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A New Estimation of Primary Radical Termination Rate

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In radical polymerization when the initiator concentration is high and/or the monomer concentration is low, a deviation is noticed from the simple expression of the polymerization rate equation

$$R_p = \left(\frac{2fk_d}{\bar{k}_t}\right)^{1/2} k_p[\mathrm{C}]^{1/2}[\mathrm{M}] \qquad (1)$$

In many papers,[1] such a deviation has been discussed in terms of the concept of primary radical termination. Here, the primary radical termination rate constant is estimated from appropriate approximations of

$$\bar{k}_t[\mathrm{N}]^2 = 2fk_d[\mathrm{C}]\left\{\frac{(1 - (\bar{k}_{ti}/k_i)([\mathrm{N}]/[\mathrm{M}]))}{(1 + (\bar{k}_{ti}/k_i)([\mathrm{N}]/[\mathrm{M}]))}\right\} \qquad (2)$$

Usually, the $\bar{k}_{ti}$ was estimated by application of eq 2 to the kinetic data obtained when [C] was only varied or/and [M] was varied.[1] This means that the $\bar{k}_{ti}$ was calculated as if $\bar{k}_t$ were independent of [C] and [M] although the $\bar{k}_t$ depends on chain length as proposed before,[2] the n being functions of [C] and [M]. In order to treat this dependence, eq 2 was modified by Ito.[3] These modifications show that, if eq 2 was used by assuming that $\bar{k}_t$ was independent of n, the $\bar{k}_{ti}$ should be overestimated. In order to avoid such overestimations, the following two methods were considered. One of them was an estimation of the $\bar{k}_{ti}$ by application of eq 2 to the data obtained by using thiol as a strong transfer agent in order to maintain the condition that n was invariable and therefore that $\bar{k}_t$ was independent of [C] and [M].[4] Recently, this method was doubted on the grounds that the effect of radical transfer to the thiols has not yet been fully understood.[6] The other method was an estimation of $\bar{k}_{ti}$ by using a relationship among [C], [M], R_p, and an average lifetime of radicals, $\bar{k}_t$ being absent from the expression.[5] However, the lifetime was obtained under the condition of nonstationary state, where [N] and $\bar{n}$ were functions of time. Introduction of the lifetime into the stationary state kinetics might yield some error. In the present paper, the $\bar{k}_{ti}$ is estimated by a new relationship among [C], [M], R_p, and $\bar{n}$, where $\bar{k}_t$ is eliminated.

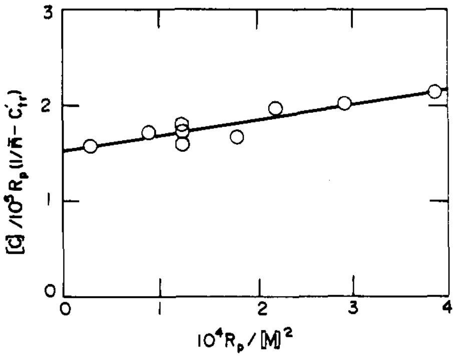

Figure 1. Application of eq 8 to the data[7] in the polymerization of MMA initiated by ABVN at 50 °C in 75% diethyl phthalate.

Theory

The rate equations for the stationary state are:[7]

$$d[\mathrm{R}]/dt = 2fk_d[\mathrm{C}] - k_i[\mathrm{M}][\mathrm{R}] - \bar{k}_{ti}[\mathrm{N}][\mathrm{R}] = 0 \qquad (3)$$

$$d[\mathrm{N}]/dt = k_i[\mathrm{M}][\mathrm{R}] - \bar{k}_{ti}[\mathrm{N}][\mathrm{R}] - \bar{k}_t[\mathrm{N}]^2 = 0 \qquad (4)$$

$$\bar{n} = \frac{k_p[\mathrm{N}][\mathrm{M}]}{\bar{k}_t[\mathrm{N}]^2 + k_{tr}[\mathrm{N}][\mathrm{S}] + \bar{k}_{ti}[\mathrm{N}][\mathrm{R}]} \qquad (5)$$

$$R_p = k_p[\mathrm{N}][\mathrm{M}] \qquad (6)$$

The $\bar{k}_t$ can be eliminated by eq 4 and 5, and we obtain:

$$k_i[\mathrm{M}][\mathrm{R}] = R_p\left(\frac{1}{\bar{n}} - C_{tr}\frac{[\mathrm{S}]}{[\mathrm{M}]}\right) \qquad (7)$$

Equations 3, 6, and 7 yield:

$$\frac{[\mathrm{C}]}{R_p(1/\bar{n} - C'_{tr})} = \frac{1}{2fk_d}\left(1 + \frac{\bar{k}_{ti}}{k_i k_p}\frac{R_p}{[\mathrm{M}]^2}\right) \qquad (8)$$

This is independent of any approximation used previously.[1]

Discussion

Equation 8 is applied to the data[7] in the polymerization of methyl methacrylate (MMA) initiated by 2,2′-azobis(2,4-dimethylvaleronitrile) (ABVN) at 50 °C (Figure 1). The values obtained are: $2fk_d = 6.6 \times 10^{-6}$ s^{-1} and $\bar{k}_{ti}/k_i k_p = 1090$ M s, which is in good agreement with the value of 1420 obtained by using the thiol as a strong transfer agent.[4]

On the application of eq 8 to the data in the polymerization of vinyl acetate (VA) initiated by ABVN[8] at 50 °C (Figure 2), $2fk_d = 7 \times 10^{-6}$ s^{-1} and $\bar{k}_{ti}/k_i k_p = 40\,000$ M s are obtained. The difference between the latter and 68 000 M s obtained[8] by eq 2 is not marked. This means that, as is well known, the VA radicals transfer easily to solvents and therefore this corresponds to the use of a strong transfer agent.[4] Further, the 40 000 is twofold less than 76 000 obtained at very high initiation rates.[9] This is consistent with the hypothesis[3,10] that the $\bar{k}_{ti}$ for reaction between R and small N is larger than that between R and large N, smaller N being formed at a higher initiation rate.

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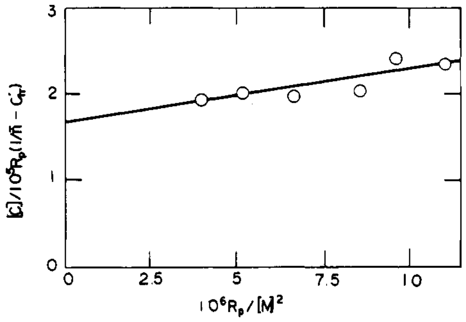

Figure 2. Application of eq 8 to the data[8] in the polymerization of VA initiated by ABVN at 50 °C in 50% ethyl acetate.

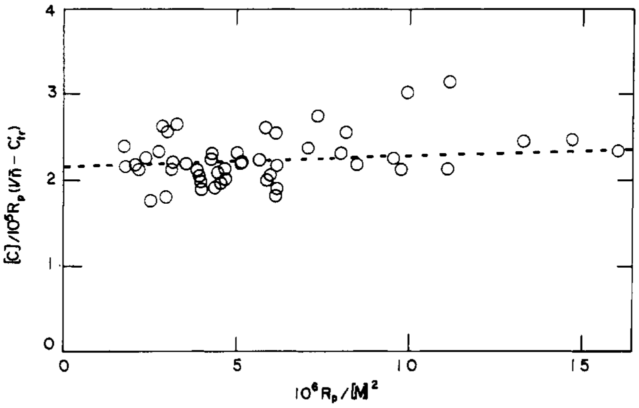

Figure 3. Application of eq 8 to the data[6] in the polymerization of MMA initiated by 2,2′-azobis(isobutyronitrile) at 60 °C.

In order to apply eq 8, the data must be obtained exactly under the condition that the primary radical termination rate is not negligibly small (perhaps when $\bar{n} < 1000$). To estimate $\bar{k}_{ti}$, eq 8 cannot be applied to data obtained under the condition that the second term ($\bar{k}_{ti}R_p/k_ik_p[M]^2$) in parentheses on the right of eq 8 is not comparable with unity, because of scattering in the data. The data[6] in Figure 3 are examples for such a scattering. For other data,[11] the calculated values of $[C]/R_p(1/\bar{n} - C'_{tr})$ also scatter regardless of $R_p/[M]^2$, and therefore the estimation of $\bar{k}_{ti}$ is impossible. Accordingly, the value $\bar{k}_{ti}/k_ik_p = 14\,500$ obtained by Deb and Kapoor,[6] which is about 14 times larger than that reported by Mahabadi and O'Driscoll,[4] and the others,[11] is meaningless. Rather, the smaller value reported by Mahabadi and O'Driscoll may be reasonable.

From the values of k_ik_p (= 42 500 M^{-2} s^{-2} for MMA and 20 900 for VA)[8] and the values of $\bar{k}_{ti}/k_ik_p$ obtained in the present paper, the $\bar{k}_{ti}$ are calculated to be 4.6×10^7 M^{-1} s^{-1} for MMA and 8.4×10^8 for VA. Here, the 4.6×10^7 is obtained at high viscosity (1.6 cP) and therefore the $\bar{k}_{ti}$ at low viscosity (0.35 cP in 75% ethyl acetate [ref 1e, p 2541]) would be estimated to be 2.1×10^8 by assuming that the rate is diffusion controlled (that is, $k_{ti} \propto 1/\text{viscosity}$). The above constants are nearly equal to the rate constants[3,12] estimated by the general theory of the diffusion-controlled reaction.

If a termination between N_n and N_1 is diffusion controlled, an average $\bar{k}_{t,1}$ (= $\sum_{n=1}^{\infty}k_{t,1n}[N_n]/[N]$) is approximated to $\bar{k}_{ti}$ (= $\sum_{n=1}^{\infty}k_{ti,n}[N_n]/[N]$).[13] This means that a distinction without a difference between $\bar{k}_{t,1}$ and $\bar{k}_{ti}$ has no effect. Rather the $\bar{k}_{ti}$ may be treated as a part of $\bar{k}_t$. This was explained by considering polymerization where the structure of the primary radical resembles that of the end radical.[10,14] Further, Ito[10] derived a new rate $k_{t,ns}$ which is controlled by translational and segmental diffusions. The deviations from $R_p \propto [C]^{1/2}[M]$ were explained by the $k_{t,ns}$, regardless of the concept of primary radical termination.[15]

Table I

R_p	polymerization rate
n	the number of monomeric units in a polymer radical
$\bar{n}$	kinetic chain length
[C]	initiator concentration
[M]	monomer concentration
[N]	total concentration of polymer radicals
$[N_n]$	concentration of polymer radical with n
[R]	primary radical concentration
[S]	solvent concentration
f	the fraction of primary radical escaping the solvent cage
k_d	initiator decomposition rate constant
k_p	propagation rate constant
k_{ti}	primary radical termination rate constant
k_t	polymer-polymer termination rate constant
k_i	rate constant of addition of primary radical on to monomer
k_{tr}	rate constant of transfer of polymer radical on to solvent
$k_{t,ns}$	rate constant of termination between N_n and N_s
$k_{ti,n}$	rate constant of primary radical termination between R and N_n
C_{tr}	k_{tr}/k_p
C'_{tr}	$k_{tr}[S]/k_p[M]$

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(13) Following ref 2, 3, and 10, $k_{t,1n} = 4\pi r(D_1 + D_S)$ and $k_{ti,n} = 4\pi r(D_i + D_S)$, where r is the reaction radius, and D_1, D_i, and D_S are the diffusion coefficients of radical $n = 1$, primary radical, and segment radical, respectively. Usually, the size of R is not so different from that of N_1 that $D_i \simeq D_1$ cannot be accepted. Thus, $k_{t,1n} \simeq k_{ti,n}$ ($\bar{k}_{t,1} \simeq \bar{k}_{ti}$) could be accepted.

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(15) This conclusion cannot be developed for polymerization having a character of $k_i \ll k_p$ at very high initiation rates, because the primary radical termination rates are so high that eq 3 and 4 must be modified. This was explained typically by the kinetic data in polymerization of VA at very high initiation rates.[9,10]