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Autoacceleration of Free-Radical Polymerization. 2. Methyl Methacrylate[1]

H. B. Lee and D. T. Turner*

Dental Research Center, University of North Carolina at Chapel Hill,
Chapel Hill, North Carolina 27514. *Received April 16, 1976*

ABSTRACT: The polymerization of methyl methacrylate was followed by dilatometry, mainly using benzoyl peroxide (0.2 to 15 wt %) as initiator at 50 and 70 °C, through the critical concentration for onset of autoacceleration in rate, ρ_p (g polymer/cm^3). Values of the number average degree of polymerization of the product below the critical concentration, $\overline{Z}_n$, were estimated from rate data and from measurements of solution viscosity. The relationship between these two measured quantities was compared with a theoretical equation derived previously on the thesis that the onset of autoacceleration corresponds to the close packing of macromolecules with unperturbed dimensions which behave as rigid spheres. A fair measure of agreement was obtained for $\overline{Z}_n < 1 \times 10^3$, i.e., experimental values of ρ_p exceeded theoretical values by not more than 30%. The discrepancy increased up to about 50% for $\overline{Z}_n > 2 \times 10^3$.

A case was made previously that the onset of autoacceleration in the rate of free-radical polymerization of methyl methacrylate occurs at the polymer concentration which corresponds to macromolecular close packing. It was assumed that the macromolecules behave as rigid spheres having a radius which can be related to values reported in the literature for unperturbed dimensions. The evidence adduced in support of this case was limited to an analysis of previously reported data.[2a] The objective of the present work is to extend data by means of experiments based mainly on the polymerization of methyl methacrylate initiated by thermal decomposition of benzoyl peroxide. Previously this system was investigated in most detail by Schulz and Harborth for peroxide concentrations up to 2 wt %.[2b] In the present work this concentration is extended up to 15 wt % in order to include data for poly(methyl methacrylate) (PMMA) of unusually low molecular weight. In order to cover the other extreme of the molecular weight spectrum, polymeric products of unusually high molecular weight were prepared in experiments without added initiator at 37 °C.

In more detail, the objective of the present work is to check the conformity of experimental data to the theoretical eq 1. This equation applies for PMMA with a random molecular weight distribution (cf. eq 16 of part 1 with $\overline{M}_n = 100\overline{Z}_n$).

$$\rho_p = 1.5 \times 10^{-24}\overline{Z}_n{}^{-1/2}\left(\frac{\overline{r_0{}^2}}{M}\right)^{-3/2} p_f \qquad (1)$$

In eq 1, ρ_p (g polymer/cm^3) is the critical concentration of PMMA at the onset of autoacceleration in the rate of polymerization. $\overline{Z}_n$ is the number average degree of polymerization of all the PMMA present at the critical concentration. Values of $(\overline{r_0{}^2}/M)^{1/2}$ are tabulated in the literature.[3] The macromolecular packing fraction, p_f, has a maximum value of 0.74 for uniform rigid spheres.

Experimental Section

Inhibitor was removed from methyl methacrylate (Polyscience Inc., Warrington, Pa.) by repeated extraction with aqueous NaOH (2%). The monomer was then repeatedly washed with distilled water and dried over $CaCl_2$. Finally, monomer was distilled under aspirator vacuum and a middle fraction selected (bp 30–35 °C). Benzoyl peroxide (Wallace and Tierman, Inc., Belleville, N.J.) was kept refrigerated in order to minimize decomposition and was used without purification.

A weighed amount of peroxide was dissolved in purified monomer and the mixture was transferred to a calibrated 1-ml pipet, which had been sealed at one end, of intermal diameter 2.8 mm and wall thickness 0.6 mm. The pipet was then immersed in a water bath maintained at constant temperature ±0.1 °C. After an induction period, usually of several minutes, the liquid began to contract and the level of the meniscus was noted periodically. At temperatures of 50 and 70 °C the course of the reaction could be followed satisfactorily to some way beyond the onset of autoacceleration. At higher conversions the method became unsatisfactory because the high viscosity of the reaction mixture resulted in poor definition of the meniscus and eventually to formation of voids.

Table I
Data Used to Calculate Values of $\bar{Z}_n$

T, °C	30	40	50	60	70	80	90
k_p	251	322	410	515	650	800	
$k_{td} \times 10^{-7}$	0.6	0.75	0.95	1.1	1.35	1.60	
$k_{tc} \times 10^{-7}$	1.5	1.5	1.45	1.45	1.4	1.45	
[M], ml^{-1}	9.294	9.183	9.074	8.969	8.865	8.764	
V_m, g^{-1} cm^3	1.076	1.089	1.102	1.115	1.128	1.141	3.39^a
A	0.403	0.582	0.826	1.17	1.57	2.11	2.75

[a] This is an extrapolated value obtained from a linear plot of log A vs. the reciprocal of absolute temperature.

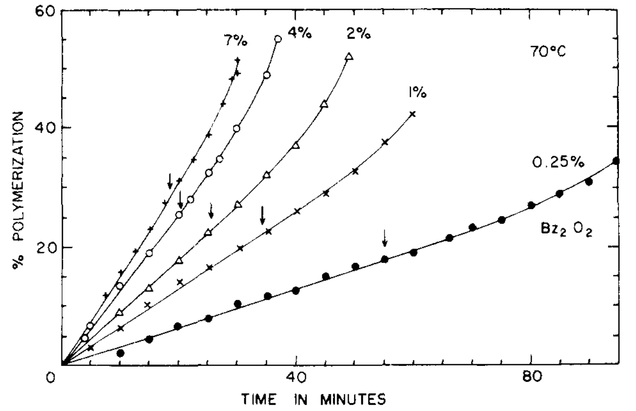

Figure 1. Polymerization of methyl methacrylate with 0.25 wt % benzoyl peroxide at 70 °C. In this and succeeding figures inhibition times are omitted.

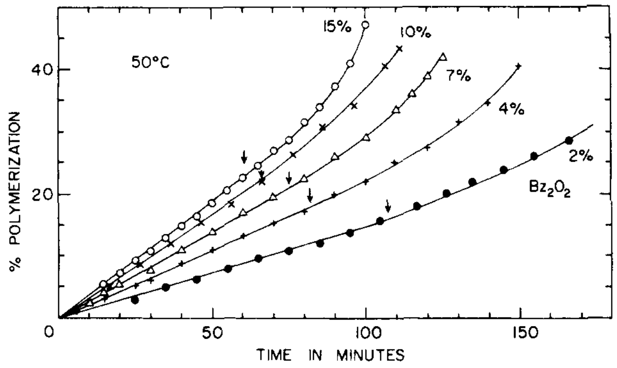

Figure 2. Polymerization of methyl methacrylate with 2.0 wt % benzoyl peroxide at 50 °C.

In some experiments the above procedure was modified in order to carry out the reaction in the absence of oxygen. In such cases the mixture of monomer and peroxide was thoroughly degassed by repeated cycles of freezing and thawing under vacuum before sealing the pipet dilatometer at $<10^{-3}$ mm.

A few experiments under vacuum were carried out with monomer alone, i.e., without any added initiator. These experiments were made using Pyrex tubes of greater internal diameter (0.6 mm) because of severe meniscus problems caused by formation of such a high molecular weight product. The polymerization reaction took place in diffuse laboratory lighting at 37 ± 0.2 °C.

Reactions were stopped rapidly by breaking the reaction tubes under benzene at room temperature. Complete dissolution of polymer was ensured by maintenance at 37 °C for 5 to 7 days. Polymer concentration was calculated from the known volume of the reaction mixture and the percent polymerization. This procedure was shown to be satisfactory by occasional concentration checks. Viscosity measurements were made at 25 °C using Ostwald-Fenske dilution viscometers. Limiting viscosity numbers were estimated by extrapolation to infinite dilution of data obtained at three concentrations.

Treatment of Experimental Data

Viscosity average molecular weights, $\bar{M}_v$, were calculated from limiting viscosity numbers, $[\eta]$ (g^{-1} 100 ml), using eq 2 which was established[4] in benzene at 25 °C by reference to light scattering studies of PMMA fractions ranging in molecular weight from 2.5×10^4 to 7.4×10^6.

$$[\eta] = 5.5 \times 10^5 M^{0.76} \quad (2)$$

Number average molecular weights, $\bar{M}_n$, were then calculated from the ratio $\bar{M}_v$:$\bar{M}_n$ (1.9:1), on the assumption that the polymeric product had a random molecular weight distribution.[5]

Estimates of the number average degree of polymerization were calculated from the rate of polymerization, R_p (mol L^{-1} s^{-1}), using eq 3. The rate was estimated from the initially linear ratio of percent polymerization vs. time of reaction. The quantity A, eq 3, was calculated from values of rate constants given by Schulz, Henrici-Olivé, and Olivé (k_p, etc.) and includes a factor which takes account of rate constants for termination by combination (k_{tc}) and disproportionation (k_{td}) of polymer radicals.[6] Monomer concentrations, [M] (mol L^{-1}), were calculated from experimental values of specific volume, V_m (g^{-1} cm^3), reported by Schulz and Harborth.[7] Data are summarized in Table I.

$$\bar{Z}_n = AR_p^{-1} \quad (3)$$

$$A = k_p^2[\mathrm{M}](k_{td} + k_{tc}/2)^{-1}$$

$$[\mathrm{M}] = 10V_m^{-1}$$

Values of critical concentration, C_c (wt %), were obtained by reference to departure from linearity of plots of log $(1 - 0.01C)$ vs. time of reaction (C is the wt % polymerization). The use of this criterion has been discussed previously[2a] and such plots are not displayed here in order to save space. Values of the density of the reaction mixture at the critical concentration, ρ_c (g cm^{-3}), were calculated from values of specific volume for monomer and dissolved PMMA reported by Schulz and Harborth.[7]

Results

Results of dilatometric runs at 70 and 50 °C are shown in Figures 1 and 2. Such data were reproduced many times but duplicate results are not presented because the good reproducibility which can be achieved in this type of reaction, both in respect of R_p and C_c, has been demonstrated previously.[7,2a] It is apparent that the present experiments involve extremely simple experimental procedures. Notwithstanding, evidence for the accuracy of the results is to be found in the agreement obtained, up to the critical concentration, with previous results of Schulz and Harborth who used more elaborate techniques.[2b,7] Specifically, this agreement may be seen by comparison of runs reported here with those previously published for the following experimental conditions: at 70 °C using 0.25, 1.0, and 2.0 wt % benzoyl peroxide; at 50 °C using 2.0 wt % peroxide (cf. ref 4).

Table II
Comparison of Values of $\overline{M}_v$ ($\times 10^{-5}$)[a] for Polymers Prepared in Air and in Vacuum

	50 °C		70 °C	
Wt % peroxide	2	1	2	4
Air	4.1, 4.0 4.2, 4.1	2.2, 2.1	1.6	1.1
Vacuum	3.8, 3.9	2.1	1.6, 1.8	1.2

[a] Each value of $\overline{M}_v$ was obtained for a separate run stopped at an arbitrary conversion of monomer before the onset of autoacceleration.

In the display of data in Figures 1 and 2, inhibition periods, usually of several minutes duration, were ignored and therefore the zero on the time axis corresponds to the first detectable onset of contraction of the reaction mixture. This procedure was adopted following Schulz and Harborth.[2b] Subsequently Schulz and Henrici studied the inhibition reaction in some detail but, from the present point of view, it will suffice to note that any consequences of this reaction appear to be negligible when viewed against the wide range of high conversions under consideration.[8] Schulz and Henrici based this conclusion on the fact that rates measured by them at various partial pressures of oxygen were in agreement with rates which previously had been reported by Arnett[9] under similar conditions but in the absence of oxygen (cf. Table I of ref 8). Of course, the neglect of oxygen in a free-radical reaction needs careful justification in any specific case and, therefore, comparisons were made in the present work under the reaction conditions stated in Table II. It was found that although rate data for ampules sealed under vacuum were more erratic, because of poorer meniscus definition, nevertheless data were reproducible and in agreement with more precise runs made in air. These comparisons are not detailed here but, instead, evidence of the similarity of results obtained in air and in vacuum is documented in respect of values of viscosity average molecular weight (Table II).

Presumably, after consumption of dissolved oxygen, the presence of air only causes inhibition at the meniscus in the more rapid reactions at 50 and 70 °C. However it would be anticipated that at considerably slower rates, which are of interest in extending measurements to include polymeric products of higher molecular weight, contact with air would become a problem because of the increased time for diffusion of oxygen into the bulk of the reaction mixture. For this reason studies of slower reactions at 37 and 30 °C were limited to experiments in ampules sealed under vacuum. The experiment made at 37 °C included no peroxide and provided the extreme case in which one week elapsed before the onset of autoacceleration (Figure 3). The erratic nature of results is due only in part to meniscus problems and probably is influenced by lack of precise control of the initiation reaction.

Values of C_c estimated from first-order plots (not shown) of the data in Figures 1 and 2 are given in Table III along with analysis of similar data reported by previous workers.[2b,10,11] The table also includes estimates of $\overline{Z}_n$. Values calculated from rate data according to eq 3, in column 8, are clearly overestimates because eq 4 neglects reduction in degree of polymerization due to chain transfer reactions. Generally, free-radical polymerization reactions of methyl methacrylate are conducted under conditions such that the neglect is justifiable. This may be permissible because the transfer constant to monomer is low. Of course, transfer to benzoyl peroxide may well assume importance when the initiator is present at 15 wt % but even under such extreme conditions the difference from estimates based on solution viscosity measurements is less than 100%. As the concern here is with the square root of $\overline{Z}_n$, it has been judged to be worth while to process such data. The other estimates of $\overline{Z}_n$, in column 10, were obtained from viscosity–molecular weight relationships except for the data of Balke and Hamielec which were obtained by gel permeation chromatography. Values of $\overline{Z}_n$ calculated from eq 2 are expected to be underestimates, a deduction made from Flory's comment that the fractions used to establish this relationship were not sharp,[12] i.e., not mono-disperse.

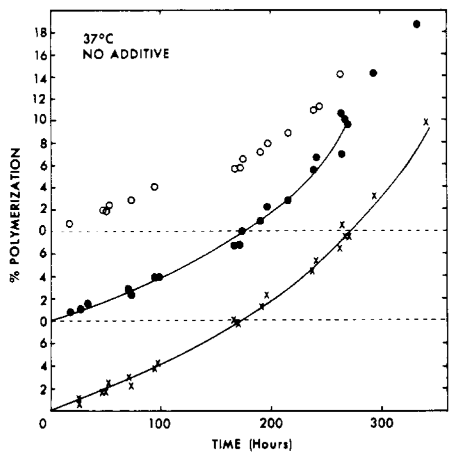

Figure 3. Polymerization of methyl methacrylate without additive under vacuum at 37 °C. Three duplicate runs are shown with offsets on the "polymerization" axis to avoid crowding of coordinate markers.

Discussion

(1) Comparison of Theory and Experiment. Equation 1 applies for a polymer with a random molecular weight distribution. The polymer formed by free-radical polymerization of methyl methacrylate generally conforms to such a distribution. Such conformity is to be expected when the termination step in the chain reaction is by disproportionation of polymer free radicals. Some termination also occurs by the combination of polymer free radicals but the relative proportion of these two reactions has not been determined precisely.[13] In the present work the authoritative analysis of Schulz, concerning relative values of k_{td} and k_{tc}, has been used but the distinction is only academic in view of present neglect of chain transfer reactions. A second related comment on the use of eq 1 is that if termination occurred solely by combination then the appropriate factor would be 1.7 instead of 1.5 (cf. eq 19 of part 1). This distinction, also, is probably of minor importance in this approach.

A first test of the theory concerns the prediction, from eq 1, that $\rho_p \overline{Z}_n^{0.5}$ = constant and, hence, that a plot of log ρ_p vs. log $\overline{Z}_n$ should have a slope of −0.5. In Figure 4 an intuitive judgement is shown of a fit of experimental data to a slope of −0.4. More objectively, a least-squares analysis gives overall slopes of −0.37 (Figure 4, bottom) and −0.32 (Figure 4, top). A precise test of the statistical significance of this difference from theory has not been possible but it does appear that there is a discrepancy and, therefore, that conformity of experimental data to the model is correspondingly approximate. To put this matter into perspective it should be noted that an alternative theoretical explanation which sought to attribute autoacceleration to an entanglement effect would be still more inconsistent with experimental results. It has been pointed out previously that, on the simplest theoretical considerations, an onset of autoacceleration due to formation of an incipient network by entanglements might be expected to conform to

Table III
Experimental Values of ρ_p and $\bar{Z}_n$

Ref	Temp, °C	Initiator, wt %	C_c, wt %	ρ_c, g/cm^3	$\rho_p = 0.01C_c\rho_c$, g polymer/cm^3	$R_p \times 10^4$, mol/L/s	$\bar{Z}_n$, (eq 3)	$100\rho_p\bar{Z}_n^{1/2}$	$\bar{Z}_n$ (eq 2)	$100\rho_p\bar{Z}_n^{1/2}$
Present work	70	0.25[a]	18	0.94	16.8	4.79	3280	960		
Present work	70	1.0[a]	22	0.95	20.8	9.24	1670	850		
Present work	70	2.0[a]	23	0.95	21.9	13.0	1210	760	790	620
Present work	70	4.0[a]	26	0.96	25.0	18.4	850	730	580	600
Present work	70	7.0[a]	29	0.97	28.0	23.5	670	730	450	590
2b, 7	50	0.25[a]	11	0.94	10.3	0.91	9070	980	7 600	900
2b, 7	50	0.50[a]	13	0.94	12.3	1.22	6770	1010		
2b, 7	50	1.0[a]	14	0.95	13.3	1.66	4980	940	3 900	830
2b, 7	50	2.0[a]	16	0.95	15.2	2.27	3640	920	2 050	690
Present work	50	4.0[a]	18	0.96	17.2	3.36	2460	850	1 440	650
Present work	50	7.0[a]	21	0.97	20.3	3.93	2100	930	1 210	700
Present work	50	10[a]	22	0.97	21.3	4.69	1760	900	950	650
Present work	50	15[a]	23	0.97	22.5	5.68	1450	860	790	630
Present work	37	0	7	0.94	16.6	0.01	*c*	*c*	50 000	1480
Present work	30	2[a]	15	0.97	14.5	0.476	8470	1330	5 470	1080
Present work	90	0.3[b]	27	0.956	25.6	37.0	743	700	650	650
Present work	90	0.5[b]	31	0.96	29.8	46.6	590	720	500	670
Present work	70	0.3[b]	19	0.94	17.8	8.2	1910	780	1 500	690
Present work	70	0.5[b]	23	0.95	21.9	10.1	1550	860	1 200	760
Present work	50	0.3[b]	16	0.95	15.2	1.47	5620	1140	4 500	1020
Present work	50	0.39[b]	16	0.95	15.2	1.70	4860	1060	3 700	930
Present work	50	0.5[b]	16	0.95	15.2	1.89	4370	1010	3 190	860

[a] Benzoyl peroxide. [b] Azobisisobutyronitrile. [c] Value of $\bar{Z}_n = 6 \times 10^5$ considered to be unreliable and not used.

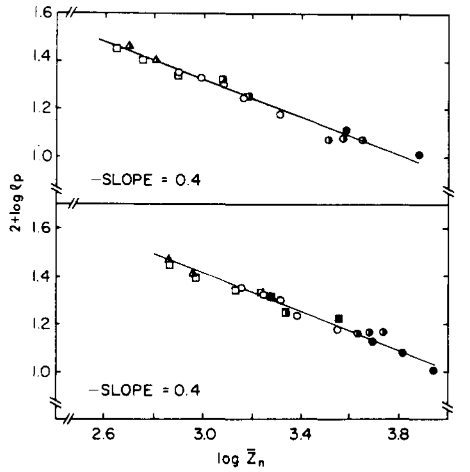

Figure 4. Plot of log ρ_p vs. log $\bar{Z}_n$, according to eq 1. Bottom: $\bar{Z}_n$ estimated from rate data. Top: $\bar{Z}_n$ estimated from the other measurements, [η], etc.

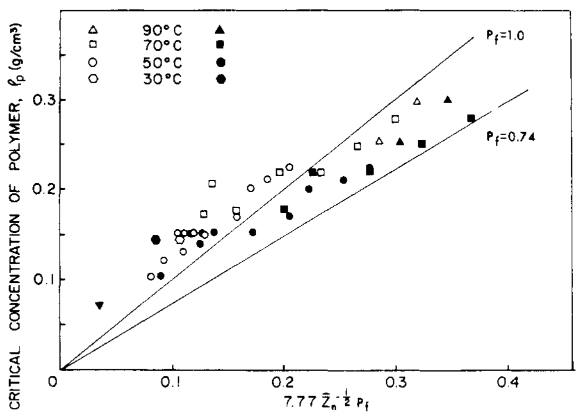

Figure 5. Plot of ρ_p vs. $7.77\bar{Z}_n^{-1/2}\rho_f$, based on eq 1: (▼) data at 37 °C without peroxide.

the relationship $\rho_p M^{1.0}$ = constant. In fact, certain properties of polymer solutions which are believed to depend on entanglements do approximate to such a relationship. For example, Lederer and Schurz reported this relationship on the basis of studies of toluene solutions of PMMA which involved measurements of viscosity with variations of molecular weight, M, and polymer concentration.[14] Subsequently Graessly and Pennline, taking into account a wider range of measurements, suggested the revised relationship $\rho_p M^{0.67}$ = constant.[15] In any event, it appears that entanglement phenomena would involve a considerably higher exponent of molecular weight than is observed in the autoacceleration phenomenon.

A second test of the theory can be made if values are assigned to $(\bar{r}_0^2/M)^{1/2}$ and p_f. A value for the former quantity was obtained by taking the mean value for all 16 values for atactic PMMA listed in the Polymer Handbook:[3] 578×10^{-11} cm; standard deviation = 48×10^{-11}. Substitution of the mean value in eq 1 gives $\rho_p = 7.77\bar{Z}_n^{-1/2}p_f$. Theoretical lines are shown for $p_f = 0.74$ and $p_f = 1.0$; the former value is the maximum possible for close packing of uniform rigid spheres (Figure 5). It will be seen that experimental data lie between limits defined by these two lines at low values of $\bar{Z}_n$. At high values of $\bar{Z}_n$, experimental values of the critical concentration, ρ_p, are greater than predicted by theory even by reference to a packing factor as high as unity. This discrepancy between theory and experiment might be attributed, most obviously, as due to an increasing inadequacy of the rigid sphere model with increase in molecular weight. Another possibility, implicit in Figure 5, is that the discrepancy might be due to the longer reaction times required for formation of polymers of higher molecular weight (cf. eq 3). This latter possibility has not been analyzed in detail because of a decision to explore, first, the adequacy and limitations of a static model because of its conceptual simplicity. Should this decision prove to be mistaken then the data in Table III would allow a revised point of departure, for modification of the model, which would take into account the time to reach the critical concentration.

The molecular weight discrepancy mentioned above can be brought out more suggestively by an empirical plot of data in

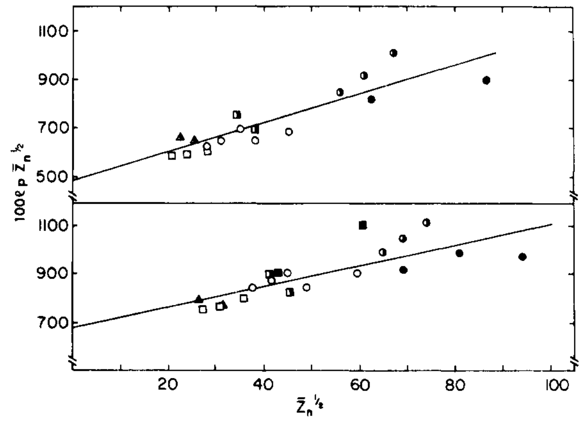

Figure 6. Empirical plot of $100\rho_p\bar{Z}_n^{1/2}$ vs. $\bar{Z}_n^{1/2}$. Bottom: $\bar{Z}_n$ estimated from rate data. Top: $\bar{Z}_n$ estimated from other measurements, [η], etc.

the form $100\rho_p\bar{Z}_n^{1/2}$ vs. $\bar{Z}_n^{1/2}$ (Figure 6). This suggests elimination of the molecular weight variable by comparison of theory with values of $100\rho_p\bar{Z}_n^{1/2}$ extrapolated to $\bar{Z}_n^{1/2} = 0$. Values obtained in this way are about 700 from rate data (Figure 6, bottom) and about 500 from other estimates of molecular weight (Figure 6, top); the latter value is considered to be more reliable for reasons discussed previously. These values are close to the theoretical value of 580 (from eq 1 with $\bar{r}_0^2/M^{1/2} = 578 \times 10^{-11}$ and $p_f = 0.74$). The increasing discrepancy from this value with increasing molecular weight may be rationalized by recognizing an obvious limitation of a rigid sphere as a model for a macromolecule. More realistically, there is an approximately Gaussian distribution of polymer chain segments with a maximum value at the center of mass and a minimum value at the periphery of the macromolecule. In the condition of close packing, at the critical concentration, some overlapping and/or distortion would occur at adjacent macromolecular peripheries. Accordingly, a more appropriate model would be a rigid core with a soft mantle. Qualitatively, it is consistent with the discrepancies noted above that the zone of the soft mantle would be expected to increase with increase in molecular weight. At the present time no persistent effort has been made to work out the implications of a revised "core and mantle" model quantitatively.

(2) Influence of Temperature. It would appear from the data in Figure 5 that there is no marked influence of temperature on the onset of autoacceleration in the range covered of 30–90 °C (the boiling point[16] of methyl methacrylate is about 101 °C). This finding is in agreement with the conclusion of Robertson[17] that there is no influence of temperature in the range 40–70 °C. Robertson's conclusion was based on studies of the concentration at which a marked increase in the termination rate constant, k_t, was first detected. Her data have been reviewed previously from the present viewpoint but without discussion of the influence of temperature.[2a] Robertson contended that a negligible temperature dependence is to be expected in cases where the diffusion of polymer radicals and the ensuing termination reaction have activation energies of similar value. She cited such values for methyl methacrylate.

Another aspect of the influence of temperature, in respect to the application of eq 1, concerns the term $(\bar{r}_0^2/M)^{1/2}$. Generally, the magnitude of this term decreases slightly with an increase in temperature[18] but, on the contrary, Schulz and Kirste have detected a trend in just the opposite sense for PMMA in a variety of solvents.[19] However the increase is only a few percent, for a rise in temperature from 30 to 60 °C, and such a small dependence may be neglected from the present point of view.

Yet another observation which should be noted is the report by Schmitt and Kovacs[20] that a second-order transition occurs at 50 °C in solutions of PMMA (about 3%) in xylene, detected by measurements of specific volume in the temperature range 25–110 °C. Too little information is available to assess the significance of this phenomenon for PMMA. More data are available for polystyrene and in this case Schmitt and Kovacs support the claim by Reiss and Benoit[21] that a transition occurs at 70 °C, in 3% solutions but not in 30% solutions. In any event, no evidence which could be related to such a change is apparent in the present data shown in Figure 5.

Conclusions

(1) Experimental data are consistent with an average value of "a" in the range 0.3 to 0.4, whereas the theory predicts a = 0.5 in the equation $\rho_p\bar{Z}_n^a$ = constant.

(2) Experimental values of $100\rho_p\bar{Z}_n^{1/2}$ ranged from about 600 to 1500 as compared to a theoretically predicted value of 580 (with $p_f = 0.74$).

(3) Experimental values of $100\rho_p\bar{Z}_n^{1/2}$ tended to increase with increase in $\bar{Z}_n$ whereas, according to theory, this product should remain constant. An empirical plot of $100\rho_p\bar{Z}_n^{1/2}$ vs. $\bar{Z}_n^{1/2}$ gave, very roughly, a straight line which allowed an estimate of the product extrapolated to zero molecular weight. Values obtained in this way are in better agreement with theory viz. about 700 with reference to estimates of $\bar{Z}_n$ from rate data and about 500 from other estimates of $\bar{Z}_n$.

(4) No dependence on temperature was detected for the onset of autoacceleration of polymerization in the range under examination of 30–90 °C. Neither is any noticeable dependence expected on theoretical grounds.

(5) In broader perspective, the theory is judged to be satisfactory in providing a first approach toward an understanding of the onset of autoacceleration of polymerization of methyl methacrylate at the molecular level. Probably, the major deficiency of the theory arises from the treatment of macromolecules as equivalent to rigid spheres. A better macromolecular model would be a hard core with a soft mantle.

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References and Notes

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Autoacceleration of Free-Radical Polymerization. 3. Methyl Methacrylate plus Diluents

H. B. Lee and D. T. Turner*

Dental Research Center, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27514. *Received April 16, 1976*

ABSTRACT: Methyl methacrylate was mixed with various liquids and then polymerized by heating with benzoyl peroxide. Conditions were found in which phase separation could be avoided despite presence of cyclohexane which is a nonsolvent for poly(methyl methacrylate) (PMMA). A critical concentration for the onset of autoacceleration in the rate of polymerization was estimated by departure from first-order kinetics. Estimates of number average degree of polymerization were obtained from rate of polymerization and also from solution viscosity data. Similar experiments were made with benzene and toluene both of which are solvents for PMMA. It was found that, for all three liquids, results conform to the macromolecular close packing theory to the same extent as do results for the monomer when polymerized alone.

At the onset of autoacceleration of polymerization of methyl methacrylate alone there is a quantitative relationship between the concentration of the polymeric product, ρ_p, and its number average degree of polymerization, $\overline{Z}_\mathrm{n}$. In broad outline, this empirical relationship conforms to a theoretical model which treats the onset of autoacceleration as due to the close packing of rigid spheres with dimensions which can be derived from measurements on unperturbed macromolecules. In more detail, discrepancies between theory and experiment are stated in part 2 of this series of papers.[1] The purpose of the present paper is to investigate whether the theory is sufficiently general to apply when methyl methacrylate is polymerized in admixture with diluents. A specific question will serve to indicate the sort of generality which is envisaged. When methyl methacrylate is polymerized alone, the theory considers the critical concentration of polymer at the onset of autoacceleration, ρ_p, expressed in grams of polymer/cm^3 of solution, i.e., per cm^3 of monomer + polymer. The further question now posed is whether this definition of ρ_p can be generalized to include polymerization in diluents if ρ_p is expressed in terms of grams of polymer/cm^3 of monomer + polymer + diluent. It would appear that this should be the case if the theory has general validity, provided that no new phenomena, such as phase precipitation, are caused through inclusion of the diluent.

In seeking an answer to the above question guidance can be obtained from previous workers. In particular, Schulz and Harborth[2] made some detailed studies of the role of benzene as a diluent and Flory[3] recognized the importance of their work by including a graphical illustration of it in his book. It would appear that the initial interest of Schulz and Harborth in the use of benzene as a diluent was in the opportunity it afforded to demonstrate unequivocally that autoacceleration can occur under isothermal conditions, i.e., under conditions such that the heat of polymerization results in only a negligibly small increase in temperature of the reaction mixture. More importantly, from the present point of view, they also provided evidence that a polymer concentration could be defined corresponding to a departure in the course of the polymerization reaction from first-order kinetics. They then used these data to reach the conclusion that the concentration of polymeric product at the onset of autoacceleration is approximately constant despite variations in the concentration of benzene. This conclusion is already fairly close to the present frame of reference except that the experimental data need to be refined and extended to take into account the influence of the degree of polymerization of the polymeric product, $\overline{Z}_\mathrm{n}$, according to eq 1 which includes other terms defined previously.[1]

$$\rho_\mathrm{p} = 1.5 \times 10^{-24}\overline{Z}_\mathrm{n}^{-1/2}\left(\frac{\overline{r_0^2}}{M}\right)^{-3/2} p_\mathrm{f} \qquad (1)$$

Other work, in which ethyl acetate was used as a diluent, was reported by Robertson[4] and seems to be important on two counts. First, her definition of a critical concentration differs in respect of method but is similar in principle, depending on detection of a marked increase in the rate "constant" for termination of the free-radical chain reaction, k_t. Second she recognized that, in addition to the concentration of the polymeric product, some further factor needs to be considered in order to define a condition of constancy at the onset of autoacceleration. Her choice for such a factor was the limiting viscosity number which is a step in the right direction as judged, in retrospect, from eq 1.

The work cited above is relatively simple in that the diluents are solvents for PMMA and hence homogeneous conditions are preserved. Of course, with certain other liquids phase separation may occur. The whole spectrum of behavior was brought out in early work by Norrish and Smith. A reaction mixture comprising 60% monomer and 40% diluent was polymerized by heating at 40 °C with benzoyl peroxide. "The diluents were chosen from good and poor solvents and also precipitants of polymethyl methacrylate, . . . ". At one extreme precipitants, such as cyclohexane, caused autoacceleration of polymerization almost at the start of the reaction with accompanying formation of an opaque firm gel. At the other extreme good solvents, such as benzene, retarded autoacceleration, relative to observations on undiluted monomer, and the reaction mixture remained clear and formed only a thin sol after polymerization.[5] Enhanced autoacceleration accompanied by precipitation of polymer due to inclusion of cyclohexane was also reported by Smets, Masquelier, and Van Tornout.[6] The general implications of such findings have been