260. *Non-stationary States in the Polymerization of Trioxan.*

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The $\geqslant Si^+ A^-$ ion-pair, where A^- is the anion of a strong acid, is a very suitable catalyst for the polymerization of trioxan. We studied the polymerization of liquid trioxan using $\geqslant Si^+ ClO_4^-$ and especially $\geqslant Si^+ HSO_4^-$ as catalysts. The polymerization is of first order with respect to initiator and of first or zero order with respect to trioxan.

Analysis of the shape of conversion curves has established an anomalous behaviour of the system trioxan–polymer–active centre. Equations have been derived which describe the course of polymerization with sufficient accuracy.

THE synthesis of polyformaldehyde has received considerable attention. Copolymers of formaldehyde have many better properties than polyformaldehyde itself; suitable raw materials are trioxane and oxygen- or nitrogen-containing heterocycles.

The ability of trioxan to polymerize has long been known, either spontaneously (especially upon melting or vaporizing) [1-5] or by initiated cationic polymerization, which is quicker and easier to control,[6-8] or initiated by radiation.[9-10]

The choice of initiator is important. It controls not only the overall reaction rate, the molecular weight of the product, and other reaction-kinetics, but also the thermal stability of the polymer. A practicable cationic initiator would have to be easily accessible; its residue bound to the polyoxymethylene chain would be a stable group inactive as a centre of depolymerization or degradation; its counter-ion would be easy to remove from the polymer; it would make possible chain-transfer with substances which form stable end-groups; it would not favour side-reactions during polymerization.

These conditions are largely met by a new initiator, the $\geqslant Si{-}O{-}Si^+ A^-$ ion-pair whose cation is a short siloxane chain terminated by a silicon ion, and the anion A^- is acid radical,[11] *e.g.*, ClO_4^- or HSO_4^-.

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EXPERIMENTAL AND RESULTS

Materials.—Trioxan, obtained by washing crude material with alcoholic potassium hydroxide, was distilled from sodium in an inert atmosphere with a column of *ca.* 8 theoretical plates. Pure trioxan was kept in a thermostatted reservoir; before use it was analysed by gas chromatography [12] on poly(ethylene glycol), and a flame-ionization detector being used. The limit of detection for formaldehyde, methyl alcohol, methylal, methyl formate and tetroxan was *ca.* 10 p.p.m. Water was determined by the Karl Fischer method. The trioxan always contained less than 50 p.p.m. of water and less than 5 p.p.m. of formic acid. Formic acid was determined by coulometric titration sensitive to 1 p.p.m.[13]

Initiator.—Sodium-dried octamethylcyclotetrasiloxane was mixed with 5% anhydrous sulphuric or perchloric acid at room temperature in the absence of air for 48 hr. The polymer so formed, terminated by silylsulphate or silylperchlorate groups, was separated by centrifuging or sedimentation from the excess of acid and dissolved in cyclohexane to yield approx. 5% solution. The amount of active substance was determined by titration of the cyclohexane solution. The required amount of this solution was measured into the reaction vessel from a burette in a stream of nitrogen. Though the initiator solution contained a little (1000 p.p.m.) water, the volume used (max. 0·1 ml.) did not raise the water content significantly.

Cyclohexane.—Cyclohexane for chromatography (Lachema) was dried by sodium and distilled.

Apparatus and Procedure.—Automatically recording [14] dilatometers measured the course of polymerization. The vessel was filled with molten trioxan, the necessary amount of initiator was added (the quantity of cyclohexane added with the initiator, 0·1 ml. for 45 g. of trioxan, was neglected) and the reaction vessel was clamped in the apparatus described previously.[14]

The calibration to connect contraction with conversion was carried out by gravimetric determination of the conversion at a known contraction after stopping the polymerization by addition of water. The relationship was accurately linear up to 20% conversion.

The amount of initiator in the polymerizing system was measured as follows: at a certain conversion the entire contents of the reaction vessel were put into excess of water at the polymerization temperature. The polymer was kept suspended in water (with dissolved trioxan) at this temperature for 20 min., then filtered off and washed. In the filtrate, acid was determined by coulometric titration. Practically the same results were obtained if dioxan (containing traces of water) instead of water was used (dioxan served as a model of trioxan incapable of polymerization).

Since the polymer filtered off did not liberate any aditional measurable amount of acid when treated with boiling water for 30 min., we conclude that all accessible acid (initiator) was determined in this way.

Results were compared with a blank in which the same amount of trioxan was dissolved in water and initiator was subsequently added.

Results.—Polymerization initiated by $\geqslant\mathrm{SiO^{+}ClO_4^{-}}$ groups was of low reproducibility. Concentrations of about 1 μmole/kg. were insufficient to initiate it at 70°, while concentrations scarcely ten times as high promoted so quick a polymerization (at the same temperature) that drops of added initiator solution became embedded in polymer formed prematurely before the initiator could dissolve. Either this resulted in complete loss of activity, or polymerization was complete within a few seconds of the addition. Later, however, we found conditions in which perchlorate active centres brought about a relatively slow polymerization.

Polymerization initiated by silyl hydrogen sulphate centres was easier to control.

A dilatometric record of the polymerization of trioxan initiated by various concentrations of $\geqslant\mathrm{Si^{+}HSO_4^{-}}$ is shown in Fig. 1. Conversion curves calculated from these records are in Fig. 2. The curves show a period of acceleration (induction period), a maximum rate, and a region of deceleration. The maximum rates are proportional to the initiator concentration (Fig. 3). The deceleration is connected with a fall in the initiator concentration as reaction proceeds; Fig. 4 shows that this fall is linear with conversion. Polymer isolated in this run had a specific surface of about 20 m.^{2}/g.

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[12] K. Otto, unpublished results.

[13] M. Přibyl, unpublished results.

[14] M. Kučera and E. Spousta, *Chem. listy*, 1963, **57**, 842.

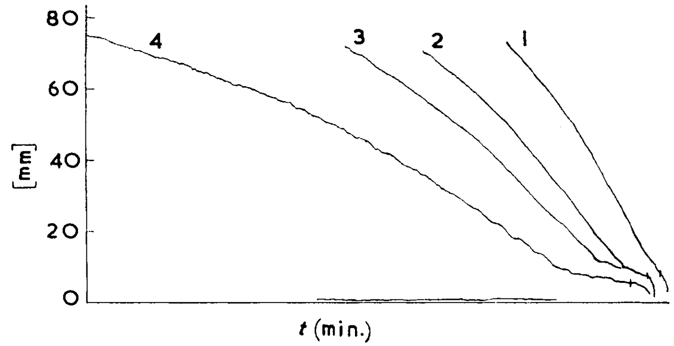

FIG. 1. Trioxan polymerization at 75°, from dilatometer.
I_0/G: 1, 192 μmoles (4·3 × 10^{-3} mole/kg.); 2, 128 μmoles (2·9 × 10^{-3} mole/kg.); 3, 96 μmoles (2·2 × 10^{-3} mole/kg.); 4, 64 μmoles (1·4 × 10^{-3} mole/kg.).

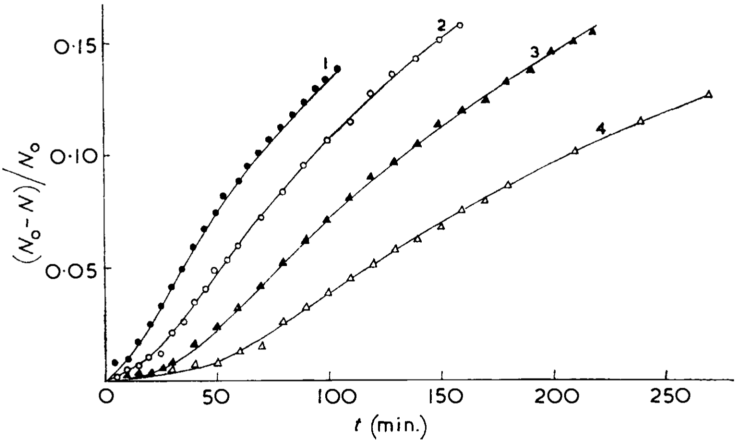

FIG. 2. Conversion curves of trioxan polymerization at 75°.
Curves as in Fig. 1.

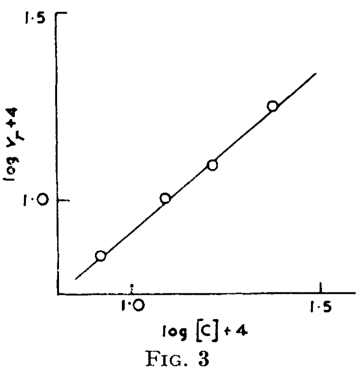

FIG. 3

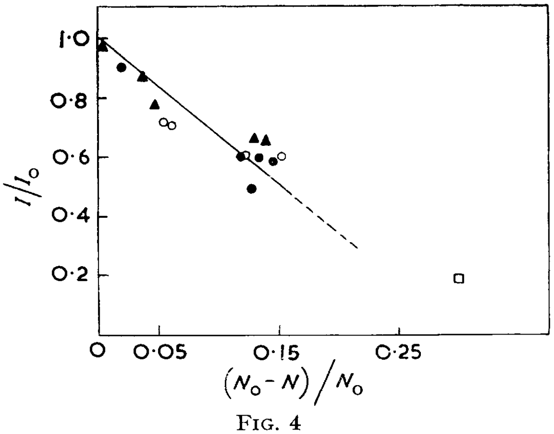

FIG. 4

FIG. 3. Dependence of log v_{overall} on log [C].

FIG. 4. Dependence of the acid concentration in the system trioxan–initiator on the conversion at 75°.
I_0/G: ○, 2·02 × 10^{-3} mole/kg extracted by dioxan. □, 2·02 × 10^{-3} mole/kg.; ●, 4·04 × 10^{-3} mole/kg.; ▲, 6·06 × 10^{-3} mole/kg. extracted by water.

DISCUSSION

Polymerization of trioxan is a reaction which precipitates insoluble polyformaldehyde from solution. As a first approximation of the polymerization rate, when the rate-determining step is the addition of trioxan to the active centre and if all initiator molecules give rise to active centres, we may write

$$-\frac{1}{G}\frac{\mathrm{d}N}{\mathrm{d}t} = k\left[\frac{N}{G}\right]^{\alpha}[C]^{\beta} \qquad (1)$$

Symbols used:

α and β govern the reaction rate with respect to trioxan and initiator ($\beta = 1$, see Fig. 3).
G = weight of the liquid phase of the polymerizing system (kg.).
N_0 = number of moles of trioxan at time 0.
N = number of moles of trioxan at time t.
C = concentration of initiator in the liquid phase of the system (mole/kg.).
k = reaction rate constant.
I = number of moles of the initiator at time t.
I_0 = original number of moles of initiator.
M = molecular weight of trioxan (kg./mole).

As molten trioxan polymerizes, the number of its molecules decreases. If the ability of all active centres to initiate were preserved, and if trioxan could diffuse to them unhindered during the whole polymerization, eqn. (1) could be written as

$$-\frac{1}{G}\frac{\mathrm{d}N}{\mathrm{d}t} = k\left[\frac{I_0}{G}\right]\left[\frac{N}{G}\right]^{\alpha} \qquad (2)$$

and upon integration (for $\alpha = 1$, $G = MN$) $= \dfrac{N_0 - N}{N_0} = \dfrac{kI_0}{N_0M}t = k_ct$ (3)

Relations derived for $\alpha = 0$ and $\alpha = 1$ differ only formally, through the value of k_c. In both cases the conversion would be linear with time. However, as Figs. 1 and 2 show, the above assumptions are not fulfilled, since the curves are not straight. This is probably due to loss of active centres by a mechanism not yet clear. This polymerization thus resembles the non-stationary ones described by Pepper.[15]

Figure 4 shows that the concentration of initiator can be expressed (for low conversions) as a function of conversion as follows:

$$\frac{I}{G} = C = \frac{I_0}{G}\left[1 - k_s'\left(\frac{N_0 - N}{N_0}\right)\right] = \frac{I_0}{G}[1 - k_s(N_0 - N)] \qquad (4)$$

From eqns. (1) and (4)

$$-\frac{1}{G}\frac{\mathrm{d}N}{\mathrm{d}t} = k\frac{N}{G}\frac{I_0}{G}[1 - k_s(N_0 - N)] \qquad (5)$$

Integration and rearrangement yields a relation (6) between conversion and time [for $\alpha = 0$ we obtain an equation differing from (6) only in the constant and in the exponent].

$$\frac{N_0 - N}{N_0} = \frac{1 - \exp\left(-kI_0k_st/M\right)}{k_sN_0} \qquad (6)$$

Two special cases of eqn. (6) can be distinguished. If $k_s = 0$, it becomes eqn. (3). If $k_sN_0 = 1$, it would correspond to the loss of initiator by deactivation being exactly compensated by the increased concentration due to decrease of the liquid phase. For this case, eqn. (6) reduces to

$$\ln N/N_0 = -kk_sI_0t/M \qquad (7)$$

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[15] D. C. Pepper, *Proc. Roy. Soc.*, 1961, *A*,**263**, 58, 88; *Proc. Chem. Soc.*, 1961, 200.

In these experiments, $k_sN_0 \neq 1$, and an approximate value $k_sN_0 \approx 3$ can be deduced from Fig. 4. The value for k_s so derived may be thought inaccurate, seeing that trioxan and water (or dioxan) may differ as regards their ability to penetrate into the vicinity of the active centres. It can, however, also be deduced from the conversion curves, if the induction periods are known.* The deduced value agrees with that derived from Fig. 3.

This value of k_s being used, the value of the propagation rate constant k can be derived from a plot of $\ln(1 - k_sN_0x)$ against t (the logarithmic form of eqn. 6). The linearity of this plot (Fig. 5) justifies the assumptions of the theory and permits extrapolation to give the length of the induction periods.

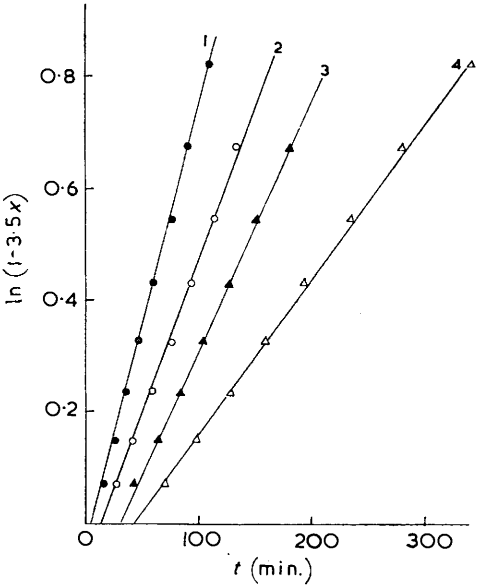

FIG. 5. Relation between $\ln(1 - k_3N_0x)$ and time for polymerization of trioxan at 75°.

Values of k and k_s are 0·56 kg. mole^{-1} min.$^{-1}$ and 0·315 mole^{-1}, respectively, when $N_0 =$ 11·1 moles/kg. at 75°.

The authors thank Dr. O. Peroutka and Dr. P. Osecký of this Institute for helpful suggestions and Dr. K. Majerová for technical assistance.

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[*Received, December 3rd,* 1963.]

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* The length of the induction periods and the value of the constant k_s were sought by a stepwise approximation by means of the logarithmic form of eqn. (6):

$$\ln(1 - k_sN_0x) = -kI_0k_st/M; \quad x = (N_0 - N)/N_0$$

Thus from the conversion curves we read conversions x_1 and x_2 corresponding to times t_1 and t_2, where $t_2 = 2t_1$ (induction periods are subtracted). It follows from eqn. (6) that

$$\frac{\ln[1 - k_s(N_0 - N_1)]}{\ln[1 - k_s(N_0 - N_2)]} = \frac{kk_sI_0t_1/M}{kk_sI_0t_2/M} = \frac{1}{2}$$

then $$[1 - k_s(N_0 - N_1)]^2 = 1 - k_s(N_0 - N_2); \quad k_s = \frac{N_0 - 2N_1 + N_2}{(N_0 - N_1)^2} = \frac{1}{N_0}\frac{2x_1 - x_2}{x_1^2}$$

x and t were taken from the experimental values of the conversion curves. For the calculation of the first approximation of $\ln(1 - k_xN_0x)$ use was made of the value of k_s as obtained from Fig. 4. The dependence of $\ln(1 - k_s'N_0x)$ on t was almost linear for $x > 0·02$, and could be extrapolated quite accurately to obtain the value for zero conversion and to obtain $t_{\text{ind.}}$, the latter being used to find more accurate values of the necessary $t_2 = 2t_1$, and thus a more accurate value of k_s. This procedure was repeated to constant k_s.