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Polymerization of Dioxolane by Triethyloxonium Hexafluorophosphate

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ABSTRACT

The polymerization of dioxolane by triethyloxonium hexafluorophosphate in methylene chloride has been studied with a view to determine the nature of the active center. NMR studies of solutions of the initiator with low ratios of monomer led to little reaction of the initiator over long times. Analysis of normal reaction mixtures showed that only a small amount of the initiator was consumed during the reaction. The polymer was studied by GPC, UV spectroscopy, and NMR. The polymer appears to consist largely of high molecular weight material with M_w/M_n less than 2, and also low molecular weight material perhaps formed by a different mechanism. The high molecular weight material appears not to have been formed by a simple linear trialkyloxonium ion, from end-group studies, and it is suggested the active center is a secondary oxonium ion on a large cyclic polymer.

The mechanism of the cationic polymerization of dioxolane is not well understood. Although several papers have appeared on the subject, there is no universally accepted structure for the active polymerizing center, or a general mechanism followed by the reaction. Some of the confusion is probably caused by the wide selection of initiators used, which undoubtedly cause minor modifications of the scheme. But most of these initiators could be expected ultimately to give a common active center, and the absence of any definite knowledge on the form of this active center hinders the complete analysis of the system.

Several types of active centers have been suggested: a linear carboxonium ion [1, 2], a linear or branched tertiary oxonium ion [3, 4], and an active center which is situated on a cyclic macromolecule which grows by ring expansion [5]. The latter center could possibly be a tertiary or a secondary oxonium ion depending on the initiator. The actual polymers produced have been suggested to be linear, completely cyclic, or a mixture of linear and cyclic polymers produced by a backbiting of a growing linear chain.

Both Plesch [6] and Jaacks [4] have advanced fairly convincing arguments against the possibility of the linear carboxonium ion, and this possibility has not been considered further here. But, nevertheless, it cannot be dismissed entirely until direct evidence for some other center is produced.

An attempt has been made here to determine the fate of the initiator, the presence of selected end groups, the NMR spectrum of the growing species, and the molecular weight distribution of the polymer formed.

The initiator chosen was triethyloxonium hexafluorophosphate because of its stability [7] and the simplicity of a mechanism if it involved a tertiary oxonium ion.

EXPERIMENTAL

Dioxolane (Eastman) was initially dried on sodium sulfate, then fractionally distilled from potassium metal. It was stored under vacuum on calcium hydride. In the later experiments a further stage of purification by condensing onto a sodium mirror was used, but it did not appear to affect the results.

Methylene chloride was used as a solvent throughout. It was fractionally distilled from calcium hydride and stored under vacuum on calcium hydride. The triethyloxonium hexafluorophosphate was prepared according to Dreyfuss [8]. It was purified by several precipitations from methylene chloride by hexane. The last precipitation was under vacuum. It was subdivided under vacuum.

All experiments were carried out in all-glass vacuum apparatuses, with the reagents added via breakseals.

The experiments were at 0°C except where stated. The equilibrium monomer concentration was taken to be 1.07 M.

The GPC calibration curve in THF was standardized by polymer samples of molecular weight determined by the viscosity relationship of Berman et al. [9].

RESULTS AND DISCUSSION

In common with most previous investigators, the polymerizations were found to have an induction period of very slow reaction, followed by a relatively fast reaction with an S-shaped monomer consumption curve. The suggestion has been made that the reaction is autocatalytic, and that the polymer produced acted as a cocatalyst [10]. Experiments were made in which polymer was added to the reaction mixture, but no shortening of the induction period was found. In fact, the presence of larger amounts of polymer caused a slowing down of the reaction, but it would be difficult to be sure this was not caused by impurities introduced with the polymer.

The NMR spectra of reaction mixtures containing low monomer-initiator ratios were measured. In Fig. 1 is shown the spectra of the initiator and reaction mixtures containing the monomer in the ratios 1:1, 1:2, and 1:5 after a reaction time of 2 hr at 0°C. The first two reaction mixture spectra show the two reagents virtually unchanged. The 1:5 ratio reaction mixture shows the presence of polymer and also minor absorbances in the region that diethyl ether absorbs. The first two reaction mixtures had less than the equilibrium concentration of monomer, and hence did not polymerize. Nevertheless there is apparently no initiator/monomer reaction on this time scale, and no measurable formation of an oxonium ion containing a dioxolane molecule.

The last reaction mixture contained more than the equilibrium monomer concentration, and polymer formed corresponding to this excess. Nevertheless, there is still little reaction of the initiator with the monomer or polymer. Some reaction has evidently occurred as an absorption of diethyl ether representing 7% of the initiator has appeared. After 24 hr this absorption of diethyl ether had grown to 16% of the initiator. But evidently there is no formation of active centers in a comparable concentration to the initiator.

Attempts were made to find the fate of the initiator during the reaction, and two methods were used. The first method was that developed by Saegusa [11], of monitoring the concentration of trialkyloxonium ion present during the reaction by terminating aliquots with sodium phenoxide solution, and measuring the

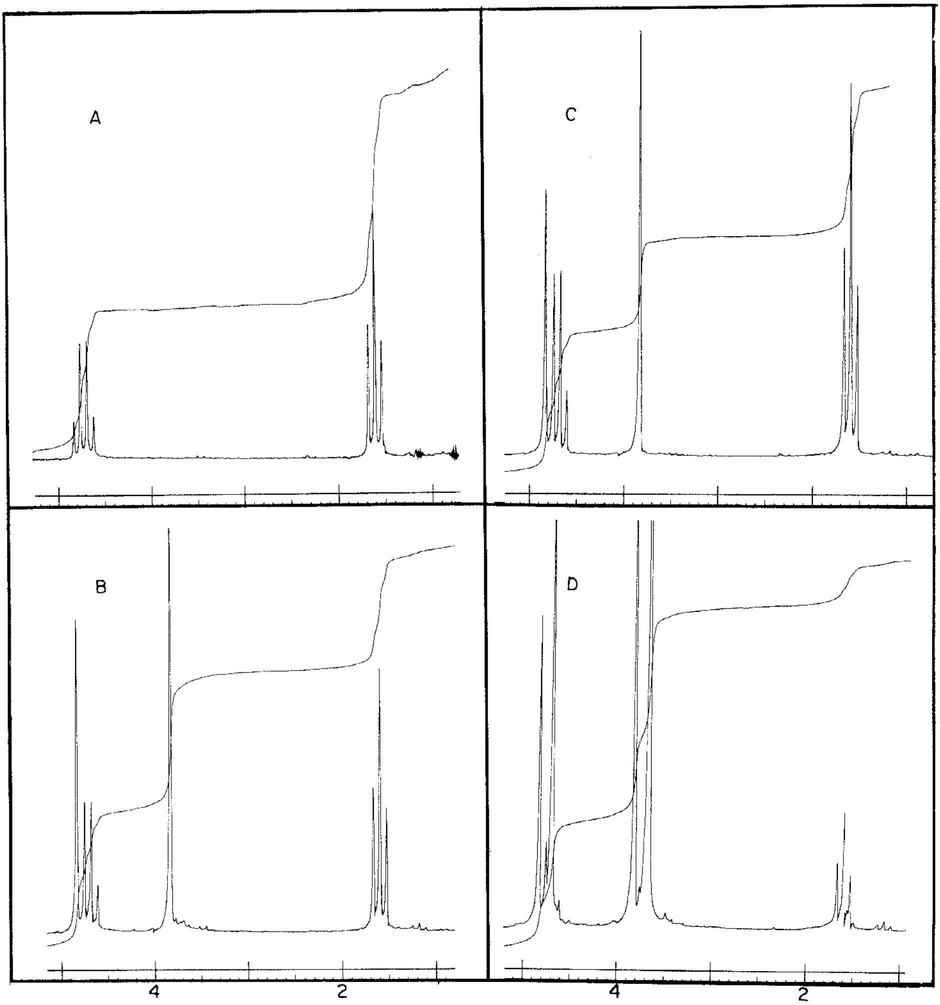


FIG. 1. ^{1}H NMR spectra of CD_2Cl_2 solutions of triethyloxonium hexafluorophosphate. A, alone; B, C, and D, with 1, 2, and 5 mole equivalent of dioxolane, respectively, after 2 hr reaction time.

concentration of phenol ethers formed by their UV absorption. This is specific for trialkyloxonium ions, either as the initiator or as a propagating species. It is also possible to determine the concentration of polymer chains containing trialkyloxonium ions by a distillation technique. The results are shown in Table 1, where it is seen

TABLE 1. Concentration of Trialkyloxonium Ions in Reaction Mixture. $[M]_0 = 2.72\,\underline{M}$ $[Et_3OPF_6]_0 = 1.15 \times 10^{-2}$. Analysis with NaOPh[a]

Time (min)	% Monomer reacted	$[C^+]_T \times 10^2$	$[C^+]_H \times 10^3$
0	0	1.14	2.12
210	24	1.03	1.73
300	50	1.11	2.18

[a] $[C^+]_T$ = total trialkyloxonium ion found. $[C^+]_H$ = higher molecular weight trialkyloxonium ion.

TABLE 2. Concentration of Et_3OPF_6 in Reaction Mixture by VPC. $[M_0] = 3.26\,\underline{M}$. $[Et_3OPF_6]_0 = 1.08 \times 10^{-2}$ [a]

Time (min)	=	0	10	40	80	160	1310
$[Et_3OPF_6] \times 10^3$	=	7.24	9.22	7.24	8.56	7.24	5.3

[a] Initiator added

that although the total concentration of trialkyloxonium ions remains fairly unchanged, very little appears as high molecular weight ethers.

The second method used depended on the reaction of trialkyloxonium hexafluorophosphate with diethylamine to form triethylamine. The triethylamine could then be analyzed by vapor phase chromatography. Unfortunately, this method is not very quantitative, as only about 85% of the initiator appeared as triethylamine; nevertheless, it gave a measure of the residual initiator. The results are shown in Table 2, and it is seen that only a small part of the initiator is consumed in the first 160 min, after which time the polymerization would be virtually at equilibrium.

An examination was made of the polymers from reaction mixtures that had been terminated by sodium phenoxide. The polymer was first precipitated with methanol, and both the precipitated high molecular weight material and the soluble polymer isolated. Both were studied in the UV spectrum to detect the presence of phenoxy end groups. Some absorption was found in both fractions in the correct region, but only enough to account for one phenoxy group per 15 chains.

The NMR spectrum of these polymers was also studied, and also that of another fraction of lower molecular weight soluble in hexane. In none of these polymers was there any evidence of absorption in the aromatic region of the spectrum. The highest molecular weight fraction showed only the two peaks typical of this polymer [12], but both low molecular weight fractions showed a small absorption at $\delta = 3.71$ and an even smaller absorption at $\delta = 1.25$. The spectrum of the lowest molecular weight sample ($M_n = 671$) is shown in Fig. 2. A peak at $\delta = 3.71$ also appears in the 5:1 reaction mixture

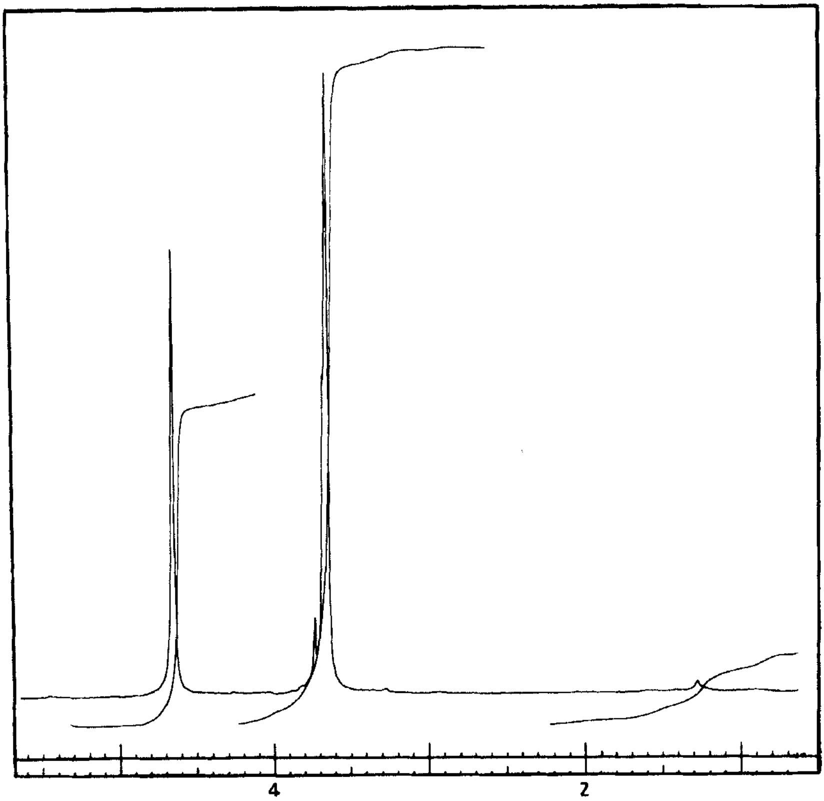
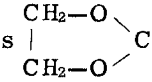


FIG. 2. ^{1}H NMR spectrum of polydioxolane molecular weight 671. CCl_4 solution of low molecular weight, methanol soluble tail.

in Fig. 1. The peak at 3.71 appears as a single peak, but it could be half of a doublet with the other half hidden in the main polymer peak. Assuming it to be a single peak, and it corresponded to the protons in an OCH_2 group, its size would correspond to one group per polymer chain.

Although it is possible that the absorption at $\delta = 3.71$ is from an end group, there also remains the possibility that it is caused by a low molecular weight cyclic polymer. A dimer or trimer could well have a discrete absorption intermediate between the monomer and polymer in the region of $\delta = 3.7$. It should be pointed out that when the polymers were dried under vacuum, they were also freed of phenetole from residual initiator. Thus it is quite possible any cyclic dimer of dioxolane would also have been removed, although any trimer would probably have been sufficiently involatile. There is no corresponding acetal CH_2 absorption, but this might coincide with the major polymer peak.

Most end groups expected from a simple linear tertiary oxonium ion polymerization would have more than a single line absorption. Exceptions are $-OCH_3$ groups, although these would absorb a little further upfield of the major absorption found here. One possible end group that could give an absorption such as the peak at $\delta = 3.71$ is  $\begin{matrix} CH_2-O\diagdown \\ | \qquad\quad CH \\ CH_2-O\diagup \end{matrix}$, formed by proton abstraction from dioxolane. If this were the initiator fragment, some other absorption would be expected for the terminating group, but the only other visible absorption is the peak at $\delta = 1.25$ which is very small in comparison.

The molecular weight distribution of the polymer produced was measured by GPC. The polymer produced during the course of the main reaction and that at the end of the reaction had a similar distribution, and a typical trace is shown in Fig. 3. During the initial slow part of the reaction, only low molecular weight polymer was formed.

The distribution shown in Fig. 3 can be divided into two parts, the main normal shaped peak of polymer insoluble in methanol,

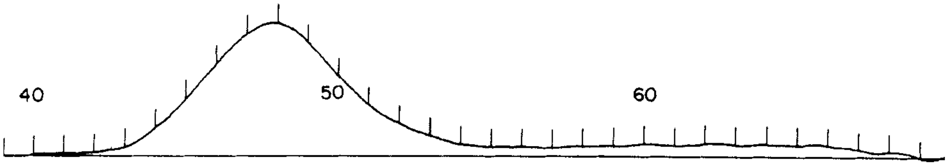


FIG. 3. Typical GPC trace of whole polydioxolane from reaction of 3.26 M dioxolane with 2.78×10^{-3} M initiator.

with a M_w/M_n between 1.5 and 2, and the tail which is largely methanol soluble where this ratio is near 2 or 3, with M_n less than 1000. It was found that there was not a uniform rise in molecular weight of the higher fraction during the course of the polymerization, Table 3. The polymerization behaved as if there was a continuous production of new high molecular weight molecules throughout the reaction, which would be in accord with the relative slow consumption of the initiator.

Also measured was the molecular weight of the polymer formed after successive addition of monomer. The first addition of monomer was allowed to react from 20 hr, and then two further additions of monomer added at intervals of 1/2 hr. The results are seen in the first half of Table 4, and show that the successive additions caused increases in the molecular weight of the high molecular weight portion. It would appear that at least some if not all of the larger polymer molecules remain living to cause this increase, as newly initiated chains would not be expected to achieve the higher molecular weight with the supplementary monomer addition. The proportion of low molecular weight material decreases in these additions, and perhaps its formation is only associated with the presence of the original initiator.

TABLE 3. Molecular Weight of High Polymer during Reaction

	Run A		Run B	
Yield (%)	35	81	17	60
Molecular weight	53,000	70,000	58,000	49,000
	$[M]_0 = 3.26$ M, $[C]_0 = 2.76 \times 10^{-3}$		$[M]_0 = 3.26$ M, $[C]_0 = 1.15 \times 10^{-2}$	

TABLE 4. Molecular Weight of High Fraction after Successive Addition of Monomer. $[C]_0 = 1.1 \times 10^{-2}$

Temperature (°C)	0	0	0	12	23	45
$[M]_{Total}$	2.04	3.23	4.45	4.45	4.45	4.45
Molecular weight, high	16,000	36,000	49,000	46,000	22,000	4,000
% of Total polymer	79	80	87	81	86	92

The high molecular weight material was found at all times to have a molecular weight greater than that calculated from the ratio of initiator to monomer consumed to form it. In this sense the reaction does not resemble other living polymerizations such as the cationionic polymerization of THF, or the anionic polymerization of ethylene oxide. But as the monomer initiator ratio increases, the ratio of such a calculated to the measured molecular weight becomes nearer to 1, as would be expected from such a system with a slow initiation rate.

On the other hand, the low molecular weight material contains many more molecules than the original initiator added. Evidently some transfer reaction must be occurring, and as it appears to decrease in importance as the original initiator is consumed, it may be associated with the initiator. That two distinct types of polymers are produced does in fact suggest that two mechanisms are in operation, one to produce the high molecular weight material and one for the low.

Two experiments were performed in which polymers were degraded. The first experiment involved the polymerization reaction described in Table 4 that had been allowed to go to completion at 0°C. The temperature was raised first to 12°C, then 23°C, and finally 45°C, in order to cause the polymer to revert to monomer. The results are also shown in Table 4. The general shape of the GPC curves remained the same with the major part of the material appearing as a higher molecular weight peak, and with a tail of lower molecular weight material. As the ratio of the peak to the tail increased somewhat at the end, it appears that both high and low molecular weight material depolymerized, with a large reduction in the average molecular weight of the major peak.

The second experiment involved adding the initiator at 0°C to a solution of a high molecular weight polymer freed of the low molecular weight tail. Only half the polymer was expected to degrade to monomer. After 24 hr the residual polymer was found not only to have decreased largely in molecular weight, but also large amounts of low molecular weight polymer had formed. From these two experiments it appears that the low molecular weight material is at least partly a consequence of the presence of the original trialkyloxonium salt.

The conclusions that can be drawn from this study are firstly that this initiator, triethyloxonium hexafluorophosphate, does not react rapidly with dioxolane. The active centers produced in the polymerization do not behave as simple trialkyloxonium ions, and the polymer produced does not have end groups expected from such a center.

In all, the behavior with this initiator agrees very well with the suggestion put forward by Plesch [5] that the growing polymer chain is a cyclic polymer, but with a secondary oxonium ion as the active center. The secondary oxonium ion would have to be produced by a slow reaction from the initial tertiary oxonium ion by some as yet unknown reaction. The active centers once produced appear to be long lived. During most of the reaction there is a simultaneous production of low molecular weight material, perhaps associated with the presence of the original initiator.

These conclusions can only be directly applied to this initiator. But it seems likely that the final active center with any initiator will be a secondary oxonium ion. This would be a very labile center, the proton interchanging quite freely in cyclic polymers. The consequence is, of course, that the chance of growth of a large ring with many ether groups is larger than that of a smaller ring. Hence the large rings would grow more rapidly than the small rings, tending to increase the disproportion between the high molecular weight peak and the tail.

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