(averaged) mechanical observations by Schmieder and Wolf[18] and a measurement of Gillham.[19] Whereas the high apparent activation energy, $E_{a_1} \gtrsim 100$ kcal/mol, is characteristic of a glass-transition process, our value of $E_{a_2} \simeq 15$ kcal/mol corresponds closely to expectation for a β relaxation. We recall a correlation by Heijboer[20] involving the activation enthalpy of a β process in kcal/mol, namely

$$E_a = 0.06 T_\beta$$

to be applied at 1 Hz. Compressibility measurements of Quach and Simha[21] yield $T_\beta = 260$ K and thus $E_a \simeq 16$ kcal/mol. The second line drawn corresponds to $E_a \simeq 32$ kcal/mol. Boyer[22] notes a similar value for the crazing process in polystyrene and suggests a stress-induced additional process, superimposed on the intrinsic β relaxation. If this were indeed to be so, it would not arise in the present experimentation.

The results of this study indicate that photon correlation spectroscopy is a powerful tool in relaxation spectroscopy encompassing the glass transition as well as sub-glass relaxations. Further investigations of different polymer structures are obviously required, including both the depolarized and the isotropic (density fluctuations) contributions. A second important aspect is the comparative investigation of densified vs. "normal" glasses. It is established that the magnitudes of the densification vary widely[23] and one may expect substantial alterations in the dynamic and quasi-equilibrium characteristics of the density fluctuations.

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Autoacceleration of Free-Radical Polymerization. 4. Predissolved Polymer

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ABSTRACT: The onset of autoacceleration of free-radical polymerization occurs when a critical concentration of polymer is formed from the monomer. This concentration can be predicted approximately from a theory which attributes the critical concentration to a condition of macromolecular close packing. The objective of the present work was to find whether quantitatively equivalent effects could be realized in the case where polymer was predissolved in monomer. Approximately, this was found when poly(methyl methacrylate) (PMMA) was predissolved in methyl methacrylate and then polymerization initiated by benzoyl peroxide. Similar experiments but with polystyrene in place of PMMA gave erratic results because of phase separation. Polystyrene predissolved in styrene was less effective in bringing on autoacceleration than in the case where polystyrene is formed in situ from monomer. It is tentatively suggested that this is because made-up solutions of polystyrene offer less resistance to the diffusion of polymer free radicals.

Rogovin and Tsaplina showed that the polymerization of methyl methacrylate is promoted by the presence of various dissolved polymers.[1] Independently, Trommsdorff, Köhle, and Lagally showed in more detail that the autoacceleration of polymerization of this monomer, initiated by benzoyl peroxide, was promoted by prior dissolution of either poly(methyl methacrylate) (PMMA) or cellulose tripropionate.[2]

The objective of the present work is to investigate whether the onset of autoacceleration caused by addition of polymer to a monomer conforms quantitatively to the same rules as were found to apply previously for polymer formed in situ during the polymerization reaction. This involves a comparison of the experimental dependence of the onset of autoacceleration, taking into account the concentration and molecular weight distribution of the

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added polymer, with predictions of a theory which attribute this effect to the close packing of macromolecules.[3]

The theoretical interest of the present work is that addition of polymer offers hope of a better defined system which would allow a more critical evaluation of the close packing theory. For example, macromolecules formed by free-radical reactions have a distribution of molecular sizes which greatly complicates a theoretical analysis. In contrast, added polymers can be selected to be monodisperse and thereby simplify the assignment of an appropriate macromolecular packing factor. More generally, the added polymer might be selected, so as to study the influence of other structural variables such as degree of branching, for example using star-shaped polystyrenes, and controlled tacticity.

Experimental Section

Commercial samples of methyl methacrylate[4] and styrene[5] were washed to remove inhibitor and then dried as described previously. Commercial samples of benzoyl peroxide[4] and azobis(isobutyronitrile) (Polysciences, Warrington, Pa.) were used as free-radical initiators.

Atactic poly(methyl methacrylate), PMMA, of weight average molecular weight (M_w) 60 600 and number average molecular weight (M_n) 33 200, in the form of beads, was used (secondary standard, Aldrich Chemical Co., Milwaukee, Wis.). Preliminary experiments showed that dissolution of this sample in methyl methacrylate followed by heating at 70 °C caused negligible polymerization; a solution containing 30% PMMA polymerized to only 2% after 60 min. Polystyrene pellets of narrow molecular weight distribution ($M_w = 179\,300$; $M_n = 170\,900$) were obtained from the National Bureau of Standards (Standard Reference Material 705).

Solutions were prepared by adding polymer to monomer in a vessel which was shielded from light. The closed vessel was gently inverted a few times each day until dissolution appeared to be complete, after 1–6 days. Solutions were made up to concentrations in the range 2–30 g of polymer per 100 mL of solution. In some cases, to be designated later, solutions were stored after dissolution appeared complete. In other cases, solutions were vigorously shaken on a Vortex mixer for 1 h but were always allowed to relax overnight before making polymerization runs.

Initiators were gently stirred into the polymer solutions and their concentrations expressed as grams of initiator per 100 g of monomer. About 1 h later solution was introduced into the bottom of a dilatometer, avoiding contact with the upper wall, by means of a Pasteur pipet with an elongated capillary delivery tube. Because of the difficulty of handling very concentrated polymer solutions the upper concentrations which could be studied in this way were as follows: PMMA, 30 g/100 mL; polystyrene, 18.2 g/100 mL.

In preliminary experiments thermocouples placed in the dilatometers showed that after immersion in a constant temperature bath (±0.1 °C) temperature equilibration occurred within 2 min. It was also shown that isothermal conditions were maintained during the polymerization reaction, at least up to the maximum conversion which could be followed by dilatometry. After temperature equilibration the meniscus began to drop a few minutes later in the case of methyl methacrylate and tens of minutes later in styrene solutions. This lapse of time, which is due to inhibition of polymerization by dissolved oxygen, was neglected. Runs of sufficient accuracy could be made for methyl methacrylate solutions using a simple pipet dilatometer[4] but runs on styrene required use of a more sensitive bulb dilatometer.[5]

The decrease in the height of the meniscus (Δh) was followed with a magnifying glass since more elaborate measurements using a travelling microscope with a telescopic lens did not give improved reproducibility of results. The weight percent conversion of monomer to polymer (c) was calculated from eq 1 in which A is the mean cross-reactional area of the capillary tube and m the mass of monomer in the dilatometer; V_p and V_m are respectively specific volumes of polymer and monomer.

$$c = 100A\Delta h/(V_m - V_p)m \qquad (1)$$

Assuming the conversion of monomer to follow first-order kinetics gives eq 2 in which t is the time and k a specific rate constant.

$$\ln(1 - 0.01c) = -kt \qquad (2)$$

Values of concentration of polymer in weight percent (c) were derived from made-up values in g of polymer/mL of solution (ρ_p) using eq 3 with the following values for specific volumes: methyl methacrylate,[6] 1.13 (70 °C); PMMA,[6] 0.8 (70 °C); styrene,[7] 1.14 (50 °C); polystyrene,[7] 0.94 (50 °C). Equation 3 is an acceptable approximation made on the assumption of no volume change on dissolution.[6]

$$c = 100\,\rho_p[\rho_p + (1 - \rho_p V_p)V_m^{-1}]^{-1} \qquad (3)$$

Results and Discussion

Experimental conditions were chosen so as to detect a marked increase in the rate of polymerization. A short inhibition period was ignored, as in previous work on monomers alone, for reasons already justified.[4,5] To avoid any misunderstanding it should be stated that in adopting this course comment is forgone on relatively small initial changes, which occur in the first few percent of a polymerization reaction, such as have been studied in more refined experiments with rigorous exclusion of oxygen and which have been given such importance by North[10] and by Schulz.[11]

Methyl Methacrylate. Initial experiments were concerned with the question of whether dissolution of PMMA in monomer could be effected completely yet without any polymerization. As the rate of dissolution of high molecular weight PMMA in its monomer is slow, a specimen of low molecular weight polymer was used which, from visual inspection, appeared to dissolve within 1 day. In order to check whether dissolution was complete and also in order to find whether any polymerization occurred during storage at room temperature, the influence of the age of the solution on subsequent polymerization at 70 °C with peroxide was studied. It was found that the age of the solution does not influence results as can be seen most directly from experiments which showed that both the initial first-order rate constant (k in eq 2) and the time to onset of autoacceleration in the rate of polymerization are not influenced. For example, a solution containing 20.6% PMMA can be run from 1 to 9 days after mixing without detectable differences in polymerization initiated at 70 °C, a few hours after addition of initiator (Figure 1).

The influence of initial polymer concentration, for solutions aged a few days, is shown in Figure 2. The results obtained with monomer alone agree with previous findings,[4] the critical concentration for onset of autoacceleration being 23 ± 1 wt % polymer. With 30 g of predissolved PMMA per 100 mL of solution the initially linear portion of the first-order plot, up to onset of autoacceleration, is already quite restricted and obviously with higher concentrations the still briefer times to onset of autoacceleration could not be monitored precisely (see Figure 2).

An attempt to define the onset of autoacceleration by reference to the initial rate of polymerization is shown by plotting values of the first-order rate constant, k, obtained from data similar to those displayed in Figure 2. Each value of k was determined for an independently prepared solution and it will be noted that the reproducibility is good (Figure 3). The results show that there is only a slight increase in k up to 25% predissolved polymer and it is concluded that autoacceleration is not brought on immediately, by the added polymer, in this range. There is insufficient evidence to judge whether autoacceleration is brought on with 30% predissolved polymer and further

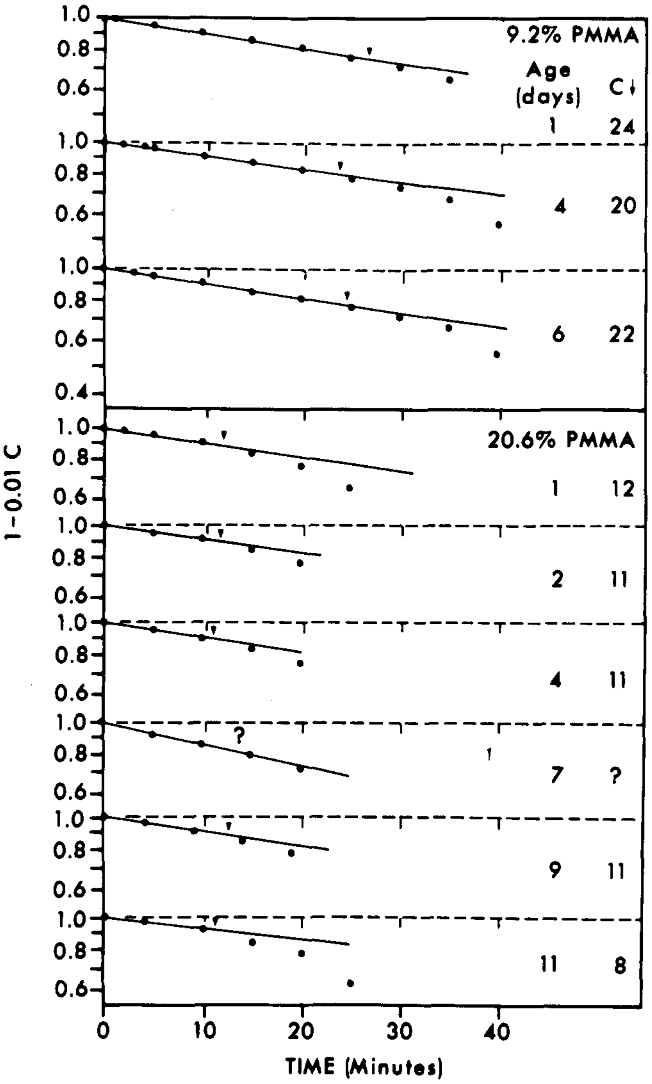

Figure 1. Influence of age of solution on polymerization of methyl methacrylate with added PMMA (Bz_2O_2, 2 wt %, calculated on monomer; temp = 70 °C). The concentrations of polymer are % w/v (i.e., g of polymer per 100 mL of solution). The onset of autoacceleration in this and subsequent figures is indicated by an arrowhead.

experiments in this region were given up, both because of the difficulty of handling such viscous solutions and also because of the limited definition of k in such cases.

A second approach to definition of the conditions which control the onset of autoacceleration is to find the concentration of added polymer which immediately causes onset of autoacceleration. Because the method used to detect the time for onset of autoacceleration from plots of data, such as Figure 2, becomes less sensitive as the critical concentration is approached, it is desirable to refer to some method of extrapolation. A method which is intuitively clear but only empirical is to plot the time of onset of autoacceleration vs. the concentration of added polymer (Figure 4). This shows a decrease in the time for onset of autoacceleration with increase in concentration of added polymer, but as the data do not follow a simple trend no definitive extrapolation could be made. Instead, it is only pointed out that the trend is not inconsistent with theoretical values calculated, according to the close packing theory, from eq 4.[12]

$$\rho_p = 1.50 \times 10^{-23} \left(\frac{\bar{r}_0^{\,2}}{M} \right)^{-3/2} \bar{M}_n^{-1/2} p_f \qquad (4)$$

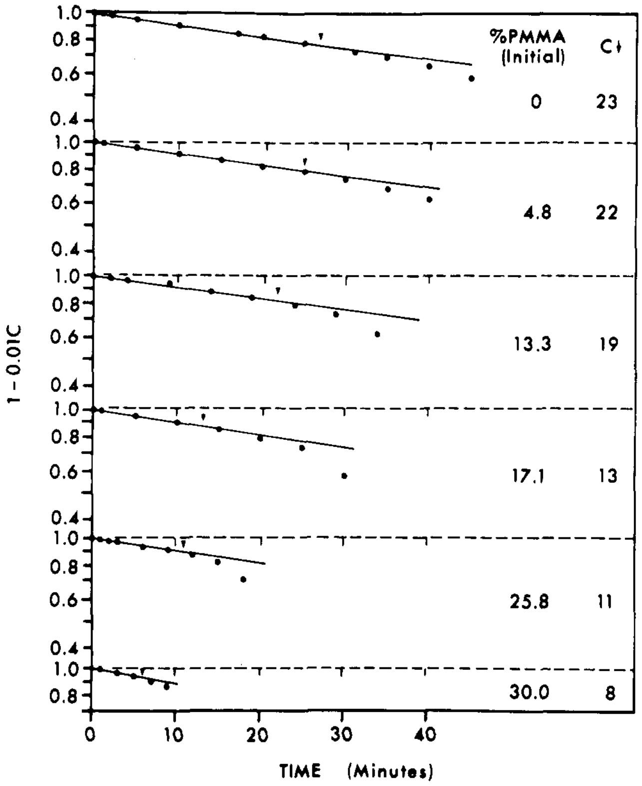

Figure 2. Influence of concentration of added PMMA on polymerization of methyl methacrylate (Bz_2O_2, 2 wt %, calculated on monomer; temp = 70 °C).

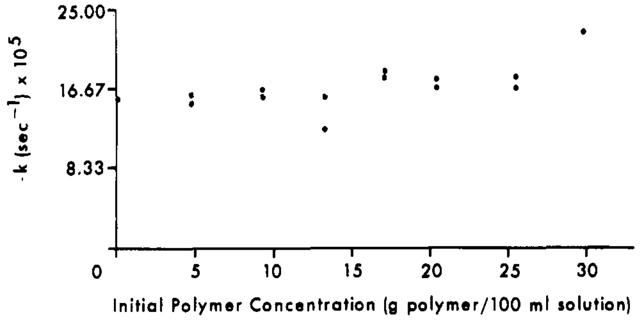

Figure 3. Influence of concentration of added PMMA on initial rate constant for polymerization of methyl methacrylate (Bz_2O_2, 2 wt %, calculated on monomer; temp = 70 °C).

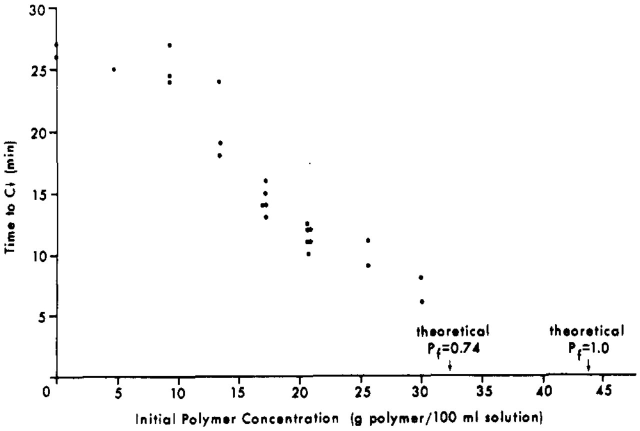

Figure 4. Empirical plot of time to onset of autoacceleration of methyl methacrylate versus concentration of added PMMA. Data from plots such as Figure 2. The theoretical values for onset of autoacceleration were calculated from eq 4.

Equation 4 approximately gives the critical concentration for autoacceleration, in g of polymer per mL of

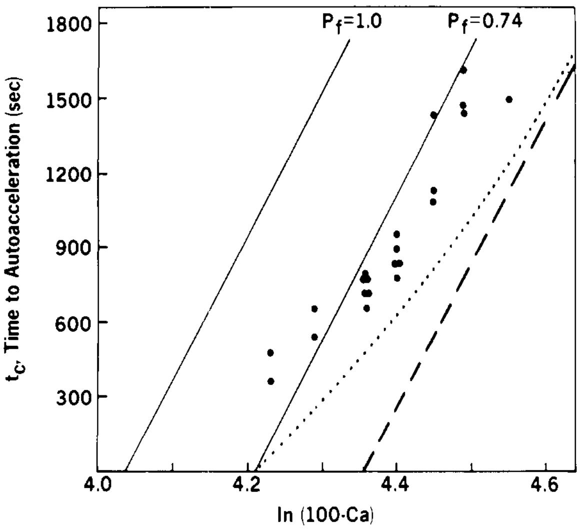

Figure 5. Plot of time to onset of autoacceleration of methyl methacrylate, t_c versus ln (100 − C_a). Data from Figure 4 plotted according to eq 8 with a slope, taken from Figure 3, of k^{-1} = (17 × $10^{-5})^{-1}$. Intercepts on ln (100 − C_a) axis calculated from eq 3 and 4, putting C_a = C_c. Full lines; $\bar{M}_n$ = 33 200. Broken line; $\bar{M}_n$ = 79 000 (p_f = 0.74). Dotted curve models, qualitatively, present experimental conditions.

solution, ρ_p, for a polymer with random molecular weight distribution. A mean value for $(\bar{r}_0^2/M)^{1/2}$ = 578 × 10^{-11} was used, as in previous work. From previous work on the polymerization of methyl methacrylate, without added polymer, the appropriate value of the packing factor, p_f, is approximately 0.74 for a polymer of $\bar{M}_n$ = 33 200.[4]

Another method of extrapolation which is more complex but which has a simple theoretical basis (Appendix) is shown in Figure 5. It will be seen that the experimental data conform roughly to the theoretical case corresponding to a packing factor closer to 0.74 than to unity.

From the above findings it is concluded that PMMA added prior to polymerization behaves similarly to polymer formed from monomer. However, the precision of data does not allow more detailed comparison with theory. In future experiments refinements might be sought by attention to a number of factors. First, a better match might be sought between the molecular weights of the added polymer and that formed from monomer. In this connection it is noted that when methyl methacrylate is polymerized alone under the conditions used in the present experiments, up to the critical concentration, it is expected to yield a product with $\bar{M}_n \simeq$ 79 000, which is about twice the molecular weight of the added polymer.[4] A theoretical plot for an added polymer of this higher molecular weight is represented by the broken line in Figure 5. Qualitatively, the actual experimental conditions should correspond to some compromise between the two theoretical cases, such as that suggested by the dotted line. The discrepancy emphasizes the need for attention to the second factor, which is to improve the precision of definition of t_c for high concentrations of polymer (cf. Figure 2). A third set of factors which should be considered concerns polymer tacticity. In the present work the polymers are "conventional" and tacticity has been neglected. However, surprisingly, it has been reported that a stereoregular polymer favors formation of a polymer with complementary tacticity. In extreme cases this results in gelation[13,14] and, presumably, should cause autoacceleration to occur earlier than predicted by the close packing theory.

A few experiments similar to those described above were made with addition of polystyrene in place of PMMA. These experiments gave erratic results but generally resulted in an onset of autoacceleration at lower polymer concentrations than would be predicted from theory. No improvement was noted when the peroxide was replaced as initiator by AZBN in order to avoid possible complications due to transfer reactions to polystyrene, and consequently of graft polymer fromation. Finally it was concluded, from observations of the development of turbidity during reaction, that complications due to phase separation made this system intractable theoretically. A similar impasse was reported previously for experiments in which methyl mathacrylate was polymerized in the presence of nonsolvents for PMMA.[15]

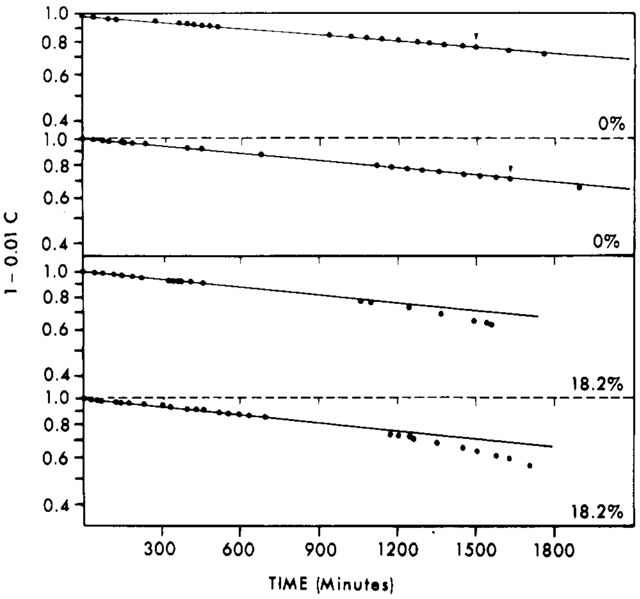

Figure 6. Influence of added polystyrene on polymerization of styrene (Bz_2O_2, 1.0 wt %, calculated on monomer; temp = 50 °C).

Part of the motivation for the experiments mentioned above was an interest in some unusual viscosity effects for ternary systems of PMMA–polystyrene–solvent reported by Cragg and Bigelow.[16] These viscosity effects were interpreted by reference to the concept of a critical concentration. Although relatively dilute solutions were studied it may be suspected in retrospect that aggregation, or incipient microphase separation, may have been a factor. A general perspective on the extreme incompatability of polymer solutions and induced aggregation in ternary systems may be obtained from a review by Morawetz.[17]

Styrene. For a monodisperse polymer ($\bar{M}_w/\bar{M}_n \approx 1$) the critical concentration is predicted theoretically from eq 5,[18] using a mean experimental value of $(\bar{r}_0^2/M)^{1/2}$ = 669 × 10^{-11}. Substitution of the value of $\bar{M}_n$ = 170 900 in eq 5 predicts values for the critical concentration of ρ_p = 0.12 g/mL and 0.16 g/mL for packing fractions of p_f = 0.74 and 1.0, respectively.

$$\rho_p = 2.0 \times 10^{-23}\left(\frac{\bar{r}_0^2}{M}\right)^{-3/2}\bar{M}_n^{-1/2}p_f \qquad (5)$$

Polymerization of the monomer alone gave reproducible estimates for the critical concentration of C_c = 21 ± 1 wt %, which is in agreement with previous results[5] obtained under similar conditions (Figure 6). In this previous work it was found that polymer formed up to the critical concentration had a molecular weight of $\bar{M}_n$ = 106 000 ($\bar{M}_w/\bar{M}_n \approx 1.5$). The gap in data collection in Figure 6 is due to an overnight break in dilatometric observations. In general it was arranged that this gap did not prevent definition of either the initial rate of polymerization or of the onset of autoacceleration, as exemplified by data for

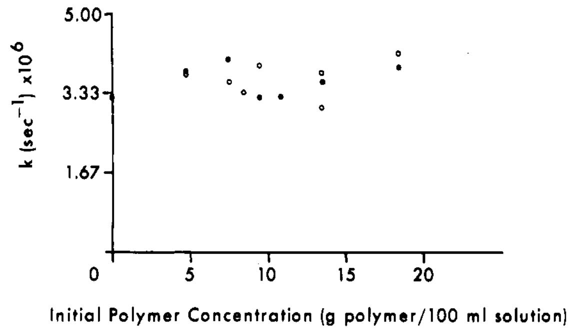

Figure 7. Influence of concentration of added polystyrene on initial rate constant for polymerization of styrene. Conditions as for Figure 6: (○) not shaken; (●) shaken.

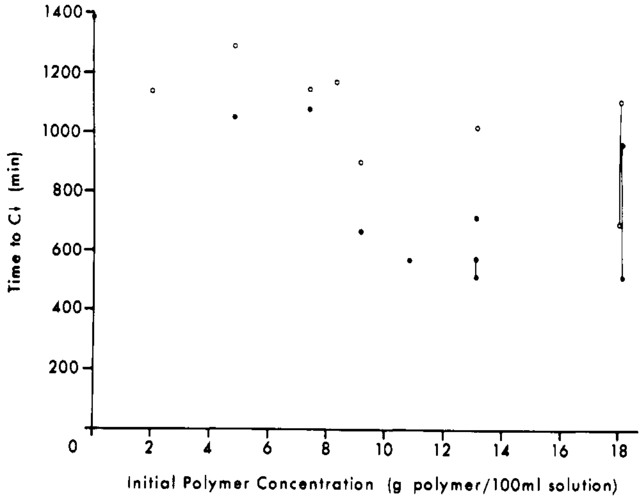

Figure 8. Empirical plot of time to onset of autoacceleration of styrene versus concentration of added polystyrene. Data from plots such as Figure 6: (○) not shaken; (●) shaken. Theoretical values for onset of autoacceleration according to eq 5 are 12 g of polymer/100 mL of solution for $p_f = 0.74$ and 16 g of polymer/100 mL of solution for $p_f = 1.0$.

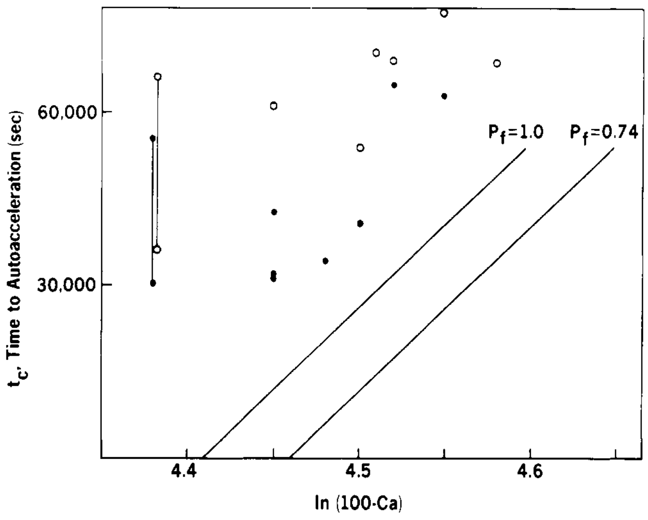

Figure 9. Plot of time to onset of autoaceleration of styrene, t_c, versus ln $(100 - C_a)$. Data from Figure 8 plotted according to eq 8 (Appendix): (○) not shaken; (●) shaken. Theoretical intercepts on the ln $(100 - C_a)$ axis were calculated using the value of $C_a \equiv C_c$ obtained from eq 5. For $p_f = 0.74$, $C_c = 13.4$; for $p_f = 1.0$, $C_c = 17.7$. Slope of $k^{-1} = (3.5 \times 10^{-6})^{-1}$ taken from Figure 7.

the monomer alone (Figure 6). However, for the most concentrated solution, because of miscalculation of this factor, only wide limits could be placed on the onset of autoacceleration and the experiment was not repeated because of the difficulty of handling highly viscous solutions.

A plot of the initial rate constant, obtained from plots similar to those of Figure 6, vs. the concentration of added polystyrene failed to detect any significant increase to a concentration of 0.18 g/mL which exceeds the upper limit, 0.16 g/mL, predicted theoretically (Figure 7). However, this does not provide decisive evidence against the occurrence of an effect because autoacceleration in styrene polymerization is small and might escape detection. More definitive results were obtained by reference to the influence of added polystyrene on the time to autoacceleration. These results show that polystyrene does decrease the time to autoacceleration but to a lesser degree than would be predicted from theory. In particular it is clear that an empirical extrapolation of data to zero time of autoacceleration would give a value for the critical concentration in excess of the theoretically predicted range of 0.12 to 0.16 g/mL (Figure 8). This discrepancy is also evident when reference is made to the simple theoretical method of extrapolation given in the Appendix (Figure 9).

In experiments of the kind described above, prior shaking of the polystyrene solutions had no detectable influence on the initial rate of polymerization (Figure 7). However, shaking did result in a decrease in the time to onset of autoacceleration although not nearly enough to bring the results into conformity with theory (Figures 8 and 9). Previously it has been suggested that shaking has a marked effect in "disentangling" polystyrene molecules even in very dilute solutions.[19] Therefore, especially in view of the much higher concentrations studied, it is possible that "disentanglement" was not achieved in the present work and that better agreement with theory might be sought by a more systematic study of this variable. Of course account would also need to be taken of the possibility of polymer degradation due to shear forces, an effect which would be expected to increase the time to autoacceleration.

The failure of added polystyrene to give results which conform quantitatively to predictions of the close-packing theory is of special interest because it may point to limitations in calculations made for a simple static model. Actually the onset of autoacceleration is governed by competing rate processes and may fail to occur at the predicted value of the critical concentration if the polymer radicals have too long a lifetime or if the restraints on their movement are too small. Polystyrene radicals do have a longer lifetime than PMMA radicals under the conditions of the present experiments but, since autoacceleration is detected near the theoretically calculated critical concentration in experiments with styrene alone, this factor cannot be decisive in the overshooting observed with added polystyrene. Instead it seems more likely that overshooting is due to smaller restraints on the movement of polymer radicals in a made-up solution as compared to one in which polystyrene is formed in situ from monomer. One somewhat trivial possibility is that the polystyrene solutions are thixotropic and that some contribution to intermolecular structure is lost when made-up solutions are delivered into a dilatometer through a capillary tube. This possibility was recognized in planning the experiments and discounted on general considerations such as a statement by Maron et al.[20] that solutions of a polystyrene of higher molecular weight ($\bar{M}_v = 240\,000$) than used in the present experiments were thixotropic only at higher concentrations than studied in the present work. Another argument against this trivial explanation is the discrepancies are observed even in more dilute solutions where thixotropy is less likely to be significant (Figure 9).

A second and more interesting speculation about discrepancies with polystyrene is that made-up solutions inherently offer less restraint to the movement of polymer radicals than do solutions prepared from monomer. In this connection it is striking that, in contrast to PMMA, made-up solutions of polystyrene can be made to flow at concentrations somewhat higher than the theoretical critical concentration. In terms of macromolecular structure, a relevant difference between the two polymers might be sought in the greater tendency of molecules of PMMA to form strong "secondary" bonds by intermolecular contacts between isotactic and syndiotactic sequences of units. This tendency in PMMA is evidenced when the mixing of a solution of an isotactic polymer with a solution of a syndiotactic polymer causes "gel" formation.[21] Possibly similar bonds are formed between occasional stereoregular sequences in conventional "atactic" polymers.

Concluding Remarks

It is concluded that: (1) added PMMA, predissolved in methyl methacrylate, is approximately equivalent to PMMA formed in situ from monomer in its influence on the onset of autoacceleration of free-radical polymerization; and (2) in contrast to the observations with PMMA, added polystyrene is less effective in bringing on autoacceleration than polymer formed in situ from styrene.

The initial objective of finding conditions which would allow a more detailed evaluation of the close packing theory appears, at present, too ambitious because of difficulties of preparing and characterizing concentrated solutions of polymers. Just the reverse, it now seems that the onset of autoacceleration might be developed as an admittedly laborious technique for providing information about the transport properties of such solutions.

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Appendix

The concentration of an added polymer, predissolved in monomer, sufficient to cause autoacceleration may be obtained empirically from plots of "added polymer concentration" vs. "observed time to autoacceleration" by extrapolation to zero time. In principle, it would be preferable to make a linear extrapolation of data which has a theoretical basis. A method is outlined below:

Let C_a be the weight percent of polymer added to the monomer. Then, $(100 - C_a)$ is the weight percent of monomer in the resulting solution. Let C be the weight percent of polymer formed from the monomer after reaction time t. C can be calculated on the assumption that polymer is formed by polymerization of monomer by a first-order reaction, i.e.,

$$C = (100 - C_a)(1 - e^{-kt}) \tag{6}$$

Eventually, after time t_c, sufficient polymer is formed which along with the added polymer causes onset of autoacceleration at the critical concentration, C_c, i.e.,

$$C_c = C_a + C \tag{7}$$

Equations 6 and 7 can be combined on the further assumption that the added polymer and the polymer formed from the monomer have equivalent influence per unit concentration on the time to reach the critical concentration, t_c

$$t_c = \frac{1}{k}[\ln (100 - C_a) - \ln (100 - C_c)] \tag{8}$$

According to eq 8 a plot of $\ln (100 - C_a)$, known from made-up values of C_a, vs. the measured time to autoacceleration, t_c, gives a straight line with a slope of k^{-1}. The value of $\ln (100 - C_a)$ extrapolated to $t_c = 0$ provides an extrapolated value of $C_c = C_a$.

In applying this simple analysis to the present data it will be noted that the assumption of formation of polymer by a first-order reaction up to the critical concentration is satisfactory (Figures 1, 2, and 6). Moreover there is evidence that k does not vary greatly in the concentraton range under consideration (Figures 3 and 7). The main objection to the present use of the analysis is that the assumption that added polymer and polymer formed from the monomer are equivalent is only a rough approximation in respect of molecular weight distribution. In more refined experiments a better match should be sought in this respect.

References and Notes

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