

# Study on kinetics of copolymerization of styrene and maleic anhydride in methyl ethyl ketone

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The compositional and rate data are measured for the alternating copolymerization of styrene and maleic anhydride in methyl ethyl ketone at 60°C with AIBN as initiator. The kinetic scheme is evaluated in terms of the participation of a monomer–monomer complex, accepting that the monomer radical at the chain end reacts only with the dissimilar monomer of the complex.  $r_1$  and  $r_2$  are determined for vanishing complex concentrations.  $r_2$  is very low but not zero. The ratios of propagation via the complex to those of normal alternating propagation could be evaluated as well as the term  $2\phi\delta_1\delta_2r_1r_2$ . The latter only for vanishing  $[M_1]$  or  $[M_2]$  respectively and for  $[M_1]=[M_2]$ . This allowed us to calculate the rate vs. composition curve for three constant overall monomer concentrations. For the lowest overall concentration the agreement between calculation and experiment is only fair, but for the overall concentrations  $[M_1] + [M_2] = 1$  and  $3 \text{ mol l}^{-1}$  it is good, thus demonstrating the possibility of describing the polymerization process by the model used here. The concept of participation of charge transfer complex between styrene and maleic anhydride is found to explain most features of copolymerization of these monomers in methyl ethyl ketone.

**(Keywords: styrene; maleic anhydride; alternating copolymerization; charge transfer complex; reaction scheme; macroradicals; cross termination)**

## INTRODUCTION

In a previous communication<sup>1</sup> we presented an analysis of the kinetics of copolymerization of styrene and maleic anhydride in dioxane at 50°C in terms of a monomer–monomer complex model and the participation of the complex in propagation. It was found that such a concept could explain most features of the system. In addition, mathematical formulations were developed which permitted evaluation of various constants such as  $r_1$ ,  $r_2$ ,  $\delta_1$ ,  $\delta_2$ ,  $\Phi$  and those representing the reactivity of the complex. The cross-termination factor  $\Phi$  was shown to play an important role in describing the kinetics and was always favoured over the mutual termination of similar radicals throughout the broad range of monomer feed compositions. It was thus concluded that both the composition of the copolymers and the rates of copolymerization in dioxane were in accord with the complex model. In our analysis, however, we neglected the reaction of a macroradical having a particular monomer end-unit with the same macromer of the complex. This assumption was made in view of the following facts:

(a) the very low homopolymerizability of maleic anhydride, thus allowing the neglect of the reaction of a maleic anhydride-ended macroradical with the maleic anhydride side of the complex;

(b) the stability of a styrene-ended macroradical is higher than that of a maleic anhydride-ended macroradical;

(c) styrene–maleic anhydride copolymers are approximately alternating.

It was felt, however, interesting and important to conduct the copolymerization in a different solvent, preferably in one which had already been reported in literature. Copolymerization of the monomer mixture in methyl ethyl ketone is such a case, for example. On the basis of compositional data of Dodgson and Ebdon<sup>2</sup> for this system, Farmer *et al.*<sup>3</sup> have calculated values of various constants applying the concept of kinetic probabilities. Two somewhat curious conclusions seem to bear out from their analysis:

(i) the value of reactivity ratio of styrene seems to be much higher than commonly reported value in styrene–maleic anhydride copolymerization;

(ii) a styrene-ended macroradical is almost equally reactive to either side of the monomer–monomer complex.

These conclusions were made by Farmer *et al.*<sup>3</sup> on the basis of compositional data. Recently Braun and Czerwinski<sup>4</sup> have used values of the various constants<sup>3</sup> for explaining the rates of copolymerization of styrene and maleic anhydride in acetone using data of Arnold and Rätzsch<sup>5</sup>. The constants seem to qualitatively describe the rate features but no conclusion could be drawn regarding quantitative description of the system.

Here we report the compositional and kinetic analysis of the copolymerization of styrene and maleic anhydride in methyl ethyl ketone at 60°C with azo-bis-isobutyronitrile (AIBN) as initiator.

## EXPERIMENTAL

Purification of the monomers and initiator and the method of polymerization have been described pre-

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viously<sup>1</sup>. The concentrations of the various complexes such as monomer-1-monomer-2, solvent-monomer-1 and solvent-monomer-2 were calculated using the values of equilibrium constants of Dodgson and Ebdon<sup>2</sup> and following the iterative method of Tsuchida *et al.*<sup>5</sup>

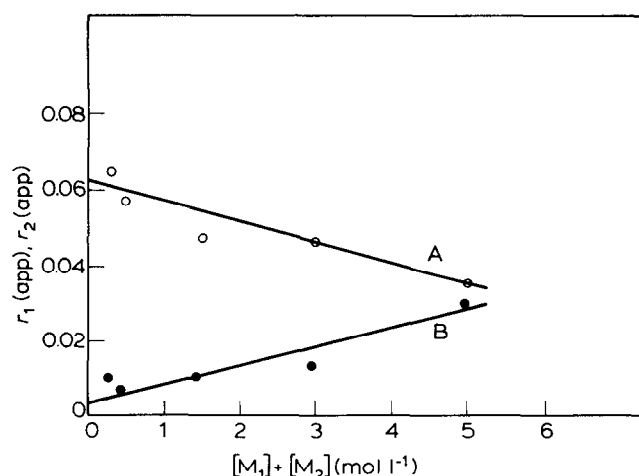
Rates of initiation for different monomer compositions and total monomer concentrations were determined using verdazyl as inhibitor as reported earlier<sup>1</sup>.

## RESULTS AND DISCUSSION

The values of apparent reactivity ratios obtained from compositional data using a modified Kelen-Tüdös plot<sup>6</sup> along with the values obtained from the data of Dodgson and Ebdon<sup>2</sup>, are shown in Table 1. The extrapolated values of reactivity ratios (Figure 1) at  $[M_1] + [M_2] = 0$  are 0.062 and 0.003 respectively. The value of  $r_2$  (maleic anhydride) is extremely small and is comparable with the reported value<sup>3</sup> obtained from bulk copolymerization data. In contrast, the value of 0.062 is much smaller compared with 0.54 which is very high by all accounts. The only difference between our method and the analytical method of Farmer *et al.*<sup>3</sup> is that, whereas we have neglected reactions between a macroradical having a particular monomer at its end with a similar monomer of the complex, they have included these reactions and hence their formulations are more general. However, if we include these reactions in the scheme of reactions for compositional analysis<sup>6</sup>, a relationship such as the following is obtained:

**Table 1** Values of apparent reactivity ratios for various total monomer concentrations in the copolymerization of styrene and maleic anhydride in methyl ketone at 60°C

Total monomer concentration ( $[M_1] + [M_2]$ ) (mol l <sup>-1</sup> )	Apparent reactivity ratios	
	$r_1$ (st)	$r_2$ (mal. anh)
5.0	0.035	0.030
3.0	0.045	0.014
1.5	0.047	0.010
0.5	0.058	0.006
0.3	0.064	0.010



**Figure 1** Variation of apparent reactivity ratios with total monomer concentrations for copolymerization of styrene and maleic anhydride in methyl ethyl ketone at 60°C: (A)  $r_1$ ; (B)  $r_2$

$$y = \frac{dM_1}{dM_2} = \frac{r_1 \frac{[M_1]}{[M_2]} + 1 + A_1 \frac{[C]}{[M_1]} + B_1 \frac{[C]}{[M_2]} + C_1 \frac{[C]^2}{[M_1][M_2]}}{r_2 \frac{[M_2]}{[M_1]} + 1 + A_2 \frac{[C]}{[M_1]} + B_2 \frac{[C]}{[M_2]} + C_1 \frac{[C]^2}{[M_1][M_2]}} \quad (1)$$

where  $A_1, A_2, B_1, B_2$  and  $C_1$  are the following constants:

$$A_1 = \frac{k_{2c}}{k_{21}} = \frac{k_{2c1} + k_{2c2}}{k_{21}}$$

$$B_1 = \left( \frac{k_{1c}}{k_{12}} + \frac{k_{1c1}}{k_{12}} + r_1 \frac{k_{2c2}}{k_{21}} \right)$$

$$C_1 = \left( \frac{k_{1c}}{k_{12}} \cdot \frac{k_{2c2}}{k_{21}} + \frac{k_{2c}}{k_{21}} \cdot \frac{k_{1c1}}{k_{12}} \right)$$

$$A_2 = \left( \frac{k_{2c}}{k_{21}} + r_2 \frac{k_{1c1}}{k_{12}} + \frac{k_{2c2}}{k_{21}} \right)$$

$$B_2 = \frac{k_{1c}}{k_{12}} = \frac{k_{1c1} + k_{1c2}}{k_{12}}$$

It is evident that if compositional data are available for the copolymers for various total monomer concentrations at equimolar feeds, the extrapolated value of  $y$  at  $[C] = 0$  should afford the value of  $r_1 + 1$ . Such an exercise results in a value of  $r_1$  which is very near to our value of 0.062. It thus seems necessary to re-evaluate various constants necessary to describe the copolymerization of styrene and maleic anhydride. Equation (1) as such is very complex to work with for a wide range of monomer feed compositions. However, it can be transformed into a simpler form under specified conditions. Thus, when  $[M_1]$  is very high, terms involving  $[C]/[M_1]$  and  $[C]^2/[M_1][M_2]$  can be neglected and one obtains

$$y = \frac{r_1 x + 1 + \left( \frac{k_{1c}}{k_{12}} + \frac{k_{1c1}}{k_{12}} + r_1 \cdot \frac{k_{2c2}}{k_{21}} \right) \frac{[C]}{[M_2]}}{\left( 1 + \frac{k_{1c}}{k_{12}} \cdot \frac{[C]}{[M_2]} \right)}$$

which on rearrangement gives

$$(y - 1 - r_1 x) \frac{[M_2]}{[C]} = \left( \frac{k_{1c}}{k_{12}} + \frac{k_{1c1}}{k_{12}} + r_1 \cdot \frac{k_{2c2}}{k_{21}} \right) - \frac{k_{1c}}{k_{12}} y \quad (2)$$

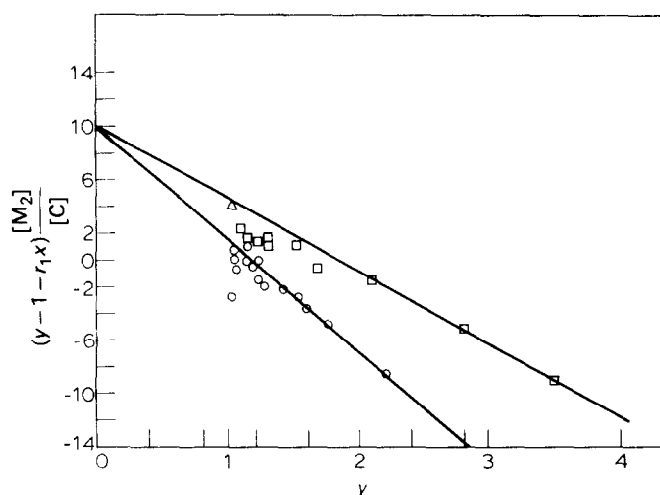
A plot according to equation (2) is shown in Figure 2. Data of Dodgson and Ebdon<sup>2</sup> for  $[M_1] + [M_2] = 5 \text{ mol l}^{-1}$  have also been plotted along with our data for  $[M_1] + [M_2] = 3 \text{ mol l}^{-1}$  and  $1.5 \text{ mol l}^{-1}$ . It is interesting to note that it is possible to extrapolate both sets of data to the same intercept within experimental error but the slopes differ. From the plot of our data, the following values for the constants are obtained from the slope

$$\frac{k_{1c1} + k_{1c2}}{k_{12}} = \frac{k_{1c}}{k_{12}} = 8.4$$

and from the intercept (10.0)

$$\frac{k_{1c1}}{k_{12}} = 1.60$$

(assuming  $k_{2c2}/k_{21} = 0$  in view of very low homopolymerizability of maleic anhydride)



**Figure 2** Plot of  $(y-1-r_1x)[M_2]/[C]$  vs.  $y$  according to equation (2). Our data (○); data of Dodgson and Ebdon<sup>2</sup> (□) in methyl ethyl ketone at 60°C

which ultimately give  $k_{1c2}/k_{12}=6.8$  and  $k_{1c1}/k_{1c2}=0.24$ . These values are smaller by factors of 3 and 5 compared with those obtained analytically<sup>3</sup>. Thus the values of both  $r_1$  and  $k_{1c}/k_{12}$  obtained from composition analysis alone seem to be overestimated. It is difficult at this stage to explain this discrepancy on the basis of experimental error or a concentration dependence of the various constants. A more rigorous analysis involving rate data may throw some light on the values of various constants. Transformation of equation (1) into a workable form for higher concentrations of  $M_2$  (maleic anhydride) is not realistic because when  $[M_2]$  is high, terms involving  $[C]/[M_2]$  and  $[C]^2/[M_1][M_2]$  cannot be neglected as the concentrations of the complex are quite appreciable even under such conditions. Values of constants signifying reactions of maleic anhydride-ended macroradicals are better obtained from analysis of rate data involving equimolar feed compositions as we will describe below. However, it is clear from the above analysis that a macroradical ending in styrene reacts preferably with the maleic anhydride side of the complex, a contention we followed previously<sup>1</sup>. The compositional equation which was deduced on the basis of reactions of macroradicals with the dissimilar monomer side of the complex only was followed with experimental data on dioxane, could not describe the compositional data in methyl ethyl ketone very well. Thus here the compositions of the copolymers seem to be much affected by reactions of macroradicals with a similar monomer in the complex.

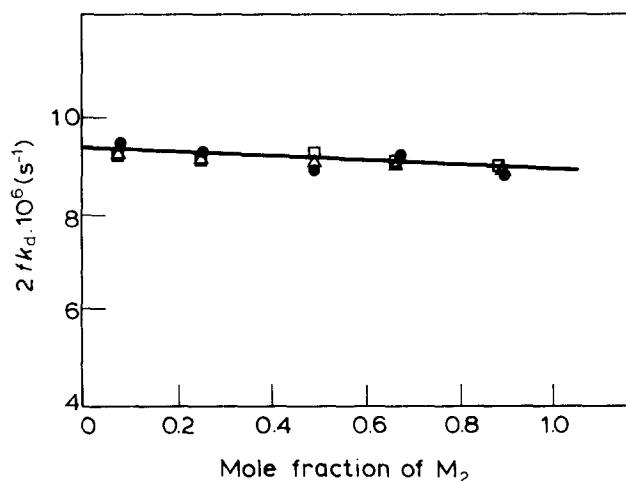
Figure 3 shows the variation of specific rates of initiation ( $2fk_d$ ) with the mole fraction of maleic anhydride in feed for three different total monomer concentrations.  $2fk_d$  is found to be independent of the total monomer concentrations and varies only slightly with monomer composition. The value of  $9.20 \times 10^{-6} \text{ s}^{-1}$  at equimolar feed agrees well with the value of  $9.56 \times 10^{-6} \text{ s}^{-1}$  (assuming  $f=0.5$ ) obtained from the relationship  $k_d=1 \times 10^{15} \exp(-30.7 \text{ kcal}/RT)$  used by Tsuchida and Tomono<sup>7</sup> for copolymerization of styrene and maleic anhydride in acetone. Figure 4 shows log-log plots of rates of polymerization (normalized to  $[I]^{0.5}=1$ ) vs. the individual monomer concentration for equimolar feeds. A slope of

about 1.45 indicates propagation via both free and complexed monomers<sup>1</sup>.

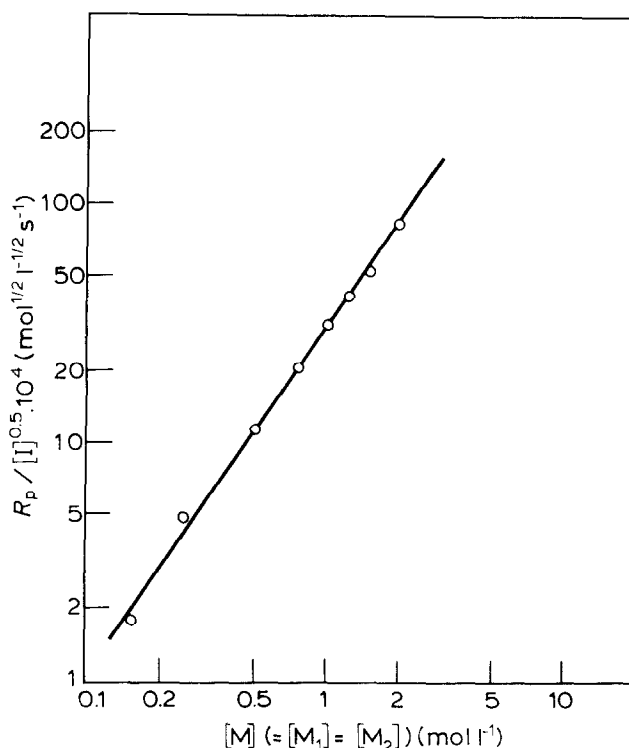
Table 2 shows values of rates of copolymerization corresponding to various monomer feed compositions and initiator concentrations for  $[M_1]+[M_2]=3 \text{ mol l}^{-1}$ ,  $1.5 \text{ mol l}^{-1}$  and  $0.5 \text{ mol l}^{-1}$  in methyl ethyl ketone at 60°C. There are well defined maxima of  $R_p$  at about 70 mol% of maleic anhydride.

#### Generalized rate relationship

We will now analyse our data in the light of the generalized formulation of the rate including all possible



**Figure 3** Variation of specific rates of initiation,  $2fk_d$  with feed compositions for three total monomer concentrations.  $[M_1]+[M_2]=3 \text{ mol l}^{-1}$  (●),  $1.5 \text{ mol l}^{-1}$  (Δ),  $0.5 \text{ mol l}^{-1}$  (□)



**Figure 4** Log-Log plot of rates of copolymerization normalized to  $[I]^{0.5}=1 \text{ mol l}^{-1}$  vs. individual monomer concentration for equimolar feed compositions in styrene-maleic anhydride copolymerization in methyl ethyl ketone at 60°C

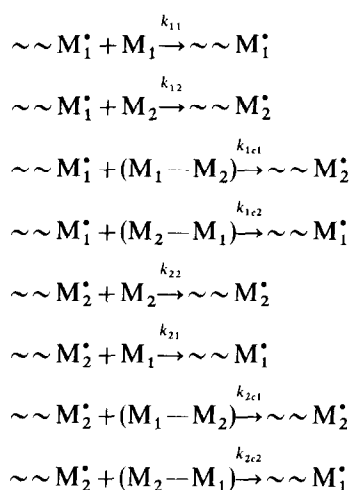
**Table 2** Values of  $R_p$ , the rate of copolymerization of styrene and maleic anhydride in methyl ethyl ketone at 60°C

$[M_1]$ (mol <sup>-1</sup> )	$[M_2]$ (mol <sup>-1</sup> )	$[I] \cdot 10^3$ (mol <sup>-1</sup> )	$[C] \cdot 10^3$ (mol <sup>-1</sup> )	$R_p \cdot 10^5$ (mol <sup>-1</sup> s <sup>-1</sup> )
2.90	0.10	3.01	8.60	3.77
2.75	0.25	3.00	23.00	6.67
2.50	0.50	2.96	42.20	12.05
2.25	0.75	2.92	57.40	15.26
2.00	1.00	2.89	68.70	19.19
1.50	1.50	2.82	78.50	28.07
1.00	2.00	2.75	71.00	34.01
0.50	2.50	2.67	45.20	32.14
0.25	2.75	2.65	24.90	28.09
1.45	0.05	2.71	1.80	1.57
1.38	0.12 <sub>5</sub>	2.70	4.30	2.65
1.25	0.25	2.67	7.90	4.60
1.12 <sub>5</sub>	0.38	2.63	10.70	5.74
1.00	0.50	2.60	12.70	7.26
0.75	0.75	2.54	14.40	9.66
0.50	1.00	2.47	12.90	10.80
0.25	1.25	2.40	8.10	9.88
0.12 <sub>5</sub>	1.37 <sub>5</sub>	2.38	4.40	8.30
0.48	0.02	2.83	0.20	0.33
0.46	0.04	2.81	0.30	0.46
0.42	0.08	2.78	0.70	0.84
0.38	0.12 <sub>5</sub>	2.74	0.90	1.39
0.33	0.17	2.71	1.10	1.81
0.25	0.25	2.65	1.30	2.50
0.17	0.33	2.58	1.10	2.86
0.08 <sub>3</sub>	0.42	2.50	0.70	2.69
0.04	0.46	2.49	0.40	2.44

$M_1$  = styrene,  $M_2$  = maleic anhydride, I = AIBN

C = styrene-maleic anhydride charge transfer complex

reactions of the monomer-monomer charge transfer complex with macroradicals having different monomer units at the macroradical ends. The possible reactions in the propagation steps can be written as follows:



where  $M_1$ ,  $M_2$  and  $(M_1 - M_2)$  or  $(M_2 - M_1)$  represent styrene, maleic anhydride and the charge transfer complex respectively. As is evident, reactions of macroradicals with either side of the complex have been included along with reactions with free monomers. The initiation and termination reactions are as reported earlier<sup>1</sup>. Considering equilibrium in the interconversion of macroradicals, we have

$$k_{12}[M_1^*][M_2] + k_{1c1}[M_1^*][C] = k_{21}[M_2^*][M_1] + k_{2c2}[M_2^*][C] \quad (3)$$

Steady state approximation for total radicals yields

$$R_i = R_t = k_{111}[M_1^*]^2 + 2k_{112}[M_1^*][M_2^*] + k_{122}[M_2^*]^2 \quad (4)$$

The rate of polymerization,  $R_p$  is the summation of all propagation reactions:

$$\begin{aligned}
 R_p = & k_{111}[M_1^*][M_1] + k_{112}[M_1^*][M_2] + k_{211}[M_2^*][M_1] + \\
 & k_{222}[M_2^*][M_2] + (k_{1c1} + k_{1c2})[M_1^*][C] \\
 & + (k_{2c1} + k_{2c2})[M_2^*][C] \quad (5)
 \end{aligned}$$

Eliminating radical concentrations in equation (5) with the help of equation (3) and equation (4), and further simplifying, one obtains

$$R_p = \frac{\left( r_1 \frac{[M_1]}{[M_2]} + 2 + r_2 \frac{[M_2]}{[M_1]} + a \frac{[C]}{[M_1]} + b \frac{[C]}{[M_2]} + c \frac{[C]^2}{[M_1][M_2]} \right) [M_2] \cdot R_i^{0.5}}{\left\{ r_1^2 \delta_1^2 + 2\phi r_1 r_2 \delta_1 \delta_2 \frac{[M_2]}{[M_1]} + r_2^2 \delta_2^2 \frac{[M_2]^2}{[M_1]^2} + a_1 \frac{[C]}{[M_1]} + b_1 \frac{[C]^2}{[M_1]^2} + c_1 \frac{[C][M_2]}{[M_1]^2} \right\}^{0.5}} \quad (6)$$

where

$$a = \frac{k_{2c}}{k_{21}} + r_2 \frac{k_{1c1}}{k_{12}} + \frac{k_{2c2}}{k_{21}}$$

$$b = \frac{k_{1c}}{k_{12}} + r_1 \frac{k_{2c2}}{k_{21}} + \frac{k_{1c1}}{k_{12}}$$

$$c = \frac{k_{1c}}{k_{12}} \cdot \frac{k_{2c2}}{k_{21}} + \frac{k_{2c}}{k_{21}} \frac{k_{1c1}}{k_{12}}$$

$$a_1 = 2 \left( r_1^2 \delta_1^2 \frac{k_{2c2}}{k_{21}} + \phi r_1 r_2 \delta_1 \delta_2 \frac{k_{1c1}}{k_{12}} \right)$$

$$b_1 = \left( r_1^2 \delta_1^2 \frac{k_{2c2}^2}{k_{21}^2} + 2\phi r_1 r_2 \delta_1 \delta_2 \cdot \frac{k_{1c1}}{k_{12}} \cdot \frac{k_{2c2}}{k_{21}} + r_2^2 \delta_2^2 \frac{k_{1c1}^2}{k_{12}^2} \right)$$

$$c_1 = 2 \left( r_2^2 \delta_2^2 \frac{k_{1c1}}{k_{12}} + \phi r_1 r_2 \delta_1 \delta_2 \frac{k_{2c2}}{k_{21}} \right)$$

Equation (6) does not involve any approximation and should thus be applicable to copolymerization systems in general. In this form the relationship is rather complex and very little reliable information can be obtained by applying it to experimental data. However, at equimolar feed compositions, it changes to

$$\frac{R_p}{R_i^{0.5} [M]} = \frac{(r_1 + r_2 + 2) + (a+b) \frac{[C]}{[M]} + c \cdot \frac{[C]^2}{[M]^2}}{\left\{ r_1^2 \delta_1^2 + 2\phi r_1 r_2 \delta_1 \delta_2 + r_2^2 \delta_2^2 + (a_1 + c_1) \frac{[C]}{[M]} + b_1 [C]^2 / [M]^2 \right\}^{0.5}} \quad (7)$$

According to equation (7), the nature of the plot of  $R_p / (R_i^{0.5} [M])$  vs.  $[C]/[M]$  will depend on the magnitudes of the various constants. Figure 5 shows a plot of  $R_p / (R_i^{0.5} [M])$  vs.  $[C]/[M]$  for equimolar feed compositions covering a range from 0.5 to 4.0 mol l<sup>-1</sup> of total monomer concentrations. All the experimental points could be covered by a straight line having the following values of slope and intercept:

$$\text{slope} = 10.94 \text{ and intercept} = 0.625$$

An examination of the various constants appearing in equation (6) shows that for the copolymerization of styrene and maleic anhydride, one can neglect  $a_1$ ,  $b_1$  and  $c_1$ . The factor  $c \cdot [C]^2 / [M]^2$  makes a negligible contribution even for very high total monomer concentrations (compare with Table 2) and its effect can also be neglected when evaluating various constants from the slope and the intercept. The constants calculated under these assumptions have the following values:

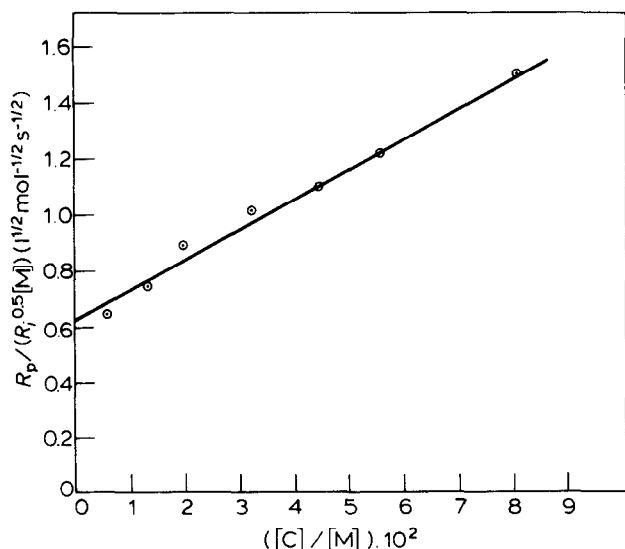


Figure 5 Variation of  $R_p / R_i^{0.5} [M]$  vs.  $[C]/[M]$  for equimolar feed compositions for styrene and maleic anhydride copolymerization in methyl ethyl ketone at 60°C

$$r_1^2 \delta_1^2 + 2\phi r_1 r_2 \delta_1 \delta_2 + r_2^2 \delta_2^2 = 10.92$$

$$(a+b) = 36.14$$

Assuming that  $k_{2c2}/k_{21}$  and  $r_2 \cdot k_{1c1}/k_{12}$  are very small compared with the others, we have

$$\frac{k_{1c}}{k_{12}} + \frac{k_{2c}}{k_{21}} + \frac{k_{1c1}}{k_{12}} = 36.14$$

using  $r_1 = 0.062$  and  $r_2 = 0.003$ . Putting  $k_{1c}/k_{12} = 8.40$  and  $k_{1c1}/k_{12} = 1.60$  as obtained from compositional analysis, we have

$$k_{2c}/k_{21} = 26.14 \approx k_{2c1}/k_{21}$$

This value is in sharp contrast to a negligible value of  $10^{-5}$  calculated analytically by Farmer *et al.*<sup>3</sup>. The overwhelming difference cannot be evidently explained in terms of experimental error. In fact, there is no reason to believe that a maleic anhydride radical should not react with the styrene side of the complex compared with its affinity to react with a free styrene molecule. Tsuchida and Tomono<sup>7</sup> have elaborately discussed this aspect and concluded that for 2-chloroethyl vinyl ether and maleic anhydride copolymerization,  $k_{2c1} \gg k_{1c2}$  and  $k_{12}$ . Nevertheless, the resulting radical having a maleic anhydride unit at the end would not be very stable and it was suggested<sup>7</sup> that a molecule of maleic anhydride is split off as a result of this reaction. It is difficult to prove such a hypothesis as has been shown in vinyl acetate-maleic anhydride copolymerization<sup>8</sup>. It should be mentioned that maleic anhydride is very efficient in forming complexes with solvents such as dioxane and methyl ethyl ketone and it is likely that the maleic anhydride radical may be stabilized as a result of interaction with the solvent.

We will now examine the analysis of a similar system made by Braun and Czerwinski<sup>4</sup> utilising kinetic constant values obtained analytically<sup>3</sup> on the basis of compositional data<sup>2</sup>. A comparison of the analytical and experimental curves reveals that as the concentration of maleic anhydride in the monomer feed increases, the discrepancy becomes more apparent. An examination of equation (7) shows that as the concentration of maleic anhydride increases, the term  $a \cdot [C]/[M_1]$  makes a major contribution which has been neglected<sup>3,4</sup>. This could explain why the maximum appears at lower maleic anhydride contents in the feed in the calculated curves<sup>4</sup>.

Having thus obtained the values of various constants necessary to treat the rate data, we will now attempt to analyse the kinetics for various feed compositions. Equation (6) can be rewritten in the following form

$$R_p = \frac{\left\{ r_1 [M_1]^2 + 2[M_1][M_2] + r_2 [M_2]^2 + \left( \frac{k_{1c}}{k_{12}} + \frac{k_{1c1}}{k_{12}} \right) [C][M_2] + \frac{k_{2c}}{k_{21}} [C][M_2] + \frac{k_{2c1}}{k_{21}} [C]^2 \right\} R_i^{0.5}}{(r_1^2 \delta_1^2 [M_1]^2 + 2\phi r_1 r_2 \delta_1 \delta_2 [M_1][M_2] + r_2^2 \delta_2^2 [M_2]^2)^{0.5}} \quad (8)$$

This equation is very similar to the equation derived without considering reactions of a macroradical (ending with a particular monomer) with a similar monomer of the complex (equation (5) of ref. 1). Designating the numerator of equation (8) as  $z$ , of which all the constants are now known, we have after some rearrangement

$$\frac{z^2 R_i}{R_p^2} = (r_1^2 \delta_1^2 [M_1]^2 + 2\phi r_1 r_2 \delta_1 \delta_2 [M_1][M_2] + r_2^2 \delta_2^2 [M_2]^2)$$

or,

$$\frac{z^2 R_i}{R_p^2 [M_1]^2} = r_1^2 \delta_1^2 + 2\phi r_1 r_2 \delta_1 \delta_2 \frac{[M_2]}{[M_1]} + r_2^2 \delta_2^2 \frac{[M_2]^2}{[M_1]^2} \quad (9)$$

Similarly,

$$\frac{z^2 R_i}{R_p^2 [M_2]^2} = r_2^2 \delta_2^2 + 2\phi r_1 r_2 \delta_1 \delta_2 \frac{[M_1]}{[M_2]} + r_1^2 \delta_1^2 \frac{[M_1]^2}{[M_2]^2} \quad (10)$$

From plots according to equations (9) and (10), both  $\delta_1$  and  $\delta_2$  can be obtained from the intercepts. The plot according to equation (9) is shown in Figure 6. The situation is quite similar to that observed for the copolymerization of styrene and maleic anhydride in dioxane at 50°C<sup>1</sup>. Instead of a quadratic increase in  $[M_2]/[M_1]$ , the curve shows a continuous decrease in slope at higher  $[M_2]/[M_1]$  values. Two conclusions can be drawn from this fact:

- (i)  $r_2 \delta_2$  is negligibly small and
- (ii)  $\phi$  is a continually decreasing function of  $[M_2]/[M_1]$ , assuming that  $r_1, r_2, \delta_1$  and  $\delta_2$  do not change with monomer composition of the feed.

The value of  $r_1^2 \delta_1^2$  obtained from the intercept is about 3.70 which gives  $\delta_1 = 31$ . This value is quite reasonable when compared with literature values of  $k_i^{0.5}/k_p$  for the homopolymerization of styrene at 60°C.

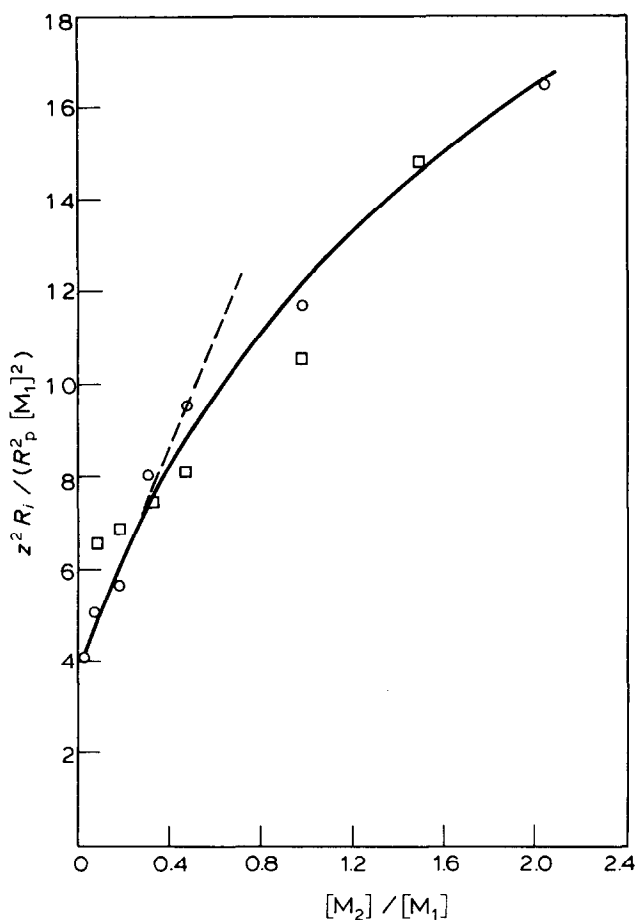


Figure 6 Plot of  $z^2 R_i / R_p^2 [M_1]^2$  vs.  $[M_2]/[M_1]$  according to equation (9) for various monomer feed compositions at two total monomer concentrations.  $[M] + [M_2] = 3 \text{ mol l}^{-1}$  (○),  $1.5 \text{ mol l}^{-1}$  (□)

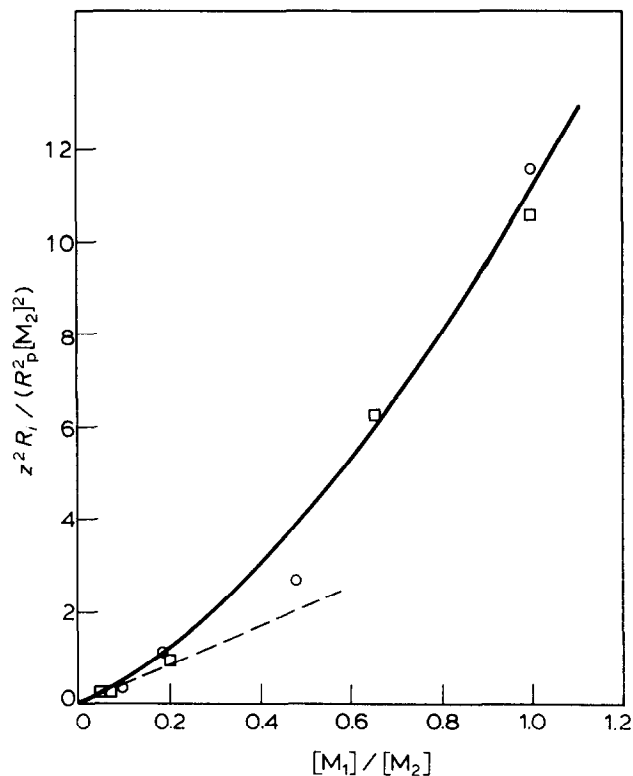


Figure 7 Plot of  $z^2 R_i / (R_p^2 [M_2]^2)$  vs.  $[M_1]/[M_2]$  according to equation (10) for various monomer feed compositions at two total monomer concentrations.  $[M_1] + [M_2] = 3 \text{ mol l}^{-1}$  (○),  $1.5 \text{ mol l}^{-1}$  (□)

The plot according to equation (10) is shown in Figure 7. An attempt to determine  $r_2^2 \delta_2^2$  from the intercept proved futile confirming that this quantity is negligible. However, a reasonably good estimate of  $2\phi r_1 r_2 \delta_1 \delta_2$  at  $[M_1] \rightarrow 0$  could be obtained from the initial slope of the plot. The values of the parameters obtained from the slopes of plots in Figure 6 and Figure 7 are as follows

$$2\phi r_1 r_2 \delta_1 \delta_2 ([M_2] \rightarrow 0) = 12.10$$

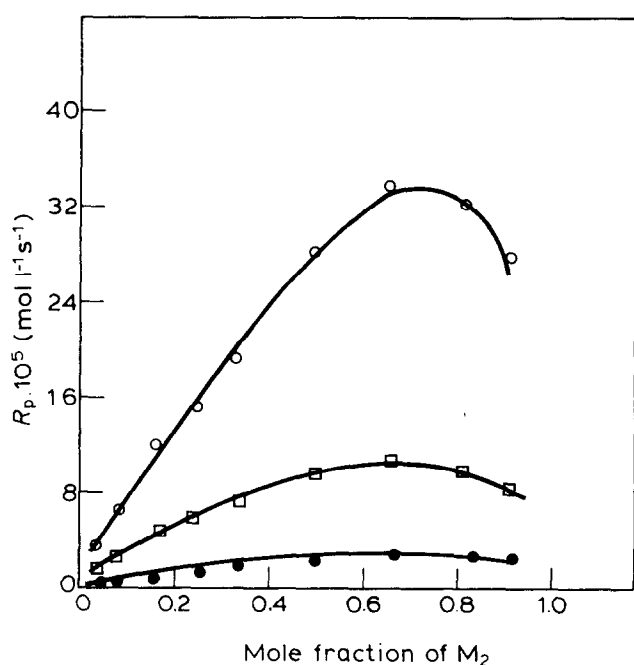
$$2\phi r_1 r_2 \delta_1 \delta_2 ([M_1] \rightarrow 0) = 4.00$$

and  $2\phi r_1 r_2 \delta_1 \delta_2 ([M_1] = [M_2]) = 7.22$

(from Figure 5)

In the absence of values of  $r_2 \delta_2$ , it is not possible to calculate absolute values of  $\phi$  for different monomer feed compositions as could be done for copolymerization in dioxane<sup>1</sup>. However, it is important to note that  $\phi$  seems to be nearly independent of the total monomer concentration, as the experimental points for different total monomer concentrations could be roughly described by a single curve (Figure 6 and Figure 7). From the values of  $2\phi r_1 r_2 \delta_1 \delta_2$ , it can be concluded that the values of  $\phi$  differ by a factor of about 3 in passing from almost pure styrene to almost pure maleic anhydride.

An examination of equation (9) and magnitudes of various constants reveal that the inclusion of reactions of macroradicals with similar monomer of the complex does not bring about substantial change in the rate-monomer feed composition relationship at least for styrene-maleic anhydride copolymerization in methyl ethyl ketone at 60°C. This is even more justified in dioxane where  $k_{2c}/k_{21}$  is yet higher still. Analytical calculations show that the term involving  $k_{1c1}/k_{12}$  incorporates a contribution rang-



**Figure 8** Comparison of calculated and experimental rates of copolymerization for styrene and maleic anhydride in methyl ethyl ketone at 60°C. (—) calculated curve; experimental data:  $[M_1] + [M_2] = 3 \text{ mol l}^{-1}$  (○),  $1.5 \text{ mol l}^{-1}$  (□),  $0.5 \text{ mol l}^{-1}$  (●)

ing from 1 to 5% in the overall rate of copolymerization which is within the range of experimental error. However, the composition of the copolymer seems to be quite sensitive to the aforesaid reaction. An examination of the compositional relationships based on inclusion and exclusion of reaction of macroradicals with a similar monomer of the complex clearly shows that the data can be reliably explained only when the former reaction is included in the analysis scheme.

Having obtained values for all the kinetic constants, we attempted to construct the analytical rate vs. feed composition curve and see how well the experimental data can describe the curve. Values of  $2\phi r_1 r_2 \delta_1 \delta_2$  for various monomer compositions were obtained from the curve encompassing the three values of this parameter at  $[M_1] \rightarrow 0$ ,  $[M_2] \rightarrow 0$  and  $[M_1] = [M_2]$ . As is evident from Figure 8, the calculated curve describes the experimental data very well indicating that the scheme adopted and the values of constants determined truly depict the course of copolymerization of styrene and maleic anhydride in methyl ethyl ketone at 60°C. The rate data for  $[M_1] + [M_2] = 0.5 \text{ mol l}^{-1}$  could not be satisfactorily described at low maleic anhydride concentration in the feed. The rates seem to be smaller than the calculated values. This may be due to loss of low molecular weight polymer during precipitation and also because of primary radical termination. We also attempted a comparison of calculated rates based on values of constants reported by Farmer *et al.*<sup>3</sup> with the experimental values. The rates calculated with  $r_2 \delta_2 = 0$  are all much less than the

experimental values (differing by a factor of about 4 at the maximum). Thus it is evident that the constant  $k_{2c}/k_{21}$ , signifying reactions of maleic anhydride-ended macroradical with the complex, has been underestimated<sup>3</sup>.

Thus the method of analysis presented here and earlier<sup>1</sup> has the advantage that, in addition to affording values of  $k_t^{0.5}/k_p$  for the easily homopolymerizable monomer, it also allows a check on the homopolymerizability of the sluggish monomer in relation to copolymerization. This is important because the contention of non-homopolymerizability, if unequivocally used for sluggish monomers, makes both  $\phi$  and  $\delta_2$  lose their importance. General  $\phi$  also can be evaluated, but in cases where  $r_2$  is very small, it is difficult to estimate  $\phi$  but values of  $2\phi r_1 r_2 \delta_1 \delta_2$  can be obtained reasonably well.

It may thus be concluded that:

(i) The essential features of the kinetics of copolymerization of styrene and maleic anhydride in dioxane and methyl ethyl ketone are similar. Incorporation of the concept of participation of a monomer-monomer complex in propagation explains all aspects of kinetics of copolymerization of this pair of monomers.

(ii) The reaction of a particular type of macroradical with a similar monomer of the complex does not play an important role in controlling the rate of polymerization. However, the composition of the copolymers seems to be sensitive to such reaction.

(iii) Detailed analysis of both composition and rate is necessary to arrive at meaningful conclusions.

(iv) Cross-termination of macroradicals in styrene and maleic anhydride copolymerization is always favoured relative to mutual termination of similar radicals.

(v) Non-homopolymerizability of maleic anhydride in solution resulting in  $r_2 \delta_2 = 0$  cannot be unequivocally used in copolymerization as  $\delta_2$  has a finite value in many solvents and  $r_2$  is not always negligible. Such assumption may lead to an unrealistic interpretation of kinetic data.

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