

The Copolymerization of Methylmethacrylate and Maleic Anhydride

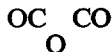
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A maximum is possible in the rate/composition curve for a copolymerization in which one monomer does not undergo homopolymerization and the termination reaction is diffusion controlled. The maximum can occur without any restriction on the value of the reactivity ratio, r_1 , provided either that the propagation ratio k_{pad}/k_{pba} satisfies certain conditions, or that the termination reaction is impeded by the introduction of the second monomer into the polymer chain.

The copolymerization of methylmethacrylate and maleic anhydride in solution at 30°C (the total monomer concentration being maintained constant) has been shown to involve a diffusion-controlled termination step. The rate of termination decreases with increasing maleic anhydride content, as would be predicted if rearrangement of the conformations of the radical chain is the rate-determining step. The rate constant for addition of methylmethacrylate radicals to maleic anhydride is less than that for addition of maleic anhydride radicals to methylmethacrylate, as would be predicted on steric considerations. Accurate determination of the propagation rate constant, maleic anhydride radical plus methylmethacrylate, and of the hypothetical termination rate constant for a chain of maleic anhydride only, has not been possible in this study.

KINETIC studies of the free-radical polymerization of methylmethacrylate and maleic anhydride are interesting in that the rate of polymerization appears to pass through a maximum with increasing mole fraction of maleic anhydride¹, although this monomer is virtually incapable of undergoing homopolymerization. Burnett² has shown that such maxima are possible in systems where one monomer does not itself polymerize, but his analysis produced the necessary condition, $r_1 < 2$, where r_1 is the monomer reactivity ratio for the compound capable of undergoing homopolymerization. Since all reported values of r_1 for this copolymerization are greater than three^{1,3}, the system has remained something of an enigma.

Two aspects of this copolymerization are worthy of further consideration: (a) the density of maleic anhydride is 50 per cent greater than that of methylmethacrylate^{1,4}, so that the total monomer molarity in a bulk polymerization increases with maleic anhydride content; (b) the termination reaction may be diffusion-controlled⁵, in which case the conventional rate equation incorporating the cross-termination factor, ϕ , is no longer applicable. Since rotation is possible about the $\text{H}_2\text{C}-\text{C}(\text{CH}_3)(\text{COOCH}_3)$ bond, but not about the $\text{HC}-\text{CH}$ bond, it is likely that substitution of



maleic anhydride for methylmethacrylate in the polymer chain will markedly affect the diffusive properties of the chain.

The effect of monomer density must depend on the kinetic order of the polymerization rate law. With methylmethacrylate polymerization the rate

varies as monomer to the power 1.1. If it is assumed that the volume of mixing for these two monomers is zero, and that the kinetic order with respect to monomer is independent of composition, the results of Blackley and Melville¹ can be normalized to a monomer density of 0.900. When this is done the maximum is markedly reduced, but is still quite discernible, *Figure 1*.

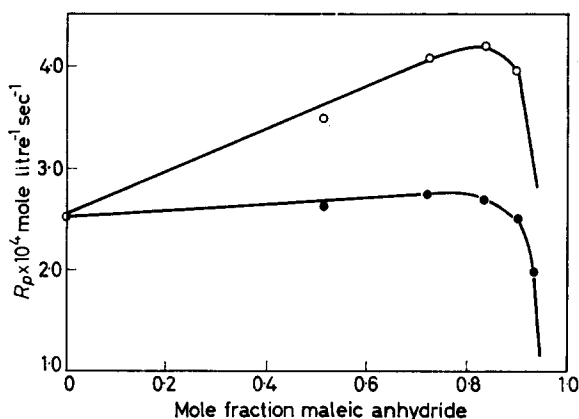


Figure 1—Rate of bulk copolymerization at 60°C (Blackley and Melville¹). O Reported rate of polymerization. ● Rate normalized to a monomer density 0.900

When the termination reaction is diffusion-controlled, the termination rate depends on the composition of the whole polymer chain and not on the chemical nature of the radical end group. Under these conditions the conventional rate expression is not valid, and it is necessary to introduce a termination rate constant $k_{t(AB)}$ which is a function of the polymer (and hence monomer feed) composition. Under these conditions if the stationary state approximation be applied in the usual way⁵,

$$\frac{R_p}{R_i^\dagger} = \frac{r_1 [A]^2 + 2 [A] [B]}{k_{t(AB)}^\dagger \{ [A] / k_{pab} + [B] / k_{pba} \}} \quad (1)$$

where k_{pij} represents the propagation rate constant for addition of radical type i to monomer type j , and R_p , R_i are the rates of polymerization and of initiation respectively. Introducing the new variables, $\epsilon_a = k_{t(AB)}^\dagger / k_{paa}$, $\xi_b = k_{t(AB)}^\dagger / k_{pba}$,

$$\frac{R_p}{R_i^\dagger} = \frac{r_1 [A]^2 + 2 [A] [B]}{\epsilon_a r_1 [A] + \xi_b [B]} \quad (2)$$

The conditions for a maximum in the rate/composition curve may be found by differentiating equation (2). Unfortunately explicit conditions can be obtained only if the composition dependence of $k_{t(AB)}$ is known. The simple extreme exists when $k_{t(AB)}$ is independent of composition, and the

two components form an ideal mixture. Then setting $[A] + f[B] = a$, where f and a are constants, equation (2) can be differentiated, and the condition for a maximum yields a quadratic equation in $[A]_{\max.}$. The equation has real positive roots when

$$fr_1 < 2 \quad (k_{paa}/k_{pba} < 2) \quad (3)$$

$$2 < fr_1 < k_{paa}/k_{pba} \quad (4)$$

Condition (3) is similar to that derived by Burnett and requires (for methylmethacrylate and maleic anhydride polymerized in bulk) that r_1 be less than three. However, condition (4) shows that rate maxima are possible for higher values of r_1 .

If the termination reaction is assumed to exhibit ideal diffusion-controlled behaviour⁵, $k_{t(AB)}$ is given by

$$k_{t(AB)} = k_{taa}x'_a + \zeta_b x'_b \quad (5)$$

Here x'_a and x'_b are the mole fractions of each monomer type in the polymer chain, k_{taa} is the termination rate constant for pure methylmethacrylate, and ζ_b is a constant representing the hypothetical rate constant for termination of chains consisting of pure maleic anhydride. The rate equation becomes

$$\frac{R_p}{R_i^{\frac{1}{2}}} = \frac{(r_1 [A]^2 + 2 [A] [B])^{3/2}}{\{k_{taa} ([A] [B] + r_1 [A]^2) + \zeta_b [A] [B]\}^{\frac{1}{2}} \left(\frac{r_1 [A]}{k_{paa}} + \frac{[B]}{k_{pba}} \right)} \quad (6)$$

and the condition for a maximum yields a cubic equation in $[A]_{\max.}$. The necessary conditions for obtaining positive real roots are then much wider, the most important one being that a maximum is possible when $k_{pna}/k_{pba} < 2 < fr_1$ so long as ζ_b/k_{taa} is less than unity. All the conditions discussed are pertinent only to the achievement of real positive values of $[A]_{\max.}$ without consideration of the further condition that $[A]_{\max.}$ must be less than or equal to the molar concentration of bulk monomer.

In this work copolymerizations have been carried out in solution so that it has been possible to maintain the total monomer concentration constant at various monomer compositions. The aim of the study was two-fold: (a) to discover whether the termination reaction is diffusion-controlled in the copolymerization of mixtures rich in maleic anhydride; and (b) to attempt evaluation of r_1 , k_{pab}/k_{pba} , and ζ_b/k_{taa} in order to assess the applicability of the conditions for a rate maximum.

EXPERIMENTAL

Materials

Methylmethacrylate, B.D.H. purified grade, was freed of inhibitor and distilled under a nitrogen pressure of 20 mm of mercury. The middle fraction was collected, and aliquot portions outgassed on the vacuum line at pressures less than 5×10^{-5} mm of mercury, prepolymerized by ultra-violet (u.v.) irradiation, and residual monomer distilled into the polymerization vessels.

Maleic anhydride was fractionally distilled under a nitrogen pressure of 12 mm of mercury and the middle fraction, b.pt 154°C, collected. Aliquot portions of molten monomer were introduced into the polymerization vessel and outgassed in contact with the solution of α,α' -azoisobutyronitrile.

AR ethyl acetate was fractionally distilled off calcium hydride. Aliquot portions were outgassed and distilled on the vacuum line.

Sucrose acetate isobutyrate (SAIB) and diisooctyl phthalate (DIOP) were treated with sodium bisulphite and activated charcoal. In order to remove trace impurities which might affect a free-radical polymerization, 1 mg of α,α' -azoisobutyronitrile was dissolved in aliquot portions of the molten esters, outgassed on the vacuum line, and the azo compound decomposed by u.v. irradiation. Prolonged irradiation over several days caused the formation of coloured polymerization retarders in the esters, so that irradiation was limited to three hours. Esters so treated did not initiate polymerization themselves, indicating that the removal of the azo compound was complete.

α,α' -azoisobutyronitrile was recrystallized three times from ethanol and once from ethyl acetate, stored in the dark at -10°C , and used in standard solutions in ethyl acetate.

Procedure

All reaction mixtures were prepared and sealed under an air pressure less than 5×10^{-5} mm of mercury.

Rates of polymerization studied at different monomer feed compositions were observed by gravimetric determination of the polymer yields, samples of each run being analysed after four different times. Each reaction vessel contained four ampoules, capacity 5 ml, into which the polymerization mixture was sealed. The ampoules were opened at 12-hourly intervals, the polymer precipitated in excess methanol at -30°C , collected on No. 4 porosity sintered glass crucibles, dried to constant weight at 100°C , and the yield calculated from the weights of polymer, ampoule plus monomers and ampoule fragments. In no case was the conversion greater than ten per cent. Yields so obtained deviated from a smooth curve by less than one per cent.

Rates of copolymerization of a mixture of monomers (1.20 molar methylmethacrylate and 2.05 molar maleic anhydride) in solvents of varying viscosities were observed using conventional dilatometers. Rates of contraction were converted to rates of polymerization by comparison of dilatometric and gravimetric runs for this monomer composition. All rate determinations were carried out in a water thermostat bath governed to $30^{\circ} \pm 0.01^{\circ}\text{C}$.

Monomer reactivity ratios were obtained by titration of the maleic anhydride in polymer using the technique of Fritz and Lisicki⁶.

Solution viscosities were determined in an Ubbelohde suspended level viscometer, and were found to be the same at the start and at the finish of each polymerization.

RESULTS

Monomer densities and solubilities

The solubility of maleic anhydride at 30°C was found to be: in ethyl acetate—1.93 mole litre⁻¹, in 50/50 v/v ethyl acetate-methylmethacrylate—4.01 mole litre⁻¹. In order to obtain reasonable rates of polymerization and measurable polymer yields, it was decided to study polymerizations at a total monomer concentration of 3.25 mole litre⁻¹. Because of the low solubility of maleic anhydride, it was found to be impracticable to study monomer compositions beyond 0.63 mole fraction maleic anhydride.

The monomer and solvent densities are required so that polymerizations of different monomer feeds can be made up to the same total volume and total monomer concentration:

Ethyl acetate 0.865 g (cm³)⁻¹

Methylmethacrylate 0.933 g (cm³)⁻¹

Maleic anhydride when dissolved in ethyl acetate 1.47 g (cm³)⁻¹.

The high density observed for maleic anhydride in solution is in agreement with that recorded by Melville and Blackley for bulk monomer.

Monomer reactivity ratios

Sixteen samples of polymer were prepared at 30°C using six different monomer feed compositions. In no case was the polymerization continued beyond ten per cent conversion. At these low conversions the dependence of polymer composition on conversion is approximately linear, so that the polymer composition corresponding to zero conversion was obtained by graphical extrapolation. The reactivity ratios were then obtained from the intersections of the lines

$$r_1 = \frac{[B]}{[A]} \left(\frac{d[A]}{d[B]} \right)_0 \left[1 - r_1 \frac{[B]}{[A]} \right] - \frac{[B]}{[A]} \quad (7)$$

The monomer and polymer compositions are listed in *Table 1*, and the reactivity ratios obtained from the six 'zero-conversion' lines are

$$r_1 = 4.63 \quad r_2 = -0.18$$

The standard deviations are 1.14 and 0.28 respectively. The ratio, r_2 , of course, can be negative only if a depropagation reaction is taking place in the copolymer. Since there is no experimental evidence for any depropagation equilibrium effects in this system, and since the variance in r_2 covers both positive and negative values, we have assumed a value of 0.00 in all calculations involving r_2 .

Although there is a disappointingly large error in the determination of r_1 , a value less than 3.0 is improbable, and the system cannot obey the $r_1 < 2$ condition discussed by Burnett.

Table 1. Monomer-polymer compositions at 30°C

$[A]/[B]_0$	$d[A]/d[B]$	% conversion	$[A]/[B]_0$	$d[A]/d[B]$	% conversion
0.587	6.13	1.89	1.56	7.96	8.69
0.587	5.25	3.12	2.56	9.85	4.28
0.587	4.67	6.01	2.56	12.19	5.19
0.906	6.02	7.66	2.56	11.20	7.56
1.40	6.92	4.53	2.56	10.57	9.36
1.40	6.69	8.61	7.19	32.47	5.73
1.56	7.52	3.13	7.19	30.01	8.52
1.56	8.05	6.68	7.19	28.36	9.74

Viscosity dependence of polymerization rate

All polymerization mixtures consisted of 1.29×10^{-3} M α, α' -azoisobutyronitrile, 1.20 M methylmethacrylate, 2.05 M maleic anhydride, and variable ratios of ethyl acetate-SAIB or ethyl acetate-DIOP.

The factor converting volume per cent monomer contraction to weight per cent conversion was determined for this monomer composition from comparison of dilatometric and gravimetric observations,

$$R_c = 2.61 \times 10^{-6} \text{ volume per cent second}^{-1},$$

$$R_g = 3.80 \times 10^{-5} \text{ weight per cent second}^{-1},$$

$$R_p = 1.23 \times 10^{-6} \text{ mole litre}^{-1} \text{ second}^{-1},$$

Conversion factor = 14.5.

Because of the high density of maleic anhydride monomer the volume contraction is small at this monomer feed composition.

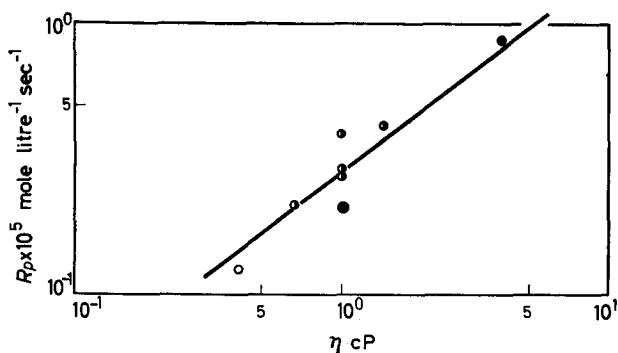


Figure 2—Viscosity dependence of copolymerization rate in solution at 30°C. 1.20 M methylmethacrylate and 2.05 M maleic anhydride. ○ ethyl acetate solvent. ◐ ethyl acetate-SAIB solvent. ● ethyl acetate-DIOP solvent

It was found that the rates of copolymerization depended on the viscosity of the solution over the complete range of viscosities studied, as is illustrated in Figure 2. Since the reaction rate increases with increasing viscosity, the termination reaction must be diffusion-controlled, even at the viscosities

corresponding to normal solution polymerization. The increase in rate also serves to verify the absence of retarder in the viscous solvent component.

Composition dependence of polymerization rates

All polymerization mixtures consisted of 1.29×10^{-3} M α, α' -azoisobutyronitrile, 3.25 M total monomer, ethyl acetate as solvent. The variation in copolymerization rate (determined from the initial slope of the yield/time observations) with monomer feed and polymer composition is listed in Table 2.

Table 2. Rates of copolymerization in solution at 30°C

x_b monomer	x'_b polymer	$R_p \times 10^5$ moles litre ⁻¹ second ⁻¹	R_p/R_{pA}
0.000	0.000	1.98	1.00
0.122	0.026	1.91	0.965
0.279	0.066	1.74	0.879
0.391	0.101	1.80	0.909
0.417	0.110	1.74	0.879
0.525	0.151	1.69	0.854
0.631	0.203	1.23	0.622

There is no detectable maximum in the rate/composition curve, although the second derivative of the curve is negative. It is possible that a maximum does exist, but that it occurs at extremely low mole fractions of maleic anhydride, the increase in rate being less than the experimental error.

DISCUSSION

Since the rate of termination, both in the homopolymerization of methylmethacrylate⁵ and in the copolymerization richest in maleic anhydride, is diffusion-controlled, it is reasonable to assume that this diffusion-dependence exists over the whole range of monomer compositions studied.

The experiments in solution at 30°C do not exhibit a rate maximum greater than experimental error. This is not in direct disagreement with the results of Blackley and Melville at 60°C, since the maximum in corrected rate at this temperature is only just larger than the experimental error. Both rate/composition curves are similar in shape, being almost independent of composition until more than 50 mole per cent maleic anhydride.

Under conditions of diffusion-controlled termination and constant monomer concentration, and with the assumption that the efficiency of initiation is independent of composition, equation (1) can be rewritten

$$\frac{R_p}{R_{pA}} = \frac{x_a^2 + 2x_ax_b/r_1}{\left(\frac{k_t(AB)}{k_{taa}}\right)^{\frac{1}{2}} \{x_a + k_{pab}x_b/k_{pba}\}} \quad (8)$$

where $[A] + [B] = a$, $[A]/a = x_a$. R_{pA} represents polymerization of A. This

equation contains the unknown variable, $k_{t(AB)}/k_{taa}$ as well as the unknown constant k_{pab}/k_{pba} , and so cannot be solved directly for both unknowns. Once the form of the composition-dependence of $k_{t(AB)}$ is known, however, solution is possible.

In order to attempt preliminary estimation of k_{pab}/k_{pba} and ζ_b/k_{taa} we have assumed that termination is 'ideal' as expressed in equation (5). Equation (8) can then be written as

$$\frac{R_p}{R_{pA}} = \frac{x_a^2 + 2x_ax_b/r_1}{\{x_a + k_{pab}x_b/k_{pba}\} \{x'_a + \zeta_b x'_b/k_{taa}\}^{\frac{1}{2}}} \quad (9)$$

k_{pab}/k_{pba} and $\zeta_b x'_b/k_{taa}$ should then be obtained from the intersections of the plots k_{pab}/k_{pba} against ζ_b/k_{taa} .

$$\frac{k_{pab}}{k_{pba}} = \frac{(x_a^2 + 2x_ax_b/r_1)(R_{pA}/R_p)}{(x'_a + \zeta_b x'_b/k_{taa})^{\frac{1}{2}} x_b} - \frac{x_a}{x_b} \quad (10)$$

Unfortunately these plots form a band of almost parallel curves, with negative slope, spanning the origin. Since neither of these ratios can be negative, the only possible interpretation is that both ratios differ from zero by a quantity which is less than the experimental error. This error is ± 0.1 and ± 0.4 for k_{pab}/k_{pba} and $\zeta_b k_{taa}$ respectively.

The conditions $r_1 \leq 2$ [solution copolymerization], $r_1 \leq 3$ [bulk copolymerization] and $k_{paa}/k_{pba} \geq r_1$ are thus not satisfied at 30°C. The certainty with which we can say that these conditions are violated depends on the accuracy with which r_1 has been measured. The values $r_1 = 3$, $r_1 = 2$, differ from the mean value by 1.4σ and 2.3σ respectively where σ is the standard deviation in r_1 . Consequently it is possible that $r_1 \leq 3$, but highly improbable that $r_1 \leq 2$. Although it might be felt that the adjustment in r_2 (-0.18 to zero) implies that a similar reduction should be made in r_1 , examination of the r_1 against r_2 experimental plots shows that a parallel adjustment in r_1 would be an increase of 0.6σ . A maximum in the rate/composition curve can now be explained only if the termination reaction is diffusion-controlled, the rate of termination increasing with maleic anhydride content of the copolymer.

It has been suggested that the rate-determining process in the termination of polymeric free radicals is a segmental rearrangement of the conformations adopted by the polymer chain in solution^{7,8}. As a methylmethacrylate unit in the chain is replaced by a maleic anhydride unit, the possibility of rotation about one carbon-carbon bond in the chain is removed. Consequently the number of possible conformations of the chain, and also the rate of rearrangement, would be reduced. Thus a value of ζ_b/k_{taa} less than unity, with the consequent possibility of a rate maximum, would be predictable on this basis. A value of k_{pab}/k_{pba} less than unity might be expected on steric considerations. Unfortunately sufficient information on the reactivity of the maleic anhydride radical is not available for theoretical prediction⁹ of this ratio.

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