

Effect of the Surrounding Polymers of a Polymer Radical on Its Termination Rate

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ABSTRACT: An effect of the surrounding polymers of a polymer radical on its termination rate has been studied in the radical polymerization of methyl methacrylate. The surrounding polymers were prepared by prepolymerization at a temperature T during time t . After t , the temperature was changed to T^* and the polymerization was continued to obtain the kinetic data. When the chain length \bar{n} of the surrounding polymers was smaller than that \bar{n}^* of the polymer radical, termination rate was found to be $\bar{k}_t \propto 1/\bar{n}$ at $\bar{n} \leq \bar{n}_c$ and $\bar{k}_t = \text{const.}$ at $\bar{n} > \bar{n}_c$ where $\bar{n}_c \approx 300 c^{-2}$ (c , polymer concentration). When $\bar{n} > \bar{n}^*$, \bar{k} is independent of \bar{n} . On the basis of the above results, the onset of the gel effect is defined to be the point at which \bar{k}_t changes abruptly at \bar{n}_c . This point was found explicitly to be the critical conversion at which $\bar{n}-x$ curve (x , conversion) and \bar{n}_c cross each other.

KEY WORDS Concentrated Polymer Solution / Temperature Changing
Method / Polymer Radical / Termination Rate / Gel Effect /

In order to treat kinetics in radical polymerization, evaluation of the termination rate between polymer radicals is necessary. When conversion is above a few percent in bulk polymerization, the excluded volume effect on the rate becomes negligibly small, and the rate constant for termination may be described as,^{1,2}

$$\bar{k}_t = \frac{4\pi pRD}{1+p} \quad (1)$$

where R is the encounter distance between polymer radicals, D , the relative translational diffusion coefficient of polymer, and p , the specific rate at distance R and is derived as,

$$p = \frac{4\pi R_s D_s}{4\pi RD} \quad (2)$$

where R_s is the reaction radius between segment radicals and D_s is the relative diffusion coefficient of the segments. When $p \ll 1$, eq 1 becomes,

$$\bar{k}_t = 4\pi R_s D_s \quad (3)$$

following modification of this equation by introducing the excluded volume effect and considering the effect of translational diffusion on the motion of a

segment, it was used to treat the experimental data obtained at low conversion.^{3,4} At a high conversion, R might approach R_s ($p \rightarrow D_s/D \gg 1$), so that eq 1 reduces,

$$\bar{k}_t = 4\pi R_s D \quad (4)$$

After D in this equation was evaluated by Stokes' law and reputation theory, eq 4 was applied to the experimental data at high conversion.⁵ Equation 1 may thus be rewritten as eq 5, in terms of eq 3 and 4.

$$\frac{1}{\bar{k}_t} = \frac{1}{\bar{k}_s} + \frac{1}{\bar{k}_t} \quad (5)$$

where $\bar{k}_t = 4\pi RD$ and eq 5 becomes eq 4 when $R \rightarrow R_s$. Equation 5 is a theoretical illustration of the change in the termination rate with increasing conversion.

In the present paper, evaluation of this change by eq 5 was done by using the kinetic data based on physical meanings. These data were obtained for the bulk polymerization of methyl methacrylate (MMA) initiated by 2,2'-azobisisobutyronitrile (AIBN) in the presence of nonreactive PMMA of various chain lengths.

EXPERIMENTAL

Commercial MMA and AIBN were purified by the method described above.⁶

The initiator and monomer in the ampoule were degassed under a vacuum of about 10^{-3} mmHg. The ampoule was maintained at a given temperature T during the proper prepolymerization time t in order to prepare the surrounding polymers of a polymer radical. Following the lapse of time t , the temperature was changed to T^* and the polymerization was continued during the proper time t^* to obtain kinetic data. Here, the chain length of the surrounding polymers was estimated by measuring the intrinsic viscosity $[\eta] = 8.12 \times 10^{-3} \bar{n}^{0.71}$ in toluene at 25°C.⁷

Formerly in preparing the surrounding polymers, the polymers of short chain length were dissolved in the polymerization solution.⁸⁻¹⁰ However, the preparation of a uniform high concentration solution of polymers of the proper chain length was difficult, as stated in ref 10. By the temperature changing method in the present paper, we were able to prepare the polymerization solution of an arbitrary concentration of polymers having the proper chain length and in which the maximum of \bar{n} was determined by the transfer of the polymer radical to the monomer and polymer. To assist in carrying out this method, polymers with $\bar{n} = 168$ and 424 were also prepared and used as the surrounding polymers of a polymer radical.

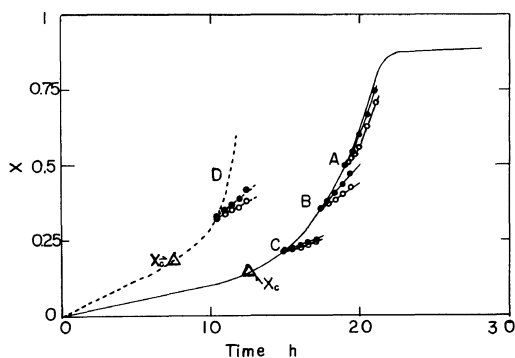


Figure 1. Time-conversion curves in polymerizations when of $\bar{n}^* > \bar{n}$ at $T = 30.0^\circ\text{C}$: ---, $[\text{C}]_0 = 0.152 \text{ mol dm}^{-3}$; —, $[\text{C}]_0 = 0.0305$; A, $x^* = 0.50$; B, $x^* = 0.36$; C, $x^* = 0.21$; D, $x^* = 0.33$ (○, $T^* = 90.0^\circ\text{C}$; ●, 80.0).

RESULTS

When the temperature was not changed ($T = T^*$ or $t^* = 0$), the usual conversion-time ($x-t$) curve was obtained (Figures 1 and 2). When the temperature was changed from 80 and 90°C to 30°C, x^*-t^* curves were obtained and are shown in Figure 1.

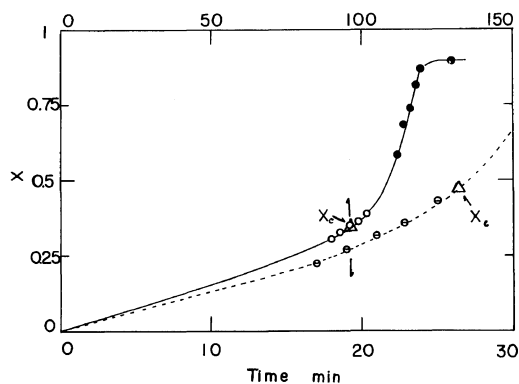


Figure 2. Time-conversion curves in polymerizations in which $\bar{n}^* < \bar{n}$: —, $T^* = 60.0^\circ\text{C}$ (○, $x^* = 0.305$; ●, $x^* = 0.584$ at $T = 30.0^\circ\text{C}$ at $[\text{C}]_0 = 0.0305 \text{ mol dm}^{-3}$); ---, $T^* = 80.0$ (○, $x^* = 0.225$ at $T = 30.0$ at $[\text{C}]_0 = 0.0305$).

Table I. Kinetic data obtained at $[\text{C}]_0 = 0.0305 \text{ mol dm}^{-3}$ at $T^* = 30.0^\circ\text{C}^a$

T °C	x_o^*	$10^5 R_p$ mol dm ⁻³ s ⁻¹	$10^{-5} \bar{k}_t$ dm ³ mol ⁻¹ s ⁻¹	\bar{n}
30.0	0	2.06	774	22300
30.0	0.210	9.05	28.7	32900
40.0	0.209	9.04	28.7	11030
50.0	0.210	8.51	31.9	7010
60.0	0.207	6.63	51.6	3710
70.0	0.214	5.01	87.3	2880
80.0	0.210	3.80	143	1600
90.0	0.215	3.30	186	780
30.0	0.360	16.7	6.07	54000
60.0	0.363	16.7	5.74	3950
70.0	0.358	15.9	6.05	3200
80.0	0.357	12.9	8.46	1510
90.0	0.361	7.42	23.4	647
30.0	0.500	23.6	2.06	82600
60.0	0.495	23.6	1.93	10200
70.0	0.508	22.1	2.06	5300
80.0	0.503	20.8	2.12	2200
90.0	0.498	17.2	2.70	1055

^a The suffix (o) denotes the initial stage.

Table II. Kinetic data obtained at $T^* = 30.0^\circ\text{C}^a$

$10^3 [C]$	T	x_o^*	$10^5 R_p$	$10^{-5} \bar{k}_t$	\bar{n}
152	30.0	0	6.52	775	10500
152	30.0	0.330	34.3	7.74	24400
152	40.0	0.327	34.2	7.79	8220
152	50.0	0.333	29.6	10.3	3810
152	60.0	0.324	17.7	28.4	1610
152	70.0	0.332	12.7	54.4	862
152	80.0	0.330	10.1	83.3	459
152	90.0	0.335	5.2	300	230
76	30.0	0.330	26.0		
30.5	30.0	0.330	16.4		40500
7.6	30.0	0.330	9.3		

^a The same units as in Table I.

Table III. Kinetic data obtained at $[C]_0 = 0.0305 \text{ mol dm}^{-3}$ when $\bar{n}^* < \bar{n}^a$

T	T^*	x_o^*	$10^5 R_p$	$10^{-5} \bar{k}_t$	\bar{n}
30.0	80.0	0.225	263	303	30500
80.0	80.0	0.225	246	302	1500
30.0	60.0	0.305	84.4	92.3	37000
60.0	60.0	0.305	82.5	91.9	4350
30.0	60.0	0.584	652	6.9	93500
60.0	60.0	0.584	642	6.9	6700

^a The same units as in Table I.

Table IV. Kinetic data obtained at 30.0°C when PMMA with a known chain length were dissolved^a

$10^3 [C]$	x	\bar{n}	$10^5 R_p$	$10^{-5} \bar{k}_t$
30.5	0.36	168	4.0	105
30.5	0.50	168	9.2	10.7
30.5	0.50	424	13.4	6.4
7.61	0.50	424	5.56	
1.90	0.50	424	2.78	
0.476	0.50	424	1.51	

^a The same units as in Table I.

When the temperature was changed from 30°C to 60 and 80°C , x^*-t^* curves were obtained as shown in Figure 2. The polymerization rate R_p was calculated from the slope of x^*-t^* line obtained at the initial stage following the change in temperature (Tables I, II, and III). The data obtained when the polymers of $\bar{n}=168$ and 424 were dissolved are shown in Table IV.

Termination rate constant was calculated by,

$$\bar{k}_t = \frac{2fk_d k_p^2 [C][M]^2}{R_p^2} \quad (6)$$

where f is the fraction of a primary radical escaping from the solvent cage ($f=0.57$),⁹ k_d is the decomposition rate constant of AIBN ($k_d=1.58 \times 10^{15} \times \exp(-15500/T) \text{ s}^{-1}$),¹¹ k_p is propagation rate constant ($k_p=4.92 \times 10^5 \exp(-2192/T) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$),¹² and $[C]$ and $[M]$ are the concentration of the initiator and monomer, respectively. The \bar{k}_t -values obtained are shown in Tables I to IV.

DISCUSSION

Polymerization Carried Out When the Chain Length of Polymer Radical is Larger than \bar{n}

As shown in Tables I and II, \bar{n} decreases with increasing T . Usually, the chain length \bar{n}^* of a polymer radical is estimated by,

$$\bar{n}^* = \frac{R_p}{2fk_d[C] + C_{tr}R_p} \quad (7)$$

where C_{tr} is the relative transfer constant. In consideration of this, it is evident that \bar{n}^* increases with increasing in R_p . At 30°C , $\bar{n}^* > 22300$ at $[C]=0.0305 \text{ mol dm}^{-3}$ and $\bar{n}^* > 10500$ at $[C]=0.152$, as expected, because of an increase in R_p with increasing x (Figure 1). Therefore, in all the polymerizations shown in Figure 1 and Tables I, II, and IV, $\bar{n}^* > \bar{n}$ is satisfied. When \bar{n} is less than the critical chain length \bar{n}_c at a given concentration, \bar{k}_t decreases with increasing in \bar{n} . When \bar{n} is larger than \bar{n}_c , \bar{k}_t is independent of \bar{n} . These relationships are presented as follows,

$$\bar{k}_t \propto 1/\bar{n} \quad \text{at } \bar{n} \leq \bar{n}_c \quad (8a)$$

$$\bar{k}_t = \text{constant} \quad \text{at } \bar{n} > \bar{n}_c \quad (8b)$$

This phenomenon resembles a well known phenomenon in the translational diffusion of polymers, which has been treated by the classical entanglement theory¹³ and the modern reputation theory.¹⁴ Based on these theories, the critical chain length n_c is estimated to be,

$$n_c = 300 c^{-\gamma} \quad (9)$$

where 300 is the critical chain length in undiluted PMMA,¹³ c is the polymer concentration, and γ is estimated to be 1 , 1.25 , and 2 .¹³⁻¹⁶ In the present

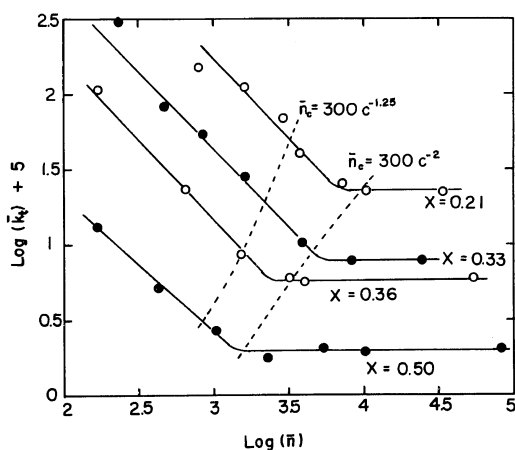


Figure 3. Relationships between \bar{k}_t and \bar{n} when $\bar{n}^* > \bar{n}$ at 30.0°C.

experiments, \bar{n}_c is close to eq 9 with $\gamma=1.25$ and 2 (Figure 3) and $\gamma=2$ is somewhat better. Thus, $n_c = 300 c^{-2}$ is used in the following discussion.

At $\bar{n} < n_c$, the proportionality of \bar{k}_t to $1/\bar{n}$ (eq 8a) is also obtained on the physical grounds that ηD_s (for eq 3) or ηD (eq 4) = constant and $\eta \propto \bar{n}^{1.3}$ where η is the solution viscosity. However, determining which one is true, eq 3 or 4, eq 8a has no effect. This is based on experimental data to be presented in a later section.

At $\bar{n} > n_c$, the termination rate derived as eq 4 corresponds to eq 8b. Since the diffusion coefficient of polymer is proportional to the entanglement density, eq 4 shows that the entanglement density is independent of the chain length of the surrounding polymers.

Polymerization in Which $\bar{n}^* < \bar{n}$

In the polymerizations shown in Figure 2 and Table III, the condition of $\bar{n}^* < \bar{n}$ is satisfied. The polymerization rate whose temperature was changed ($T=30^\circ\text{C} \rightarrow T^*=60$ or 80), was slightly larger than R_p , whose temperature was not changed. This slight difference is based on the difference in $[C]$, k_d which increases with change in temperature. When the difference in $[C]$ is modified, the respective difference in $[C][M]^2/R_p^2$ ($\propto \bar{k}_t$) can not be detected (Table III). It is concluded that the termination rate is independent of \bar{n} when $\bar{n}^* < \bar{n}$.

Graessley¹⁷ has discussed the complexity of the diffusion of a polymer in a polydispersity system. Although the radical polymerization system is essen-

tially polydispersity, the diffusion of a polymer radical in terms of \bar{k}_t is not as complex as he maintains. At least, in the present cases, in treating diffusion of a polymer radical, the introduction of eq 8 is necessary, but the others are trivial.

Definition of the Onset of the Gel Effect

Formerly, a termination rate was presented in terms of a critical conversion at which the solution exhibited an abrupt change in viscosity.¹⁸ In particular, such a change is marked when the autoacceleration of polymerization rate appears. Thus, in order to join a quantitative understanding of this autoacceleration, the onset of the gel effect is defined by the close packing theory.¹⁹ Also Dionisio *et al.*²⁰ defined the onset of the gel effect as the point at which the segmental diffusion-controlled termination rate is equal to the translational rate ($\bar{k}_s = \bar{k}_T$). However, the above treatments do not stem from the familiar physical bases shown by eq 8 and 9. Furthermore, after the excluded volume effect has disappeared, both \bar{k}_s and \bar{k}_T decrease slowly with increasing x at $\bar{n} \leq \bar{n}_c$. Therefore, the critical conversion x_c at the onset of the gel effect is vague, when the $x-t$ curve does not change abruptly. These cases are the bulk polymerization at a lower initiation rate in Figure 1 ($[C]=0.0305$ mol dm⁻³ at 30°C) and that at high temperature (80°C) as shown in Figure 2.

In the present paper, the best definition for the onset of the gel effect is made by eq 9. That is, the onset of the gel effect is the point at which \bar{k}_t changes abruptly at \bar{n}_c . The value of x_c at this point

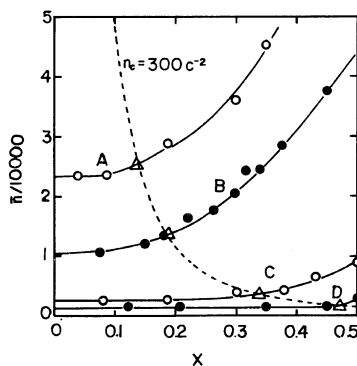


Figure 4. Determination of the critical conversion x_c (Δ): A, $x_c=0.13$ at 30.0°C at $[C]_0=0.0305$ mol dm⁻³; B, $x_c=0.19$ at 30.0°C at $[C]_0=0.152$; C, $x_c=0.34$ at 60.0°C at $[C]_0=0.0305$; D, $x_c=0.47$ at 80.0°C at $[C]_0=0.0305$.

can be found explicitly as the cross point between $\bar{n}-x$ curve and eq 9 (Figure 4). The x_c values are shown in Figures 1 and 2. It is apparent that x_c corresponds to the onset of the gel effect.

Dependence of R_p on $[C]$

At $x > 0.1$, the excluded volume effect has disappeared.²³ When \bar{n}^* is larger than 1000, the effect of D on D_s also disappears.^{3,4} Thus, the termination rate does not depend on \bar{n}^* , provided it is segmentally diffusion-controlled (eq 3). However, if it is translationally diffusion-controlled (eq 4), it depends on \bar{n}^* . To clarify this, an examination of the dependence of \bar{k}_t on \bar{n}^* is presented below. In accordance with previous reports,^{6,21} if the termination rate is defined as $k_t \propto \bar{n}^{*-2a}$, the polymerization rate is given by,

$$R_D \propto [C]^{A(a)} \quad (10)$$

where $A(a) = (1-2a)/2(1-a)$ when the non-reacting polymers are produced by termination only. $A(a) = (2-3a)/(4-2a)$ when the polymers are produced by both termination and the transfer. $A(a) = 1/2$ when they are produced only by transfer. For a typical

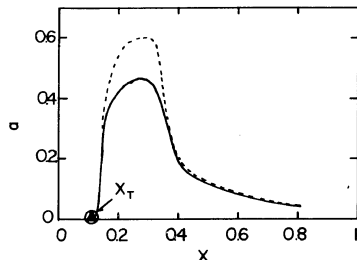


Figure 5. Relationship between a and x obtained in the polymerization at 45.0°C when $[C]_0 \geq 0.025 \text{ mol dm}^{-3}$:⁶ —, $A(a) = (1-2a)/2(1-a)$; ---, $A(a) = (2-3a)/(4-2a)$.

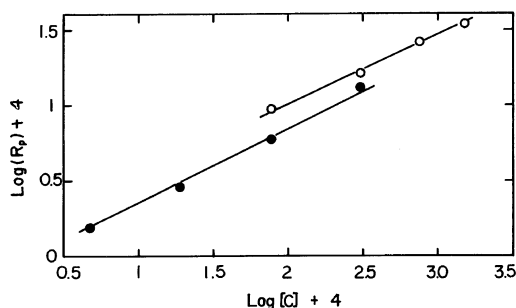


Figure 6. Relationship between R_p and $[C]$ at 30.0°C : \circ , $x=0.33$; \bullet , $x=0.50$ ($\bar{n}=424$).

illustration of eq 10, the relationship between a and x is shown in Figure 5. At $x < 0.12$, a is found to be zero. With increasing x , a increases, since the termination predominates and its rate depends on n^* . At $x > 0.3$, a decreases with increasing x . The critical conversion $x_c = 0.13$ obtained in the polymerization at $[C]_0 = 0.0305 \text{ mol dm}^{-3}$ at 30°C (Figure 1) is equal to the conversion x_T at which a is taken off the base line. However, the other x_c values are different from $x_T = 0.12$, i.e. $x_c = 0.47$ in the polymerization at 80°C in Figure 2. Perhaps, at $x > x_T$, the termination rate may be translationally diffusion-controlled and eq 4 may be used. A critical conversion defined by Dionisio *et al.*²⁰ may correspond to x_T , since $\bar{k}_s = \bar{k}_T$.

In this paper, in order to estimate the long chain length $\bar{n}_c = 7100$ at $x = 0.21$, the initiation rate at 30°C was made so slow that the transfer predominates at $x > 0.2$. Also a higher initiation rate ($[C] > 0.16 \text{ mol dm}^{-3}$) was experimentally impossible in obtaining correct kinetic data.

Consequently, as estimated from eq 7 and Tables I, II, and IV, $2fk_d[C] < C_{tr}R_p$ may be actual at $x > 0.2$, where $C_{tr} \approx 10^{-5}$.²² Thus, in view of eq 10, $A(a)$ reduces to $1/2$, even if the termination rate depends on chain length (Figure 6). This case corresponds to the polymerization at $x > 0.5$ in Figure 5.

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