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Kinetics of Polymerization of 1,3-Dioxolan Initiated by $C_6H_5CO^+SbF_6^-$ and $(C_6H_5)_3C^+SbF_6^-$ Salts

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ABSTRACT

Polymerizations of 1,3-dioxolan initiated by oxycarbenium salt $C_6H_5CO^+SbF_6^-$ and triphenylmethylium salt $(C_6H_5)_3C^+SbF_6^-$ proceed with induction periods. $C_6H_5CO^+SbF_6^-$ initiates polymerization by a direct addition, while initiation with $(C_6H_5)_3C^+SbF_6^-$ proceeds through the intermediately formed 1,3-dioxolan-2-ylium salt. Kinetic analysis of polymerization of 1,3-dioxolan, initiated by oxycarbenium salt or triphenylmethylium salt revealed that, in spite of different chemisty of initiation, both processes proceed with a slow initiation on monomer and fast initiation on polymer. The pertinent kinetic equations were derived and it was found, that the rate constant of propagation ($\bar{k}_p$) does not depend on the structure of initiator used, being equal to 25 ± 5 liter/mole-sec (0°C, CH_2Cl_2 or CH_3NO_2).

INTRODUCTION

Difficulties in the quantitative analysis of the kinetics of polymerization of 1,3-dioxolan (I) are, at least partially, connected with a much higher rate of propagation than the rate of initiation. This gives eventually kinetic curves with autoacceleration periods [1-3]. The chemistry of initiation was studied in detail only for the 1,3-dioxolan-2-ylium salts in connection with their ambident reactivities [4].

Recently, we observed that in the polymerization of I initiated with benzoylium hexafluoroantimonate ($C_6H_5CO^+SbF_6^-$) (II), II was quantitatively introduced into the macromolecules as the polymer endgroups, indicating that initiation proceeds by a direct addition of the oxocarbenium cation [5].

The degrees of polymerization calculated on the basis of the reacted monomer and initiator were within an experimental error (avg. ±15%) equal to the degrees of polymerization measured either from endgroups (UV or ^{1}H-NMR) or osmometrically. These findings indicate that polymerization proceeded without any noticeable transfer and that the concentration of macrocycles formed, e.g., by back-biting reaction (including also the end-to-end closure), is not higher than the error in the determination of $\overline{DP}_n$. This is even higher than the concentration of macrocycles that can be expected according to Jacobson-Stockmayer theory [6].

In this paper the kinetics of polymerization of I initiated by II is described and compared with the kinetics of polymerization of I initiated with $(C_6H_5)_3C^+SbF_6^-$ (III), in which initiation is preceded by hydride anion transfer from I to III.

Because of the low solubility of II in CH_2Cl_2, CH_3NO_2 was used as a solvent for this system. Polymerization with III was studied in both CH_2Cl_2 and CH_3NO_2, and results for both solvents are compared.

EXPERIMENTAL

1,3-Dioxolan (I) (Koch & Light) was purified by several distillations from sodium and stored on a vacuum line in a reservoir closed with a Teflon stopcock over Na/K alloy. According to GLC the total concentration of impurities was lower than 0.01%.

Methylene dichloride solvent was washed several times with fuming sulfuric acid, then with 5% solution of $NaHCO_3$, and finally with water, dried with $CaCl_2$, and fractionated several times from CaH_2. CH_2Cl_2 was stored on a vacuum line in a reservoir closed with a Teflon stopcock over a sodium mirror. The concentration of impurities (GLC) was lower than 0.005%. The concentration of H_2O is below 10^{-6} M, if a sodium mirror is used [7].

Nitromethane solvent was purified by several fractionated vacuum distillations from CaH_2 and stored on a vacuum line, in a reservoir closed with a Teflon stopcock. The concentration of impurities (GLC) was lower than 0.01%.

1,3-Dioxolan-2-ylium hexafluoroantimonate (IV) was prepared and purified as described elsewhere [4].

Triphenylmethylium hexafluoroantimonate (III) (Ozark-Mahoning, Tulsa, Oklahoma) was purified as described previously [4].

Benzoylium hexafluoroantimonate (II) was prepared from benzoyl fluoride and antimony pentafluoride by mixing both compounds in SO_2 solvent at -50°C. The solid, colorless or slightly yellow salt precipitates upon addition of Freon 113. After isolation, this salt was purified by dissolution in liquid SO_2 and precipitation with Freon 113. The colorless product was finally washed several times with CH_2Cl_2 and dried under vacuum. All of the described operations were performed on the vacuum line. Final purity, based on the ^1H NMR data was $> 95\%$ [8].

Freon 113 may also be used as the reaction medium. In this case, II precipitates immediately after mixing the solutions of SbF_5 and C_6H_5COF in Freon 113 at -50°C. After isolation, II may be purified by dissolution in CH_3NO_2 and precipitation with CH_2Cl_2. Purity of II is usually better if prepared by the former method.

Polymerization was conducted in dilatometers sealed in vacuo. Final purification of reagents and filling of the dilatometers were performed by using a standard vacuum-line technique.

RESULTS AND DISCUSSION

Kinetics of 1,3-Dioxolan Polymerization Initiated by $C_6H_5CO^+SbF_6^-$

Kinetics of polymerization of I was studied dilatometrically in CH_3NO_2 solvent. Semilogarithmic anamorphoses of typical kinetic curves are shown in Fig. 1.

The rate of polymerization increases initially, and eventually reaches a constant value. In our previous paper [5], it was shown, that initiation in this system proceeds quantitatively and that macromolecules contain the initiator fragment $C_6H_5C(O)O-$ as one of the endgroups. Thus, it is reasonable to assume that the stationary stage of polymerization starts, when the initiation is completed. The concentration of active species becomes at this stage equal to the starting concentration of initiator $[II]_0$.

If the mechanism of polymerization were described by a simple kinetic scheme, with merely slow initiation and fast propagation:

$$\text{II} + \text{I} \xrightarrow{k_i} M^*$$

$$M^* + n\text{I} \xrightarrow{k_p} \text{poly-I}^* \qquad k_p > k_i \qquad (1)$$

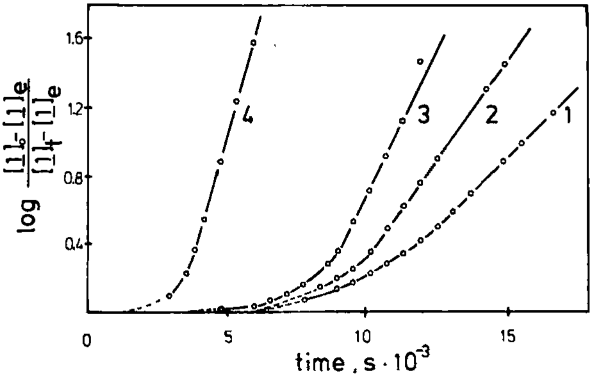


FIG. 1. Kinetic curves of 1,3-dioxolan (I) polymerization initiated with varying concentrations of $C_6H_5CO^+SbF_6^-$ (II): (1) 1.15×10^{-4} M; (2) 1.75×10^{-4} M; (3) 3.50×10^{-4} M; (4) 5.00×10^{-4} M. 0°C; CH_3NO_2; $[I]_0 = 3.0$ M.

then the kinetics of an acceleration period should have been described by the Eq. which is a solution of scheme (1) [9]:

$$\log\left(\frac{-d\ln\{([I]_0-[I]_e)/([I]_t-[I]_e)\}}{dt}\,\frac{1}{\bar{k}_p[II]_0}+1\right) = -\frac{k_i}{2.303}\int_0^t [I]_t\,dt \qquad (2)$$

In order to verify the validity of Eq. (2) for the system under study, the values of $d\ln\{([I]_0 - [I]_e)/([I]_t - [I]_e)\}/dt$ for a given t were determined graphically as tangents of a plot of $\ln\{([I]_0 - [I]_e)/([I]_t - [I]_e)\}$ versus time, and the corresponding integrals were calculated from the area under a kinetic curve ($[I]_t$ vs time). The values of $\bar{k}_p$ were determined from the linear parts of kinetic curves, as described in the next paragraph.

The plots of the left-hand side of Eq. (2) against $\int_0^t [I]_t dt$ were however found to be nonlinear, their curvature indicating that the rate of initiation increases with increasing conversion of I into poly-I (Fig. 2).

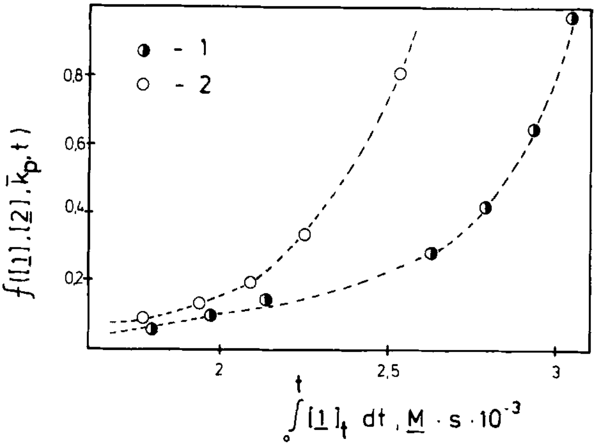
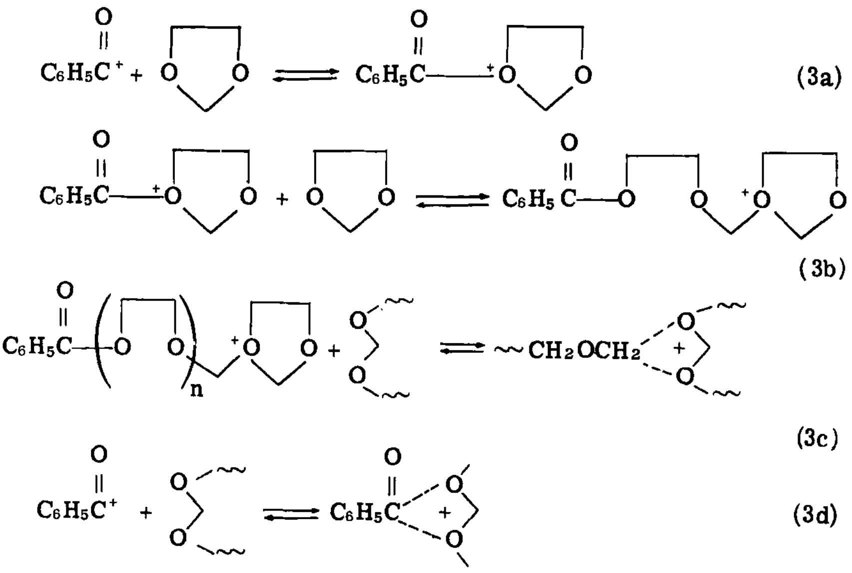
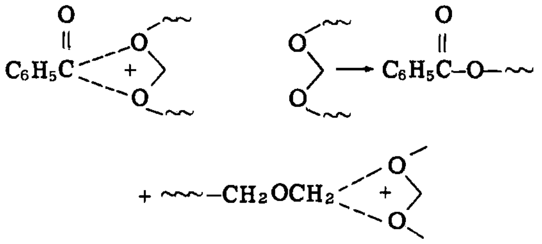


FIG. 2. Kinetic curves of 1,3-dioxolan (I) polymerization initiated with varying concentrations of $C_6H_5CO^+SbF_6^-$ (II), plotted according to Eq. (2): (1) $[II]_0 = 1.75 \times 10^{-4}$ M; (2) $[II]_0 = 3.50 \times 10^{-4}$ M. 0°C; CH_3NO_2; $[I]_0 = 3.0$ M. $f([I], [II]k_p, t) = -\log\{1 - d\ln[([I]_0 - [I]_e)/([I]_t - [I]_e)]/dt\, k_p[II]_0\}$.

Thus, to account for the observed autocatalytic kinetic curves, we propose the scheme of initiation shown in Eqs. (3), in which the polymer takes part in the initiation reaction (anions omitted):





(3e)

The rates of cationation [reactions (3a) and (3d)] are apparently high, the reaction in both cases being a reversible process. The next step of the reaction, i.e., addition of the second monomer molecule [reaction (3b)] is also reversible. This reaction involves a nucleophilic attack of the oxygen atom of the incoming monomer molecule on the carbon atom in α position to the oxygen bearing the positive charge. The forward reaction (3b) should be slow, because of the steric hindrance involved due to the presence of a bulky $C_6H_5C(O)-$ moiety, which makes difficult an approach of the second monomer molecule.

This factor is probably responsible for a complete inhibition of the similar reaction with an oxonium ion, bearing a still more bulky moiety $(C_6H_5)_3C-$, as will be discussed in the next paragraph. Consequently, in the reaction path described by Eqs. (3a)-(3c) there is at least one relatively slow and reversible reaction. Thus, the conditions are created, when even in the presence of a low amount of poly-I, formed slowly through reactions (3a)-(3c), the majority of initiator reacts rather through reaction path described by Eqs. (3d)-(3e), because this part of the scheme involves an irreversible transformation of initiator into growing species [reaction (3e)]. The net effect, would be the increasing importance of reactions (3d) and (3e), with increasing concentration of poly-I. Thus, the oxonium ions formed in the reversible reactions (3a)-(3c), would serve only as a kind of reservoir of $C_6H_5CO^+SbF_6^-$ ions which are used up in an irreversible reaction (3e). The rate of reaction (3e) increases with increasing concentration of poly-I. Scheme (3) is too complicated to be analyzed quantitatively. The validity of this scheme for our system, however, can be examined by an approximate treatment, in which scheme (3) is reduced to the simpler scheme (4):

$$\begin{aligned}
&\text{II} + \text{I} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Ox} \rightleftharpoons \text{M}^* \text{ (slow)}\\
&\text{M}^* + \text{I} \overset{\bar{k}_p}{\rightleftharpoons} \text{poly-I (P) (fast)} \qquad (4)\\
&\text{II} + \text{poly-I} \xrightarrow{k_{iP}(\text{eff})} \text{M}^* \text{ (fast)}
\end{aligned}$$

where: $k_{ip}(\text{eff})$ is the effective rate constant of initiation, Ox denotes an oxonium ion formed in reaction (3a), and M* is the active species (oxonium ions) of various polymerization degrees n, where $n > 2$.

Solution of scheme (4), given in the Appendix, leads to the Eq. (5):

$$\ln\left(1 - \frac{d\ln([I]_0 - [I]_e)/([I]_t - [I]_e)}{dt}\,\frac{1}{k_p[II]_0}\right) = -k_{ip}(\text{eff})\int_0^t([I]_0 - [I]_t)dt + \ln\left(1 + \frac{k_1}{k_{-1}}[I]_t\right) \qquad (5)$$

The apparent rate constants k_1, k_{-1}, and $k_{ip}(\text{eff})$ have no simple physical meaning; thus, by using Eq. (5) one can only prove whether the proposed kinetic scheme and experimental results are compatible. If the kinetic scheme indeed describes the process, then the plot of the left-hand side of Eq. (5) against $\int_0^t([I]_0 - [I]_t)dt$ should give a straight line. Because $[I]_t$ changes slowly during the acceleration period, it was assumed that $1 + (k_1/k_{-1})[I]_t = \text{const}$. The corresponding plots, constructed for three typical kinetic runs according to Eq. (5) are shown in Fig. 3. The linearity of the plots indicates, that the kinetic analysis is in agreement with a proposed reaction scheme and that the propagating active species are predominantly formed in the reaction of II with poly-I. The effective rate constant of initiation with poly-I derived from this approximate treatment was found to be $k_{ip}(\text{eff}) = 4.7 \times 10^{-3}$ liter/mole-sec (0°C, CH_3NO_2).

Kinetics of 1,3-Dioxolan Polymerization Initiated by $(C_6H_5)_3C^+SbF_6^-$

Initiation of polymerization of I by $(C_6H_5)_3C^+SbF_6^-$ (III) proceeds through an intermediate formation of the hydride transfer reaction product: 1,3-dioxolan-2-ylium salt (III), while oxonium ion, formed in the parallel reaction, does not lead directly to macromolecules [3].

The hydride transfer reaction is relatively fast $k_H \sim 10^{-2}$ liter/mole-sec at 25°C; thus neither characteristics of an early stage of polymerization nor its rate during the stationary period of polymerization changes, if preformed IV is used as initiator instead of III [3].

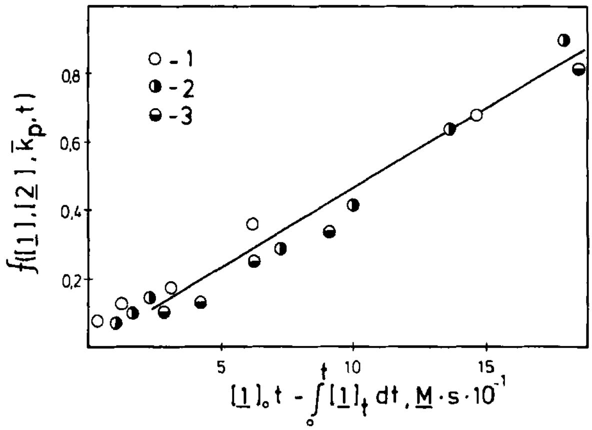
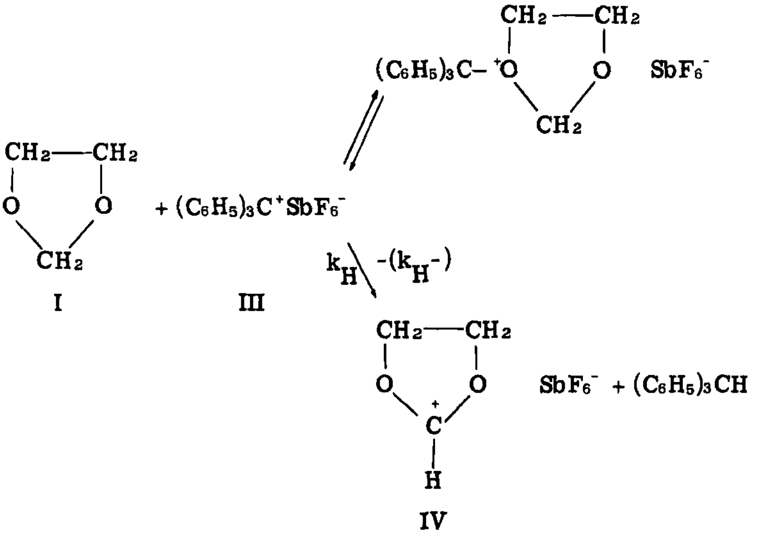
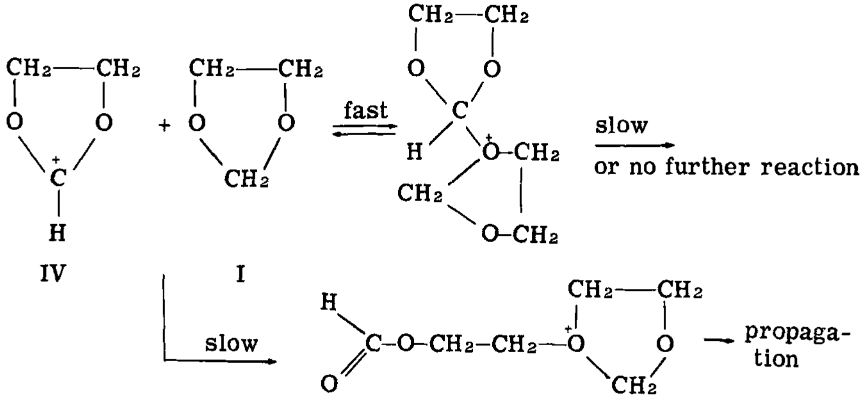


FIG. 3. Kinetic curves of 1,3-dioxolan (I) polymerization initiated with varying concentrations at $C_6H_5CO^+SbF_6^-$ (II), plotted according to Eq. (5): (1) 1.15×10^{-4} M; (2) 1.75×10^{-4} M; (3) 3.50×10^{-4} $\underline{M}$. 0°C; CH_3NO_2; $[I]_0 = 3.0$ $\underline{M}$; $f([I], [II], \bar{k}_p, t) = -\ln(1- d\ln \{([I]_0 - [I]_e)/([I]_t - [I]_e)\}/dtk_p[I]_0)$.

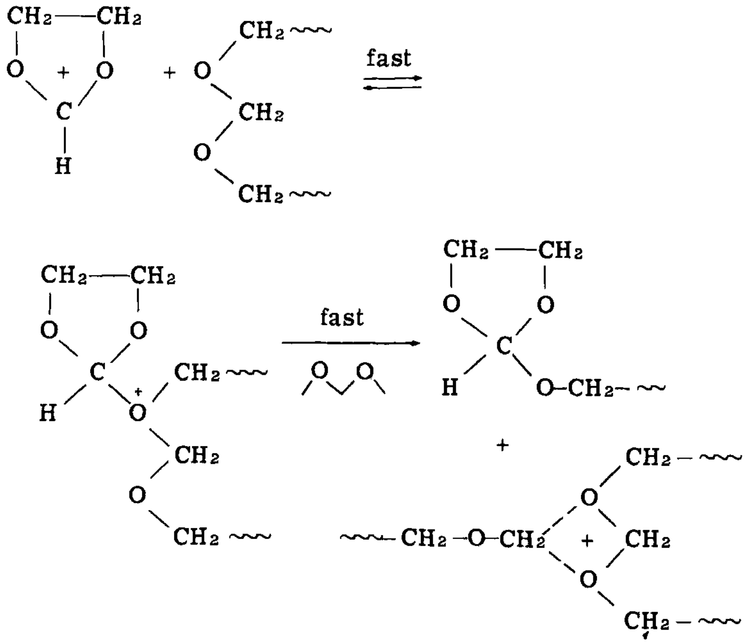


(6)

According to our model studies, IV reacts with I and poly-I with different rate constants, the rate constant of reaction with poly-I (k_{ip}) being much higher than the rate constant of reaction with I [4]. The chemistry of these reactions is shown in scheme (7):



(7a)



(7b)

Applying a concept of two parallel initiation reactions, described in scheme (7), and proceeding with different rate constants, one obtains the formal kinetic scheme (8):

$$\begin{aligned} &IV + I \xrightarrow{k_{iM}} M^* \\ &M^* + nI \underset{}{\overset{\bar{k}_p}{\rightleftharpoons}} \text{poly-}I \\ &IV + \text{poly-}I \xrightarrow{k_{ip}} M^* \end{aligned} \tag{8}$$

where M* denotes active species and $k_{ip} \gg k_{iM}$.

Solution of this scheme, similar to that given in the Appendix, leads to the Eq. (9):

$$\frac{1}{t}\ln\left(1 - \frac{d\ln\{([I]_0 - [I]_e)/([I]_t - [I]_e)\}}{dt} \Big/ \bar{k}_p[IV]_0\right) = -k_{ip}[I]_0 - (k_{iM} - k_{ip})\int_0^t [I]_t dt/t \tag{9}$$

Formally a similar kinetic scheme was also proposed by Enikolopyan and Rosenberg [10], although the mathematical treatment of these authors did not give access to the corresponding rate constants, namely, k_{iM} and k_{ip}.

Following the method described above, values of $d\ln\{([I]_0 - [I]_e)/[I]_t - [I]_e)\}/dt$ were determined as tangents of a plot of $[I]_t$ versus time for a given time and the corresponding integrals were calculated by measuring the area under the curve of a plot of $([I]_0 - [I]_e)/([I]_t - [I]_e)$ versus time. A typical plot, constructed according to Eq. (9), is given in Fig. 4.

After applying the same treatment to the number of kinetic curves an average value of k_{ip} was found equal to $6 \pm 2 \times 10^{-3}$ liter/mole-sec (0°C, CH_3NO_2) the k_{iM} value being too low to be determined by this method. The upper limit of k_{iM} was estimated to be 10^{-4} liter/mole-sec at 0°C. The same kinetic pattern was observed for the polymerization of I in methylene chloride solution. Induction periods are,

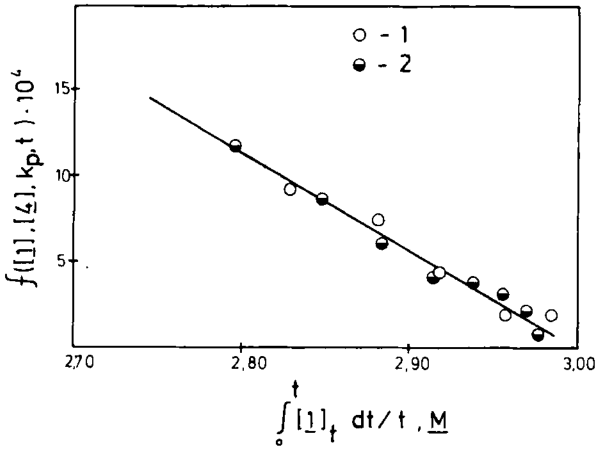


FIG. 4. Kinetic curves of 1,3-dioxolan (I) polymerization initiated with various concentrations of 1,3-dioxolan-2-ylium hexafluoroantimonate (IV), plotted according to Eq. (9): (1) [IV] = 4.40×10^{-4} M; (2) [IV] = $4.60 \times 10^{-}$ M. 0°C; CH_3NO_2; $[I]_0 = 3.0$ M.

$f([I], [IV], \bar{k}_p, t) = 1/t\,(-\,d\ln\{([I]_0 - [I]_e)/[I]_t - [I]_e)\}/dt\, k_p\, [IV]_0 + 1).$

however, longer than for polymerizations carried out in CH_3NO_2 solvent, indicating that k_{ip} is lower in methylene chloride. Indeed, by using the method described above, it was found that k_{ip} is equal to $3 \pm 1 \times 10^{-3}$ liter/mole-sec (10°C, CH_2Cl_2 solvent).

The logical consequence of such a scheme of initiation, according to which active species are formed predominantly in the fast reaction of an initiator with poly-I should be the possibility of decreasing the length of the induction period by introducing a poly-I from the beginning of the reaction. Instead of poly-I, the low molecular weight model of a unit of poly-I, namely, dimethoxymethane ($CH_3OCH_2OCH_3$) was used. Preliminary results, showing the removal of the autoacceleration period by addition of dimethoxymethane were discussed earlier by Penczek [3].

Kinetic curves (semilogarithmic anamorphoses) of polymerization of I initiated with IV in the presence of dimethoxymethane are shown in Fig. 5. Thus, in agreement with the proposed initiation scheme, addition of a model of poly-I at the beginning of polymerization results in considerable increase of a rate of initiation. Kinetics of this polymerization is also, as expected, described by Eq. (9), provided that concentration of polymer, being equal to $[I]_0 - [I]_t$ for the

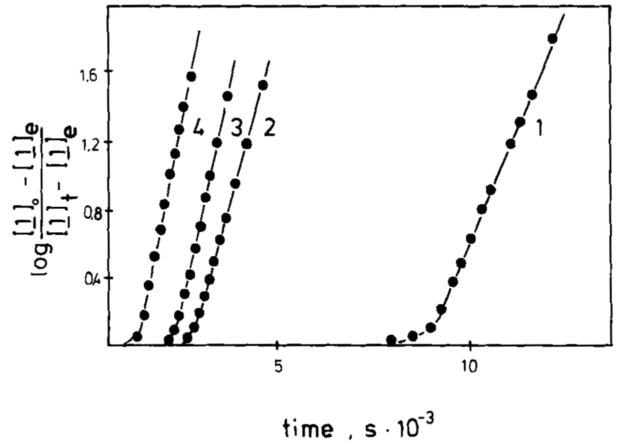


FIG. 5. Kinetic curves of 1,3-dioxolan (I) polymerization initiated with 1,3-dioxolan-2-ylium hexafluoroantimonate (IV) in the presence of dimethoxymethane: $[CH_3OCH_2OCH_3]_0$ = (1) 0; (2) 0.02 M; (3) 0.80 M; (4) 1.10 M. 25°C; CH_2Cl_2; $[I]_0 = 3.0$ M; $[IV]_0 = 1.7 \times 10^{-4}$ M.

polymerization in the absence of diethoxymethane is expressed as $([I]_0 - [I]_t) + [\text{dimethoxymethane}]$.

Analysis of kinetics plots gives values of k_{ip} slightly higher than those obtained for polymerization in the absence of dimethoxymethane and equal to $k_{ip} = 5 \pm 2 \times 10^{-3}$ liter/mole-sec (10°C, CH_2Cl_2 solvent) (3 ± 1 liter/mole-sec without dimethoxymethane added).

Taking into account the fact, that, because of insufficient accuracy of our kinetic measurements in the region of low conversion, the scattering of our results is rather high, the agreement between these two k_{ip} values is an additional argument for the validity of the proposed mechanism of polymerization.

Kinetics of the Stationary Period of Polymerization and Determination of $\bar{k}_p$

After completion of the autoacceleration period, polymerization of I initiated with either II or III becomes a steady-state process. Thus

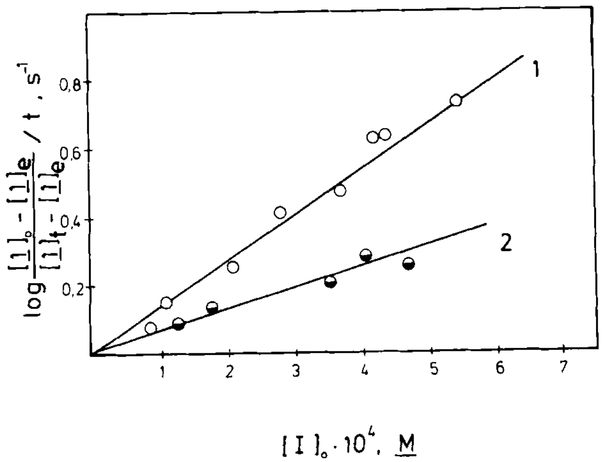


FIG. 6. Dependence of the rate of the stationary polymerization of 1,3-dioxolan on the starting concentration of initiator: (1) $(C_6H_5)_3C^+SbF_6^-$, 25°C, CH_2Cl_2; (2) $C_6H_5CO^+SbF_6^-$; 0°C; CH_3NO_2.

the semilogarithmic anamorphoses of the conversion curves are linear until equilibrium conditions ar reached. In the previous sections of this paper, it was assumed that, the concentration of active species at this stage of polymerization, is equal to the starting concentration of an initiator. For the polymerization of I initiated by II, it was shown in an independent study [5] that if polymerization is stopped even before equilibrium is reached (during the stationary stage), then all of the initiator (± 15%) is incorporated into poly-I as end groups. On this basis and taking into account the linearity of the semilogarithmic plots, we assumed that equality $[M^*] = [II]_0$ holds. In agreement with this assumption, the rate of polymerization was found to be proportional to the starting concentration of initiator, as it is shown in Fig. 6 for both initiators II and III.

Thus, the rate constant of propagation $\bar{k}_p$ can be determined from the slopes of the semilogarithmic plots:

$$\bar{k}_p = \ln \{([I]_0 - [I]_e)/([I]_t - [I]_e)\}/[II]_0 t \tag{12}$$

From Fig. 6, $\bar{k}_p$ was found to be equal to 25 ± 5 liter/mole-sec (0°C, CH_3NO_2). The notation $\bar{k}_p$ indicates that this value does not discriminate between ions and ion pairs.

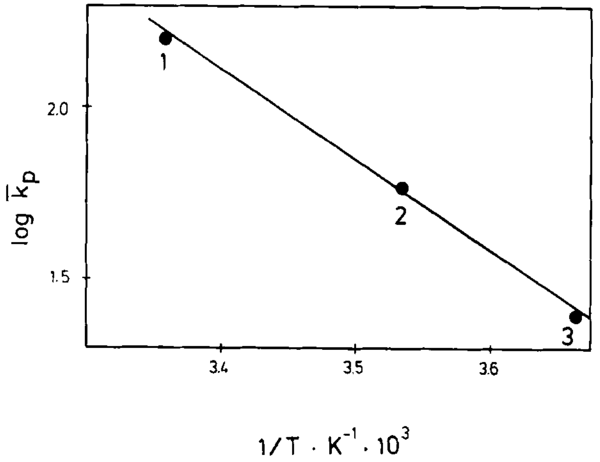


FIG. 7. Dependence of the logarithm of the apparent rate constant of 1,3-dioxolan propagation on reciprocal of absolute temperature: (1, 2) $(C_6H_5)_3C^+SbF_6^-$, CH_2Cl, $CH_3OCH_2OCH_3$ added; (3) $C_6H_5CO^+SbF_6^-$, CH_3NO_2.

These values are slightly higher than the apparent rate constants of propagation of polymerization of I initiated with $(C_6H_5)_3C^+SbF_6^-$ in CH_2Cl_2 solvent ($\bar{k}_p$ = 10 liter/mole-sec at 0°C). In the latter system it was found, however, that in the presence of dimethoxymethane not only is the rate of initiation higher, but also the measured rate constant of propagation increases approximately by a factor of 2. These findings were tentatively explained by assuming that during the induction period, the concentration of $-OCH_3$ groups (formed as a result of H^- ion transfer from I to the transient . . . $-O\overset{+}{=\!=}CH_2$ cations) becomes lower with increasing concentration of dimethoxymethane [3]. Methoxy groups participate in the formation of the nonreactive oxonium ions, decreasing in this way the number of the active species. In the presence of dimethoxymethane, induction periods are considerably shortened; thus hydride transfer reaction, being a source of $-OCH_3$ groups, is less important, and the apparent rate constants of propagation eventually reach, at a certain concentration of dimethoxymethane added, their true value [3]. In CH_3NO_2 solvent the rate of initiation is higher; consequently the hydride transfer reaction is of little importance.

In Fig. 7 the dependence of ln $\bar{k}_p$ on 1/T is given. Points at 25°C and 10°C represent the average values of $\bar{k}_p$ in CH_2Cl_2 solvent with dimethoxymethane added, while the point at 0°C represents an average $\bar{k}_p$ value determined in CH_3NO_2. Points fit the straight line, which indicates that $\bar{k}_p$ is essentially independent of the polarity of the solvent.

APPENDIX

The solution of the kinetic scheme described by Eq. (4)

$$\mathrm{In} + \mathrm{M} \xrightleftharpoons[k_{-1}]{k_1} \mathrm{Ox} \xrightarrow{k_{iM}} \mathrm{M}^*$$

$$\mathrm{M}^* + n\mathrm{M} \xrightleftharpoons{\bar{k}_p} \mathrm{P}$$

$$\mathrm{In} + \mathrm{P} \xrightarrow{k_{ip}} \mathrm{M}^*$$

with

$$k_{ip} \gg k_{iM}$$

where Ox denotes oxonium ion $R\!-\!\overset{+}{O}\!-\!CH_2OCH_2CH_2$, M* is the active species of various degrees of polymerization and P denotes polymer. The concentration of the active species is equal to:

$$[\mathrm{M}^*] = [\mathrm{In}]_0 - [\mathrm{In}] - (k_1/k_{-1})[\mathrm{In}][\mathrm{M}] = [\mathrm{In}]_0 - [\mathrm{In}]\ \{1 + (k_1/k_{k-1})[\mathrm{M}]\} \tag{A-1}$$

The rate of disappearance of initiator is given by equation:

$$-\,d[\mathrm{In}]/dt = k_{iM}(k_1/k_{-1})[\mathrm{In}][\mathrm{M}] + k_{ip}[\mathrm{In}][\mathrm{P}] \tag{A-2}$$

If $k_{ip} \gg k_{iM}$, the first term in Eq. (A-2) may be neglected:

$$-\,d[\mathrm{In}]/dt = k_{ip}[\mathrm{In}][\mathrm{P}] \tag{A-3}$$

The concentration of polymer, expressed in terms of concentration of monomer units being incorporated into polymer, equals to:

$$[P] = [M]_0 - [M] \tag{A-4}$$

Thus:

$$-d[In]/dt = k_{ip}\,[In]\,([M]_0 - [M]) \tag{A-5}$$

After integration of Eq. (A-5) one obtains:

$$\ln([In]_0/[In]) = k_{ip}\int_0^t ([M]_0 - [M])\,dt \tag{A-6}$$

or

$$[In] = [In]_0 \exp\{k_{ip}\int_0^t ([M]_0 - [M])dt\} \tag{A-7}$$

Substitution of Eq. (A-7) into Eq. (A-1) gives the following expression for a concentration of active species:

$$[M^*] = [In]_0\left(1 - \exp\{k_{ip}\int_0^t ([M]_0 - [M])dt\}(1 + [k_1/k_{-1}][M])\right) \tag{A8}$$

The rate of monomer disappearance, in the case of reversible propagation, is given by Eq. (A-9):

$$d\ln\{([M]_0 - [M]_e)/([M]_t - [M]_e)\}/dt = \bar{k}_p[M^*] \tag{A9}$$

Substitution of Eq. (A-8) into Eq. (A-9) leads to the expression:

$$d\ln\{([M]_0 - [M]_e)/([M]_t - [M]_e)\}/dt =$$

$$\bar{k}_p[In]_0\left(1 - \exp\{k_{ip}\int_0^t ([M]_0 - [M]_t)dt\}(1 + [k_1/k_{-1}][M]_t)\right) \tag{A-10}$$

after rearrangement one obtains a final equation:

$$\ln\left(1 - d \ln \{([M]_0 - [M]_e)/([M]_t - [M]_e\}/dt \, \frac{1}{\bar{k}_p [\mathrm{In}]_0}\right) =$$

$$-k_{ip} \int_0^t ([M]_0 - [M]_t)\, dt + \ln\left(1 + \frac{k_1}{k_{-1}} [M]_t\right) \qquad \text{(A-11)}$$

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