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

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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, $\overline{Z}_n$. 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, $\overline{Z}_n$, according to eq 1 which includes other terms defined previously.[1]

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

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

Table I
Values of ρ_p, $\bar{Z}_n$, and Derived Quantities from Previous Experimental Data

Added liquid	Liquid, vol % = 100 (1 − x)	Temp, °C	Initiator, wt %	$C = 100y$, wt % polymerization	ρ_p,[c] g/cm^3	(M), mol/L	$R_p \times 10^4$, mol/L/s	$\bar{Z}_n$	$100\rho_p\bar{Z}_n^{1/2}$	$7.77\,\bar{Z}_n^{-1/2}$
Benzene	60	50	1[a]	70	0.27	3.78	0.67	2130	1240	0.170
Benzene	40	50	1[a]	45	0.26	5.66	0.97	3310	1500	0.135
Benzene	20	50	1[a]	32	0.25	7.55	1.31	4370	1650	0.118
Monomer alone	0	50	1[a]	22	0.21	9.44	1.66	5390	1540	0.106
Benzene	60	70	1[a]	70	0.27	3.78	3.84	740	740	0.285
Benzene	40	70	1[a]	42	0.24	5.66	5.66	1130	810	0.231
Benzene	20	70	1[a]	32	0.24	7.55	7.42	1540	940	0.198
Monomer alone	0	70	1[a]	25	0.24	9.44	9.24	1930	1050	0.177
Ethyl acetate	50	60	1[b]	60	0.29			930	920	0.255
	30	60	1[b]	40	0.27			1550	1100	0.198
	10	60	1[b]	20	0.17			1830	770	0.182
Monomer alone	0	60	1[b]	20	0.19			2000	890	0.175

[a] Benzoyl peroxide (data of Schulz and Harborth[2b]). [b] Azobisisobutyronitrile (data of Robertson[4]). [c] ρ_p from eq 2 and using data of Schulz and Harborth:[10] 50 °C, $V_m = 1.10$, $V_p = 0.835$; 60 °C, $V_m = 1.115$, $V_p = 0.840$; 70 °C, $V_m = 1.13$, $V_p = 0.845$.

discussed extensively in respect of both precipitating and homogeneous reactions.[7-9]

Discussion of Previous Data

The conformity of previous data to eq 1 can be seen in perspective best by comparison with plots of ρ_p vs. $f(\bar{Z}_n)$ according to eq 2. This equation was obtained from eq 1 by substitution of a mean value of $(\overline{r_0^2}/M)^{1/2} = 578 \times 10^{-11}$ cm and can be used with parametric choices for values of the macromolecular packing factor, p_f.[1]

$$\rho_p = 7.77\bar{Z}_n^{-1/2}p_f \qquad (2)$$

Previous workers have reported values of the volume fraction of monomer (x) in the made-up mixture with diluent ($1 - x$) and also the weight fraction of monomer converted to polymer at the onset of autoacceleration (y). The corresponding mass of polymer per unit volume (ρ_p in g/cm^3) can be calculated from eq 3 in which V_m and V_p are respectively the specific volumes of monomer and polymer at the temperature of the polymerization reaction (suitable values have been determined by Schulz and Harborth[10]). Strictly, values of x should also be referred to the reaction temperature but this factor, along with other minor refinements such as the possibility of volume changes or mixing, are neglected as being unimportant for present purposes.

$$\rho_p = [V_p + V_m(1/xy - 1)]^{-1} \qquad (3)$$

Values of wt % polymerization ($100y$) at the onset of autoacceleration were estimated by Schulz and Harborth, with benzene as diluent, on the criterion of departure from first-order kinetics and are given in Table 4 of their paper. Values of $\bar{Z}_n$ are also given elsewhere in their paper but these will not be used here on the grounds that their viscosity–molecular weight relationship was subsequently found to need revision. Instead, values of $\bar{Z}_n$ are calculated from their initial rates of polymerization, R_p, using eq 3 of part 2. As explained previously, this procedure generally gives overestimates especially in cases where chain transfer occurs.[1] However, chain transfer is not expected to be a source of considerable error in the case of benzene which approximates to an inert diluent, as pointed out by Schulz and Harborth.[2]

In general, the preferred method of estimation of $\bar{Z}_n$ is from measurements of solution properties. In the case of Robertson's experiments, using ethyl acetate as diluent, values of limiting viscosity number were reported in her Table 4. Her analysis of data did not require calculation of molecular weights from these particular viscosity numbers, but for other purposes she did make use of a viscosity–molecular weight relationship which is used here again. Robertson's values of critical concentration are also given in Table 4 of her paper.

Values obtained as above are given in Table I and are used to calculate values of the product $100\rho_p\bar{Z}_n^{1/2}$. This is not a constant as required by eq 2 but varies by a factor of about 2. On the other hand, there does not seem to be any consistent variation which can be attributed to the presence of a diluent. In particular the values obtained in experiments with diluent do not differ systematically from those obtained in its absence (cf column 10, Table I).

Theoretical plots of eq 2, with $p_f = 0.74$ and 1.0, are shown in Figure 1. Results of previous experiments without diluent fall within the areas bounded by the broken curves. It will be seen that the data from Table I (columns 6 and 11) do not conform to eq 2 and, for the most part, do not agree with results obtained in experiments which differed mainly in that they did not include diluent. Again, however, it is to be noted that two out of three of the controls in the diluent experiments (i.e., samples without diluent) are also discrepant.

From the above overview it is concluded that the data obtained previously with diluents can be brought within the focus of the close-packing macromolecular model but that further work is needed to check whether sufficient experimental precision can be achieved to test conformity with eq 2.

Experimental Section

The liquids used were of analytical reagent grade. Experimental techniques were as described previously,[1] the dilatometric runs being made with the presence of air.

Results and Discussion

(1) The Influence of a Precipitant. Cyclohexane. Polymerization reactions in which precipitation occurs are outside the scope of the macromolecular close packing theory but it is pertinent to find conditions in which a nonsolvent can be included without causing precipitation, as this would allow investigation of extreme conditions in solution just short of precipitation. Cyclohexane is a good choice because not only was it included in the work of Norrish and Smith but it was subsequently studied in more detail by Hayden and Melville. These latter authors found that initially, under their reaction conditions, the polymeric product remained dissolved unless the cyclohexane exceeded 10 to 30% of the initial mixture. They also pointed out that cyclohexane acts merely as a diluent and that chain transfer is negligible.[11]

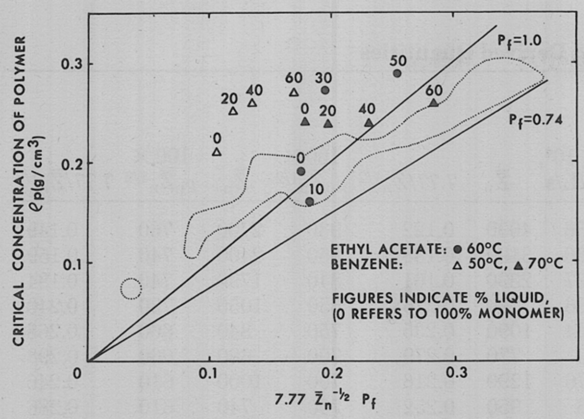

Figure 1. Plot of ρ_p vs. $7.77\bar{Z}_n^{-1/2}p_f$. The full lines are drawn according to eq 1 with $(\bar{r}_0^2/M)^{1/2} = 578 \times 10^{-11}$ cm. The two areas bounded by broken lines define the limits of experimental data obtained previously in experiments without diluents.[1]

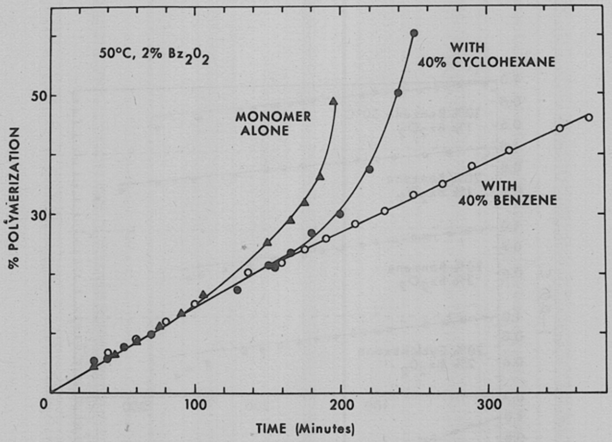

Figure 2. Polymerization of methyl methacrylate with cyclohexane and benzene as diluents (50 °C).

In a first set of experiments the influence of cyclohexane (40%) was compared with that of benzene, which is a solvent for PMMA. The experimental conditions (50 °C) were similar to those of Norrish and Smith (40 °C) except that they used an order of magnitude less peroxide (0.25 wt %). The results in Figure 2 agree with previous findings inasmuch as the onset of autoacceleration is retarded by inclusion of benzene. They differ in that whereas Norrish and Smith, and also Smets et al., found cyclohexane to accelerate the onset of autoacceleration, relative to undiluted monomer, retardation is observed in the present experiments. When a similar experiment is run at the lower temperature of 24 °C the retardation is even more pronounced than it is in the case where benzene is the diluent (Figure 3). Thus two sets of experiments which bracket the initial rate of polymerization in the work of Norrish and Smith both give a quite different result.

A reasonable explanation for the results described above can be based on an examination of the opaque precipitate which is formed before or near the onset of autoacceleration. In the faster reaction (at 50 °C) this precipitate extends throughout the reaction mixture (Figure 4A) but, in contrast, in the slower reaction (at 24 °C) the heavier "gel" phase precipitates to the bottom of the dilatometer (Figure 4B). In the latter case there obviously must be an accompanying decrease in polymer concentration in the clear supernatant layer and this would provide a sufficient reason for a marked retardation in the onset of autoacceleration. These observations are not necessarily inconsistent with the findings of Norrish and Smith nor contrary to their view that the formation of a gel phase can bring on autoacceleration by causing hindrance to the radical termination reaction. It seems more likely to be a matter of a phase transformation giving rise to a complicated variety of rate effects with relatively slight changes in reaction conditions.

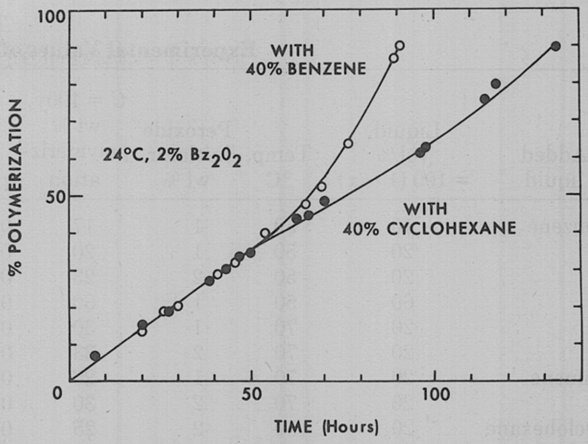

Figure 3. Polymerization of methyl methacrylate with cyclohexane and benzene as diluents (24 °C).

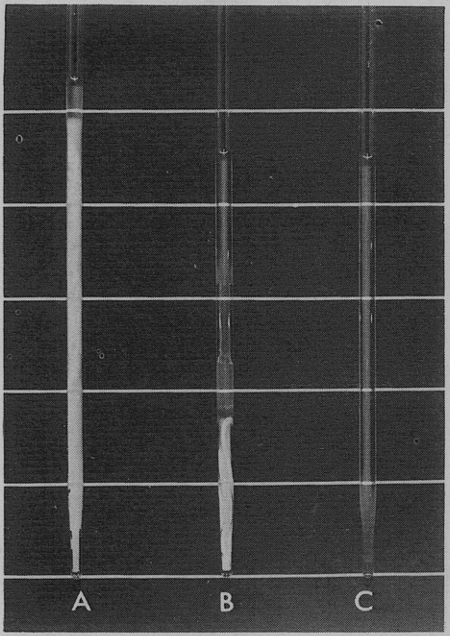

Figure 4. Appearance of reaction mixtures beyond the onset of autoacceleration: (A) Conditions of Figure 2, phase separation throughout reaction mixture (cyclohexane); (B) Conditions of Figure 3, partial phase separation (cyclohexane); (C) Homogeneous reaction under all conditions (benzene, etc.).

As a result of experiments of the kind described above, conditions were found in which 20% cyclohexane could be used as a diluent without causing any precipitation up to conversions well beyond the onset of autoacceleration. The important finding which results is that, in the absence of precipitation, cyclohexane has an influence on autoacceleration which is indistinguishable from that of a solvent for PMMA, i.e., benzene (Figure 5).

(2) The Influence of Diluents which are Solvents for PMMA. The onset of autoacceleration in mixtures including benzene or toluene, both of which are solvents for PMMA, was

Table II
Experimental Values of ρ_p, $\overline{Z}_n$, and Derived Quantities

Added liquid	Liquid, vol % = 100 (1 − x)	Temp, °C	Peroxide initiator, wt %	C = 100y, wt % polymerization	ρ_p, g/cm^3	$R_p \times 10^4$, mol/L/s	$\overline{Z}_n$	$7.77/\overline{Z}_n^{1/2}$	$100 \times \rho_p\overline{Z}_n^{1/2}$	$\overline{Z}_n$	$100 \times \rho_p\overline{Z}_n^{1/2}$	$7.77/\overline{Z}_n^{1/2}$
Benzene	10	50	1	17	0.146	1.66	4030	0.122	930	2700	760	0.149
	20	50	1	20	0.150	1.66	3190	0.138	850	2400	740	0.159
	20	50	2	23	0.174	2.27	2330	0.161	840	1790	740	0.184
	60	50	1	60	0.224	1.66	790	0.276	630	1050	730	0.240
	20	70	1	30	0.226	9.24	1090	0.235	750	840	660	0.268
	20	70	2	33	0.251	13.0	770	0.279	700	680	660	0.298
Toluene	20	70	1	26	0.194	7.76	1290	0.216	700	1000	610	0.246
	20	70	2	30	0.226	10.6	950	0.252	700	740	610	0.286
Cyclohexane	20	50	2	25	0.186	2.47	2140	0.168	860	1370	690	0.210
	20	70	1	30	0.222	8.05	1250	0.219	790	840	640	0.268
	20	70	2	33	0.246	11.1	910	0.254	730	630	620	0.310
Monomer alone	0	50	2	16	0.152	2.27	3640	0.129	920	2050	690	0.172
	0	70	1	22	0.208	9.24	1670	0.190	850			
	0	70	2	23	0.219	13.0	1210	0.223	760	790	620	0.277

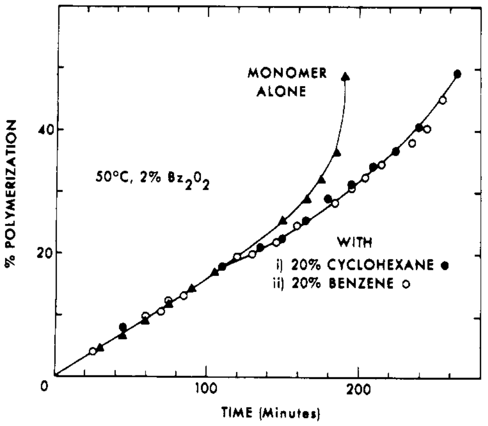

Figure 5. Polymerization of methyl methacrylate with cyclohexane as diluent, short of phase precipitation.

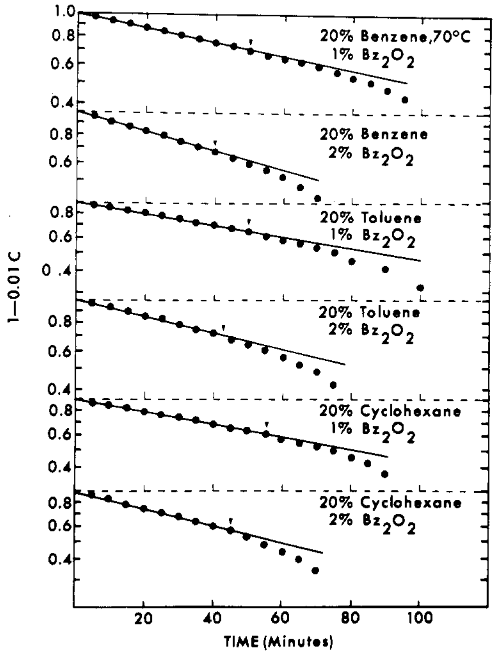

Figure 6. Homogeneous polymerization data with diluents, plotted according to first-order kinetics.

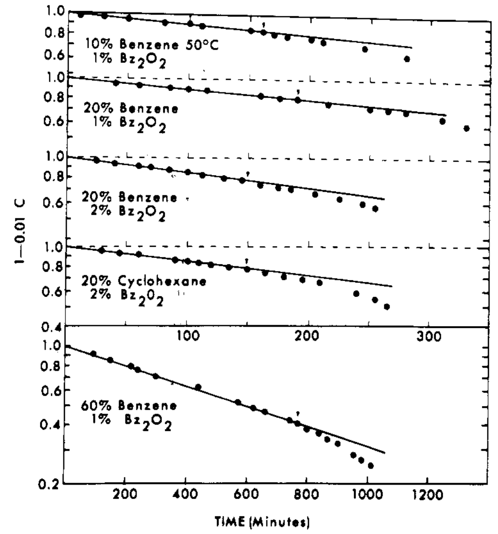

Figure 7. Homogeneous polymerization data with diluents, plotted according to first-order kinetics.

detected by departure from first-order kinetics. Results, along with ones for other homogeneous systems which include cyclohexane, are shown in Figures 6 and 7; the arrows indicate the critical concentration for autoacceleration. It is considered important to display these data because the relatively fine distinctions to be made subsequently go beyond the approximate conclusion of Schulz and Harborth that the onset of autoacceleration can be defined solely by reference to the polymer concentration, i.e., without taking account of its degree of polymerization.

(3) Comparison of Theory and Experiment. Experimental values of ρ_p, $\overline{Z}_n$, and derived quantities are given in Table II. These data are treated, with reference to eq 1, in a manner similar to that described previously[1] and, consequently, a brief discussion will suffice.

According to eq 1 a log–log plot of ρ_p vs. $\overline{Z}_n$ should have a slope of −0.5. The experimental data indicate slopes of −0.4 and −0.35 for values of $\overline{Z}_n$ estimated respectively from rate and viscosity date (Figure 8). A similar discrepancy was noted previously for experiments without diluents.

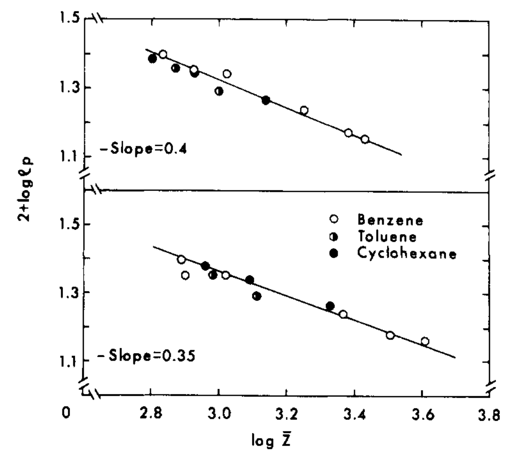

Figure 8. Plot of log ρ_p vs. log $\overline{Z}_n$.

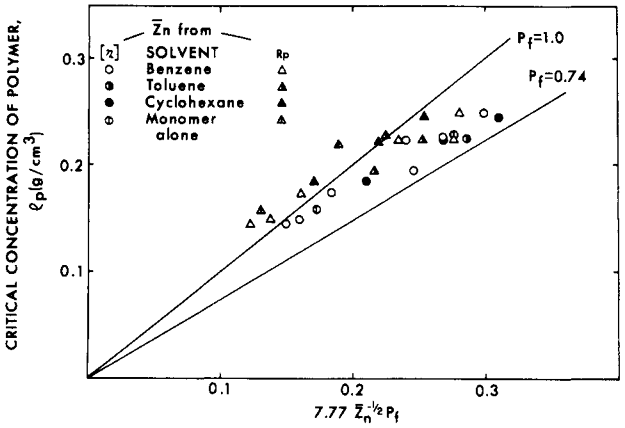

Figure 9. Plot of ρ_p vs. 7.77 $\overline{Z}_n{}^{-1/2}p_f$.

Data are plotted according to eq 2 in Figure 9. It is apparent that greater precision has been achieved than for the plot of previously reported data in Figure 1 and comparison with data for undiluted systems show a closely similar trend (cf. enclosed areas in Figure 1 or, in more detail, part 2).

Conclusions

(1) Diluents of methyl methacrylate give values of ρ_p and $\overline{Z}_n$ which conform to the close packing model for macromolecules to the same degree of approximation as data obtained in the bulk polymerization of the monomer alone.

(2) The above statement is true for both solvents and nonsolvents of·PMMA provided precipitation does not occur up to the onset of autoacceleration.

Future Work

Future work is desirable to check whether the theory applies with viscous diluents and transfer agents. The former task should be informative because of the increasing knowledge of the influence of viscosity on the early stages of polymerization.[12,13] The latter is desirable to extend measurements to include low molecular weight products obtained at longer reaction times than investigated up to this point.[14] This would provide a more severe test of the range of applicability of a static model.[1]

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