Radical polymerization initiated by primary radicals with similar structure to the end radical on the polymer

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1,1′-Azobisethyl-1-phenylethane and dimethyl-2,2′-azobisisobutylate decompose to yield 1-phenylethyl radical (PER) with a similar structure to the end radical on polystyrene (ST) and 1-methyl-1-methylcarboxylate ethyl radicals with that of poly(methylmethacrylate) (MMA). The data on the polymerizations of ST and MMA initiated by the above primary radicals at 60°C are treated by using some equations obtained before. Rate constants of termination between small polymeric radicals such as the primary radicals are estimated to be $\bar{k}_{\mathrm{tST:ST}} = 5.2 \times 10^8 l\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$ and $\bar{k}_{\mathrm{tMMA:MMA}} = 1.1 \times 10^8$. A rate constant of primary radical termination between PER and polyMMA radical is also estimated to be $\bar{k}_{\mathrm{ti}} = 3.1 \times 10^8$ ($\simeq \bar{k}_{\mathrm{tST:MMA}}$). From these values, $\bar{k}_{\mathrm{tST:MMA}}/(\bar{k}_{\mathrm{tST:ST}}\bar{k}_{\mathrm{tMMA:MMA}})^{1/2}$ is calculated to be 1.3, which is close to unity. However, it differs from $\phi \simeq 13$ obtained before for cross-termination in polymerization between ST and MMA.

(Keywords: 1-phenylethyl radical; 1-methyl-1-methylcarboxylate ethyl radical; styrene; methylmethacrylate; termination between small radicals; primary radical termination; cross-termination)

INTRODUCTION

In radical polymerization when the initiator concentration is high and/or the monomer concentration is low, there is a deviation from the polymerization rate equation:

$$R_{\mathrm{p}} = \left(\frac{2fk_{\mathrm{d}}}{\bar{k}_{\mathrm{t}}}\right)^{1/2} k_{\mathrm{p}}[C]^{1/2}[M] \qquad (1)$$

Such a deviation has been treated in terms of the concept of primary radical termination[1-7], the chain length dependence of termination rate[8-10] or both[11]. In order to examine the chain length dependence of termination rate, it is better to avoid treatment of the primary radical termination. This may be done when an initiator producing the primary radicals with a similar structure to the end radical on the polymer is used, because the rate constant of primary radical termination is approximated to that of termination between polymer radical and small radical with $n = 1$ and that of addition of primary radical onto monomer is also approximated to that of propagation. In view of this, the data[2] on the polymerization of styrene (ST) initiated by 1,1′azobis-1-phenylethane (PER) was analysed[10], where 1-phenylethyl radical (PER) is produced as a primary radical and its structure resembles that of the end radical of polyST. However, the data were obtained when large polymers were produced, therefore the chain length dependence was not marked and could not be examined sufficiently, where the dependency is weaker for termination between larger polymer radicals[8-11]. In the polymerization of methacrylonitrile initiated by 2,2′-azobisisobutyronitrile (AIBN)[12], the data were obtained when small polymers were formed, where 1-methyl-1-cyanoethyl radical (MCER) is produced and its structure resembles that of the end radical on poly(methacrylonitrile). However, when $n < 10$, the propagation rate constant increased with decreasing chain length. Thus, the chain length dependency was not examined sufficiently either.

In the present work, the polymerizations of ST and methyl methacrylate (MMA) initiated by APE and dimethyl-2,2′-azobisbutylate (DMAB) were carried out under the condition that rather small polymers were formed, where DMAB decomposes to yield 1-methyl-1-methylcarboxylate ethyl radical (MMCER) with a similar structure to the end radical on polyMMA. The rate constants of termination are calculated from the data obtained, by using equation (1). Further, when disproportionation predominates, the relationship between chain length and polymerization rate is given by[13]:

$$\frac{[C]}{R_{\mathrm{p}}(1/\bar{n} - C_{\mathrm{trM}} - C_{\mathrm{trS}}[S]/[M])} = \frac{1}{2fk_{\mathrm{d}}}\left(1 + \frac{\bar{k}_{\mathrm{ti}}}{k_{\mathrm{i}}k_{\mathrm{p}}} \cdot \frac{R_{\mathrm{p}}}{[M]^2}\right) \qquad (2)$$

where the term of $\bar{k}_{\mathrm{t}}$ is absent. This is applied to the data on the polymerization of MMA initiated by APE. The value obtained for $\bar{k}_{\mathrm{ti}}/k_{\mathrm{i}}k_{\mathrm{p}}$ is used to discuss cross termination in copolymerization between MMA and ST.

EXPERIMENTAL

Commercial ST and MMA were purified by methods described in earlier papers[4,11]. APE was prepared as described before[14]. DMAB was supplied by Wako Pure Chemical Industries, Ltd.

Mixtures of monomer, initiator and ethyl acetate as solvent were placed in an ampoule and degassed at about 10^{-3} mm Hg by the freeze–thaw technique. The ampoule was maintained at 60.0 ± 0.02°C during proper polymerization time. The molecular weight of polymers produced was rather small, as shown in *Tables 1* and *2*, the weight loss on the purification of the polymers was not negligible. Further, the separation of the initiators could not be carried out satisfactorily, when $[C]$ was high. Accord-

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Table 1 Kinetic data on the polymerization of styrene

Initiator	$[C]$ (m l^{-1})	$[M]$ (m l^{-1})	$[S]$ (m l^{-1})	η (cp)	$10^6 R_p$ (l m^{-1} s^{-1})	$\bar{n}$
APE	0.20	7.96	0	0.481	45.3	1484
APE	0.20	3.98	4.86	0.394	16.6	584
APE	0.20	1.99	7.29	0.356	6.95	246
APE	0.20	0.995	8.51	0.333	2.97	103
APE	0.20	0.497	9.12	0.325	1.2	43
DMAB	0.0125	4.17	5.04		28.1	500
DMAB	0.00313	4.18	5.04		14.8	958
	0	4.18	5.04		1.6	5144

ingly, the conversions were estimated by gel permeation chromatography (g.p.c.). The molecular weight was obtained by g.p.c. To calculate the molecular weight of polyMMA, the g.p.c. calibration curve for polyST was modified by method described before[15]. Viscosities of the polymerization solution at 60.0°C were measured in the presence of about 0.01% 1,1-diphenyl-2-picrylhydrazyl.

RESULTS AND DISCUSSION

The data on the polymerization of ST are shown in *Table 1*. Relationship between chain length and polymerization rate is given by[21]:

$$\frac{1}{\bar{n}}=C_{\mathrm{trM}}+C_{\mathrm{trS}}\cdot\frac{[S]}{[M]}+C_{\mathrm{trC}}\cdot\frac{[C]}{[M]}+(1+\lambda)fk_{\mathrm{d}}\cdot\frac{[C]}{R_{\mathrm{p}}} \quad (3)$$

or

$$\frac{1}{\bar{n}}=C_{\mathrm{trM}}+C_{\mathrm{trS}}\cdot\frac{[S]}{[M]}+C_{\mathrm{trC}}\cdot\frac{[C]}{[M]}+\frac{(1+\lambda)\bar{k}_{\mathrm{t}}}{k_{\mathrm{p}}^{2}}\cdot\frac{R_{\mathrm{p}}}{[M]^{2}} \quad (4)$$

Because of the chain length dependence of termination rate, an application of equation (4) is not better when $[C]$ is higher and/or $[M]$ is lower, in order to estimate transfer constant. When $[C]$ is lower, equation (4) should be better applicable because transfer predominates and the chain length dependence disappears[11]. Thus, equation (4) is applied to the data obtained when DMAB was used as initiator, where $[M]=4.18$ mol l^{-1} and $[S]=5.04$ (*Figure 1*). When $[C]\leqslant 0.0125$ mol l^{-1}, it is applicable. From the intercept, $(C_{\mathrm{trM}}+C_{\mathrm{trS}}[S]/[M])$ is found to be 9.6×10^{-5}. Due to $C_{\mathrm{trM}}=6.0\times10^{-5}$,[17] C_{trS} is calculated to be 3.0×10^{-5}.[16] By using $C_{\mathrm{trM}}=6.0\times10^{-5}$ and $C_{\mathrm{trS}}=3.0\times10^{-5}$, the data on the polymerization initiated by APE are analysed by equation (3). There is a good linear relationship between $(1/\bar{n}-C_{\mathrm{trM}}-C_{\mathrm{trS}}[S]/[M])$ and $[C]/R_{\mathrm{p}}$, where the intercept is zero (*Figure 1*). Thus, the transfer to APE should be negligibly small. In the polymerization of ST, the coupling between polymer radicals predominates $(\lambda\simeq 0)$[18], then fk_{d} is calculated to be 1.38×10^{-7} s^{-1} and f is found to be 0.52 where $k_{\mathrm{d}}=2.66\times10^{-7}$ s^{-1}.[14]

The data on the polymerization of MMA are shown in *Table 2*. As stated in the Introduction, DMAB decomposes to yield MMCER whose structure resembles that of the end radical on polyMMA. Therefore, equation (3) is applied to the data on the polymerization initiated by DMAB (*Figure 2*), where $C_{\mathrm{trM}}=1.03\times10^{-5}$ and $C_{\mathrm{trS}}=1.32\times10^{-5}$ are used[20]. Apparently, $(1/\bar{n}-C_{\mathrm{trM}}-C_{\mathrm{trS}}[S]/[M])$ is proportional to $[C]/R_{\mathrm{p}}$. Thus, the transfer to DMAB is neglible. In the polymerization of MMA, disproportionation predominates $(\lambda\simeq 1)$[19], therefore fk_{d} is calculated to be 4.05×10^{-6} s^{-1} and f is found to be 0.50, where $k_{\mathrm{d}}=8.11\times10^{-6}$ s^{-1} is used[20].

In the polymerizations of ST initiated by PER and MMA initiated by MMCER, the rate constants of termination are calculated by the equation (1) with the above values for fk_{d}, where $k_{\mathrm{p}}=178$ l mol^{-1} s^{-1} for ST and 545 for MMA are used[21]. The values obtained for $(\eta\bar{k}_{\mathrm{t}})$ are shown in *Figure 3*. These values may be analysed by [10]:

$$\bar{k}_{\mathrm{t}}=\sum_{n=1}^{\infty}\sum_{s=1}^{\infty}k_{\mathrm{t,ns}}\frac{[N_{\mathrm{n}}]}{[N]}\frac{[N_{\mathrm{s}}]}{[N]} \quad (5)$$

$$k_{\mathrm{t,ns}}=k\left[\frac{1}{n\alpha_{n}{}^{3.25}}+\frac{1}{s\alpha_{s}{}^{3.25}}+\left(\frac{32}{3\pi}\right)^{1/2}\sigma\left(\frac{1}{n^{1/2}\alpha_{n}{}^{3.25}}+\frac{1}{s^{1/2}\alpha_{s}{}^{3.25}}\right)+\rho\left(\frac{1}{\alpha_{n}{}^{0.60}}+\frac{1}{\alpha_{s}{}^{0.60}}\right)\right] \quad (6)$$

where:

$$\alpha=1 \qquad \text{at } n\leqslant n_{\alpha} \quad (7a)$$

$$\alpha=\alpha_{0}n^{e} \qquad \text{at } n>n_{\alpha} \quad (7b)$$

In order to evaluate termination between polyST radicals, $\alpha_0=0.68$, $e=0.0697$ and $1/\sigma=2.17$ are used[10], then n_{α} is calculated to be 53. The most probable value for $k/k_{\mathrm{p}}{}^{2}$ is found to be 9800 mol s l^{-1} in ethyl acetate. Considering the inverse proportionality of termination rate to viscosity, such a value is changed to 6400 in the bulk polymerization which is in agreement with 4980 obtained previously[10]. The value for ρ is found to be 0.118 which is in the range of $\rho=0.111\sim0.151$. When $k/k_{\mathrm{p}}{}^{2}=6800$ and $\rho=0.118$ (this work) and $k/k_{\mathrm{p}}{}^{2}=4980$ and $\rho=0.1416$ (ref. 10), the $\bar{k}_{\mathrm{t}}$-values are calculated at given $\bar{n}$-values.* Theoretical curves are shown in *Figure 3*. To evaluate

Table 2 Kinetic data on the polymerization of MMA

Initiator	$[C]$ (m l^{-1})	$[M]$ (m l^{-1})	$[S]$ (m l^{-1})	η (cp)	$10^6 R_p$ (l m^{-1} s^{-1})	$\bar{n}$
DMAB	0.050	9.01	0	0.361	816	2194
DMAB	0.050	4.51	5.04	0.334	390	962
DMAB	0.050	2.25	7.58	0.323	175	439
DMAB	0.050	1.13	8.85	0.318	83.8	196
DMAB	0.050	0.563	9.48	0.316	34.4	80
DMAB	0.050	0.282	9.80	0.314	15.6	38
DMAB	0.050	0.141	9.95	0.313	7.2	18
APE	0.20	8.80	0	0.361	272	4148
APE	0.20	4.40	4.86	0.336	142	2340
APE	0.20	2.20	7.29	0.325	72.5	1130
APE	0.20	1.10	8.51	0.319	32.6	520
APE	0.20	0.550	9.12	0.317	14.1	229
APE	0.20	0.275	9.42	0.315	5.5	91
APE	0.20	0.138	9.57	0.314	2.4	43
APE	0.20	0.069	9.65	0.314	1.0	22

Units are the same in *Table 1*

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* In this calculation, the values of $fk_{\mathrm{d}}[C]/R_{\mathrm{p}}$ must be found. This is done by using equation (3), that is: $fk_{\mathrm{d}}[C]/R_{\mathrm{p}}=(1/\bar{n}-C_{\mathrm{trM}}-C_{\mathrm{trS}}[S]/[M])/(1+\lambda)$

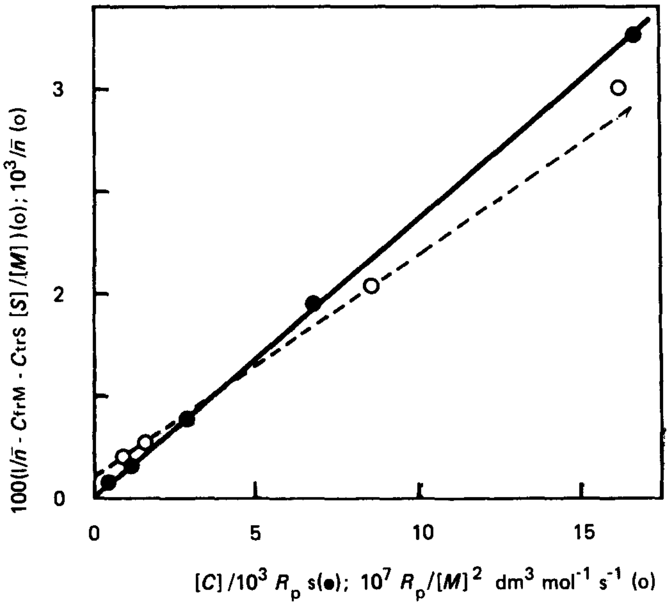

Figure 1 An analysis of the data on the polymerization of styrene by equation (3) ((●) initiated by APE), where C_{trS} is estimated from the data obtained in the absence of initiator or in the presence of DMAB (○) by using equation (4)

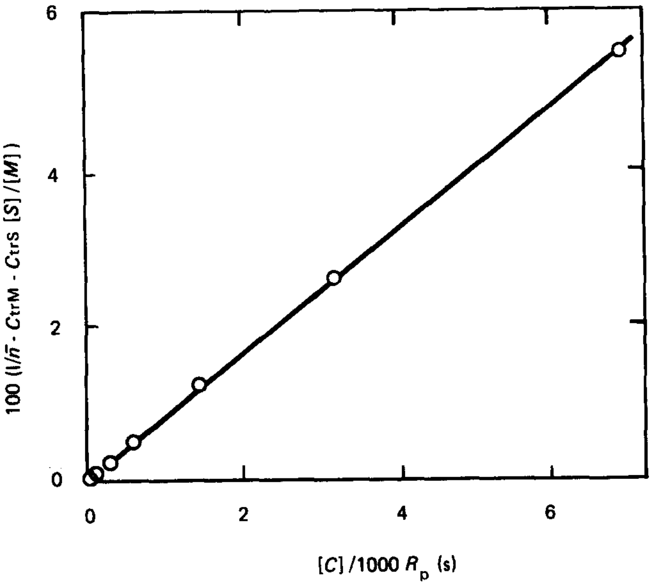

Figure 2 Relationship between chain length and polymerization rate in the polymerization of MMA initiated by DMAB

termination between polyMMA radicals, $\alpha_0 = 0.645$, $e = 0.0967$ and $1/\sigma = 1.80$ are used[10] where $n_x = 93$. The most probable value for $k/k_p{}^2$ is calculated to be $104\,\text{mol s l}^{-1}$ which is in good agreement with 134.2 obtained before[10]. The value for ρ is found to be 0.278 which is in agreement with 0.244. By using $k/k_p{}^2 = 104$ and $\rho = 0.278$, the $\bar{k}_t$-values are calculated* and shown in *Figure 3*.

When primary radical termination is important, a general equation between chain length and polymerization rate is given by:

$$\frac{fk_d[C]}{R_p(1/\bar{n} - C_{trM} - C_{trS}[S]/[M])} = \frac{1 + \bar{k}_{ti}R_p/k_ik_p[M]^2}{1 + \lambda + (1-\lambda)\bar{k}_{ti}R_p/k_ik_p[M]^2} \quad (8)$$

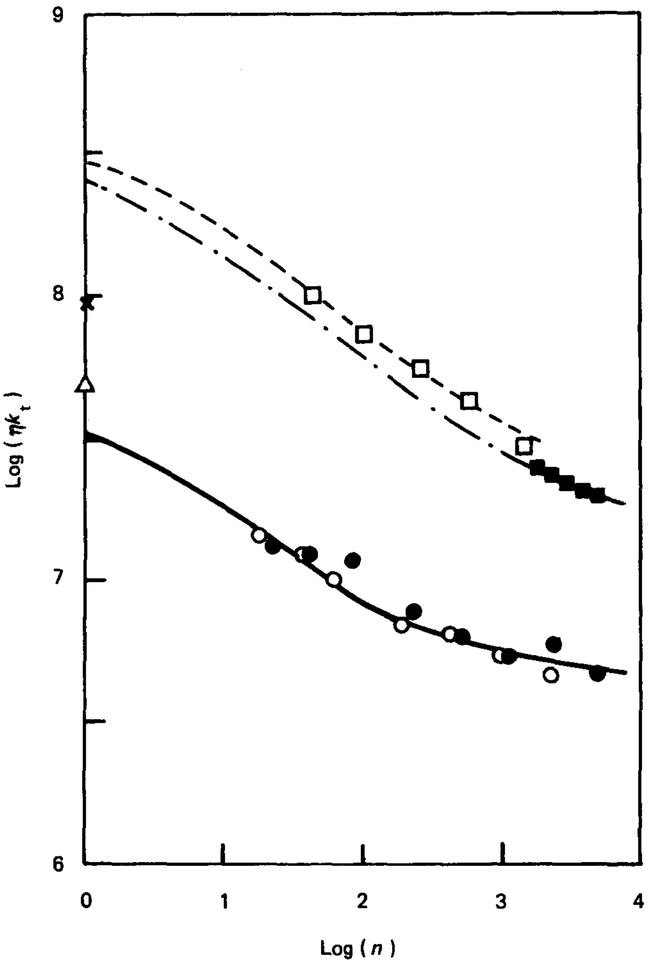

Figure 3 Chain length dependency of termination rate in the polymerization of styrene ((□) this work, (■) ref. 3) initiated by APE and in that of MMA initiated by DMAB (○) and APE (●) where (x) $\bar{k}_{tiMMA:APE}$, (△) $k_{tiMMA\text{-}AIBN}$, (···) calculated when $k/k_p{}^2 = 6400\,\text{mol s l}^{-1}$ and $\rho = 0.118$, (–·–) $k/k_p{}^2 = 4980$ and $\rho = 0.141$, (———) $k/k_p{}^2 = 104$ $\rho = 0.278$

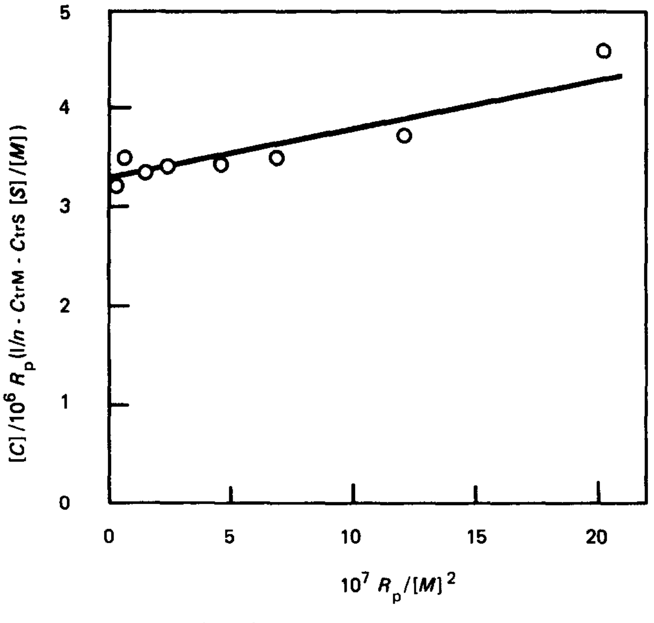

Figure 4 An estimation of the term of primary radical termination in the polymerization of MMA initiated by APE

When $\lambda \simeq 0$, equation (8) becomes equation (3). Thus, even if the primary radical termination is important, its term cannot be estimated by using equation (8). This means that the term of the primary radical termination cannot be obtained from the data on the polymerization of ST. When $\lambda \simeq 1$, equation (8) becomes equation (2). The equation (2) is applied to the data on the polymerization of MMA initiated by APE (*Table 2*). A linear relationship between $[C]/(1/\bar{n} - C_{trM} - C_{trS}[S]/[M])$ and $R_p/[M]^2$ is shown in *Figure 4*. The value for f is found to be 0.58, which is in a good agreement with 0.52 obtained in the polymerization of ST. The term of primary radical termination is found to be $\bar{k}_{ti}/k_i k_p = 1800\ \text{l mol s}^{-1}$. By using this value, the $\bar{k}_t$-values are calculated by[1–7]:

$$\bar{k}_t = \frac{2fk_d k_p{}^2[C][M]^2}{R_p{}^2} \cdot \frac{(1 - \bar{k}_{ti}R_p/k_i k_p[M]^2)}{(1 + \bar{k}_{ti}R_p/k_i k_p[M]^2)} \qquad (9)$$

and shown in *Figure 3*. These termination rates correspond to those obtained in the polymerization initiated by DMAB and are close to the curve calculated by equations (5)–(7). To estimate the value of $\bar{k}_{ti}$, k_i is calculated by:

$$k_i \simeq k_{pST:MMA} = k_{pST:ST}(k_{pST:MMA}/k_{pST:ST}) \qquad (10)$$

When $k_p = 178\ \text{l mol s}^{-1}$ and $k_{pST:ST}/k_{pST:MMA} = 0.52$,[21,22] k_i is calculated to be 315, then $\bar{k}_{ti}$ is estimated as $3.1 \times 10^8\ \text{l mol}^{-1}\ \text{s}^{-1}$, which is twice as much as $k_{tiAIBN} = 1.4 \times 10^8$ estimated from the value of[22]: $\bar{k}_{ti}/k_i k_p = 950$. The value as $\bar{k}_{ti} = 3.1 \times 10^8$ is interesting to evaluate cross-termination rate in copolymerization between ST and MMA. As shown in *Figure 3*, the rate constants of termination between small radicals are calculated to be $\bar{k}_{tST:ST} = 5.2 \times 10^8$ and $\bar{k}_{tMMA:MMA} = 1.1 \times 10^8$ at $\bar{n} = 1$. Thus, a mean value is found as:

$$\delta \equiv \frac{\bar{k}_{tST:MMA}}{(\bar{k}_{tST:ST}\bar{k}_{tMMA:MMA})^{1/2}} = 1.3$$

where $\bar{k}_{tST:MMA} \simeq k_{ti}$. Such a value is close to unity and nearly equal to $\delta \simeq 0.70 \sim 0.95$ obtained for reaction between MCER and PER[24]. However, it differs from $\phi = 13$ obtained for the cross-termination between polyST radical and polyMMA one by Walling[23]. Recently, Fukuda *et al.*[25] stated that the termination rate constant in the copolymerization between ST and MMA is close to the composition average of the termination rate constants of homopolymerizations or ϕ is close to unity. The present result as $\delta = 1.3$ is consistent with the Fukuda *et al.* result.

NOMENCLATURE

$R_p \equiv$ polymerization rate
$\bar{n} \equiv$ average of chain length
$[C] \equiv$ initiator concentration
$[M] \equiv$ monomer concentration
$[S] \equiv$ solvent concentration
$f \equiv$ the fraction of primary radicals escaping the solvent cage
$k_d \equiv$ decomposition rate constant
$k_i \equiv$ rate constant of addition of primary radical on to monomer
$k_p \equiv$ propagation rate constant
$\bar{k}_t \equiv$ rate constant of termination between polymer radicals
$\bar{k}_{ti} \equiv$ rate constant of primary radical termination
$\lambda \equiv$ ratio of disproportionation in all termination
$c_{trA} \equiv$ transfer constant to A ($A \equiv M$, S and C)
$\eta \equiv$ solvent viscosity
$n,s \equiv$ degree of polymerization
$[N_n] \equiv$ concentration of polymer radical with n
$[N] \equiv$ total concentration of polymer radical
$k_{t,ns} \equiv$ rate constant of termination between polymer radicals with n and s
$k \equiv$ constant being inversely proportional to viscosity
$\alpha \equiv$ the chain expansion parameter due to intermolecular interaction between polymers
$\sigma \equiv$ the ratio of a constant length defined for the excluded volume to the length of a link
$\rho \equiv$ a mobility factor of segment in a polymer chain
$\alpha_0, e, n_\alpha \equiv$ constants
$k_{pA:B} \equiv$ rate constant of propagation of radical A to monomer B
$\bar{k}_{tA:B} \equiv$ rate constant of termination between radicals A and B

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