

Evaluation of Termination Rate by the Free Volume Theory in Radical Polymerization

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ABSTRACT: Kinetic data on the radical polymerization of methyl methacrylate are treated in terms of termination rate equations based on Stokes law and the reptation model. The values of k/k_p^2 obtained are independent of initiation rate, where k corresponds to the rate constant of the diffusion-controlled reaction between segment radicals and k_p is the propagation rate constant. When x (conversion) is less than 0.5, an equation as $k/k_p^2 \propto \exp(-1.1/V_f)$ (V_f , free volume) is obtained. When $x > 0.5$, k/k_p^2 deviates from such an equation. This deviation may show that the propagation rate decreases with increasing in x , since this rate becomes diffusion-controlled.

KEY WORDS Radical Polymerization / Methyl Methacrylate / Termination Rate / Stokes Law / Reptation Model / Free Volume / Propagation Rate / Diffusion-Controlled Reaction /

In order to treat the kinetic data of radical polymerization at high conversion, it is assumed that the termination rate between polymer radicals depends on chain length, as described by $k_{t,ms} \propto (n^{-a} + s^{-a})^{1-3}$ since the rate is translational diffusion-controlled. The parameter a was the same constant throughout the range of chain length. However, the modern concept of reptation shows that the diffusion coefficient of polymer, of which $n > n_c$, is proportional to n^{-2} (this corresponds to $a=2$).⁴⁻⁶ When $n \leq n_c$, the coefficient is proportional to $n^{-1/2}$ ($a=1/2$) on the basis of Stokes law. Accordingly, the termination rate is described by⁷

$$k_{t,ms} = k(\zeta_n + \zeta_s) \quad (1)$$

$$(\zeta = n^{-1/2} \text{ at } n \text{ (or } s) \leq n_c,$$

$$\zeta = n_c^{3/2} n^{-2} \text{ at } n \text{ (or } s) > n_c; n_c \propto c^{-1.25})$$

The k -values were calculated by the application of eq 1 to the experimental data at a high initiation rate. These values are examined by eq 2 based on the free volume theory.

$$\ln k = \text{const} - \frac{\gamma^* v^*}{V_f} \quad (2)$$

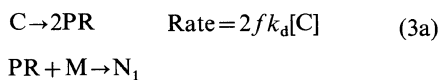
It was found that the relationship between $\ln k$ and V_f^{-1} is linear when $x < 0.5$. But when $x > 0.5$, $\ln k$

deviates from such a line. In the present paper, the termination rate in the wide range of initiation rate is calculated by eq 1 and its modified equation for the rate of termination in terms of the branched polymer radical. The k -values obtained are discussed in more detail.

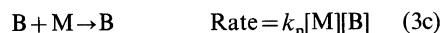
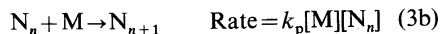
THEORY

The polymerization reaction scheme is shown below.

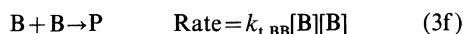
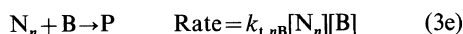
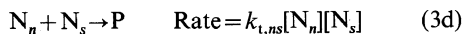
Initiation:



Propagation:



Termination:



Transfer to monomer and polymer:



The rate equations at stationary state are:

$$\frac{d[N]}{dt} = 2fk_d[C] - \bar{k}_t[N]^2 - \bar{k}_{tB}[N][B] + k_{trm}[B][M] - k_{trp}[N][P] = 0 \quad (4)$$

$$\frac{d[B]}{dt} = k_{trp}[N][P] - k_{trm}[B][M] - \bar{k}_{tB}[N][B] - k_{t, BB}[B]^2 = 0 \quad (5)$$

Polymerization rate is:

$$R_p = k_p[M]([N] + [B]) \quad (6)$$

In the above equations, the rate of termination between linear polymer radicals is given by⁷

$$\bar{k}_t = 2k\bar{k} \left(\bar{k} = \sum_{n=1}^{\infty} [N_n] / [N] \right) \quad (7)$$

When a radical transfers to a polymer, the polymer repropagates and becomes a branched polymer radical. In that the diffusion of the branched polymer should be hindered markedly by the entanglement, eq 1 must be modified. Actually, the problem of diffusion of branched polymers is extremely complicated.⁸ Thus, assuming that the diffusion coefficient of the branched polymer is negligibly less than that of the linear polymer, eq 1 may be modified as:

$$k_{t, nB} \simeq k\zeta, \quad \bar{k}_{tB} \simeq k\bar{k}, \quad \text{and} \quad k_{t, BB} \simeq 0 \quad (8)$$

\bar{k} can be calculated by following the similar methods reported before,^{7,9,10} where $g(n)$ ($= [N_{n-1}] / [N_n]$) must be modified into:

$$g(n) = 1 + C_{tr} + \frac{fk_d[C]}{R_p} \left(1 + \frac{\zeta}{\bar{k}} \right) + \frac{\zeta C_{trp}(fk_d[C]/R_p)}{\bar{k}(fk_d[C]/R_p + C_{trm})} \quad (9)$$

By using \bar{k} , k/k_p^2 is described by:

$$\frac{k}{k_p^2} = \left(1 + \frac{C_{trm}}{fk_d[C]/R_p + C_{trm}} \right) \left(\frac{fk_d[C]/R_p}{\bar{k}[M]^2} \right) \quad (10)$$

DISCUSSION

The equations described here are applied to the kinetic data obtained in the polymerization of methyl methacrylate (MMA), where n_c , C_{trm} , V_f , and k_d (when 2,2'-azobisisobutyronitrile (AIBN) is used) are shown in ref 7. The value of f is set up as 0.57 for the initiation efficiency of primary radicals yielded by decomposition of AIBN.¹¹ For the decomposition of benzoyl peroxide (BPO), the fk_d -values obtained before¹⁹ are used. At 50 and 70°C, C_{trp} for the middle group on polymer coil was obtained as 2.2×10^{-5} , but C_{trp} for the end was much greater than this value.^{12,13} The repropagating radicals yielded by the transfer to the end are still linear. This means that the transfer to the end group should be neglected here. Since the value as 2.2×10^{-5} approximates to C_{trm} , transfer should be valid,¹⁴ and is adopted in the present cases.

The k and \bar{k} -values were calculated for polymerization at a low initiation rate ($[AIBN]_0 = 0.00625 \text{ mol dm}^{-3}$, at 45°C)³ (Table I). The relationship based on eq 2 is shown in Figure 1. A line with the slope of $\gamma^*v^* = 1.1$ is obtained when $x < 0.5$. The other line is also obtained at $x > 0.5$, but its slope is less (0.17). The k and \bar{k} -values are calculated for polymerizations initiated by BPO¹⁹

Table I. The k/k_p^2 and \bar{k} -values calculated for polymerization of MMA initiated by AIBN ($[C]_0 = 0.00625 \text{ mol dm}^{-3}$) at 45°C³

x	$10^5 fk_d[C]$	1000 \bar{k}	k/k_p^2 ^a	k/k_p^2 ^b
	R_p			
0.1	7.24	18.18	5280	5280
0.15	6.08	14.69	4288	4288
0.2	4.64	10.96	3137	3147
0.25	3.39	8.17	2134	2134
0.3	2.42	6.22	1387	1387
0.35	1.608	4.80	789	789
0.4	1.093	4.02	445	445
0.45	0.800	3.66	264	265
0.5	0.539	3.43	131.2	131.8
0.55	0.479	3.59	94.6	95.7
0.6	0.458	3.76	77.0	78.3
0.65	0.447	4.14	60.9	60.9
0.7	0.445	4.67	47.4	50.7
0.75	0.938	6.18	108	123

^a Obtained by eq 1.

^b Appendix.

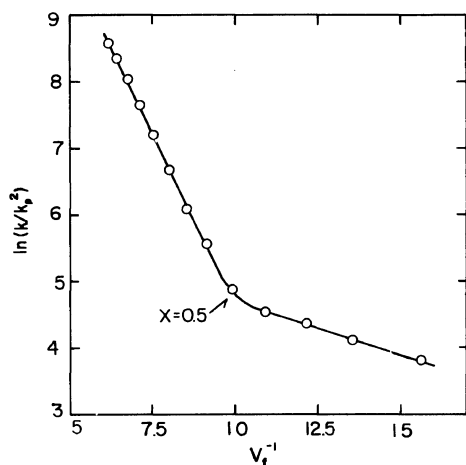


Figure 1. Relationship between k/k_p^2 and V_f in polymerization of MMA initiated by AIBN ($[C]_0=0.00625$ mol dm⁻³) at 45°C.³

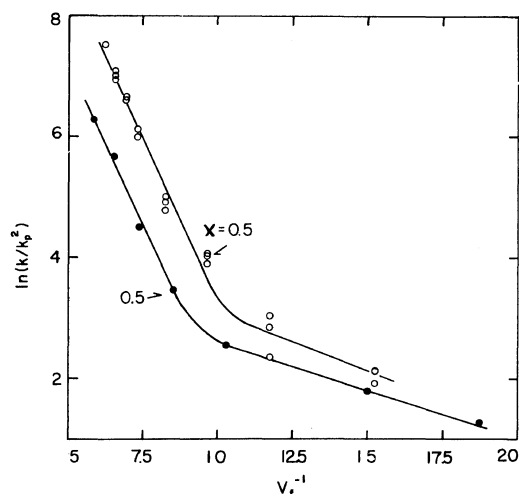


Figure 2. Relationship between k/k_p^2 and V_f in polymerization of MMA initiated by BPO at (○) and 70°C (●).¹⁹

(Table II). The relationship between $\ln(k/k_p^2)$ and V_f^{-1} is shown in Figure 2. The slope of the line at $x < 0.5$ was found to be 1.1 for initiation rate at any temperature. The slope at $x > 0.5$ is about 0.2 (50°C) and 0.18 (70°C). Lines having the same characteristics as the above were obtained in polymerizations at high initiation rates.⁷ All values obtained for the slopes are shown in Table IV. As already shown, γ^*v^* is independent of the initiation rate and temperature. However, very recently, it was shown that

Table II. The k/k_p^2 and \bar{k} -values calculated for the polymerization of MMA initiated by BPO¹⁹

x	$10^5 f k_d / R_p$	$1000 \bar{k}$	k/k_p^2
0.15 ^a	2.611	8.559	1911
0.2	1.766	6.207	1202
0.3	0.888	3.927	454.0
0.4	0.440	3.176	188.1
0.5	0.296	3.248	57.84
0.6	0.195	3.482	21.20
0.7	0.148	4.213	8.473
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0.2 ^b	4.73	11.25	1059
0.25	3.78	8.966	793.5
0.3	2.44	6.370	452.6
0.4	1.136	4.228	146.7
0.5	0.619	3.726	48.76
0.6	0.284	3.613	10.38
0.7	0.284	4.455	6.789
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0.2 ^c	8.69	17.18	1130
0.25	6.18	12.50	730.9
0.3	3.88	8.547	400.0
0.4	1.621	4.921	119.3
0.5	0.997	4.221	50.12
0.6	0.594	4.101	17.37
0.7	0.485	4.835	8.188
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0.2 ^d	8.46	17.60	537.3
0.3	5.46	11.44	290.7
0.4	2.44	6.613	90.49
0.5	1.354	5.183	12.53
0.6	0.915	5.198	12.53
0.8	0.801	7.322	3.573

^a $[C]_0=0.25\%$ at 50°C.

^b 1.0% at 50°C.

^c 2.0% at 50°C.

^d 0.25% at 70°C.

the diffusion of a polymer is affected by the size of its surrounding polymers.^{15,16} The constant value of $\gamma^*v^*=1.1$ was obtained for a mixture of polymers of different chain length; therefore this value may not be recognized as a correct value without a more detailed examination. Daoud and Genes¹⁵ stated that, when $n_d \gg n_p$, the diffusion coefficient of a polymer with n_d in the presence of large amounts of polymers with n_p is not proportional to n^{-2} (the reptation model), but $n^{-1/2}$ (the Stokes law). This may be visualized in the polymerization of MMA in a large amount of polyMMA with $n_p=794$.¹¹ In this experiment, $[N] \ll [P]$ and n_p is considerably shorter

Table III. The k/k_p^2 -values calculated for polymerization of MMA initiated by AIBN in the presence of known amounts of poly (MMA) with $n_p = 794$ at 50°C^{11}

x^*	$10^5 f k_d [C] / R_p$	k/k_p^2 ^a	k/k_p^2 ^b
0.0936	15.35	4650	4588
0.1618	15.90	4231	3855
0.2413	12.27	2892	2236
0.2993	7.58	1672	1049
0.3089	7.395	1737	1059
0.3947	5.196	1012	494.2
0.4121	4.644	697.2	325.4
0.4261	4.429	629.1	285.5

^a Obtained by eq. 1

^b Obtained by $k_{t,ns} = k(n^{-1/2} + s^{-1/2})$.

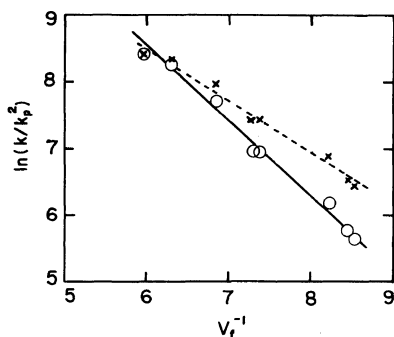


Figure 3. Relationship between k/k_p^2 and V_f in polymerization of MMA initiated by AIBN at 50°C^{11} : \times , eq 1; \circ , $k_{t,ns} = k(n^{-1/2} + s^{-1/2})$.

than n_d ($\approx \bar{p} > 3200$). Further, kinetic data are obtained when $x^* < 0.43$ (this means that $n_c > 900$). Therefore, the polymer radicals, which diffuse by following the reptation model, are probably negligibly small. The other polymer radicals may diffuse by following Stokes law. In order to compare the difference between the reptation model and Stokes law, k/k_p^2 was calculated by eq 1 and $k_{t,ns} = k(n^{-1/2} + s^{-1/2})$ (Table III). The relationships between $\ln(k/k_p^2)$ and V_f^{-1} are shown in Figure 3. From eq 1, the slope is found to be 0.75. From Stokes law, the slope was found to be 1.15 and this is in a good agreement with the values in Table IV. Thus, the $\gamma^*v^* = 1.1$ obtained for usual radical polymerizations are probably correct.

When $x > 0.5$, the slopes of linear relationships between $\ln(k/k_p^2)$ and v_f^{-1} are about 0.2, which is

Table IV. The slopes obtained by linear relationship between $\ln(k/k_p^2)$ and V_f^{-1}

Initiator	Temp °C	γ^*v^*	Slope ($x > 0.5$)	References
AIBN	50	1.15	—	11
AIBN	45	1.1	0.17	3
AIBN	50	1.0	—	7, 18
AIBN	70	1.0	0.20	7, 18
AIBN	90	1.0	0.22	7, 18
BPO	50	1.1	0.2	19
BPO	70	1.1	0.18	19

independent of the initiation rate and temperature. Without the final stage of polymerization, f is independent of x and the displacement of radical position by propagation⁷ is not marked, as shown in Appendix. Perhaps, the slope at $x > 0.5$ is considerably less than γ^*v^* , and thus shows a decrease in propagation rate constant with an increase in conversion. Horie *et al.*¹⁷ stated that the propagation rate constant is independent of conversion when $x < 0.4$, but decreases with further promotive polymerization, since the rate becomes diffusion-controlled. This is consistent with the present case. However, the actual relationship between k_p and v_f are more complex than those obtained here.¹⁷ On making more detailed consideration, k/k_p^2 at $x > 0.5$ must be obtained by extending the Brooks experiment,¹¹ and then the most probable relationship between k_p and v_f can be discussed. This will be carried out in the following paper.

APPENDIX

The relationship between f and f_0 at high initiation rate is given by:

$$\frac{f}{f_0} = \frac{R_p[C]_0(1/\bar{p}_n - C_{trm})}{R_{p0}[C](1/\bar{p}_{n0} - C_{trm})} \quad (\text{A1})$$

where the suffix (0) is designated as the initial stage of polymerization ($t=0$). The introduction of R_p , $[C]$, \bar{p}_n , and C_{trm} -values, shown before,⁷ into eq A1 yields $1 \geq f/f_0 > 0.9$ at $x < 0.8$. This shows an independency of f on x .

On considering the displacement of radical position by propagation,⁷ eq 9 is rewritten as;

$$g(n) = 1 + C_{tr} + \frac{fk_d[C]}{R_p} \left(1 + \frac{\zeta + \kappa}{\bar{k} + \kappa} \right) + \frac{(\zeta + \kappa)C'_{trp}(fk_d[C]/R_p)}{(\bar{k} + \kappa)(fk_d[C]/R_p + C_{trm})} \quad (A2)$$

where $\kappa = 5.3 \times 10^{-10} \exp(1.1/V_f)$ at 45°C . The k/k_p^0 -values obtained by eq A2 are in good agreement with those obtained by eq 9 when $x \leq 0.7$ (Table I). This means that the relationship between k/k_p^2 and V_f is independent of the displacement of the radical position by propagation without the final stage of polymerization.

NOMENCLATURE

t	, time
R_p	, polymerization rate
$[C]$, initiator concentration
PR	, primary radical
$[M]$, monomer concentration
$[N_n]$, concentration of linear polymer radical with n
n	, the number of monomeric units in a polymer (chain length)
$[N]$, total concentration of linear polymer radical
$[B]$, concentration of branched polymer radical
$[P]$, concentration of non-radical polymer
x	, conversion
f	, the fraction of PR escaping from the solvent cage
k_d	, initiator decomposition rate constant
k_p	, propagation rate constant
$k_{t,ns}$, rate constant of termination between N_n and N_s
\bar{k}_t	, average rate constant of termination between N and N
$k_{t,nB}$, rate constant of termination between N_n and B
\bar{k}_{tB}	, average rate constant of termination N and B
$k_{t,BB}$, rate constant of termination between B and B
k_{trm}	, rate constant of transfer of radical to monomer
k_{trp}	, rate constant of transfer of radical to polymer
C_{trm}	, k_{trm}/k_p
C_{trp}	, k_{trp}/k_p

C'_{trp}	, $k_{trp}[P]/k_p[M]$ ($C_{tr} = C_{trm} + C'_{trp}$)
\bar{p}_n	, the number-average degree of polymerization
k	, rate constant of reaction between segment radicals
η_c	, critical chain length
n_d	, chain length of diffusing polymer
n_p	, chain length of non-diffusing polymer
c	, the polymer concentration
x^*	, weight fraction of polymer added in polymerization solution
γ^*	, an overlap factor
v^*	, the critical free volume sufficient to permit a segment to jump in after the displacement of another segment

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