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Autoacceleration of Free-Radical Polymerization.
1. The Critical Concentration

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ABSTRACT: It is suggested that the onset of marked autoacceleration in the rate of polymerization of methyl methacrylate by free radicals occurs when the concentration of polymer approximates to a condition of macromolecular close packing. In a model adopted from previous studies of the flow properties of concentrated polymer solutions, the macromolecules are treated as equivalent to uniform rigid spheres with a radius which is calculated from unperturbed dimensions. This model is generalized to take account of the influence of molecular weight distribution. Published data on the polymerization of methyl methacrylate are analyzed and shown to fit the model sufficiently well to indicate that it will provide a basis for reaching a quantitative understanding of the onset of autoacceleration at the molecular level.

The purpose of the present series of papers is to enquire whether the *onset* of autoacceleration in the rate of free radical polymerization, along with an accompanying increase in molecular weight,[1-9] can be understood quantitatively by reference to a simple model which attributes the effect to the onset of close packing of macromolecules in the reaction mixture.

Critical Concentration

The viscosity and related transport properties of polymer solutions increase abruptly at a critical concentration of polymer the value of which depends on molecular weight. The abruptness of such changes has been explained in terms of either entanglements or the close packing of discrete macromolecular coils.[10-16] In their simplest exposition these explanations differ concerning the value to be predicted for the exponent "a" in the product $\rho_p M^a$, where ρ_p is the concentration of polymer at the critical concentration (g cm^{-3}) and M is the molecular weight; $a = 1.0$ (entanglements) and $a = 0.5$ (macromolecular close packing).

(i) Entangled Networks. A condition for incipient network formation may be expressed in terms of the weight average degree of polymerization, $\bar{P}_w$, and the probability that a mer is chemically cross-linked, p_x (eq 1).[17] According to F. Bueche this expression may be extended to include entangled networks, i.e., ones which involve only physical cross-links (entanglements), by introduction of a slippage factor, s, which takes values ranging from zero to unity according to the lifetime of the entanglement (eq 2).[18] In eq 2, p_e represents the probability that a mer is entangled.

$$\bar{P}_w p_x = 1 \tag{1}$$

$$\bar{P}_w p_e s , 1 \tag{2}$$

To develop eq 2 to introduce a dependence on the concentration of polymer in solution, ρ_p, it is necessary to relate this term to a measure of the entanglements. Bueche has suggested eq 3, which is an intuitive relationship supported by some experimental evidence. In eq 3, $\bar{P}_{n,e}$ is the number average degree of polymerization between adjacent entanglements on a given molecule, and the constant has an arbitrary value. Recognizing the identity of p_e^{-1} and $\bar{P}_{n,e}$, eq 2 and 3 give the required dependence on molecular weight and concentration (M being proportional to $\bar{P}_w$ if s is assumed to be constant (eq 4)).

$$\rho_p \bar{P}_{n,e} = \text{constant} \tag{3}$$

$$\rho_p M = \text{constant} \tag{4}$$

(ii) Macromolecular Close Packing. Following previous authors,[12] the simplest case to consider is that in which all the macromolecules have the same molecular weight, M. If the macromolecules are considered to be equivalent to rigid spheres of radius r which, at the critical concentration, form a close-packed array which occupies a volume fraction of the solution, p_f, then the number of macromolecules per unit volume, N, is given by eq 5. Also, it is given by the product of the number of moles of macromolecules per unit volume, $\rho_p M^{-1}$, and Avogadro's number, N_A (eq 6). The radius of a Gaussian coil, and hence that of its equivalent sphere, can be expressed (eq 7) in terms of M if the molecular weight exceeds some relatively small value (cf. Cornet).[19] The required dependence on concentration and molecular weight is given by rearrangement of eq 5 to 7 (eq 8).

$$N = \frac{\text{tot vol of macromolecules in unit vol}}{\text{vol of each macromolecule}} = \frac{3p_f}{4\pi r^3} \tag{5}$$

$$N = \rho_p N_A / M \tag{6}$$

$$r = k' M^{1/2} \qquad (k' \text{ is a constant}) \tag{7}$$

$$\rho_p M^{1/2} = 3p_f / 4\pi k'^3 N_A \tag{8}$$

Macromolecular Close Packing in More Detail

Experimental data by Onogi et al.[12] and Asai[13] provide evidence that in certain polymer solutions, at the critical concentration, the product $\rho_p\overline{M}_n^{1/2}$ approximates closely to a constant value whereas $\rho_p\overline{M}_n$ increases markedly with increasing molecular weight. Here $\overline{M}_n$ refers to number average molecular weight and comparison with eq 8 led to the contention that the critical concentration is due to macromolecular close packing. A more exacting test of this contention would be possible if a numerical value could be predicted for product $\rho_p\overline{M}_n^{1/2}$. Equation 8 is unsuitable for this purpose because it involves a constant of unknown value (k'). However, Onogi et al. have indicated how such a value may be calculated from known values of the unperturbed root-mean-square end-to-end distance of macromolecules, $\bar{r}_0^2$. This treatment, which was limited to the case in which all the macromolecules have the same molecular weight, M, is discussed in the following section. A subsequent section then extends this treatment to take account of the influence of molecular weight distribution.

(i) Value of the Equivalent Radius. A theoretical value for the product $\rho_p M^{1/2}$ is most sensitive to the value chosen for the radius of the equivalent sphere because this occurs as a cubed term in the calculation. In an early use of the concept of macromolecular packing of random coils to calculate a critical concentration Boyer and Spencer chose a value derived from a limiting viscosity number, a choice which would seem to be appropriate for isolated macromolecules.[20] Subsequent workers[10,11] independently followed a similar procedure despite the fact that, unlike Boyer and Spencer, they were concerned with trying to account for phenomena occurring in much more concentrated solutions. This procedure seems inappropriate in light of evidence that as the concentration increases the coils contract. Simha has devoted considerable effort to the development of a theoretical treatment of the contraction of coils and has succeeded in calculating the extent of such an effect up to moderate concentrations of polymer.[21] However, the extreme position on the extent of coil contraction has been taken by Maron, who considered the process to continue even into the concentration range where the volume fraction of polymer approaches unity.[22] In contrast, in such an extreme case, the consensus of opinion[23] is that considerable interpenetration of coils does occur.[23,24]

To give an impression of the extent of the contraction of coils, values of average macromolecular radius have been calculated from data reported by Maron, Nakajima, and Krieger[22] and plotted against the volume fraction of a sample of polystyrene in solution (the basis of the calculations is indicated in the caption to Figure 1). The trend demonstrates a number of features which are believed to be qualitatively correct. First, in very dilute solutions the macromolecular radius is greater in a "good" solvent (toluene) than in a "poor" solvent (methyl ethyl ketone). Second, as the solution becomes more concentrated the coils progressively contract and any difference due to solvent "power" becomes negligible. Third, it shows the relatively small magnitude of error involved in a choice of a value for the macromolecular radius appropriate for a concentrated solution.

If reliable data of the kind shown in Figure 1 were available, then the most satisfactory procedure for choosing a value of the macromolecular radius would be by reading off the ordinate corresponding to the experimentally observed critical concentration. In the absence of such data the choice of a value must be made in a more arbitrary way. In this respect, Onogi et al. made use of the convenient idea that the appropriate dimensions for the equivalent sphere are those of the unperturbed macromolecule[19,25] (eq 9). Substitution of this value for r in eq 5 and equating the resulting expression to eq 6 provides the required relationship (eq 10). For some purposes, comparison with experiment is facilitated by replacement of ρ_p (grams of polymer/cm^3) by the product $0.01C_c\rho_c$ in which C_c is the critical concentration in wt % and ρ_c is the density of the polymer solution at the critical concentration in g cm^{-3} (eq 11).

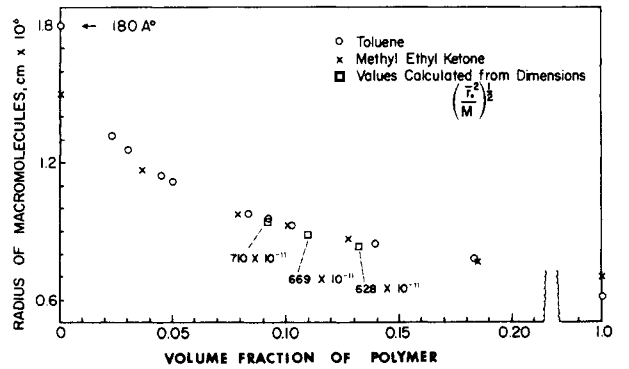

Figure 1. Dependence of radius of macromolecules in solution on volume fraction of polymer. The radius (r) was calculated from $r = (3/4\pi)(V_p\epsilon M/N_A)^{1/3}$. The specific volume of polystyrene $V_p = 1.05$ g^{-1} cm^3; $M = 2.4 \times 10^5$; ϵ is a factor by which the volume fraction of polymer has to be multiplied to obtain the effective hydrodynamic volume of the macromolecules. Values of ϵ were taken from Tables III and IV of ref 22.

$$r = \frac{5.11}{6\pi}\left(\frac{\bar{r}_0^2}{M}\right)^{1/2} M^{1/2} \tag{9}$$

$$\rho_p M^{1/2} = \frac{3}{4\pi N_A}\left(\frac{5.11}{6\pi}\left(\frac{\bar{r}_0^2}{M}\right)^{1/2}\right)^{-3} p_f \tag{10}$$

$$C_c\rho_c M^{1/2} = 2.00 \times 10^{-21}\left(\frac{\bar{r}_0^2}{M}\right)^{-3/2} p_f \tag{11}$$

Values for the square root factor which occurs in eq 9 to 11 have been discussed by Flory[26] and subsequently, in greater detail, by Kurata and Stockmayer.[27] The "Polymer Handbook" lists 31 estimates for atactic polystyrenes covering a wide range of experimental conditions[28] (mean value = 669 $\times 10^{11}$; standard deviation= 41 $\times 15^{-11}$ cm). Values of r obtained in the above manner agree with the results calculated from the data of Maron et al. (Figure 1).

(ii) Influence of Molecular Weight Distribution. The previous treatment which assumes that all the macromolecules are the same size can be generalized to provide expressions which are more useful for comparison with experimental data obtained for polymers having a distribution of molecular weights. The general treatment involves the summation of contributions to the critical value of the packing fraction, p_f, from the number of x-mers per cm^3, n_x, each x-mer having an equivalent radius of r_x (eq 12).

$$p_f = \sum_{x=1}^{\infty} n_x \frac{4}{3}\pi r_x^3 \tag{12}$$

A convenient distribution function for n_x, especially appropriate for the vinyl polymers of interest, is that of the Schulz type[29] in which n_0 is the total number of monomer units per cm^3, $\bar{x}_n$ is the number average degree of polymerization, and k is a numerical parameter which specifies a particular type of distribution (eq 13). For example, $k = 1$ corresponds to the distribution obtained from a polymerization reaction in which termination of the polymer radicals is by disproportionation.

$$n_x = \frac{n_0}{x}\left(\frac{k}{\bar{x}_n}\right)^{k+1}\left(\frac{x^k}{k!}\right)\exp\left(\frac{-kx}{\bar{x}_n}\right) \tag{13}$$

Substitution of n_x (eq 13) in eq 12 and replacement of the summation by an integration gives eq 14 which provides a solution for the number of monomer units per cm^3, n_0. It will be seen, also, that the unperturbed dimensions have been introduced for the equivalent radius via eq 9.

$$p_\mathrm{f} = \int_0^\infty n_\mathrm{x} \frac{4}{3} \pi r_\mathrm{x}^3 \,\mathrm{d}x$$

$$= \frac{n_0}{\bar{x}_\mathrm{n}^2} \frac{4}{3} \pi \left(\frac{5.11}{6\pi} \left(\frac{\bar{r}_0^2}{M}\right)^{1/2}\right)^3 M_0^{3/2} \Gamma\left(\frac{3}{2} + 1\right) \bar{x}_\mathrm{n}^{5/2} \qquad (14)$$

The solution for n_0 can be substituted in eq 15, in which M_0 is the molecular weight of a mer, to provide an expression for ρ_p, the mass of polymer per cm^3 at the critical concentration (eq 16).

$$\rho_\mathrm{p} = \frac{n_0}{N_\mathrm{A}} M_0 \qquad (15)$$

$$\rho_\mathrm{p} = 1.50 \times 10^{-23} \left(\frac{\bar{r}_0^2}{M}\right)^{-3/2} \overline{M}_\mathrm{n}^{-1/2} p_\mathrm{f} \qquad (k = 1) \quad (16)$$

A similar procedure can be followed for the case of $k = 2$, which corresponds to a distribution in which termination is by the combination of polymer radicals, to give eq 17.

$$\rho_\mathrm{p} = 1.70 \times 10^{-23} \left(\frac{\bar{r}_0^2}{M}\right)^{-3/2} \overline{M}_\mathrm{n}^{-1/2} p_\mathrm{f} \qquad (k = 2) \quad (17)$$

Equations 16 and 17 may be expressed in a form similar to eq 11:

$$C_\mathrm{c} \rho_\mathrm{c} M^{1/2} = 2.00 \times 10^{-21} \left(\frac{\bar{r}_0^2}{M}\right)^{-3/2} p_\mathrm{f} \quad \text{(monodisperse)} \quad (18)$$

$$C_\mathrm{c} \rho_\mathrm{c} \overline{M}_\mathrm{n}^{1/2} = 1.70 \times 10^{-21} \left(\frac{\bar{r}_0^2}{M}\right)^{-3/2} p_\mathrm{f} \qquad (k = 1) \quad (19)$$

$$C_\mathrm{c} \rho_\mathrm{c} \overline{M}_\mathrm{n}^{1/2} = 1.50 \times 10^{-21} \left(\frac{\bar{r}_0^2}{M}\right)^{-3/2} p_\mathrm{f} \qquad (k = 2) \quad (20)$$

(iii) The Macromolecular Packing Factor. The simplest approach to the packing of macromolecules in solution is to assume that they can be treated as a contiguous array of inpenetrable spheres at the critical concentration. In the monodisperse case (eq 18) close packing would result in a value of $p_\mathrm{f} = 0.74$ while an appropriate value for a randomly packed array[30] would be 0.64. For the distributions corresponding to $k = 1$ and 2 (eq 19 and 20) the ratios of weight to number average molecular weight are only 2.0 and 1.5, respectively. For such distributions it is reasonable to accept Cornet's judgement in selecting a value for a packing factor that "errors are not very large for molecular weight distributions of moderate width".

A more serious conceptual problem concerns the question of whether a macromolecule in solution does, indeed, behave like a rigid inpenetrable sphere. This question has already been mentioned in connection with the alternative possibility of overlapping of coils. A related problem is whether segments of the coil would diffuse into the "interstices of the lattice" prior to the critical concentration. If this does occur and if the equivalent sphere model is nevertheless retained as an approximation then larger packing fractions might be used than would be physically appropriate for rigid spheres. Actually, on the basis of a match between experimental data on solution viscosity and a hard sphere model, Onogi et al. did suggest a packing factor of unity. However, Cornet rightly pointed out that a match is likely to be coincidental.[19]

In view of the uncertainties in making a decision about a value for the macromolecular packing fraction, this factor is retained without evaluation in a tabulation of theoretical values of the product $C_\mathrm{c} \rho_\mathrm{c} \overline{Z}_\mathrm{n}^{1/2}$ (Table I). This product was calculated from eq 18, 19, and 20 for the various molecular weight distributions.

Table I
Theoretical Values of $C_\mathrm{c} \rho_\mathrm{c} \overline{Z}_n^{1/2}$ for PMMA[a–c]

Distribution	$\overline{M}_\mathrm{w}/\overline{M}_\mathrm{n}$	Values of $(\bar{r}_0^2/M) \times 10^{11}$ 530	 578	 626
Monodisperse	1.0	$1340p_\mathrm{f}$	$1030p_\mathrm{f}$	$810p_\mathrm{f}$
$k = 1$	1.5	$1140p_\mathrm{f}$	$880p_\mathrm{f}$	$690p_\mathrm{f}$
$k = 2$	2.0	$1110p_\mathrm{f}$	$780p_\mathrm{f}$	$610p_\mathrm{f}$

[a] The mean value of all 16 values listed for atactic PMMA in the Polymer Handbook[28] is 578×10^{-11} cm. The other two values are for the mean value ±1 the standard deviation of 48×10^{-11} cm. [b] $\overline{M}_\mathrm{w}$ is the weight average molecular weight. $\overline{M}_\mathrm{n} = 100\, \overline{Z}_\mathrm{n}$. [c] $\overline{Z}_\mathrm{n}$ has been used in place of $\overline{M}_\mathrm{n}$ in order to conform to the convention established in studies of solution properties.

Critical Concentration in Free-Radical Polymerization

It is suggested that the macromolecular close packing model be adopted for comparison with the onset of the autoacceleration effect in free radical polymerization on the assumption that the critical concentration, C_c, can be identified with the wt % conversion of monomer to polymer at which the onset of autoacceleration is detected experimentally.

In order to put the application of the model into perspective a brief comparison will be made of some previous treatments of the diffusion controlled polymerization of methyl methacrylate. Below the critical concentration growing polymer free radicals diffuse through the monomer with relative ease and mutually terminate in pairs. Any diffusion control of the reaction at this stage, such as has been discussed by North,[6] is considered to be of minor importance relative to the subsequent abrupt changes which occur at the critical concentration. Above the critical concentration, polymer free radicals would be constrained to move through paths of uniformly high segment density. Under such conditions their mobility would be limited by entanglements and the autoacceleration effect would be more pronounced. The course of reactions carried to such high conversions has been discussed recently by Cardenas and O'Driscoll.[31]

The above comments suffice to indicate that the macromolecular close packing model is not inconsistent with previous treatments of diffusion controlled polymerization reactions. Instead it differs in limiting attention to the *onset* of autoacceleration. The main advantage of this focusing of attention is that it allows the prediction of quantitative relationships between C_c and $\overline{Z}_\mathrm{n}$ in terms of unperturbed macromolecular dimensions.

Critical Concentration in the Polymerization of Methyl Methacrylate

Dilatometric data showing percent polymerization vs. time for the free radical reaction of methyl methacrylate, initiated by benzoyl peroxide, Bz_2O_2, at 50 and 70 °C, have been tabulated by Schulz and Harborth.[32] Results obtained for four experiments made under similar conditions are plotted in Figure 2, each successive run being displaced arbitrarily on the "polymerization" axis to avoid overcrowding of coordinate markers. These early but exemplary results show, first, that there is an approximately constant rate of polymerization up to a conversion of monomer approaching about 20%; this is under approximately isothermal conditions. Second, the initial rate is reproducible. The third conclusion to be drawn is that a region can be recognized in which there is an upturn in the plot of conversion vs. time which appears to be fairly reproducible. From the present point of view it is most impor-

Table II
Comparison of Values of $C_c\bar{Z}_n$ and $C_c\rho_c\bar{Z}_n^{1/2}$, Calculated from Experimental Data

T, °C	Initiator, wt %	$\bar{M}_w/\bar{M}_n$ (at C)[a]	C_c, wt %	ρ_c, g/cm^3	$\bar{Z}_n$ × 10^{-3}	$C_c\bar{Z}_n$ × 10^{-4}	$C_c\rho_c\bar{Z}_n^{1/2}$	Ref
50	Bz_2O_2, 0.25		11	0.94	7.6	8.4	900	32, 33[b]
50	Bz_2O_2, 1.0		17	0.96	3.9	6.6	1020	32, 33[b]
50	Bz_2O_2, 2.0		17	0.96	3.0	5.1	890	32, 33[b]
50	AZBN, 0.3	2.2 (11.5)	19	0.96	4.5	8.6	1220	36
50	AZBN, 0.4	2.3 (16.7)	20	0.97	3.7	7.4	1180	36
50	AZBN, 0.5	2.3 (14.8)	19	0.96	3.9	7.4	1140	36
70	AZBN, 0.3	2.1 (11.6)	28	0.97	1.5	4.2	1050	36
70	AZBN, 0.5	2.1 (14.1)	33	0.98	1.2	4.0	1120	36
90	AZBN, 0.3	1.9 (25.1)	40	0.99	0.65	2.6	1010	36
90	AZBN, 0.5	2.0 (30.4)	41	0.99	0.5	2.1	910	36
40	AZBN, 0.1		4	0.93	33	13	680	39[c]
50	AZBN, 0.1		6	0.90	17	10	700	39[c]
60	Bz_2O_2, 0.3		8	0.92	11	8.8	770	39[c]
70	AZBN, 0.1		14	0.93	5.8	8.1	990	39[c]

[a] C designates the conversion (wt %) for which the molecular weights were measured. [b] Molecular weight data from G. V. Schulz.[38] [c] Molecular weight data calculated from the limiting viscosity numbers tabulated by Robertson using the relationship given in her paper.[39] The mean value of $C_c\rho_c\bar{Z}_n^{1/2}$ = 970; standard deviation = 170.

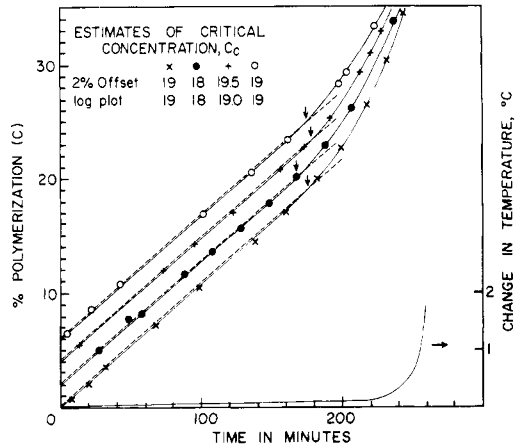

Figure 2. Reproducibility of isothermal conversion of methyl methacrylate to polymer. Monomer plus 1 wt % Bz_2O_2 at 50 °C (Schulz and Harborth).[32] Results of four runs are successively offset on the "polymerization" axis to avoid overcrowding of coordinate markers.

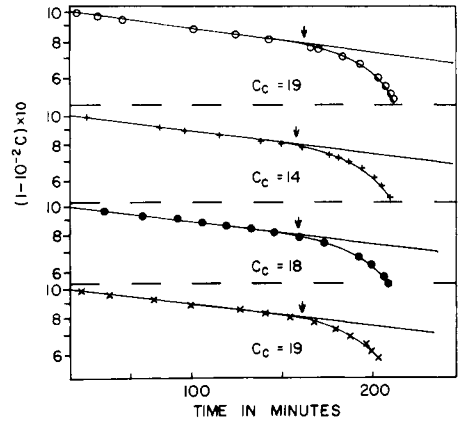

Figure 3. Data of Figure 2 replotted according to first-order kinetics.

tant to decide whether results such as those shown in Figure 2 can provide a precise value for the polymer concentration at the onset of the upturn.

Schultz and Harborth defined the "beginning of acceleration" by reference to the concentration at which departure from first-order kinetics was observed.[33] Stannett's more direct definition, given in a paper on radiation-induced polymerization, is by identification of departure from initial linearity in a direct plot of data such as that displayed in Figure 2.[34] Both these definitions are somewhat subjective in that they require visual identification of a point on a tangent. A similar problem is encountered in definition of a yield stress from tensile stress–strain curves of certain metals and in such cases the convention is followed by taking a 2% offset which is drawn parallel to the initially linear portion of the curve.[35] A value for the yield stress is then taken by reference to the point of intersection of the experimental curve with the offset line. By analogy with this convention, a 2% offset has been indicated by a broken line in Figure 2 and a critical degree of polymerization defined by an arrowhead. This corresponds to the wt % polymer in the reaction mixture at the upturn, i.e., to the critical concentration at the onset of marked acceleration in the rate of polymerization. A replot of the same data of Schulz and Harborth according to first-order depletion of monomer is shown in Figure 3 and a critical concentration defined by an arrowhead. Results obtained by the two methods are similar to within an accuracy of 5% as shown by the table in the inset of Figure 2.

Apart from the above work there are not many precise tabulated data on record which document the polymerization of methyl methacrylate through the autoacceleration region. A notable exception is an extensive compilation by Balke and Hamielec[36] for free radical reactions initiated by azo-bis-isobutyronitrile (AZBN) at 50, 70, and 90 °C. The scatter of these data is somewhat greater than that of Schulz and Harborth but does not prevent approximate definition of a critical concentration as illustrated for dilatometric runs made at 50 °C with 0.3, 0.4, and 0.5 wt % AZBN (Figure 4).

The value of the compilation of Balke and Hamielec is increased by their inclusion of extensive molecular weight data obtained by the method of gel permeation chromatography. Such data can be used to define a critical reaction time by reference to an upturn in molecular weight. This corresponds to a critical reaction time estimated by departure of rate data from first-order kinetics. The plots (similar to Figure 3) made to obtain such estimates are not displayed but the results are indicated by the arrowheads in Figure 5. Balke and Hamielec

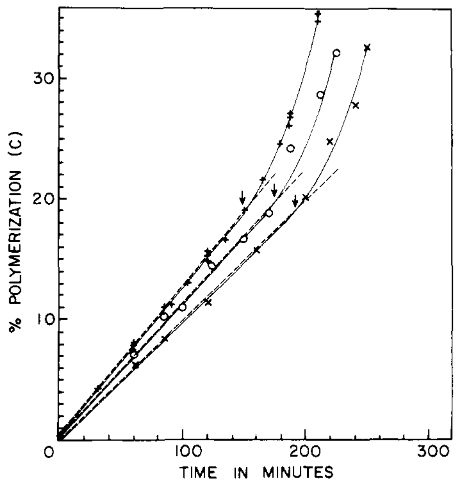

Figure 4. Conversion of methyl methacrylate to polymer with variations in initiator concentration: 50 °C; initiator, AZBN; (X) 0.3 wt %; (O) 0.39 wt %; (+) 0.5 wt % (Balke and Hamielec).[36]

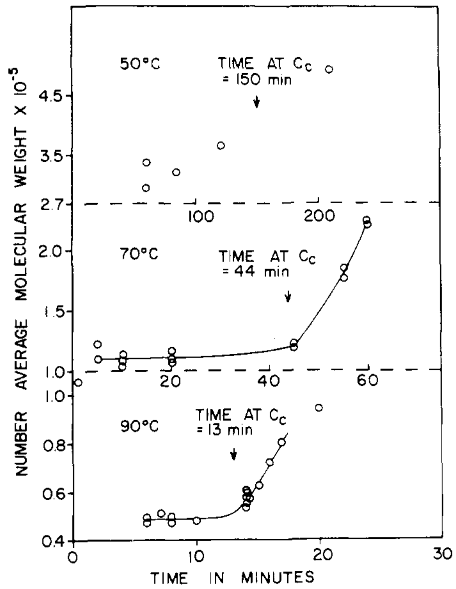

Figure 5. Dependence of $\overline{M}_n$ of PMMA on time and temperature of polymerization (Balke and Hamielec).[36]

pointed out that their highest molecular weight data are less reliable and, therefore, it is not surprising that such data do not allow definition of a critical reaction time (Figure 5, top). In summary of the use of molecular weight data to define the onset of autoacceleration, its advantage is that it may sometimes be a more sensitive technique. On the other hand, this advantage is generally offset by the greater labor involved in making numerous accurate molecular weight measurements. This disadvantage is especially serious in polymerization studies, because the continuous monitoring of molecular weight during the reaction is usually impractical.

Comparison of Experiment and Theory

The results of experiments which provide values of the number average degree of polymerization, $\overline{Z}_n$, at or just below the initial concentration, C_c, are listed in Table II. For consistency, all the values of C_c were estimated by reference to departure of rate data from first-order kinetics. Values for the density of the reaction mixture at the critical concentration, ρ_c, were calculated using specific volumes reported by Schulz and Harborth.[32] The experimental data show that the value of the product $C_c\rho_c\overline{Z}_n^{1/2}$ is much closer to constancy than that of the product $C_c\overline{Z}_n$. Therefore, on this criterion, the data are consistent with the model for macromolecular close packing rather than the one outlined for network formation by entanglements. In order to proceed to a more exacting test of the macromolecular close packing model it is first necessary to decide on the appropriate molecular weight distribution. With reference to an analysis of reaction mechanisms the parameter k, in eq 13, lies between 1 and 2 depending on the relative incidence of termination by disporportionation and combination. Moreover, the value of k probably decreases, between these limits, with increase in temperature of the polymerization reaction.[37] On the basis of experimentally determined ratios of $\overline{M}_w$ and $\overline{M}_n$ the appropriate choice, at least in the temperature range of 50 to 90 °C, appears to be $k = 1$ since this is consistent with experimental observations that $\overline{M}_w/\overline{M}_n = 2$ (Table II).[36] Hence by reference to Table I the appropriate value of $C_c\rho_c\overline{Z}_n^{1/2}$ is between $780p_f$ ($k = 1$) and $880p_f$ ($k = 2$), with a weighting toward the former value. Even if p_f is arbitrarily selected as unity, this theoretical value is somewhat lower than the mean experimental value obtained from all the values in Table II of 970 (standard deviation = 170). Nevertheless the agreement is close enough to suggest that the close packing model will serve as a useful guide to further experiments and can provide a basis for an understanding of autoacceleration at the molecular level.

Conclusions

(1) A model for macromolecular close packing of random coils treated as equivalent to uniform rigid spheres with a radius corresponding to unperturbed dimensions has been extended to include molecular weight distributions which apply to certain vinyl polymers prepared by free radical mechanisms, including PMMA and polystyrene.

(2) The novel suggestion is made that the onset of autoacceleration in the rate of free radical polymerization of methyl methacrylate corresponds approximately to the condition of macromolecular close packing.

(3) Data taken from the literature, covering a wide range of experimental conditions, have been analyzed to provide experimental values for the product $C_c\rho_c\overline{Z}_n^{1/2} = 970 \pm 170$. Approximately, this is consistent with the prediction from the model that this value should remain constant when values of C_c and $\overline{Z}_n$ vary.

(4) The value predicted by the model for a polymer formed with a random molecular weight distribution is $C_c\rho_c\overline{Z}_n^{1/2} = 780p_f$. For close packing of rigid spheres the maximum value of p_f is 0.74 and, on this basis, the predicted value is 580. Therefore the experimentally observed values are somewhat higher than that predicted by the simple model. Nevertheless, the agreement is sufficient to provide a basis for an understanding of the autoacceleration phenomenon at the molecular level.

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

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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, $\bar{Z}_n$, 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 $\bar{Z}_n < 1 \times 10^3$, i.e., experimental values of ρ_p exceeded theoretical values by not more than 30%. The discrepancy increased up to about 50% for $\bar{Z}_n > 2 \times 10^3$.

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 $\bar{M}_n = 100\bar{Z}_n$).

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

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. $\bar{Z}_n$ 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.