methanol-insoluble part was investigated. The observed values of elementary analysis of the polymer agreed with those calculated for the structure $\lbrack\!-\mathrm{C(CH_3){=}(C_6H_5)}-\rbrack_n$ independent of polymerization conditions. The softening points of poly(phenylpropyne)'s having a molecular weight greater than 4000 were in a range of 230–240 °C regardless of the polymerization conditions and these values were much higher than those of poly(phenylacetylene)'s.[8-11]

Figure 4 shows the ir spectra of poly(phenylpropyne) and poly(phenylacetylene) which were obtained in benzene by $\mathrm{WCl_6{\cdot}Ph_4Sn}$ at 60 °C. Poly(phenylacetylene) produced under these conditions seems to be rich in the trans structure.[8] However, the ir spectra of poly(phenylpropyne)'s were almost unaffected by polymerization solvent and temperature. As to poly(phenylpropyne), absorptions were seen at 2960 and 2870 cm^{-1} due to the C–H streching vibration of the methyl group, and at 1370 cm^{-1} due to the C–H deformation vibration of the methyl group. These absorptions are not observed in the ir spectra of poly(phenylacetylene)'s. Therefore, the poly(phenylpropyne)'s must possess methyl side groups. Also, an absorption (870 cm^{-1}) due to the polyene proton which appears in polyphenylacetylene)'s was not observed in poly(phenylpropyne)'s. Four absorptions in a range of 1700–2000 cm^{-1} and absorptions at both 760 and 695 cm^{-1} are characteristic of monosubstituted benzene. From these observations, it can be concluded that poly(phenylpropyne) possesses methyl and phenyl side groups and the main chain of poly(phenylpropyne) consists of a polyene structure.

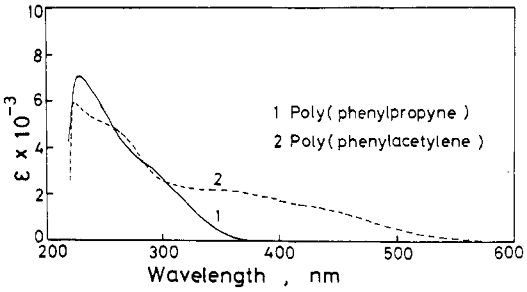

Figure 6. Uv and visible spectra of poly(phenylpropyne) and poly(phenylacetylene) produced by $\mathrm{WCl_6{\cdot}Ph_4Sn}$ in benzene; polymerization conditions are the same as in Figure 4.

^{1}H NMR spectra of poly(phenylpropyne)'s and poly(phenylacetylene)'s formed under various conditions were compared. The spectra of poly(phenylacetylene)'s consisted of one broad peak at about δ 7. The peaks of polyene and phenyl protons seem to be overlapping each other. On the other hand, the spectra of poly(phenylpropyne) consisted of two broad peaks at δ 6.5 and 1.5. The former peak is assigned to phenyl protons and the latter to methyl protons. The ratio of peak areas of the phenyl and methyl protons was approximately 5.2:3.0, which agrees with the value for the structure estimated by means of ir spectra. Thus ^{1}H NMR spectra also endorsed that poly(phenylpropyne) possesses methyl and phenyl side groups.

Figure 5 shows the ^{13}C NMR spectra of poly(phenylpropyne) and poly(phenylacetylene) produced in benzene. In the spectrum of poly(phenylacetylene), peaks were observed only in a range of δ 125–145, which are attributed to the aromatic and olefinic carbons. In the spectrum of poly(phenylpropyne), a peak was seen at δ 21.5 in addition to the peaks of aromatic and olefinic carbons. The peak at δ 21.5 was assigned to the methyl side group because the methyl carbon of β-methylstyrene shows a peak at δ 18.6.[12] These results also indicate that poly(phenylpropyne) possesses methyl and phenyl side groups and a polyene structure, and that the polymerization proceeds via the opening of the carbon–carbon triple bond without isomerization.

The geometrical structure of poly(phenylacetylene) was determined by means of the ir spectrum; absorptions at 870 and 739 cm^{-1} were attributed to a cis structure.[9] On the other hand, the geometrical structure of poly(phenylpropyne) cannot be determined in this manner because poly(phenylpropyne) does not possess protons on the main chain. It was, however, inferred by construction of its molecular model (CPK formula model) that the polymer has mostly a trans structure because the steric hindrance between the bulky groups is very large in the cis structure. Even the trans-type structure cannot take a planar conformation according to the molecular model; it must be distorted. This agrees with the results of uv spectrum.

Poly(phenylacetylene) having a high molecular weight is a reddish-brown powder.[8] On the contrary poly(phenylpropyne) is a white powder. The uv and visible spectra of poly(phenylpropyne) and poly(phenylacetylene) are shown in Figure 6. In the poly(phenylacetylene) the absorption was observed over a wide range of 220–600 nm in uv and visible spectra. On the other hand, in the poly(phenylpropyne) the maximum absorption was observed at 230 nm. $\epsilon_{\max}$ was ca. 7000, and no absorption existed in a range where wavelength is greater than 380 nm. These results support that the polyenes of poly(phenylpropyne) are not in the conjugated state due to the steric effect of two bulky groups, methyl and phenyl.

In conclusion, phenylpropyne was polymerized by $WCl_6 \cdot Ph_4Sn$ to a polymer with a molecular weight of several thousand, and the polymer obtained was linear and possessed methyl and phenyl side groups.

References and Notes

(1) T. Masuda, K. Hasegawa, and T. Higashimura, *Macromolecules*, **7**, 728 (1974).

(2) Part 4 of this series: T. Masuda, K. Q. Thieu, N. Sasaki, and T. Higashimura, *Macromolecules*, preceding paper in this issue.

(3) For a review, see C. W. Bird, "Transition Metal Intermediate in Organic Synthesis", Academic Press, New York, N.Y., 1967, p 1.

(4) For a review, see I. Wender and P. Pino, Ed., "Organic Synthesis via Metal Carbonyls," Vol. I. Interscience, New York, N.Y, 1968, p 343.

(5) P. S. Woon and M. F. Farona, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 1749 (1974).

(6) S. Reich and S. Koehler, *Chem. Ber.*, **46**, 3727 (1913).

(7) R. Adams, Ed., "Organic Reactions", Vol. I, Wiley, New York, N.Y., 1942, p 251.

(8) T. Masuda, N. Sasaki, and T. Higashimura, *Macromolecules*, **8**, 717 (1975).

(9) R. J. Kern, *J. Polym. Sci., Part A-1*, **7**, 621 (1969).

(10) Y. Okamoto, A. Gordon, F. Movsovicius, H. Hellman, and W. Brenner, *Chem. Ind.* (*London*), 2004 (1961).

(11) K. Higashiura, K. Tanimoto, N. Hamachi, and M. Oiwa, *Kogyo Kagaku Zasshi*, **66**, 374 (1963).

(12) K. Izawa, T. Okuyama, and T. Fueno, *Bull. Chem. Soc. Jpn.*, **46**, 2881 (1973).

The Reaction of Polyoxyethylene Glycols with Epichlorohydrin. Factors Affecting the Composition and Yield of Volatile Products

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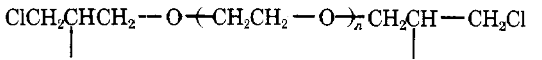
ABSTRACT: The side reactions which accompany the addition of α-hydro-ω-hydroxypoly(oxy-1,2-ethanediyl) (I) (average molecular weight of 588 and 1480) to epichlorohydrin (ECH) catalyzed by boron trifluoride etherate have been studied. Dioxane arises solely from I while the other products, identified as *cis*- and *trans*-4-chloromethyl-2-methyl-1-3-dioxolane (CMMD) and 2-chloromethyl-1,4-dioxane (CMD), are derived from both I and ECH. Various additives, water, 3-chloro-1,2-propanediol, 1,4-butanediol, and tetrahydrofuran, were evaluated for effectiveness in reducing the formation of volatile products. Only water proved effective at the levels tested. With I of molecular weight 1480, and no water added, about 14–16% dioxane was produced. With 1–1.5% water dioxane was reduced to 3–4% with corresponding reductions in CMD but not in CMMD. CMMD can be produced from I, 3-chloro-1,2-propanediol, and catalyst even when no ECH is present. Although dioxane is suppressed when water is present, the average molecular weight of the adduct is less than that of the starting material.

The cationic polymerization of ethylene oxide catalyzed by boron trifluoride etherate produces substantial quantities of 1,4-dioxane as well as α-hydro-ω-hydroxypoly(oxy-1,2-ethanediyl) (I), hereinafter referred to as "polyoxyethylene glycol" (POEG).[1] In addition, POEG will, in the presence of ethylene oxide and the catalyst, partially depolymerize to yield dioxane and some 2-methyl-1,3-dioxolane. A subsequent study showed that the depolymerization of POEG to yield dioxane without the formation of 2-methyl-1,3-dioxolane can be effected by the addition of triethyloxonium fluoroborate with neither ethylene oxide nor boron trifluoride etherate being present.[2]

Alcohols, including POEG, react with 1-chloro-2,3-epoxypropane (epichlorohydrin, ECH) in the presence of boron trifluoride etherate[3] to yield, in the case of POEG, useful products such as II



$$\underset{\displaystyle OH}{ClCH_2CHCH_2}-O\!\left(CH_2CH_2-O\right)_n CH_2\underset{\displaystyle OH}{CH}-CH_2Cl$$

II

having end groups capable of being converted into the epoxide function. The purpose of this investigation was to determine the nature and quantity of volatile products formed in the POEG–ECH reaction catalyzed by boron trifluoride etherate. For the purposes of this study, volatile products were defined as those materials which can be stripped from the neutralized reaction mixture at 115 °C and 2 Torr.

Results and Discussion

Nature of the Volatile Products. The earlier work[1] with POEG, ethylene oxide, and boron trifluoride etherate revealed the presence of dioxane and 2-methyl-1,3-dioxolane, both of which might arise either from the polymer, or from ethylene oxide, or from both. In the reaction with ECH dioxane must arise solely from the POEG and any products containing chlorine must arise, at least in part, from ECH. The volatile product from a typical run was analyzed by GLC and was found to consist of five substances: dioxane, a trace of ECH, and three substances with longer retention times than ECH. Peaks 3 and 4 were close together and the fifth and last peak emerged several minutes later.

GLC–mass spectrometric analysis showed that the substances responsible for peaks 3, 4, and 5 all had parent masses of 136 and contained one chlorine atom. Peaks 3 and 4 together had fragmentation patterns different from that of peak 5. NMR spectra for gas chromatographic fractions repre-

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