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Methyl Methacrylate Polymerization at High Conversion. I. Influence of the Molecular Weight of the Polymer Produced*

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ABSTRACT

Data obtained in the polymerization of methyl methacrylate at high conversion show that both the conversion at which the gel effect appears and the value of k_t at a given conversion depend upon the molecular weight of the dead polymer.

Hayden and Melville have shown that at the conversion where the gel effect is present, the termination rate constant k_t at a given temperature and conversion is a function of the initiation rate [1]. This dependence, which leads to a change in reaction order with conversion [2], can be due to a change of k_t with the size of the growing radicals or to a dependence of k_t upon the molecular weight

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of the polymer produced in the reaction [1, 3-5]. Furthermore, the conversion at which the gel effect appears at a given temperature depends on the initiation rate and on the presence of chain transfer agents added to the reaction mixture [1, 2, 6, 7]. These dependencies can also be due to one or both of the factors already mentioned.

In the present communication we report experimental data showing that the molecular weight of the dissolved polymer is a significant factor in determining both the conversion at which the gel effect appears and the termination rate constant in the accelerated region.

The polymerization rate was followed dilatometrically in a mushroom-type dilatometer [2]. A small amount of sample (generally 0.25 ml) was laid over the mercury surface in such a way that the thickness of the solution was less than 1 mm. Under these conditions the results obtained were independent of the sample, showing that self-heating is not a significant source of error [8]. Di-tert-butyl peroxide (K & K Laboratories) was employed as initiator. Light of $\lambda > 300$ nm was employed to increase the initiation rate. All measurements were carried out at 77° C.

The polymerizations were carried out with constant light intensity to a given conversion. The irradiation was then stopped, and the subsequent thermal polymerization measured. The reaction rates measured under these conditions were compared with those obtained when a similar sample was thermally polymerized. By this method we can change independently the size of the growing radical and the molecular weight of the dissolved polymer. Some of the results obtained are shown in Fig. 1 and 2.

Figure 1 shows the data obtained for run A, in which the light was cut off in the unaccelerated region (16% conversion). From this point on, the polymerization continues at a rate similar to that of the thermal polymerization at low conversion (see curve B). Since the initiation rate must be the same in both cases, this result indicates that the mean size of the growing radicals must be the same. In spite of this, the thermal reaction becomes clearly accelerated when the conversion reaches 10%, while the rate of polymerization of run A remains practically constant up to nearly 20% conversion. This type of experiment clearly shows that the molecular weight of the dissolved polymer is a significant parameter in determining the conversion at which the gel effect appears.

In Fig. 2 the data obtained when the light was cut off in the accelerated region (32% conversion) are given. Figure 2 also includes data obtained in the thermal polymerization (curve D). In spite of the fact that the rates of initiation must be the same after cutting the light off, the rates of polymerization given by the slopes of curves C and D are significantly different. It is worth mentioning that the

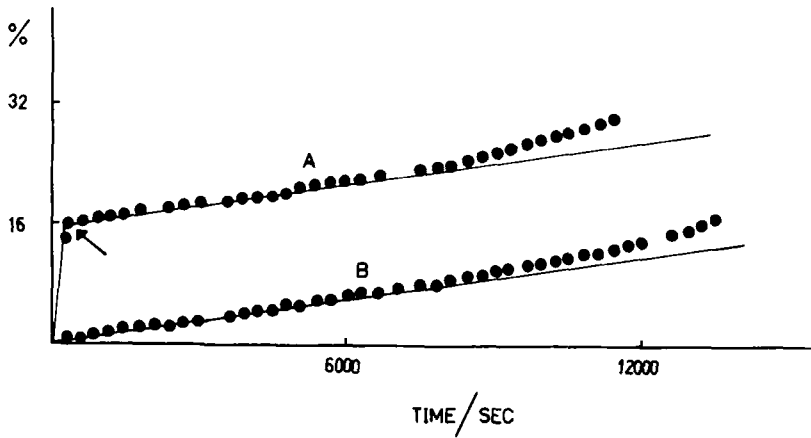


FIG. 1. Experimental data for (A) a run photoinitiated to the point indicated by the arrow; (B) thermal polymerization.

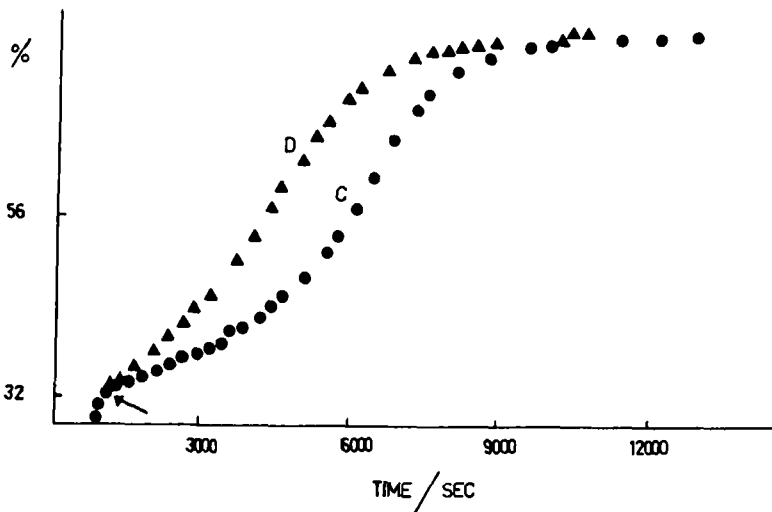


FIG. 2. Experimental data for (C) a run photoinitiated to the point indicated by the arrow; (D) thermal polymerization (the time scale has been displaced to overlap the data of curve C at the point indicated by the arrow).

possible errors (cooling of the solution after cutting the light off [8], time lag before reaching a new "pseudo" stationary state, or production of a catalyst during the irradiation [9], would lead to the opposite result (an apparent higher rate for run C).

The order in initiation a can be defined by Eq. (1):

$$a = \log (R_{p, \text{light}}/R_{p, \text{dark}}) / \log (R_{I, \text{light}}/R_{I, \text{dark}}) \quad (1)$$

where the R_p denote polymerization rates and the R_I are initiation rates.

At a given conversion, a can be measured in two ways. By relating the data of thermal polymerization to those obtained in photopolymerization we obtain a_2 . This method implies that both the mean size of the growing radicals and the reaction media change when the rate of initiation changes (since it is changing the mean size of the polymer produced). Alternatively, by measuring the rate of polymerization before and after cutting the light off we obtain a_1 . This method permits us to analyze how the reaction rate depends upon the rate of initiation in the same reaction medium.

Some of the results obtained by applying Eq. (1) to our experimental data are shown in Table 1. The difference between the values of a_1 and a_2 obtained at a given conversion can be attributed to the dependence of k_t on the molecular weight of the dissolved

polymer. The same conclusion can be reached from an analysis of the data obtained by Fujii [11], who, working under conditions such that the reaction media could be considered as nearly constant, found an order in initiation of 0.5 in spite of the decrease of a_2 with conversion [2].

The fact that the values of a_1 given in Table 1 are lower than 0.5 can be attributed to a dependence of k_t upon the mean size of the growing radical [3, 4] or to an increase in primary recombination at high initiation rates [2, 12]. On the other hand, the differences between a_1 and a_2 cannot be attributed to primary recombination, since this would imply that the primary recombination increases when the mean size of the dissolved polymer decreases.

The data obtained can be put on a more quantitative basis by employing the following simplified mechanism. If we consider that the termination is a second-order reaction and that we can apply a point-to-point steady-state treatment even in the accelerated region [1], we can obtain Eq. (2):

$$R_p/R_p' = (R_I/R_I')^{1/2} (k_p/k_p') (k_t'/k_t)^{1/2} (f/f') \quad (2)$$

TABLE 1. Experimental Data

Conversion (%)	P/P ^a	PM/PM ^b	Termination rate ratios ^c		
			a ₁	a ₂	(k _t /k _t ') ₁ (k _t /k _t ') ₂ (k _t /k _t ') ₃
0			0.5 ^d	0.5 ^d	
9	15-40	15-40		0.5	1.0
17	28-75	22-57		0.42	0.35
	40	1	0.51	1.1	
	1.05	40			0.30
28	1.9	80			0.28
	60-120	40-80		0.35	
	120	80			0.11
	80	1	0.44	0.38	
35	2	55			0.25
	2.4	80			0.20
	40	1		0.55	
	55	1		0.35	
	80	55			0.15
	130	80			0.07
41	1.3	45			0.45
	1.9	70			0.25
	40	1	0.43	0.55	
	50	1	0.42	0.35	
	14	14		0.46	
	50	40		0.35	0.25
	106	70			0.10
48	1.2	35			0.60
	2	100			0.25
	40	1		0.20	

(continued)

TABLE 1 (continued)

Conversion (%)	P/P' ^a	PM/PM' ^b	Termination rate ratios ^c			
			a ₁	a ₂	(k _t /k _t ') ₁	(k _t /k _t ') ₂
48	50	35				0.12
	80	1	0.41		0.25	
	160	100		0.30		0.07

^aP/P' denotes the relative size of the growing radicals.

^bPM/PM' denotes the relative mean molecular weight of the dissolved polymer. These values must be considered only as rough estimates.

^c(k_t/k_t')₁ = difference in termination rate constant due to differences in the mean size of the growing radicals; (k_t/k_t')₂ = difference in termination rate constant due to differences in mean size of the growing radicals and molecular weight of the dead polymer; (k_t/k_t')₃ = difference in termination rate constant that can be associated to differences in the molecular weight of the dissolved polymer.

^dAssumed value [10].

where *f* measures the initiation efficiency. The primed terms in Eq. (2) differ from the corresponding unprimed ones in the molecular weight of the dissolved polymer and/or in the mean size of the growing radicals. If we assumed *k_p* and *f* are independent of differences in the reaction media or *R_I*, then Eq. (2) can be rearranged to give Eq. (3):

$$k_t'/k_t = (R_p/R_p')^2 (R_I'/R_I) \quad (3)$$

This equation measures the relative value of *k_t* at a given conversion under different experimental conditions (i.e., differences in the reaction media and/or in the initiation rate). Furthermore, the relative sizes of the growing radicals can be estimated by use of Eq. (4):

$$P'/P = (R_p R_I') / (R_p' R_I) \quad (4)$$

since chain transfer can be neglected under our experimental conditions [13].

Data obtained by employing Eqs. (3) and (4) are shown in Table 1. Before analyzing these results it is worth discussing the error introduced by neglecting primary recombination. If we represent by α the fraction of radicals lost in primary recombination under conditions of high initiation rate (where the effect is going to be more important), Eq. (3) must be modified to

$$k_t/k_t' = (R_I/R_I') (R_p'/R_p) / (1 - \alpha) \quad (5)$$

where k_t' measures the termination rate constant under conditions of high initiation rate. The values of $(k_t/k_t')_1$ and $(k_t'/k_t')_2$ given in Table 1 have been obtained on neglecting α and must be then considered as lower limits of k_t/k_t' . On the other hand, the $(k_t/k_t')_3$ values would be nearly independent of primary recombination.

An analysis of the data given in Table 1 shows that the values of k_t/k_t' measured in the same medium are very little sensitive to the mean size of the growing radicals. Even at 40% conversion, changing P by a factor 40 changes k_t by less than a factor of 2. Also the values of $(k_t/k_t')_3$ indicate that the influence of the reaction medium is significant. If we disregard the small differences in mean radical sizes, the data obtained show that k_t can change by a factor 4 due to changes in the reaction medium.

The present results show that, although the main factor affecting k_t is the percentage of conversion, the mean size of the dissolved polymer influences its value considerably. The mean size of the growing radicals also seems to modify k_t , but the importance of this effect could have been overestimated in the present work by neglecting primary recombination.

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