RATE CONSTANTS IN RADICAL POLYMERISATION REACTIONS

By G. M. BURNETT, PH.D.

(CHEMISTRY DEPARTMENT, UNIVERSITY OF BIRMINGHAM)

THE application of physicochemical methods to the elucidation of the mechanism of free radical reactions has, in the past few years, progressed to a point at which it is possible to place the whole problem of radical reactivity on a more fundamental basis. This is most necessary and desirable in order to obtain a better understanding of those reactions in which it is known that free radicals participate. The goal of this type of investigation must be, in the long run, to establish a relationship between the nature of the molecular architecture of the radical and its reactivity, and so far only the fringe of this major problem has been touched. Two general types of radical reaction have now reached the stage of being capable of interpretation in terms of the fundamental rate constants of the reactions. For oxidation processes involving hydrocarbons it has been established that the general scheme representing the course of reaction is

$$\begin{array}{lll}
\text{Initiation:} & \left.\begin{array}{rl} & \text{Production of radicals by benzoyl peroxide} \\ \text{or} & RO_2H + h\nu \\ \text{or} & 2RO_2H \end{array}\right\} & \longrightarrow \text{radicals of the type } R\text{—} \text{ or } RO_2\text{—} \\
\text{Propagation:} & R\text{—} + O_2 & \longrightarrow RO_2\text{—} \\
 & RO_2\text{—} + RH & \longrightarrow RO_2H + R\text{—} \\
\text{Termination:} & \left.\begin{array}{l} RO_2 + RO_2\text{—} \\ R\text{—} + RO_2\text{—} \\ R\text{—} + R\text{—} \end{array}\right\} & \longrightarrow \text{non-radical products}
\end{array}$$

In the above scheme, RH and RO_2H represent the hydrocarbon and its hydroperoxide, and R— and RO_2— are the radicals. The present situation in this type of reaction, *i.e.*, the oxidation of olefin hydrocarbons, has recently been reviewed,[1] so in this discussion the results of these investigations will not be considered in detail.

Polymerisation reactions involving olefinic compounds afford a very powerful tool in the study of radical processes. Here the radical nature of the reaction has been established beyond all doubt. The mechanism involves the formation of free radicals which add on to the double bond of the olefin so that the radical is perpetuated, this process being repeated until the free radical is finally destroyed, usually by reaction with another of its own kind. Recently it has been found possible to evaluate the reaction velocity constants for these polymerisation processes.[2, 3, 4]

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[1] J. L. Bolland, *Quart. Reviews*, 1949, **3**, 1.

[2] G. M. Burnett and H. W. Melville, *Nature*, 1945, **156**, 661; *Proc. Roy. Soc.*, 1947, *A*, **189**, 456.

[3] P. D. Bartlett and C. G. Swain, *J. Amer. Chem. Soc.*, 1945, **67**, 2273; 1946, **68**, 2381.

[4] C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc.*, 1948, *A*, **192**, 309.

I. The Mechanism of Polymerisation Reactions *

The separate reaction steps which take place in a polymerisation process may be formulated as follows, for a general monomer $CH_2{:}CXY$, in which X and Y are substituents, one of which is generally hydrogen:

Initiation: Production of free radicals by

$$\left.\begin{array}{ll} & 2CH_2{:}CXY \\ \text{or} & CH_2{:}CXY + h\nu \\ \text{or} & R\text{—} + CH_2{:}CXY\end{array}\right\} \longrightarrow \begin{array}{l}\text{radicals with free}\\ \quad\text{end} \sim\!\sim CH_2{\cdot}CXY\text{—}\end{array} \qquad k_i \qquad \begin{array}{r}(1)\\(2)\\(3)\end{array}$$

Propagation:

$$\sim\!\sim CH_2{\cdot}CXY\text{—} + CH_2{:}CXY \longrightarrow \sim\!\sim CH_2{\cdot}CXY{\cdot}CH_2{\cdot}CXY\text{—} \qquad k_p \qquad (4)$$

Transfer to monomer:

$$\sim\!\sim CH_2{\cdot}CXY\text{—} + CH_2{:}CXY \longrightarrow CH_2{\cdot}CHXY + \text{—}CH{:}CXY \qquad k_f \qquad (5)$$

Transfer to polymer:

$$\sim\!\sim CH_2{\cdot}CXY\text{—} + P \longrightarrow P\text{—} + \sim\!\sim CH_2{\cdot}CHXY \qquad k_x \qquad (6)$$

Termination:

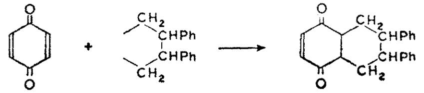
$$2 \sim\!\sim CH_2{\cdot}CXY \longrightarrow \text{inactive products} \qquad k_t \qquad (7)$$

In general, reaction-velocity constants are derived only for very low monomer conversions (usually of the order of 1%), so the reaction involving transfer to polymer may be neglected for the present. Thus four constants have to be determined in order to characterise uniquely this type of free-radical reaction.

The various steps of the reaction have now to be discussed in greater detail. P. J. Flory [6] first postulated the bimolecular nature of all steps of the overall process; thus the initiation reaction in purely thermal polymerisation must be by the interaction of two monomer radicals. This may give rise to either a single molecule possessing *two* unpaired electrons or two molecules each of which have a *single* free electron. Styrene being taken as an example, this may be formulated as:

$$\begin{array}{rl} & 2Ph{\cdot}CH{:}CH_2 \longrightarrow \text{—}CH_2{\cdot}CHPh{\cdot}CHPh{\cdot}CH_2\text{—} \\ \text{or} & 2Ph{\cdot}CH{:}CH_2 \longrightarrow Ph{\cdot}CH_2{\cdot}CH_2\text{—} + Ph{\cdot}CH{:}CH\text{—}\end{array}$$

It is now considered most likely that the initiation step involves the formation of a diradical rather than of two monoradicals. The evidence which most favours this postulation is derived from the inhibition of the polymerisation of styrene by *p*-benzoquinone. From this reaction an adduct, whose molecular weight agrees with the addition of two molecules of styrene to one of quinone, has been isolated.[7, 8] It is thought that such an addition falls into the Diels–Alder type of reaction, *i.e.*,



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[5] *Trans. Faraday Soc.*, 1944, **40**, 1.

[6] *J. Amer. Chem. Soc.*, 1937, **59**, 241.

[7] W. Kern and K. Fueurstein, *J. pr. Chem.*, 1941, **158**, 186.

[8] H. W. Melville and W. F. Watson, *Trans. Faraday Soc.*, 1948, **44**, 886.

* The terminology adopted in this review is based on that of G. Gee and H. W. Melville [5] and used in all subsequent work by Melville's school. More recently, there has been a tendency to employ numerical subscripts. The corresponding nomenclature of other workers is k_1 for k_i; [4] k_2 for k_p; [3, 4] k_3 for either k_f [4] or k_t; [3] k_4 for k_t [4]; k_5 for k_f.[3]

In photochemical initiation, the absorption of a quantum of light energies raises the energy level of the π electrons of the double bond to such an extent as to create a free diradical. Although this will be true of almost all monomers studied, exceptions can arise. T. T. Jones and H. W. Melville [9] showed that, in the case of methyl vinyl ketone, a second initiation process played a part in the reaction. This, in essence, was the normal photolysis of a ketone:

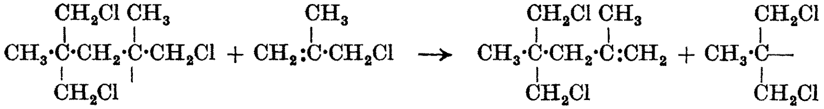
$$\mathrm{CH_3{\cdot}CO{\cdot}CH{:}CH_2 \longrightarrow CH_3{—} + CH_2{:}CH{—} + CO}$$

The third method of initiating polymerisation is by the use of a catalyst such as peroxides and certain azo-compounds or photosensitisers. In each case the compound first breaks down to give free radicals which are capable of adding on to the monomer molecule in order to give free-radical chain carriers.

The propagation step is straightforward and requires no further explanation. In the transfer reaction shown in the above scheme, the radical is assumed to abstract a hydrogen atom from the monomer which then acquires free-radical characteristics. There is, however, a certain duality in this reaction since it is possible that the hydrogen atom is donated by the radical to the monomer with a similar result, *i.e.*,

$$\mathrm{\sim\!\sim CH_2{\cdot}CXY{—} + CH_2{:}CXY \longrightarrow \sim\!\sim CH{:}CXY + CH_3{\cdot}CXY{—}}$$

It is thought that this may be the case in the polymerisation of styrene,[10] and has been definitely shown to be true in the dimerisation of methallyl chloride in which a chlorine atom is donated by the monomer to the dimeric radical: [11]



$$\mathrm{CH_3{\cdot}\underset{\underset{CH_2Cl}{|}}{\overset{\overset{CH_2Cl}{|}}{C}}{\cdot}CH_2{\cdot}\underset{|}{\overset{\overset{CH_3}{|}}{C}}{\cdot}CH_2Cl + CH_2{:}\overset{\overset{CH_3}{|}}{C}{\cdot}CH_2Cl \longrightarrow CH_3{\cdot}\underset{\underset{CH_2Cl}{|}}{\overset{\overset{CH_2Cl}{|}}{C}}{\cdot}CH_2{\cdot}\overset{\overset{CH_3}{|}}{C}{:}CH_2 + CH_3{\cdot}\underset{\underset{CH_2Cl}{|}}{\overset{\overset{CH_2Cl}{|}}{C}}{—}}$$

Although it is agreed that the termination does involve the simultaneous destruction of two active centres, there is considerable controversy over the exact chemical nature of this reaction. The two radicals may lose their activity either by direct combination, *viz.*,

$$\mathrm{\sim\!\sim CH_2{\cdot}CXY{—} + {—}YXC{\cdot}CH_2\sim\!\sim \longrightarrow \sim\!\sim CH_2{\cdot}CXY{\cdot}CXY{\cdot}CH_2\sim\!\sim}$$

or by disproportionation:

$$\mathrm{\sim\!\sim CH_2{\cdot}CXY{—} + {—}YXC{\cdot}CH_2\sim\!\sim \longrightarrow \sim\!\sim CH{:}CXY + \sim\!\sim CH_2{\cdot}CHXY}$$

Although these two processes cannot be distinguished kinetically, it is obvious that the precise nature of this step will have a profound effect on the molecular weight of the product ultimately formed. The evidence on either side is somewhat inconclusive, although several significant points emerge from the data available. For combination it has been established that in the polymerisation of methyl methacrylate catalysed by hydroxyl radicals (derived from hydrogen peroxide in a redox system) the resulting

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[9] *Proc. Roy. Soc.*, 1946, *A*, **187**, 19.

[10] C. H. Bamford, Internation Colloquium on Macromolecules, Amsterdam, 1949.

[11] F. R. Mayo, K. E. Wilzbach, and R. Van Meter, *J. Amer. Chem. Soc.*, 1948, **70**, 4069.

polymer contains *two* hydroxyl groups per molecule.[12] From this result it has been assumed that the growing radicals are terminated by a combination reaction, but the introduction of a second hydroxyl group might arise from a transfer reaction with either hydrogen peroxide or water (used as a solvent) or by the termination of a growing chain by a hydroxyl radical. Many radicals are known to combine almost exclusively, *e.g.*, $MeO{\cdot}C_6H_4{\cdot}\underset{\bullet}{C}H{\cdot}CH_2{\cdot}CH_3$ [13] and *p*-xylyl,[14] although the latter disproportionates in the gas phase. C. C. Price [15] has pointed out that radicals of the type $(CH_3)_2\dot{C}{\cdot}CO_2R$ combine exclusively, and argues, by analogy, that polymethyl methacrylate radicals having a very similar structure ought to do likewise. In this type of work, however, argument by analogy is rather dangerous, since many large radicals have been shown to disproportionate to a very great extent, *e.g.*, *n*-octyl radicals.[16] In polymerisation reactions carried out under conditions in which the initial step is the formation of diradicals, *i.e.*, thermal and photochemical initiation, it can be shown that the molecular weight of the final polymer will be dependent of the rate of reaction if combination occurs, and will be inversely proportional to the rate when dismutation is the terminating process.[17] This can readily be shown to be true in theory, but thus far no such independence of molecular weight of rate of reaction has been established. Using the viscosity technique, Bamford and Dewar [4] have demonstrated that if there is disproportionation the rate of change of viscosity will be dependent on $I^{(1-\alpha)/2}$, whereas for combination the rate will be proportional to $I^{1/2}$, when the intensity of illumination, I, is high. They have not so far found the latter condition to be true. Further, J. Weiss [18] has shown that for radicals which possess an appreciable dipole moment, there is a greater tendency for the radicals to disproportionate. Since most polymer radicals do have a dipole moment, the more conclusive evidence appears to be in favour of disproportionation. As was pointed out earlier, however, there is no certainty that diradicals are formed in either thermal or photochemical initiation, so the evidence is by no means above criticism, despite the fact that the bulk of experimental data does point to diradical initiation. A possible way of removing this impasse might be by the use of photosensitisers which give free diradicals as a result of photolysis. Such a photosensitiser, *cyclo*hexanone, has already been shown to be effective in promoting the polymerisation of vinyl chloride.[19] A photosensitiser of this type would effectively remove all ambiguity with regard to the exact nature of the initiation process, and so the viscosity method or a direct measurement of the molecular weight as a function of rate could be readily applied with the object of obtaining a unique result.

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[12] J. H. Baxendale, S. Bywater, and M. G. Evans, *J. Polymer Sci.*, 1946, **1**, 237.

[13] M. S. Kharasch, H. C. McBay, and W. H. Urry, *J. Org. Chem.*, 1945, **10**, 401.

[14] M. Swarc, *Faraday Soc. Discussions*, 1947, **2**, 138.

[15] *Ibid.*, p. 402.

[16] C. H. Bamford and R. G. W. Norrish, *J.*, 1938, 1531.

[17] See, *e.g.*, C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc.*, 1949, *A*, **197**, 356.

[18] *Faraday Soc. Discussions*, 1947, **2**, 104.

[19] L. Valentine, Ph.D. Thesis, Aberdeen, 1949.

II. Rate Constants for the Polymerisation of Single Monomers

The methods which have been employed in these investigations have been the technique of intermittent illumination and the viscosity method. From the kinetic scheme detailed in the previous section it can be shown that, when the quasi-stationary state is reached, *i.e.*, when the rate of chain initiation equals the rate of termination, the rate of polymerisation can be expressed as

$$\text{rate} = k_p k_t^{-1/2} I^{1/2}[M] \quad . \quad . \quad . \quad . \quad (8)$$

where I is the rate of initiation and $[M]$ the monomer concentration. Also the degree of polymerisation (*i.e.*, the osmotically measurable chain length) of the polymer will be

$$\bar{P} = \frac{\text{rate of conversion of monomer}}{\text{rate of formation of polymer}} = \frac{k_p}{k_f + k_t^{1/2} I^{1/2}/[M]}$$

which may be rewritten as

$$\bar{P}^{-1} = k_f/k_p + k_t^{1/2} I^{1/2}/k_p[M]$$

Substitution of the value of $I^{1/2}$ from (8) leads to

$$\bar{P}^{-1} = k_f/k_p + k_t(\text{rate})/k_p^2[M]^2 \qquad (9)$$

Hence if the reciprocal degree of polymerisation is plotted against the rate of conversion a linear relationship will be found, the gradient of the line being $k_t/k_p^2[M]$, so that the ratio of $k_p/k_t^{1/2}$ may be found. At the same time the intercept of the straight line represented by equation (9) on the $\bar{P}^{-1}$ axis will give k_f/k_p.

It now falls to determine a second ratio between propagation and termination constants which will enable all the reaction velocity coefficients to be determined uniquely. Such a quantity is the lifetime of the growing polymer chain, which is defined by

$$\tau = \frac{\text{number of active centres per unit volume}}{\text{number of centres destroyed per unit volume per unit time}}$$
$$= k_t[P]^{-1} = (k_t I)^{-1/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where $[P]$ is the concentration of active centres which under steady state conditions will be $(I/k_t)^{1/2}$. The lifetime of the active centres is most readily obtained by means of the rotating sector technique. The theory of this experimental method has been fully set out by Burnett and Melville,[2] and similar treatments of the problem have been published with certain extensions to take into account steady dark reactions.[20, 21] This difference in treatment is most necessary in the case of oxidation processes when the thermal dark rate is appreciable, but this condition can also arise in polymerisation reactions, especially for those in which photosensitisers have been used to start chain growth. From equation (10) it is evident that

$$\tau^{-1} = k_t(\text{rate})/k_p[M]$$

so that a plot of the reciprocal lifetime against rate of monomer conversion

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[20] G. Gee and L. Bateman, *Proc. Roy. Soc.*, 1948, *A*, **195**, 376.

[21] M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, *J. Amer. Chem. Soc.*, 1949, **71**, 497.

will give the value of k_p/k_t, and hence a combination of the two series of measurements will yield k_p, k_t, and k_f. The value of k_i, if not determined otherwise, can be found from the thermal rate of polymerisation, which will be

$$\text{rate} = k_i^{1/2}k_p[M]^2/k_t^{1/2}$$

since the rate of initiation is $k_i[M]^2$. As $k_p/k_t^{1/2}$ is known, k_i may be easily calculated.

Several assumptions have been tacitly made in the foregoing description, and since these are of vital importance it is necessary to comment on them more fully. The most important probably is the fact that the analysis above assumes that the distribution of radicals throughout the reaction system is uniform. In using photochemical initiation this implies that the absorption of light must be very weak. It is a good criterion that, for average size reaction vessels the extinction coefficient should not exceed 0·05 and should if possible be lower. Secondly, it has been assumed that the reactivity of the radical is independent of molecular size. It will be shown later that this assumption may constitute an oversimplification of the problem, but as a first approximation, at least, it is valid. In the third place, it has become fairly common practice to " trigger " polymerisation with photosensitisers, but the compounds used must not be chosen indiscriminately. The photosensitiser must, as a molecule, take no part in the reaction other than to act as a source of free radicals which must be capable of very rapid addition to the olefinic double bond and must not, in any other way, enter into the course of the reaction. If these conditions are not fulfilled the tendency will be for the rate of reaction to cease to be proportional to the square root of the light intensity and so the theory of intermittent illumination will no longer be applicable.

It is evident from equation (9) that if the transfer velocity coefficient becomes large the value of the ratio k_f/k_p may become sufficiently high to bring about an apparent independence of molecular weight on the rate of polymerisation. In such instances it becomes necessary to determine the rate of chain initiation directly. This is most conveniently accomplished by the use of inhibitors or retarders.* It has been found that *p*-benzoquinone has the ability to suppress completely certain polymerisation reactions.[2, 8, 22, 23] The time of complete inhibition is normally proportional to the quinone concentration and, on the assumption that one quinone molecule stops one polymer chain, it is possible to compute the rate of initiation. More recently, a second method has been found which may prove to be more reliable. Certain azo-compounds, notably α-azobis*iso*butyronitrile (1 : 1′-dicyanoazopropane), have been found to react with very great efficiency with most monomers. Since these compounds are also good photosensitisers, it follows that the rate of initiation can be found by a comparison of the rates of polymerisation under thermal and photochemical

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[22] S. Foord, *J.*, 1940, 48.

[23] M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, *J. Amer. Chem. Soc.*, 1949, **71**, 2610.

* See Melville and Watson [8] for distinction between these terms.

conditions. This is possible since the first-order constant for the thermal decomposition of the initiating material can be determined with very great precision.[24]

The viscosity method elaborated by Bamford and Dewar has the advantage that it requires only simple apparatus, and from a series of simple measurements it is possible to determine with ease the rate constants for thermal initiation, propagation, termination, and transfer. In essence, the method makes use of the fact that the rate of a photochemical chain reaction does not fall to zero—or to the thermal dark rate—immediately the source of illumination is removed, and also that the maximum rate of reaction is not set up until an appreciable time after the light is switched on. The kinetic scheme used by the authors is as follows:

$$\begin{array}{llcll}
\text{Initiation:} & 2\mathrm{M} & \longrightarrow & \mathrm{D_2} \text{ or } 2\mathrm{X} & k_i \\
\text{Propagation:} & \mathrm{M} + \mathrm{X} & \longrightarrow & \mathrm{X} & k_p \\
\text{Transfer:} & \mathrm{D_2} + \mathrm{M} & \longrightarrow & \mathrm{D_1} + \mathrm{R} & 2k_f \\
 & \mathrm{D_1} + \mathrm{M} & \longrightarrow & \mathrm{P_1} + \mathrm{R} & k_f \\
 & \mathrm{R} + \mathrm{M} & \longrightarrow & \mathrm{P_2} + \mathrm{R} & k_f \\
\text{Termination:} & \mathrm{D_2} + \mathrm{X} & \longrightarrow & \mathrm{D_1} + \mathrm{Q} & 2k_t \\
 & \mathrm{D_1} + \mathrm{X} & \longrightarrow & \mathrm{P_1} + \mathrm{Q} & k_t \\
 & \mathrm{R} + \mathrm{X} & \longrightarrow & \mathrm{P_2} + \mathrm{Q} & k_t \\
 & 2\mathrm{X} & \longrightarrow & 2\mathrm{Q} & k_t
\end{array}$$

in which D_2 is a free diradical, D_1 a free monoradical derived from an original diradical, R a radical formed by the transfer reaction, X any radical end, P_1 and P_2 polymers derived from diradicals and transfer radicals, respectively, and Q any dead centre. Houwink's viscosity equation being used in the form $[\eta] = K(M_0\bar{P})^\alpha$, where K and α are constants, and allowance being made for the difference in viscosity behaviour between polymer derived from diradicals and from transfer radicals, it can be shown that the rate of change of viscosity for thermal polymerisation is

$$\frac{\mathrm{d}\eta}{\mathrm{d}t} = K'M_0[M]^2(k_p{}^2/k_t)^{(1+\alpha)/2}k_i{}^{(1-\alpha)/2}\frac{\beta + \frac{1}{2}(2+\alpha)}{(\beta + 1)^{1+\alpha}}$$

where η, the ideal specific viscosity, is $[\eta]c$, c being the polymer concentration in base moles per litre, and K' is related to K. For photochemical initiation

$$\frac{\mathrm{d}\eta}{\mathrm{d}t} = K'M_0[M]^2(k_p/k_t)^{(1+\alpha)/2}k_i{}^{(1-\alpha)/2}\frac{\beta + \frac{1}{2}(2+\alpha)\xi}{(\beta + \xi)^{1+\alpha}}$$

where $\beta = k_f(k_ik_t)^{-1/2}$ and $\xi = (1 + AI)^{1/2}$, A being a constant and I the relative light intensity. Measurement of $\mathrm{d}\eta/\mathrm{d}t$ over a range of light intensities enables one to calculate β, $(k_p/k_t)^{(1+\alpha)/2}k_i{}^{(1-\alpha)/2}$, and A. A further relationship is provided by the molecular weight of the thermal polymer, which is given by

$$\bar{P}_n = 2k_p(k_ik_t)^{-1/2}/(2\beta + 1)$$

The only further relationship required to enable the computation of the individual rate constants to be carried out is obtained by making use of the fact that the rate of polymerisation does not fall to the dark rate imme-

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[24] F. M. Lewis and M. S. Matheson, *J. Amer. Chem. Soc.*, 1949, **71**, 747.

diately the light is removed. The authors define the after-effect as the difference between the measured specific viscosity and that which would have been obtained had the rate of reaction fallen to the dark rate on switching off the light. The analysis for this is complex and requires for its solution the assumption that α can be expressed as m/n, where m and n are small integers. Measurement of the after-effect allows k_t to be computed and so all the other velocity constants can be determined.

The Values of Rate Constants in Polymerisation Reactions.—Now that the methods of measurement have been detailed, and bearing in mind the assumptions which have been made, we are in a position to consider the results obtained for a number of representative investigations covering only the first stages of the reaction, and carried out in the medium of the pure monomer.

Vinyl Acetate.—The first monomer to be studied with a view to determining the rate constants was vinyl acetate. Results on this particular compound are somewhat divergent, probably owing in part at least to the very great difficulty of its purification. Hydrolysis of the ester leads to formation of acetaldehyde and acetic acid, the former being described as both a retarder [25] and under certain conditions a photosensitiser as a result of photolysis of the aldehyde. A new technique was evolved by P. D. Bartlett and K. Nozaki [26] whereby the monomer was partly polymerised *in vacuo* before the final distillation. This method seems to be very advantageous since all anomalous behaviour is avoided. The results of a number of independent investigations are shown in Table I.

TABLE I

Rate constants for vinyl acetate polymerisation

Temp.	k_i.	k_p.	$k_t \times 10^{-7}$.	k_f.	Method.	Source.
		(l. mole^{-1}sec.$^{-1}$).				
15·9° . .	—	750	39·2	—	Rot. sector	(2) & (27)
25 . .	—	1100	8	—	do.	(3)
25 . .	—	2024	11·76	*ca.* 5[a]	do.[b]	(23)[d]
25 . .	—	1954	11·78	0·23	do.[c]	(28)[d]
0 . . .	0	2800	22	0·14	Viscosity	(29)

(*a*) This measurement was made at 50°.
(*b*) With α-azobis*iso*butyronitrile as photosensitiser.
(*c*) With di-*tert*.-butyl peroxide as photosensitiser.
(*d*) For the purposes of comparison the published results have been doubled, since these authors have assumed combination to be the termination reaction whereas the others assumed disproportionation.*

As was mentioned above, one of the main differences in the study of vinyl acetate polymerisation is that the transfer constant is rather high so

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[25] H. W. Melville and F. R. Tuckett, *J.*, 1947, 1201, 1211.

[26] *J. Amer. Chem. Soc.*, 1946, **68**, 2377.

* Throughout this review all results are compared on the basis of disproportionation, *i.e.*, all published American results have been doubled.

that it is not generally possible to use the molecular-weight method to compute $k_p/k_t^{1/2}$. In view of this, it is necessary to determine the rate of photochemical initiation directly, an operation which must always be fraught with some degree of uncertainty. The inhibitor technique has been most usually employed,[2, 23, 28] the first two sets of workers using *p*-benzoquinone, which appears to be a highly efficient inhibitor of vinyl acetate no doubt on account of the exceptionally high activity of the growing radical and the relative inertness of the monomer. Bartlett and Kwart, on the other hand, have made use of duroquinone in their inhibition experiments. The values calculated by G. Dixon-Lewis [29] were obtained by using a method depending on Bamford and Dewar's viscosity technique, a modification being introduced to allow for the fact that the thermal polymerisation rate is zero. When it is considered that one cannot reasonably expect that the final results will be correct to much less than a factor of 2, on account of the rather involved experimental methods employed as well as the complexity of the reaction itself, the results detailed in Table I will be seen to be, on the whole, in remarkably good agreement. It should be pointed out that the first results published by Burnett and Melville [2] have been corrected to allow for two points over which there has been much controversy. All the reaction constants in the table refer to single-radical ends, whereas in the original paper diradicals alone were considered. This means that the original k_p and k_t values have been divided by 2 and 4 respectively. The k_t value has also been corrected to allow for a slightly non-uniform distribution of radicals in the reaction system.[27] The photosensitisers used by the American investigators [23, 28] were examined to ensure that they took no part in the polymerisation other than that of starting the reaction chains. Furthermore, Matheson and his co-workers have made due allowance for the considerable dark rate experienced at 25° with the azo-type photosensitiser, and Bartlett and Kwart arranged that their measured dark rate was less than 0·6% of the photo-rate, under which conditions the effect of the dark rate is negligible.

It is naturally more fundamental to compare the frequency factors and energies of reaction for the various steps of the chain process rather than to deal with the absolute values of the rate constants at definite temperatures. Since we are concerned with bimolecular reactions it is well known that the velocity coefficients can be expressed in the form $k = A \exp(-E/RT)$, where A is the frequency factor (having a normal value of 10^{11}—10^{12}) and E is the energy of activation for the reaction. The following table shows the results obtained by such analyses :

Energies of activation and frequency factors for vinyl acetate polymerisation

A_p.	A_t.	A_f.	E_p.	E_t.	E_f.	Source.
$8\cdot3 \times 10^{5}$	$3\cdot92 \times 10^{8}$	—	4·4	0	—	(2) & (27)
$4\cdot86 \times 10^{8}$	$8\cdot32 \times 10^{11}$	—	7·32	5·24	—	(23)
$9\cdot8 \times 10^{5}$	$2\cdot2 \times 10^{8}$	$9\cdot9 \times 10^{3}$	3·2	0	6·1	(29)

The agreement between the energies of activation in the first and the third set of results is within the expected experimental error of ± 1 kcal., and the frequency factors also lie well within expected divergence. The very high values of the activation energies and frequency factors given by Matheson *et al.*[23] are surprising and may be due, at least in part, to the method of determination of the rates of initiation, *i.e.*, the use of *p*-benzoquinone in the case of monoradical initiation. The very high value for the termination energy is all the more astonishing since it had been assumed that the termination reaction involved combination—a step which has usually been associated with zero or very low energies. In view of the wide discrepancies in the energy and frequency factors it would appear most desirable to conduct a reinvestigation of this phase of the reaction. On the whole, the greatest attention to all possible sources of error appears to have been paid by Bartlett and Kwart, but so far these workers have not attempted to investigate the effect of temperature on the velocity constants.

Styrene.—The polymerisation of styrene has been studied by numerous workers, using both the accepted methods to determine the rate constants for the reaction steps. Again there is a certain amount of divergence of opinion but, in certain respects, agreement is closer than in the case of vinyl acetate. The values which have been determined are shown below.

Rate constants for styrene polymerisation

Temp.	k_i.	k_p.	k_t.	k_f.	Method.	Source.
		(l. mole^{-1}sec.$^{-1}$).				
0° .	$4{\cdot}51 \times 10^{-18}$	6·91	$1{\cdot}83 \times 10^{6}$	$7{\cdot}47 \times 10^{-5}$	Viscosity	(4)
25 .	$1{\cdot}32 \times 10^{-16}$	18·7	$2{\cdot}79 \times 10^{6}$	$6{\cdot}68 \times 10^{-4}$	do.	(4)
30 .	—	51·9	$1{\cdot}05 \times 10^{7}$	$1{\cdot}66 \times 10^{-3}$	Rot. sect.[a]	(30)
30 .	—	135	$1{\cdot}7 \times 10^{8}$	—	do.[b]	(31)

(*a*) Photosensitised by benzoyl peroxide.
(*b*) Photosensitised by bisazopropane, but full details are not yet available.

Here again there is some discrepancy, but it is not yet possible to comment adequately on these results since the details of Matheson's work are not known. Even so, the differences between the energies of activation, in particular, are too high to allow any great reliance to be placed on the figures of the last table.

The Reviewer has made some measurements of the photochemical overall energy of activation for styrene. The justifiable assumption being made that the energy for the initiation step is zero, this determination gives $(E_p - \frac{1}{2}E_t)$. The measured value of this quantity comes out at 5·50 kcals.

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[27] G. M. Burnett, H. W. Melville, and L. Valentine, *Trans. Faraday Soc.*, 1949, **45**, 960.

[28] P. D. Bartlett and K. Kwart, *J. Amer. Chem. Soc.*, in the press.

[29] *Proc. Roy. Soc.*, 1949, *A*, **198**, 510.

[30] H. W. Melville and L. Valentine, *Trans. Faraday Soc.*, in the press.

[31] M. S. Matheson, unpublished results.

per mole, which is in much closer agreement with Bamford and Dewar's results (5·1 kcals.) than with Matheson's (7·5 kcals.). From the energies of activation for the termination and transfer reactions a rather interesting point arises. If disproportionation is the operative chain-termination mechanism, this implies the abstraction of a hydrogen atom from one radical to saturate the other, *i.e.*, there is a rupture of a C–H bond. In the same way the transfer reaction requires a C–H bond to be broken, and yet the difference in the energies of activation necessary to bring this about is very high indeed, so it must be deduced that there is some very fundamental difference between the nature of the two reactions.

Energies of activation and frequency factors for styrene polymerisation

A_i.	A_p.	A_t.	A_f.	E_i.	E_p.	E_t.	E_f.	Source.
$1{\cdot}23 \times 10^{12}$	$1{\cdot}02 \times 10^{6}$	$3{\cdot}07 \times 10^{8}$	$1{\cdot}50 \times 10^{7}$	37·0	6·5	2·8	14·2	(4)
—	$3{\cdot}80 \times 10^{8}$	$2{\cdot}4 \times 10^{10}$	—	—	9·0	3·0	—	(31)

Methyl Methacrylate.—The polymerisation of methyl methacrylate has been the subject of a vast number of investigations because of the many abnormalities which, even now, have been only partly explained. The study of this reaction has been complicated by the fact that reproducibility of results has been difficult to obtain, especially from worker to worker. Again this appears to be bound up with the question of purity of the monomer. C. H. Bamford and M. J. S. Dewar [32] have gone to considerable lengths to obtain exceptionally pure monomer, their method giving high reproducibility in initial measurements, but agreement with other workers is lacking so far. The results for the reaction velocity coefficients are set out below. If the expected discrepancy factor of 2 is borne in mind, the results of this table are in quite good agreement. This is all the more surprising on account of the very anomalous behaviour of methyl methacrylate under normal polymerisation conditions. The results obtained by the rotating sector are in comparatively good agreement although the discrepancy in the termination constant might be considered to be somewhat

Rate constants for methyl methacrylate polymerisation

Temp.	k_i.	k_p.	k_t.	k_f.	$k_p{}^2/k_t$.	k_f/k_p.	Method.	Source.
23·6°	—	310	$6{\cdot}6 \times 10^{7}$		$1{\cdot}46 \times 10^{-3}$		Rot. sect.[a]	(33)
30	—	286	$2{\cdot}44 \times 10^{7}$	$7{\cdot}50 \times 10^{-3}$	$3{\cdot}35 \times 10^{-3}$	$1{\cdot}17 \times 10^{-5}$	do.[a]	(21)
0	$6{\cdot}82 \times 10^{-15}$	41·6	$2{\cdot}69 \times 10^{6}$	$6{\cdot}13 \times 10^{-4}$	$5{\cdot}11 \times 10^{-4}$	$1{\cdot}28 \times 10^{-5}$	Viscosity	(32)
50	—	—	—	—	$1{\cdot}14 \times 10^{-2}$	$8{\cdot}5 \times 10^{-5}$	—[b]	(34)

(*a*) Direct photo-initiation.
(*b*) Benzoyl peroxide-accelerated reaction.

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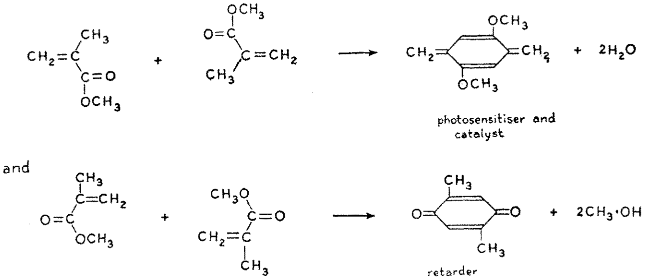
[32] *Proc. Roy. Soc.*, 1949, *A*, **197**, 356.

[33] H. W. Melville and M. H. Mackay, *Trans. Faraday Soc.*, 1949, **45**, 332.

[34] G. V. Schulz and G. Harborth, *Makromol. Chem.*, 1947, **1**, 106.

high. The main difference between the results may in fact be in the purification techniques. Although both Melville and Matheson state that reproducibility was obtained in their experiments, the work of Bamford and Dewar was complicated by the fact that the rates observed were not wholly reproducible. They were forced then to modify their system of calculation to allow for this by always carrying their after-effect experiments to the same rate of reaction. They attribute this non-reproducibility to two factors, (*a*) formation of a photocatalyst, and (*b*) thermal production of an inhibitor. Chemically both these reactions appear possible by side reactions with elimination of either water or méthyl alcohol :



Since the other authors found no evidence of the thermal polymerisation which is higher than that of styrene under comparable conditions, it may be that their monomer contained traces of inhibitor which would lead to higher values of k_t. On account of the complexity of the reaction at temperatures higher than about 10°, Bamford and Dewar did not determine the energies of activation for the steps of the reaction. Melville and Mackay report that the energy of activation of the propagation step is 4·4 kcals. per mole, giving a frequency factor of $5{\cdot}5 \times 10^5$, while the termination reaction does not have any measurable energy of activation but is probably of the order of 1 kcal./mole. This leads to a frequency factor $> 10^8$. Matheson and his collaborators, by measuring the rate constants at four different temperatures, find that

$$k_p = 10{\cdot}26 \times 10^6 \exp(-\ 6310/\boldsymbol{RT})$$
$$k_t = \ 2{\cdot}72 \times 10^9 \exp(-\ 2840/\boldsymbol{RT})$$
$$k_f = \ 5{\cdot}50 \times 10^6 \exp(-\ 12280/\boldsymbol{RT})$$

Extrapolation of Schulz and Harborth's results at two temperatures gives good agreement with Bamford and Dewar's data. The only other investigation of the thermal rate of polymerisation of methyl methacrylate is described in a short paper by C. Walling and E. R. Briggs.[35] They compute the value of the initiation rate constant at three temperatures above 100° : k_i is $0{\cdot}70 \times 10^{-15}$ l. mol.$^{-1}$sec.$^{-1}$. The energy of activation for initiation is found to be 22 kcals., giving a frequency factor considerably less than unity (0·36). From the rates of thermal polymerisation it is evident that the purity of the monomer leaves much to be desired despite the care taken

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[35] *J. Amer. Chem. Soc.*, 1946, **68**, 1141.

to avoid contamination by air. If Bamford and Dewar's hypothesis regarding the formation of inhibitor at high temperatures is accepted, then the explanation of the low rates found by the Americans is obvious. It is therefore probable that these results can be disregarded.

p-*Methoxystyrene.*—Extending the work of Bamford and Dewar, R. W. E. Axford [36] has investigated the polymerisation of *p*-methoxystyrene with the object of determining the effect of the introduction of the *p*-methoxy-group into the styrene molecule. The general characteristics of the reaction were similar to those of styrene, but the monomer polymerises much less rapidly. A comparison of the velocity constants at 0° for these two monomers is shown below. Except in the case of thermal initiation, all the rate constants are considerably less than those for styrene. Axford estimates that the energy of activation for the initiation reaction is 30 kcals. per mole which, as might be expected, is less than that for styrene (38 kcals.). Thus it appears that the introduction of the methyl group has the effect of lowering the " polymerisation capacity " of styrene, a fact which has been predicted from other considerations.[37] This reduction in activity will be due either to a reduction in the reactivity of the radical by more resonance stabilisation or to reduction in monomer activity. The former seems to be more likely as it appears that the radical reactivity plays a major rôle in determining the rate of polymerisation (see below).

Rate constants for styrene and p-*methoxystyrene at* 0°

	Styrene.	*p*-Methoxystyrene.
k_i	$4{\cdot}51 \times 10^{-18}$	$5{\cdot}94 \times 10^{-16}$
k_p	$6{\cdot}91$	$2{\cdot}92$
k_t	$1{\cdot}83 \times 10^{6}$	$1{\cdot}06 \times 10^{6}$
k_f	$7{\cdot}47 \times 10^{-5}$	$5{\cdot}78 \times 10^{-5}$
k_f/k_p . . .	$1{\cdot}08 \times 10^{-5}$	$1{\cdot}98 \times 10^{-5}$

Methyl Acrylate.—Methyl acrylate is a monomer of considerable theoretical interest because of its close resemblance to the methacrylate. Despite this similarity in chemical structure the vapour-phase polymerisation of these two monomers showed several very significant differences, as was demonstrated by H. W. Melville.[38] Thus it is of importance to see whether these anomalies are repeated in the liquid phase and to what the differences can be attributed. Using the sector technique, M. S. Matheson [39] has been able to determine the propagation and termination velocity constants for a number of temperatures from which he has deduced that

$$k_p = 2{\cdot}0 \times 10^{8} \exp(-\,7100/\boldsymbol{RT})$$
$$k_t = 5{\cdot}60 \times 10^{10} \exp(-\,3100/\boldsymbol{RT})$$

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[36] *Proc. Roy. Soc.*, 1949, *A*, **197**, 374.

[37] P. P. Shorygin and N. V. Shorygina, *J. Gen. Chem. Russia*, 1939, **9**, 845.

[38] (*a*) *Proc. Roy. Soc.*, 1937, *A*, **163**, 511 ; (*b*) *ibid.*, 1938, *A*, **167**, 99.

[39] Unpublished results.

It is advantageous to compare these figures with those obtained by the same author for methyl methacrylate for which

$$k_p = 10{\cdot}2 \times 10^8 \exp(-\ 6300/\boldsymbol{R}T)$$
$$k_t = 2{\cdot}60 \times 10^9 \exp(-\ 2800/\boldsymbol{R}T)$$

Here there is a very close similarity in the energies of activation for the two monomers, so attention need be paid only to the frequency factors. From these results it is evident that the propagation reaction in the case of methacrylate is about 5 times more efficient than that of the acrylate but the efficiency of interaction of the radicals is reversed, so that the termination rate of acrylate is very much greater than that of methacrylate. Since the resonance energy of both monomers and their derived radicals cannot be expected to differ by very much, this difference in radical interaction efficiency must be attributable to the steric hindrance induced by the presence of the methyl group directly attached to the carbon atom of the double bond of methyl methacrylate. A similar explanation was invoked by Melville [38a] to account for the differences in polymerisation characteristics in the gas phase.

Butyl Acrylate.—A further ester of acrylic acid, namely, butyl acrylate, has been investigated by A. F. Bickel and H. W. Melville.[40] It would not be expected that the introduction of the butyl group in place of methyl would produce any profound effect on the polymerisation characteristics of this monomer, since the butyl group is well separated from the radical end. Nevertheless, the behaviour of this monomer is rather peculiar in many respects, the most significant being the fact that large deviations from the theoretical intermittent illumination curve have been obtained. This naturally makes the evaluation of the lifetime somewhat uncertain, but by working on the part of the experimental curve giving closest agreement with theory the following values of the propagation and termination velocity constants were found :

$$k_p = 4{\cdot}4 \times 10^4 \exp(-\ 2100/\boldsymbol{R}T)$$
$$k_t = 1{\cdot}8 \times 10^4 \text{ (with no energy of activation)}$$

In this case the frequency factors for both reactions are very low indeed, implying that the reactions are both very inefficient. This is true more particularly of the termination step, for it has been found that the most probable frequency factor is of the order of 10^8. There appears to be no apparent reason for the very considerable differences between the constants found for butyl and those of methyl acrylate since it is evident that the presence of the butyl group will make little difference to the resonance energy of the molecule or radical.

Comparison of Radical Reactivities.—The question now arises as to whether any deductions can be made as to the radical activities merely on the basis of the results which have been set out in the preceding discussion. Before undertaking such a comparison of reactivities it must be remembered that the rate constant for propagation and transfer reactions must depend

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[40] *Trans. Faraday Soc.*, in the press.

on the reactivity of the monomer as well as that of the radical. As a very rough guide therefore it can be stated that as the radical reactivity increases that of the monomer molecule will decrease. As an example the styryl radical can exist in a number of resonance forms which tend to stabilise the radical, while the effect of resonance on the molecule will tend to make the olefinic link more reactive. The following table shows the values of some ratios which make such a comparison possible.

Rate constants at 25°

Monomer.	k_p.	$k_t^{1/2} \times 10^{-3}$.	$k_f \times 10^{3}$.	$k_t^{1/2}/k_p$.	$k_f/k_p \times 10^{5}$.
Butyl acrylate[41] . .	13·1	0·134	—	10·2	—
Styrene[30]	39·5	2·81	1·1	71·3	2·79
Methyl methacrylate[21] .	275	5·0	—	57·2	—
Vinyl acetate[27] . .	750	22·3	970[a]	30	107

(*a*) Calculated from the data of Dixon-Lewis.[29]

From this table, which admittedly contains only a few of the monomers studied, it will be seen that, despite the great variation in the values of the individual constants, the magnitude of $k_t^{1/2}/k_p$ does not vary to the same extent. Indeed, it appears that the reactivity of the radicals towards monomer and another radical of the same kind cannot be significantly different between different monomers. Also, since these monomers are arranged in the order of their reactivities in copolymerisation, the data give credence to the rough guide stated above as will be seen from the values of $k_t^{1/2}$ (this is chosen as a better quantitative measure of the reactivity of the radical than k_t, which must refer to the interaction of two radicals). It is interesting that the order is preserved in the propagation constants, which would suggest that it is the reactivity of the radical and not that of the monomer which is of major importance. The most surprising feature is the trend shown by the transfer constant. This one would assume would depend more on the strength of the C–H bond than on radical reactivity. As mentioned previously, the reaction may be due to a donation of a hydrogen atom from the radical to monomer. If this were true one might reasonably expect the radical to be again of the greater importance.

Variation of Rate Constants with Molecular Size.—Early workers in the field of polymerisation kinetics assumed that there was a variation in the value of the rate constants for each step of the reaction, this usually being expressed as a function of molecular size. More recently, the accepted view has been that the reactivity of the radical is independent of chain length. Some experiments have been carried out with the intention of verifying this feature. In their original investigation of the polymerisation of vinyl acetate, Burnett and Melville[2] showed that doubling the chain length produced a negligible change in the rate constants, from which it was deduced that for chains containing more than 100 monomer units the

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[41] Results of M. S. Matheson communicated by Prof. H. Mark at International Colloquium on Macromolecules, Amsterdam, 1949.

velocity constants were independent of molecular size. On revising the figures of that paper with the aid of Burnett, Melville, and Valentine's data,[27] it is found that the ratio k_p/k_t is $1{\cdot}26 \times 10^{-6}$ and $1{\cdot}34 \times 10^{-6}$ for chain lengths of 176 and 352 respectively. Thus it will be seen that there is no proportionality between these values and the chain length and, furthermore, the variation of 7% is well within experimental error. Some similar experiments in the case of methyl methacrylate and styrene show greater divergence, as shown in Table II.[44] The variation in methyl methacrylate is again probably not significant, but with styrene the difference appears to be sufficiently great to be outside probable experimental error so that in this case, at least, there seems to be a definite variation in the rate constants under the two conditions used. It will be noted that in these cases there is a decrease in the ratio for the higher chain lengths, which would indicate there is either an increase in the efficiency of the termination reaction or a decrease in that of propagation.

TABLE II

Variation of rate constants with molecular size

Monomer.	Degree of polymerisation.	$k_p/k_t \times 10^6$.	Ratio.
Methyl methacrylate . .	4500 17000	10·94 10·04	1·09
Styrene	390 2000	1·24 0·88	1·41

Variation in Rate Constants with Environment.—The course of polymerisation of methyl methacrylate has been noticed by a number of workers to be subject to a self-acceleration.[42] The effect was shown to occur under isothermal conditions and to depend on the rate of initiation and the temperature. Since the higher the initiation rate and the higher the temperature the greater the amount of polymer formed before self-acceleration commenced, it was evident that this effect could be correlated with the viscosity of the solution of polymer in monomer. This was further verified by increasing the initial viscosity of the monomer by the addition of cellulose tripropionate. Under these conditions it was found that the self-acceleration was apparent from the start of the reaction, indicating that the necessary conditions for self-acceleration could be simulated in this way. It has been shown that this effect can be duplicated in solution in which the monomer solvent is either a poor solvent or a precipitant for the polymer. The same autocatalytic type of curve was obtained.[43] At the same time as the increase in molecular weight takes place it was found that there was an increase in the molecular weight of the resulting polymer. This can be

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[42] See, *e.g.*, E. Trommsdorff, Colloquium of High Polymers, Freiburg, 1944 (Reprinted in B.I.O.S. Report No. 363, Item No. 22).

[43] R. R. Smith and R. G. W. Norrish, *Nature*, 1942, **150**, 336.

true only if either the rate of propagation increases or alternatively if the rate of termination decreases. It is difficult to see how the first alternative can be true since one would expect, if anything, a decrease in propagation due to a lowering of the mobility of the monomer. Thus it is almost necessary to accept the second alternative. The reduction in rate of termination can be imagined as due to the fixation of the growing radicals in the viscous medium and so prevents those radicals from making contact. In the case of solution it seems to be most plausible to suppose that, owing to the fact that the polymer molecule will tend to coil in poor solvents, the active ends of the radicals will become buried and hence be inaccessible to the other radicals but, at the same time, the diffusion of the monomer to the active centre must not be seriously impeded.

It is possible to interpret the phenomenon on a somewhat different basis. C. Walling [44] has suggested that in a poor solvent the monomer will be preferentially adsorbed on the polymer, so causing a submicroscopic phase separation and effectively " blanketing " the active radical end. Although the two explanations predict similar results, there seems to be more support for the coiling of the molecule since it is also applicable to those cases in which the polymer is insoluble in its own medium, there then generally being a violent self-acceleration, *e.g.*, acrylonitrile.[42]

The polymerisation of vinyl acetate carried out in *n*-hexane solution (which brings about precipitation of the polymer) has been investigated in order to ascertain which of the alternatives given above is correct.[45] It was shown that, whereas the propagation constant varied slightly—the variation was within experimental error and could be discounted—the value of the rate constant for illumination fell by a factor of 5. This substantiates the view that the rate of the termination reaction is lowered by the change in environment. This fact is itself somewhat peculiar, since it had previously been considered that radical reactions were insensitive to changes in environment.

Similar results were obtained by Matheson and his co-workers [21] in the polymerisation of pure methyl methacrylate. Here, after the inception of the self-acceleration, the value of the termination constant fell by a factor of 100 while the propagation constant again remained sensibly unchanged. If methyl methacrylate is polymerised in aqueous medium with a redox catalyst system, the value of $k_p/k_t^{1/2}$ has been found to be 12·3 at 25°.[46] An estimate of this ratio for pure monomer can be obtained from the data of Schulz and Harborth,[34] and at 25° $k_p/k_t^{1/2}$ for pure monomer is found to be $5{\cdot}2 \times 10^{-2}$. If it is again assumed that the rate constant for propagation is unchanged, then this implies that the termination constant has been decreased by a factor of about 60,000. This very great change is not actually unreasonable since the use of water as a solvent is a rather extreme case.

J. H. Baxendale and M. G. Evans [47] have attempted to deal with the

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[44] *Faraday Soc. Discussions*, 1947, **2**, 285.

[45] G. M. Burnett and H. W. Melville, *Proc. Roy. Soc.*, 1947, *A*, **189**, 494.

[46] J. H. Baxendale, M. G. Evans, and J. H. Kilham, *Trans. Faraday Soc.*, 1946, **42**, 668.

[47] *Ibid.*, 1947, **43**, 210.

problem of reactions in which the polymer is precipitated in terms of the coagulation of colloidal particles. The velocity constant for such conditions should then be described in the form

$$k_t = \frac{8\boldsymbol{R}T}{3000\eta}\left\{\frac{2 + r_1/r_2 + r_2/r_1}{4}\right\}$$

where r_1 and r_2 are the radii of the particles, and if polymer chains of n_1 and n_2 units can be assumed to be spheres because of severe coiling the above equation becomes

$$k_t = \frac{8\boldsymbol{R}T}{3000\eta}\left\{\frac{2 + (n_1/n_2)^{1/3} + (n_2/n_1)^{1/3}}{4}\right\}$$

By using assumptions of this type it is possible to deduce the effect of the addition of emulsifiers, since these will alter the charge on the colloid particles and hence affect the rate of coagulation. These views being taken into account, it is evident that the viscosity and also the activation energy of viscous flow will enter into the termination constant of the reaction. The only possible weakness in the above discussion appears to be in the fact that coagulation does not appear necessarily to occur simultaneously with termination, as the above postulates seem to indicate.

A further phenomenon which has also been found in the case of methyl methacrylate but has so far not been investigated elsewhere may have some bearing on the subject under discussion. In their investigation of the catalysed polymerisation of this monomer Schulz and Harborth [34] measured the average degree of polymerisation at different monomer conversions. As has been stated, an increase in molecular weight was encountered in agreement with the theory of viscosity action in methyl methacrylate. If the " instantaneous " degree of polymerisation is defined by $\overline{\overline{P}} = \mathrm{d}m/\mathrm{d}n$, where n is the number of molecules of polymer, and if the average degree of polymerisation is $\overline{P} = m/n$, then it can be shown that $\overline{P}$ and $\overline{\overline{P}}$ are related by the equation

$$\overline{\overline{P}} = \frac{\overline{P}}{1 - (m/\overline{P})\mathrm{d}\overline{P}/\mathrm{d}m}$$

Investigation shows that the value of the instantaneous degree of polymerisation rises to very high values, being as high as 47,000 under certain conditions. At the same temperature the value of k_f/k_p is $8{\cdot}5 \times 10^{-5}$, so that in theory the maximum possible degree of polymerisation ought to be 12,000. Now the question which has to be answered is whether in some way the value of the transfer constant has altered during the viscous phase of the reaction. Since the transfer reaction involves a monomer molecule, this appears to be unlikely because the constancy of the propagation rate constant implies that the mobility of the monomer is unaltered. So far no concrete proposals have been given to account for this type of reaction, but it may be that transfer to polymer to some extent might account for this increase in molecular weight above the limiting value. The resurgence of growth of dead polymer has been shown to be possible in the case of the copolymerisation of styrene and butadiene (G.R.-S.).[49]

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[48] F. T. Wall, *J. Amer. Chem. Soc.*, 1947, **69**, 1761. [49] *Ibid.*, 1948, **70**, 3695.

Emulsion Polymerisation of Styrene.—In the original discussion of the rate constants for various monomers, two investigations were omitted since it was felt that they fitted more logically into a discussion of anomalous results. The polymerisation of styrene as an emulsion has been the subject of an investigation by W. V. Smith [50] based on a theory of emulsion polymerisation due to W. V. Smith and R. H. Ewart.[51a] The value of k_p determined by this method is given as $3{\cdot}5 \times 10^{10} \exp(-11700/\boldsymbol{RT})$. This is very much greater than the value obtained in polymerisation of the pure monomer at the same temperature, and the energy of activation is very much greater than that generally accepted. Smith also finds molecular weights very much in excess of the limiting value set by k_f/k_p and contends, therefore, that the published values of the rate constants for transfer reactions must be too high. This seems to be rather unlikely in view of the considerable accuracy with which the determinations can be made. The mechanism of emulsion polymerisation is not as well defined as that of the pure monomer, and it may be that a situation similar to that obtaining in high conversion polymers may be operating.

Vinylidene Chloride.—This monomer, which has considerable commercial interest, has two peculiarities in that the polymer is insoluble in the monomer and is also crystalline. An investigation of the reaction was carried out by J. D. Burnett and H. W. Melville [51] in order to ascertain the effect of precipitation on the values of the kinetic constants. Rates of polymerisation and overall energies of activation were found to be quite normal for this monomer despite the unusual properties of the polymer. The velocity constants evaluated by means of the sector technique and using direct photoinitiation gave the following results :

Rate constants for vinylidene chloride polymerisation

Temp.	k_p.	k_t.			E_p.	E_t.
	(l. mole^{-1}sec.$^{-1}$).		A_p.	A_t.	(kcals./mole).	
15° . . .	2·3	$0{\cdot}23 \times 10^5$	10^{16}	10^{30}	25	40
25	8·6	$1{\cdot}75 \times 10^5$				
35	36·8	$18{\cdot}0 \times 10^5$				

The frequency factors and energies of activation in this case are exceptionally high and indeed the former can have no meaning since they exceed the normal collision frequency. It seems therefore that here some factor has been neglected which has the effect essentially of increasing the measured energy of activation and this in turn brings about an increase in the frequency factor. This complication, without much doubt, can be ascribed to the crystalline nature of the polymer, which means that the polymer is not swollen, and further one might expect that the heats of crystallisation and solution will come into the energy terms.

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[50] *J. Chem. Physics*, 1948, **16**, 592.

[51] (*a*) *Trans. Faraday Soc.*, in the press ; (*b*) J. D. Burnett, Ph.D. Thesis, Aberdeen, 1949.

III. Polymerisation in Solution

When a polymerisation reaction takes place in solution there is always the possibility that the growing radicals will react with the solvent to give dead polymer and a further radical by the reaction

$$R— + XS \longrightarrow RX + S— \qquad k'_f$$

This type of reaction was first investigated by F. R. Mayo,[52] who showed that in the case of the thermal polymerisation of styrene the degree of polymerisation of the polymer, *i.e.*, the osmotically measured chain length, was related to the molar ratio of solvent to monomer by the equation

$$\bar{P}^{-1} = \bar{P}_0^{-1} + (k'_f/k_p)(XS/M)$$

where P and P_0 are the degrees of polymerisation in solution and in pure monomer, and (XS/M) is the molar ratio of solvent to monomer. It will be seen that the above equation will give a linear relationship between reciprocal degree of polymerisation and the solvent–monomer ratio. It should also be noted that the relationship holds only for fairly long chains. The consequences of shortening the chains will be considered later. The work was extended considerably, and the technique of measurement much refined, by R. A. Gregg and F. R. Mayo,[53] who obtained the results shown in Table III.

TABLE III

Thermal polymerisation of styrene in hydrocarbon solvents^a

Solvent.	$k'_f \times 10^4$ (l. mole^{-1}sec.$^{-1}$). 60°.	$k'_f \times 10^4$ (l. mole^{-1}sec.$^{-1}$). 100°.	E'_f, kcals./mole.	A'_f.
Benzene	1·06	31	21·3	$8·9 \times 10^9$
tert.-Butylbenzene	3·52	92·5	20·2	$6·0 \times 10^9$
Toluene	7·35	109	16·6	$5·7 \times 10^7$
Ethylbenzene	39·6	274	12·0	$2·8 \times 10^5$
*iso*Propylbenzene	48·5	336	12·0	$3·4 \times 10^5$
Diphenylmethane	135	705	10·2	$6·4 \times 10^4$
Triphenylmethane	206	1340	11·6	$1·3 \times 10^6$
Fluorene	4420	20800	9·6	$1·2 \times 10^6$
Pentaphenylethane	118×10^4	—	—	—
*cyclo*Hexane	1·42	26·8	19·9	$1·4 \times 10^9$
n-Hexane ^{a}	24·8	160	11·5	$8·9 \times 10^4$
Decalin	23·6	—	—	—

Values of k'_f, E'_f, A'_f calculated from data of Bamford and Dewar.[4]
(*a*) Non-solvent for polymers.

C. H. Bamford and M. J. S. Dewar,[54] using a similar technique, have obtained the results shown in Table IV. It will be seen from the figures of Tables III and IV that the values of k'_f vary very considerably, and in fact this measurement may be used as a method of determining the activity of free radicals towards other molecules. This is of particular interest in

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[52] *J. Amer. Chem. Soc.*, 1943, **65,** 2324.

[53] *Faraday Soc. Discussions*, 1947, **2,** 328.

[54] *Ibid.*, p. 314.

organic chemistry and comparison with many organic reactions comes readily. In the series of aromatic compounds investigated it will be seen that benzene is less reactive than toluene, ethylbenzene, or *iso*propylbenzene. This presumably must be ascribed to the presence in the latter of α-hydrogen atoms. This is further substantiated by the fact that as the lability of the α-hydrogen atom increases the efficiency of the transfer reaction increases also, and if all the hydrogen atoms of the methyl group of toluene are blocked by methyl groups as in *tert.*-butylbenzene the activity is decreased. These results indicate that radical attack occurs preferentially at the α-hydrogen atoms. The other series which can be readily investigated is that of di- and tri-phenylmethane and fluorene whose activity is in that order, this being bound up with the decreasing strength of the methane carbon–hydrogen bond. The acidities of these hydrocarbons [55] show a very close parallel with the value of Mayo's transfer constant, *i.e.*, k_f'/k_p. The identity of these orders must be due to the same factors, increasing resonance stabilisation of the radical formed by the loss of a hydrogen atom or of the negative ion by the loss of a proton. Similar conclusions cannot, however, be reached in many other cases.

TABLE IV

Thermal polymerisation of styrene in solution

Solvent.	$k_f' \times 10^4$ (l. mole^{-1}sec.$^{-1}$). 60°.	80°.	100°.	E_f', kcals./mole.	A_f'.
Carbon tetrachloride .	5300		30400	11·3	$1·3 \times 10^{7a}$
,, ,, .	8040	19400	45400	10·7	$7·6 \times 10^7$
Carbon tetrabromide	159×10^4	282×10^4	—	6·7	$3·92 \times 10^6$
s.-Dichloroethane .	19	116	—	21·2	$1·26 \times 10^{11}$
s.-Dibromoethane .	—	30	111·2	16·2	$2·99 \times 10^8$
Toluene [b]	—	4·2	17	18·2	$6·68 \times 10^8$
Ethylbenzene [b] . .	—	14·3	41	18·2	$1·60 \times 10^9$
Benzene [b]	—	1·6	6·7	19·1	$8·79 \times 10^8$

(*a*) Gregg and Mayo ; [53] other results by Bamford and Dewar.[54]
(*b*) Calculated from Mayo's data,[52] using $K = 4·57 \times 10^{-3}$, $\alpha = 0·65$ in the viscosity equation.

For halogenated compounds the efficiency as transfer agents is very much increased. Thus the rate of the transfer reaction in the series $CH_2Cl·CH_2Cl$, $CHCl_2·CHCl_2$, CCl_4 increases in that order, which one would expect from the fact that increase in chlorine constant enhances the stability of the radical. Bromine derivatives are more active than the corresponding chlorine compounds, probably by virtue of the lower bond energy of the carbon–bromine bond. The very high value of k_f' for the carbon tetrabromide makes it possible to prepare very low-molecular-weight compounds and in fact the monomeric adduct, $Ph·CHBr·CH_2·CBr_3$, has been isolated.[56]

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[55] (*a*) J. B. Conant and G. W. Wheland, *J. Amer. Chem. Soc.*, 1932, **54**, 1212 ; (*b*) W. K. McEwen, *ibid.*, 1936, **58**, 1124.

[56] M. S. Kharasch, E. V. Jensen, and W. H. Urry, *ibid.*, 1947, **69**, 1100.

This incidentally shows that the point of radical attack must be on the β-carbon atom of the styrene side chain.

Of all the transfer agents the most potent class are the thiols, all of which appear to have transfer-reaction velocity coefficients greater than the normal propagation rate constant. This feature appears to be independent of the nature of the hydrocarbon attached to the thiol group. Results foı the ratio k'_f/k_p are shown below for some common thiols.

Polymerisation of styrene in the presence of thiols

Thiol.	k'_f/k_p :		E'_f.	A'_f.
	60°.	100°.		
tert.-Butanethiol	3·7	2·3	5·8	$1{\cdot}22 \times 10^6$
Dodecanethiol	14·8	—	—	—
3-Ethoxypropanethiol . . .	21	13·7	3·9	$4{\cdot}1 \times 10^5$
Ethyl thioglycollate . . .	58	—	—	—

An interesting method of determining the ratio of k'_f/k_p is the use of the radioactive isotope of sulphur, ^{35}S, which is incorporated in the thiol. This method was devised by C. Walling.[57] The determinations of the value of k'_f were made by using active *n*-butanethiol with the monomers styrene, vinyl acetate, methy methacrylate, and methyl acrylate. The results are shown below:

Transfer constants for n-*butanethiol*

Monomer.	k_p.	k'_f/k_p.	k'_f.
Styrene	207[a]	22	4550
Methyl methacrylate . . .	367[b]	0·67	246
Vinyl acetate	3700	48	178000
Methyl acrylate	—	1·69	—

(*a*) Calculated from Bamford and Dewar.[4]
(*b*) Calculated from Matheson.[21]

It is evident that the study of the reactivity of radicals derived from monomers may be undertaken by a comparison of the values of k'_f for a number of monomers undergoing polymerisation in the same solvent. Unfortunately, only a few experiments have been performed in this connection. The polymerisation of vinyl acetate in carbon tetrachloride was shown to give a value of k'_f of 430 at 55° as compared with the value of 0·85 for styrene at 60°.[58] An investigation of radical reactivity was carried out by K. Nozaki,[59] using the techniques of transfer reactions and copolymerisation in order to attempt to correlate the nature of substituents in ethylene

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[57] *J. Amer. Chem. Soc.*, 1948, **70**, 2561.
[58] G. M. Burnett and H. W. Melville, *Faraday Soc. Discussions*, 1947, **2**, 322.
[59] *Ibid.*, p. 337.

with the stability of the radical formed during polymerisation. He showed that this order was

$$C_6H_5\cdot > CH_2{:}CH\cdot > \cdot CN \simeq \cdot CO_2Me > Cl > \cdot CH_2R \simeq \cdot OAc > \cdot H$$

Reference to the last table shows that the order of activity seems to have been altered slightly, since the activity of the apparently heavily stabilised styryl radical is greater than that of either methyl acrylate or methacrylate, both of whose substituent groups give only slight stabilisation. On the whole, however, the order given by Nozaki is fairly rigidly followed.

Using exceptionally high concentrations of carbon tetrachloride for the thermal polymerisation of styrene, up to a ratio of solvent to monomer of 400 to 1, F. R. Mayo[60] has investigated the effect of chain length on the ratio k'_f/k_p. With the very short chains involved in this reaction it is necessary to modify, to some extent, the equations which have been used previously, since it is evident that the consumption of monomer in side reactions will be comparable to that taken up in the polymerisation reaction. The results recorded in this work show that at 76° the ratio of k'_f/k_p is 0·0006 (or less) for one styrene unit, 0·0025 for two units, 0·007 for three units, and for four or more units the value is constant at 0·0115. Studies of the rate of reaction showed that, on account of the very great difficulty in obtaining the lowest molecular weights corresponding to one unit of styrene, it is the transfer-rate coefficient k'_f rather than k_p which varies. The assumption of constancy of the rate coefficients therefore requires some qualification defining the chain length. It will be noticed that, in this case, there is some similarity between those results reported here and those obtained in investigations of the effect of molecular size on the propagation and termination reaction velocity constants[41] (Table II). In the latter case the value of k_p/k_t decreased but k'_f/k_p increased with molecular size. The significance of this trend is rather obscure since in the first instance there is a comparison of a radical–molecule reaction and an inter-radical reaction, whereas in the second case both reactions are of radical–molecule nature.

It is evident that, following a transfer reaction with solvent, the radical produced from the solvent must itself be capable of carrying on the reaction chain, *i.e.*, it must be capable of adding on to the double bond of the monomer. It seems to be thus far an impossible task to evaluate the rate constant for this type of reaction. This is unfortunate since it means that a powerful tool is denied to the physical chemist for the investigation of radical attack on the monomer double bond. A measure of the reaction velocity constant for the attack of the solvent fragment on the monomer would give a measure of the activity of the monomer by using the same solvent, or, by keeping to a single monomer, the activity of many radicals could be investigated.

It will have been noticed that throughout the entire range of results which have been presented here there is the trend that with high energies of activation high frequency factors are also found. This was first pointed out by Gregg and Mayo[53] in connection with the frequency factors and

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[60] *J. Amer. Chem. Soc.*, 1948, **70**, 3689.

energies of activation for a number of hydrocarbon solvents in the polymerisation of styrene. In this case, there was found to be a linear relationship between the logarithm of the frequency factor and the energy of activation. This has recently been extended by C. H. Bamford and M. J. S. Dewar [61] to a number of other reactions including the autoxidation of tetralin.[62] They show that if the energy of activation is much less than 20 kcals. per mole it is unlikely that the frequency factor will appreciably exceed 10^7. This is in direct contradiction to the normally accepted value of 10^{11}—10^{12}. A similar relationship holds in the case of oxidation reactions, as has been pointed out by Bolland,[1] and is also known to be true in the case of ionic reactions.[63] As yet the source of this relationship is unknown.

IV. Copolymerisation *

Monomer Reactivity Ratios.—In recent years the study of copolymerisation has been prosecuted with increasing vigour on account of the unique information which the results afford on the reactivity of radical types. Not only can the familiar monomers undergo copolymerisation, but many compounds, which do not themselves form high polymers, can copolymerise with other monomers. In some cases, the peculiar situation arises in which two monomers, neither of which polymerises alone, copolymerise with each other, *e.g.*, maleic anhydride and stilbene. Most of the work carried out has been with systems of two monomers. If these monomers are denoted by A and B, then there are two possible modes of initiation, in the case of either radical or photochemical chain starting :

$$\mathrm{A} \longrightarrow \mathrm{P}_1 \quad \text{rate} = X_a \qquad (11)$$

$$\mathrm{B} \longrightarrow \mathrm{Q}_1 \quad \text{rate} = X_b \qquad (12)$$

in which P and Q are the active radicals derived from monomers A and B. There will evidently be four propagation reactions

$$\left.\begin{array}{llll} \mathrm{P} + \mathrm{A} & \longrightarrow & \mathrm{P} & \text{rate} = k_{p,aa}[\mathrm{P}][\mathrm{A}] \\ \mathrm{P} + \mathrm{B} & \longrightarrow & \mathrm{Q} & \text{rate} = k_{p,ab}[\mathrm{P}][\mathrm{B}] \\ \mathrm{Q} + \mathrm{A} & \longrightarrow & \mathrm{P} & \text{rate} = k_{p,ba}[\mathrm{Q}][\mathrm{A}] \\ \mathrm{Q} + \mathrm{B} & \longrightarrow & \mathrm{Q} & \text{rate} = k_{p,bb}[\mathrm{Q}][\mathrm{B}] \end{array}\right\} \qquad (13)$$

In the rate constant $k_{p,ab}$, the first subscript denotes the nature of the radical end, in this case P derived from monomer A, and the second denotes the monomer concerned in the reaction, *i.e.*, B. If, as is most likely, the chains are stopped by the mutual destruction of two active ends, then the possible reactions will be

$$\left.\begin{array}{l} \mathrm{P} + \mathrm{P} \\ \mathrm{P} + \mathrm{Q} \\ \mathrm{Q} + \mathrm{Q} \end{array}\right\} \longrightarrow \text{non-radical products} \quad \left.\begin{array}{l} \text{rate} = k_{t,aa}[\mathrm{P}]^2 \\ \text{rate} = k_{t,ab}[\mathrm{P}][\mathrm{Q}] \\ \text{rate} = k_{t,bb}[\mathrm{Q}]^2 \end{array}\right\} \qquad (14)$$

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[61] *Nature*, 1949, **163**, 256.

[62] *Proc. Roy. Soc.*, 1949, *A*, **198**, 252.

[63] R. A. Fairclough and C. N. Hinshelwood, *J.*, 1937, 538.

* The terminology used throughout this section is that adopted by Melville's school. In this case the main difference from other workers is the use of σ and μ for monomer reactivity ratios which are currently denoted by r_1 and r_2 by most American workers. Other symbols are almost universally accepted.

If the monomers can undergo purely thermal polymerisation then there are three possible initiation reactions, *viz.*:

$$\left.\begin{array}{l}\mathrm{A} + \mathrm{A}\\ \mathrm{A} + \mathrm{B}\\ \mathrm{B} + \mathrm{B}\end{array}\right\} \longrightarrow \text{radical products}$$

So far no investigation has shown the "crossed" initiation term to be significant (see below).

If the normal approximation is introduced that the reaction chains will be long, then the consumption of monomer will be confined solely to the propagation reactions. Hence the consumption of the individual monomers is

$$-\,\mathrm{d}[\mathrm{A}]/\mathrm{d}t = k_{p,aa}[\mathrm{P}][\mathrm{A}] + k_{p,ba}[\mathrm{Q}][\mathrm{A}]$$

and

$$-\,\mathrm{d}[\mathrm{B}]/\mathrm{d}t = k_{p,bb}[\mathrm{Q}][\mathrm{B}] + k_{p,ab}[\mathrm{P}][\mathrm{B}]$$

Also since under the stationary state conditions,

$$k_{p,ab}[\mathrm{P}][\mathrm{B}] = k_{p,ba}[\mathrm{Q}][\mathrm{A}]$$

it can be shown that

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}[\mathrm{B}]} = \frac{[\mathrm{A}]}{[\mathrm{B}]}\,\frac{\sigma[\mathrm{A}] + [\mathrm{B}]}{[\mathrm{A}] + \mu[\mathrm{B}]}$$

where $\sigma = k_{p,aa}/k_{p,ab}$ and $\mu = k_{p,bb}/k_{p,ba}$, these being called the monomer reactivity ratios and defining, in effect, the activity of the monomers towards

TABLE V

Monomer reactivity ratios[66]

Monomer A.	σ.	Monomer B.	μ.	$\sigma\mu$.	Temp.	Ref.
Styrene . . .	0·52	Methyl methacrylate	0·46	0·24	60°	(67)
,, . . .	0·75	Methyl acrylate . .	0·20	0·15	70	(68)
,, . . .	0·75	,, ,, . .	0·18	0·13	60	(67)
,, . . .	0·30	Methacrylonitrile .	0·16	0·048	60	(69)
,, . . .	0·41	Acrylonitrile . . .	0·04	0·016	60	(70)
,, . . .	0·54	β-Chloroethyl acrylate	0·10	0·054	60	(69)
,, . . .	2·0	Vinylidene chloride .	0·14	0·28	60	(70)
,, . . .	55	Vinyl acetate . . .	0·01	0·55	60	(71)
,, . . .	0·043	Maleic anhydride .	0	0	80	(72)
,, . . .	8·5	Methyl maleate . .	0·03	0·026	60	(73)
,, . . .	0·21	Methyl fumarate . .	0·25	0·053	60	(73)
,, . . .	1·16	*p*-Methoxystyrene .	0·82	0·94	60	(74)
,, . . .	0·74	*p*-Chlorostyrene . .	1·025	0·76	60	(74)
,, . . .	0·64	*m*-Chlorostyrene . .	1·09	0·70	60	(74)
,, . . .	0·56	*o*-Chlorostyrene . .	1·64	0·92	60	(75)
,, . . .	0·20	2 : 5-Dichlorostyrene	0·80	0·16	70	(76)
Methyl methacrylate	0·67	Methacrylonitrile . .	0·65	0·43	60	(69)
,, ,,	1·2	Acrylonitrile . . .	0·15	0·18	60	(70)
,, ,,	20	Vinyl acetate . . .	0·015	0·30	60	(71)
,, ,,	0·29	*p*-Methoxystyrene .	0·32	0·093	60	(74)
,, ,,	0·50	α-Methylstyrene . .	0·14	0·07	60	(75)
Vinyl acetate . .	0·10	Methyl acrylate . .	9·0	0·90	60	(74)
,, ,, . .	0·17	Ethyl maleate . .	0·043	0·007	60	(73)
,, ,, . .	0·011	Ethyl fumarate . .	0·444	0·005	60	(73)
Maleic anhydride .	0·03	Stilbene	0·03	0·009	60	(73)

the same radicals. This copolymer composition equation, derived independently by F. R. Mayo and F. M. Lewis [64] and by T. Alfrey and G. Goldfinger,[65] has proved to be of immeasurable importance in studying the reactivities of monomers. By means of sensitive analytical techniques the monomer reactivity ratios for a wide range of monomer pairs have been determined, a selection of these being set out in Table V.

Since the monomer reactivity ratios are ratios of propagation constants, it would not be expected that the values of σ and μ would vary very much with temperature. Table VI shows results obtained from two widely differing temperatures. The data show quite conclusively that there is a slight but definite difference in the monomer reactivity ratios at the higher temperatures. The authors [77] showed further that the entropy changes differed, in most cases, only slightly from zero, so that whether two monomers

TABLE VI

Effect of temperature on monomer reactivity ratios

Type.	Monomer reactivity ratios : 60°.	Monomer reactivity ratios : 131°.	$\Delta H_1 - \Delta H_2$ (cals./mole).	$\Delta S_1 - \Delta S_2$ (E.U./mole).
Styrene	0·520 ± 0·026	0·590 ± 0·026	480 ± 250	0·12 ± 0·68
Methyl methacrylate	0·460 ± 0·026	0·536 ± 0·026	580 ± 280	0·19 ± 0·76
Styrene	0·747 ± 0·028	0·825 ± 0·005	380 ± 140	0·54 ± 0·36
Methyl acrylate. .	0·182 ± 0·016	0·238 ± 0·005	1020 ± 340	0·66 ± 0·86
Styrene	6·52 ± 0·05	5·48 ± 0·56	−660 ± 480	1·87 ± 1·36
Ethyl maleate . .	0·01	—	—	—
Styrene	0·301 ± 0·024	0·400 ± 0·014	1070 ± 320	0·82 ± 0·82
Ethyl fumarate .	0·0697 ± 0·0041	0·0905 ± 0·0008	990 ± 290	−2·35 ± 0·73
Styrene	0·742 ± 0·030	0·816 ± 0·015	360 ± 170	0·48 ± 0·43
p-Chlorostyrene .	1·032 ± 0·030	1·042 ± 0·015	35 ± 120	0·40 ± 0·32

[64] *J. Amer. Chem. Soc.*, 1944, **66**, 1594.

[65] *J. Chem. Physics*, 1944, **12**, 205.

[66] Many other ratios are to be found in a review on copolymerisation by R. Simha and L. A. Wall, *J. Nat. Bur. Stand.*, 1948, **41**, 521.

[67] F. M. Lewis, F. R. Mayo, W. Cummings, E. R. Briggs, and C. Walling, *J. Amer. Chem. Soc.*, 1948, **70**, 1519.

[68] T. Alfrey, E. Merz, and H. Mark, *J. Polymer Sci.*, 1946, **1**, 37.

[69] F. M. Lewis, C. Walling, W. Cummings, E. R. Briggs, and W. J. Wenisch, *J. Amer. Chem. Soc.*, 1948, **70**, 1527.

[70] F. M. Lewis, F. R. Mayo, and W. F. Hulse, *ibid.*, 1945, **67**, 1701.

[71] F. R. Mayo, C. Walling, F. M. Lewis, and W. F. Hulse, *ibid.*, 1948, **70**, 1523.

[72] T. Alfrey and E. Lavin, *ibid.*, 1945, **67**, 2044.

[73] F. M. Lewis and F. R. Mayo, *ibid.*, 1948, **70**, 1533.

[74] C. Walling, E. R. Briggs, K. B. Wolfstirn, and F. R. Mayo, *ibid.*, p. 1537.

[75] C. Walling, E. R. Briggs, and K. B. Wolfstirn, *ibid.*, p. 1543.

[76] T. Alfrey and T. G. Harrison, *ibid.*, 1946, **68**, 299.

[77] F. R. Mayo, F. M. Lewis, and C. Walling, *Faraday Soc. Discussions*, 1947, **2**, 285.

will copolymerise or not seems to depend solely upon a difference with a maximum of about 3 kcals. in the free energies of activation for the two competing reactions of a free radical.

The reactivities of monomers and the ease with which they enter copolymerisation appear to be influenced by three main factors : (1) General overall reactivities of monomers towards all types of radicals ; (2) tendency of monomers to alternate on entering the copolymer ; (3) steric effects. The reactivities of the monomers can be found from the reciprocals of the ratios set out in Table V, but until sufficient values of $k_{p,aa}$ have been determined there is little point in comparing monomer reactivity towards different radicals. Attention has to be focussed rather on the reactivity of monomers toward the same radical. Certain trends are, however, found in most cases, although these may not be always duplicated as the radical type changes. For the exception it is generally found that there is a high tendency to alternate on entering the copolymer.

Since the value of the propagation constants of styrene, methyl methacrylate, and vinyl acetate are relatively well established, it is possible to evaluate the rate constants for the crossed type of propagation reaction. The values of rate constants for the interaction of radical and monomer are set out in Table VII.[78]

TABLE VII

Propagation rate constants of the type $k_{p,ab}$ *for some copolymer pairs at* 60°

	Styrene.[a]	Vinyl acetate.[b]	Methyl methacrylate.[a]
Styrene	59	$2\cdot6 \times 10^{5}$	386
Methyl methacrylate	114	$1\cdot8 \times 10^{5}$	177
Acrylonitrile	147	$4\cdot3 \times 10^{4}$	131
Methyl acrylate	79	$2\cdot6 \times 10^{4}$	—
Vinylidene chloride	29·5	$2\cdot6 \times 10^{5}$	70
Vinyl chloride	3·5	$1\cdot1 \times 10^{4}$	14
Vinyl acetate	1·1	$2\cdot63 \times 10^{3}$	8·9
Allyl acetate	0·66	$4\cdot4 \times 10^{3}$	7·7
Ethyl fumarate	197	$2\cdot4 \times 10^{5}$	—
Ethyl maleate	9·1	$1\cdot5 \times 10^{4}$	8·9
trans-Dichloroethylene	1·8	$2\cdot7 \times 10^{3}$	—
cis-Dichloroethylene	0·26	$4\cdot2 \times 10^{2}$	—

(*a*) Calculated from the data of Bamford and Dewar. [4,32]
(*b*) Calculated from Dixon-Lewis's data. [29]

Here some points are immediately apparent. The reactivities of the three radicals, those derived from styrene, vinyl acetate, and methyl methacrylate, fall into their expected order of reactivity, *i.e.*, vinyl acetate $\gg$ methyl methacrylate $>$ styrene. This is in agreement with the effect of substituents in stabilising radicals already given by Nozaki,[59] *i.e.*, $\cdot$Ph $>$ $\cdot CO_2Me \simeq \cdot Me > \cdot OAc$. It will also be noted that the values of the

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[78] C. H. Bamford, *Faraday Soc. Discussions*, 1947, **2**, 317.

rate constant for some of the reactions involving vinyl acetate radicals rise to very high orders ($> 10^5$). This would suggest by analogy with other radical reactions (see above) that the energy of activation for these processes is very low. This is further substantiated by the fact that the orders of magnitude of these velocity constants are of the same order as those normally associated with radical–radical reactions. Hence, the nature of the substituent does appear to have a profound effect on the stability of the radical.

It will be seen from Table VII that there is a general trend in the values of the propagation constants, which tend to become less as one goes down the table. There are some notable exceptions which require further consideration. In copolymerisation reactions generally two distinct types of reaction—the ideal and the alternating—have been distinguished. In the case of ideal copolymerisation, the nature of the radical end in no way affects the addition of the next monomer molecule to the chain, although some slight preference may be shown. In the ideal case, in which the copolymer is formed in a purely random manner, $\sigma = \mu^{-1}$, so that $\sigma\mu$ will be unity. Alternation is easily detected, since 1 : 1 copolymers will be formed over a wide range of monomer mixtures. This must imply that radicals with free ends derived from monomer A will preferentially react with monomer B and *vice versa*. Thus the nature of the radical end determines the addition of the next monomer unit. This must mean that the constant, $k_{p,aa}$, for both monomers must be very much less than the constant for the crossed propagation reaction, so that both σ and μ will be small and $\sigma\mu$ will approach zero. As with all wide generalisations, it is difficult to fit individual cases into either class with certainty, but the value of the product of the monomer reactivity ratios can be taken as a very good indication of the tendency of a monomer pair to alternate. Table V gives the values of $\sigma\mu$ for a number of monomer pairs, and it will be seen that in some cases unity is closely approached while in others the values lie below 0·5, showing a tendency to alternate, and some do in fact reach zero, showing complete alternation.

Three lines of attack have been developed with a view to elucidate the nature and underlying cause of alternation. The first of these has been elaborated by C. C. Price [79] and by T. Alfrey and C. C. Price.[80] These workers assume that the controlling factor is the activation energy, which is lowered by an electrical charge effect between radical and monomer. The rate constants for the addition of radicals to monomer can then be expressed in the form

$$\begin{aligned} k_{p,aa} &= A_{aa}\exp(-\,\Delta F_a/RT) \\ &= A_{aa}\exp[-\,(p_a + q_a + \varepsilon_a{}^2)] \end{aligned}$$

and

$$\begin{aligned} k_{p,ab} &= A_{ab}\exp(-\,\Delta F_{ab}/RT) \\ &= A_{ab}\exp[-\,(p_a + q_b + \varepsilon_a\varepsilon_b)] \end{aligned}$$

in which the A factors denote probability factors, p_a denotes a reactivity factor for the end group, q_a and q_b similar factors for monomers A and B,

[79] "Reactions at Carbon Carbon Double Bonds", 1940.

[80] *J. Polymer Sci.*, 1946, **1**, 83.

and ε_a and ε_b are electrical (charge) terms. If it is assumed that there is no steric hindrance (*i.e.*, $A_{aa} = A_{ab}$) and that the same charge is conferred on both radical and monomer by the same substituent, then

$$k_{p,aa} = P_a Q_a \exp(-\varepsilon_a{}^2)$$
$$k_{p,ab} = P_a Q_b \exp(-\varepsilon_a \varepsilon_b)$$

where P_a is characteristic of the radical end and Q_a and Q_b are general monomer reactivities. Hence the monomer reactivity ratios can be written in the form

$$(Q_a/Q_b) \exp[-\varepsilon_a(\varepsilon_a - \varepsilon_b)]$$

and

$$(Q_b/Q_a) \exp[-\varepsilon_b(\varepsilon_b - \varepsilon_a)]$$

By this method the monomer can be classified in terms of a general reactivity (Q) and a polar factor (ε). As a result of a thorough study of the copolymerisation of styrene with various substituted styrenes, it was concluded that these ideas, although giving a sound enough qualitative picture of the reactions, could not be made sufficiently quantitative.[81]

M. G. Evans [82] has shown that in the case of the interaction of radical A with monomer B to give a radical F, the heat of reaction can be split into several terms as follows

$$H = (-R_A - R_M + R_F) - D_{C:C} + D_{C\cdot C}$$

where R are resonance energies, and the D terms are dissociation energies. Changes in the activation energies will be given by

$$\Delta E = \alpha \Delta H = \alpha(R_A + R_M - R_F)$$

For values of propagation constants in monomer reactions therefore

$$k_{p,a}/k_{p,b} = \exp[(-E_a + E_b)/\boldsymbol{R}T]$$
$$= \exp[-\alpha(R_{M,a} - R_{M,b})/\boldsymbol{R}T]$$

When this is checked against reasonable values for the resonance energy of methyl methacrylate, styrene, and vinyl acetate, it gives values of α completely at variance with those computed from the energies of activation for the propagation steps and the heats of reaction. This disagreement may, however, be due to the fact that in the above treatment all entropy changes have been neglected.

Mayo, Lewis, and Walling [81] investigated the copolymerisation of a number of substituted styrenes with styrene, methyl methacrylate, and maleic anhydride, which show an increasing tendency to alternate with the styrene group of monomers. They deduce that the alternating effect is not wholly a polar one. This conclusion was reached as a result of comparing the reactivities obtained with Hammett's σ constant,[83] defined by $\log(k/k_0) = \sigma\rho$, where k and k_0 are the velocity constants for substituted and unsubstituted benzene, σ is characteristic of the substituent and ρ of the reaction. The σ constant has been interpreted in terms of the ability of the substituent to donate electrons to or withdraw them from the locus

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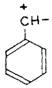
[81] F. R. Mayo, F. M. Lewis, and C. Walling, *J. Amer. Chem. Soc.*, 1948, **70**, 1529.

[82] *Faraday Soc. Discussions*, 1947, **2**, 321.

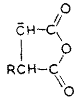
[83] " Physical Organic Chemistry ", 1940.

of reaction. For styrene and substituted styrenes in which the tendency to alternate is negligible the correlation between reactivity and the Hammett constant is very good. Certain discrepancies begin to appear when methacrylate is the monomer, and with maleic anhydride all correlation between the two quantities disappears. It is therefore concluded that the phenomenon is best explained in terms of the electron-accepting and -donating capacities of carbonyl conjugated and aromatic systems with a subsequent increase in the stability of the active complex due to resonance.

In the case of styrene and maleic anhydride electron donation would result in structures of the types (I) and (II). The styrene portion would be stabilised by resonance between 26 possible structures, while the carbonyl portion becomes the relatively stable enolate ion. For the attack of the styrene radical on a conjugated double bond, similar resonance stabilisation can occur. Not only does this explain the cause of alternation in a qualitative manner, but it also indicates why maleic anhydride has a greater tendency to alternate than methyl methacrylate, since the former has two carbonyl groups over which the odd electron and the charge can be distributed.



(I.)



(II.)

This theory is very similar to that adopted by J. Weiss [84] to explain the formation of coloured complexes between these compounds, although this type of complex must be carefully distinguished from the active complexes which the above theory requires.

At the same time C. C. Price,[85] using the values of σ and μ obtained by a variety of workers, has pointed out that the correlation between the alternation in charge due to substitution and the Hammett constant is very good, as the following table shows. Price therefore concludes that his theory is quite adequate to deal with the problem, and it has, at any rate, the definite advantage that it enables the worker to put figures to the phenomena rather than deal in purely qualitative principles.

Correlation between Hammett's constant and E *values for copolymerisation of substituted styrenes*

Substituent.	$\Delta\varepsilon$.	σ [83].	Substituent.	$\Delta\varepsilon$.	σ [83].
p-Dimethylamino-	− 0·6	− 0·44	*p*-Iodo- . . .	0·35	0·28
p-Methoxy- . .	− 0·3	− 0·27	*p*-Bromo- . . .	0·45	0·23
p-Methyl- . . .	− 0·1	− 0·17	*m*-Chloro- . . .	0·45	0·37
m-Methyl- . . .	0	− 0·07	*m*-Bromo- . . .	0·55	0·38
(Hydrogen). . .	(0)	(0)	*p*-Cyano- . . .	1·1	1·0 [a]
p-Chloro- . . .	0·35	0·23	*p*-Nitro- . . .	1·2	1·27 [a]

(*a*) The values are for phenol derivatives.

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[84] *J.*, 1942, 255.

[85] *J. Polymer Sci.*, 1948, **3**, 772.

That steric effects do play an important part in copolymerisation processes can be seen from Tables V and VII in which it will be noted for instance that ethyl maleate is much less reactive than the corresponding fumaric ester. In the former, the whole molecule with the exception of the ethyl groups will be in the same plane, whereas in the latter only one carbethoxy-group can be coplanar with the double bond. Hence the resonance contribution of the maleate to a radical adduct will be much less than that of the fumarate, so it can be predicted that for this reason alone the fumarate will be the more active. In addition to this resonance effect there will be the purely geometrical steric hindrance of the bulky carbethoxy-groups which would tend to impede the approach of the attacking free radical. Complications such as these appear to be incapable of explanation on the basis of Price's theory.

Termination in Copolymerisation.—As was shown previously, three possible termination reactions can be envisaged as occurring in copolymerisation reactions. To obtain information regarding these constants it is necessary to find the rate of copolymerisation. The analysis of the rates of reaction for such systems has been carried out by H. W. Melville, B. Noble, and W. F. Watson.[86] If the termination reaction scheme is

$$\begin{array}{llll} P_r + P_s & \longrightarrow & M_r + M_s & k_{t,rs,aa} \\ P_r + Q_s & \longrightarrow & M_r + M_s & k_{t,rs,ab} \\ Q_r + Q_s & \longrightarrow & M_r + M_s & k_{t,rs,bb} \end{array}$$

the reaction velocity coefficients require to be split in some way in order to cope with the mathematical analysis. As a first approximation it is taken that

$$\left.\begin{array}{l} k_{t,rs,aa} = k_{t,r,a} + k_{t,s,a} \\ k_{t,rs,ab} = k_{t,r,a} + k_{t,s,b} \\ k_{t,rs,bb} = k_{t,r,b} + k_{t,s,b} \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad (17)$$

which implies that the terminating capacity of a radical is the same for like and unlike radicals. This is, however, somewhat crude, so that a more general form of (17) has to be applied, *i.e.*,

$$k_{t,rs,ab} = k_{t,r,ab} \cdot k_{t,s,ab} \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

By using a system of kinetic analysis similar to that of Gee and Melville,[5] the following expressions have been derived. Using the assumptions of equation (17), we have

$$\frac{-\,\mathrm{d}\{[\mathrm{A}] + [\mathrm{B}]\}}{\mathrm{d}t} = \frac{\{\sigma[\mathrm{A}]^2 + 2[\mathrm{A}][\mathrm{B}] + \mu[\mathrm{B}]^2\}(X_a + X_b)^{1/2}}{\sigma\delta_a[\mathrm{A}] + \mu\delta_b[\mathrm{B}]} \quad . \quad (19)$$

and using equation (18), we have

$$\frac{-\,\mathrm{d}\{[\mathrm{A}] + [\mathrm{B}]\}}{\mathrm{d}t} = \frac{\{\sigma[\mathrm{A}]^2 + 2[\mathrm{A}][\mathrm{B}] + \mu[\mathrm{B}]^2\}(X_a + X_b)^{1/2}}{\{\sigma^2\delta_a{}^2[\mathrm{A}]^2 + 2\phi\delta_a\delta_b\sigma\mu[\mathrm{A}][\mathrm{B}] + \mu^2\delta_b{}^2[\mathrm{B}]^2\}^{1/2}} \quad . \quad (20)$$

in which $\delta_a = (k_{t,r,aa})^{1/2}/k_{p,aa}$; $\delta_b = (k_{t,r,bb})^{1/2}/k_{p,bb}$; $\phi = (k_{t,r,ab} \cdot k_{t,s,ab})/(k_{t,ra} \cdot k_{t,sb})$. If $\phi = 1$ then it is evident that equation (20) will reduce to equation (19). All of the constants in equation (20) are known from monomer experiments and from copolymer composition except ϕ, so that a study of the rate will

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[86] *J. Polymer Sci.*, 1947, **2**, 229.

immediately determine whether ϕ is unity or not. If $\phi > 1$ then it must immediately follow that the termination reaction between unlike radicals is preferred to that between like radicals. The problem of determining the rate of copolymerisation is naturally a somewhat complex one, but this has now been accomplished with considerable success.[87, 88] Melville and his collaborators have investigated the systems styrene–methyl methacrylate and styrene–butyl acrylate, and Walling has studied the copolymerisation of styrene with methyl methacrylate, methyl acrylate, and vinyl acetate. In the case of styrene–methacrylate it was found that the addition of small quantities of styrene brought about a marked reduction in the rate of reaction while further additions produced no comparable effect, as is shown in the following table.

Rate of copolymerisation of styrene and methyl methacrylate

Mole fraction of styrene	0	0·052	0·195	0·418	0·804	1·000
Rate, moles % per hour	4·65	1·88	1·13	0·82	0·80	1·10

On the assumption that the rate of initiation will vary linearly with monomer composition, the value of ϕ for this system will be approximately 45, indicating preferential " crossed " termination. When the rates of initiation are determined by osmotic pressure molecular-weight measurements it is found that the above assumption is invalid, and by making the necessary calculations it was found that the value of $\phi = 14$ gave a very good fit with the experimental rates. Since the termination constants for the individual monomers are known, it is possible to evaluate the velocity constant for the reaction between styrene radicals and methacrylate radicals. This was found to be $2{\cdot}06 \times 10^8$ l. mole^{-1}sec.$^{-1}$ compared with 8×10^6 for the interaction of styrene radicals and $2{\cdot}7 \times 10^7$ for methacrylate radicals. Thus it will be clearly seen that there is a definite preference for the termination of the chains to take place by the interaction of unlike radicals. It has been suggested that a possible explanation of the non-linearity of the measured rates of initiation as a function of monomer composition may be that unlike radicals, for some reason, probably due to polarity, combine rather than disproportionate. This postulate does give a closer agreement to the supposed linear variation of initiation with monomer composition and gives an upper limit of 30 to the value of ϕ.

The position with the butyl acrylate–styrene is not so clear as for the methacrylate–styrene systems. In this case no single value of ϕ appears to be capable of covering the whole range of monomer compositions : the values of ϕ vary considerably but are again very much greater than unity, having a most probable value of the order of 150.

The results obtained by Walling for the methacrylate–styrene copolymerisation give a value of ϕ very close to that already given ($\phi = 13$). Some

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[87] E. J. Arlman, H. W. Melville, and L. Valentine, International Colloquium on Macromolecules, Amsterdam, 1949.

[88] C. Walling, *J. Amer. Chem. Soc.*, 1949, **71**, 1930.

discrepancies in the actual working out of this value may give a slight alteration but will not seriously disturb the general agreement between the two sets of results. In the investigation of the methyl acrylate–styrene system, the reaction was carried out at 60°, α-azobis*iso*butyronitrile being used as catalyst. The rates of polymerisation show the same trend as reported by Melville *et al.*, *i.e.*, the addition of small amounts of styrene causes a large reduction in the rate of reaction, whereas further addition has little effect. The value of ϕ stated to fit the rate curve is given as 40, but the values of δ_a and δ_b are suspect and closer study reveals an arithmetical error which has the effect of raising the value of ϕ to about 300.* In any case, it is evident that the crossed termination mechanism is again very much favoured. Purely thermal initiation being used in the styrene–methacrylate copolymerisation, the rate of initiation will be

$$I = k_{t,aa}[\mathrm{A}]^2 + k_{i,ab}[\mathrm{A}][\mathrm{B}] + k_{i,bb}[\mathrm{B}]^2$$

where the k_i terms are rate constants for thermal initiation. Walling makes the assumption that the rate constant for the thermal polymerisation of methyl methacrylate is very much less than that of styrene, and on this basis calculates that $k_{i,ab}$ will be 6×10^{-12} l. mole^{-1}sec.$^{-1}$ as compared with $2{\cdot}15 \times 10^{-12}$ for pure styrene. The work of Bamford and Dewar [32] makes it unlikely that the assumption used here is correct, so little can be said as to the value of the initiation constant for " crossed " initiation or whether indeed it occurs at all.

In the foregoing discussion it is evident that in all cases the value of ϕ will be greater than unity, so it is desirable to have an explanation of the underlying reason why termination between two unlike radicals should be preferred to other types of termination. Melville, Arlman, and Valentine suggest that there is a possible electronic explanation of this phenomenon derived along the lines of the Alfrey–Price theory mentioned in connection with monomer reactivity.[79] Modifications which are introduced allow the termination constants to be written in the form

$$\begin{aligned} k_{t,aa} &= A_{aa}P_a{}^2 \exp(-\ \varepsilon_a{}^2) \\ k_{t,bb} &= A_{bb}P_b{}^2 \exp(-\ \varepsilon_b{}^2) \\ k_{t,ab} &= A_{ab}P_aP_b \exp(-\ \varepsilon_a\varepsilon_b) \end{aligned}$$

where the A's are probability factors, P_a and P_b are general reactivities of radicals, and ε_a and ε_b are electrical charge terms. Substitution in the definition of ϕ and squaring gives

$$\phi = \frac{k_{t,ab}}{k_{t,aa}k_{t,bb}} = \frac{A_{ab}{}^2}{A_{aa}A_{bb}}\cdot\frac{1}{\sigma\mu} \quad . \quad . \quad . \quad . \quad . \quad (21)$$

since from equations (15) and (16) $\sigma\mu = \exp(-\ \varepsilon_a{}^2 + 2\varepsilon_a\varepsilon_b + \varepsilon_b{}^2)$.

Reference to the data of Table V shows that the value of $\sigma\mu$ for methacrylate–styrene copolymerisation is 0·24. Thus this alone will not be capable of raising the value of ϕ to the order of 14. It is, therefore, evident that the probability factor for crossed termination must also be exceptionally high, in order that the necessary value of ϕ can be approached. This may

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* The Reviewer's thanks are due to Dr. L. Valentine for pointing out some of the arithmetical errors in this paper.

be due to steric effects which, as usual, can be purely geometrical or may also give rise to greater or less stability of the radicals on the grounds of resonance alone. Again, the methyl acrylate–styrene system gives a value of $\sigma\mu$ which is only about 0·5 times that of the former system, so it is evident that a further enhanced probability factor will be necessary to give a ϕ value of 300. At the same time one might in the latter case expect an increased probability of mixed termination in view of the removal of a blocking methyl group between methacrylate and acrylate molecules. Preliminary experiments which have been carried out with *p*-methoxystyrene–styrene systems for which $\sigma\mu \simeq 1$ tend to show that in this case the value of ϕ is much lower than those quoted and may indeed approximate closely to unity,[89] thus indicating that no longer is crossed termination preferred.

The following table sets out the values of individual velocity coefficients which have been obtained in this work.

Rate constants in copolymer reactions

Reaction between :		Rate constant (l. mole^{-1}sec.$^{-1}$).	Energy of activation (kcals. per mole).	Frequency factor.
Radical.*	Molecule.			
		At 25°.		
Styrene	Styrene	39·5	6·0	8·9 × 10^{5}
Styrene	Butyl acrylate	89·7	—	—
Butyl acrylate	Butyl acrylate	22·5	6·0	5·1 × 10^{5}
		13·1	2·1	4·4 × 10^{4}
Butyl acrylate	Styrene	77·0	—	—
Styrene	—	7·9 × 10^{6}	2·0	2·2 × 10^{8}
Butyl acrylate	—	1·6 × 10^{4}	0	1·6 × 10^{4}
Styrene Butyl acrylate	—	5·7 × 10^{7} (mean value)	—	—
		At 30°.		
Styrene	Methyl methacrylate	95	5·5	8·5 × 10^{5}
Methyl methacrylate	Styrene	545	4·4	8·5 × 10^{5}
Methyl methacrylate	Methyl methacrylate	230	5·0	9·5 × 10^{5}
Methyl methacrylate	—	2·7 × 10^{7}	1·0	1·5 × 10^{8}
Methyl methacrylate Styrene	—	2·1 × 10^{8}	—	—
		At 60°.		
Methyl acrylate	Methyl acrylate molecule [a]	4692	701	2 × 10^{8}
Styrene	Methyl acrylate	79	—	—
Methyl acrylate	Styrene	2·3 × 10^{4}	—	—
Methyl acrylate [a]	—	5·36 × 10^{6}	3·1	5·60 × 10^{10}
Methyl acrylate Styrene [b]	—	1·49 × 10^{9}	—	—

(*a*) Matheson.[39] (*b*) ϕ is taken as 300.

* Where a second species is not given, reaction is between two identical radicals.

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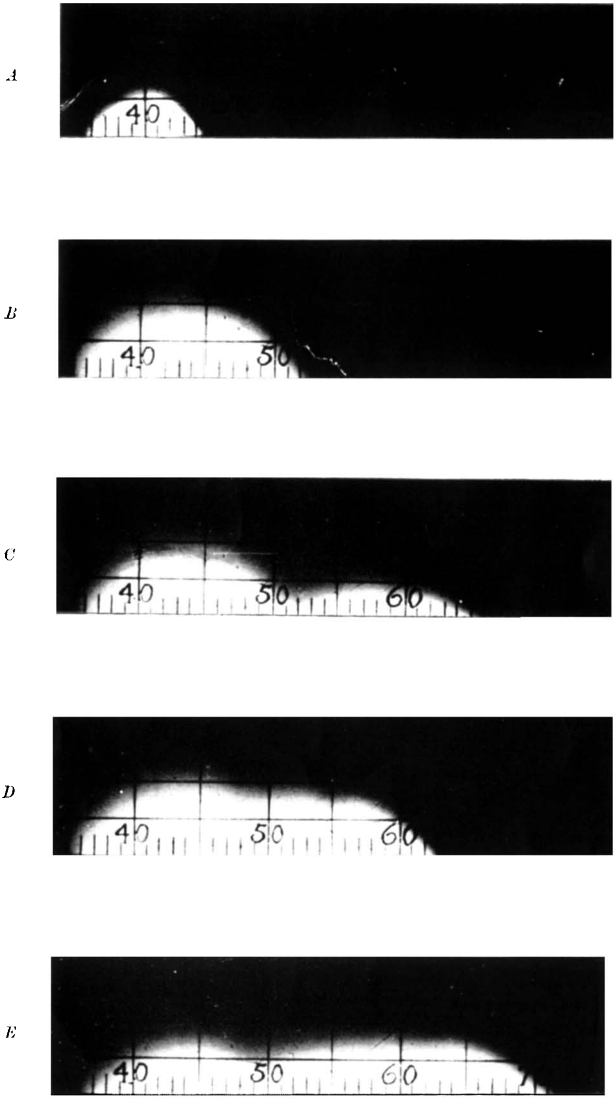
[89] L. Valentine, unpublished data.

In the oxidation of hydrocarbons there are also three possible termination reactions and in this case the assumption made is equivalent to a value of $\phi = 1$ for crossed termination. In the light of copolymerisation experiments it may be necessary to revise this view, although there seems to be some support for the original assumption in that the radicals are very similar and there is little variation in the values of termination constants as the hydrocarbon is varied.[20]

The Reviewer would like to record his thanks to Prof. P. D. Bartlett and Dr. M. S. Matheson for their help in forwarding manuscripts of unpublished papers and for other data incorporated in this review.



A chloride emulsion

B bromide emulsion

C *B* dyed with cyanine

D *B* dyed with *iso*cyanine

E *B* dyed with pinacyanol

PLATE 1

Wedge spectrograms.