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ELECTROINITIATED POLYMERIZATION OF TRIOXANE IN CHLORINATED HYDROCARBONS

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Abstract—The electroinitiated polymerization of trioxane in chlorinated hydrocarbons, with tetrabutylammonium perchlorate as background electrolyte, has been investigated. The initiation always involves perchlorate oxidation but the polymerization exhibits different features in the various solvents. It has been found that in 1–2 dichloroethane the polymerization, once started by a short pulse of current, proceeds without any induction period to moderate conversion of monomer to polymer. The initial rate of polymerization depends linearly on the monomer conc. and on the initiating charge, so allowing determination of some kinetic parameters. On the other hand, the electroinitiated polymerization of trioxane in dichloromethane requires continuous current to give reasonable conversions; it exhibits induction periods and acceleration which cannot be simply related to the current.

1. INTRODUCTION

Since the report by Staudinger and Kern [1], the polymerization of trioxane has been the subject of several patents for the technological preparation of high mol. wt polyoxymethylenes. It is better to produce these polymers from the solid trimer (trioxane) than from gaseous monomeric formaldehyde because of both the higher stability of trioxane and its easier purification and handling.

Recently much work has been done to elucidate the kinetics of trioxane polymerization which exhibits some peculiarities such as induction periods, heterogeneity and autoacceleration [2–5]. Some of these characteristics are due to the fact that the growing ends, unlike those in the cationic polymerization of vinyl compounds, are stabilized as oxonium ions; consequently initiation can be faster than propagation [6]. For this reason, one can probably understand that different results were obtained with different catalysts and different media, and that the polymerization exhibits a characteristic and complicated behaviour in each solvent [6]. For electrolytic initiation, it was recently found that trioxane polymerization in strongly polar solvents, e.g. acetonitrile, leads to polyoxymethylene oligomers with a poor current yield [7] whereas the same reaction in benzonitrile or nitrobenzene starts with a low charge transfer giving polymers of higher mol. wt [8]. In the anode initiated bulk polymerization of molten trioxane [9], a charge of 3×10^{-3} C per g of trioxane starts a very fast propagation with complete conversion of the monomer to high mol. wt polyoxymethylene ($\simeq 3 \times 10^5$) within less than 10^2 sec.

The present work investigated the anode initiated polymerization of trioxane in solvents of moderate polarity, viz. the chlorinated hydrocarbons, 1–2 dichloroethane and dichloromethane: the process could be compared with the reaction initiated by chemical catalysts in the same media [2, 5] and with the anode initiated polymerization of the similar cyclic compound 1–3 dioxolane [10].

2. EXPERIMENTAL

2.1 *Materials*

Trioxane (TRO), a Merck reagent grade, was distilled under nitrogen and over CaH_2; the fraction boiling at 114° was collected [11]. Tetrabutylammonium perchlorate (TBAP) was prepared from tetrabutylammonium hydroxide, Fluka reagent grade, and from perchloric acid, RP C. Erba reagent grade; the crude product was recrystallized from ethanol–water and dried in a vacuum oven at 60°. 1–2 Dichloroethane and dichloromethane were both RP C. Erba chemicals; after washing with H_2SO_4 and $NaHCO_3$, they were twice distilled over CaH_2. The other reagents were commercial products.

2.2 *Apparatus and procedure*

The experimental equipment was substantially the same as used previously [7–9]. Electrolyses were performed by using amperostat with high output potential in an U-shaped cell where only the anode compartment was filled with monomer solution: the cathode compartment was entirely filled with mercury and was separated from the other compartment by a G4 sintered glass disc. The working anode was a platinum net with an area of about 2 cm^2: the anode reaction started the polymerization process; the corresponding cathode reaction was the discharge on mercury of tetrabutylammonium ions with the formation of tetraalkylammonium amalgam. During the polymerization the monomer solution was mechanically stirred at 500 rev/min and maintained at the reaction temperature by thermostatically controlled heating jackets. Current-potential curves were obtained in the same cell using an Amel 557/SU potentiostat employing a Pt microanode and an $Ag/AgClO_4$ reference electrode.

The kinetic runs were performed by sampling the monomer solution at various reaction times, adding it either to NH_3–methanol (runs in 1-2 dichloroethane) or NH_3–propanol (runs in dichloromethane) and determining by VC. the monomer to polymer conversion.

All the VC. determinations were carried out using a Fractovap C. Erba mod. G.V. vapour phase chromatograph; the analysis conditions were: 2 m column packed with chromosorb W 80–100 mesh + 10 per cent polyethylene glycol 20 M at 80°; nitrogen carrier at a flow rate of 50 ml/min; flame ionization detector.

The mol. wts of the polymer were determined by viscometric measurements at 25° in hexafluoroacetone sesquihydrate [12].

Analysis of the experimental data (least squares procedure) was carried out by a 9100 Hewlett–Packard calculator equipped with a 9125 plotter.

3. RESULTS AND DISCUSSION

3.1 *Anode reaction*

Before investigating the polymerization of trioxane (TRO) in chlorinated hydrocarbons, some experiments were performed in order to ascertain the nature of the anode generated catalyst which initiates the cationic polymerization. Much information can be obtained from a study of the steady state current (*i*) vs potential (*E*) obtained for tetrabutylammoniumperchlorate (TBAP) solutions in dichloromethane both in the absence and in the presence of TRO (see Fig. 1). It can be seen that the anode discharge for the TBAP/dichloromethane system remains substantially unaffected by repeated additions of fair amounts of TRO thus showing that the electrode process is always related to the TBAP–dichloromethane system. However, using different background electrolytes, the electrode reaction can be shifted either to more negative potentials (with tetrabutylammonium bromide) or to some more positive potentials (with tetrabutylammonium tetrafluoroborate) remaining always unaffected by the presence in solution of TRO. The background electrolyte oxidation is consequently the only noticed anode process.*

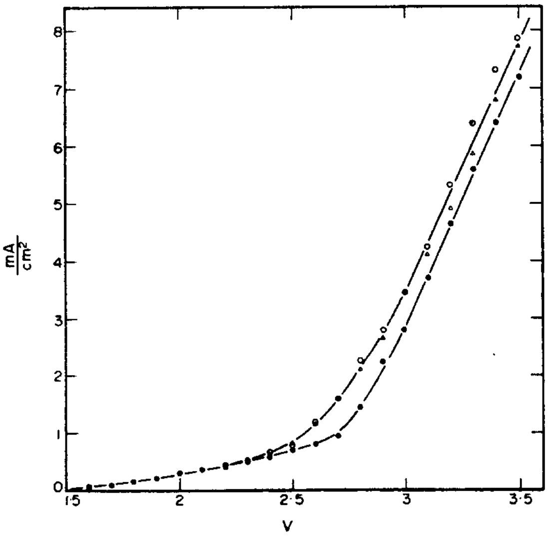

Fig. 1. Polarization curves obtained at 25° in dichloromethane for the system constituted by: ● TBAP 6×10^{-2} moles l^{-1} alone; △ TBAP + TRO 0·22 moles l^{-1}; ○ TBAP + TRO 0·9 moles l^{-1}.

Now, noting that the perchlorate oxidation involves H^+ ion formation [13], catalysis by the anode reaction using a perchlorate background is probably analogous to initiation by perchloric acid [9].

3.2 *Kinetics in* 1–2 *dichloroethane*

It was found that, on electrolysing for a few seconds with a 10–20 mA cm^{-2} current density a monomer solution in 1–2 dichloroethane, the polymerization started and went to several per cent conversion without any further supply of current. Figure 2 shows some typical kinetic patterns obtained for the same initial monomer conc. ($[M]_0$ = 1·84 moles l^{-1}) which were started by different amounts of charge. Monomer and solvent concentrations were calculated from the weights added at room temperature assuming densities 1·110 g/ml for TRO and 1·256 g/ml for 1–2 dichloroethane. It is clear from Fig. 2 that both the initial rate of monomer consumption and the limiting conversion are related to the charge initially furnished to the system. No substantial induction periods and no acceleration are present, suggesting that all the active centres are formed within a short time, probably within the electrolysis time. Under these conditions, supposing that the charge transfer for unit volume is equivalent to the free proton concentration, the same concentration of active centres [M*] should be instantaneously formed, according to scheme (I)–(II)

$$H^+ + M \rightarrow M^* \text{ very fast} \qquad (I)$$

$$M^* + M \rightarrow M_2^* \text{ propagation} \qquad (II)$$

Further, the concentration of active centres [M*] should not greatly diminish during the first stage of the reaction, as the polymerization goes on for a time several orders of magnitude longer than the duration of the electrolysis, so a simple kinetic law of the type (I):

$$-\frac{d[M]}{dt} = k_p[M^*][M]_0 \qquad (1)$$

may be tested for analysis of the kinetic data. According to this equation, the initial slope of the monomer fractional consumption plot should be con-

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* Similar behaviour was observed in 1–2 dichloroethane.

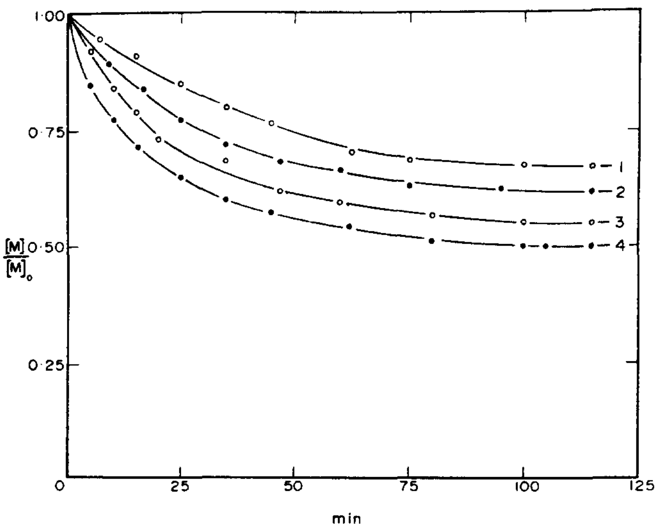

Fig. 2. Kinetics of TRO polymerization in 1–2 dichloroethane at 60° initiated by different anode charge transfers. The numbers refer to the runs of Table 1.

stant involving both the furnished charge [F] (Faraday/l) and the specific rate constant k_p:

$$-\frac{d[M]/[M]_0}{dt} = k_p[F]. \qquad (2)$$

Table 1 shows, for the various conditions, the initial rate so obtained from the experiments of Fig. 2 and from similar runs at different initial monomer concentrations. The remarks regarding the absence of both induction and acceleration apply also to the runs not illustrated in Fig. 2.

Equations (1) and (2) indicate a linear dependence of the rate on the initial charge transfer; the $(-d[M]/[M]_0/dt)$ values of Table 1 plotted against the respective values of [F] lie on straight lines as shown in Fig. 3 where the three lines refer to three values of $[M]_0$. The slopes of these lines, which should indicate the true value of k_p, are similar for the different $[M]_0$ values, showing the linear dependence on monomer conc. of Eqn. (1), assumed as the basis of the present kinetic analysis.

It is apparent that the straight lines of Fig. 3 do not

Table 1. Initial rates of electroinitiated TRO polymerization at 60°

Run	Initial monomer. conc $[M]_0$ (mole l^{-1})	10^4 × initiating charge [F] (Faraday l^{-1})	Initial rate $-\frac{d[M]/[M]_0}{dt}$ (min^{-1})	Fractional limiting conversion $[M]_L/[M]_0$
1	1·84	2·070	0·031	0·50
2	1·84	1·520	0·016	0·55
3	1·84	1·265	0·013	0·62
4	1·84	1·015	0·008	0·67
5	3·24	2·270	0·050	0·58
6	3·24	1·820	0·037	0·60
7	3·24	1·135	0·025	0·62
8	3·24	0·910	0·020	0·67
9	4·36	1·565	0·030	0·65
10	4·36	1·175	0·020	0·71
11	4·36	1·015	0·0125	0·71
12	4·36	0·782	0·010	0·74

TBAP = 2·22 × 10^{-2} moles l^{-1}.
The average values of k_p l moles^{-1} min^{-1} – 2 obtained from Fig. 3 are:
220 ± 70 for $[M]_0$ = 1·84 moles l^{-1}.
213 ± 40 for $[M]_0$ = 3·24 moles l^{-1}.
268 ± 100 for $[M]_0$ = 4·36 moles l^{-1}.

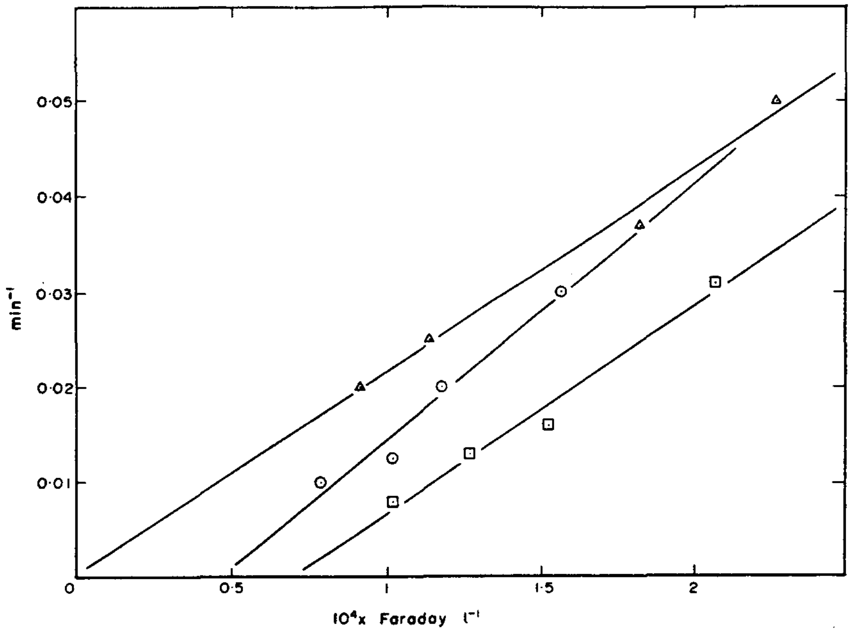

Fig. 3. Initial polymerization rates vs the charge transfers for different initial monomer conc.: □ $[M]_0$ = 1·84 moles l^{-1}; △ $[M]_0$ = 3·24 moles l^{-1}; ⊙ $[M]_0$ = 4·36 moles l^{-1}.

all start from the origin as required by Eqn. (2). This fact is probably accounted for by realizing that the three sets of experiments of Table 1 were performed from three mother solutions of different $[M]_0$, consequently for each set there is a different threshold charge which is probably consumed by impurities in the system.

Table 2 shows the kinetic results obtained at various temperatures with the same initial monomer concentration. The specific rate constants (k_p) thus obtained, from the Arrhenius equation, give an activation energy for propagation of 14·7 ± 4·6 kcal/mole.

The reduction in rate and eventual cessation of polymerization well before complete conversion indicate a termination process destroying the active centres. The nature of this process which determines the form of the kinetics will now be briefly discussed.

(a) It might be a termination reaction involving traces of impurity of the solutions. Even if the systems are affected by some impurities, as indicated by the threshold charge necessary for starting the polymerization, the associated decay of the active centres does not seem the sole termination reaction on the basis of this experiment: on furnishing a further charge to a polymerizing system after it has reached its limiting conversion, the polymerization starts again with initial rate and subsequent deceleration comparable to the previous values.

(b) There might be termination with the polymer: this possibility can be disregarded since experiments performed in the presence of dead polymer showed no significant change in the average "life" of the active centres.

(c) According to the findings of Onyon and Taylor

Table 2. Initial rates of electroinitiated TRO polymerization at 40° and 80°

Run	Temp.	10^4 × initiating charge [F] (Faraday l^{-1})	Initial rate $\frac{-d[M]/[M]_0}{dt}$ (min^{-1})	Fractional limiting conversion $[M]_l/[M]_0$
13	40	3·670	0·012	0·65
14	40	2·290	0·005	0·77
15	40	1·550	0·002	0·82
16	80	2·250	0·150	0·42
17	80	1·350	0·090	0·42
18	80	0·905	0·064	0·49

$[M]_0$ = 3·24 moles l^{-1}.
TBAP = 2·22 × 10^{-2} moles l^{-1}.
The average values of k_p(l $moles^{-1}$ min^{-1}) are: 48 ± 16 at 40°; 643 ± 128 at 80°.

for TRO polymerization in cyclohexane [14], both self-termination and termination with the solvent remain the most likely processes in the system.

These reactions indicate a first-order or pseudo-first-order decay [owing to the practical constancy of solvent concentration of the active centres as in (3)]:

$$[M^*] = [M^*]_0 e^{-k_t t}, \tag{3}$$

where the constant k_t may include the solvent concentration. Taking into account Eqn. (3), it can be easily shown [14] that integration of Eqn. (1) from $t = 0$ to $t = \infty$ (i.e. when the monomer consumption has reached its limiting value), gives Eqn. (4):

$$\ln \frac{[M]_1}{[M]_0} = \frac{k_p}{k_t} [M^*]_0, \tag{4}$$

which suggests a linear dependence of the limiting conversion of the monomer to polymer on the initiator conc.

The results of Tables 1 and 2 show a dependence of the limiting value of the fractional monomer consumption on the charge initially supplied, even if there is appreciable scatter of results.

If termination involves the solvent, on substituting k_t [Solvent] for k_t, Eqn. (4) implies an inverse dependence on the solvent not shown by the kinetic data. One has to conclude that, apart from the effect of the impurities, self-termination is in the experimental range investigated the main process for destruction of centres. This result is far from being established, although for example the idea of self-termination by recombination with the counter-ion associated with the growing end is valid for high ionic conc. solutions, it seems unlikely with the perchlorate ion [15]. Solvent intervention, at least as a transfer agent, during the polymerizations is indicated by the data on mol. wt.

3.3 *Molecular weights of the polyoxymethylenes obtained in* 1–2 *dichloroethane*

The reaction mechanism and the polymerization process in principle can be further clarified by consideration of both the changes of the polymer mol. wt during the course of a run and the reaction variables affecting the same.

Table 3 reports the variation of polymer mol. wt with conversion at three temperatures: it also shows the development at various stages of reaction of the number of polymer moles formed for each initiating act, i.e. for Faraday transferred.

One can observe that the mol. wt of the polymer at an early stage of the reaction is lower than that of the subsequent polymer; the ratio [polymer moles]/[Faraday] is high enough to indicate a facile transfer reaction with an agent which is thereby consumed well before the reaction is complete. The most likely agent of this type is water, in traces, as already pointed out for the electroinitiated bulk polymerization of TRO [9]. However, the occurrence of another transfer reaction operating in the later stages is indicated by the progressive increase (especially in the polymerizations at 60° and 80°) in the number of moles formed and the slight decrease of mol. wts at the highest conversions. The intervention of the solvent as the transfer agent responsible for this last behaviour seems confirmed by the data of Table 3, where polymerization runs 35–39 performed at different initial monomer concentrations

Table 3. Polymer mol. wt dependence on fractional conversion

Run	Fractional conversion	$\overline{M}_v$	[Polymer moles]/[Faraday]*
Conditions: $t = 40°$; $[M]_0 = 3{\cdot}24$ ml^{-1}; TBAP = $2{\cdot}22 \times 10^{-2}$ ml^{-1}; F = $3{\cdot}67 \times 10^{-4}$ Faraday l^{-1}			
19	0·08	4·000	15·5
20	0·16	6·750	18·3
21	0·22	8·750	19·2
22	0·29	12·000	18·3
23	0·34	12·000	21·8
Conditions: $t = 60$; $[M]_0 = 3{\cdot}24$ ml^{-1}; TBAP = $2{\cdot}22 \times 10^{-2}$ ml; F = $2{\cdot}27 \times 10^{-4}$ Faraday l^{-1}			
24	0·05	7·000	9·2
25	0·10	13·500	9·6
26	0·16	21·000	9·8
27	0·25	17·500	18·5
28	0·28	16·500	22·0
29	0·40	16·000	32·0
Conditions: $t = 80°$; $[M]_0 = 3{\cdot}24$ ml^{-1}; TBAP = $2{\cdot}22 \times 10^{-2}$ ml^{-1}; F = $2{\cdot}25 \times 10^{-4}$ Faraday l^{-1}			
30	0·15	20·000	9·7
31	0·25	24·000	13·1
32	0·35	29·000	15·5
33	0·39	28·000	17·3
34	0·46	28·000	21·4

* This ratio is approximate being computed from $\overline{M}_v$.

Table 4. Polymer mol. wt dependence on solvent and initiator concentrations at 60° and 35 min reaction time

Run	$[M]_0$	$[\text{Dichloroethane}]/[M]_0$	$([F] \times 10^4)$	Fractional conversion	$\bar{M}_v$
35	7·87	0·577	2·20*	0·75	38,000
36	5·80	1·155	1·62*	0·50	26,000
37	5·12	1·445	1·43*	0·430	22,500
38	4·60	1·740	1·28*	0·420	21,000
39	3·81	2·300	1·07*	0·33	19,000
40	5·80	1·55	0·407	0·20	25,000
41	5·80	1·55	0·815	0·40	25,000
42	5·80	1·55	3·27	0·625	21,500

* Runs performed with the same $[F]/[M]_0$ ratio.

and stopped at the same reaction time (35 min), exhibit a noticeable decrease of mol. wt with increase of the initial [Solvent]/[Monomer] ratio: this fact can be recognized more clearly by considering both the different conversions obtained here and the molecular weight dependence on conversion shown in Table 3.

The reasonable independence of the molecular weight on the initiator concentration exhibited by runs 36, 40–42 of Table 4 (performed at the same [S]/[M] ratio but started by different amounts of charge) indicates that initiator concentration appears as a first order quantity in all the kinetic terms (if the polymerization degree is regulated by the ratio of rates of chain limiting processes to propagation). This fact may indirectly support previous kinetic conclusions.

3.4 *Kinetics in dichloromethane*

Unlike the results obtained in 1–2 dichloroethane, the electroinitiated polymerization of TRO in dichlormethane exhibits the following peculiarities. At the current densities adopted previously, high conversions of monomer into polymer can be obtained only by a continuous electric feed; once the electrolysis is stopped, the post-polymerization of TRO is substantially reduced, e.g. after 20 min of continuous anodic charge transfer at the total current intensity of 50 mA, the amount of monomer consumed reaches the limiting value of only ~ 15 per cent.

The reactions moreover exhibit induction times which are related to the initial monomer concentration and to the current intensity as shown by the kinetic

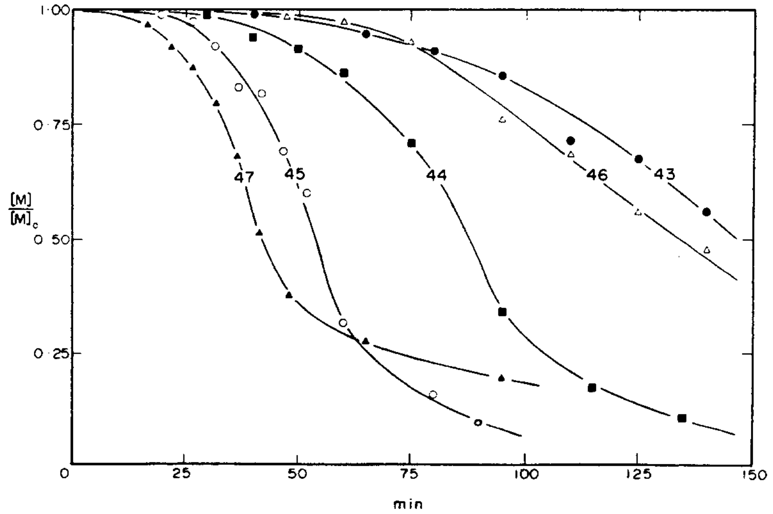

Fig. 4. Kinetics of TRO polymerization in dichloromethane at 30° obtained for various (continuous) current intensities. The numbers refer to the runs of Table 5.

runs of Fig. 4. Runs 43–45 refer to the same $[M]_0$ and different current intensities whereas runs 46–47 differ also for $[M]_0$. Rigorous analysis of these results is clearly difficult as the kinetic law which may apply to the first stage of the reaction in an homogeneous phase is less reliable at higher conversions,* where the polymerization propagates mainly heterogeneously on the surfaces of the crystals [5, 16].

The kinetics at different current intensities indicate for different induction times a comparable charge consumption corresponding to about 10^{-2} M/l conc.: such an impurity level is unreasonable so this charge seems to be related more reasonably to the establishment of some equilibrium in the solution [16, 17] where the kinetics of the process is not yet shifted to polymer formation. However, with all its limitation, a kinetic treatment of the data to relate the polymerization to the continuous anode charge transfer can be attempted as follows.

At any time, as indicated by the postpolymerization experiment, there is a net difference between the number of active centres produced by the current (I in Faraday/l sec) and the rate of their destruction according to the equation:

$$\frac{d[M^*]}{dt} = I - k_t[M^*], \tag{5}$$

where, as previously, the termination can be pseudo-first-order by the hypothesis of solvent intervention (in this second case k_t includes the solvent concentration). Substitution into Eqn. (3) of the value for $[M^*]$ obtained by integration of Eqn. (5) and subsequent integration gives:

$$-\ln\frac{[M]}{[M]_0} = \frac{k_p}{k_t} I\left(t - \frac{1}{k_t} + \frac{1}{k_t}e^{-k_t t}\right), \tag{6}$$

which leads to:

$$-\frac{1}{It}\ln\frac{[M]}{[M]_0} = k_p/k_t\left(1 - \frac{1}{k_t t} + \frac{1}{k_t t}e^{-k_t t}\right). \tag{7}$$

By extrapolating this equation to $t = \infty$, one obtains k_p/k_t as limiting value.

Figure 5 shows that the kinetic runs of Fig. 4 roughly satisfy Eqn. (7).

Equation (7) does not take into account both the induction phenomena and any acceleration effect other than that due to the increase of active centres [2, 5].

For different values of $[M]_0$, the plots of Fig. 5 tend to different asymptotes: that is, if Eqn. (7) with all previous remarks is still valid for the runs of Fig. 4, increasing solvent concentration leads to decreasing k_p/k_t values, thus indicating a possible solvent intervention in the termination. This fact would agree with the much more limited "life" of the active centres in dichloromethane than in 1-2 dichloroethane: moreover the k_p/k_t values, deduced from Fig. 2 (ranging from ~20

Table 5. Mol. wts of polymers obtained in dichloromethane at 30°

Run	$[M]_0$	$10^5 \times I$ (Faraday l^{-1} sec^{-1})	$\bar{M}_v$
43	3·14	0·293	2500
44	3·14	0·487	1800
45	3·14	0·780	2600
46	1·81	0·560	1800
47	4·95	0·387	2500

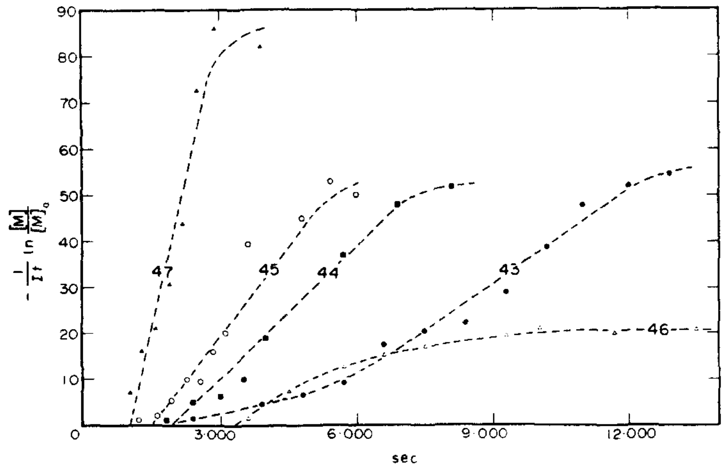

Fig. 5. Kinetics runs of Fig. 4 plotted according to Eqn. (7). The numbers refer to the runs of Table 5.

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* After prolonged electrolysis the increasing acidity might also cause some depolymerization, but the extent of this reaction was shown not to be substantial by electrolysing under the same conditions a polyoxymethylene sample.

to ~80) are not in disagreement with the molecular weight of the polymers reported in Table 5 taking also into account the possible transfer reactions which affect the mol. wts.

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REFERENCES

1. H. Staudinger and W. Kern, *Die hochmolecularen organischen Verbindungen*, p. 224. Springer, Berlin (1932).
2. W. Kern and V. Jaacks, *J. Polym. Sci.* **48**, 399 (1960).
3. M. Kucera and E. Spousta, *J. Polym. Sci.* **A, 2**, 3431 (1964).
4. M. Kucera and E. Spousta, *J. Polym. Sci.* **A, 2**, 3443 (1964).
5. L. Leese and M. W. Baumber, *Polymer* **6**, 269 (1965).
6. S. Okamura, T. Higashimura and T. Miki, *Progr. Polym. Sci. Japan* **3**, 97 (1972).
7. G. Mengoli and G. Vidotto, *Makromolek. Chem.* **165**, 137 (1973).
8. G. Mengoli and G. Vidotto, *Makromolek. Chem.* **165**, 145 (1973).
9. G. Mengoli and G. Vidotto, *Makromolek. Chem.* **175**, 893 (1974).
10. G. Mengoli and S. Valcher, *Europ. Polym. J.* in press.
11. M. Sakamoto, I. Ishigaki, M. Kumakura, H. Yamashina, T. Iwai, A. Ito and K. Hayashi, *J. Makromol. Chem.* **1**, 639 (1966).
12. L. Höhr, V. Jaacks, H. Cherdron, S. Iwabuchi and W. Kern, *Makromolek. Chem.* **103**, 279 (1967).
13. A. M. Maki and D. H. Geske, *J. chem. Phys.* **30**, 1356 (1959).
14. P. F. Onyon and K. J. Taylor, *Europ. Polym. J.* **1**, 133 (1965).
15. S. Penczek, J. Fejgin, P. Kubisa, K. Matyjaszewski and M. Tomaszewicz, *Makromolek. Chem.* **172**, 243 (1973).
16. R. Mateva, G. Wegner and G. Lieser, *Polym. Lett.* **11**, 369 (1973).
17. P. S. Raman and V. Mahadevan, *Makromolek. Chem.* **165**, 153 (1973).

Résumé—On étudie la polymérisation du trioxane amorcée électriquement en milieu hydrocarbures chlorés, avec le perchlorate de tetrabutylammonium comme électrolyte de base. L'amorçage implique toujours l'oxydation du perchlorate mais la polymérisation présente des caractéristiques différentes suivant la nature du solvant. On a trouvé que dans le dichloro-1,2-éthane, la polymérisation qui débute par une impulsion de courant de courte durée, procède ensuite sans période d'induction pour atteindre une conversion modérée. La vitesse initiale de polymérisation croît linéairement avec le concentration de monomère et la charge d'amorçage, permettant ainsi la détermination de quelques paramètres cinétiques. Par ailleurs, la polymérisation di trioxane dans le dichlorométhane nécessite un courant continu pour atteindre des conversions raisonnables; on observe dans ce cas des périodes d'induction et d'accélération qui ne peuvent pas être reliées de manière simple au courant.

Sommario—E' stata investigata la polimerizzazione del triossano elettroiniziata in solventi clorurati con perclorato di tetrabutilammonio come elettrolita di supporto. Il meccanismo di inizio coinvolge in ogni caso la ossidazione dello ione perclorato ma il processo di polimerizzazione ha caratteristiche proprie nei solventi esaminati. Si è cosi trovato che in 1,2-dicloroetano la polimerizzazione una volta innescata con un rapido impulso di corrente va avanti senza tempi di induzione a moderate conversioni di monomero in polimero.

Le velocità iniziali di polimerizzazione dipende linearmente dalla conc. monomerica e dalla carica fornita inizialment: è cosi possibile la determinazione di alcuni parametri cinetici. D'altra parte la polimerizzazione elettroiniziata del triossano in diclorometano richiede una somministrazione continua di corrente per ottenere ragionevoli conversioni: si verificano inoltre periodi di induzione e di accelerazione che non possono esser messi in relazione con gli effetti della corrente.

Zusammenfassung—Untersucht wurde die elektroinitiierte Polymerisation von Trioxan in chlorierten Kohlenwasserstoffen mit Tetrabutylammoniumperchlorat als Elektrolyten. Die Initiierung erfolgt immer unter Oxidation des Perchlorats, jedoch zeigt die Polymerisation in verschiedenen Lösungmitteln unterschiedliche Charakteristiken. Es wurde gefunden, daß in 1,2-Dichloräthan die Polymerisation, gestartet durch einen kurzen Stromstoß, ohne Induktionsperiode mit mäßigem Umsatz erfolgt. Die anfängliche Polymerisationsgeschwindigkeit hängt linear ab von der Monomerkonzentration und von der initiierenden Ladung; daraus können einige kinetische Parameter bestimmt werden. Auf der anderen Seite erfordert die elektroinitiierte Polymerisation von Trioxan in Dichlormethan als Lösungsmittel einen ständigen Stromfluß, um zu größeren Umsätzen abzulaufen; hier tritt eine Induktionsperiode auf und eine Beschleunigung, die in keinen einfachen Zusammenhang zu dem Strom gebracht werden können.