

Kinetics of Radical Polymerization with Primary Radical Termination

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(Received June 18, 1981)

ABSTRACT: The polymerization initiated by 1-phenylethyl radical (PER) and diphenylmethyl radical (DPMR) at 50°C was studied to clarify the causes of deviation in the polymerization rate R_p from $R_p \propto [C]^{1/2}[M]$ ($[C]$, initiator concentration and $[M]$, monomer concentration). In the polymerization of styrene initiated by PER, the term defined as primary radical termination (PRT) can not be used to explain the deviation, because of $k_i \approx k_p$ (k_i , rate constant of addition of primary radical to monomer and k_p , propagation rate constant). Thus, the deviation should be explained by the dependence of polymer-polymer termination (PPT) on chain length. In the polymerization initiated by DPMR, both the PRT term and the dependence of PPT on chain length are necessary to explain the deviation, because of $k_i \ll k_p$, where $k_i = 37 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (styrene) and 2.5 (methyl methacrylate).

KEY WORDS Phenylethyl Radical / Diphenylmethyl Radical / Primary Radical Termination / Polymer-Polymer Termination / Styrene / Methyl Methacrylate /

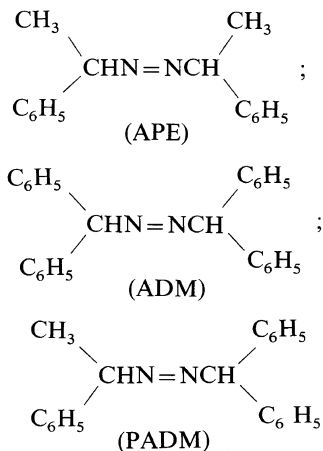
In the polymerization of styrene, methyl methacrylate (MMA), and methacrylonitrile (MA) initiated by 2,2'-azobisisobutyronitrile (AIBN), the rate constant of addition of a primary radical to a monomer has been estimated to be $k_i = k_{pMA}(k_{p12}/k_{p11})$ where k_{pMA} and k_{p12}/k_{p11} are designated as the rate constant of the homopolymerization of MA and $1/r_1$ in the copolymerization of MA (M_1)- M_2 system, respectively.^{1,2,11} The k_i -value obtained is nearly equal to the propagation rate constant of the respective homopolymerization (that is, $k_i \approx k_p$). If this is true, an approximation as $\bar{k}_{ti}/k_i k_p \approx \bar{k}_{t,1}/k_p^2$ can be used. That is, $\bar{k}_{t,1}$ may be treated as a part of \bar{k}_t .^{2,3} Therefore, the deviation of polymerization rate from eq 1 can not be explained on the basis of the primary radical termination rate, but rather by the dependence of polymer-polymer termination rate on the chain length.¹⁻³

$$R_p \propto [C]^{1/2}[M] \quad (1)$$

If $k_i \ll k_p$ is satisfied, the effect of primary radical

termination is important to explain the deviation from eq 1. This has been typically illustrated in terms of a kinetic treatment of the polymerization of vinyl acetate (VA) initiated by AIBN.⁴

In the present paper, the polymerization of styrene and MMA in the presence of 1-azobisphenylethane (APE),⁵ azobisdiphenylmethane (ADM),⁶ and 1-phenylethylazodiphenylmethane (PADM)⁷ was studied to reconfirm the above explanation.



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The primary radicals formed by the decomposition of these azo initiators are the 1-phenylethyl radical: $\text{CH}_3\dot{\text{C}}\text{HCH}_2\text{C}_6\text{H}_5$ (PER) and the diphenylmethyl radical: $\text{C}_6\text{H}_5\dot{\text{C}}\text{HCH}_2\text{C}_6\text{H}_5$ (DPMR). The structure of PER resembles that of the end radical of polymer in the polymerization of styrene, and therefore the prediction that $k_i \approx k_p$ is satisfied. On the other hand, DPMR is more stable than PER, in view of resonance theory.⁶ Thus, it is expected that the rate constant of addition to the monomer is considerably smaller than the propagation rate constant. That is, the condition that $k_i \ll k_p$ is satisfied. The data obtained are treated by the kinetic equations reported before.^{2,4}

EXPERIMENTAL

APE, ADM, and PADM were prepared by methods described in earlier articles.⁵⁻⁷ Commercial styrene and MMA were also purified by a method described earlier.⁴ The polymerization solutions containing the above azo initiators were prepared at about 10^{-3} mmHg by the freeze-thaw technique. The polymerization was conducted at $50.0 \pm 0.05^\circ\text{C}$. The conversions were estimated by liquid chromatography. The ultimate conversion was below 8%. The values of \bar{n} were estimated from M_n obtained by gel permeation chromatography (GPC). Here, M_n of polystyrene was estimated by using a GPC calibration curve made by the relationship between the molecular weight M of the polystyrene standard and elution volume. To estimate M_n of poly(MMA), this curve was modified by in accordance with the fact that $[\eta]M$ was independent of the kind of polymer at given elution volume.^{8,9}

RESULTS AND DISCUSSION

The kinetic data obtained are shown in Tables I through IV. Clearly, the deviation of R_p from eq 1 is seen in the data obtained in any polymerization system. That is, $(R_p/[C]^{1/2}[M])$ increases with a decrease in $[C]$. In order to explain similar deviations, the effect of primary radical termination was considered,¹⁰ without examining the dependence of the polymer-polymer termination rate on the chain length. On the other hand, some theoretical treatments indicate that the polymer-polymer termination depends on chain length, where the

chain length is a function of $[C]$ and $[M]$.^{3,11-13} To avoid this confusion, an equation not involving the polymer-polymer termination was derived.² Considering the transfer to initiator, this equation is expressed as,

$$\frac{fk_d[C]}{R_p(1/\bar{n} - C_{\text{trM}} - C_{\text{tri}}[C][M])} = 1 + \frac{\bar{k}_i R_p}{k_i k_p [M]^2} \quad (2)$$

If the primary radical termination rate is negligibly small (that is, inequality 3 is adoptable), eq 2 reduces to eq 4.

$$1 \gg \frac{\bar{k}_i R_p}{k_i k_p [M]^2} \quad (3)$$

$$\frac{[M]}{[C]} \left(\frac{1}{\bar{n}} - C_{\text{trM}} \right) = C_{\text{tri}} + fk_d \cdot \frac{[M]}{R_p} \quad (4)$$

Setting up $C_{\text{trM}} = 4.0 \times 10^{-5}$,¹⁴ eq 4 is fitted to the data obtained in the polymerization initiated by PER (Table I). A good linear relationship based on eq 4 obtained (Figure 1). This means that the inequality 3 can be used. Accordingly, the primary

Table I. Bulk polymerization of styrene initiated by APE at 50.0°C

[C]	$10^5 R_p$	\bar{n}	$10^6 R_p/[C]^{1/2}[M]$
mol dm ⁻³	mol dm ⁻³ s ⁻¹		dm ^{3/2} mol ^{-1/2} s ⁻¹
0.200	1.901	2310	5.34
0.100	1.484	3710	5.75
0.050	1.120	5011	6.07
0.025	0.861	7413	6.55
0.0125	0.617	9485	6.60

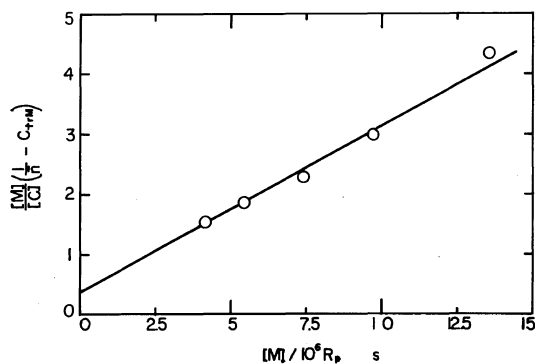


Figure 1. Application of eq 4 to the data in the polymerization of styrene initiated by APE (Table I).

Table II. Polymerization of styrene initiated by ADM at 50.0°C

[C]	[M]	$10^5 R_p$	\bar{n}	$10^5 R_p/[C]^{1/2}[M]$
mol dm ⁻³	mol dm ⁻³	mol dm ⁻³ s ⁻¹		dm ^{3/2} mol ^{-1/2} s ⁻¹
0.1033 ^a	2.00	1.1, 0.9		1.7, 1.4
0.1033 ^a	4.01	3.44		2.67
0.1033 ^a	8.04	14.9	107	5.76
0.0258	8.28	10.68	238	8.03
0.00646	8.36	7.16	542	10.66
0.00161	8.36	4.49	1178	13.39
0.000404	8.36	2.56	2435	15.24
0.000101	8.36	1.401	4980	16.67

^a Benzene was used as solvent.

Table III. Polymerization of MMA initiated by ADM at 50.0°C

[C]	[M]	$10^5 R_p$	\bar{n}	$10^5 R_p/[C]^{1/2}[M]$
mol dm ⁻³	mol dm ⁻³	mol dm ⁻³ s ⁻¹		dm ^{3/2} mol ^{-1/2} s ⁻¹
0.1040 ^a	1.09	1.9, 1.5		5.3, 4.2
0.1040 ^a	2.18	5.16		7.17
0.1040 ^a	4.36	22.5		15.63
0.1040	8.72	68.8	412	23.9
0.0260	8.99	52.7	843	36.3
0.00650	9.04	33.1	1725	45.4
0.00163	9.04	20.6	3239	55.7
0.000460	9.04	12.02	6403	66.0
0.0001202	9.04	6.88	14500	75.4

^a Benzene was used as solvent.

radical termination term ($\bar{k}_{ti}/k_i k_p$) is unnecessary. f and C_{tri} were estimated from the slope and intercept of the line and are shown in Table V. Previously, the deviation of R_p from eq 1 was explained by considering only primary radical termination, without examining the data on \bar{k}_i as a function of \bar{n} .¹⁵ In view of eq 4, this explanation is incorrect. Therefore, the deviation of R_p from eq 1 should be explained by the dependence of polymer-polymer termination rate, where $\bar{k}_{ti}/k_i k_p \approx \bar{k}_{t,1}/k_p^2$ because of $k_i \approx k_p^{1-3}$ as stated in the Introduction.

On the other hand, eq 4 cannot be used for treating the data obtained in the polymerization initiated by DPMR (Tables II and III), since a negative value is obtained for C_{tri} . This means that primary radical termination is important in this case. To apply eq 2 to the data shown in Tables II and III, the value of $\bar{k}_{ti}/k_i k_p$ must be determined. To estimate this value, eq 5 must be used.⁴

$$R_p = \frac{k_i k_p}{\bar{k}_{ti}} [M]^2 \quad (5)$$

In the present case, eq 5 is applicable to the data obtained for styrene at $[M] \leq 8.04$ mol dm⁻³ and $[C] = 0.1033$ and for MMA at $[M] \leq 4.36$ mol dm⁻³ and $[C] = 0.104$, as seen in Figure 2. $\bar{k}_{ti}/k_i k_p$ was found to be 4.5×10^5 mol s dm⁻³ (styrene) and 8.5×10^4 (MMA). To treat the data in Tables II and III, eq 2 is rewritten as:

$$\frac{[M]}{[C]} \left(\frac{1}{\bar{n}} - C_{triM} \right) = C_{tri} + f k_d \left[\frac{[M]}{R_p (1 + \bar{k}_{ti} R_p / k_i k_p [M]^2)} \right] \quad (6)$$

Applicability of eq 6 to the data obtained in the polymerization of styrene can be seen in Figure 3, since C_{tri} is a positive value. The values obtained are

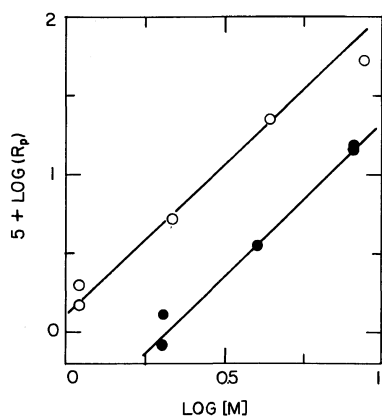


Figure 2. Application of eq 5 to the data in the polymerization of styrene (●, [ADM]=0.1033 mol dm⁻³ in Table II) and MMA (○, 0.104 in Table III).

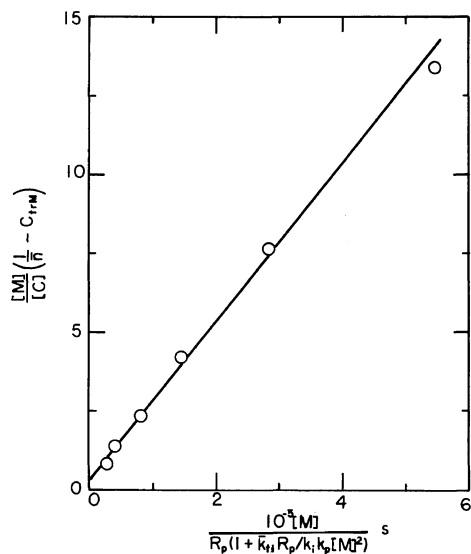


Figure 3. Application of eq 6 to the data in the polymerization of styrene initiated by ADM (Table II), where $\bar{k}_{ti}/k_i k_p = 4.5 \times 10^5$ mol s dm⁻³.

shown in Table V. In order to apply eq 6 to the data obtained in the polymerization of MMA, C_{trM} is set as 1.08×10^{-5} .¹⁶ This applicability is shown in Figure 4. The values obtained for C_{tri} and f are shown in Table V.

To apply eq 2 to the data obtained in the polymerization initiated by both PER and DPMR (Table IV), it is rewritten as:

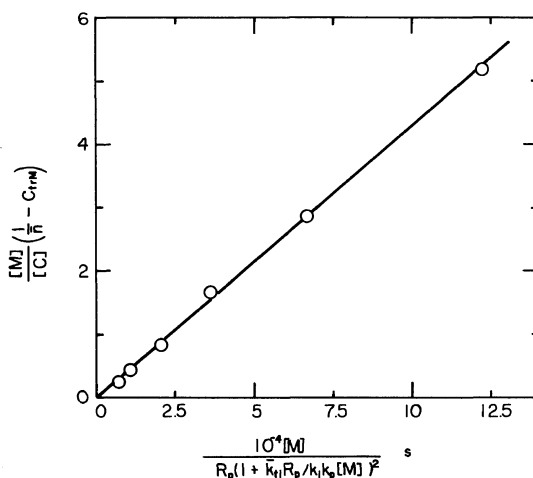


Figure 4. Application of eq 6 to the data in the polymerization of MMA initiated by ADM (Table III), where $\bar{k}_{ti}/k_i k_p = 8.5 \times 10^4$ mol s dm⁻³.

Table IV. Bulk polymerization of styrene initiated by PADM at 50.0°C

[C]	$10^5 R_p$	\bar{n}	$10^5 R_p/[C]^{1/2}$ [M]
mol dm ⁻³	mol dm ⁻³ s ⁻¹		dm ^{3/2} mol ^{-1/2} s ⁻¹
0.0560	9.56	389	4.60
0.0140	4.98	918	5.06
0.00350	2.70	1965	5.46
0.000875	1.429	3670	5.79
0.000219	0.760	8036	6.14

$$2R_p \left(\frac{1}{\bar{n}} - C_{trM} - C_{tri} \frac{[C]}{[M]} \right) = \frac{fk_d[C]}{1 + \bar{k}_{ti1}R_p/k_{i1}k_p[M]^2} + \frac{fk_d[C]}{1 + \bar{k}_{ti2}R_p/k_{i2}[M]^2} \quad (7)$$

Because $1 \gg \bar{k}_{ti1}R_p/k_{i1}k_p[M]^2$ as shown before, eq 7 should be reduced to:

$$\frac{[M]}{[C]} \left(\frac{1}{\bar{n}} - C_{trM} \right) = C_{tri} + fk_d \frac{[M]}{2R_p} \left(1 + \frac{1}{1 + \bar{k}_{ti2}R_p/k_{i2}k_p[M]^2} \right) \quad (8)$$

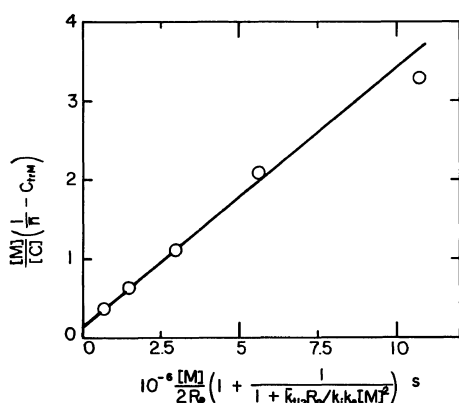


Figure 5. Application of eq 8 to the data in the polymerization of styrene initiated by PADM (Table IV), where $\bar{k}_{ti}/k_i k_p = 4.5 \times 10^5 \text{ mol s dm}^{-3}$.

The applicability of eq 8 is shown in Figure 5. The values obtained for C_{tr} and f are shown in Table V, and C_{trPADM} are somewhat smaller than C_{trADM} . In view of the above, it may be said that the kinetic treatment based on eq 2 has been experimentally verified.

The primary radical termination rate is probably diffusion-controlled. This means that $\bar{k}_{tiAIBN} \approx \bar{k}_{tiADM}^{-1-3}$.

Thus, to estimate the value of k_i , the following equation may be used,

$$k_{iADM} \approx \frac{k_{iAIBN}(\bar{k}_{ti}/k_i k_p)_{AIBN}}{(\bar{k}_{ti}/k_i k_p)_{ADM}} \quad (9)$$

The values used here are: $(\bar{k}_{ti}/k_i k_p)_{AIBN} = 27900 \text{ mol s dm}^{-3}$, $k_{iAIBN} = 595 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for styrene at 50°C and $(\bar{k}_{ti}/k_i k_p)_{AIBN} = 1420$, $k_i = 149$ for MMA at

50°C .^{17,18} The calculated values are shown in Table V, where the prediction that $k_i \ll k_p$ is satisfied. In the above discussion, if the steric effect for \bar{k}_{tiADM} is larger than that for \bar{k}_{tiAIBN} , (meaning that $\bar{k}_{tiADM} < \bar{k}_{tiAIBN}$), $k_i \ll k_p$ should be satisfied more completely.

CONCLUSION

In the polymerization of styrene and MMA initiated by DPMR initiated by the dimethylcyanomethyl radical (DCMR),⁴ $k_i \ll k_p$ is satisfied, and therefore the primary radical termination term is important in explaining the deviation of R_p from eq 1. On the other hand, in the polymerization of styrene and MMA initiated by PER and DCMR,¹ the radical termination term is unnecessary and the deviation of R_p from eq 1 is explained only by the dependence of the polymer-polymer termination rate on the chain length, because $k_i \leq k_p$. In the polymerization of styrene, $k_{iAIBN} = 595 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ is considerably larger than $k_p = 123$. $\bar{k}_{ti}/k_i k_p$ at $k_i > k_p$ is smaller than that at $k_i = k_p$. Thus, when $k_i > k_p$, primary radical termination is not important in explaining the deviation of R_p from eq 1.

NOMENCLATURE

R_p	, polymerization rate
\bar{n}	, number average degree of polymerization
[C]	, initiator concentration
[M]	, monomer concentration
f	, the fraction of primary radical escaping from the solvent cage

Table V. Values obtained in polymerization initiated by azo initiators at 50.0°C

Monomer	Initiator	$10^8 k_d^a$	f	C_{tr}	k_p^b	k_i
		s^{-1}			$\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	
Styrene	APE	5.75	0.41	0.0075	123	123
Styrene	PADM	668	0.46	0.2 ± 0.05	123	123, 37
Styrene	ADM	6070	0.48	0.3 ± 0.1	123	37
MMA	ADM	6070	0.58	0	285	2.5
VA	AIBN				2640	7.92^c

^a Calculated by the respective Arrhenius equations in ref 5—7.

^b From ref 19.

^c From ref 18.

k_d	, initiator decomposition rate constant
k_p	, propagation rate constant
k_i	, rate constant of addition of primary radical to monomer (k_{i1} is for PER, k_{i2} for DPME)
\bar{k}_{ti}	, primary radical termination rate constant (\bar{k}_{ti1} is for PER, \bar{k}_{ti2} for DPME)
$\bar{k}_{t,1}$, rate constant of termination between polymer radical and radical with one monomer unit
C_{trM}	, the relative transfer constant of polymer radical to monomer
C_{tri}	, the relative transfer constant of polymer radical to initiator
$[\eta]$, intrinsic viscosity
M_n	, number-average molecular weight

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