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A Simple Dilatometric Method of Determining the Rate Constants of Chain Reactions. II. The Effect of Viscosity on the Rate Constants of Polymerization Reactions[1]

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The simple dilatometric technique previously reported has been used to measure the ratios k_t/k_p in mixed solvents whose viscosities could be adjusted over a 1000-fold range. With values of k_t/k_p^2 obtained from stationary state measurements and molecular weight determinations it has been possible to measure values of k_t and k_p for butyl acrylate and methyl methacrylate. In both cases k_p seems to be independent of viscosity. For methyl methacrylate k_t is inversely proportional to viscosity over the entire range (1000-fold). Termination in butyl acrylate is more complex and its k_t can be interpreted in terms of a model involving competition between translational diffusion and chemical activation. A kinetic scheme is presented for diffusion-controlled reactions. The results of three different molecular models are applied to the viscosity controlled termination constants for the acrylates and shown to bracket the data reasonably well.

A. Introduction

The evaluation of absolute rate constants of polymerization reactions usually involves the independent determination of different ratios of the constants. In the investigation of the propagation and termination reactions the ratios k_p/k_t and $k_p/k_t^{1/2}$ are the most readily obtained. The former can be determined from a dilatometric study[3] of the non-stationary phase of photo-sensitised polymerizations. The accuracy of this determination is augmented and not decreased by departures from isothermal stability of the system. The ratio $k_p/k_t^{1/2}$ may be evaluated from a study of the molecular weights of the polymer formed under stationary state conditions.

Rate constants k_p and k_t have been obtained for *n*-butyl acrylate and methyl methacrylate. Certain factors must be taken into account in the choice of a suitable solvent including monomer in which to study the reaction. It is necessary that the solvent be of low reactivity and preferably not susceptible to radical transfer reactions. In order to obtain significant information concerning the termination reaction the solvent should be of high solvating power for the polymeric as well as the monomeric material. If this is not the case reduced termination rates due to the "trapping" of radicals in polymer[4-6] or enhanced propagation rates[7] may be observed. It is also essential that the solvent be of low viscosity and that polymerization be carried only to low conversion, in order to avoid reduced termination rates due to the Trommsdorff or "gel" effect.[6] Neglect of these factors is suggested as a reason for the variation in values of radical lifetimes and hence the ratio k_p/k_t reported in the literature for these monomers.[8]

In spite of the current interest in the kinetics of high conversion polymerization and concomittant phenomena,[6,8] little attention has been paid to the use in these reactions of solutions of high viscosity. A viscous solvent permits study of the reaction without the presence of a high concentration of polymer, thereby eliminating crosslinking or gel formation. It is now currently accepted that in viscous media the termination reaction, involving two radical chains, becomes diffusion controlled, whereas the slower propagation reaction, involving the relatively small monomer molecule is little affected. In order to effect a rigorous kinetic analysis of such a system, it is necessary to introduce varying reactivities for radicals of different chain length. This difference is principally due to the variation in the diffusivity of the species. In this instance it has been possible to attribute changes in rate constants directly to the viscosity effect without the alternative possibility of effects due to pressure, as for example in the studies of Norrish on polymerizations at high pressure.[9] Hamann[10] has reported the role of high viscosities (obtained by the use of high pressure techniques) on some etherification reactions. He was able to show that viscosities of about 10^8 poises can be obtained in certain solvents at pressures of 4×10^4 atmospheres, and bimolecular etherification reactions are then diffusion controlled.

In the present work the effect of solvent viscosity at atmospheric pressure on the kinetics of polymerization is reported. In connection with the determination of the rate constants in viscous media, measurements were first made in non-viscous solvents and the results of these observations are reported as a preliminary section.

B. Experimental

Materials.—Reagent grade monomers were treated with NaOH soln. to remove inhibitors, washed and dried over anhydrous $CaSO_4$. The dry monomers were purified by a reduced pressure distillation under nitrogen through a 3 ft. column packed with Fenske helices at a reflux ratio of 10:1. Aliquot portions of the central fraction of the distillate were then outgassed on the vacuum line at pressures of less than 10^{-5} mm., prepolymerized to 10% conversion and residual monomer distilled directly into the reaction vessel, in this work the dilatometer filling vessel. Reagent grade volatile solvents were dried over sodium wire, fractionally distilled under nitrogen and then outgassed on the vacuum line. Traces of peroxides were decomposed by irradiation with ultraviolet light in the presence of small amounts of monomer.

Samples of polyethylene oxides were obtained from Union Carbide, Ltd. (Carbowax series), and polyethylene oxide polypropylene oxide block copolymers from Wyandotte

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(3) S. W. Benson and A. M. North, THIS JOURNAL, **80**, 5625 (1958).

(4) R. G. W. Norrish and R. R. Smith, *Nature*, **150**, 336 (1942).

(5) G. M. Burnett and H. W. Melville, *Proc. Roy. Soc.* (*London*), **A189**, 494 (1947).

(6) G. V. Schulz and G. Harborth, *Makromol. Chem.*, **1**, 104 (1947).

(7) R. H. Ewart, C. P. Rowe, J. R. McCartney and P. Debye, *J. Chem. Phys.*, **14**, 687 (1946).

(8) See for example: G. M. Burnett, "Mechanism of Polymer Reactions," Interscience Publishers, New York, N. Y., 1954, Chapter VII, Sections 3 and 4.

(9) F. M. Merret and R. G. W. Norrish, *Proc. Roy. Soc.* (*London*), **A206**, 309 (1951).

(10) S. D. Hamann, *Trans. Faraday Soc.*, **54**, 507 (1958).

Chemical Corp. (Pluronic and Tetronic series). These liquids are slightly hygroscopic, involatile surface active materials and consequently difficult to purify. The liquids were dried over anhydrous $CaSO_4$ and traces of aldehydes removed with solid sodium bisulfite. After treatment with activated charcoal, the liquids were outgassed on the vacuum line and subjected to ultraviolet irradiation in the presence of a trace of α,α'-azo-isobutyronitrile. Samples so treated exhibited constant viscosity, no inhibition or retardation of polymerisation and a transfer constant of the same order as ethyl acetate.

Apparatus.—All polymerization runs were prepared using the standard high vacuum techniques. Three types of dilatometer were used to follow the course of the reactions. The non-stationary phase of reactions in non-viscous media could be followed in conventional dilatometers only when the rate of radical decay was not greater than the rate of cooling of the dilatometer.[3] For cylindrical dilatometers of diameter 1 cm. and length 10 cm. cooling "half-lives" of about 50 seconds limited observation to a study of butyl acrylate. In order to study the radical decay of methyl methacrylate use was made of dilatometers which had high rates of cooling. These were constructed from a thin glass tube fitted into a tube of radius 1 mm. greater and with the ends joined by "Dewar" seals. In this way the liquid under observation is contained between two walls 1 mm. apart, and, the inner tube being open at each end allows efficient circulation of the thermostat bath water. Such dilatometers of volume 10 cc. had cooling "half-lives" of about 5 seconds. For observations of polymerizations in viscous media conventional mercury recording dilatometers were used.

The movement of the meniscus in the dilatometer stem was observed using a travelling microscope fitted with an eye-piece containing a graduated scale of length equivalent to 0.25 cm. For fast reactions the time that the meniscus crossed each scale division was recorded as an impulse from a telegraph key on a pen recorder geared to a chart speed of 8'' per minute. In this way impulses at intervals down to 0.3 second could be recorded and accurately measured. At shorter times the accuracy of determination is limited by the accuracy of the time of depression of the telegraph key, not by measurement of the trace.

Molecular weights were determined by viscosity measurements on benzene solutions of the polymers in standard high precision Ostwald viscometers. These had a flow time for solvent at 30° of 700 seconds. The viscosity of the polymerization solutions was measured in standard Ostwald viscometers and also in a "Falling-Ball" viscometer. The latter consisted of a precision capillary of length 40 cm. and diameter 2 mm. A precision stainless steel ball-bearing of diameter 1.7 mm. was allowed to fall down the capillary. The capillary was mounted in a vertical position on a rotating plate fitted with a "stop" to ensure that the position of the capillary was constant after rotation.

Cooling constants of the dilatometer and contents were measured before and after every polymerization run and were found not to change when polymerization was carried to low conversions. Under the same conditions the viscosity of polymerization mixtures was found to be unchanged before and after each run.

C. The Propagation and Termination Rate Constants in Non-viscous Media

In order to investigate the usefulness of the dilatometric method of determining the ratio k_t/k_p[3] and also verify the literature values of the ratio, determinations were made in non-viscous solvents chemically similar and also chemically dissimilar to the monomer and viscous solvents studied.

The value of k_t/k_p is obtained from experimental measurement of the rate of contraction of the dilatometer contents as a function of time in the post-irradiation period of a photo-initiated polymerization using the equation[3]

$$(\Phi - 1)e^{\kappa t} = A_0B + A_1Be^{(\kappa - k_1)t} \qquad (1)$$

where Φ is the ratio of the rate of contraction at a time, t, after cessation of illumination to the rate of contraction after infinite time (*i.e.*, the "dark" rate) κ is the Newtonian cooling constant of the system, $B = \alpha H/\gamma\sigma\rho$ where α is the coefficient of thermal expansion of the liquids in the dilatometer. H is the molar heat of the polymerization reaction, γ is the % volume change for 1% monomer reaction, σ is the specific heat and ρ the density of the liquid contents. k_1 is given by $2k_tR_d/k_p(\mathrm{M})$ where R_d is the rate of contraction after infinite time; A_0 and A_1 are constants of integration.

The function on the left-hand side is experimentally measurable, so that by choosing three times and the corresponding rates of contraction it may be treated as three simultaneous equations in the three unknowns A_0B, A_1B and k_1. Solving only for k_1 leads directly to k_t/k_p. In practice, we have found it convenient to use this algebraic method to solve for the quantity A_0B whereupon a plot of $\ln[(\Phi - 1)\exp(\kappa t) - A_0B]$ against t, will give a line of slope $\kappa - k_1$ and intercept $\ln(A_1B)$ (see 1st paper).

n-Butyl acrylate was studied in the monomer as solvent and also in benzene, ethyl acetate and n-butyl propionate. It was observed that neither benzene nor the monomer itself was a "good solvent" for the polymeric material. This was illustrated by the onset of gelation (accompanied by increased rates of polymerization and reduced rates of termination) at low conversion. The ratio k_t/k_p was determined in monomer as solvent at varying concentrations and was found to exhibit increasing values at conversions as low as 1%. The results of these determinations are set forth in Table I. While the determinations of the ratio in the "poorer" solvents, benzene and monomer, show good agreement with the literature value, it is apparent that the increase in k_t in the "better" solvents represents a more reliable value. The choice of the two esters as solvents in which to study the polymerization is justified by the low transfer coefficients reported[11-15] and by qualitative measurement of the solubility of polybutyl acrylate

TABLE I[a]

VALUES OF THE RATIO k_p/k_t AT 30° FOR n-BUTYL ACRYLATE IN VARIOUS SOLVENTS

Solvent	$k_p/k_t \times 10^4$	$R_p \times 10^4$	$t_{1/2}$, sec.
Monomer	12.5	27.3	75
Benzene	14.1	15.8	75
Ethyl acetate	8.33	1.46	57
n-Butyl propionate	8.40	2.76	53
Monomer	15.	(Melville and Bickel[16] extrapolated from 25°)	

[a] The rate of polymerization during the photostationary light period, R_p, the corresponding half-life of the radicals, $t_{1/2}$, and one literature value are included for comparative purposes. Units of R_p are mole/liter-sec.

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(11) K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946).

(12) S. Palit and S. K. Das, *Proc. Roy. Soc.* (*London*), **A226**, 82 (1954).

(13) G. M. Burnett and H. W. Melville, *ibid.*, **A189**, 456, 495 (1947); *Faraday Soc. Disc.*, 322 (1947).

(14) S. Basu, J. N. Sen and S. R. Palit, *Proc. Roy. Soc.* (*London*), **A202**, 485 (1950).

(15) S. K. Das, S. R. Chatterjee and S. R. Palit, *ibid.*, **A227**, 252 (1955).

TABLE II

VALUES OF THE RATIO k_p/k_t FOR METHYL METHACRYLATE IN VARIOUS SOLVENTS

Temp., °C.	Solvent	$k_p/k_t \times 10^5$	$R_p{}^a \times 10^5$	$t_{1/2}$, sec.	
40	Ethyl acetate	2.3	2.5	22	M
30	Monomer	4.0	1.7	54	
30	Ethyl acetate	1.4	1.7	17.5	
30	Diethyl ether	4.6	2.5	22	
30	Monomer	0.7	(extrap. from 23.6° ref. (17)-sector)		
30	Monomer	1.2		(ref. (18)-sector)	
30	Monomer	5.4	(extrap. from 0°)	(ref. (19)-viscosity)	
30	Monomer	1.3	(extrap. from 15°)	(ref. (20)-thermal)	
30	Monomer	1.1	(ref. (21)-sector)		

[a] R_p in units of liter/mole-sec.

with the concentration corresponding to gel formation.[16]

Methyl methacrylate was studied in the monomer as solvent and also in ethyl acetate and diethyl ether. A considerably prolonged photo-after effect is observed with this monomer. For this reason only those studies carried out at exceptionally low conversions and at times when the rate of polymerization is appreciably greater than the dark rate were considered for the determination of the rate constants. The results of these determinations, together with some literature values are set forth in Table II. The literature values of this ratio, with the exception of that obtained from a study of viscosity agree rather closely with an average of 1.1. While the value observed in ethyl acetate as solvent is in agreement with this, our experimental determination in monomer as solvent was conducted in rather a higher conversion and is consequently felt to be somewhat in error. Again an increase in the ratio is observed in the "poor solvent," diethyl ether.

The molecular weights of polymethyl methacrylates prepared in ethyl acetate under stationary state conditions were determined from viscosity measurements using the relationship between intrinsic viscosity and number average molecular weight of Baxendale, Bywater and Evans.[22] From the plot of reciprocal degree of polymerization against the rate of polymerization, Fig. 1, the ratios $k_p/k_t^{1/2} = 9.64 \times 10^2$ and $k_f/k_p = 2.0 \times 10^{-5}$ were obtained. Since all the polymerizations were carried out at a constant solvent/monomer ratio, k_f is a measure of the combined transfer to monomer and to solvent. From these three ratios of the various rate constants, individual values were obtained as: $k_p = 404$, $k_t = 1.76 \times 10^7$ and $k_f = 8.08 \times 10^{-3}$, all liter/mole sec. at 40°.

D. Studies in Viscous Media

A determination of the independent rate constants for the polymerization of methyl methacrylate in a solution of visocsity 120 cp. at 40° was made. Using the dilatometric method of studying the non-stationary phase of the reaction the ratio k_t/k_p was found to be 2.15×10^2.

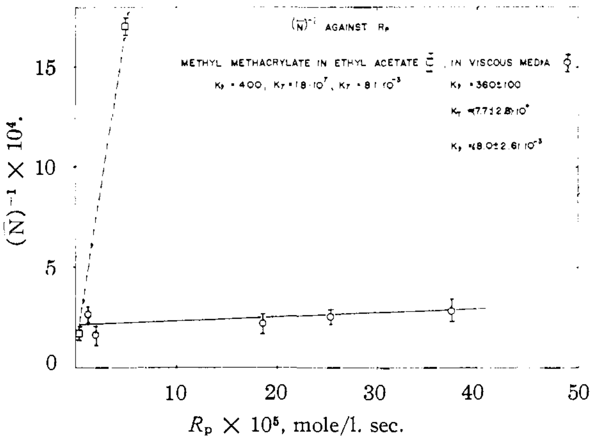

Fig. 1.—Inverse degree of polymerization against rate of polymerization: methyl methacrylate in ethyl acetate ☐ and in polyethylene oxide–polypropylene oxide copolymer ○ at 40°.

A study of the molecular weights of the polymers formed at different rates of polymerization was carried out by viscosity measurements. The results of such a study are plotted on Fig. 2. On the same figure are plotted the results of molecular weight determinations of polymers prepared in ethyl acetate. The slope of the plot of reciprocal degree of polymerization against the rate of polymerization in viscous medium is so small that the error of its measurement is large. However, from this plot the ratio k_t/k_p^2 is obtained as 0.60 ± 0.30, and from the intercept the ratio k_f/k_p is $4.0 \pm 1.0 \times 10^{-5}$. These three ratios allow the individual rate constants to be evaluated as, $k_p = 360 \pm 100$, $k_t = 7.7 \pm 2.8 \times 10^4$ and $k_f = 8.0 \pm 2.6 \times 10^{-3}$ all liter/mole sec. It is at once apparent that the propagation rate constant is the same as that in non-viscous media, of 1/300 the viscosity, within the limits of experimental error.

Since the determination of the individual rate constants necessitates the preparation and molecular weight determination of a number of polymers and since the determination of the ratio k_t/k_p^2 is inaccurate in solutions of high viscosity, it was decided to make use of the assumption that the propagation rate constant, found to have the same

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(16) H. W. Melville and A. F. Bickel, *Trans. Faraday Soc.*, **45**, 1049 (1949).

(17) H. W. Melville and M. H. Mackay, *ibid.*, **45**, 323 (1949).

(18) M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, THIS JOURNAL, **71**, 497 (1949).

(19) C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc.* (*London*), **A197**, 356 (1949).

(20) N. Grassie and H. W. Melville, *ibid.*, **A207**, 285 (1951).

(21) L. Valentine Thesis, Aberdeen, 1949.

(22) J. H. Baxendale, S. Bywater and M. G. Evans, *Trans. Faraday Soc.*, **42**, 237 (1946). Using the relation of J. Bischoff and V. Desreux, *J. Poly. Sci.*, **10**, 437 (1953), would change all values of k_p by less than 15% and k_t by less than 30%.

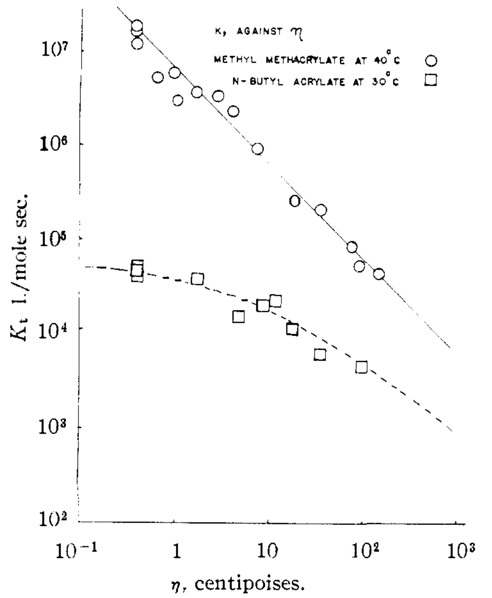

Fig. 2.—Termination rate constant against solvent viscosity: □, methyl methacrylate at 40°, O, *n*-butyl acrylate at 30°.

value at viscosities of 0.4 and 120 cm. is constant over the whole range of intermediate viscosities. Since the internal pressure of such a system of solvents would be expected to be constant over the range and since the viscosity of such a solvent seems to be due to frictional interactions of the large solvent molecules rather than due to specific intermolecular attractions, such an approximation does not seem unreasonable. Any variation in k_p would be less than the experimental error incurred by molecular weight measurements.

The value of k_p was therefore measured carefully at a viscosity of 0.4 cp., and this value, 404 liter/mole-sec., adopted as a constant value over the viscosity range. In order to evaluate k_t, it was now only necessary to measure the ratio k_t/k_p, which could be done accurately in the solutions of high viscosity.

Using various mixtures of ethyl acetate and polyethylene oxide–polypropylene oxide co-polymer, it was found that the solvent viscosity could be varied continuously from 0.400 to 1000 cp. Using a 1.56 molar solution of monomer in this range of solvents, determinations were made of the ratio k_t/k_p for methyl methacrylate at 40° and for *n*-butyl acrylate at 30°. The determinations at the lower temperature are hampered by the fact that the cloud points of the solvent and of polymer solutions in the viscous solvent lie in this temperature region. The appearance of opacity in the solution causes light absorption and polymerization rates to be non-uniform and consequently less precise.

Calculation of the termination rate constant using the single value for the propagation rate constant yielded values which decreased regularly with increasing viscosity as are illustrated in Fig. 2. It is apparent immediately that in the case of methyl methacrylate the termination reaction is dependent on viscosity, as inverse first power, even in the "non-viscous" solvents. It is therefore meaningless to refer to the termination of this monomer as becoming diffusion controlled with increasing viscosity, since under normal conditions it is already viscosity dependent. In this case the measured termination rate constant, k_t, is a direct measure of the "diffusion rate constant," k_d (see eq. 6). The "chemical rate constant" for the termination of this monomer is too high to measure.

The termination of *n*-butyl acrylate expresses a more complex dependence on viscosity over this range. At viscosities close to those of normal solvents it appears to be almost independent of the viscosity of the solution, as would be the case if the reaction was controlled by a slower chemical step. At increasing viscosities the reaction becomes more dependent upon the viscosity of the solution until at the region around 10^2 to 10^3 cp. it is again dependent upon the inverse first power of the solution viscosity. This behavior may be interpreted as an increasing diffusion control of a reaction in which the "diffusion" and "chemical" rate constants are of the same order of magnitude.

The discussion of these observations is aided by the use of a model of the kinetic scheme for diffusion controlled reactions which is provided in the following section.

E. Propagation and Termination Rate Constants in Viscous Solvents

The bimolecular reaction between two molecular species present in low concentration in solution can be regarded as a successive, three state process. First two molecules must come into contact, a process dependent on the diffusion constants of the species in solution. Secondly the reactive parts of the molecules must come within a certain distance of each other and possibly assume a certain configuration. Thirdly, after all positional factors are favorable, chemical reaction takes place. For most chemical reactions in normal solution the third process requires large activation energies and is the slowest and rate-determining step of the three. But for many fast reactions such as the termination of free radicals, the first and second steps may be slower than the third and the reaction is then said to be "diffusion controlled."

This three stage mechanism for the termination of free radicals $\mathrm{R}_{\dot{A}}$ and $\mathrm{R}_{\dot{B}}$ can be represented by

$$\mathrm{R}_{\dot{A}} + \mathrm{R}_{\dot{B}} \underset{2}{\overset{1}{\rightleftarrows}} (\mathrm{R}_{\dot{A}}.\mathrm{R}_{\dot{B}})$$

$$(\mathrm{R}_{\dot{A}}.\mathrm{R}_{\dot{B}}) \underset{4}{\overset{3}{\rightleftarrows}} (\mathrm{R}_A\text{:}\mathrm{R}_B)_p$$

$$(\mathrm{R}_A\text{:}\mathrm{R}_B)_p \xrightarrow{c} \text{Stable Products } (e.g.\ \mathrm{R}_A\mathrm{R}_B) \quad (2)$$

Here $(\mathrm{R}_{\dot{A}}.\mathrm{R}_{\dot{B}})$ represents the pair of radicals in collision but not having the correct orientation for chemical reaction, while $(\mathrm{R}_A\text{:}\mathrm{R}_B)$ represents the collision pair with all active groups in proper orientation. By including the reverse step to the chemical reaction, c, it is possible to include the interesting case of cage effects in unimolecular or bimolecular decompositions. If stationary state kinetics are applied to this scheme, assuming that $(\mathrm{R}_{\dot{A}}.\mathrm{R}_{\dot{B}})$ and $(\mathrm{R}_A\text{:}\mathrm{R}_B)_p$ are present in small concentration, the rate of formation of products is given by

$$\frac{\mathrm{d\ Prod}}{\mathrm{d}t} = \frac{k_1k_3\left[\frac{k_c}{k_4 + k_c}\right]}{k_2 + k_3\left[\frac{k_c}{k_4 + k_c}\right]}(\mathrm{R_A^{\cdot}})(\mathrm{R_B^{\cdot}}) \qquad (3)$$

Assuming that the over-all radical concentration is low (*i.e.*, precluding such rapid initiation that the equilibrium concentration of collision pairs is not proportional to the square of the radical concentration) k_t, the second-order termination constants is given by

$$k_t = \frac{k_1k_3\left(\frac{k_c}{k_4 + k_c}\right)}{k_2 + k_3\left(\frac{k_c}{k_4 + k_c}\right)} = \frac{k_1k_3}{k_2k_4}\left\{\frac{\frac{k_4k_c}{k_4 + k_c}}{1 + \frac{k_3}{k_2}\left(\frac{k_c}{k_4 + k_c}\right)}\right\} \qquad (4)$$

In the case of a very slow chemical reaction, $k_c << k_4$ and this reduces to

$$k_t = \frac{k_1k_3k_c}{k_2k_4\left[1 + \frac{k_3k_c}{k_2k_4}\right]} = \frac{K_pk_c}{1 + K_p\frac{k_c}{k_1}} \qquad (5)$$

where $K_p = k_1k_3/k_2k_4$ is the equilibrium constant for the formation of active pairs. In the sense employed here $(\mathrm{R_A{:}R_B})_p$ is not to be identified with a transition state species but rather with a loose "near-neighbor" or "cage" complex. When $k_1 << K_pk_c$ this reduces further to the diffusion controlled rate $k_t \rightarrow k_1$. In the other extreme $k_1 >> K_pk_c$, then $k_t \rightarrow K_pk_c$ and diffusion plays no role in the reaction scheme.

When the chemical step is very fast, $k_c >> k_4$ and equation 3 reduces to

$$k_t \longrightarrow \frac{k_1k_3}{k_2 + k_3} = k_d \qquad (6)$$

which would be the rate constant for a wholly diffusion controlled reaction. The constants k_1 and k_3 refer to the two different kinds of diffusion processes of which at present only k_1, the rate constant related to translational diffusion is accessible to independent measurement. The constant k_3 has different meanings depending upon the physical models chosen to interpret the reaction. For simple, small radicals the formulation of k_t in terms of their diffusion constants is relatively simple since such species can be represented by hard spheres. This is also true of large, closely coiled molecules such as proteins whose shapes may be well defined. The problem of specifying models for long chain molecules whose configurations may change considerably in time is more difficult. Three different models have been investigated, and the theoretical implications of these will be reported in detail in a subsequent publication. Their results however will be used here in the last section.

F. Discussion

For a process in which chemical activation and diffusion play comparable roles, such as the termination process in butyl acrylate, equation 4 provides a method of analysis. If the data of Fig. 2 be expressed in the manner of equation 4, we have after rearrangement

$$\frac{1}{k_t} = \frac{1}{k_1} + \frac{k_4k_2}{k_1k_3}\left(\frac{1}{k_4} + \frac{1}{k_c}\right) = \frac{1}{k_1} + \frac{1}{K_p}\left(\frac{1}{k_4} + \frac{1}{k_c}\right) = \frac{1}{k_d} + \frac{1}{k'_c} \qquad (7)$$

where k_d has been defined by equation 6 and k_c' represents $K_p{\cdot}k_c$. If k_d can be represented by k_d'/η where η is the solution viscosity (as has been suggested by experimental observation), the over-all termination rate constant is given by

$$\frac{1}{k_t} = \frac{\eta}{k_d'} + \frac{1}{k_c'} \text{ or } k_t = k_c' - \frac{k_c'}{k_d'}(k_t\eta) \qquad (8)$$

k_c' and k_d' may then be found from a plot of k_t against $k_t\eta$.[23]

Data for the termination of butyl acrylate plotted in this way are illustrated in Fig. 3. From Figs. 2 and 3 the values of k_c' and k_d' for the two monomers are obtained as

Methyl methacrylate, $k_d' = 6.3 \times 10^6$; at 40° (k_c' unmeasurable, but) $\geqslant 10k_d' \geqslant 6 \times 10^7$

Butyl acrylate at 30° $k_d' = 7.0 \times 10^5$; $k_c' = 4.9 \times 10^4$

with k_d' in units of liter-cp./mole sec. and k_c' in liter/mole sec.

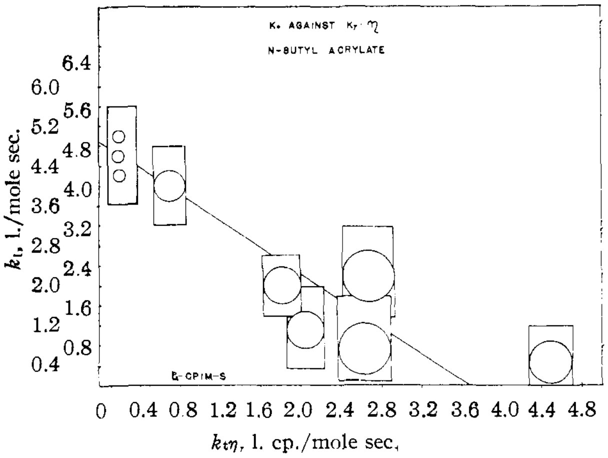

Fig. 3.—Termination rate constant against the product termination rate constant × solvent viscosity; *n*-butyl acrylate at 30°.

From these figures it is possible to draw certain conclusions. The diffusion processes in the case of methacrylate are 10 times faster than those of butyl acrylate. It seems more likely that this difference arises in k_3 than in k_1. Even more remarkable is the fact that the chemical termination constant of methyl methacrylate is at least a thousand times larger than that for butyl acrylate. Since $k_c' = k_c{\cdot}K_p$, part of this difference may lie in differing values of the equilibrium constant, K_p.

It is unlikely that this difference could exceed the value of ten encountered as the ratio of the diffusion rate constants for the two species. It therefore remains that the chemical, inter-radical reaction of methyl methacrylate is at least one hundred times as fast as that for butyl acrylate, a difference suggesting that the activation energy of the reaction in the case of the butyl acrylate is at least 3 kcal./mole greater than in the case of methyl methacrylate.

Also from the values of the constants k_c' and k_d' it is apparent that the termination of butyl acrylate will become diffusion controlled only when k_d'/η is

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[23] For graphical purposes this is a more sensitive method of plotting than that given by $1/k_t$ against η.

considerably less than 5×10^4 liter/mole sec. that is when η is considerably greater than 15 cp. In view of the current interest in high conversion polymerization, it appears that information yielded by a study such as this, combined with a knowledge of the viscosity of polymer solutions as a function of concentration, can suggest a concentration at which the "gel-effect" will become important (in absence of cross-linking reactions).

Three models representing the bimolecular termination reaction of macroradicals in solution have been investigated. These will be discussed in detail in a subsequent publication, but the comparison of numerical values derived theoretically from these models with the experimental results is appropriate at this point.

The first model has been conveniently named the "Ball and Chain" model. The reaction is simplified by considering the reaction as occurring when two methyl radicals (the chain ends) diffuse together with a mobility characterized by the diffusion constant for the polymer chain. In this way all the diffusion processes are reduced into a consideration of one translational diffusion. Such a model predicts a diffusion controlled termination constant for radicals A terminating with radicals, B

$$k_d = \frac{2RTP_{AB}r_{AB}}{3{,}000\eta x_0}\left(\frac{1}{n_A^{1/2}} + \frac{1}{n_B^{1/2}}\right) \qquad (9)$$

where r_{AB} is the radius of the sphere into which the two methyl radicals diffuse in order to be close enough to react, in this case considered as the diameter of a methyl group. P_{AB} is a probability factor to correct for the fact that radicals are attached to long chains which may prevent interdiffusion from certain angles; n_A and n_B are the number of monomer units in each chain; x_0 is the length of a carbon–carbon bond in the chain.

The model predicts the observed dependence of the constant upon the inverse first power of viscosity and also predicts that it is inversely proportional to the square root of the chain length of the species involved. Choosing as representative values for a polymerization system $\eta = 1 \times 10^{-2}$ poises, $r_{AB} = 3 \times 10^{-8}$ cm., $x_0 = 1.5 \times 10^{-8}$cm., $P_{AB} = 1/4$, and assuming that the average rate constant can be obtained from this formula by substitution of an average radical size, 10^3 monomer units, k_d is found to be 7×10^7 liter/mole sec., or $k_d' = 7 \times 10^7$ liter cp./mole sec. This value of k_d' is seen to be about ten times higher than the value encountered for methyl methacrylate but may be considered as a maximum possible value for the diffusion rate constant for a polymer of such a chain length.

The second model which has been investigated is the "Rigid Sphere" model. The polymer chains are assumed to be solid spheres in solution with the radical end occupying a certain small area on the surface of the sphere. The translational diffusion rate constant is calculated using the usual diffusion formula, and the positional diffusion is approximated by the probability that the areas containing the radical ends are the areas of the spheres which come into contact. The distance between contact and non-contact is then postulated as the diameter of one solvent molecule. This yields the expression

$$k_d = \frac{RT}{3.8 \times 10^4\pi^2\eta}\left(\frac{\sigma_E^4}{\sigma_s x_0^3}\right)\left[\frac{1}{n_A^{1/2}} + \frac{1}{n_B^{1/2}}\right]^3 \qquad (10)$$

where σ_E^2 is the cross sectional area of the chain ends, σ_s is the diameter of a solvent molecule and the other symbols are defined as before (eq. 9).

This model predicts that the rate constant is again proportional to the inverse first power of viscosity but predicts that it is inversely proportional to the chain length to the power 3/2. Since $\sigma_s \sim \sigma_E \sim 3 \times 10^{-8}$ cm. and again assuming an average value of 10^3 for n_A and n_B, a value of 2×10^4 liter/mole sec. is predicted for k_d, or $k_d' = 2 \times 10^4$ liter cp./mole sec. This value is lower than the experimental results. However, the model is not a true picture of the behavior of polymer chains in a "good" solvent, since it neglects the mobility of the radical end groups.

The third model which has been considered is that suggested by the hydrodynamic treatments of linear polymers. The polymer chains are represented by a random coil with a Gaussian distribution of mass from the center of gravity. Solvent molecules can then diffuse through the outer regions of the coil, and collisions between coils are inelastic, occurring with some interpenetration of the coiled chains. The translational diffusion rate constant is calculated using standard hydrodynamic formulas for such a system and configurational diffusion computed from the rate of diffusion of the radical chain ends in the volume of interpenetration during the collision. Such a treatment leads to an over all diffusion rate constant

$$k_d = 5 \times 10^{20}\,\frac{D_E^2\eta}{T}\left[\left(\frac{n_A}{n_B}\right)^{1/4} + \left(\frac{n_B}{n_A}\right)^{1/4}\right]^2 \qquad (11)$$

where D_E is the "internal" diffusion constant of the chain end over a small distance in the outer portion of the polymer coil. Since in a good solvent in the outer region of the polymer coil the chain end is almost surrounded by a nearest neighbor shell of solvent molecules, D_E is inversely proportional to solvent viscosity, and the over all diffusion rate constant will be inversely proportional to the first power of viscosity. This expression predicts that in a monodisperse system the termination rate constant is independent of the chain length (neglecting the fact that in non-ideal solvents D_E will have a slight dependence upon chain length). Also in heterodisperse systems the dependence upon chain length is much less than that predicted by the other models.

Assuming that D_E in a good solvent might have a value of $D_S/3$ where D_S is the self diffusion constant for the solvent and that termination occurs predominately between small and large radicals, it is possible to obtain an approximate value for k_d. Choosing a value of 1×10^{-5} for D_S at a viscosity of 1×10^{-2} poises and assuming that on the average radicals of chain length 50 react with those of length 1000, the diffusion rate constant is evaluated as $k_d = 1.1 \times 10^6$ liter/mole sec. or $k_d' = 1.1 \times 10^6$ liter cp./mole sec. This value is seen to lie between the two observed values and is in fair agreement with the experimental results.

The approximate values predicted by the three models are only reported here as a comparison with measured rate constants. The detailed discussion of the merits and flaws of the models, as well as their more rigorous application to hetero-disperse systems, will be reported in the subsequent publication.

In conclusion it may be stated that the dilatometric method of measuring the ratio k_t/k_p has been found effective over a viscosity range from 0.4 to 200 cp., and values of the termination and propagation rate constants have been calculated from this ratio over the range. Whereas the propagation (and also the transfer) rate constant is unchanged, the termination constant undergoes a considerable reduction. A consideration of the termination reaction as being composed of successive diffusion and chemical processes reveals that the termination of methyl methacrylate is diffusion controlled over the complete range, whereas the slower termination of butyl acrylate is only diffusion controlled at viscosities greater than 15 cp. Both experimental and preliminary theoretical considerations postulate that the diffusion controlled rate constant be proportional to the inverse first power of the solvent viscosity. Unfortunately the experiments performed here were not sufficiently precise as to be able to observe any dependence of the termination rate constant upon the chain length of the radicals involved.

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, UNION CARBIDE CHEMICALS COMPANY]

The Polymerization of Styrene by *n*-Butyllithium[1]

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The rate of polymerization of styrene initiated by *n*-butyllithium has been studied at temperatures from 20 to 50° in benzene and toluene solution. For *n*-butyllithium concentrations less than 0.020 *M* the rate of propagation is proportional to the concentrations of both catalyst and styrene. For higher catalyst concentrations the rate is proportional to the monomer concentration but independent of the catalyst concentration. The degree of polymerization is determined by the ratio of monomer to catalyst. There is no termination reaction, and the rate of initiation is about one-fifth the rate of propagation. The activation energy for propagation is 17 kcal./mole. A polymerization mechanism is proposed to explain these observations.

Introduction

Although there have been many investigations of the kinetics of the cationic polymerization of styrene,[2] the quantitative aspects of the anionic polymerization of this monomer have received little attention. Noteworthy among the few papers on this subject is an excellent study of the kinetics of polymerization in liquid ammonia initiated by potassium amide by Higginson and Wooding.[3] More recently, Korotkov investigated the polymerization of dienes and their copolymerization with styrene in the presence of alkali metal alkyls.[4]

The use of lithium alkyls as catalysts for the polymerization of styrene has been described.[5,6] Although this polymerization proceeds with extreme rapidity in tetrahydrofuran solution,[5] we have found that in hydrocarbon solvents the polymerization is much slower, requiring about 0.5–4.0 hr. for complete conversion at room temperature. In order to learn more about the mechanism of this polymerization, a study of the kinetics of the reaction was undertaken. Since aromatic hydrocarbons are good solvents for both polystyrene and the reactants, benzene and toluene were used as diluents. All of the polymerizations described herein proceeded homogeneously.

Experimental

Materials.—Commercial styrene (Union Carbide Chemicals Company) was distilled at 20 mm. pressure from Linde 5-A Molecular Sieve immediately before use and stored over Molecular Sieve or calcium hydride. Reagent grade benzene or toluene was dried by passing through a column of Molecular Sieve directly into the reaction vessel or by storing over Molecular Sieve or calcium hydride. *n*-Butyllithium was prepared in 60–80% yields from *n*-butyl chloride and lithium metal sand in benzene or hexane solution.[7] The lithium chloride was allowed to settle and the clear, supernatant liquid was transferred and stored under nitrogen. The concentration was determined by acid titration.

Molecular Weight Dependence.—All operations were conducted with the rigorous exclusion of air and moisture. The apparatus consisted of a one-liter flask fitted with a stirrer, thermometer and 125-ml. graduated dropping funnel. The top of dropping funnel was connected through a three-way stopcock to flasks containing benzene and styrene, respectively, stored over calcium hydride. The reaction flask and dropping funnel were dried by heating to about 100° at 0.5 mm. pressure. High purity nitrogen was used to break the vacuum. Styrene, 50–100 ml., was transferred to the graduated dropping funnel by applying nitrogen pressure to the styrene reservoir. After determining the volume, it was transferred to the reaction flask. Benzene, 400 ml., was similarly added to the flask. An accurately measured quantity (0.001–0.025 mole) of *n*-butyllithium solution was added with stirring from a calibrated pipet at room temperature. Polymerization began almost immediately and was essentially complete in 0.5–2.0 hr. External cooling was applied when necessary to keep the temperature below about 70°. Otherwise no attempt was made to control temperature in these runs. The polystyrene was recovered by precipitation in methanol, washed thoroughly with methanol and dried. Yields were quantitative. Intrinsic viscosities were determined in benzene solution at 30°.

Rate Measurements.—Reactants were mixed in a 100-ml., graduated volumetric flask fitted with a stopcock in the

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[1] Presented in part at the 133rd Meeting of the American Chemical Society, San Francisco, April, 1958.

[2] D. C. Pepper, *Quart. Rev.* (*London*), **8**, 114 (1954).

[3] W. C. E. Higginson and N. S. Wooding, *J. Chem. Soc.*, 760 (1952).

[4] A. A. Korotkov, Paper presented at the International Union of Pure and Applied Chemistry Meeting, Prague, Sept., 1957; *Angew. Chem.*, **70**, 85 (1958).

[5] M. Morton, H. L. Stephens and J. L. Hall, Paper presented at the 132nd Meeting of the American Chemical Society, New York, Sept., 1957.

[6] A. Zilkha, M. Albeck and M. Frankel, *J. Chem. Educ.*, **35**, 345 (1958).

[7] T. D. Perrine and H. Rapoport, *Anal. Chem.*, **20**, 635 (1948).