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Specific Nature of the Polymerization of Heterocyclics

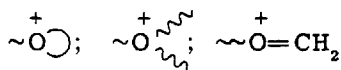
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This report deals primarily with oxyheterocyclics since this class of compounds is the best studied with regard to the laws of polymerization of heterocyclics.

Compared with the ionic polymerization of vinyl compounds, the following are the specific features of the polymerization of oxyheterocyclics:

1. The active centers of polymerization are the more stable oxonium or carboxonium ions of different structures rather than



carbonium ions (or ion pairs, which are not of great importance in this case). The reactivity and structure of the active growing oxonium ion depends on the nature of the monomer polymerized. As is generally known, the affinity of carbocations for nucleophilic agents is much higher than that of oxonium ions. This causes considerable kinetic differences in the polymerization of heterocyclics and vinyl compounds.

2. Chain propagation of heterocycles is a substitution reaction rather than an addition reaction as in the case of vinyl monomers. Therefore, transfer rate constants and chain propagation become comparable values.

3. The macromolecule formed during polymerization contains the same heteroatoms in the main chain as the monomer and may react with all active parts of the system.

Lewis acids and oxonium salts are typical cationic catalysts for the polymerization of oxyheterocyclics.

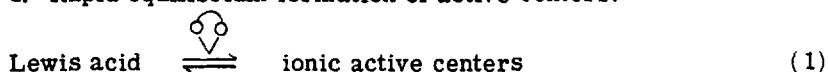
It is of extreme importance to determine the ratio of the concentration of growing ionic particles existing at any given moment to the initial concentration of the catalyst.

Our investigations have shown this ratio to be much less than unity for acetal systems in the following two ways:

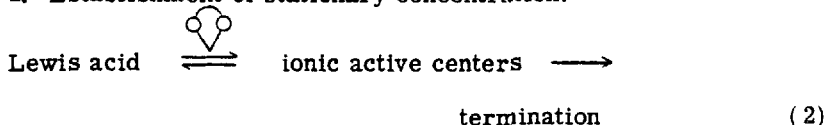
1. Kinetically, by studying the polymerization of dioxolane and exchange reactions of linear acetals (methyl acetal, ethyl acetal).
2. By directly measuring the concentration of R^+ and by NMR.

Figure 1 shows that the reaction proceeds without an induction period. This may occur only in three cases:

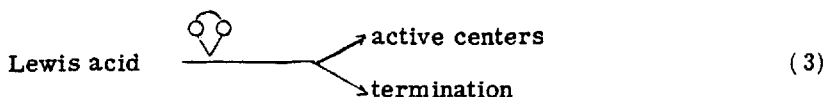
1. Rapid equilibrium formation of active centers:



2. Establishment of stationary concentration:



3. Rapid irreversible initiation followed by a parallel termination reaction (it is assumed that termination and initiation reactions are of the same order as catalyst):



The first equilibrium takes place in the case of dioxolane polymerization since the molecular weight is linearly proportional to the degree of conversion, whereas with the addition of $\text{CH}_3\text{OCH}_2\text{Cl}$ [1] the rate of polymerization of dioxolane increases 30 times.

Similar results were obtained for dioxolane polymerization with HCl under the action of $\text{CH}_3\text{OCH}_2\text{Cl}$ and also for the exchange reaction of linear acetals. This shows conclusively that the concentration of ionic centers was considerably lower than the initial concentration of the Lewis acid.

The NMR method was used for studying the acetal + Lewis acid

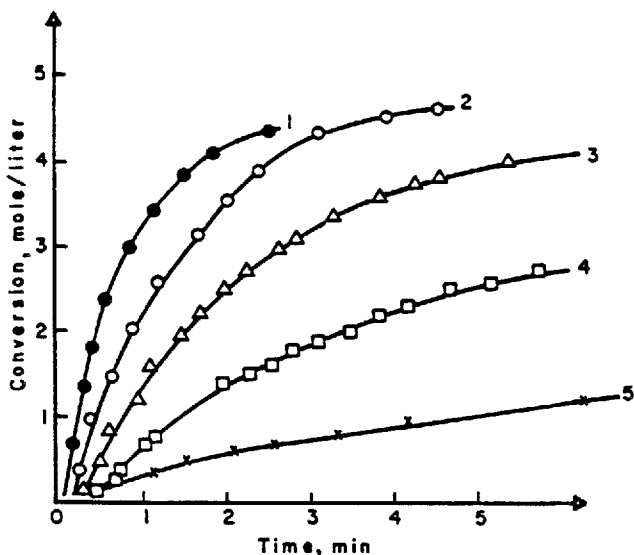
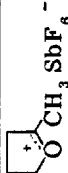


FIG. 1. Kinetic curves of dioxolane polymerization in the $\text{Et}_3\text{O}^+\text{SbCl}_6^- + \text{CH}_3\text{OCH}_2\text{Cl}$ system. $[\text{Et}_3\text{O}^+\text{SbCl}_6^-]$ and $[\text{CH}_3\text{OCH}_2\text{Cl}]$ are equal to: (1) 1.5×10^{-3} and 2.4×10^{-1} ; (2) 1.5×10^{-3} and 6×10^{-2} ; (3) 5×10^{-4} and 6.7×10^{-2} ; (4) 1.5×10^{-3} and 2.7×10^{-2} ; (5) 5×10^{-4} and 1.3×10^{-2} mole/l. $[\text{Dioxolane}]_0 = 6.4$ mole/l. $T = 20^\circ$ in CH_2Cl_2 .

systems under different conditions [2]. The only difference observed was a displacement of the CH_2 - and CH_3 -group bands towards the weak field in the $\text{CH}_3\text{-OCH}_2\text{-OCH}_2\text{Cl} + \text{SbCl}_5$ or SnCl_4 systems (with methylene chloride as solvent). No new bands indicating the formation of $\text{CH}_3\text{-O-CH}_2^+$ were observed in the 9τ region. The formation of $\text{CH}_3\text{-O-CH}_2^+$ was observed in a stronger polar solvent (CH_3NO_2) and at a lower temperature (-30°C) in the $^+\text{CH}_2\text{O-CH}_3 + \text{SbCl}_5$ system, but even in this case ionization is not complete ($< 40\%$).

The catalyst SbF_5 is of particular significance. Its activity is much higher than that of other Lewis acids (SbCl_5 , BF_3 , etc.). The high activity of SbF_5 is not necessarily due to the influence of a counterion on the chain propagation stage for it is known that counterions practically do not affect the initial rate of polymerization of tetrahydrofuran. The nature of the counterion may, in principle, influence the reaction rate by changing the ratio between free ions and ionic pairs, but the counterion cannot sufficiently affect the

TABLE I

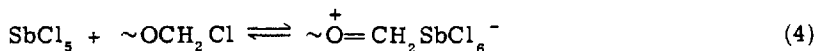
$\text{Ph}_3\text{C}^+\text{SbCl}_6^-$	$\text{Ph}_3\text{C}^+\text{Sb}^-\text{Cl}_6$	$\text{Ph}_3\text{C}^+\text{SbF}_6^-$	$\text{Ph}_3\text{C}^+\text{ClO}_4^-$	$\text{Et}_3\text{O}^+\text{SbCl}_6^-$	
(1)	(1)	(3)	(2)	(3)	(3)
1.4×10^{-4}	4.3×10^{-4}	1.7×10^{-4}	2.5×10^{-4}	2.4×10^{-4}	2×10^{-4}

dissociation constant of ionic pairs (see Table 1). Therefore, in the case of SbF_5 a large portion of Lewis acid was present in the form of an ionic particle.

But in what form was the portion of Lewis acid that had not converted into the ionic state present in the system? Our NMR, spectroscopic, cryoscopic, and other studies showed the un-ionized portion of Lewis acid present in the form of complex compounds with the monomer. For example, SnCl_4 forms a complex with dioxolane in a 1:2 ratio at 25°C with $K_{\text{equil}} = 50 \text{ l/mole}$.

General considerations lead one to presume that there is only partial ionization of Lewis acids in common solvents. There seems little likelihood that this is the case, however, when oxonium salts are used as polymerization catalysts. This is backed up by the work of Saegusa [3] which shows that the concentration of active centers was practically the same as the initial concentration of the catalyst for tetrahydrofuran polymerization on $\text{Et}_3\text{O}^+\text{BF}_4^-$ salt. However, experimental results indicate that in the case of oxonium salts the concentration of ionic active centers during the polymerization of cyclic acetals is significantly lower than the concentration of the original salt. It was established that introduction of $\text{CH}_3\text{OCH}_2\text{Cl}$ into the dioxolane + $\text{Et}_3\text{O}^+\text{SbCl}_6^-$ system results in reaction acceleration. The reaction proceeds without an induction period or self-acceleration (see Fig. 1). Chloromethyl ether introduced in the course of polymerization acted in the same way as when it was introduced at the very outset. The initial rate of the reaction was proportional to the concentration of $\text{Et}_3\text{O}^+\text{SbCl}_6^-$ with a constant concentration of chloromethyl ether. The relationship between the initial reaction rate and the concentration of chloromethyl ether is shown in Fig. 2.

The observed acceleration can be accounted for by proceeding from the assumption that the original salt $\text{Et}_3\text{O}^+\text{SbCl}_6^-$ decomposes under the action of dioxolane into neutral products with SbCl_5 and $\sim\text{OCH}_2\text{Cl}$ among them. The concentration increase of active centers when chloromethyl ether is added is due to the following reaction:



This mechanism is supported by the fact that dioxolane polymerization with $\text{Et}_3\text{O}^+\text{SbCl}_6^-$ and with SbCl_5 proceeds at practically the same rate.

The BF_4^- counterion was found to be much more stable than SbCl_6^- in acetal medium. Even when the system is thoroughly dried, dioxolane polymerization on $\text{Et}_3\text{O}^+\text{BF}_4^-$ proceeds with an induction period. The kinetics of the exchange reaction of ethylal and methylal is of an autocatalytic nature under the action of this salt. NMR studies

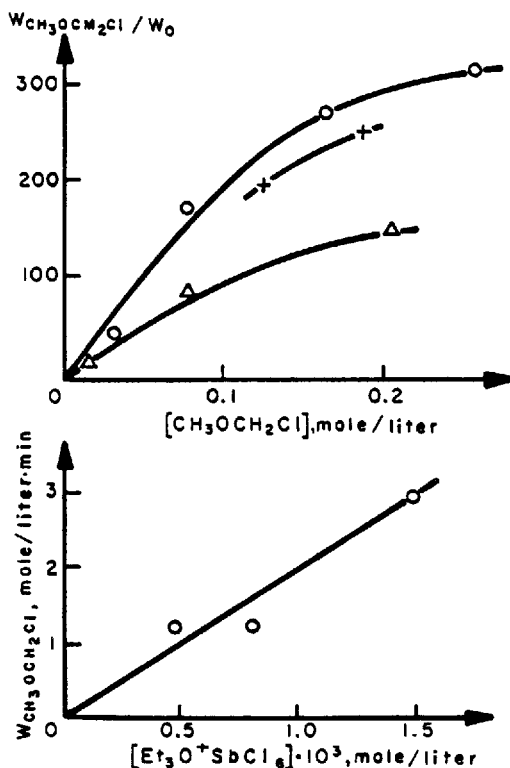


FIG. 2. Kinetic dependence of dioxolane polymerization on $Et_3O^+SbCl_6^- + CH_3OCH_2Cl$. Top: Dependence of relative polymerization rate on the concentration of CH_3OCH_2Cl : (○) $[Et_3O^+SbCl_6^-] = 1.5 \times 10^{-3}$ mole/l, $T = 20^\circ C$; (△) $[Et_3O^+SbCl_6^-] = 5 \times 10^{-4}$ mole/l, $T = 20^\circ C$; (+) $[Et_3O^+SbCl_6^-] = 1 \times 10^{-3}$ mole/l, $T = 12^\circ C$. Bottom: Dependence of polymerization rate on concentration of $Et_3O^+SbCl_6^-$: $[CH_3OCH_2Cl] = 6 \times 10^{-2}$ mole/l, $T = 20^\circ C$; $[dioxolane]_0 = 7.4$ mole/l in CH_2Cl_2 .

regarding the interaction of $Et_3O^+BF_4^-$ (0.1 mole/l) with methylal (0.1 mole/l) in a methylene chloride solution at $20^\circ C$ on nuclei H^+ and F^{19} indicate that both Et_3O^+ and BF_4^- undergo marked transformation in a period comparable with the reaction time [4].

Moreover, the addition of CH_3-OCH_2Cl had no effect on the catalytic activity of this salt during the processes of polymerization and exchange reactions of linear acetals.

The data obtained lead to the conclusion that in this case the original salt $\text{Et}_3\text{O}^+\text{BF}_4^-$ slowly converts to active centers under the action of some as yet unknown mechanism for the time comparable with the reaction time. According to this mechanism, additions of strong donors should react with the active centers and vigorously reduce the maximum reaction rate. The basicity of the donor is in direct proportion to the extent of its inhibiting capacity. As can be seen from Fig. 4, the strongest donors are tetrahydrofuran ($\text{pK} = 5$), dioxolane ($\text{pK} = 7.45$), and diethyl ether ($\text{pK} = 6.48$). Rapid equilibrium achievement should give a similar effect. Indeed, additives in this case simply reduce the portion of ionic particles that are capable of conducting the polymerization.

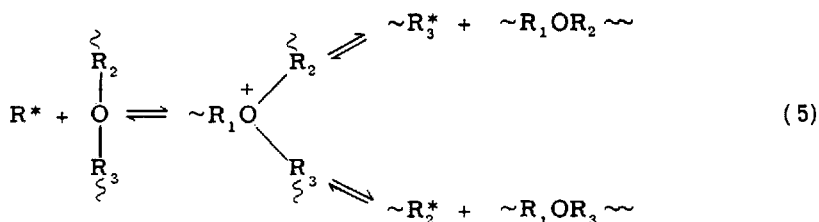
One can decide between these two mechanisms by studying the relation between the degree of polymerization and the time and degree of conversion. The degree of polymerization is linearly proportional to the degree of conversion in all cases. This means that no kinetic chain termination occurs. If, therefore, equilibrium formation of active centers occurs (even slowly), the additives will reduce the molecular weight increase of the derived macromolecules, but at the same extent of the reaction the degree of polymerization should also be the same. If complete kinetic termination of the active centers takes place (stable addition of the active center to the additive), the reaction rate is inversely proportional to the degree of polymerization at the same extent of the reaction. The lower reaction rate corresponds to the higher degree of polymerization, i.e., to a small number of growing chains.

Thus, in the case of $\text{Et}_3\text{O}^+\text{BF}_4^-$ and BF_3 , slow formation of very stable active centers takes place.

Let us consider some general mechanisms of macromolecular participation in the polymerization of heterocyclics.

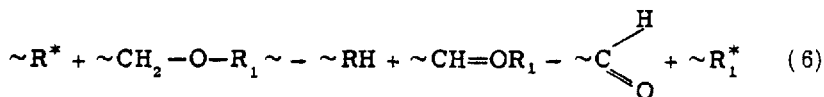
There are two such mechanisms in cationic polymerization [5, 6].

1. Formation of onium ions:



In this case any electrophilic particles including the growing active center or catalyst molecule attack any heteroatom of the macro-chain yielding an onium ion which can decompose in several directions, either regenerating the active center in homopolymerization or forming a new active center in copolymerization.

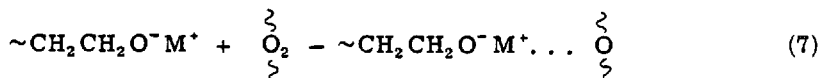
2. Hydride ion migration reactions:



The macromolecule in this case acts as a hydride ion donor. The resulting polymer cation may then decompose into two fragments, as illustrated in Reaction (6). The growing active center and catalyst molecules (carboxonium and carbonium salts, Lewis acids, protonic acids) may act as hydride acceptors.

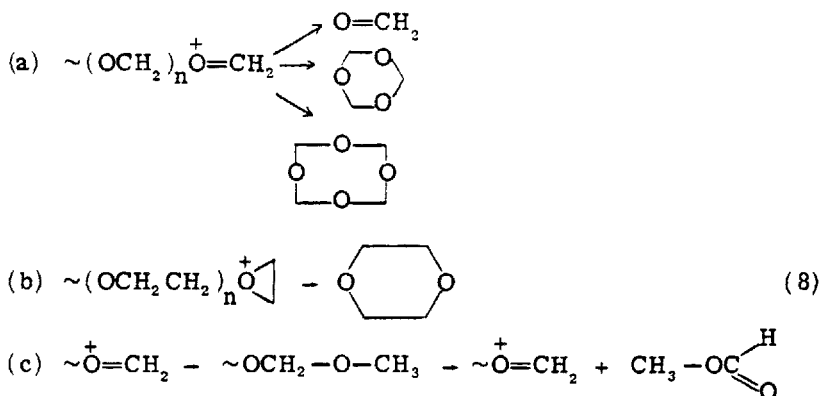
If in Reactions (5) and (6) the active electrophilic particle consists of the growing active center, a chain transfer reaction takes place; if it consists of original salt molecules, an initiation reaction takes place.

The most general mechanism of anionic polymerization of heterocycles is solvation of the counterion by the heteroatom of the macrochain:



What are the kinetic effects stemming from the above-mentioned reactions? Most important are the effects of these reactions on the properties of the polymer formed (molecular weight, molecular weight distribution, end group distribution, unit sequence distribution in copolymers). As follows from their mechanism, Reactions (5) and (6) should result in a statistical rearrangement of heterogeneous sequences in polymers (the end groups and units of various chemical natures). The intense effect of these reactions on polymer molecular weight distribution should be taken into consideration. In chain propagation only one additional unit is added to the length of the macromolecule, whereas in transfer reactions the unit added is comparable in length with the average chain. We shall not dwell on these problems as they have already been discussed [5, 7-11]. Let us simply note that interchain exchange reactions (Reaction 5) are also of practical interest as a special type of polymer synthesis and modification [5].

One of the possible effects of Reactions (5) and (6) may be the formation of low-molecular by-products due to the intramolecular nature of these reactions:



It is obvious in this case that a study of polymer kinetics by polymer accumulation and monomer consumption should have different results. The kinetic curve derived from polymer accumulation may not only lag behind the curve derived from monomer consumption, but even the shape of the kinetic curve may differ.

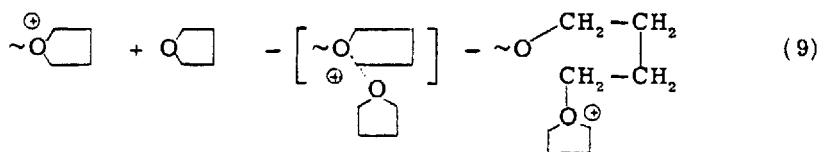
It should be noted that in some cases the formation of low molecular cycles predominates. Thus, during cationic polymerization of ethylene oxide, polymerization may be directed toward the formation of 1,4-dioxane as an end product.

It is also obvious that these reactions should be considered when determining the relative monomer reactivities for copolymerization reactions.

Let us consider how the above-mentioned macromolecular reactions affect the different elementary formation processes of macromolecules.

CHAIN PROPAGATION

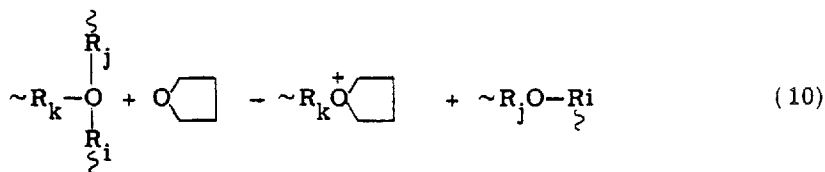
Owing to research on the polymerization mechanism of cyclic ethers, mainly with regard to tetrahydrofuran, it can be demonstrated that the growing active center in this case is a trialkyloxonium ion and the propagation reaction proceeds according to the bimolecular nucleophilic substitution mechanism (S_N2):



which is generally accepted at present. But what is the role of the "polymer" active centers $\left(\begin{array}{c} \zeta \\ \sim \text{O}^+ \\ \zeta \end{array} \right)$ in this process?

Kinetic studies of the polymerization of 5-, 4-, and 3-membered cycles made in our laboratory and by other research workers provide the following information.

There is a decrease in the rate of the propagation reaction on acyclic trialkyloxonium ions as the cycle size diminishes:



In the case of 4- and 3-membered oxides the rate of the propagation reaction on acyclic trialkyloxonium ions is so low that formation of such acyclic ions, resulting from the reaction of a growing trialkyloxonium ion with the polymer, may be considered to be a termination process of the reaction chain in the kinetic sense.

This relation between the reactivities of cyclic and acyclic trialkyloxonium ions in the series of 5-, 4-, and 3-membered oxides is not difficult to understand, considering that there is a sharp rise in the cycle stress in this series.

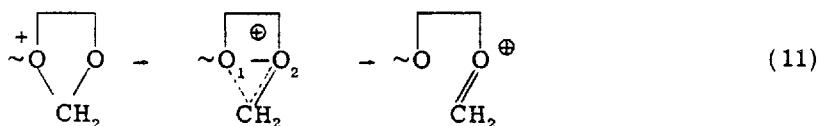
It should be noted that the rate constant for chain propagation of tetrahydrofurane on the acyclic trialkyloxonium ion is somewhat lower than on the cyclic ion. It has an insignificant effect on the total polymerization rate of tetrahydrofurane, since the concentration of acyclic trialkyloxonium ions, determined by the relation between the basicity and concentration of the monomer and polymer, is considerably lower than the concentration of cyclic trialkyloxonium ions.

It is far more difficult to explain the nature of the active center and the polymerization mechanism of cyclic acetals. Although a good deal of research has been done on this in different laboratories, further investigation is required.

For purposes of brevity we shall not dwell at length on the proof. Instead we shall point out that based on a critical analysis of the kinetics of separate polymerization of cyclic acetals and of copolymerization with vinyl monomers, aldehydes, and cyclic ethers of model exchange reactions of linear acetals and of data on the kinetics and mechanism of well-studied related nucleophilic substitution reactions of acetals (particularly acid-catalyzed hydrolysis reactions

of acetals, ketals, and orthoesters), we have concluded that for the polymerization of cyclic acetals the actual growing active centers are carboxonium ions which form during monomolecular decomposition of the trialkyloxonium ion [12].

It should be stressed that, unlike other known S_N1 substitution reactions at the saturated carbon ion (hydrolysis of haloid esters, for example), hydrolysis and other nucleophilic substitution reactions for acetals and orthoesters maintain the S_N2 mechanism in a wide range of experimental conditions and chemical structures of the substrate and reagent [12]. Such stability is remarkable and, we believe, is associated with the specific nature of the carboxonium ion in the transition state. It is felt that the transition state is quasi-bimolecular with synchronic breaking of $C-O_1$ bonds and formation of $C=O_2$ bonds for nucleophilic substitution reactions of acetals, ketals, and orthoesters, including polymerization reactions of cyclic acetals:



i. e., from the viewpoint of formal kinetics, the reaction proceeds according to the S_N1 mechanism and actually to the quasi-bimolecular mechanism.

Such an approach explains the relatively low activation energy values and high pre-exponential factors for the nucleophilic substitution reactions of acetals (polymerization hydrolysis and others). In this way the low requirements with regard to the geometry of the transition state, typical of S_N1 reactions, are combined with low activation energy values, characteristic of S_N2 reactions.

Let us consider the specific kinetic features of dioxolane polymerization under the action of triethyloxoniumhexachloroantimonate, which provides rapid initiation from the standpoint of S_N1 mechanisms. We have discovered that the kinetic curve cannot be described by the simple function where α and α_p are the current and equilibrium degrees of completion of dioxolane polymerization, respectively, and C_0 is the catalyst concentration.

$$d\alpha/dt = K_p C_0 (\alpha_p - \alpha) \quad (12)$$

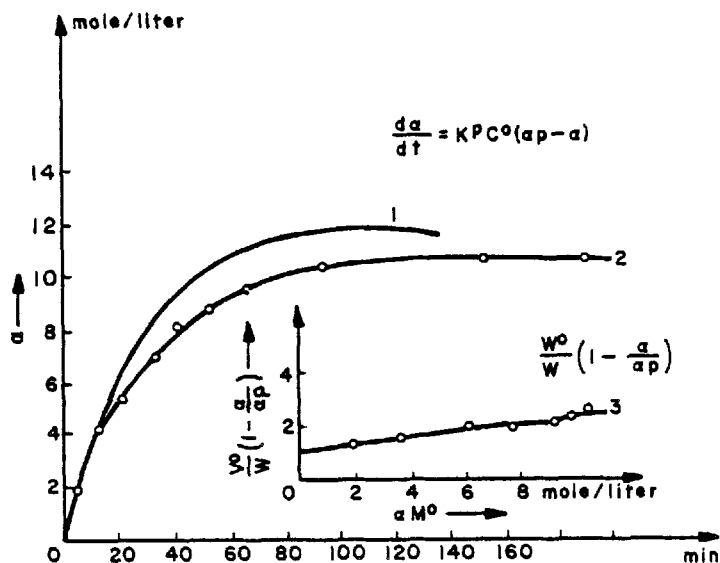


FIG. 3. Kinetic curves of dioxolane block polymerization under the action of triethyloxoniumhexachloroantimonate at 40°C. $C_0 = 3 \times 10^{-3}$ mole/l. (1) Calculated according to Eq. (11). (2) Experimental curve. (3) Dependence of $\frac{V_p}{V_p^0} \left(1 - \frac{\alpha}{\alpha_p}\right)$ on αM_0 .

Figure 3 shows that the experimental curve gradually lags behind the rate curve (the rate constant for propagation is estimated by the initial rate of polymerization). Special experiments show that the trivial cause of termination of active centers is not connected with this phenomenon. We have assumed that the decrease of the polymerization rate is associated with the interaction of the growing active center with a macromolecule, forming an inactive acyclic trialkyloxonium ion:



The formation of such polymer oxonium ions has been shown by directly measuring the viscosity of the "living" and terminated polymer. Such reactions should be indicated by the formation of

macromolecular aggregates containing labile bonds and an increase in the viscosity of the system. This was actually observed. The destruction of labile oxonium ions under the action of some nucleophilic reagent leads to a sharp decrease in the viscosity of the polymerizing system, as was expected.

Thus the ratio of the viscosity of the "living" polymer to the viscosity of the terminated polymer η_l/η_t , derived from dioxolane polymerization ($M_0 = 3$ moles/l), was equal to 2.8 at 30° C in a methylene chloride solution in the presence of triethylhexachloroantimonate ($C_0 = 1 \times 10^{-3}$ mole/l).

The η_l/η_t value may be determined on the basis of the following considerations.

The viscosity of concentrated polymer solutions is known to be described by the empirical equation

$$\eta = AC^5 \bar{M}_w^{3.4} \quad (14)$$

where A is a constant, C is the polymer concentration, and \bar{M}_w is the weight-average molecular weight.

The viscosity of the "living" polymer solution in this case may be described as

$$\eta_l = A(\alpha M_0)^5 \left[\frac{\alpha M_0}{C_0} M_g^\beta (1 + K_1 \alpha M_0) \right]^{3.4} \quad (15)$$

where αM_0 is the polymer yield,

$$C_0 \frac{1}{1 + K_1 \alpha M_0} = \sum_1^\infty R_1$$

is the number of chains, β is the polydispersion coefficient, M_g is the molecular weight of a polymer unit, and K_1 is the equilibrium constant of Reaction (13).

For the terminated polymer:

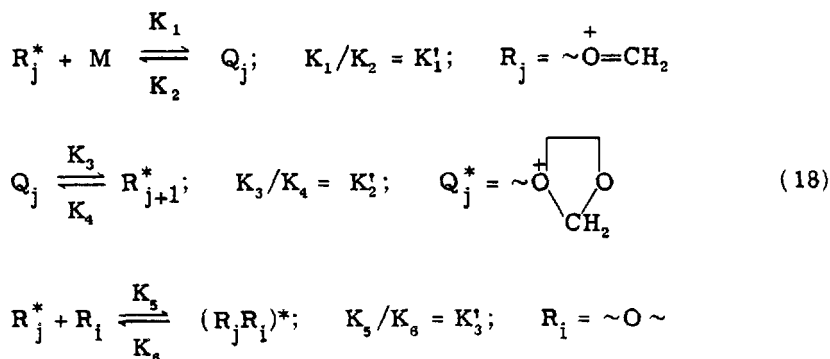
$$\eta_t = A(\alpha M_0)^5 \left[\frac{\alpha M_0}{C_0} M_g^\beta \right]^{3.4} \quad (16)$$

Hence

$$\eta_l/\eta_t = (1 + K_1 \alpha M_0)^{3.4} \quad (17)$$

The ratio η_1/η_t —calculated according to this formula using the value of $K_1 = 0.17$ l/mole determined from kinetic data (see Fig. 3)—is equal to 2.72, which coincides well with the value found experimentally.

The formation of complexes of growing active centers with macromolecules made it possible to describe the experimental kinetic curve of dioxolane polymerization. The kinetic scheme of the process may be marked down as follows:



The subscripts indicate the degree of polymerization.

It is not difficult to show that the polymerization rate equation for this scheme should be written as

$$\frac{d\alpha}{dt} = K_p C_o (\alpha_p - \alpha) = \frac{K_1 K_3 C_o (\alpha_p - \alpha)}{K_2 + K_3 + K_4 + K_1 M_o + [K_3' (K_2 + K_3) - K_1] \alpha M_o} \tag{19}$$

at $t = 0$

$$\left(\frac{d\alpha}{dt} \right)_0 = K_{\text{eff}o} C_o (\alpha_p - \alpha) = \frac{K_1 K_3}{K_1 + K_2 + K_3 + K_1 M_o} C_o (\alpha_p - \alpha) \tag{20}$$

where

$$\alpha_p = \frac{M_o - M_p}{M_o}; \quad M_p = \frac{K_1 K_3}{K_2 K_4} = \frac{1}{K_1' K_2'}$$

From Eq. (12) follows that

$$\frac{1}{K_{\text{eff}}} = \frac{K_2 + K_3 + K_4}{K_1 K_3} + \frac{1}{K_3} M_0 \quad (21)$$

Experimental checking of this equation has shown that $1/K_{\text{eff}}$ is not determined by M_0 within the limits of experimental error (Fig. 4). This denotes that $K_2 + K_3 + K_4 \gg K_1 M_0$.

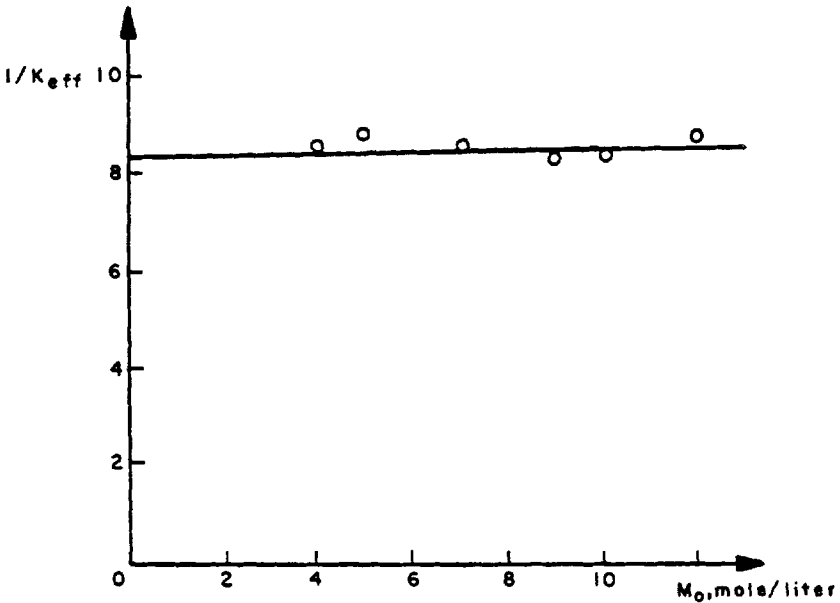


FIG. 4. Dependence of dioxolane polymerization effective rate constant reverse value on the initial monomer concentration.

For convenient experimental checking, Eq. (20) may be re-written as

$$\frac{W_0}{W} \left(1 - \frac{\alpha}{\alpha_p} \right) = 1 + \beta + K\alpha M_0 \quad (22)$$

where

$$\beta = \frac{K_4 + K_1 M_0}{K_2 + K_3}; \quad K = K'_3 - \frac{K_1}{K_2 + K_3}$$

and W and W_0 are the current and initial polymerization rates, respectively. The experimental kinetic curves of dioxolane polymerization with $\frac{W_0}{W} \left(1 - \frac{\alpha}{\alpha_p} \right)$ as a function of αM_0 are well described

by a straight line. Its intercept on the ordinate axis that is equal to unity (Fig. 3) shows $\beta \ll 1$, i.e., $K_2 + K_3 \gg K_4 + K_1 M_0$. Thus $K = K'_3$. The equation can now be simplified to give:

$$\frac{d\alpha}{dt} = K_1 C_0 (\alpha_p - \alpha) \frac{1}{1 + K'_3 \alpha M_0} \quad (23)$$

The equilibrium constant $K'_3 = 0.17$ l/mole is not temperature dependent within the limits of experimental error. This may be connected with different degrees of solvation of ions R_j^* and $(R_j R_1)^*$.

It is clear from the above discussion that, as a result of low basicity of the polymer system components, the acting catalyst is predominately in the form of carboxonium ions. Their concentration decreases with the conversion due to the formation of complexes with the developing macromolecules. Assuming that the dioxolane polymerization rate decrease is connected with the formation of a complex of the growing active center with a macromolecule, this effect should be artificially brought about by introducing polymers or polymer chain low-molecular analogs at the very outset of polymerization. In this case a decrease in the initial polymerization rate is to be expected. The extent of the decrease is directly proportional to the concentration of the additive. This was fully confirmed experimentally. The kinetic curves of dioxolane polymerization in the presence of methylal are tabulated in Fig. 5. The equilibrium constant of the reaction between the growing active center and a methylal molecule can be calculated from the depression of the initial rate according to

$$\frac{W_0}{W} \left(\frac{M_0^E - M_1}{M_0 - M_1} \right) = 1 + K_2 E_0 \quad (24)$$

where M_0^E and M_0 are the initial monomer concentrations with and without methylal addition, respectively, M_1 is the equilibrium monomer concentration, E_0 is the initial methylal concentration, and W and W_0 are the dioxolane polymerization rates with and without methylal addition, respectively. It equals 0.38 l/mole at 40°C. The difference in the basicity of polydioxolane and methylal is seen from the differences in the equilibrium constants of the reactions of the growing active center with the two molecules.

During the copolymerization of heterocycles, in addition to macromolecules and macromolecular fragments, "foreign" chains also react with the growing active centers [14].

Let us examine tetrahydrofuran and dioxolane copolymerization. Dioxolane polymerization kinetic curves in the presence of diethyl ether, modeled on the polytetramethylene oxide chain, are presented in Fig. 6. It is seen that the initial ether concentration increases inversely as the initial polymerization rate. The equilibrium constant derived from the depression of the initial rates is 0.89 l/mole at 40°C.

Figure 7 presents the kinetic curves of tetrahydrofuran polymerization in the presence of methylal, a low-molecular polydioxolane chain analog. The decrease in the polymerization rate noted in this case is associated with the formation of less active ions during the reaction between methylal and the growing active centers.

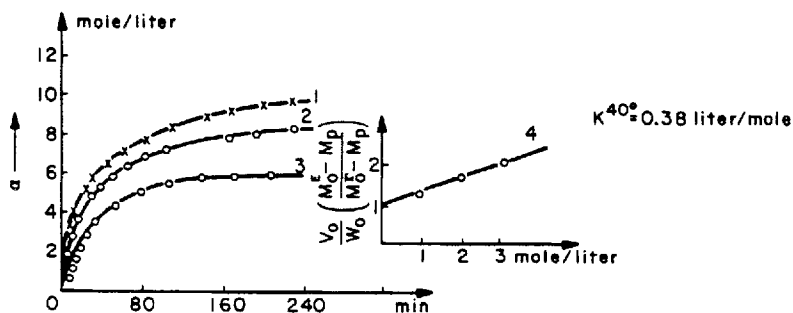


FIG. 5. Kinetic curves of dioxolane polymerization at 40°C under the action of $(C_2H_5)_3O^+SbCl_6^-$ ($C_0 = 3 \times 10^{-3}$ mole/l in the presence of methylal additions; M_0 and X_0 in moles/liter: (1) 12.9, 1.0; (2)

11.5, 2.0; (3) 10.1, 3.0; (4) dependence of $\frac{V_0}{W_0} \left(\frac{M_0^E - M_p}{M_0^r - M_p} \right)$ on E_0 (see explanation in text).

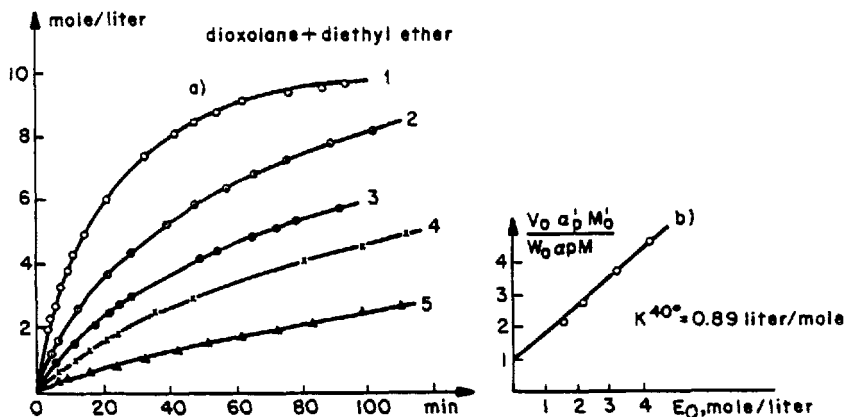


FIG. 6. (a) Kinetic curves of dioxolane polymerization in the presence of diethyl ether additions, in moles/liter: (1) 0; (2) 1.5; (3) 2.0; (4) 3.0; (5) 4.0; $C_0 = 3 \times 10^{-3}$ mole/l; $T = 40^\circ\text{C}$. (b) Influence of diethyl ether additions on the initial rate of dioxolane polymerization.

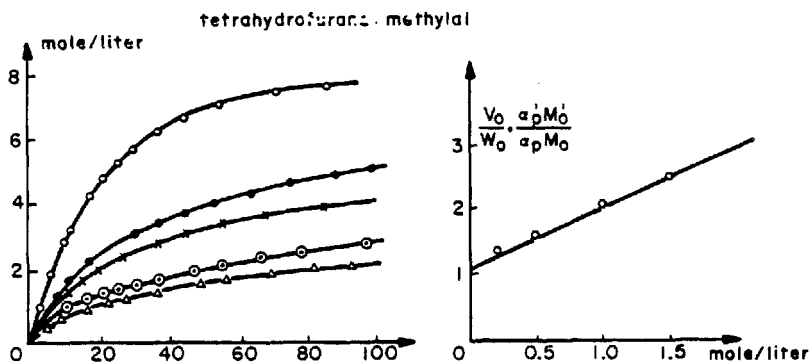


FIG. 7. Kinetic curves of tetrahydrofuran polymerization in the presence of methylal additions. $C_0 = 7 \times 10^{-3}$ mole/l; $T = 40^\circ\text{C}$; X_0 , in moles/liter: (O) 0; (●) 0.25; (×) 0.5; (⊙) 1.0; (Δ) 1.5.

The examples presented in this report clearly show the copolymerization mechanism of heterocyclics to be very complex and that the resulting macromolecules take part in donor-acceptor interactions with all electrophilic particles of the system. These reactions change the concentration of the active centers in the course of polymerization. This, in the final analysis, determines the specific kinetic features of the copolymerization of heterocyclics. In view of this we note that the ionic polymerization of heterocyclics cannot be described by the usual simple laws of copolymerization (the Mayo-Lewis equation). Copolymerization constants of heterocyclics published in the literature should be treated with caution since the reactions of growing active centers with macromolecules have not been taken into account.

A detailed study of the copolymerization mechanism of heterocycles with regard to reactions of the forming macromolecules should be made in each case to determine the relative monomer reactivities. Overlooking possible reactions of macromolecules in the course of formation of heterochain polymers may lead to serious errors in both the interpretation of experimental results and the explanation of the mechanisms of these reactions.

FORMATION OF ACTIVE CENTERS

An S-shaped kinetic curve has been obtained in many polymerization reactions of heterocyclics.

For instance, these are the processes that are involved in dioxolane polymerization with some Lewis (boron trifluoride etherate and antimony pentafluoride) and protonic acids (HClO_4 and HSO_3F). Examples are the kinetic curves of dioxolane polymerization under the action of boron trifluoride [15] (Fig. 8). It will be observed from Fig. 8 that the maximum induction period and rate of polymerization of dioxolane depend on the catalyst concentration, the former being inversely proportional and the latter directly proportional to the catalyst concentration.

A mathematical analysis of possible schemes of the observed processes provides evidence for concluding that autocatalysis is required to explain the experimental results. It may be assumed from general considerations that the catalyst not only reacts with monomer molecules, but also with polymer chains:



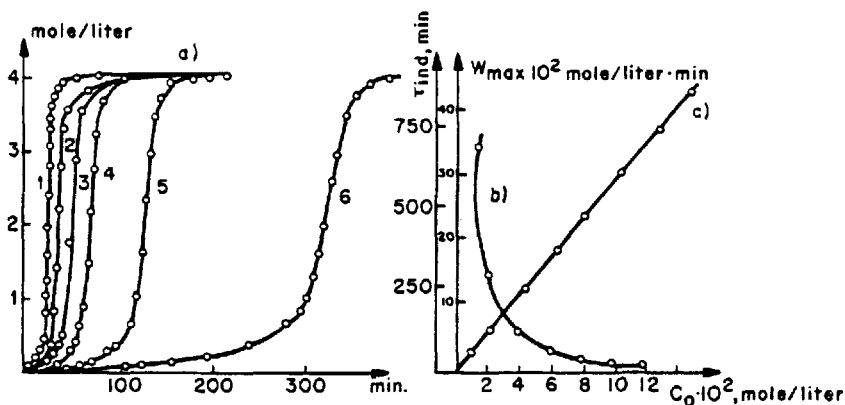


FIG. 8. (a) Kinetic curves of dioxolane polymerization in methylene chloride solution at 20°C under the action of $(C_2H_5)_2O \cdot BF_3$ [in (moles/liter) $\times 10^2$]: (1) 9.5; (2) 8; (3) 6; (4) 4; (5) 3; (6) 1. (b) Dependence of induction period on catalyst concentration. (c) Dependence of maximum rate on catalyst concentration.

If $K_2 \gg K_1$ and $K_1 \ll K_p$, the reaction would naturally be autocatalytic.

A direct result of this mechanism is the observed decrease of the induction period when polymer of low-molecular additives are introduced into the polymerizing system. This is evident from Fig. 8. Similar effects are found by using polymer or low-molecular analog additives in oligoxolane polymerization in the presence of SbF_5 and protonic acids. It should be noted that in the latter case the ratio of the reactivities of cyclic and acyclic acetals is the same as for the well-studied acid hydrolysis reaction for acetals.

The reaction between the catalyst and polymer has also been studied by direct destruction of polydioxolane under the action of boron trifluoride etherate [16]. The catalytic destruction of polydioxolane was carried out in a specially designed vacuum viscometer. The viscosity of the solvent of the initial polydioxolane solution and the kinetics of the changes of viscosity after mixing the catalyst with the polymer solution were determined in a single experiment.

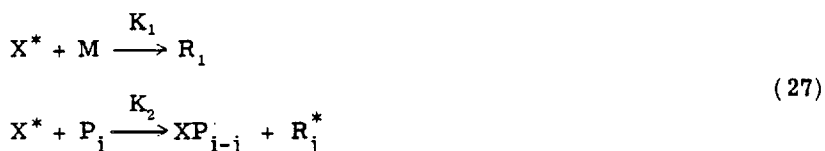
We have made a detailed mathematical analysis of the polymerization process, taking into consideration that initiation proceeds according to Scheme (25) and the process of catalytic destruction of polydioxolane. The relationships obtained for the maximum rate, the induction period, and the rate of catalytic destruction were compared with the experimental results. It should be noted that these results are in full

accord with the proposed kinetic mechanism, which takes into account the participation of macromolecules during the formation of active centers. The values of the constants of the elementary steps were found to be as follows: $K_1^{2.0} = 3.5 \times 10^{-4}$ l/mole sec; $K_2^{2.0} = 3.2 \times 10^{-2}$ l/mole sec; $K_p = 6.8 \times 10^{-2}$ l/mole sec; $K_2/K_1 = 38$.

There is another possible mechanism with regard to the participation of macromolecules in initiation processes (or rather, reinitiation processes) that may occur during the polymerization of heterocyclics in the presence of low-molecular transfer agents [17]. Generally, as a result of chain transfer to the low-molecular compound XY, an active fragment X^* may form:



Its reactivity in relation to the monomer differs from that of the growing active center. Reinitiation may proceed with the reaction of the active fragment X^* and monomer and polymer molecules:



If $K_2 \gg K_1$ and $K_1 \ll K_p$, there should be an unusual autocatalytic-type consumption of the chain transfer agent (according to the physical viewpoint and calculations). This was actually observed in studying dioxolane polymerization under the action of trialkyloxonium salts in the presence of p-nitrophenol. The chain transfer kinetics was spectrophotometrically controlled by the accumulation of p-nitrophenoxy end groups.

A similar effect should be observed during polymerization of cyclic acetals in the presence of any other transfer agents which form protons due to chain transfer.

In conclusion, mention should be made of the formation reactions of active centers, their nature, and their reactivities during the polymerization of cyclic acetals. Many laboratories have recently used direct spectroscopic (NMR on various nuclei, UV spectroscopy) and conductive methods to study model reactions in working on this problem. It has been found that various chemical conversions of the counterion take place and that the concentration of growing active centers is much lower than the catalyst concentration. It should be noted that up to now no direct correlation has been established

between the conversion of active particles in the system and the rate of polymerization. The results obtained thus far are of a qualitative nature. There is no doubt that a strictly quantitative approach is essential for comprehending the complex diversity of chemical conversions that occur during the initiation of the polymerization of cyclic acetals by various catalytic systems and for understanding the mechanisms of these interesting processes.

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