Estimation of Molecular Weight in Terms of the Gel Effect in Radical Polymerization

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ABSTRACT: In consideration of the modern idea of reptation, it is proposed that the rate of termination is proportional to $n^{-1/2}$ (n =chain length) when n is less than a critical chain length n_c , but the rate is proportional to n^{-2} when $n > n_c$. The molecular weight in terms of the gel effect is calculated by using such a rate. This molecular weight fits sufficiently to the experimental molecular weight obtained previously in a radical polymerization of methyl methacrylate. Further, the rate constant of termination between small polymer radicals is discussed by the free volume theory.

KEY WORDS Molecular Weight / Radical Polymerization / Gel Effect / Reptation Model / Termination Rate / Methyl Methacrylate / Free Volume /

In studying the gel effect in radical polymerization, it was found that the termination rate between polymer radicals depends on their chain length,^{1–3} since the rate is translational diffusion-controlled. Here, a typical equation, describing such dependence, is

$$k_{t,ns} \propto (n^{-a} + s^{-a}) \quad (1)$$

where $k_{t,ns}$ is the rate constant of termination between polymer radicals of chain length n and s , and a is the parameter set to be the same constant in the all range of chain length. Generally, the n -dependence of the coefficient of translational diffusion at $n > n_c$ is markedly larger than that at $n \leq n_c$, where n_c is a critical chain length and has been estimated by the classical idea of polymer entanglement^{4–6} and the modern idea of reptation.^{7–10} Thus, on the assumption that the rate is proportional to the coefficient of the translational diffusion, a in eq 1 should not be the same constant for all chain length. Recently, in order to study the gel effect, certain methods based on the classical idea of entanglement have been proposed.^{11–14} The author has formulated the rate equation only when the transfer of polymer radical to solvent predominates, no equation could be formulated when such a transfer was not predominant, owing to the difficulty involved. In the other methods,^{12,13} the termination rate at $n \leq n_c$ was distinguished from the termination

rate at $n > n_c$, because of the entanglement density. However, in spite of the n -dependence of the translational diffusion,^{4–10} this dependence was not considered. In this paper, eq 1 is modified by the modern idea of reptation.^{7–10} The molecular weight of a polymer is estimated by this modified equation.

THEORY

The termination rate equation is rewritten as^{1,2}

$$k_{t,ns} = 4\pi RD \quad (2)$$

where R is reaction radius between the end radicals of the polymers and D is the relative diffusion coefficient explained below. When $n \leq n_c$, Einstein and Stokes' relation, given by eq 3, may be adopted for evaluating the diffusion of the polymers.^{1,2}

$$D = D_0(n^{-1/2} + s^{-1/2}) \quad (3)$$

where D_0 is the diffusion coefficient of monomer unit. When $n > n_c$ reptation^{7–10} shows that the diffusion coefficient of the polymer is proportional to n^{-2} . Thus, D is given by

$$D = D_0 n_c^{3/2} (n^{-2} + s^{-2}) \quad (4)$$

Introducing eq 3 and 4 into eq 2, eq 1 is rewritten as

$$k_{t,ns} = k(\zeta_n + \zeta_s) \quad (5)$$

($\zeta = n^{-1/2}$ at $n, s \leq n_c$; $\zeta = n_c^{3/2} n^{-2}$ at $n, s > n_c$)

where $k = 4\pi RD_0$, and n_c is evaluated by

$$n_c = \frac{(18\pi^2)^{1/2}}{A} c^{-1.25} \quad (6)$$

where c is the polymer concentration and A is a constant depending on size of the monomer.⁹

The rate equation for radical polymerization is

$$\begin{aligned} \frac{d[N_n]}{dt} &= k_p[N_{n-1}][M] - k_p[N_n][M] \\ &- \sum_{s=1}^{\infty} k_{t,ns}[N_n][N_s] - k_{tr}[S][N_n] = 0 \end{aligned} \quad (7)$$

where k_p and k_{tr} are the rate constants of propagation and transfer, respectively; $[M]$, $[S]$, and $[N_n]$ are the concentrations of monomer, solvent, and polymer radical with n , respectively. Using the same method as in previous papers,^{15,16} the equation for the fraction of polymer radicals with n was determined as

$$\frac{[N_n]}{[N]} = \frac{F(n)}{F(1) + F(2) + \cdots + F(\infty)} \quad (8)$$

$$F(n) = \frac{1}{g(1)} \cdot \frac{1}{g(2)} \cdots \frac{1}{g(n)} \quad (9)$$

$$g(n) = 1 + C_{tr} + \frac{fk_d[C]}{R_p} (1 + \zeta/\bar{k}) \quad (10)$$

$$\bar{k} = \sum_{s=1}^{n_c} s^{-1/2} \frac{[N_s]}{[N]} + n_c^{3/2} \sum_{s=n_c+1}^{\infty} s^{-2} \frac{[N_s]}{[N]} \quad (11)$$

$$\left([N] = \sum_{s=1}^{\infty} [N_s] \right)$$

where $C_{tr} = k_{tr}[S]/k_p[M]$, f is the fraction of a primary radical escaping from solvent cage, k_d is the decomposition rate constant of the initiator, $[C]$ is the initiator concentration, and R_p is the polymerization rate. To estimate the $\bar{k}$ -value, eq 8—11 is solved numerically. That is, an appropriate $\bar{k}$ -value is set up. The computation based on eq 8—11 yields a more probable value. Repeating such computation causes $\bar{k}$ to converge the most probable value. By using this value, the most probable $[N_n]/[N]$ can be calculated.

When disproportionation predominates, the production rate of the non-reacting polymer with n is

$$R_{t,n} = \sum_{s=1}^{\infty} k_{t,ns}[N_n][N_s] + k_{tr}[S][N_n]$$

$$= fk_d[C] \left(1 + \frac{\zeta}{\bar{k}} + \frac{C_{tr}R_p}{fk_d[C]} \right) \frac{[N_n]}{[N]} \quad (12)$$

Thus, the instantaneous fraction $\phi(n)$ of a non-reacting polymer with n becomes

$$\begin{aligned} \phi(n) &= \frac{R_{t,n}}{\sum_{n=1}^{\infty} R_{t,n}} \\ &= \left(\frac{1 + \zeta/\bar{k} + R_p C_{tr}/fk_d[C]}{2 + R_p C_{tr}/fk_d[C]} \right) \frac{[N_n]}{[N]} \end{aligned} \quad (13)$$

By using $\phi(n)$, the instantaneous number-average degree of polymerization $\bar{p}_n$ and the instantaneous weight-average one $\bar{p}_w$ can be described as

$$\bar{p} = \sum_{n=1}^{\infty} n\phi(n) \quad (14a)$$

$$\bar{p}_w = \frac{\sum n^2 \phi(n)}{\sum n\phi(n)} \quad (14b)$$

The integrated number-average degree of polymerization $\bar{P}_n$ and the integrated weight-average one $\bar{P}_w$ at conversion x are^{12,17-19}

$$\bar{P}_n = \frac{x}{\int_0^x dx/\bar{p}_n} \quad (15a)$$

$$\bar{P}_w = \frac{1}{x} \int_0^x \bar{p}_w dx \quad (15b)$$

DISCUSSION

Molecular Weight

Balke and Hamielec¹⁹ obtained extensive data for finding the relationship among molecular weight, conversion, and time in the polymerization of methyl methacrylate (MMA) initiated by 2,2'-azobisisobutyronitrile (AIBN). They estimated the theoretical molecular weight by the conventional equation, assuming that the termination rate is independent of the chain length. In spite of the extensive modification of this equation, the calculated weight-average degree of polymerization deviated from the experimental data. In the present paper, it is shown that the rate equations described

in the preceeding section fit sufficiently to the Balke and Hamielec data.

In the termination between poly(methyl methacrylate) (PMMA) radicals, disproportionation predominates.^{19,20} Thus, eq 12 is adopted without any modification for coupling. $[N_n]/[N]$ can be calculated when $f k_d [C]/R_p$, n_c , and C_{tr} are known. $f k_d [C]/R_p$ ($[C]=[C]_0 \exp(-k_d t)$ where $[C]_0$ is the initial concentration of initiator and t is time) is estimated from the Balke and Hamielec data (Table I to III). Here, the decomposition rate is estimated by²¹

$$k_d = 1.58 \times 10^{15} \exp(-15500/T) \text{ s}^{-1}$$

where T is the absolute temperature. Berry and Fox²² estimated a critical chain length as 300 from rheological experiments with undiluted PMMA ($c=1$). Brooks¹⁴ used this value for explaining the data of the polymerization rate of MMA. In the present paper, the critical chain length is also estimated by using 300. That is, by setting $n_c=300$ at $c=1$, eq 6 becomes

$$n_c = 300 c^{-1.25}$$

Table I. The calculated instantaneous degree of polymerization from the experimental data¹⁹ in the polymerization of MMA at 50°C in the presence of $[AIBN]=0.5\%$ ^a

x	$10^5 f k_d / R_p$	$1000 \bar{K}$	$\bar{P}_n$	$\bar{P}_w$	$10^{-7} k$
0	15.0	28.57	3223 3218 ^d 3218 ^b	8774 6435 ^d 7191 ^b	
0.15	13.97	26.02	3460 3458 ^c 3446 ^d	9877 9399 ^c 6892 ^d	
0.2	10.26	18.70	4695 4687 ^c 4630 ^d	15368 12653 ^c 9259 ^d	43.3
0.25	6.86	12.64	6944 6914 ^c 6758 ^d	22910 18024 ^c 13513 ^d	25.6
0.3	5.42	9.578	8649 8615 ^c 8389 ^d	28985 22389 ^c 16779 ^d	18.66
0.35	3.75	6.642	11739 11579 ^c 11655 ^d	41410 31850 ^c 23310 ^d	11.25
0.4	2.526	4.502	16301 16369 ^c 16308 ^d	54371 42243 ^c 32615 ^d	6.53
0.45	1.954	3.642			4.12
0.5	1.012	2.107			1.602
0.55	0.855	1.766			1.120
0.6	0.866	1.735			0.940

^a $k_d = 0.00000233 \text{ s}^{-1}$, $C_{trm} = 0.0000108$, $k_p = 559 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

^b Obtained by Appendix 1.

^c Equation 16 when $a=1/2$.

^d Equation 16 when $a=0$.

In previous papers,^{12,19} transfer to the monomer was neglected. However, this transfer is important at high conversion. The importance of this transfer is shown by comparing $fk_d[C]/R_p$ and the transfer constant with the monomer C_{trm} , as is also shown by eq 10. Here, C_{trm} is estimated by²³

$$\log_{10} C_{trm} = -1.13 - \frac{1240}{T}$$

As is shown in Table I to II, C_{trm} is comparable to $fk_d[C]/R_p$ at high conversion; thus, the transfer to the monomer cannot be neglected. It is recognized that the transfer to AIBN is negligible.²⁴⁻²⁷ Also, the concentration of AIBN is not comparable with that of MMA in the present polymerization. Thus, the transfer to AIBN is neglected in the present calculation.

The values calculated are shown in Table I to III. At low conversion, the instantaneous molecular weight is equal to the integrated molecular weight which is expected to be the experimental molecular weight. However, even though the calculated number-average degree of polymerization is in a good agreement with the experimental degree of polymerization, the calculated weight-average de-

gree of polymerization deviated from the experimental degree of polymerization ($p_w=7195$ at $x=0.0801$ at 50°C and 2680 at $x=0.04$ at 70°C in the presence of $[AIBN]=0.5\%$). This may be caused by the fact that the n -dependence of the termination rate is $n^{-1/2}$ for the whole range of chain length, because n_c becomes infinite. However, at a conversion so low that $x \rightarrow 0$, the n -dependence of the rate is less than $n^{-1/2}$ when $n > 100$.^{15,16,28-30} Thus, the average degree of polymerization is calculated by the author's method¹⁵ (Appendix 1 and Table I to III). Certainly, the method in Appendix 1 is better than that based on eq 5, since the values obtained in Appendix fit the experimental data. At about $x \approx 0.1$, a correct calculation of molecular weight is very difficult, since the relationship between the expansion of the polymer coil, and conversion is very complex,³¹ and the lower limit of conversion, to which eq 5 is applicable is not fully known. The aim of the present paper is not to set forth the kinetics at low conversion, but at a conversion high enough so that the gel effect becomes important. Consequently, more detailed research has not been carried out, and $\bar{p}_w$ has been designated as the experimental value of 7200 ($x=0$ to 0.1 at 50°C),

Table II. The calculated instantaneous degree of polymerization from the experimental data¹⁹ in the polymerization of MMA at 70°C in the presence of $[AIBN]=0.5\%$ ^a

x	$10^4 fk_d[C]/R_p$	$1000 \bar{\kappa}$	$\bar{p}_n$	$\bar{p}_w$	$10^{-7} k$
0	4.35	47.76	1127 1127 ^b	3051 2689 ^b	
0.2	4.33	46.90	1137	3222	45.0
0.25	3.20	38.10	1529	4606	27.4
0.3	2.34	29.74	2092	6615	17.45
0.35	1.797	23.19	2702	8767	11.21
0.4	1.342	17.44	3526	12101	7.23
0.45	1.016	13.30	4609	15875	4.66
0.5	0.839	10.76	5540	18640	3.22
0.55	0.682	8.632	6661	22242	2.25
0.6	0.475	6.128	9185	30130	1.239
0.65	0.402	5.161	10466	33892	0.821
0.7	0.408	4.921	10456	33954	0.662
0.75	0.345	4.175	11463	39285	0.394
0.8	0.35	3.995	11441	39325	0.276
0.85	1.38	11.42	3437	12459	

^a $k_d=0.0000382 \text{ s}^{-1}$, $C_{trm}=0.0000181$, $k_p=830 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

^b Obtained by Appendix 1.

Table III. The calculated instantaneous degree of polymerization from the experimental data¹⁹ in the polymerization of MMA at 90°C in the presence of [AIBN]=0.5%^a

x	$10^4 f k_d [C]/R_p$	$1000 \bar{k}$	$\bar{P}_n$	$\bar{P}_w$	$10^{-7} k$
0	10.68	73.95	466 464 ^b	1256 1194 ^b	
0.2	0.51	69.96	522	1411	28.9
0.25	9.18	68.54	541	1478	25.6
0.3	6.68	57.44	736	2109	15.02
0.35	6.23	54.10	787	2325	12.66
0.4	4.96	45.25	983	3046	8.59
0.45	3.67	36.18	1321	4247	5.19
0.5	2.67	27.43	1793	5972	3.11
0.55	2.095	21.79	2275	7564	2.01
0.6	1.845	18.83	2563	8597	1.473
0.65	1.71	17.00	2756	9290	1.099
0.7	1.63	15.56	2856	9894	0.830
0.75	1.413	13.31	3235	11300	0.520
0.8	0.954	9.382	4622	15790	0.221
0.85	0.738	7.378	5796	18936	
0.9	1.729	13.87	2722	9404	

^a $k_d = 0.000460 \text{ s}^{-1}$, $C_{\text{trm}} = 0.0000286$, $k_p = 1180 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.^b Obtained by Appendix 1.

2700 (0 to 0.15 at 70°C), and 942 (0 to 0.2 at 90°C) in the presence of [AIBN]=0.5%. The $\bar{P}_n$ is calculated by the present method for the whole range of conversion. Molecular weight may be calculated by eq 16 as well as by eq 5 and so the importance of the reptation model can thus be seen.

$$k_{t,ns} = k(n^{-a} + s^{-a}) \quad (16)$$

where $a=0$ applies to conventional case¹⁹ and $a=1/2$ to the conventional diffusion-controlled reaction. It is surprising that the difference between the instantaneous number average derived from eq 5 and that from eq 16 can be scarcely detected, as is shown in Table I, and any calculated number average fits the experimental data. Thus, the importance of reptation and the n -dependence of the rate can not be discussed by the number average. The weight average determined by eq 16 when $a=0$ is least (Table I) and deviates completely from the experimental data at 50 and 70°C (Figures 1 and 2). The weight average calculated by eq 16 when $a=1/2$ is not the best fit for the data at 50°C (Figure 1) and at 70°C without the final stage of polymerization (Figure 2). The weight average determined by eq 5 is the best fit for the data at any temperature without

the final stage (Figures 1 to 3). In conclusion, the weight average determined by the reptation fits sufficiently the experimental data. However, at the final stage, the weight average calculated by eq 5 at 70°C deviates slightly from the data, but the weight average calculated by eq 5 at 90°C deviates considerably. The deviation at 90°C cannot be neglected, and so is discussed later.

Termination Rate

The average of the termination rate is

$$\begin{aligned} \bar{k}_t &= \sum_{n=1}^{\infty} \sum_{s=1}^{\infty} k_{t,ns} \frac{[N_n]}{[N]} \frac{[N_s]}{[N]} \\ &= 2k\bar{k} \end{aligned} \quad (17)$$

Introduction of eq 17 into the conventional rate equation yields

$$k = \left(\frac{f k_d [C]}{R_p} \right) \left(\frac{[M]^2}{\bar{k} R_p} \right) k_p^2 \quad (18)$$

k can be estimated by using the values in Tables I to III and the propagation rate as³⁰

$$k_p = 4.92 \times 10^5 \exp(-2192/T) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Figure 1. Estimation of the integrated molecular weight. Experimental data $\bar{P}_n$ (●) and $\bar{P}_w$ (○) in the polymerization of MMA at 50°C in the presence of [AIBN]=0.5%.¹⁹ (—), the degree of polymerization calculated by eq 5; (---), the degree of polymerization calculated by eq 16 when $a=1/2$; (- · -), the degree of polymerization calculated by eq 16 when $a=0$.

Figure 2. Estimation of the integrated molecular weight for the experimental data¹⁹ in the polymerization of MMA at 70°C in the presence of [AIBN]=0.5%. The same symbols in Figure 1.

The $2k$ -value obtained (Table I to III) is in 10^9 to 10^8 $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ at $x \approx 0.2$ and this is reasonable,

Figure 3. Estimation of the integrated molecular weight for the experimental data¹⁹ in the polymerization of MMA at 90°C in the presence of [AIBN]=0.5%. The same symbols in Figure 1.

because of the good agreement with the rate constant of the diffusion-controlled reaction between small reactants.^{32,33} With an increase in the polymer concentration, k decreases. Such a decrease may be studied by the free volume theory.^{3,34} That is, k at the free volume may be given by

$$\ln k = \text{const} - \frac{\gamma^* v^*}{V_f} \quad (19)$$

where γ^* is an overlap factor and v^* is the critical free volume sufficient to permit a segment to jump in the place where another segment displaces. V_f is estimated by Kelley and Buche's equation.^{35,36}

$$V_f = \{ [25 + 0.48(T - T_{gp})]c + [25 + (T - T_{gm})(1 - c)] \} / 1000 \quad (20)$$

where T_{gp} and T_{gm} are the glass-transition temperatures of the polymer and monomer, respectively. As is shown in Figure 4 the relationship between $\ln k$ and $1/V_f$ when $x < 0.5$ would be the line with a slope of $\gamma^* v^* \approx 1.0$ at any temperature. However, when $x > 0.5$, the experimental data deviate from eq 19.

The reason for the experimental-data deviation

Figure 4. Relationship between k and the free volume at 50 (○), 70 (●), and 90 (◐)°C.

from eq 19 is: (1) f might decrease with the promotion of polymerization above 0.5. In the past, it was not shown that f is not variable when $x > 0.5$.^{14,37} (2) k_p might decrease with an increase in x .³⁸ (3) The displacement of radical position on the polymer chain moves not only by translational diffusion, but also by propagation. That is, when the radical adds one-monomer unit ($N_n + M \rightarrow N_{n+1}$), the radical position moves a distance l which is twice the carbon-carbon bond length. Such a movement is independent of the translational diffusion. The number of monomer units added is $k_p[M][N]/[N] = k_p[M] s^{-1}$.^{2,39} Such an addition is also random. Therefore, following the diffusion theory of a particle, this movement may be evaluated by

$$D_{\text{pro}} = \frac{l^2}{6} k_p[M] \quad \text{cm}^2 \text{s}^{-1} \quad (21)$$

The extent of D_{pro} is estimated to be $10^{-12} \sim 10^{-13} \text{ cm}^2 \text{s}^{-1}$, since $l \approx 3 \times 10^{-8} \text{ cm}$ and $k_p[M] \approx 1000 \text{ s}^{-1}$.^{31,40} Perhaps, D_0 may be $10^{-6} \text{ cm}^2 \text{s}^{-1}$ at $x = 0.2$. By expanding the line in Figure 4 in the range of $x > 0.5$, the D_0 at the final stage is estimated to be $10^{-9} \text{ cm}^2 \text{s}^{-1}$. Now, we consider a polymer radical with $n = 60000$, which is a typical size, as is shown in Appendix 2. Its diffusion coefficient is $10^{-9} \times (300/60000)^2 = 2.5 \times 10^{-14} \text{ cm}^2 \text{s}^{-1}$ which is less than D_{pro} . That is, at the final stage, the displacement of the radical position by D_{pro} may not be neglected. When the above problems are cleared up, the deviation of the experimental data from eq 19 may be explained. Further, the displacement

of the radical position by the propagation may be important for explaining why the calculated $\bar{P}_w$, using eq 5, deviates from the experimental $\bar{P}_w$ at 90°C at the final stage. That is, D_{pro} is larger at higher temperatures, because of larger k_p , and the termination rate is larger than $(2/3)\pi l^2 R k_p[M]$ even if $D \rightarrow 0$. The upper limit of the polymer size may be controlled by the rate, as $(2/3)\pi l^2 R k_p[M]$, and is less than the limit calculated by using eq 5. Thus, it may be expected that the calculated $\bar{P}_w$ using $k_{t,ns} = 4\pi R(D + D_{\text{pro}})$ fits the experimental data.

APPENDIX

1. At very low conversion, the term $\xi/\bar{k}$ in eq 10, 12, and 13 is rewritten as

$$[(k_1 n^{-e_1} + k_2 n^{-e_2} + \rho k_3 n^{-e_3}) / (k_1 \bar{k} + k_2 \bar{k}_2 + \rho k_3 \bar{k}_3)],$$

with the notation in ref 15. The molecular weight in the table is calculated accordingly, with the same parameters for k_j , e_j ($j = 1$ to 3), and ρ in ref 15.

2. Because of the n -dependence of $k_{t,ns}$, the number-average degree of polymerization of the radical is not equal to that of the non-reacting polymer, but $\bar{n} = \sum n[N_n]/[N]$. When $x = 0.5$ at 50°C, $\bar{n} = 54600$. Thus, $\bar{n} = 60000$ is a typical size when $x > 0.5$.

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