KINETICS OF SOLUTION POLYMERISATION OF TRIOXANE—I

POLYMERISATION DURING INDUCTION PERIOD

M. N. CHANDRASHEKARA, D. DESAI and M. CHANDA

Department of Chemical Engineering, Indian Institute of Science, Bangalore-560012, India

(Received 4 September 1984; in revised form 15 April 1985)

Abstract—A study has been made of the solution polymerisation of trioxane in 1,2-dichloroethane with boron trifluoride diethyl etherate as the initiator during the induction period. The experimental parameters varied were initiator concentration, initial trioxane concentration and temperature. The rates of trioxane consumption, tetraoxane production and formaldehyde production and the rate of increase in the amount of soluble linear oligomers increased with increase in the initial concentrations of initiator and trioxane and with increase in temperature. The results also indicate an equilibrium between formaldehyde and cationic species. A kinetic model is proposed for polymerisation of trioxane during the induction period. The model proposes three parallel irreversible reactions between trioxane and cationic species and a reversible reaction between formaldehyde and cationic species. The scheme involves five rate constants which are determined from statistical fit of experimental data. The predictions of concentration-time profiles for various species are in excellent agreement with the experimental results.

1. INTRODUCTION

The polymerisation of trioxane to form polyoxymethylene is industrially important [1]. One commercially attractive and scientifically interesting way of carrying out this polymerisation is to conduct it in solution. This solution polymerisation of trioxane has attracted considerable attention [2-12]. An unusual feature of the solution polymerisation is the existence of an induction period during which no polymer precipitates out; precipitation starts only after the induction period. Though considerable information is available on the polymerisation during the precipitation period [3-5], not much is known about the behaviour of the system during the induction period [6-12].

Jaacks and Kern [6] were the first to establish that formaldehyde is produced during the induction period. They also suggested that the precipitation of polymer starts only after an equilibrium concentration of formaldehyde is reached. It has also been suggested [7] that the induction period can be reduced or eliminated by an initial addition of formaldehyde to the reaction mixture. On the other hand, Miki *et al.* [8] found that, though the presence of sufficient formaldehyde leads to instant turbidity when initiator is added, the amount of precipitate does not increase with time. Thus, according to them, the true induction period is not changed by the addition of formaldehyde.

Rakova *et al.* [9, 10] have divided the induction period into two parts, one associated with slow initiation and another with the accumulation of formaldehyde. They have also given an expression for total induction time in terms of the monomer and initiator concentrations. On the other hand, Hladky *et al.* [11] observed that the induction period is independent of monomer concentration when the

reaction is carried out in a solvent mixture (heptane nitrobenzene) with dielectric constant equal to that of trioxane. However, the dilatometric method used by these investigators gives no information on the nature and quantity of the various products formed during the reaction. Miki *et al.* [12] on the other hand have established by GLC the existence of cyclic oligomers, like tetraoxane and pentoxane, during the polymerisation of trioxane.

Thus, the information available so far refers to the occurrence of an induction period, the effects of various factors on it and the various products formed during the induction period. Not much is known, however, about the kinetic behaviour of the reacting system during the induction period.

We now report an experimental study and modelling of the kinetic behaviour during the induction period of trioxane polymerisation in 1,2-dichloroethane with boron trifluoride diethyl etherate as initiator. The parameters studied are initiator concentration, initial trioxane concentration and temperature.

2. EXPERIMENTAL

The polymerisations were carried out in a 1 litre resin kettle fitted with stirrer, immersed in a thermostat maintained to within $\pm 0.1^\circ$. Samples were withdrawn from the reaction mixture with a hypodermic syringe; they were immediately run into a weighed amount of chilled isopropanol to stop reaction. The parameters studied were temperature, catalyst concentration and initial concentration of trioxane. The reaction was studied at 35, 40, 45 and 50° . Earlier investigators [3] studied this reaction with a high ratio of catalyst to water. In this study, this ratio was kept very low. The concentration of water was fixed at 5 mmol/l by the addition of measured quantities of deionised water. The concentration of the catalyst, boron trifluoride ethyl etherate, ranged from 1 to 5 mmol/l. The

Table 1. Experimental conditions

Experiment number	Temperature (°C)	Initial monomer concentration $[M]_0$ (mol l ⁻¹)	Initial initiator concentration $[I]_0$ (mol l ⁻¹)
1	35.0	4.0	0.003
2	35.0	4.0	0.004
3	35.0	4.0	0.005
4	40.0	4.0	0.002
5	45.0	4.0	0.001
6	45.0	4.0	0.002
7	45.0	4.0	0.003
8	45.0	4.0	0.004
9	50.0	3.0	0.001
10	50.0	3.0	0.002
11	50.0	3.0	0.003
12	50.0	4.0	0.001
13	50.0	4.0	0.002
14	50.0	5.0	0.002

Solvent = 1,2-dichloroethane. Initiator = boron trifluoride diethyl etherate. Concentration of water = 5 mmol l⁻¹.

initial concentration of trioxane varied from 2 to 5 mol/l. The experimental conditions are presented in Table 1.

The 1,2-dichloroethane used as solvent was purified as described [13]. Trioxane was purified by washing a solution in CH₂Cl₂ with NaOH and Na₂SO₃ solutions. The organic phase was then dried over anhydrous Na₂SO₄. The trioxane was crystallised from this solution, dissolved in 1,2-dichloroethane and stored over lithium aluminium hydride to remove traces of moisture and other reactive impurities. The concentration of water in the trioxane solution was determined by Karl-Fischer titrations. Boron trifluoride diethyl etherate, was first vacuum distilled and then dissolved in 1,2-dichloroethane.

The samples withdrawn from the reaction mixture were analysed for trioxane, formaldehyde and tetroxane. The formaldehyde in the sample was determined by iodometric titration; the trioxane and tetroxane in the sample were determined by gas chromatography using a column filled with 10% polyethylene glycol monostearate-4000 coated on Fluoropak-80 and flame-ionisation detector. The isopropanol used to stop reaction in the sample also served as an internal standard in the gas-chromatographic analysis. The "cut and weigh" procedure was employed to measure the areas of peaks of the chromatogram.

3. DEVELOPMENT OF KINETIC MODEL

3.1. Material balance

The material balance was calculated for all the experiments. In all cases, the amounts of formaldehyde and tetroxane produced did not correspond to the trioxane consumed. Further, this difference increased with reaction time suggesting that some trioxane produces soluble linear oligomers. These oligomers could be dead or alive, and their total weight can be calculated in the following way:

$$G = [M]_0 - [M]90 - [T]120 - [F]30$$

where $[M]_0$ represents initial trioxane concentration, and $[M]$, $[T]$ and $[F]$ represent concentration of trioxane, tetroxane and formaldehyde at any time t .

3.2. Consumption of trioxane

The consumption of trioxane can be presented as

where M represents trioxane and P represents the

growing cations. The kinetics of consumption can be written as:

$$-\frac{d[M]}{dt} = k'[M]^p[P]^q \quad (1)$$

Assuming that $[P]$ is proportional to the initial concentration of initiator $[I]_0$, equation (1) can be written as

$$-\frac{d[M]}{dt} = k'\alpha[M]^p[I]_0^q$$

where α includes the proportionality constant. It may be noted that several previous workers have in fact, assumed $[P]$ to be equal to $[I]_0$ at a given temperature [4, 14].

A plot of initial rate of trioxane consumption vs $[I]_0$ at various values of $[M]_0$ was linear indicating the order of reaction to be 1 with respect to initiator. Similarly, plots of $\log(-d[M]/dt)$ vs $\log[M]$ gave parallel straight lines having slope close to 2, indicating second order reaction with respect to trioxane. Equation (1) thus becomes

$$-\frac{d[M]}{dt} = k'\alpha[M]^2[I]_0$$

which on integration gives

$$\frac{1}{[M]} = \frac{1}{[M]_0} + k'\alpha[I]_0t$$

Putting $k = k'\alpha$ gives

$$\frac{1}{[M]} = \frac{1}{[M]_0} + k[I]_0t \quad (2)$$

Figure 1 depicts a plot of $1/[M]$ vs t data for various $[I]_0$ values. It is evident that equation (2) satisfies the data extremely well. Further, a constant value (for k) is obtained if the slopes of various lines are divided by the appropriate $[I]_0$ values. This result supports the assumption of linear proportionality between $[P]$ and $[I]_0$.

3.3. Conditions at the end of the induction period

Table 2 shows concentrations of tetroxane and formaldehyde at the end of the induction period ($t = t^*$) at 50° for various values of $[M]_0$. It is evident that the formaldehyde concentration at $t = t^*$ is

Fig. 1. Plot of $1/[M]$ vs time at different initiator concentration. $[M]_0 = 4.0$ mol/l, temperature = 35.0° .

independent of $[M]_0$, whereas that of tetroxane is not. This suggests an equilibrium between cationic species P and formaldehyde and the absence of such an equilibrium between cationic species and tetroxane at $t = t^*$.

3.4. Kinetic model

Based upon the above analysis of experimental data, the following kinetic model can be written for the polymerisation of trioxane during the induction period:

It should be noted that the species P consists of cationic molecules produced by reactions (B1) and

(B2) as well as other cationic molecules of greater chain lengths. P is seen from reaction scheme (B) to be ion pairs. Reactions (B1) and (B2) are the ionisation reactions and indicate the manner in which ion pairs are generated by the initiator. Reaction (B3) corresponds to initiation, propagation and formation of formaldehyde and tetroxane reaction. Reaction (B4) is the reversible reaction between formaldehyde and the cationic species. The model postulates that the trioxane (M) reacts with the cationic species (P) to form an activated species P' which at once undergoes three parallel rapid reactions by which a fraction x is converted into tetroxane, a fraction y into formaldehyde and a fraction $(1-x-y)$ into the cationic species P. Reaction (B5) is the chain transfer reaction producing dead linear oligomer.

Based on the arguments given in Section 3.2, we also have $k_1 = k'_1\alpha$, $k_2 = k'_2\alpha$, $k_{tr} = k'_{tr}\alpha$. The molar rates of consumption of M and of production of F and T are given by the following equations:

$$-\frac{d[M]}{dt} = k[I]_0[M]^2 \quad (3)$$

$$\frac{d[T]}{dt} = kx[I]_0[M]^2 \quad (4)$$

$$\frac{d[F]}{dt} = 3ky[I]_0[M]^2 - k_1[F][I]_0 + k_2[I]_0 \quad (5)$$

The rate of increase in weight of dead linear oligomers can be given by

$$\frac{dW_D}{dt} = k_{tr}[I]_0[H_2O]M'_D \quad (6)$$

where W_D represents the weight of dead linear oligomers and M'_D is their average molecular weight at time t . The rate of gain in the weight of cationic (living linear) oligomers is given by:

$$\begin{aligned} \frac{dW_L}{dt} = & k(1-x-y)[I]_0[M]^2M'_M + k_1[F][I]_0M'_F \\ & - k_2[I]_0M'_F - k_{tr}[I]_0[H_2O]M'_D \\ & - kx[I]_0[M]^2M'_F \end{aligned} \quad (7)$$

where W_L is the weight of living linear oligomers. The last term in equation (7) represents the loss of one CH_2O unit from cationic molecules required to produce one tetroxane molecule from one trioxane molecule. M'_M and M'_F are the molecular weights of trioxane and formaldehyde respectively. Further by definition

$$G = W_L + W_D \quad (8)$$

Table 2. Concentration of tetroxane and formaldehyde at the end of the induction period

Experiment number	Temperature ($^\circ\text{C}$)	$[M]_0$ (mol l $^{-1}$)	$[I]_0$ (mol l $^{-1}$)	t^* (min)	$[T]^*$ (mol l $^{-1}$)	$[F]^*$ (mol l $^{-1}$)
9	50	3.0	0.001	105	0.121	0.134
10	50	3.0	0.002	38	0.121	0.131
12	50	4.0	0.001	65	0.148	0.137
13	50	4.0	0.002	27	0.147	0.134
14	50	5.0	0.002	17.5	0.162	0.133

$[M]_0$ = initial monomer concentration; $[I]_0$ = initial initiator concentration; t^* = induction time; $[T]^*$ = tetroxane concentration at t^* ; $[F]^*$ = formaldehyde concentration at t^* .

Equations (6), (7) and (8) lead to

$$\frac{dG}{dt} = k(1-x-y)[I]_0[M]^2M'_M + k_1[F][I]_0M'_F - k_2[I]_0M'_F - kx[I]_0[M]^2M'_F \quad (9)$$

Equation (9) is rearranged to

$$\frac{d(G/M'_M)}{dt} = k(1-4/3x-y)[I]_0[M]^2 + [1/3][F][I]_0k_1 - [1/3]k_2[I]_0 \quad (10)$$

Dividing equation (5) by 3 and adding to equation (10) leads to:

$$\frac{d}{dt} \{ [F]/3 + G/M'_M \} = k(1-(4/3)x)[I]_0[M]^2 \quad (11)$$

Equations (3), (4), (5) and (11) represent the kinetic behaviour of the reacting system in the interval $0 \leq t \leq t^*$. The solutions of these equations with the initial conditions

$$\begin{aligned} t=0, [M] &= [M]_0 \\ [T] &= 0 \\ [F] &= 0 \\ G &= 0 \end{aligned} \quad (12)$$

are as follows:

$$[M] = \frac{[M]_0}{(1+at)} \quad (13)$$

$$[T] = kx[I]_0[M]_0^2(t-at^2+a^2t^3) \quad (14)$$

$$\begin{aligned} [F] &= \left[\left\{ \frac{1}{k_1[I]_0} + \frac{2a}{k_1^2[I]_0^2} + \frac{6a^2}{k_1^3[I]_0^3} \right\} 3ky[I]_0[M]_0^2 \right. \\ &\quad \left. + \frac{k_2}{k_1} \right] (1 - e^{-k_1[I]_0t}) + 3ky[I]_0[M]_0^2 \\ &\quad \times \left[-\frac{2at}{k_1[I]_0} + \frac{3a^2t^2}{k_1[I]_0} - \frac{6a^2t}{k_1^2[I]_0^2} \right] \end{aligned} \quad (15)$$

and

$$\begin{aligned} \{ G/M'_M + [F]/3 \} &= k(1-(4/3)x)[I]_0[M]_0^2 \\ &\quad \times (t-at^2+a^2t^3) \end{aligned} \quad (16)$$

where

$$a = k[I]_0[M]_0 \quad (17)$$

The equations (14)–(16) are obtained based upon the first three terms of the binomial expansion of $[1/(1+at)^2]$.

Equations (13)–(17) describe the variation of molar concentrations of trioxane [M], tetraoxane [T], formaldehyde [F] and variation of $\{[F]/3 + G/M'_M\}$ with time during the induction period $0 \leq t \leq t^*$. To employ the equations (13)–(17) for numerical calculations, one needs the values of constants k , x , y , k_1 and k_2 .

3.5. Evaluation of constants

The five constants k , x , y , k_1 and k_2 can be evaluated as follows

(i) The slope of the linear plot of $1/[M]$ vs t [equation (2)] is $k[I]_0$, giving the value of k .

(ii) Once k is known, x can be obtained from the least squares fit of the experimental data of $[T]$ vs t to equation (14).

(iii) At $t = t^*$, $k_1[F]^*[I]_0 = k_2[I]_0$.

This yields:

$$\frac{k_1}{k_2} = \frac{1}{[F]^*} \quad (18)$$

and

$$y = \frac{(d[F]/dt)_{t=t^*}}{3k[I]_0[M]^*2} \quad (19)$$

Equation (18) gives a relationship between k_1 and k_2 in terms of experimentally measured (or extrapolated) value of $[F]$. So once k_1 is fixed, k_2 also is fixed.

From the experimental data, one knows values of $(d[F]/dt)_{t=t^*}$ and $[M]^*$. ($[M]^* = [M]$ at $t = t^*$ and $[F]^* = [F]$ at $t = t^*$.) Using these values one can find, from equation (19), the values of y . However, this value of y is only an initial estimate, as the value of the derivative at $t = t^*$ from the data is not very accurate. The exact value has to be decided along with the value of k_1 , such that $[F]$ vs t data are properly explained.

(iv) At $t = 0$, $[F] = 0$; and one has

$$3ky[I]_0[M]_0^2 + k_2[I]_0 = (d[F]/dt)_{t=0}$$

Table 3. Kinetic parameters evaluated from individual experiments and their averages

Temperature (°C)	$[M]_0$ (mol l)	$[I]_0$ (mol l)	Individual constants					Average constants				
			k	x	y	k_1	k_2	k	x	y	k_1	k_2
35	4.0	0.003	0.059	0.492	0.037	2.7	0.184	0.059	0.512	0.040	2.667	0.182
		0.004	0.059	0.530	0.042	2.7	0.184					
		0.005	0.059	0.515	0.042	2.6	0.177					
40	4.0	0.002	0.111	0.577	0.049	6.0	0.450	0.111	0.595	0.052	6.250	0.469
		0.004	0.111	0.613	0.054	6.5	0.488					
45	4.0	0.001	0.200	0.415	0.040	10.0	0.970	0.200	0.495	0.040	11.500	1.116
		0.002	0.202	0.492	0.041	14.0	1.358					
		0.003	0.200	0.480	0.039	10.0	0.970					
		0.004	0.201	0.595	0.040	12.0	1.164					
50	3.0	0.001	0.360	0.408	0.044	24.0	3.192	0.360	0.500	0.049	24.83	3.300
		0.002	0.361	0.542	0.044	24.0	3.192					
		0.003	0.360	0.555	0.044	24.0	3.192					
	4.0	0.001	0.361	0.444	0.044	24.0	3.192					
		0.002	0.359	0.511	0.044	24.0	3.192					
	5.0	0.002	0.360	0.542	0.069	29.0	3.857					

Units of rate constants: k , $l^2 \text{ mol}^{-2} \text{ min}^{-1}$; k_1 , $\text{mol}^{-2} \text{ min}^{-1}$; k_2 , min^{-1} .

Fig. 2. Effect of initiator concentration on trioxane consumption. $[M]_0 = 4.0$ mol/l, temperature = 35.0° .

Once the initial estimate of y has been made, this equation will yield the value of k_2 . This again is only an approximate value because the value of $(d[F]/dt)_{t=0}$ from the experimental data will be approximate. The exact value of k_2 will be decided, along with the exact values of y and k_1 , to satisfy $[F]$ vs t data.

4. RESULTS AND DISCUSSIONS

Table 3 shows the constants k , x , y , k_1 and k_2 calculated using the procedure outlined earlier for the experiments mentioned in Table 1. Table 3 also shows the average values of k , x , y , k_1 and k_2 for various temperatures.

Figures 2–13 present the $[M]$ vs t , $[F]$ vs t , $[T]$ vs t and $\{[F]/3 + G/M'_M\}$ vs t plots in the period $0 \leq t \leq t^*$ for various experimental conditions. The experimental data are represented by various symbols; theoretical predictions based on equations

Fig. 3. Effect of initiator concentration on tetroxane production. $[M]_0 = 4.0$ mol/l, temperature = 35.0° .

Fig. 4. Effect of initiator concentration on formaldehyde production. $[M]_0 = 4.0$ mol/l, temperature = 35.0° .

(13)–(17) are presented by lines. The solid lines are based on the best constants obtained for the individual experiments, whereas the broken lines are based on average constants at the given temperature. It is evident from these figures that the trioxane concentration $[M]$ decreases monotonically with time, whereas the concentrations of formaldehyde, $[F]$ and tetroxane, $[T]$ and the amount of linear soluble oligomers (both dead or alive) represented by G/M'_M increase monotonically with time. This is expected from the reaction scheme (B) and is predicted by the theoretical curves. The monotonicity also implies that the rate of formaldehyde production from trioxane and species P always remains greater than the rate of formaldehyde consumption by reaction (B4).

Figures 2–13 also show that the theoretical predictions based on the average constants are very close to the predictions based on the constants from individual experiments.

Fig. 5. Effect of initiator concentration on $\{[F]/3 + G/M'_M\}$. $[M]_0 = 4.0$ mol/l, temperature = 35.0° .

Fig. 6. Effect of initial trioxane concentration on trioxane consumption. $[I]_0 = 0.002$ mol/l, temperature = 50.0°

Figures 2–5 show the effect of variation in initial initiator concentration on the $[M]$ vs t , $[T]$ vs t , $[F]$ vs t and $\{[F]/3 + G/M_M'\}$ profiles. Evidently, the rates of trioxane consumption, tetroxane production and formaldehyde production, and rate of increase in amount of linear soluble oligomers (represented by G/M_M') increase with increase in the initial initiator concentration. This is understandable, as the increased initiator concentration would lead to more collisions between cationic molecules and trioxane molecules, which in turn leads to higher rates of trioxane consumption and product formation. This behaviour is also expected from equations (13)–(17). In fact, theoretical predictions based on equations (13)–(17) not only predict the correct trend but also explain the data fairly well. Particularly encouraging is the fact that the constants k and x determined from

Fig. 7. Effect of initial trioxane concentration on tetroxane production. $[I]_0 = 0.002$ mol/l, temperature = 50.0°

Fig. 8. Effect of initial trioxane concentration on formaldehyde production. $[I]_0 = 0.002$ mol/l, temperature = 50.0°

the data of $[M]$ vs t and $[T]$ vs t , when substituted in equation (16), explain the data of $\{[F]/3 + G/M_M'\}$ vs t fairly well (see Fig. 5).

Figures 6–9 show the effect of variation in initial trioxane concentration, $[M]_0$ on $[M]$ vs t , $[T]$ vs t , $[F]$ vs t and $\{[F]/3 + G/M_M'\}$ vs t profiles. It is apparent that the rates of trioxane consumption and product formation increase with increase in the initial concentration of trioxane. This again is understandable and fits in with the molecular collision picture. Again, this effect of $[M]_0$ is also reflected by the model. The theoretical predictions based on equations (13)–(17) explain the trend as well as the actual data of Figs 6–9 fairly well.

Figures 10–13 exhibit the effect of variation in temperature on the changes with time of various quantities. The Figures show that the rates of tri-

Fig. 9. Effect of initial trioxane concentration on $\{[F]/3 + G/M_M'\}$. $[I]_0 = 0.002$ mol/l, temperature = 50.0°

Fig. 10. Effect of temperature on trioxane consumption. $[M]_0 = 4.0$ mol/l, $[I]_0 = 0.002$ mol/l.

Fig. 11. Effect of temperature on tetroxane production. $[M]_0 = 4.0$ mol/l, $[I]_0 = 0.002$ mol/l.

Fig. 12. Effect of temperature on formaldehyde production. $[M]_0 = 4.0$ mol/l, $[I]_0 = 0.002$ mol/l.

oxane consumption and product formation increase with rise in the temperature, as expected. Once again, the theoretical predictions based on equations (13)–(17) not only explain the correct trend but also explain the data reasonably well.

Figure 14 shows the linear Arrhenius plots for the average values of k , k_x , k_y , k_1 and k_2 . Interestingly, the Figure shows that the slopes of the average values of k , k_x and k_y are the same, showing that the activation energies for all the reactions given by (B3) are the same. This supports the central hypothesis of the model that there is a single very short-lived activated species P' which leads to various products.

It is evident from Figs 2–13 that the induction period, t^* , decreases as the initial concentrations of initiator and trioxane and the temperature increase. Also the concentration of formaldehyde at t^* is independent of the initial concentrations of initiator and trioxane, but increases with increase in temperature. These findings agree with those of Jaacks and Kern [6] and confirm their hypothesis about the

Fig. 13. Effect of temperature on $\{[F]/3 + G/M_w\}$. $[M]_0 = 4.0$ mol/l, $[I]_0 = 0.002$ mol/l.

Fig. 14. Arrhenius plots of various rate constants. (○) k , (△) k_x , (×) k_y , (●) k_1 , (▲) k_2 .

existence of an equilibrium between formaldehyde and cationic species at $t = t^*$.

Miki *et al.* [14] have found that in the post-induction period the tetroxane concentration remains constant (they view this constant value as equilibrium value). They also found that this constant value increases with increase in initial trioxane concentration. The present results (Table 2) also corroborate this trend. However, the present model does not consider that the tetroxane equilibrates with cationic species at $t = t^*$. The good agreement between theory and experiments for various $[T]$ vs time data lends support to this approach.

Miki *et al.* [12] also concluded that the solution polymerisation of trioxane during the post-induction period occurs by the following mechanism:

However, our present results suggest that the reversibility of these reactions is negligible during the induction period. Our results further indicate that the species P' is highly unstable and its concentration during the induction period is negligible since it is consumed as soon as it is formed.

5. CONCLUSIONS

The present study indicates that the rates of trioxane consumption, tetroxane production and formaldehyde production and the rate of increase in amount of soluble linear oligomer increase with increase in initial concentrations of initiator and trioxane and with increase in temperature. Further, the hypothesis that tetroxane, formaldehyde and growing cationic chains are produced from a single highly unstable species by three parallel very rapid reactions leads to a model which satisfactorily explains the observed kinetic behaviour of the system.

Acknowledgement—The financial assistance provided by Council of Scientific and Industrial Research, Government of India to one of the authors (M. N. Chandrashekara) is gratefully acknowledged.

REFERENCES

1. M. Sittig, *Hydrocarb. Process. Petrol. Refin.* **41**, 131 (1962). *Hydrocarb. Process.* **45**, 155 (1966).
2. K. Weissmehl, E. Fischer, K. Gutweiler, H. D. Hermann and H. Cherdron, *Angew. Chem. Int. Ed.* **6**, 526 (1967).
3. S. Okamura, T. Higashimura and T. Miki, *Progress in Polymer Science, Japan* (Edited by S. Okamura and M. Takayanagi), Vol. 3, p. 97. Wiley, New York (1972).
4. P. S. Raman and V. Mahadevan, *Makromolek. Chem.* **178**, 1367 (1977).
5. C. S. Hsia Chen, *J. Polym. Sci., Polym. Chem. Ed.* **14**, 143 (1976).
6. V. Jaacks and W. Kern, *J. Polym. Sci.* **48**, 399 (1960).
7. G. Odian, *Principles of Polymerisation*, p. 474. McGraw-Hill, New York (1970).
8. T. Miki, T. Higashimura and S. Okamura, *Bull. chem. Soc., Japan* **39**, 36 (1966).
9. G. V. Rakova, J. M. Romanov and N. S. Enikolopyan, *Vysokomolek. Soedin.* **6**, 2178 (1964).
10. N. S. Enikolopyan, V. T. Irshak, I. P. Kravchuk, O. A. Plichov, G. V. Raveva, I. M. Ramanov and G. N. Savushkina, *J. Polym. Sci. C16*, 2453 (1967).
11. B. Hladky, M. Kucera and K. Majerova, *Colln Czech. chem. Commun.* **32**, 4162 (1967).
12. T. Miki, T. Higashimura and S. Okamura, *J. Polym. Sci. A-1*, **5**, 95 (1967).
13. J. A. Riddick and W. B. Bunger, *Organic Solvents, Techniques of Chemistry* (Edited by A. Weissberger), Vol. II, 3rd edn. Wiley-Interscience, New York (1970).
14. T. Miki, T. Higashimura and S. Okamura, *J. Polym. Sci. A-1*, **5**, 2977 (1967).
15. M. Kucera and E. Spousta, *J. Polym. Sci. A*, **2**, 3431 (1964).