

## STUDIES IN COPOLYMERIZATION

### THE SYSTEMS METHYL METHACRYLATE + *p*-METHOXYSTYRENE AND STYRENE + *m*-VINYL PHENOL

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The system methyl methacrylate + *p*-methoxystyrene, and to a lesser extent, that of styrene + *m*-vinyl phenol have been studied at 60° C, with 2-azo-*bis*-(isobutyronitrile) as initiator.

Using the dilatometric technique the polymerization of methyl methacrylate has been followed up to 10 % conversion for various concentrations of initiator. The molecular weights of the polymers have been measured in benzene solution, and the  $\delta = k_i/k_p$  constant calculated to be 6.8. For the methyl methacrylate + *p*-methoxystyrene system, the rate of polymerization has been found to fall quite sharply as the mole fraction of *p*-methoxystyrene is increased. Molecular weight studies reveal that the rate of initiation for the copolymer system is directly proportional to the monomer composition. There

is found to be a drift in the value of  $\phi$  from 12 to 27 as the concentration of *p*-methoxystyrene is increased.

In the styrene + *m*-vinyl phenol system, the rate of polymerization increases gradually as the styrene content is decreased. A value of  $\phi \leq 1$  fits the results quite well.

This is the fifth in a series of papers which is concerned with the kinetics and mechanisms of copolymerization reactions; a brief account of these investigations has already been given.<sup>1</sup> The last paper<sup>2</sup> discussed the styrene + *p*-methoxystyrene system, for which  $\phi$ , a measure of the extent to which interaction between unlike radicals is preferred, was found to have a value of unity.  $\phi$  is defined by  $\phi = k_{t12}/(k_{t11}k_{t22})^{1/2}$ , where  $k_{t11}$  and  $k_{t22}$  are the termination rate constants for the two monomers  $M_1$  and  $M_2$ , and  $k_{t12}$  is the rate constant for the interaction of two unlike radicals.

The system styrene + methyl methacrylate has been widely investigated<sup>3, 4, 5</sup> and  $\phi$  has been found to have a value of 14 over the whole monomer range. By substituting *p*-methoxystyrene for styrene, the main interest in this work lies in discovering the magnitude and variation of  $\phi$ . It has been suggested<sup>5</sup> that the increased rate of reaction between unlike radicals is primarily due to polarity differences, and so considering the similar polarities of styrene and *p*-methoxystyrene,  $\phi$  for the methyl methacrylate + *p*-methoxystyrene system would be expected to have a value in the vicinity of 14.

Another peculiar feature of copolymerization reactions has been the variation of the rate of initiation with monomer composition.<sup>3, 5</sup> 2-azo-*bis*-(isobutyronitrile) is used as initiator, as it has been claimed<sup>4</sup> that this substance gives almost equal rates of initiation for all monomers, the rate of initiation being determined solely by the rate of fission of the initiator into free radicals. For the styrene + *p*-methoxystyrene system, there was found to be no great difference in the rates of initiation for the two monomers, and the initiation varied directly as the monomer composition. The rate of initiation was, however, much smaller than that expected from the rate of decomposition of the initiator, assuming that each fragment of the initiator started one polymer chain.

Since it has been deduced<sup>5</sup> that  $\phi^2 \propto 1/r_1r_2$ , where  $r_1r_2$  are the monomer reactivity ratios, a value of  $\phi < 1$  would be expected if  $r_1r_2 > 1$ . Values of  $r_1r_2$  much greater than unity cannot, of course, be expected, since this would mean that each monomer preferred to polymerize separately rather than to copolymerize. Out of 220 monomer pairs,<sup>6</sup> only 6 have values of  $r_1r_2$  significantly greater than unity. It is significant that 4 of these pairs involve either dienes or monomers yielding insoluble polymers, and so present considerable difficulties. It was suggested to us<sup>7</sup> that the system styrene + *m*-vinylphenol might repay attention in this connection; a short investigation of this system has therefore been made.

#### THE METHYL METHACRYLATE + *p*-METHOXYSTYRENE SYSTEM

##### EXPERIMENTAL

The rates of polymerization were determined by the same methods, and under the same conditions, as those used for the copolymerization of styrene and *p*-methoxystyrene.<sup>2</sup> The methyl methacrylate<sup>3</sup> and *p*-methoxystyrene<sup>2</sup> were purified as previously described. 2-azo-*bis*-(isobutyronitrile) was again used as an initiator for the reaction.

The densities of methyl methacrylate monomer and polymer at 60°C were taken to be 0.897 and 1.191, respectively.<sup>8</sup> These data give a percentage volume contraction of 24.68 for 100% conversion. Previous experiments<sup>2</sup> gave a value of 16.23% for *p*-methoxystyrene. For the copolymers, use was made of the copolymer composition equation, the monomer reactivity ratios used being those given by Walling *et al.*<sup>9</sup> Polymers were isolated by precipitation with methanol, followed by a further process of solution in benzene and precipitation.

Osmotic pressures were measured in benzene solution at 25°C by the static method, equilibrium being reached in just under 3 h.

## RESULTS

EVALUATION OF THE  $\delta = k_t^{\frac{1}{2}}/k_p$  CONSTANT FOR METHYL METHACRYLATE.—The values of the rate constants for the polymerization of methyl methacrylate are known<sup>3,10</sup> but not at 60°. Uncertainty in the energies of activation ruled out extrapolation to this temperature, so that a determination of  $\delta$  at 60° was necessary. The true thermal rate at 60° C was found to be of the order of 0.1 %/h initially, but fell off gradually with time, as shown in fig. 1. Bamford and Dewar<sup>11</sup> maintain that this fall-off is due to the formation of an inhibitor, but as the initiated reaction was studied for only 5-10 % polymerization (1-2 h), the formation of inhibitor in this time is negligible. As the initiated rates were always greater than 4 %/h, the slow thermal reaction is of little importance.

A batch of reaction vessels was prepared using varying amounts of initiator, and the rates of polymerization at 60° measured. The rate measurements are given in table 1, whilst the rates of polymerization are shown in fig. 1. It is worth noting that the rate for an initiator concentration of 1 g/l. is not in agreement with that found by Walling,<sup>4</sup> whose data yield  $R/C^{\frac{1}{2}} = 7.85$ . However, the value of  $R/C^{\frac{1}{2}} = 9.8$  has been found by other workers in these laboratories<sup>20</sup> and is quite reproducible.

As can be seen from fig. 1, the rate of polymerization is exactly constant up to 7 % 0.54 (B) and 1.016 (C) g/l. For the true thermal reaction, the full time axis is 50 h conversion, but afterwards there is a very slight deviation from linearity. The rate measurements in table 1 refer to the first 7 % of reaction. The constancy of  $R/C^{\frac{1}{2}}$  indicates that mutual termination is operating.

The  $\Pi/C$  against  $C$  curves for these polymers are shown in fig. 2; the form of the  $\Pi/C$  against  $C$  curve for the polymer of lowest molecular weight agrees well with that found for photo-polymers of methyl methacrylate.<sup>12</sup> A curve of the same shape was then fitted to the more scattered experimental points for the other polymers. The results of the molecular weight determinations are shown in table 2, and  $1/\bar{P}$  is plotted as a function of the rate of polymerization in fig. 3.

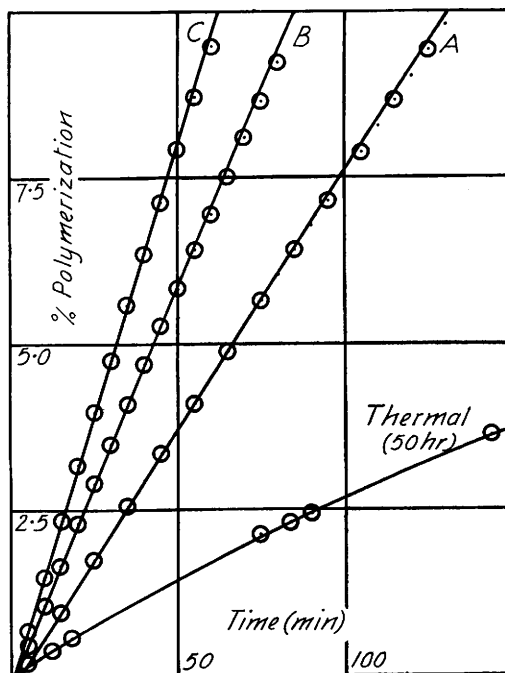


FIG. 1.—Polymerization of methyl methacrylate at initiator concentrations of 0.725 (A).

TABLE 1.—VARIATION OF THE RATE OF POLYMERIZATION OF METHYL METHACRYLATE WITH THE CONCENTRATION OF INITIATOR

concn. of initiator, $C$ (g/l.)	rate ( $R$ ) (%/h)	$R/C^{\frac{1}{2}}$
0.225	4.65	9.83
0.54	7.13	9.70
1.016	9.78	9.70

TABLE 2.—MOLECULAR WEIGHT DATA FOR METHYL METHACRYLATE

rate of polymerization, $R$ (moles l. <sup>-1</sup> sec. <sup>-1</sup> $\times 10^4$ )	mol. wt.	$1/\bar{P} (\times 10^4)$
1.16	840,000	1.19
1.78	630,000	1.59
2.44	520,000	1.92

Since there is some uncertainty in the  $\Pi/C$  against  $C$  extrapolations, the fact that all 3 points lie on a good straight line is perhaps rather fortuitous. The plot of  $1/\bar{P}$  against  $R$  satisfies the equation

$$1/\bar{P} = k_f/k_p + (\delta/(M))^2 R,$$

with

$$k_f/k_p = 0.55 \times 10^{-4},$$

and

$$(\delta/(M))^2 = 0.57, \delta = 6.8.$$

Taking  $\delta_{30} = 22.5$ ,<sup>12</sup> and  $k_f/k_p = 1.4 \times 10^{-5}$  at  $0^\circ\text{C}$ ,<sup>11</sup> the values of the activation energies  $E_p - \frac{1}{2}E_t$ ,  $E_f - E_p$  are calculated to be 8.0 kcal and 4.0 kcal respectively. These values do not compare too favourably with those of  $E_p - \frac{1}{2}E_t = 5$  kcal,  $E_f - E_p = 5.9$  kcal, calculated by Bamford and Dewar using the results of Schulz and Harborth for  $50^\circ$  and  $70^\circ\text{C}$ . From these results, however, the value of  $\delta_{60}$  is calculated to be 7.45, which is in fair agreement with that experimentally obtained. Matheson *et al.*<sup>14</sup> give  $E_p - \frac{1}{2}E_t = 4.9$  kcal;  $E_f - E_p = 6.0$  kcal, values which agree well with those of Bamford and

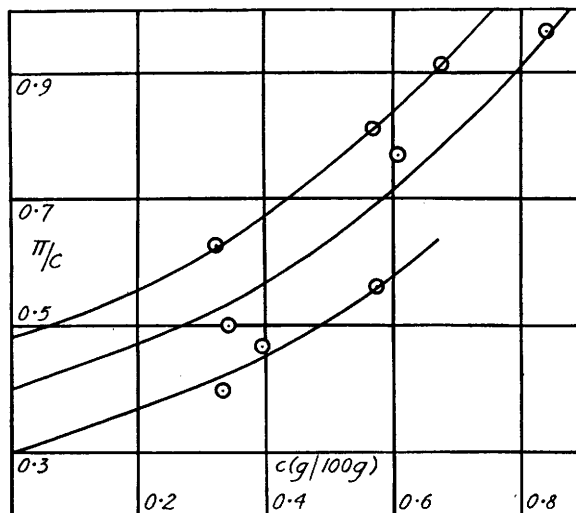


FIG. 2.—Variation of  $\Pi/C$  with  $C$  for various polymethyl methacrylates ( $\Pi$  in cm benzene)

Dewar. It seems likely, then, that the value of  $\delta$  found in this work is too low whilst that for  $k_f/k_p$  is too high. In order that the present results may be directly comparable to those previously obtained in these laboratories, however, the experimental values are used.

Substituting the known values of  $R$ ,  $(M)$  and  $\delta$  in the expression

$$R = \delta^{-1}(M)I^{\frac{1}{2}},$$

the rate of initiation ( $I$ ) is calculated to be  $3.36 \times 10^{-8}$  moles  $\text{l}^{-1} \text{sec}^{-1}$ , when  $R$  has been corrected to a concentration of initiator of 1 g/l. This value is subject to the experimental errors involved in osmotic pressure measurements, and these are considerable, for high molecular weights. In previous work,  $I$  was found to be  $3.3$  and  $2.1 \times 10^{-8}$  moles  $\text{l}^{-1} \text{sec}^{-1}$  for styrene and *p*-methoxystyrene respectively. Also, assuming that each molecule of initiator on thermal decomposition gives rise to 2 free radicals, each of which initiates a polymer chain,  $I = 12.2 \times 10^{-8}$  moles  $\text{l}^{-1} \text{sec}^{-1}$  as calculated from the data of Lewis and Matheson.<sup>15</sup> From the values of the rate of initiation obtained for the 3 monomers, it would appear that all the initiator fragments do not, in fact, start radical chains. The claim that 2-azo-*bis*-(isobutyronitrile) does give a constant rate of initiation for different monomers is more justified, although the experimentally measured value is considerably lower than that expected from the rate for the decomposition of the initiator.

**THE COPOLYMERIZATION OF METHYL METHACRYLATE AND *p*-METHOXYSTYRENE.**—The actual copolymerization was studied by the same techniques as those used for previously investigated systems. Having knowledge of the monomer reactivity ratios, and the weights of the two monomers added to each reaction vessel, the contraction in volume was easily converted into a percentage polymerization. In each case, the polymer produced was weighed, the weight being in good agreement ( $\pm 4\%$ ) with the calculated value.

Various monomer mixtures were made up, the concentration of 2-azo-bis-(isobutyronitrile) being 1 g/l. in each case. The rate of polymerization was determined in the usual manner, the reaction being followed to about 10 % conversion, in order to obtain appreciable amounts of the copolymers for molecular weight determinations. The conversion-time plots were almost linear, yet as for the separate monomers, deviation from linearity became more pronounced after 8 % conversion. Fig. 4 shows the relationship between the rate of polymerization (corrected to an initiator concentration of 1 g/l.) and the mole fraction of *p*-methoxystyrene ( $M_2)_0$ . The shape of the curve is very similar to that obtained for the styrene + methyl methacrylate system,<sup>3, 4</sup> although the fall in the rate is not so sharp for small concentrations of *p*-methoxystyrene.

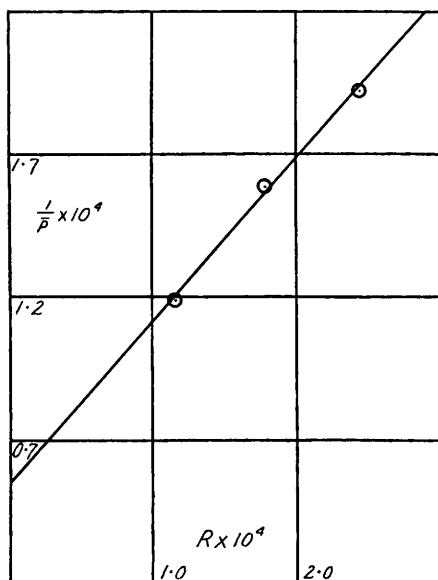


FIG. 3.—Variation of the degree of polymerization with the rate (moles l.<sup>-1</sup> sec.<sup>-1</sup>).

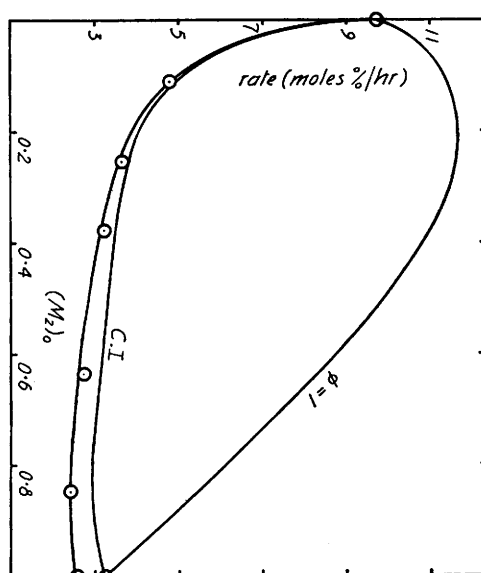


FIG. 4.—Variation of the rate of polymerization with the mole fraction of *p*-methoxystyrene in the monomer mixture ( $M_2)_0$ . C.I. = constant initiation = that for methyl methacrylate.

These results were then substituted in the appropriate kinetic expression,<sup>16</sup> viz.,

$$R = \frac{\{r_1 M_1\}^2 + 2(M_1)(M_2) + r_2 (M_2)^2\} I^{\frac{1}{2}}}{\{r_1^2 \delta_1^2 (M_1)^2 + 2\phi r_1 r_2 \delta_1 \delta_2 (M_1)(M_2) + r_2^2 \delta_2^2 (M_2)^2\}^{\frac{1}{2}}}, \quad (1)$$

where  $M_1$  and  $M_2$  represent methyl methacrylate and *p*-methoxystyrene respectively, assuming the rate of initiation to be constant and equal to that for *p*-methoxystyrene alone. ( $I = 2.1 \times 10^{-8}$  moles l.<sup>-1</sup> sec.<sup>-1</sup>.) For this system  $r_1 = 0.29$ ,  $r_2 = 0.32$ ,<sup>9</sup>  $\delta_1 = 6.8$ , and  $\delta_2 = 21.2$ . There was found to be a drift in the value of  $\phi$  from 5 to 23 as the mole fraction of *p*-methoxystyrene was increased. As the theory does not predict any variation in the value of  $\phi$ , it was advisable to try and measure the rates of initiation of the copolymerizing systems. This cannot be done with complete accuracy by molecular weight measurements, but approximate values can be obtained by using the procedure adopted for the styrene + *p*-methoxystyrene system. It was found that  $k_f/k_p = 0.55 \times 10^{-4}$  for methyl methacrylate, and  $0.74 \times 10^{-4}$  for *p*-methoxystyrene,<sup>2</sup> so to a first approximation, the transfer term for the copolymerizing system can be taken to be  $0.65 \times 10^{-4}$ . This transfer constant is a composite quantity since there are 4 possible transfer coefficients involved, viz. transfer by interaction of polymethyl methacrylate radicals and also poly-*p*-methoxystyrene radicals with the 2 monomers. Two of those are already known from the polymerization behaviour of the individual monomers. Since these latter coefficients are comparable in magnitude, neither may be neglected and hence from the one piece of new experimental information (the molecular weight of the copolymer)

the other 2 cross-transfer coefficients cannot at present be evaluated. The rate of initiation for each monomer mixture was then calculated from the expression

$$I = R(1/\bar{P} - 0.65 \times 10^{-4}).$$

The molecular weights of various copolymers were determined, the copolymers being chosen so as to span the range of monomer mixtures. The results are shown in table 3, and the  $\Pi/C$  against  $C$  curves are plotted in fig. 5. Variation in the composition of the polymers has no effect on the value of Huggins'  $\mu$  constant, which gives a measure of the interaction between solute and solvent.

TABLE 3.—RATES OF INITIATION FOR THE COPOLYMER SYSTEM

expt. no.	(M <sub>2</sub> ) <sub>0</sub> (mole fraction)	rate ( $R$ ) (moles l. <sup>-1</sup> sec. <sup>-1</sup> ) $\times 10^5$	$\bar{P}$	(moles l. <sup>-1</sup> sec. <sup>-1</sup> ) $\times 10^8$	mole fraction of M <sub>2</sub> in co-polymer	Huggins' $\mu$ value
—	0.0	24.2	—	3.36	0.0	0.46
3	0.11	11.46	2680	3.50	0.24	0.46
5	0.255	8.47	2160	3.33	0.375	0.46
1	0.381	6.71	2060	2.86	0.49	—
2	0.635	5.75	2260	2.16	0.57	0.46
—	0.85	5.02	—	—	0.725	—
—	1.0	5.1	—	2.10	1.0	0.4552

Fig. 6 gives the plot of the rate of initiation against the mole fraction of *p*-methoxystyrene in the monomer mixture (M<sub>2</sub>)<sub>0</sub>. A straight line drawn by the method of least squares satisfies every point within the limits of the experimental error. Thus it seems reasonable to assume that the rate of initiation varies directly with the monomer composition. Substitution in eqn. (1) of the values for  $I$  taken from the graph in fig. 6 yielded the results shown in table 4 and fig. 7.

TABLE 4.—VARIATION OF  $\phi$  WITH MONOMER COMPOSITION

(M <sub>2</sub> ) <sub>0</sub>	$I$ (corrected) (moles l. <sup>-1</sup> sec. <sup>-1</sup> ) $\times 10^8$	$\phi$	$\phi$ (assuming constant $I = 2.1 \times 10^{-8}$ moles l. <sup>-1</sup> sec. <sup>-1</sup> )
0.11	3.22	11.7	4.8
0.255	3.04	17.9	9.0
0.38	2.88	26.1	14.9
0.635	2.56	26.9	19.7
0.85	2.29	27.0	23.1

As for constant initiation, there is a drift in the value of  $\phi$ . Although it is not so great as for the styrene + butyl acrylate<sup>5, 17</sup> system, this variation in  $\phi$  does rather conflict with the constant values of 1 and 14 obtained for the styrene + *p*-methoxystyrene and styrene + methyl methacrylate systems.

Assuming constant initiation (= that for methyl methacrylate) and taking  $\phi$  to be unity, the theoretical rate was calculated for each copolymer and plotted against the mole fraction of *p*-methoxystyrene in the monomer mixture (fig. 3). Thus it is seen that it is only the comparatively high values of  $\phi$  which bring the theoretical rate of polymerization into line with that which is experimentally obtained. Plotting the rate of polymerization, calculated for constant initiation (= that for methyl methacrylate), against monomer composition (fig. 3), the general shape of the curve is only slightly altered.

#### THE STYRENE + *m*-VINYLPHENOL SYSTEM

##### EXPERIMENTAL

The *m*-vinyl phenol as obtained from British Resin Products Ltd. was 80 % pure, and stabilized with metol. Distillation at about 40° under reduced pressure to remove the inhibitor produced a colourless oily liquid, which when left in the air at room temperature readily polymerized, turning brown during the process. The *m*-vinyl phenol was stored at -30° C. The only information in the literature gives the b.p. = 114° C/16-17 mm.<sup>18</sup> The main impurity of the *m*-vinyl phenol, as stated by the manufacturers, was *m*-ethyl phenol, a substance difficult to remove. As only limited quantities of the monomer were available, a procedure to separate these substances could not be evolved and the crude monomer was used. Except where otherwise stated, all calculations were made assuming the monomer to be 100 % pure.

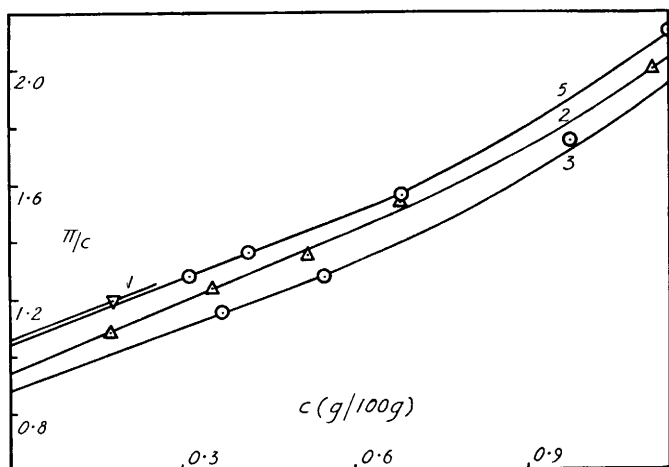
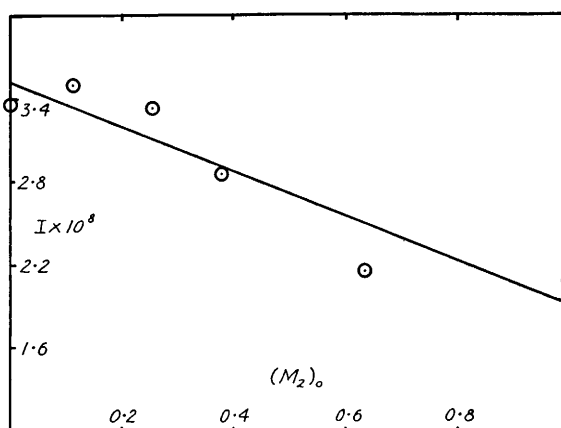
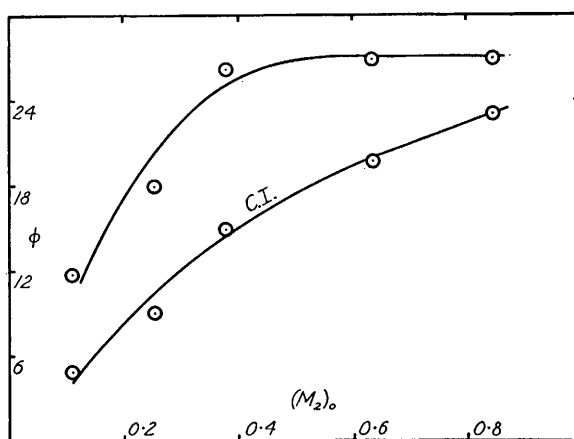
FIG. 5.—Variation of  $\Pi/C$  with  $C$  for various copolymers.

FIG. 6.—Variation of the rate of initiation with the monomer composition.

FIG. 7.—Variation of  $\phi$  with the monomer composition.  $C.I.$  = constant initiation = that for *p*-methoxystyrene.



Poly *m*-vinyl phenol, a white and fibrous solid, is soluble in ethyl alcohol, ethyl acetate and acetone, and insoluble in benzene. The polymer was isolated by slowly running a concentrated alcohol solution into a large excess of benzene, which was kept well agitated with a glass rod. The polymer has a great tendency to adhere to glass and so most of the polymer was collected round the stirring rod. After being hardened in fresh benzene, the polymer was easily scraped from the glass rod, and finally dried in an oven at 100° C. Being slightly hygroscopic, the polymer was kept in a desiccator.

It was found to be impossible to distil *m*-vinyl phenol on the high vacuum line, so the reaction vessels (volume  $\cong 5$  cm<sup>3</sup>) were filled before being attached to the line, then degassed and sealed off in the usual way. The volume of the monomer was calculated from the tube dimensions. In the copolymerizing system, the volume of the *m*-vinyl phenol was obtained by subtracting the known volume of styrene distilled from the total volume, again obtained from the tube dimensions.

The polymerization at 60° C initiated by 2-azo-*bis*-(isobutyronitrile), was followed by the dilatometric method up to 10 % conversion. The contraction against time plots were linear up to 7 % conversion, but afterwards there was a slight divergence from linearity. Because reliable values for the densities of the monomer and polymer were not available, the polymer was always weighed.

After polymerization, the bulb of the reaction vessel was crushed in a glass mortar, and the contents covered with benzene. The precipitated polymer was disintegrated by a pestle and collected in a no. 3 S.G. crucible together with the glass fragments. After being dried at the pump for 2 h, the polymer was dissolved in a minimum of absolute alcohol, and the solution filtered under suction. The remaining glass chips were washed twice with alcohol, and the combined polymer solutions ( $\sim 30$  cm<sup>3</sup>) concentrated to 5 cm<sup>3</sup> in an oven at 100° C before being added to benzene in the manner described above.

Although rather tedious, and not too accurate in the quantitative sense, this method had the advantage of precipitating the polymer in a condition suitable for carbon-hydrogen analysis. It served also to measure the density of the monomer at 60° C, for weighing the tube with monomer, and the glass fragments after washing with alcohol gave the weight of *m*-vinyl phenol used. A value of 1.014 was obtained from four determinations by this method for the density at 60° C.

Substituting the results obtained in the relationship,

$$\text{wt. of polymer} = \frac{\text{volume contraction} \times \rho_{\text{monomer at } 60^\circ \text{ C}} \times 10^2}{\% \text{ volume contraction for } 100 \% \text{ conversion } (F)}$$

a mean value of  $F = 15$  % was calculated. This value is quite similar to the value of  $F = 16.3$  % obtained for styrene by density measurements at 60° C. Using this value of 15 %, the rate of polymerization was easily calculated from the contraction against time plot.

The pure thermal rate at 60° C varied considerably, generally being  $\sim 1$  %/h, but as it was always much lower than the initiated rate, it was completely ignored. Using the initiator, the reproducibility was not all that could be desired, but the logarithmic plot

TABLE 5.—DEPENDENCE OF RATE ON INITIATOR CONCENTRATION

rate (%/h)	initiator concentration (g/l.)
3.94	0.25
6.10	0.53
7.97	0.76
9.18	1.03
9.66	1.02

of rate against initiator concentration gave a reasonably straight line having a slope of 0.63. This suggested that most of the chains were being stopped by mutual termination. Table 5 gives the rate measurements.

Assuming the rate of initiation to be the same as for styrene at an initiator concentration of 1 g/l., i.e.  $I = 3.3 \times 10^{-8}$  moles l.<sup>-1</sup> sec<sup>-1</sup>,  $\delta$  was calculated to be 7.

Various compositions of styrene and *m*-vinyl phenol were polymerized using an initiator concentration of 1 g/l., and as usual there was a small decrease in rate after 7 % conversion. When each reaction vessel was immersed in the thermostat at 60° C, a faint white precipitate settled to the bottom of the tube. This was in all probability poly-*m*-vinyl phenol, thus indicating that the monomer had slightly polymerized, either during the initial distillation, or on storing at  $-30^\circ \text{ C}$ . An attempt was made to measure the extent of the polymerization by treating the original monomer with benzene. No polymer was, however, obtained by this method. The copolymer could not be isolated by the normal technique of precipitation with methanol, as the poly-*m*-vinyl phenol was soluble in alcohol. The method adopted was to precipitate the polymers rich in *m*-vinyl

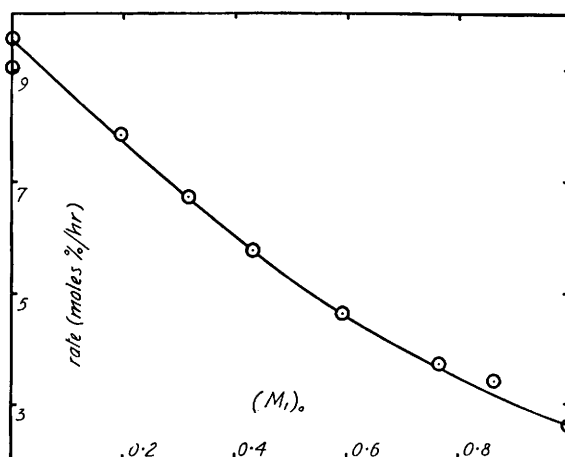


phenol from alcohol with benzene, and the polystyrene-rich polymers from benzene using *n*-hexane. Copolymers produced from a monomer mixture having a mole fraction of *m*-vinyl phenol in the range 0.35-0.7, could not be isolated by this procedure. The copolymers were dried in an oven at 100° overnight, and then subjected to a carbon-hydrogen analysis. Basing the results on the experimental oxygen content, the composition of each copolymer was calculated, the results being given in table 6.

TABLE 6.—ANALYSIS OF COPOLYMERS

(M <sub>1</sub> ) <sub>0</sub> (mole fraction of styrene in monomer mixture)	% carbon	% hydrogen	% oxygen	wt. fraction of polystyrene in copolymer
0.0	77.06	6.79	16.15	—
0.195	79.30	7.06	13.64	0.155
0.315	80.90	7.15	11.95	0.260
0.765	87.94	7.39	4.67	0.710
0.865	90.06	7.29	2.65	0.835
1.0	92.03	7.83	0.0	1.0

The analysis of poly-*m*-vinyl phenol consistently gave a different composition from that of C=80 %, H=6.66 %, expected from the formula. The low value for the carbon may be due to the hygroscopic nature of the polymer, despite the fact that all the polymers were kept in a desiccator until required for analysis.

FIG. 8.—Variation of the rate of polymerization with the mole fraction of styrene in the monomer mixture (M<sub>1</sub>)<sub>0</sub>.

Using the copolymer composition equation, the values of the reactivity ratios were calculated by the method of Arlman and Melville<sup>17</sup> to be  $r_1$  (styrene) = 0.91,  $r_2$  = 1.21, and  $r_1 r_2$  = 1.10. Knowing these values, the rate of polymerization was determined and plotted against the mole fraction of styrene in the monomer mixture (M<sub>1</sub>)<sub>0</sub>. As can be seen from fig. 8, there is a steady increase in rate as the styrene content is decreased. An attempt was made to calculate  $\phi$  by substituting these rate data into eqn. (1) and putting  $\delta_2$  = 7; the results are shown in table 7.

Considering the impurity of the *m*-vinyl phenol, and the rather unsatisfactory method of precipitation of the copolymers, only a limited amount of work has been done on this system, and the results given must be regarded as semi-quantitative only.

TABLE 7.—VALUES OF  $\phi$  FOR STYRENE + *m*-VINYL PHENOL

mole fraction styrene	$\phi$
0.195	0.5
0.315	0.4
0.430	0.7
0.590	0.2
0.765	<0
0.865	<0

## DISCUSSION

The results obtained here for the rates of initiation serve only to accentuate the difference noticed previously between the measured rate of initiation, and that calculated from the rate of decomposition of the initiator. 2-azo-*bis*-(*iso*-butyronitrile) at 60° C initiates chains at a rate of  $2.3 \times 10^{-8}$  moles  $\text{l}^{-1} \text{sec}^{-1}$  for styrene, *p*-methoxystyrene, methylmethacrylate and all mixtures of these monomers, although the rate of production of radicals is  $12 \times 10^{-4}$  moles  $\text{l}^{-1} \text{sec}^{-1}$ ,<sup>17</sup> (also confirmed by Bawn and Mellish<sup>19</sup> recently). This discrepancy remains unexplained. It may be that there is a definite wastage of initiator fragments, and that only about 25 % of them start chains, the remainder perhaps combining to form  $(\text{CMe}_2\text{CN})_2$ .

The results for the copolymerizations are in general agreement with those obtained for other systems. There is obviously a flaw in the experimental technique for styrene + *m*-vinyl phenol, since negative values of  $\phi$  are calculated for two of the compositions. However, it seems likely that a value of  $\phi \leq 1$  fits the facts quite well. It was felt that the accurate results that might have been obtained from a more careful study of the system would not have justified the extra labour involved, since the system showed no interesting abnormalities.

The methyl methacrylate + *p*-methoxystyrene system is also in agreement with expectation. The value of  $\phi$  is greater than that for the pair styrene + methyl methacrylate, in accordance with the fact that the product of the reactivity ratios is smaller for this pair (see, e.g., ref. (2) for a discussion of this point). As was pointed out in a previous paper,<sup>2</sup> a relation between  $\phi$  and Price's *e*-factors can be deduced, e.g.

$$\phi^2 = \frac{A_{12}^2}{A_{11}A_{22}} \exp (e_1 - e_2)^2,$$

where  $A_{12}$ ,  $A_{11}$  and  $A_{22}$  are the temperature-independent factors for the three termination reactions and  $e_1$ ,  $e_2$  are electrical charge factors. The higher value of  $\phi$  for *p*-methoxystyrene over styrene in copolymerization with methyl methacrylate ( $e = 0.4$ ) can thus be regarded as arising from the greater electronegativity of *p*-methoxystyrene, which has  $e = -1.05$ ,<sup>21</sup> compared with  $-0.8$  for styrene. On the other hand, the system styrene + diethyl fumarate,<sup>22</sup> with  $(e_1 - e_2) = 2$ , has  $\phi = 7.75$ , a value much lower than would have been expected on the basis of polarities. It seems likely that the bulky 1:2-carbethoxy groups exercise steric hindrance so as to overcome the favourable dipolar attractions.

The most difficult matter to account for is the variation of  $\phi$  with composition observed in all these systems in which  $\phi$  is greater than unity. The variation seems to be larger the higher the value of  $\phi$ . In contrast to this behaviour is the fact that the reactivity ratios are independent of composition and naturally of the methods of initiation and termination of polymerization. This means that the 4 radical-molecule interactions involved in the propagation of copolymerization are independent of composition, and that the effective concentrations of the monomers are their molar concentrations. Correspondingly the radical concentrations are accurately given by the copolymer composition equation. The variation of  $\phi$  with composition would therefore seem to be due to change in environment. In radical-radical interactions of a single monomer, the environment can materially reduce the value of the termination coefficient if the viscosity of the medium is increased, or if the radicals are made to contract in a medium which is a poor solvent for the polymer. There is as yet no evidence that in a good solvent environment has any effect on the termination coefficient. On the other hand, it is well known that the efficiency of the initiation of polymerization owing to the thermal or photochemical decomposition of a radical-producing molecule does vary considerably with environment. It is therefore reasonable to suppose that in the reverse process of radical-radical interaction a similar influence can be exerted.

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