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Methyl Methacrylate Polymerization at High Conversion. II. Factors Determining the Onset of the Gel Effect

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ABSTRACT

The free volume at the onset of the gel effect depends both on chain length and temperature. For high molecular weights, the conversion at which the gel effect appears can be related to the critical entanglement.

Balke and Hamielec have proposed that the onset of the gel effect in the bulk polymerization of methyl methacrylate occurs at a characteristic free-volume value [1]. Cárdenas and O'Driscoll have introduced the concept of polymer entanglement to describe quantitatively the main factors of the bulk polymerization carried out to high conversion, but retained some elements of the free-volume theory to characterize the onset of the gel effect [2]. Nevertheless, there seems to be some incompatibility between the two theories, since the amount of entanglement, for a given conversion, depends upon the molecular weight of the polymer while the free volume is almost independent of it. If a critical amount of entanglement must be

reached to produce the gel effect, the conversion at which the effect appears must be sensitive to the molecular weight of the polymer and cannot then be determined exclusively by the free volume which, for high molecular weights, is determined exclusively by the conversion.

In order to investigate which factors determine the onset of the gel effect, we have carried out measurements of the rate of methyl methacrylate polymerization over a wide range of experimental conditions. A similar study was carried out by O'Driscoll, Wurtz, and Husar employing styrene [3]. These authors concluded that, although the gel effect appears before than the critical entanglement determined from viscosimetric measurements, both effects obey approximately the same equations.

EXPERIMENTAL

The reaction rates were measured dilatometrically, and the experimental set up was similar to that described elsewhere [4].

Limiting conversions, free volumes, and volume fractions were evaluated by use of the formulae and data given by Horie et al. [5] and Balke and Hamielec [1].

Furthermore, the volume contraction was assumed to be directly related to the conversion [1].

RESULTS AND DISCUSSION

Some of the experimental results obtained are shown in Fig. 1. The mean length of the polymer chain produced was estimated by use of Eq. (1):

$$\bar{X} = (k_p^2/k_t)[M]^2/(R_p)_0 \quad (1)$$

where $[M]$ is the initial monomer concentration, and $(R_p)_0$ is the initial polymerization rate. The values of (k_p^2/k_t) were taken from data of Schultz et al. [6] obtained at very low conversion. The value of \bar{X} was assumed to be independent of the conversion till the onset of the gel effect [1, 2]. For long chain lengths, a small correction was added to Eq. (1) to take into account chain transfer to the monomer. When the values estimated with the aid of Eq. (1) were compared with

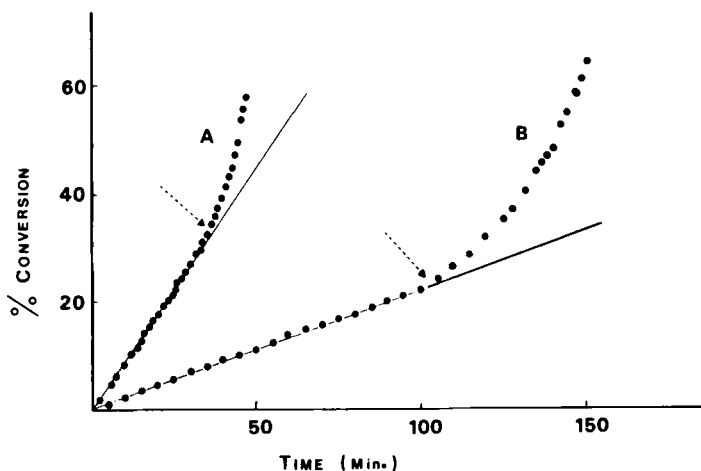


FIG. 1. Experimental data: (A) thermal polymerization initiated by AIBN (10^{-2} M) at 79° C; (B) thermal polymerization initiated by AIBN (10^{-3} M) at 75° C.

those obtained from the intrinsic viscosity of the polymer produced [7], the differences were less than a factor of 2 in all cases considered. Equation (1) was preferred due to the difficulty in evaluating \bar{X} from viscosity measurements over a wide range of molecular weights. The use of Eq. (1) can overestimate \bar{X} at high initiation rates due to the neglect of primary recombination. The possible influence of this effect will be considered in the following discussion.

The first aim of the present work was to test the hypothesis that a critical free-volume value is the only factor that determines the onset of the gel effect. One of the difficulties associated with this type of analysis is how to define the onset of the gel effect. This difficulty is stressed by the data obtained by North and Reed [8], which show that a first-order reaction in monomer cannot be assumed even at very low conversion. In all our experimental determinations, the reaction rate was nearly constant till a given conversion where a sharp increase in rate could be observed. We define then the onset of the gel effect as the point where a clear increase in polymerization rate could be observed. These points are indicated by an arrow in Fig. 1. The differences between the values of the critical concentration obtained by this method and those obtained by analytical methods. (i.e., that employed by Balke and Hamielec [1]) are not significant to the following discussion.

TABLE 1. Dependence of $(V_f)_c$ on Chain Length at 77° C

Chain length	Initiator ^a	T _g (°C)	Percentage conversion at onset of gel effect	$(\phi_p)_c$	$(V_f)_c$
13800	peroxide (t)	114	11.6	0.087	0.190
13400	peroxide (t)	114	10.8	0.081	0.190
4200	AIBN (t)	114	22.5	0.175	0.173
2800	peroxide (p)	114	20.8	0.16	0.176
2250	AIBN (t)	113	26	0.205	0.167
1250	AIBN (t)	112	28	0.222	0.164
1100	AIBN (t)	112	32	0.25	0.158
950	AIBN (t)	111.5	33	0.265	0.155
680	peroxide (p)	110.5	34	0.27	0.154
630	peroxide (p)	110.5	33	0.26	0.15
140	peroxide (p)	96.5	50	0.43	0.123

^a(t) denotes thermal polymerization; (p) denotes photochemical polymerization.

Dependence of the Free Volume at the Critical Point with \bar{X} at a Given Temperature

In Table 1 the values of the polymer volume fraction at the critical point $(\phi_p)_c$ are given as a function of the chain length of the polymer at 77° C. From these values, and by using the formulas given by Horie et al. [5] and Balke and Hamielec [1], the values of the free volumes at the critical point $(V_f)_c$ can be evaluated. The values so obtained are included in Table 1. From these data we can see that there is a dependence of $(V_f)_c$ on \bar{X} . The free volume at which the gel effect appears increases when the molecular weight of the polymer produced increases. The critical values of 0.151 assumed by Balke and Hamielec [1] corresponds, at this temperature, to an \bar{X} of approximately 600.

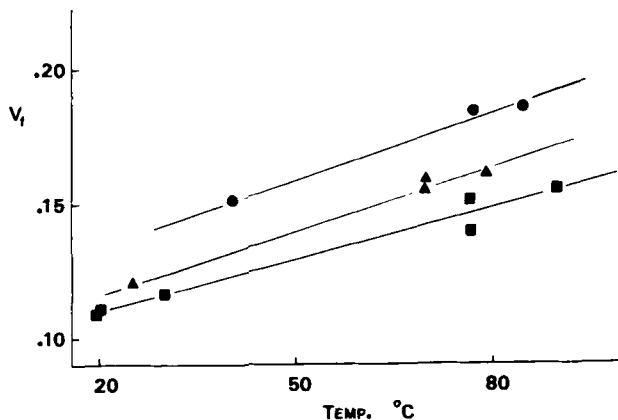


FIG. 2. Dependence of the free volume at the onset of the gel effect on temperature: (●) chain length 7500; (▲) chain length 1000; (■) chain length 440.

Dependence of $(V_f)_c$ on Temperature

Balke and Hamielec [1] have assumed that, independently of the polymerization rate and temperature, the onset of the gel effect occurs consistently at a free volume of about 0.151. On the other hand, the results of Cárdenas and O'Driscoll indicate some dependence of $(V_f)_c$ at the onset of the gel effect with temperature [2].

Since in the present work we have shown that the $(V_f)_c$ depends, at a given temperature, on the mean size of the growing radicals, it is interesting to note whether $(V_f)_c$, at a given \bar{X}_n , is independent of temperature.

The results obtained, shown in Fig. 2, indicate that $(V_f)_c$ increases when the temperature increases.

We can conclude that the free volume at the onset of the gel effect depends appreciably both on chain length and temperature.

The autoacceleration has been related to entanglement of the growing radicals [2]. It is of interest to examine if its onset can be related to a critical amount of entanglement. The viscosity of polymer solutions at zero shear rate shows a critical point at a given volume fraction which is simply related to the mean molecular weight \bar{X} by Eq. (2) [2, 10]:

$$K_c = (\phi_p)_c \bar{X}^\beta \quad (2)$$

where K_c is a constant for a given polymer-solvent pair. This singular point has been related to a critical amount of entanglement (one or two entanglements per polymer molecule). From this point, the viscosity increases much faster with the polymer percentage, due to the fact that the polymer molecules cannot move freely as single units. If the gel effect takes place at a critical entanglement value, a similar equation can be expected to relate the polymer volume fraction and the mean molecular weight of the polymer being produced [3]. Furthermore, the entanglement must depend both upon the molecular weight of the dead polymer and the size of the growing radicals [4].

If a relationship like that shown in Eq. (2) relates the chain length to the polymer volume fraction at the onset of the gel effect, a plot of $\log (\phi_p)_c$ against chain length should be linear and almost independent of temperature. All the data obtained in the present work, as well as most data previously reported, are shown in Fig. 3. This

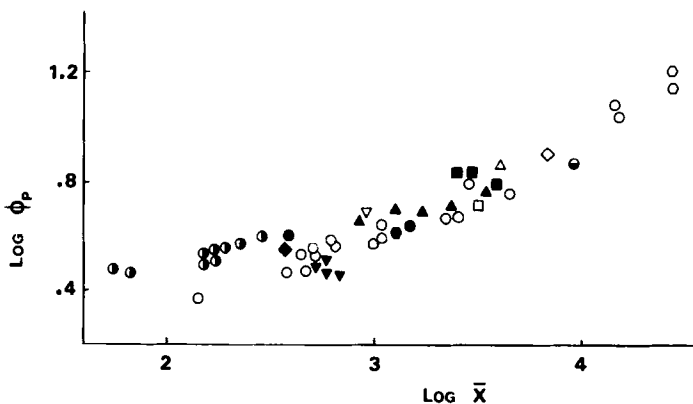


FIG. 3. Relationship between the polymer volume fraction at the onset of the gel effect and the chain length: (\circ) temperatures between 75 and 79°C, this work; (\circ) 66°C, this work; (\square) 58°C, this work; (\triangle) 52°C, this work; (\diamond) 43°C, this work; (∇) 25°C, this work; (\bullet) 20°C, this work; (\bullet) 20°C, data of Naylor and Billmeyer [9]; (\blacklozenge) 30°C, data of Naylor and Billmeyer [9]; (\blacktriangle) 70°C, data of Schultz [7]; (\blacksquare) 50°C, data of Balke and Hamielec [1]; (\bullet) 70°C, data of Balke and Hamielec [1]; (\blacktriangledown) 90°C, data of Balke and Hamielec [1]; (\circ) 86°C, this work.

figure shows that the value of $(\phi_p)_c$ is almost independent of temperature but that an equation like Eq. (2) does not hold over the entire experimental range considered. At low values of \bar{X} , the values of $(\phi_p)_c$ are less sensitive to changes in the chain length of the polymer.

It must be considered that neglect of primary recombination in the evaluation of \bar{X} can overestimate its value at high initiation rates. If this correction were appreciable the curvature of the plot shown in Fig. 3 would be still more pronounced.

The slope of the plot shown in Fig. 3 approaches a value of 0.5 at high values of \bar{X} . The values of K_c obtained by using Eq. (2) with $\beta = 0.5$ are shown in Fig. 4 as a function of \bar{X} . We can see from this figure that, at high \bar{X} , the value of K_c remains almost constant at a value of 10. We can conclude then that for polymer of high molecular weight, the onset of the gel effect, independently of the temperature can be predicted by use of Eq. (3). The values of \bar{X} and K_c are then

$$(\phi_p)_c = 10/(\bar{X})^{0.5} \quad (3)$$

of the order expected from viscometric measurements and are similar to those employed by Cárdenas and O'Driscoll to explain the behavior of the polymerization in the accelerated region. We can conclude then that, at least for high molecular weight polymer, entanglement and gel effect seem to be closely related phenomena. This requires that the termination rate constant must become controlled by the diffusion of the whole polymer and not by the segmental

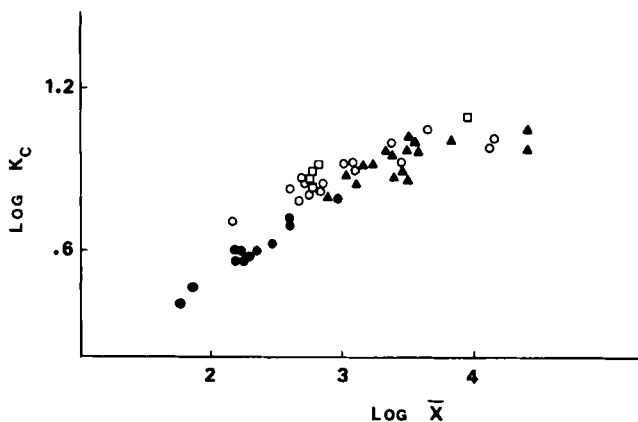


FIG. 4. Values of K_c obtained by using Eq. (2) with $\beta = 0.5$.

diffusion (which should be little influenced by the entanglement). The gel effect appears then when the diffusion of the center of mass of the growing radical, due to entanglement, becomes the rate-determining step.

On the other hand, the gel effect observed at very low molecular weight cannot be explained in terms of entanglement, since, for \bar{X} below 100, critical entanglement is not reached even in the pure polymer [10]. For these values of \bar{X} , the gel effect appears at conversions higher than 30%. Under these conditions, the polymer concentration must increase the microviscosity in the neighborhood of the growing radical, decreasing both the diffusion of the center of mass and the segmental diffusion. This dependence of microviscosity on conversion (and hence of k_t) would be less sensitive to the molecular weight, and must depend primarily upon ϕ_p .

In conclusion, our data would indicate that for high molecular weights, the gel effect appears at low conversions (where the microviscosity can be considered nearly constant) and is determined by the chain length. On the other hand, the autoacceleration observed at very low molecular weight is probably due mainly to an increase in microviscosity in the neighborhood of the growing radicals.

REFERENCES

- [1] S. T. Balke and A. E. Hamielec, J. Appl. Polym. Sci., **17**, 905 (1973).
- [2] J. N. Cárdenas and K. F. O'Driscoll, J. Polym. Sci. Polym. Chem. Ed., **14**, 883 (1976).
- [3] K. F. O'Driscoll, W. Wertz, and A. Husar, J. Polym. Sci. A-1, **5**, 2159 (1967).
- [4] E. Abuin, L. Contreras, E. Gruttner, and E. A. Lissi, J. Macromol. Sci.-Chem., **A11**, 65 (1977).
- [5] K. Horie, I. Wita, and H. Kambe, J. Polym. Sci. A-1, **6**, 2663 (1968).
- [6] G. V. Schultz and G. Henrici-Olivé, Z. Physik. Chem. (Frankfurt), **27**, 1 (1960).
- [7] G. V. Schultz, Z. Physik. Chem. (Frankfurt), **8**, 290 (1956).
- [8] A. M. North and G. A. Reed, Trans. Faraday Soc., **57**, 859 (1961).
- [9] M. A. Naylor and F. W. Billmayer, Jr., J. Amer. Chem. Soc., **75**, 2181 (1953).
- [10] R. S. Porter and J. F. Johnson, Chem. Rev., **66**, 1 (1966).

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