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Copolymerization. XIII.[1] Over-all Rates in Copolymerization. Polar Effects in Chain Initiation and Termination

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Studies of free radical catalyzed copolymerizations have, in the past, dealt chiefly with the composition of the products formed. Within this field, an adequate theory, based upon the copolymerization equation,[2] has been developed relating the compositions of copolymer and feed in terms of two ratios of rate constants, the "monomer reactivity ratios," and has been subjected to exhaustive experimental test.[3] Since the composition of a copolymer is determined, essentially, by the relative reactivities of the monomers present toward the different free radicals in the system, copolymer composition studies have also helped to throw light on the broader problem of the effect of radical and olefin structure on radical addition reactions.[3a,4,5]

The problem of over-all rates, however, has received only qualitative discussion[3a,6] chiefly because of its greater complexity. Thus, while the *composition* of a copolymer is determined by the four rate constants for chain growth (resolvable into two ratios) the *rate* of a copolymerization involves, as well, the rate constants for chain initiation and termination. Despite this difficulty, two developments now make an attack on the problem of over-all rates feasible, and, in fact, experimentally quite simple. The first of these is a kinetic analysis by Melville, Noble and Watson[7] which indicates that most of the rate-constants may be combined into independently measurable ratios. The second is the discovery in this Laboratory that polymerization initiators of the type of 2-azo-bis-isobutyronitrile decompose unimolecularly at the same rate in a variety of solvents,[8] and that the fragments start polymerization efficiently in a variety of monomers. This paper describes an experimental investigation using this initiator with three monomer pairs. Results are in reasonable agreement with the equations of Melville, Noble and Watson. Further, taken with recent determinations of the separate rate constants for the individual monomers,[9] they permit an estimate of the absolute rates of "crossed" chain initiation and termination and suggest the existence of polar phenomena in the processes of radical formation and interaction, similar to those arising in radical addition reactions.[2a,3a,4,5]

Derivation of Equations.—Expressions for over-all rates of copolymerization for a variety of possible cases have been derived by Melville, Noble and Watson.[7] The development given below, while leading to some of the same expressions, is considerably shorter and is directed particularly toward the cases actually observed experimentally. The assumptions employed, which are listed below, appear well established for oil-phase radical polymerizations leading to high molecular-weight products. The first two are the same as those used in the treatment of copolymer compositions: (a) steady-state assumptions are valid, *i. e.*, we are dealing with chains of long length, but short life compared to the over-all reaction. (b) Rate constants for the reaction of a growing chain depend only upon the monomer unit at the growing end, and not upon chain length or further composition.[10] (c) Chain termination is by bimolecular radical interaction. Experimentally, this appears to be a requirement for the formation of high molecular weight polymers, since any faster competing method of radical destruction leads to short chains, as in the polymerization of allyl acetate.[11]

By assumption (b) the over-all rate of monomer disappearance is given by

$$\frac{-\mathrm{d}([\mathrm{M}_1] + [\mathrm{M}_2])}{\mathrm{d}t} = k_{11}[\mathrm{M}_1\cdot][\mathrm{M}_1] + k_{21}[\mathrm{M}_2\cdot][\mathrm{M}_1] + k_{12}[\mathrm{M}_1\cdot][\mathrm{M}_2] + k_{22}[\mathrm{M}_2\cdot][\mathrm{M}_2] \quad (1)$$

where, in keeping with nomenclature in previous papers in this series,[12] $[\mathrm{M}_1]$ and $[\mathrm{M}_2]$ are concentrations of the two monomers and k_{21} is the rate constant for attack of a growing chain ending in an M_2 unit upon M_1 etc. By assumptions (a) and (c) the two steady-state equations may also be

$$k_{21}[\mathrm{M}_2\cdot][\mathrm{M}_1] = k_{12}[\mathrm{M}_1\cdot][\mathrm{M}_2] \quad (2)$$

$$I = k_{t_1}[\mathrm{M}_1\cdot]^2 + 2k_{t_{12}}[\mathrm{M}_1\cdot][\mathrm{M}_2\cdot] + k_{t_2}[\mathrm{M}_2\cdot]^2 \quad (3)$$

written where I represents the rate at which kinetic chains are started, and K_{t_1} the rate of termination of chains by interaction of two M_1 type

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[1] For the preceding paper in this series, see Walling, Seymour and Wolfstirn, THIS JOURNAL, **70**, 1554 (1948).

[2] (a) Mayo and Lewis, *ibid.*, **66**, 1594 (1944); (b) Wall, *ibid.*, **66**, 2050 (1944); (c) Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944).

[3] (a) Mayo, Lewis and Walling, THIS JOURNAL, **70**, 1529 (1948); (b) Chapin, Hamm and Fordyce, *ibid.*, **70**, 538 (1948); (c) Agron, Alfrey, Bohrer, Haas and Wechsler, *J. Polymer Sci.*, **3**, 157 (1948). Further references will be found in these papers.

[4] Price, *ibid.*, **1**, 83 (1946).

[5] (a) Walling, Briggs, Wolfstirn and Mayo, THIS JOURNAL, **70**, 1537 (1948); (b) Walling, Seymour and Wolfstirn, *ibid.*, **70**, 1554, 2559 (1948).

[6] Bartlett and Nozaki, *ibid.*, **68**, 1495 (1946).

[7] Melville, Noble and Watson, *J. Polymer Sci.*, **2**, 229 (1947).

[8] Lewis and Matheson, THIS JOURNAL, **71**, 747 (1949).

[9] (a) Matheson, Bevilacqua, Auer and Hart, Abstracts of papers presented at the St. Louis Meeting of the Am. Chem. Soc., September, 1948; (b) Matheson, Aver, Bevilacqua and Hart, THIS JOURNAL, **71**, 497 (1949).

[10] To some extent, this assumption may be replaced by the more general one that this constancy applies only to some of the rate constant ratios; *cf.* ref. 7.

[11] Bartlett and Altschul, THIS JOURNAL, **67**, 812, 816 (1945).

[12] *Cf.* Alfrey, Mayo and Wall, *J. Polymer Sci.*, **1**, 581 (1946).

radicals, etc.[13] Solving (2) and (3) simultaneously for $[M_1.]$ and substituting into (1) we obtain

$$\frac{-\mathrm{d}([M_1] + [M_2])}{\mathrm{d}t} = \frac{(k_{21}k_{11}[M_1]^2 + 2k_{12}k_{21}[M_1][M_2] + k_{22}k_{12}[M_2]^2)(I)^{1/2}}{(k_{t_1}k_{21}^2[M_1]^2 + 2k_{t_{12}}k_{21}k_{12}[M_1][M_2] + k_{t_2}k_{12}^2[M_2]^2)^{1/2}} \qquad (4)$$

The transformation of (4) into (5), a form equivalent to one of the expressions of Melville, Noble

$$\frac{-\mathrm{d}([M_1] + [M_2])}{\mathrm{d}t} = \frac{(r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2)I^{1/2}}{(\delta_1^2r_1^2[M_1]^2 + 2\phi\delta_1\delta_2r_1r_2[M_1][M_2] + \delta_2^2r_2^2[M_2]^2)^{1/2}} \qquad (5)$$

and Watson, now requires only the substitutions

$$r_1 = k_{11}/k_{12},\ r_2 = k_{22}/k_{21},\ \delta_1^2 = k_{t_1}/k_{11}^2,\ \delta_2^2 = k_{t_2}/k_{22}^2,$$
$$\phi^2 = k^2_{t_{12}}/k_{t_1}k_{t_2}$$

and some simple algebra.

Since the quantities r_1 and r_2 are the familiar monomer reactivity ratios, measurable from copolymer composition studies, and δ_1 and δ_2 are simply the ratios of the square root of the rate constants for chain termination to the rate constants for chain growth for the individual monomers, measurable, for example, by rate studies at known rates of chain initiation, or molecular weight determinations under conditions of negligible chain transfer, the only ratio not independently measurable is ϕ, the factor giving the relation between $k_{t_{12}}$, the rate constant for "crossed" termination, and the geometric mean of the rate constants for chain termination of each monomer alone (k_{t_1} and k_{t_2}). Actually, if a means of producing constant chain initiation is available, independent determination of δ_1 and δ_2 is unnecessary, and all that is required is a series of measurements of relative polymerization rates on a number of monomer mixtures including the two pure monomers alone. Equation (5) may be put in the form

$$\frac{-\mathrm{d}([M_1] + [M_2])}{\mathrm{d}t} = \frac{(r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2)(I^{1/2}/\delta_1)}{[r_1^2[M_1]^2 + 2\phi r_1r_2[M_1][M_2]\delta_2/\delta_1 + r_2^2[M_2]^2(\delta_2/\delta_1)^2]^{1/2}} \qquad (6)$$

In the case of pure M_1, (6) becomes

$$\mathrm{d}\ln[M_1]/\mathrm{d}t = I^{1/2}/\delta_1 \qquad (7)$$

and, since

$$\frac{\mathrm{d}\ln[M_1]}{\mathrm{d}\ln[M_2]} = \frac{\delta_2}{\delta_1} \qquad (8)$$

δ_2/δ_1 may be obtained simply by comparing the polymerization rates of the two monomers alone. Rate measurements in copolymerization now permit the determination of ϕ and detecting any unusual rate of crossed termination. Next, in cases where k_{t_1} and k_{t_2} are known, the absolute value of $k_{t_{12}}$ may be calculated. Finally, in systems where ϕ is known, rate measurements may be employed to determine the kinetics of chain initiation under other conditions, for example, to study the existence and rate of "crossed" thermal initiation.

Copolymerization Rates with Constant Chain Initiation.—Initial experiments were carried out on the pair styrene–methyl methacrylate which has received extensive study in this Laboratory and for which monomer reactivity ratios and δ's are known. All experiments were carried out at 60° using one gram/liter of 2-azo-bis-isobutyronitrile as initiator. One-cc. samples of known compositions were polymerized to low conversion in sealed tubes in the absence of air and worked up by transfer to tared test-tubes, most of the solvent removed *in vacuo*, the polymer redissolved in a little xylene and finally dried to constant weight *in vacuo* at 60°. The technique, which appears adequate for very small samples,[14] is more rapid than the repeated precipitations followed by sublimation of solvent from a frozen benzene solution usually employed in this Laboratory for the isolation of larger quantities of polymer.[15] Results are listed in Table I.

TABLE I

RATES OF COPOLYMERIZATION OF STYRENE–METHYL METHACRYLATE AT 60° IN PRESENCE OF 1 G./L. OF 2-AZO-BIS-ISOBUTYRONITRILE

Mole fract. styrene	Time, hr.	Yield, wt. %	Rate × 10^5, moles/l./sec.
1.000	2	5.11	5.92
	4	8.00, 9.48	4.64, 5.45
0.758	2	3.92	4.61
	4	7.50	4.43
.579	2	4.08	4.82
	4	7.94	4.75
.378	2	4.68	5.67
	4	8.87	5.38
.1906	1	3.17	7.78
	2	6.48	7.95
.0913	0.5	2.35	11.6
	1	4.11	10.2
.000	0.5	3.99	19.8
	1	7.81	19.4

An idea of the validity of the assumption of constant chain initiation required for a treatment of these data may be obtained as follows. At 60° in xylene the rate constant for unimolecular decomposition of 2-azo-bis-isobutyronitrile is 1.0×10^{-5} sec.$^{-1}$ and varies little with change of solvent.[8] If all fragments start chains, I is thus 2×10^{-5} [initiator]. Taking $\delta_1 = 47.3$ for styrene[9] its expected polymerization rate may be calculated from Equation (7) as 6.16×10^{-5} mole/liter/sec., compared with an average experimental value of 5.82×10^{-5}. Similarly, for methyl methacrylate $\delta_2 = 1.76$[9] and the calculated and experimental values for the rate become 26.5×10^{-5} and 19.9×10^{-5}, respectively. The agreement is well within the experimental errors in δ's.

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[13] The factor of 2 in front of $k_{t_{12}}$ is introduced to make all the k_t's proportional since, for example, in solution containing equal concentrations of $M_1\cdot$ and $M_2\cdot$, although any $M_1\cdot$ will collide with another $M_1\cdot$ as often as with an $M_2\cdot$, there will, in all, be twice as many $M_1\cdot$, $M_2\cdot$ collisions as $M_1\cdot$. $M_1\cdot$ ones. Our k_{t_1}, thus is equal to the $2k_t$ of Matheson, *et al.*[9]

[14] *Cf.* Walling, THIS JOURNAL, **70**, 2561 (1948).

[15] Lewis and Mayo, *Ind. Eng. Chem., Anal. Ed.*, **17**, 134 (1945).

If ϕ is now calculated from the data of Table I, taking $\delta_2/\delta_1 = 0.293$, $r_1 = 0.52$ and $r_2 = 0.46$, values of 17.1, 13.6 and 7.8 are obtained for the reaction mixtures containing mole fractions of styrene of 0.579, 0.378 and 0.1906, respectively. Choosing an average value of $\phi = 13$, the theoretical curve for rate *vs.* composition is plotted in Fig. 1, and compared with the experimental data. The fit is only fair, high styrene compositions giving higher rates and low styrene lower rates than are actually observed. However, all the points are fitted by values of ϕ between 6 and 19, and the deviation of experiment from the curve for $\phi = 1$ is unmistakable.

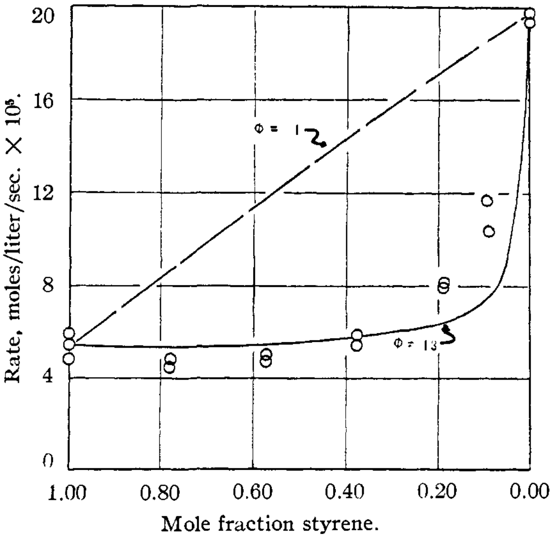

Fig. 1.—Observed and calculated rates of polymerization of styrene–methyl methacrylate at 60° in the presence of 1 g./l. 2-azo-bis-isobutyronitrile.

The values for the rate constants for chain termination of both styrene and methyl methacrylate at 60° have recently been reported by Matheson, Bevilacqua, Auer and Hart,[9] and from these the value for the cross-termination constant 2 $k_{t_{12}}$ may be calculated as 13 × $\sqrt{9.86 \times 1.87} \times 10^7 = 55.8 \times 10^7$, ± ~50%, or appreciably higher than that for either monomer alone.

If the reasonable assumption is made that 2-azo-bis-isobutyronitrile is as effective in starting polymerization chains in other monomers as in styrene and methyl methacrylate, by using the procedure described above, ϕ may be determined for other monomer pairs for which δ_1 and δ_2 are not individually known. In Fig. 2 are plotted the results of a series of experiments carried out on styrene–methyl acrylate at 60°. Since methyl acrylate polymerizes very rapidly and shows a pronounced acceleration with increasing solution viscosity, the monomer mixtures were diluted with an equal volume of ethyl acetate, and the catalyst concentration reduced to 50 mg./liter. Taking $\delta_2/\delta_1 = 0.0304$, from rate measurements in the pure monomers[16] r_1(styrene) $= 0.75$, $r_2 = 0.18$,[3a] the best fit to the points is given by $\phi = 40$, and failure of the experiments to follow the equation for $\phi = 1$ is plainly apparent. Again, however, the fit of a single ϕ value to all the experimental points is only fair. In principle, ϕ could be determined by this technique for any monomer pair for which the monomer reactivity ratios are known. However, for many pairs one (or both) monomer reactivity ratio is very small, and cannot be accurately determined. Although this prevents the determination of ϕ, it makes possible a very simple calculation of the over-all rate for at least some compositions. Thus, if r_2 approaches zero the rate equation (5) may be written

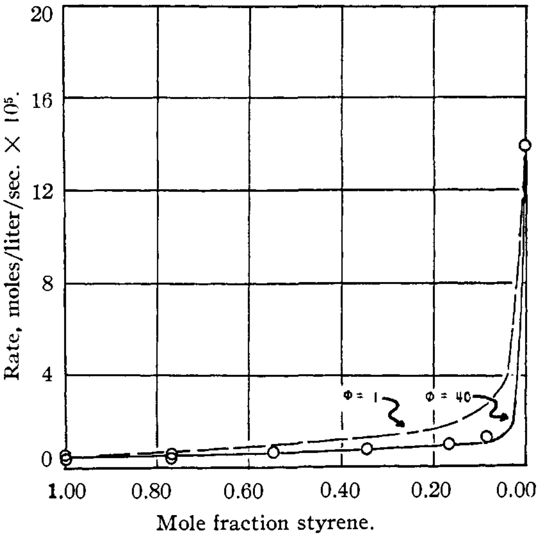

Fig. 2.—Observed and calculated rates for the copolymerization of styrene–methyl acrylate at 60°.

$$\frac{-\,d([M_1] + [M_2])}{dt} = ([M_1] + \frac{2}{r_1}[M_2])\frac{I^{1/2}}{\delta_1} \quad (9)$$

a form which should be a good approximation for systems high in M_1 but which, of course, fails as pure M_2 is approached. Inspection of (9) shows that, for $r_1 > 2$ (for monomers of equal molar volumes), polymerization rates will decrease with increasing M_2, while, with $r_1 < 2$, they will increase.

Styrene–vinyl acetate provide an example of such a system. Here, r_1(styrene) $= 55$ and $r_2 \sim 0.02$[3a] so that addition of vinyl acetate to styrene should decrease the rate of polymerization. Results of experiments carried out at 60° with 1 g./liter of catalyst are shown in Fig. 3.

The trend is in the right direction, but points lie somewhat below the theoretical line.[17] The pronounced inhibiting effect of very small quanti-

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(16) Independent measurement of δ_2 by Dr. Matheson of this Laboratory indicates a value of $\delta_2/\delta_1 = 0.0284$, and thus gives further justification for the assumption of constant initiation in this system.

(17) Actually they lie slightly below the values expected if vinyl acetate were behaving as a pure diluent. Although the sample employed had been carefully distilled and stored in the ice-box, the ease with which vinyl acetate develops inhibitors is well known.

ties of styrene upon vinyl acetate polymerization has been noted in a previous paper from this Laboratory.[3a] How great this inhibition may be, or how little styrene it takes to produce it cannot be calculated from Equation (9), but requires a knowledge of r_2 as well. Taking $r_2 = 0.02$ and $\delta_2/\delta_1 = 0.141$ the theoretical relation has been plotted in Fig. 3, and indicates a maximum inhibition at about 2% styrene. At this point the rate should be approximately 1/100 that in pure vinyl acetate for the same rate of chain initiation. A lower value of r_2 would lead to even greater inhibition by smaller quantities of styrene and unpublished work from this Laboratory suggests that this is actually the case.

The Thermal Initiation of Copolymerization.—The initiation of styrene polymerization by a bimolecular reaction between two styrene molecules appears well established,[18,19] and there is evidence for a similar but slower initiation in the polymerization of methyl methacrylate.[20] In the case of a mixture of the two, however, the possibility of "cross-initiation" between a molecule of styrene and one of methacrylate must also be considered, and the total initiation reaction may be the sum of three terms[21]

$$I_{\text{Thermal}} = k_{I_1}[M_1]^2 + 2k_{I_{12}}[M_1][M_2] + k_{I_2}[M_2]^2 \quad (10)$$

Of the three, k_{I_1} and k_{I_2} are known from measurements on the single monomers. The cross initiation term may be determined by the following procedure. Since, for any one monomer mixture the polymerization rate is proportional to $I^{1/2}$, the thermal rate in pure styrene is related to the rate in the presence of a given amount of 2-azo-bis-isobutyronitrile (assuming that the initiated rate is large compared to the thermal)

$$\frac{(\mathrm{d}[M_1]/\mathrm{d}t)_{\text{init.}}}{(\mathrm{d}[M_1]/\mathrm{d}t)_{\text{th.}}} = \left(\frac{I_{\text{init.}}}{I_{\text{th.}}}\right)^{1/2} \quad (11)$$

Thus, by measuring the ratio of rates, the ratio of I's may be obtained. Now, if the ratio of thermal and initiated rates (using the same amount of initiator) are measured for a monomer mixture, $I_{\text{init.}}$ will, by the assumptions of the preceding section, be the same, so the ratio (where subscript zero refers to pure styrene) may be determined.

$$\frac{I_{\text{th}}}{I_{0\text{th}}} = \frac{[M_1]^2}{[M_1]_0^2} + \frac{2k_{I_{12}}}{k_{I_1}}\frac{[M_1][M_2]}{[M_1]_0^2} + \frac{k_{I_2}}{k_{I_1}}\frac{[M_2]^2}{[M_1]_0^2} \quad (12)$$

From measurements on two mixtures, the two ratios may in principle be calculated. However, since k_{I_2}/k_{I_1} is very small,[20] the last term may be neglected and the relative magnitude of the cross-initiation term calculated from a single mixture. Rates from experiments on three mixtures, heated 43 hrs. at 60° (approx. 5% reaction) are listed in Table II, together with the calculated ratios. Although the spread is comparable to that found in the measurement of ϕ, the existence of a marked cross-initiation reaction appears clearly evident. Taking k_{I_1} as 2.15×10^{-12} (from the rate in pure styrene and $\delta_1 = 47.3$), the numerical value of $k_{I_{12}}$ is 6×10^{-12}.

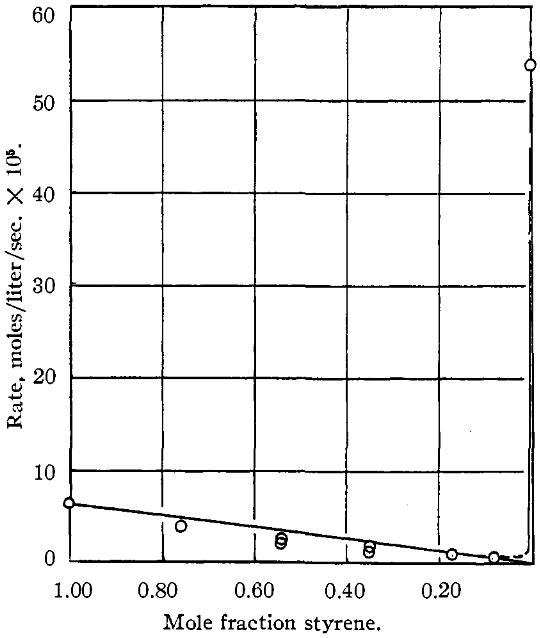

Fig. 3.—Observed and calculated rates of copolymerization of styrene–vinyl acetate at 60° (solid line, Equation (9), dashed line, Equation (8)).

TABLE II

RATES OF THERMAL POLYMERIZATION OF STYRENE–METHYL METHACRYLATE AT 60°

Mole fraction styrene	Rate × 10^6, moles/liter/sec.	$k_{I_{12}}/k_{I_1}$
1.000	2.15[a]	..
0.650	1.91	1.21
.490	3.24	4.78
.336	2.81	2.45
.000	0.24[20]	Av. 2.8

[a] Average value from Gregg and Mayo, THIS JOURNAL, **70**, 2373 (1948). This result is in good agreement with previous values.

Discussion.—Although the experiments described in the preceding sections are of a rather preliminary nature, they indicate that in the cases studied, over-all rates of copolymerization follow the equations of Melville, Noble and Watson with reasonable precision,[22] and it is hoped that they will encourage other workers to investigate additional systems. In this regard, it may be pointed out again that systems in which r_1 is

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[18] Walling, Briggs and Mayo, THIS JOURNAL, **68**, 1145 (1946). This paper summarizes previous references.

[19] Goldfinger and Lauterbach, *J. Polymer Sci.*, **3**, 145 (1948).

[20] Walling and Briggs, THIS JOURNAL, **68**, 1141 (1946).

[21] The unlikelihood of unimolecular initiation (on energetic grounds) was first pointed out by Flory, *ibid.*, **59**, 241 (1937). Accordingly, here, only bimolecular reactions are considered.

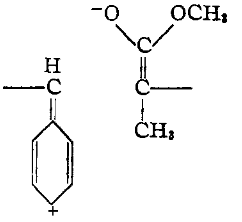
[22] It should perhaps be pointed out that, in a number of the expressions of Melville, Noble and Watson, concentrations are expressed in mole fractions. Except for monomers of equal molar volumes, this requires a dependence of rate upon monomer activity rather than concentration as assumed here.

appreciable and r_2 approaches zero are particularly simple, so that from Equation (9) measurement of the slope of a composition *vs.* rate plot should permit an independent determination of r_1. Of particular interest, too, are systems where other than bimolecular chain termination is possible. Melville, Noble and Watson have developed the equations for termination by the reaction of the growing polymer with monomer and these might be expected to apply to some copolymerizations of monomers such as allyl acetate (with only termination by reaction with allyl acetate being considered). On the other hand, Bartlett and Nozaki[6] have suggested that chain termination in the allyl acetate–maleic anhydride system may be of a mixed or bimolecular type.

Although the compositions of copolymers formed in emulsion are predicted by the same equations as those for homogeneous reaction, except insofar as monomer concentrations are changed by solution in the aqueous phase,[23] it should be noted that over-all rates of reaction should no longer be expected to obey the same sort of equations. If the picture of emulsion polymerization developed by Smith and Ewart[24] and shown to apply to styrene polymerization[25] is of general validity, the expression for polymerization rate should be proportional to the concentration of emulsion particles and the quantity V or rate/unit radical concentration in the treatment of copolymerization developed by Wall,[2b] *i. e.*, in terms of the units used in this paper

$$V = \frac{k_{11}k_{12}(r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2)}{k_{22}r_1[M_1] + k_{11}r_2[M_2]} \qquad (13)$$

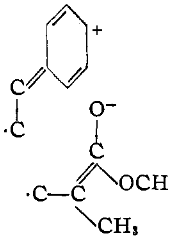
Aside from their connection with copolymerization, the determination of rate-constants for "cross" termination and initiation has importance in the broader field of free radical chemistry. Probably the most important observation which has come from the study of copolymer compositions has been the recognition of the "alternating effect": The fact that the order of reactivity of olefins is greatly affected by the nature of the attacking radical, apparently through the participation of polarized forms in the transition state in which, perhaps, important contributions are made by structures where actual electron transfer has taken place between reactants.[3a,5a] The possibility of similar increased reactivity in radical coupling reactions has been suggested by Bartlett and Nozaki[26] on the basis of the low dissociation of unsymmetric hexaphenylethanes, and seems plainly apparent in the large values of ϕ in the styrene–methyl methacrylate and styrene–methyl acrylate systems. If the picture developed to account for the alternating effect has validity, this increased reactivity should arise from contributions of forms such as



(I)

to the transition state. Since ϕ more or less parallels $1/r_1r_2$ as a measure of heightened reactivity, its larger value (*e. g.*, 13 *vs.* 4 for styrene–methacrylate) indicates that, as might be expected, a radical is more easily polarized and more easily accepts or gives up an electron than does a stable monomer molecule. Data on additional systems showing a tendency to alternate in copolymerization would be of great interest, but it should be noted that, as r_1 and r_2 become small, their precise measurement (and accordingly any sort of accurate solution of Equation (8)) becomes increasingly difficult. Also, with increasing values of the cross-termination constant, the danger of termination becoming diffusion controlled increases.

Consideration of the bimolecular rate constants for thermal initiation of styrene (2.09×10^{-12}), methyl methacrylate (1.9×10^{-15}) and for crossed-initiation of the two (6×10^{-12}) presents the possibility that here, too, a "polar effect" is to be found, involving transition-state forms such as



II

and suggests that the greater initiation constant for styrene compared with methacrylate arises from its "amphoteric" character. Since both benzyl carbanions and carbonium ions present possibilities for resonance, electron transfer between two styrene molecules may take place, and such polar forms may be important in the transition state. Actually, styrene–methyl methacrylate show only a moderate tendency to alternate in copolymerization, and much larger values of the specific rate of cross-initiation might be expected for more strongly alternating pairs such as styrene–maleic anhydride. In practice, the difficulty of preventing copolymerization of such mixtures is well known, although the increased ease of reaction involves, too, the high rate of the chain-growth reaction. Since in copolymerization butadiene rather closely resembles styrene,[3a] rapid thermal initiation might be expected in mixtures of butadiene with carbonyl or nitrile-conjugated monomers. Actually, in the absence of catalyst a Diels Alder reaction occurs, and the question

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[23] (a) Fordyce and Chapin, THIS JOURNAL, **69**, 581 (1947). (b) Fordyce and Ham, *ibid.*, **69**, 695 (1947).

[24] Smith and Ewart, *J. Chem. Phys.*, **16**, 592 (1948).

[25] Smith, THIS JOURNAL, **70**, 3695 (1948).

[26] Bartlett and Nozaki, *ibid.*, **69**, 2299 (1947).

might be raised whether here, too, a diradical is formed which readily forms a six-membered ring rather than adding further olefin units. The insensitivity of the Diels Alder reaction to medium and to polar catalysts is in keeping with such a biradical intermediate, while the ineffectiveness of free radical sources as catalysts presents no difficulty since they produce single radicals. On the other hand, the transition state of the Diels–Alder reaction has usually been pictured as involving the simultaneous formation of two new bonds. However, the close parallel between the resonance forms advanced by Woodward[27] for the Diels–Alder reaction and structures such as II suggest that, in either case there is a very close mechanistic parallel between the two.

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Summary

Kinetic expressions have been developed for the over-all rate of copolymerization of two monomers which are in agreement with those of Melville, Noble and Watson,[7] and, which, when the rate of chain initiation is known, contain only one unknown parameter.

Experimental determination of rates of polymerization, using 2-azo-bis-isobutyronitrile as a constant radical source, show reasonable agreement with theory for the systems styrene–methyl methacrylate, styrene–methyl acrylate, and styrene–vinyl acetate.

In both the first two pairs a relatively rapid cross-termination reaction is detected, and is suggested as arising from a "polar effect" in radical coupling reactions parallel to that producing alternation in copolymerization.

Rate measurements of the rates of *uncatalyzed* copolymerization of styrene–methyl methacrylate indicate a bimolecular initiation reaction involving one molecule of each monomer, and more rapid than the bimolecular initiation in either monomer alone. The analogy to the Diels–Alder reaction is pointed out.

PASSAIC, NEW JERSEY RECEIVED DECEMBER 23, 1948

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[27] Woodward, THIS JOURNAL, **64**, 3058 (1942).

[CONTRIBUTION FROM THE WESTERN REGIONAL RESEARCH LABORATORY,[1a] ALBANY, CALIF.]

Optical, Crystallographic, and X-Ray Diffraction Data for Limonin and Some of its Solvates

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During attempts to prepare pure limonin ($C_{26}H_{30}O_8$) by extraction from citrus fruits,[1b] crystalline products were obtained by the addition of methanol to the methylene chloride solution of the purified limonin. A plate type and two prismatic types of crystals were usually present in the fresh product, but the two prismatic types would change to the plate type on standing a day or two in contact with the saturated solution.

Microscopic observation of behavior plus X-ray tests as reported below have shown that the three kinds of crystals are unsolvated limonin and two solvates of limonin. Analyses reported by Emerson[1] show that the two solvates are limonin monomethylene chloride solvate and limonin hemimethylene chloride solvate. The properties of limonin acetic acid solvate are also reported.

Microscopical Examination and Optical Properties.—All data reported below were obtained at 25° except where otherwise noted. Refractive indices were obtained by immersion methods with sodium light. In some cases it was necessary to mount crystals on a stage goniometer in order to obtain the principal refractive indices and to determine the optic orientation. Table I lists the optical properties of all the compounds except limonin hemimethylene chloride solvate, which is too unstable to determine accurately.

Limonin.—Crystals of this compound are shown in Figs. 1 and 2. When limonin is recrystallized from hot ethanol, methanol, butanol, or acetone, crystals of the stable plate type are obtained, but the habit may vary considerably with rate of growth, nature of the solvent, and presence of impurities. Rapid growth favors the very thin rhomb-shaped plates and hexagonal forms which tend to grow in laminated aggregates (Fig. 1). Slow growth favors the thick plates (Fig. 2) with beveled edges replacing the acute ends of the other type. These two types of crystals were at first thought to be different in composition, but a determination of their optical properties proved that they are identical.

When a cautery needle is held close above the cover glass over a few crystals of limonin, the crystals melt without transformation. The viscous melt becomes vitreous if cooled rapidly, but birefringent bladed crystals will grow if the melt is cooled slowly. Such crystals were not investigated further.

The optical properties reported for limonin by

[1a] Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

[1b] Emerson, THIS JOURNAL, **70**, 545 (1948).