

## Evaluation of Termination Rate by Segmental and Translational Diffusions in Radical Polymerizations

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(Received May 4, 1979)

**ABSTRACT:** A diffusion coefficient of a segment is proposed from the fact that the  $M$ th segment from the end arrives at the place where the  $N$ th segment is located by jumping  $(N - M)$  times. By using this and the translational diffusion coefficient derived previously, a termination-rate equation is formulated. After such an equation is applied to the diffusion-controlled model terminations, it is also applied to the polymerization rates in the polymerizations of styrene and methyl methacrylate (MMA) initiated by azo compounds, without any modification for reactions in terms of primary radicals. The mobility factor of a segment, which denotes the ratio of the segmental mobility to the mobility of a particle of the segment size, is estimated to be 0.24 for PMMA and 0.14 for polystyrene; these values would be independent of solvent properties.

**KEY WORDS** Segmental Diffusion / Translational Diffusion / Termination / Polymerization Rate / Methyl Methacrylate / Styrene / Segmental Mobility /

Termination rates have been treated by assuming that they would be segmental diffusion-controlled. Such an assumption was applied to the experimental results that the rate was inversely proportional to solvent viscosity and independent of  $n$  (the number of monomeric units) of polymer radical.<sup>1-3</sup> Certainly, the inverse proportionality has been supported by many workers. However, the  $n$ -independence has not been supported sufficiently, because an  $n$ -dependence, which is less than  $\sqrt{n}$ , has been estimated theoretically.<sup>4-6</sup> This writer<sup>5</sup> estimated such a dependence by considering the excluded volume only. Horie *et al.*,<sup>4</sup> and Mahabadi and O'Driscoll<sup>6</sup> estimated it by the excluded volume and another  $n$ -dependence of segmental diffusion. In such estimations, the segment radicals approach each other by only the segmental diffusion. However, this is not sufficient. If this were absolutely correct, the segments could not approach when  $D_S$  (the diffusion coefficient of a segment) = 0. However, it is apparent that, even if  $D_S = 0$ , any point along the polymer chain can move by translational diffusion. This is true absolutely. Thus, during encounter between the polymers, the points where the radicals are located can also move relatively and approach each other by the translational diffusion. These

movements can not be neglected when  $n$  is small.

Actually,  $D_S$  is not zero. Thus, an available diffusion for the encounter between the polymer radicals would be written as

$$D_A = D_T + D_S \quad (1)$$

where  $D_T$  is the translational diffusion coefficient of a polymer. Such a diffusion was considered in terms of a Ball and Chain Model by Benson and North.<sup>7</sup> The diffusing jump of a bead as a segment has been considered in many papers dealing with the computation analysis of dynamics in terms of translational diffusion of a polymer in solution. For instance, Verdier and Stockmayer<sup>8</sup> deals only that a bead jumps  $\nu_0$  times in unit time. When the excluded volume is effective, a modification of their model for the jump becomes necessary.<sup>9</sup> Generally, for the jump of any segment, the segment should be located according to a Gaussian distribution, even if the excluded volume is effective.<sup>13</sup> In the present paper, a diffusion coefficient of a segment for which a familiar Gaussian distribution<sup>13</sup> can be kept is proposed. The experimental data in terms of the termination rates are explained by evaluating  $D_S$  and  $D_T$  by such a segmental diffusion coefficient and by the translational diffusion one proposed previously.<sup>11</sup>

## THEORY

*Diffusion Coefficients*

The translational diffusion coefficient has been formulated by solving an equation in terms of the Oseen formula.<sup>10,11</sup> By neglecting the fluctuation in the Oseen formula, Kurata and Yamakawa<sup>11</sup> obtained

$$D_T = \frac{kT}{\zeta} \left[ \frac{1 + (32/3\pi)^{1/2} \sigma n^{1/2}}{n\alpha^{0.652}} \right] \quad (2)$$

where  $k$  is Boltzmann's constant,  $T$  is absolute temperature,  $\zeta$  is the friction constant of a segment,  $\alpha$  is the chain expansion factor due to intermolecular interaction between polymers, and  $\sigma$  is the ratio of a constant length defined for the excluded volume to the length of a link and can be approximated to the ratio of the mean square end-to-end distance for freely jointed monomeric unit to the unperturbed dimension.<sup>11,12</sup>

Generally, the density of segments of a polymer can be described by a Gaussian distribution.<sup>13</sup> On the other hand, the probability that a diffusing particle is located at a given place is also described by another Gaussian distribution. Now we consider the  $M$ th segment from the end as a diffusing segment, and the place where the other  $N$ th segment is located. Such a place is a typical one at which the  $M$ -th segment can arrive by performing jumps for  $(N-M)$  times. Because the  $(N-M)$  jumps correspond to the  $v_0$ ,<sup>8</sup> the square average distance from the starting position is

$$\bar{r}^2 = \frac{1}{6} l^2 \alpha^2 v_0 \quad (3)$$

where  $l$  is the diameter of a segment. Thus, such a distance can be recognized as a diffusion coefficient of a segment. Since a particle of a segment size is placed separately in solution, its diffusion coefficient is evaluated to be  $kT/\zeta$  (Einstein's equation). However, the real segment can not be placed separately. This should decrease the mobility of the segment. Evaluating such a decrease by a factor  $\rho$ , the diffusion coefficient of a segment would be described as

$$D_s = \left( \frac{kT}{\zeta} \right) \rho \alpha^2 \quad (4)$$

*Termination Rate in the Monodispersity of Reacting Polymers*

The termination rate equation was derived as<sup>5,6</sup>

$$k_t = k_s F^* \quad (5)$$

where  $k_s$  is a rate constant of the bimolecular reaction between segment radicals and  $F^*$  denotes the excluded-volume effect. Following Flory's relation,<sup>13</sup>  $F^*$  is derived to be  $\alpha^{-1.84}$ .<sup>15</sup> On the basis of Fujita and Norisuye's relation, for  $\alpha \leq 1.5$ ,<sup>16</sup> it is also derived to be<sup>6</sup>

$$F^* = \alpha^{-2.6} \quad (6)$$

As is stated by Flory,<sup>17</sup> the Fujita and Norisuye relation gives the best fit to the experimental data. Thus, eq 6 should be a better fit to the termination rate. When  $\alpha > 1.5$ , the best relation between the familiar interaction parameter  $z$  and  $\alpha$  is<sup>16</sup>

$$z = 0.6(\alpha^5 - \alpha^2)$$

which is rewritten as<sup>11,13</sup>

$$X = 3.2(\alpha^2 - 1)$$

This author<sup>18</sup> formulated a relationship between  $F^*$  and  $X$  as

$$F^* = (X/2 + 1)^{-0.92}$$

Thus, when  $\alpha > 1.5$ , the above equations yield

$$F^* = (1.6\alpha^2 - 0.6)^{-0.92} \quad (7)$$

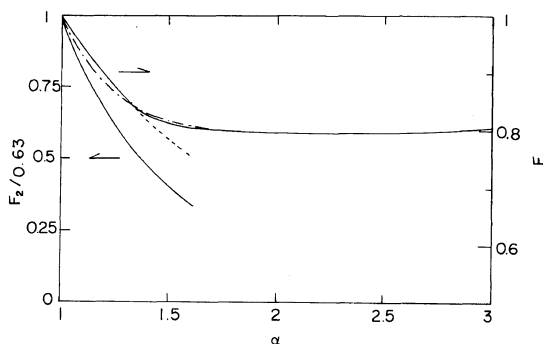
By using eq 1, 2, and 4 to 7, the termination-rate constants proposed previously<sup>4-6</sup> can be modified

$$k_t = k \left[ \left( \frac{1}{n} + \frac{\sigma'}{n^{1/2}} \right) \alpha^{-2.65} + \rho \right] F \quad (8)$$

$$F = \begin{cases} \alpha^{-0.6} & (\alpha \leq 1.5) \quad (8a) \\ \alpha^2 (1.6\alpha^2 - 0.61)^{-0.92} & (\alpha > 1.5) \quad (8b) \end{cases}$$

where  $k = 8\pi RkT/\zeta$  ( $R$ , reaction radius) and  $\sigma' = (32/3\pi)^{1/2}$ .

As is proved by Mahabadi and O'Driscoll<sup>6</sup> and stated later in detail, Mandelkern and Flory's approximation<sup>14</sup> is not suitable when  $n < 100$ , because  $\sigma' n^{1/2}$  in eq 2 and 8 is comparable with unity when estimated from the Kurata and Yamakawa treatment.<sup>11</sup> Such an approximation is not adopted in eq 8, which is quite similar to the rate equation derived by Horie *et al.*<sup>4</sup> When  $100 < n < 3000$ , eq 8 is similar to the rate equations proposed by Horie *et*



**Figure 1.** The  $\alpha$ -dependences of termination rates when  $\rho \gg (1+n+\sigma'/n^{1/2})$  ( $k_1 \propto F$  in eq 8a --- and 8b - - -; and  $k_1 \propto F_2 = \alpha^{-2.6} - 0.37\alpha^{-3.34}$  in the Mahabadi and O'Driscoll rate<sup>6</sup>).

al.,<sup>4</sup> and Mahabadi and O'Driscoll.<sup>6</sup> When  $n > 3000$ , eq 8 differs very much from the rate equations proposed previously, as is shown in Figure 1, where the  $\alpha$ -dependences of the rates are given.

#### Termination Rate in Polydispersity of Reaction Polymers (Radical Polymerization)

In order to treat the termination rate between different size polymers, the approximation  $a^2 + b^2 \approx 2ab$  has been used.<sup>6,18</sup> When the excluded volume is important, a rate equation which includes a multiplication may be convenient. However, as was estimated above, the  $n$ -dependence based on the excluded volume is considerably less than that based on the translational diffusion. Generally, a better relative diffusion has been given by a sum of two diffusion coefficients. By using the summation and a relationship such as  $\alpha = K'n^{b'}$  ( $K'$  and  $b'$  are constants),<sup>18</sup> the termination rate of eq 8 can be rewritten as eq 9 for the rate of termination between the polymers with  $n$  and  $s$ .

$$k_{1,ns} = \frac{k}{2} [k_1(n^{-e_1} + s^{-e_1}) + k_2(n^{-e_2} + s^{-e_2}) + \rho k_3(n^{-e_3} + s^{-e_3})] \quad (9)$$

$$k_1 = K'^{-3.25}; \quad k_2 = \sigma' K'^{-3.25}; \quad k_3 = K'^{-0.6};$$

$$e_1 = 1 + 3.25b'; \quad e_2 = \frac{1}{2} + 3.25b'; \quad e_3 = 0.6b'$$

An average termination rate is given by

$$\bar{k}_1 = \sum_{n=1}^{\infty} \sum_{s=1}^{\infty} k_{1,ns} \frac{[N_n]}{[N]} \frac{[N_s]}{[N]} \quad ([N] = \sum [N_n]) \quad (10)$$

$$= k(k_1 \bar{k}_1 + k_2 \bar{k}_2 + \rho k_3 \bar{k}_3) \quad (11)$$

$$\bar{k}_j = \sum_{n=1}^{\infty} n^{-e_j} \left( \frac{[N_n]}{[N]} \right) \quad (12)$$

where  $[N_n]$  is the concentration of  $n$ -polymer radicals. The  $\bar{k}_j$  will be calculated below. The rate eq 13 is rewritten as eq 16 by using eq 14 and 15

$$\begin{aligned} \frac{d[N_n]}{dt} &= k_p [N_{n-1}] [M] - k_p [N_n] [M] \\ &\quad - \sum_{s=1}^{\infty} k_{1,ns} [N_n] [N_s] = 0 \end{aligned} \quad (13)$$

where  $k_p$  is the rate constant of propagation and  $[M]$  is the monomer concentration.

$$\begin{aligned} g(n) &= 1 + C_{tr} + \frac{fk_d[C]}{R_p} \\ &\quad \times \left( 1 + \frac{k_1 n^{-e_1} + k_2 n^{-e_2} + \rho k_3 n^{-e_3}}{k_1 \bar{k}_1 + k_2 \bar{k}_2 + \rho k_3 \bar{k}_3} \right) \end{aligned} \quad (14)$$

where  $f$  is the fraction of primary radicals escaping the solvent cage,  $k_d$  is the rate constant for the decomposition of initiator,  $[C]$  is the initiator concentration,  $R_p$  is the polymerization rate, and  $C_{tr}$  is the transfer constant.

$$\frac{[N_n]}{[N_1]} = \frac{1}{g(1)} \cdot \frac{1}{g(2)} \cdots \frac{1}{g(n)} = F(n) \quad (15)$$

$$\frac{[N_n]}{[N]} = \frac{F(n)}{F(1) + F(2) + \cdots + F(\infty)} \quad (16)$$

The factor  $\rho$  is estimated by

$$\frac{fk_d[C][M]^2}{R_p^2} = \frac{k}{2k_p^2} [(k_1 \bar{k}_1 + k_2 \bar{k}_2) + (k_3 \bar{k}_3) \rho] \quad (17)$$

The order of the numerical computations is

(1) An appropriate  $\rho$ -value is set. Then the other appropriate  $\bar{k}_j$ -values are set. The computations based on eq 12 and 14–16 yield more probable  $\bar{k}_j$  values. Repeat of such computations yields the most probable  $\bar{k}_j$  at the appropriate  $\rho$ .

(2) Application of the method of least squares (Appendix) to the values obtained in the order (1) yield more probable  $\rho$ -values. The repeats of (1) and (2) yield the most probable  $\bar{k}_j$  at the most probable  $\rho$ .

## DISCUSSION

### Termination Rate in Monodispersity

The data for the rate constants  $2k_R$  of bimolecular relations between poly(ethylene oxide) radicals produced a linear relation, based on the treatment proposed by Benson and North.<sup>19</sup> In the present paper, a linear relation based on eq 8 is also obtained (Figure 2) for the above data and the  $\alpha$ -values calculated by Horie *et al.*<sup>4</sup> Here,  $\sigma$  is set to be 0.494, which is calculated by Mark and Flory's datum.<sup>41</sup> The  $k$  and  $\rho$  are calculated to be  $1.104 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and 0.05639, respectively, by the method of least squares (Appendix). These values are in good agreement with  $1.3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and 0.04, which are estimated in ref 19.

Recently, Horie and Mita<sup>20</sup> examined the effects of molecular weight and solvent on the rate constants  $k_q$  for the quenching of the phosphorescence of polystyrylbenzil by polystyrylanthracene (model reaction for diffusion-controlled termination). At a high molecular weight ( $n \approx 3000$ ), they recognized a marked difference between  $(k_{q,\alpha} = 1.03/k_{q,1.37})_{\text{exptl}} = 0.66$  and  $(k_{q,1.03}/k_{q,1.37})_{\text{calcd}} = 1.8$ , which is calculated by their equation and also estimated by the Mahabadi and O'Driscoll equation. On the other hand, as is estimated easily in Figure 1, eq 8 yields  $(k_{q,1.03}/k_{q,1.37}) = 1.2$ , which is a better fit to the experimental value. Therefore their data are treated by using eq 8. Here,  $\sigma = 1/2.17$  in various solvents at

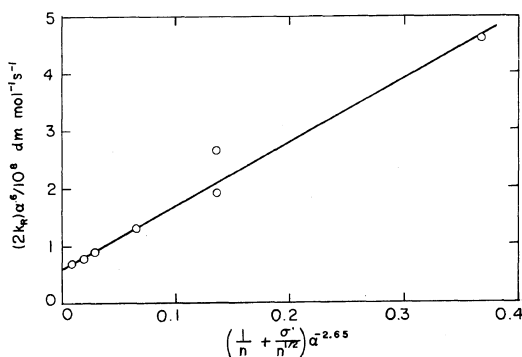


Figure 2. Application of eq 8 to the Borgwardt *et al.* kinetic data.<sup>19</sup>

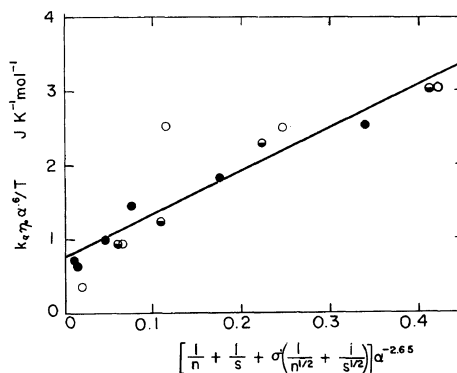


Figure 3. Application of eq 8 to the Horie and Mita kinetic data<sup>20</sup> at 40°C in benzene (○), butanone (●), and cyclohexane (◐) (the axis of abscissa, which is  $B_i \alpha^{0.6}$  in Table V, is calculated to be

$$[1/n + 1/s + \sigma(1/n^{1/2} + 1/s^{1/2})] \alpha^{-2.65},$$

because  $s$  for polystyrylbenzil differs slightly from  $n$  for polystyrylanthracene).

–9 to 68°C is used. Especially, when cyclohexane is used as solvent, the data are scattered considerably (Figure 3). By using the method in the Appendix, the values which correspond to  $(k, \rho)$  are calculated to be 5.509 and 0.1376 in benzene, 5.920 and 0.1101 in butanone, and 5.903 and 0.1418 in cyclohexane; no marked differences based on solvent property could be recognized. Application of the method of least squares to all the data yields (5.797, 0.1308), from which the line shown in Figure 3 is produced.

The above values for  $k$  are equal to the rate constants of a diffusion-controlled reaction between small molecules and were discussed previously.<sup>19,20</sup> Benson and North<sup>7</sup> estimated the value corresponding to the  $\rho$  as  $N_L^{-1/2} = 100^{-1/2} = 0.1$  ( $N_L$  is some characteristic segmental length associated with segmental diffusion), which is reproduced approximately as  $\rho = 0.05639$  or 0.1308 in the above model reactions. Such values can be also reproduced by the analysis of the kinetic data in radical polymerizations based on eq 8, and therefore are discussed in the following section in detail.

Horie and Mita<sup>20</sup> proposed a kinetic excluded volume in order to explain the facts<sup>20–23</sup> that the rates in poor solvents are less than that in good solvents at high molecular weight. The kinetic excluded volume is evaluated as a deviation of the actual rate from the theoretical rate, where the  $\alpha$ -dependence is approximated by that in the rate equation derived by Mahabadi and O'Driscoll,<sup>6</sup> as is

shown in Figure 1. On the other hand, when the actual rate is evaluated by eq 8, the corresponding deviation is considerably less, because  $k_i \propto F = \alpha^{-0.6}$  when  $\alpha \leq 1.5$ . When  $\alpha > 1.5$ ,

$$F = 0.65\alpha^{0.16} \left( 1 + \frac{0.35}{\alpha^2} + \dots \right) \quad (18)$$

That is, as is apparent in Figure 1,  $F \approx 0.8$  ( $1.5 < \alpha \leq 2.5$ ) and  $F$  increases by  $\alpha^{0.6}$  ( $\alpha > 2.5$ ). It is thus impossible to decide whether the kinetic excluded volume is effective or not when  $n < 4000$ , because the deviation of the data from eq 8 is not marked.

#### Termination Rate in Radical Polymerization

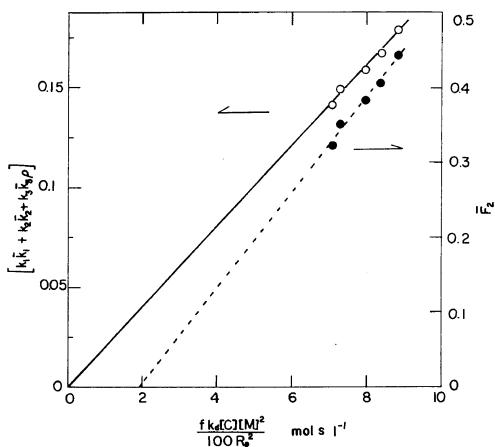
When the structure of a primary radical resembles that of the end radical of a polymer,<sup>24</sup> the primary radical termination rate constant  $\bar{k}_{ti}$  would be approximated by a rate constant  $\bar{k}_{i,1}$  ( $= \sum k_{k,\ln}[N_n]/[N]$ ) of the termination rate between the polymer radical with an arbitrary size and a radical with  $n=1$  (that is,  $\bar{k}_{ti} \approx \bar{k}_{i,1}$ ). The rate constant  $k_i$  of addition of the primary radical to monomer is approximated by  $k_p$  (that is,  $k_i \approx k_p$ ). Here, eq 9–17 would be applied to the kinetic data, without any modification in terms of reactions of primary radicals. A polymerization of styrene initiated by 1,1'-azobis-1-phenylethane (APE)<sup>25</sup> should satisfy the above conditions. The  $f k_d = 1.63 \times 10^{-7} \text{ s}^{-1}$  and  $C_{tr} = 6.0 \times 10^{-5}$  at 60°C are used.<sup>26,28</sup> The  $\alpha = 0.680 n^{0.0967}$  is obtained by the previous data.<sup>15,19,20</sup> By setting  $\rho = 0.13$  as an initial value,  $(k/2k_p^2, \rho)$  converge as (5002.1, 0.14093), (4798.7, 0.14169), and (4980.9, 0.14161), which are equal to the fifth values. The final data are shown in Table I when  $\rho = 0.14161$ . Proportionality based on eq 17 is shown in Figure 1.

**Table I.** The values obtained in terms of  $\bar{k}_j$  in the polymerization of styrene initiated by APE at 60°C<sup>25a</sup>

$y_i$	$B_i$	$C_i$	$\bar{k}(\bar{F}_2)$
886.4	0.054536	0.87786	0.17895(0.44347)
839.4	0.044682	0.86547	0.16731(0.40557)
797.4	0.037775	0.85520	0.15895(0.38231)
728.1	0.029759	0.84082	0.14889(0.35243)
708.6	0.023957	0.82796	0.14127(0.32815)

<sup>a</sup>  $y_i = f k_d [C][M]^2 / R_p^2$ ;  $B_i = k_1 \bar{k}_1 + k_2 \bar{k}_2$ ;  $C_i = k_3 \bar{k}_3$ ;  $\bar{k} = k_1 \bar{k}_1 + k_2 \bar{k}_2 + (k_3 \bar{k}_3) \rho$ .

The same data are treated by the rate equation proposed by Mahabadi and O'Driscoll,<sup>6</sup> but the proportionality of  $\bar{F}_2$  ( $= k_1 \bar{k}_1^2 - k_2 \bar{k}_2^2 + k_3 \bar{k}_3^2$ , with the notation in ref 43) to  $[C][M]^2/R_p^2$  could not be recognized, as is shown in Table I and Figure 4.

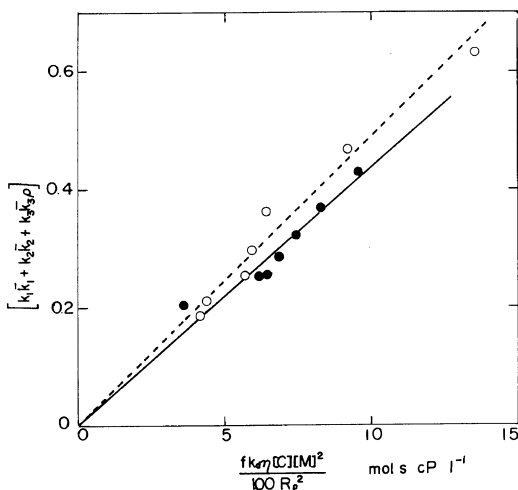


**Figure 4.** Proportionality based on eq 17 in the polymerization of styrene initiated by APE.<sup>25</sup>

In the preceding paper,<sup>43</sup> the kinetic data in the polymerizations of styrene initiated by 2,2'-azobis(2,4-dimethyl valeronitrile) (ABVN)<sup>15</sup> and methyl methacrylate (MMA) initiated by 2,2'-azobisisobutyronitrile (AIBN)<sup>31</sup> were treated by the rate equation proposed by Mahabadi and O'Driscoll. In order to fit to the data, their equation was modified for the primary radical termination. This means that their rate could not fit to the termination between small radicals as primary radicals, because they employed Mandelkern and Flory's approximation<sup>16</sup> for the translational diffusion of a polymer. Following Kurata and Yamakawa,<sup>11</sup> this modification is examined by  $[1 + \sigma' n^{1/2} \approx \sigma' n^{1/2}]$ . Horie *et al.*<sup>4</sup> set  $\sigma' = 0.75$ , which is in good agreement with  $\sigma' = 0.845$  for polystyrene in the present paper. Thus, at least when  $n < 100$ ,  $\sigma' n^{1/2}$  is comparable with unity and the Mandelkern and Flory approximation would not be adopted. This might be indicated by the fact that the rate equation derived by Mahabadi and O'Driscoll deviates from the experimental data when  $n < 1000$ , because the  $n$ -dependence of the latter is larger than that of the former.<sup>42</sup> Further, if the modification in terms of the primary radical termination were correct, the  $n$ -dependence of  $\bar{k}_1$  in  $\theta$ -solvent might disappeared. This is not correct,

because eq 8 and the other rate equations<sup>4,6</sup> show the  $n$ -dependence based on the diffusion even if  $\alpha = 1$ . On the other hand, eq 8, in which the Mandelkern and Flory approximation is not adopted, can fit to the data regardless of the modification for the primary radical termination, as is shown below.

On the application of eq 9–17 to the data in the polymerization of styrene initiated by ABVN at 50°C,<sup>15</sup> the values  $\alpha = 0.649 n^{0.107}$  (styrene–benzene = 1 : 1) and  $\alpha = 0.845 n^{0.033}$  (styrene–benzene–ethylalcohol = 3 : 1 : 2) are used.<sup>15,29,30,43</sup> From the  $k_d$  obtained previously<sup>32,33</sup> and the  $f$  estimated by using 2,2'-diphenyl-1-picrylhydrazyl in the present work, the  $fk_d$  is calculated to be  $(7.2 \pm 0.2) \times 10^{-6} \text{ s}^{-1}$ , which is equal to the value obtained previously.<sup>34</sup> The proportionality based on eq 17 is shown in Figure 5. The slopes are calculated to be 2051 for the former and 2146 for the latter, which are close to each other.



**Figure 5.** Proportionality based on eq 17 in the polymerization of styrene initiated by ABVN<sup>15</sup> in styrene–benzene (O) and styrene–benzene–ethylalcohol (●).

The data in the polymerization of MMA–AIBN at 60°C are treated by setting  $\sigma = 1/1.80$ ,<sup>30,35</sup> and  $\alpha = 0.645 n^{0.0967}$ .<sup>36,37,43</sup> The values calculated are shown in Table III and Figure 6, when  $k/k_p^2 = 134.2$  and  $\rho = 0.2442$ . Here, in experiment 1 in Baldwin's data,<sup>31</sup> an average chain length was estimated to be  $\bar{n} (= R_p/2fk_d[C]) \approx 3$  and therefore

$$R_p = k_i[M][R] + k_p[M][N] \approx k_p[M][N] \quad (19)$$

**Table II.** The values obtained in terms of  $\bar{k}_j$  in the polymerization of styrene initiated by ABVN at 50°C<sup>15</sup>

$y_i^* \text{ }^a$	$B_i$	$C_i$	$\bar{k}$
1353.7 <sup>b</sup>	0.49258	1.0287	0.63228
922.0 <sup>b</sup>	0.33268	0.99654	0.46801
642.4 <sup>b</sup>	0.23054	0.96794	0.36190
591.9 <sup>b</sup>	0.16799	0.94421	0.29621
572.9 <sup>b</sup>	0.12752	0.92409	0.25301
439.0 <sup>b</sup>	0.088379	0.89827	0.21036
415.8 <sup>b</sup>	0.064978	0.87832	0.18425
954.7 <sup>c</sup>	0.27850	1.0133	0.43136
828.4 <sup>c</sup>	0.21686	1.0055	0.36854
748.3 <sup>c</sup>	0.17069	0.99821	0.32127
686.1 <sup>c</sup>	0.13460	0.99099	0.28409
643.3 <sup>c</sup>	0.10674	0.98400	0.25518
614.8 <sup>c</sup>	0.10518	0.97752	0.25088
359.7 <sup>c</sup>	0.058132	0.96584	0.20388

<sup>a</sup>  $y_i^* = fk_d \eta [C][M]^2 / R_p^2$  ( $\eta$ , solvent viscosity).

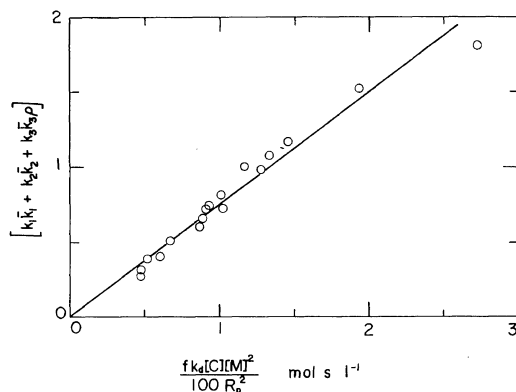
<sup>b</sup> Styrene–benzene. <sup>c</sup> Styrene–benzene–ethyl alcohol.

**Table III.** The values obtained in terms of  $\bar{k}_j$  in the polymerization of MMA initiated by AIBN at 60°C<sup>31</sup>

$y_i$	$B_i$	$C_i$	$\bar{k}$
272.7	1.5268	1.2108	1.8041
196.8	1.2523	1.1179	1.5253
145.7	0.89838	1.0893	1.1644
133.8	0.81322	1.0810	1.0772
116.9	0.73981	1.0732	1.0019
126.7	0.72011	1.0701	0.98146
100.7	0.54958	1.0492	0.80583
93.06	0.48981	1.0401	0.74383
91.08	0.47674	1.0380	0.73025
103.3	0.47371	1.0375	0.72710
88.79	0.40406	1.0252	0.5444
87.72	0.35077	1.0145	0.59854
66.82	0.26291	0.99307	0.50544
60.40	0.16471	0.95966	0.39909
52.95	0.14214	0.94943	0.37402
49.71	0.082766	0.91296	0.30574
49.16	0.047077	0.87654	0.26115

would not be adopted ( $[R]$ , the primary radical concentration), due to the difference between  $k_i$  and  $k_p$ .<sup>34,43</sup> Further, the shrinkage depends on  $n$  when  $n$  is short.<sup>38</sup> In spite of this, Baldwin neglected such a dependence. This yielded some error when  $\bar{n} \approx 3$ . Thus, experiment 1 in the Baldwin data was not used.

As is apparent in the above, the applicability of



**Figure 6.** Proportionality based on eq 17 in the polymerization of MMA initiated by AIBN.<sup>31</sup>

eq 9—17, without any modifications for the reactions in terms of primary radicals, shows that such approximations as  $\bar{k}_{ii} \approx \bar{k}_{i,1}$  and  $k_i \approx k_p$  or  $k_i > k_p$  would be satisfied.<sup>24</sup> When  $k_i \ll k_p$ , a modification should be necessary, as is illustrated in the polymerization of vinyl acetate initiated by AIBN.<sup>39</sup> That is, the primary radical concentration is high and its termination rate should be increased when  $k_i \ll k_p$ . Usually, a bimolecular reaction between radicals would be diffusion-controlled, and its maximum would be  $10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . This is supported by the fact that the rate constant of reaction between dimethylcyanomethyl radical and methylphenylmethyl radical can be approximated by that between methylphenylmethyl radicals.<sup>26</sup> In conclusion, under the condition that  $k_i \ll k_p$  is not satisfied, to obtain  $\bar{k}_{ii}/k_i k_p$  from the relation between  $R_p$  and  $[C]$  is difficult, because of the  $n$ -dependence of  $\bar{k}_i$ . However, the  $\bar{k}_{ii}/k_i k_p$  obtained by using a transfer agent as butanethiol would be exact, because the polymer size would be independent of  $[C]$ .<sup>46</sup>

### Mobility of a Segment

The  $\rho$ -values obtained are shown in Table IV. For polystyrene, the mobility of the end segment, which is obtained by the model reactions, is in good agreement with that obtained by the polymerizations. The average is  $\rho = 0.14$ , which would be independent of solvent property. The  $\rho$  for PMMA is about double that of polystyrene. This would be reasonable, in view of the similarity to the results obtained by the kinetic data in copolymerization.<sup>40</sup> The  $\rho$  for poly(ethylene oxide) is about four times less than that of PMMA. This should also be reasonable, because the radicals on poly(ethylene oxide) are located randomly. That is, the mobility of the middle point is less than that of the end. This is supported by the similarity to the results obtained in terms of the nuclear Overhauser effect for the mobility of the carbon of the polymer chain.<sup>44</sup>

### APPENDIX

1. In order to analyze the data which are scattered, the method of least squares<sup>45</sup> is suitable. Equations 8 or 17 are rewritten as

$$y_i = x_j(B_i + \rho_j C_i) \quad (\text{A1})$$

where  $y_i$ ,  $B_i$ , and  $C_i$  denote  $(k_i \text{ or } f k_d [C][M]^2/R_p^2)$ ,  $[(1/n + \sigma'/n^{1/2})\alpha^{-3.25} \text{ or } k_1 \bar{k}_1 + k_2 \bar{k}_2]$ , and  $(\alpha^{-0.6} \text{ or } k_3 \bar{k}_3)$ , respectively, for the  $i$ -th sample ( $i = 1$  to 6 in Table V);  $x_j$  and  $\rho_j$  correspond to the values of  $(8\pi R k \text{ or } k/2k_p^2)$  and  $\rho$  which are obtained by the  $j$ -th computations. Equation A1 is rewritten as

$$\begin{aligned} Y_i &= y_i(x_j + \Delta x_j, \rho_j + \Delta \rho_j) - y_i(x_j, \rho_j) \\ &= \Delta x_j \frac{\partial y_i}{\partial x_j} + \Delta \rho_j \frac{\partial y_i}{\partial \rho_j} + d_i \end{aligned} \quad (\text{A2})$$

**Table IV.** The mobility factor  $\rho$

Polymer	Solvent	$\rho$	Method
Poly(ethylene oxide)	Water	0.05639	Pulseradiolysis <sup>19</sup>
Polystyrene	Benzene	0.1376	Triplet probe <sup>20</sup>
Polystyrene	Butanone	0.1108	Triplet probe <sup>20</sup>
Polystyrene	Cyclohexane	0.1418	Triplet probe <sup>20</sup>
Polystyrene	Styrene	0.1416	Polymerization <sup>25</sup>
Polystyrene	Styrene-benzene	0.1358	Polymerization <sup>15</sup>
Polystyrene	Styrene-benzene-ethyl alcohol	0.1509	Polymerization <sup>15</sup>
PMMA	Benzene	0.2442	Polymerization <sup>31</sup>

where  $d_i$  denotes a deviation. Setting  $y_i(x_j + \Delta x_j, \rho_j + \Delta \rho_j)$  = the value measured,  $\Delta x_j$  and  $\Delta \rho_j$  can be calculated by solving

$$\frac{\partial \Sigma(d_i)^2}{\partial x_j} = 2 \Sigma \left[ \frac{\partial y_i}{\partial x_j} \left( \Delta x_j \frac{\partial y_i}{\partial x_j} + \Delta \rho_j \frac{\partial y_i}{\partial \rho_j} - Y_i \right) \right] = 0 \quad (\text{A3})$$

$$\frac{\partial \Sigma(d_i)^2}{\partial \rho_j} = 2 \Sigma \left[ \frac{\partial y_i}{\partial \rho_j} \left( \Delta x_j \frac{\partial y_i}{\partial x_j} + \Delta \rho_j \frac{\partial y_i}{\partial \rho_j} - Y_i \right) \right] = 0 \quad (\text{A4})$$

which are obtained under the condition that the summation

$$\Sigma(d_i)^2 = \Sigma \left( \Delta x_j \frac{\partial y_i}{\partial x_j} + \Delta \rho_j \frac{\partial y_i}{\partial \rho_j} - Y_i \right)^2 \quad (\text{A5})$$

is minimized. Better values  $(x_{j+1}, \rho_{j+1})$  are generated as  $(x_j + \Delta x_j, \rho_j + \Delta \rho_j)$ . Repetition of the above converges  $(x_j, \rho_j)$  to the most probable values. For the data in Table V, setting  $(x_1 = 6.5, \rho_1 = 0.1)$  as initial values,  $(x_2, \rho_2)$  are calculated to be (5.509428741, 0.1319072311), and  $(x_3, \rho_3)$  are equal to  $(x_4 = 5.509428744, \rho_4 = 0.137644012)$ .

**Table V.** Application of the method of least square to the Horie and Mita kinetic data<sup>20</sup> in benzene at 40°C

$i$	$y_i$	$B_i$	$C_i$
1	2.4	0.323	0.949
2	1.7	0.1628	0.931
3	1.3	0.0677	0.902
4	0.87	0.0319	0.872
5	0.53	0.0115	0.827
6	0.59	0.0105	0.824

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