European Polymer Journal Vol. 17, pp. 641 to 644, 1981
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0014-3057/81/060641-04$02.00/0

NON-IDEAL KINETICS IN VINYL POLYMERIZATION

NOTE ON PRIMARY RADICAL TERMINATION IN BENZOYL PEROXIDE INITIATED POLYMERIZATION OF VINYL CHLORIDE IN DICHLOROETHANE SOLUTION

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(*Received* 6 *August* 1980)

Abstract—The kinetics of vinyl chloride polymerization initiated by benzoyl peroxide doubly labelled with ^{14}C and ^{3}H were studied in 1,2-dichloroethane solution at 60°. The importance of primary radical termination in the polymerization is examined by kinetic analysis and by analysis of polymers for combined initiator fragments.

INTRODUCTION

The ideal relationship for free-radical polymerization is

$$R_p = \left(\frac{2fk_dk_p^2}{k_t}\right)^{\frac{1}{2}} [\mathrm{M}]\,[\mathrm{I}]^{\frac{1}{2}}. \qquad (1)$$

Deviations are often discussed in terms of (i) diffusion effects; (ii) formation of electron donor-acceptor complexes; (iii) chain transfer to solvent; and (iv) primary radical termination. Orders in initiator >0.5 and in monomer >1.0 have been predicted and experimentally found [1–3] for polymerizations in which there is primary radical termination. In this communication, the extent of primary radical termination in vinyl chloride polymerization in dichloroethane solution is discussed in terms of the kinetic analysis of Bamford *et al.* [4] and Deb and Gaba [5].

EXPERIMENTAL

Materials

Vinyl chloride monomer (VCM) and 1,2-dichloroethane (DCE) were purified as described previously [6]. Doubly labelled benzoyl peroxide† (tritium in the benzene ring and ^{14}C in the carboxyl carbon) was purified by precipitation with methanol from acetone solution and dried in a vacuum desiccator.

Polymerization

Polymerization rates in dichloroethane solution were measured at 60° in dilatometers at 0.56, 2.7 and 3.5 M monomer using various concentrations of the initiator. Polymerization was allowed to proceed to about 10% conversion; the polymer was recovered by precipitation with excess methanol and purified from traces of uncombined initiator fragments by repeated precipitation from solutions in deperoxidised tetrahydrofuran.

Assay of polymer samples for combined initiator fragments

Polymer samples were assayed for ^{14}C and tritium by liquid scintillation counting. Count rates were obtained for: (a) polymer solution (2–3% w/v in cyclohexanone); (b) polymer solution with large activity excess of [^{3}H]toluene standard; (c) polymer solution with large activity excess [^{14}C]hexadecane standard; and (d) a blank. The mathematical relationship [7] correlating count rate with the relative abundances of ^{3}H- and ^{14}C-initiator fragments in the polymer was used to determine the variation of the ratio $C_6H_5COO^{\bullet}/(C_6H_5COO^{\bullet} + C_6H_5^{\bullet})$ with monomer and initiator concentrations.

RESULTS AND DISCUSSION

The variation of rate of polymerization with initiator concentration is shown in Fig. 1. It will be seen that, although straight lines can be drawn through the experimental points, the plots for 0.56 and 2.7 M monomer do not pass through the origin, suggesting that the order with respect to initiator may not be strictly 0.5; kinetic orders of 0.34, 0.42 and 0.51 were obtained for 0.56, 2.7 and 3.5 M monomer respectively. These results indicate that primary radical termination may be important in this system.

Primary radical termination (PRT)

The principal reactions of primary radicals are:

$$R^{\bullet} + M \xrightarrow{k_i} M_1^{\bullet} \text{ initiation}$$

and

$$R^{\bullet} + P^{\bullet} \xrightarrow{k_{prt}} \text{primary radical polymer termination}$$

where R$^{\bullet}$ represents a primary radical and P$^{\bullet}$ a polymer radical; k_i and k_{prt} are the rate constants for initiation and primary radical termination respectively. The importance of primary radical termination should depend on both monomer and initiator concentrations, tending to be most significant at low monomer concentrations and high initiator concentrations. The situation is more complicated for

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† This compound was made by Dr W. Brendlein from a mixture of [^{3}H]benzoic acid and [^{14}C]benzoic acid.

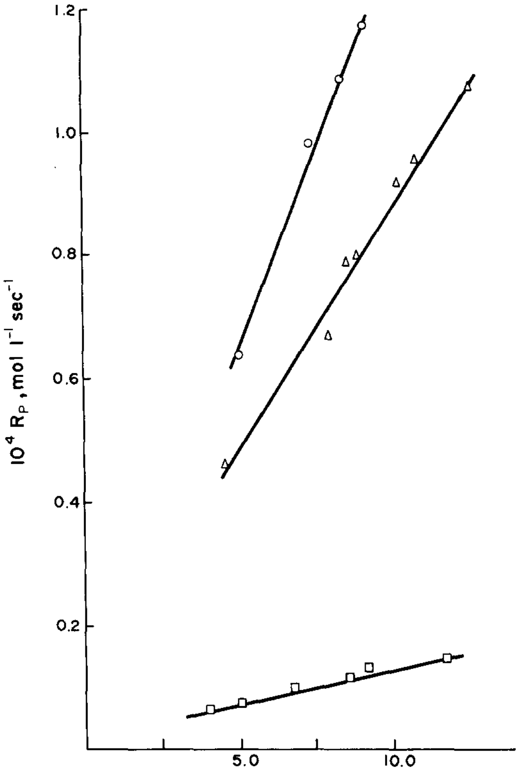

Fig. 1. Dependence of the rate of polymerization, R_p, on initiator concentration at 0.56 (□) 2.7 (△) and 3.5 M (○) monomer at 60°.

polymerization initiated by benzoyl peroxide where the secondary dissociation of the primary radical competes with the "normal" initiation process

$$C_6H_5COO^\cdot \xrightarrow{k_d'} C_6H_5^\cdot + CO_2.$$

The phenyl radical so formed may initiate polymerization

$$C_6H_5^\cdot + M^\cdot \xrightarrow{k_i} M_i$$

or engage in termination

$$C_6H_5^\cdot + P^\cdot \xrightarrow{k_{prt}} \text{polymer}$$

at rates significantly different from those of the primary radical.

One of the earliest mathematical treatment for primary radical termination was developed by Bamford *et al.* [4]. By considering the relative probabilities of occurrence of three radical combination reactions, viz. (i) recombination of primary radicals; (ii) primary radical termination; and (iii) combination of growing polymer radicals, and by assuming that the rate constant for primary radical termination is a geometric mean of the combination reactions (i) and (iii) above, the authors obtained.

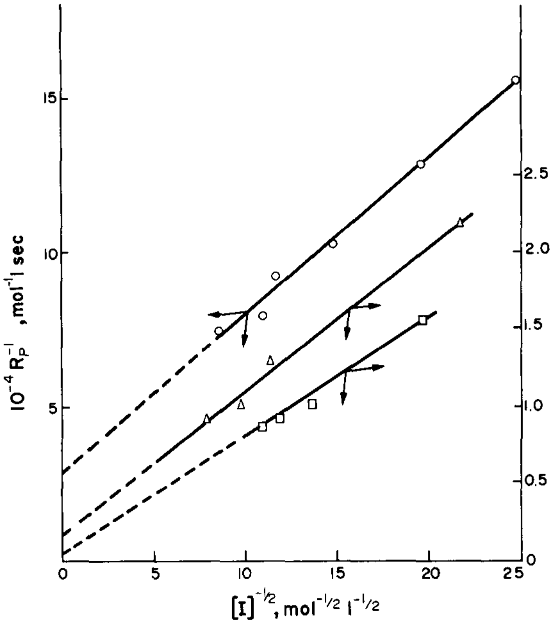

Fig. 2. Primary radical termination: plots of $1/R_p$ vs $1/[I]^{\frac{1}{2}}$ for the polymerization of 0.56 (○), 2.7 (△) and 3.5 M (□) monomer at 60°.

$$\frac{1}{R_p} = \frac{k_t^{\frac{1}{2}}}{k_p \Sigma [M]^2} + \frac{k_t^{\frac{1}{2}}}{k_p (2k_d)^{\frac{1}{2}}} \cdot \frac{1}{[M][I]^{\frac{1}{2}}} \qquad (2)$$

where $\Sigma = k_i/(\sigma k_{prt})^{\frac{1}{2}}$ and σ is the geometric mean constant. Figure 2 shows the data from this study presented as plots of $1/R_p$ vs $1\,[I]^{\frac{1}{2}}$. The plots show that primary radical termination becomes an important kinetic feature at low monomer concentrations. The value of the primary radical termination term $k_t^{\frac{1}{2}}/(k_p\Sigma)$ calculated from the straight line plots are shown in Table 1.

The decrease in the $k_t^{\frac{1}{2}}/(k_p\Sigma)$ term from 9.00×10^3 mol l^{-1} at 0.56 M monomer to 2.45×10^3 mol l^{-1} at 3.5 M monomer might be thought to indicate a dependence of the primary radical termination term on monomer concentration.

The errors involved in the extrapolation of the straight line passing through the experimental points for polymerization 3.5 M monomer and the relatively small intercept of the straight line on the vertical axis lead to the suggestion that $k_t^{\frac{1}{2}}/(k_p\Sigma)$ is virtually constant at 8.0×10^3 mol l^{-1}. However, this treatment does not take into account the secondary dissociation of the primary radicals.

Table 1. Primary radical termination in vinyl chloride polymerization in dichloroethane solution

[M] (mol l^{-1})	Slope	Intercept	$k_t^{\frac{1}{2}}/k_p(2k_d)^{\frac{1}{2}}$ (mol$^{\frac{1}{2}}$ l$^{-\frac{1}{2}}$ sec)	$k_t^{\frac{1}{2}}/(k_p\Sigma)$ (mol l^{-1})
0.56	5.90×10^3	2.87×10^4	1.85×10^4	9.00×10^3
2.70	9.36×10^2	1.02×10^3	2.53×10^3	7.44×10^3
3.50	8.37×10^2	2.01×10^2	2.93×10^3	2.45×10^3

Table 2. Dependence of R_i/R_{prt} on [I] and [M] at 60°

[M] (mol l^{-1})	10^3 [I] (mol l^{-1})	R_i/R_{prt}
0.56	1.61	0.11
0.56	13.66	0.05
2.70	2.15	0.35
2.70	15.98	0.15
3.50	2.64	0.42
3.50	8.50	0.23

More recently, Deb and Gaba [5] developed a kinetic analysis for primary radical termination in systems where the decomposition of the primary radicals competes with initiation process. The authors based their analysis on the reaction scheme.

$$\mathrm{I} \xrightarrow{k_d} 2\mathrm{R}^{\bullet} \text{ production of primary radicals; } 2fk_d[\mathrm{I}]$$

$$\mathrm{R}^{\bullet} + \mathrm{M} \xrightarrow{k_i} \mathrm{M}_i \text{ initiation by } \mathrm{R}^{\bullet}\text{; } k_i[\mathrm{R}^{\bullet}][\mathrm{M}]$$

$$\mathrm{M}_1^{\bullet} + \mathrm{M} \xrightarrow{k_p} \mathrm{P}^{\bullet} \text{ propagation; } k_p[\mathrm{M}^{\bullet}][\mathrm{M}]$$

$$\mathrm{R}^{\bullet} \xrightarrow{k_d'} \mathrm{R}^{\bullet\prime} \text{ decomposition of primary radical; } k_d'[\mathrm{R}^{\bullet}]$$

$$\mathrm{R}^{\bullet\prime} + \mathrm{M} \xrightarrow{k_i'} \mathrm{M}_i \text{ initiation by } \mathrm{R}^{\bullet\prime}\text{; } k_i'[\mathrm{R}^{\bullet\prime}][\mathrm{M}]$$

$$\mathrm{R}^{\bullet} + \mathrm{P}^{\bullet} \xrightarrow{k_{prt}} \text{dead polymer; primary radical termination } k_{prt}[\mathrm{R}^{\bullet}][\mathrm{P}^{\bullet}]$$

$$\mathrm{R}^{\bullet\prime} + \mathrm{P}^{\bullet} \xrightarrow{k_{prt}'} \text{dead polymer; termination by } \mathrm{R}^{\bullet\prime} k_{prt}'[\mathrm{R}^{\bullet\prime}][\mathrm{P}^{\bullet}]$$

$$\mathrm{P}_a^{\bullet} + \mathrm{P}_b^{\bullet} \xrightarrow{k_t} \text{dead polymer; mutual termination of growing chains } k_t[\mathrm{P}^{\bullet}]^2.$$

By considering the stationary states for $[\mathrm{R}^{\bullet}]$, $[\mathrm{R}^{\bullet\prime}]$ and $[\mathrm{P}^{\bullet}]$ and by assuming that (i) mutual termination of benzoyloxy and phenyl radicals, (ii) primary radical transfer, and (iii) termination of macroradicals by phenyl radicals are negligible, the authors obtained the relationship.

$$\log \frac{R_p^2}{[\mathrm{I}][\mathrm{M}]^2} = \log \frac{2fk_d k_p^2}{k_t} - 0.8684 \frac{k_{prt}/(k_i k_p)}{1 + k_d'/(k_i[\mathrm{M}])} \cdot \frac{R_p}{[\mathrm{M}]^2}. \quad (3)$$

The data from this study are presented in Fig. 3 as plots of $\log R_p^2/([\mathrm{I}][\mathrm{M}]^2)$ vs $R_p/[\mathrm{M}]^2$. From the slopes of the plots, values for

$$[(k_{prt}/(k_i k_p)]/\{1 + k_d'/(k_i[\mathrm{M}])\}$$

of 9.89×10^4 and 1.59×10^5 mol l^{-1} sec were obtained for polymerization of 0.56 and 2.7 M monomer respectively. By putting 3.90 for k_d'/k_i [7], an average value for $k_{prt}/k_i k_p$ of 4.62×10^5 mol l^{-1} sec is obtained. It is interesting that the value of $k_{prt}/k_i k_p$ obtained here is about the same order of magnitude as, but somewhat larger than, the values reported for the styrene–benzene-AZBN system [5].

The implications of the value of $k_{prt}/k_i k_p$ obtained from this study can be assessed by comparing the rate of initiation, R_i, with the rate of primary radical termination, R_{prt}.

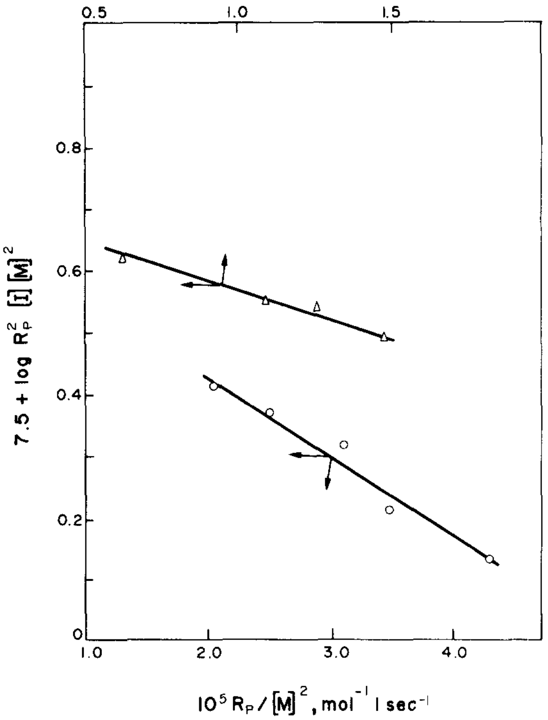

Fig. 3. Primary radical termination: semilogarithmic plots of $R_p^2/[\mathrm{I}][\mathrm{M}]^2$ vs $R_p/[\mathrm{M}]^2$ for the polymerization of 0.56 (○) and 2.7 M (△) monomer at 60°.

$$\frac{\text{Rate of initiation}}{\text{Rate of PRT}} = \frac{R_i}{R_{prt}} = \frac{k_i[\mathrm{R}^{\bullet}][\mathrm{M}]}{k_{prt}[\mathrm{R}^{\bullet}][\mathrm{P}^{\bullet}]} = \frac{k_i[\mathrm{M}]}{k_{prt}[\mathrm{P}^{\bullet}]}. \quad (4)$$

The rate of polymerization

$$R_p = [\mathrm{P}^{\bullet}]k_p[\mathrm{M}] \quad (5)$$

so that

$$\frac{R_i}{R_{prt}} = \frac{k_i k_p}{k_{prt}} \cdot \frac{[\mathrm{M}]^2}{R_p}. \quad (6)$$

By substituting the value of $k_{prt}/k_i k_p$ and the polymerization data from this study into Eqn 6, the ratio R_i/R_{prt} shown in Table 2 is obtained.

The results show the expected dependence of PRT on both monomer and initiator concentrations. However, the low values of R_i/R_{prt} seem unlikely as these would suggest that at 0.56 M monomer and 0.0137 M initiator, the rate of initiation is only 5–10% of the rate of primary radical termination. It appears that, although PRT affects the polymerization kinetics of VCM in DCE, the kinetic analysis of Deb and Gaba leads to an unreliable prediction of its importance.

One of the most important assumptions made by Deb and Gaba is that termination of macroradicals by phenyl radicals is negligible. The authors justified this assumption by considering that $[\mathrm{C_6H_5^{\bullet}}] \ll [\mathrm{C_6H_5OO^{\bullet}}]$ and $k_{prt}' \sim k_{prt}$ without justifying these assumptions. If $[\mathrm{C_6H_5^{\bullet}}] \ll [\mathrm{C_6H_5COO^{\bullet}}]$, it would

Table 3. Variation of the degree of incorporation of phenyl and benzoyloxy radicals with initiator concentration in the polymerization of 0.56 M monomer at 60°

10^3 [I] (mol l^{-1})	$10^5(C_6H_5COO^{\cdot} + C_6H_5^{\cdot})$	$10^5(C_6H_5COO^{\cdot})$	$\frac{C_6H_5COO^{\cdot}}{(C_6H_5COO^{\cdot} + C_6H_5^{\cdot})}$
1.61	1.71	0.64	0.37
2.64	2.19	0.71	0.32
4.62	3.08	1.08	0.35
7.51	2.51	0.89	0.36
8.42	2.87	0.92	0.32
9.70	3.79	1.32	0.35

Table 4. Variation of the degree of incorporation of phenyl and benzoyloxy radicals with initiator concentration for polymerization of 2.7 M monomer at 60°

10^3[I] (mol l^{-1})	$10^5(C_6H_5COO^{\cdot} + C_6H_5^{\cdot})$	$10^5(C_6H_5COO^{\cdot})$	$\frac{C_6H_5COO^{\cdot}}{(C_6H_5COO^{\cdot} + C_6H_5^{\cdot})}$
6.36	7.38	3.68	0.50
7.60	7.75	3.52	0.45
7.80	9.66	4.83	0.50
10.44	9.29	4.60	0.50
11.56	12.96	6.13	0.47
15.98	11.71	5.63	0.48

Table 5. Variation of the degree of incorporation of phenyl and benzoyloxy radicals with initiator concentration in the polymerization of 3.5 M monomer at 60°

10^3 [I] (mol l^{-1})	$10^5(C_6H_5COO^{\cdot} + C_6H_5^{\cdot})$	$10^5(C_6H_5COO^{\cdot})$	$\frac{(C_6H_5COO^{\cdot}}{(C_6H_5COO^{\cdot} + C_6H_5^{\cdot})}$
3.64	3.87	2.01	0.52
5.41	5.68	3.16	0.56
7.22	6.87	3.77	0.55
8.50	7.21	3.98	0.55

be expected that the ratio $[C_6H_5COO^{\cdot}]/([C_6H_5^{\cdot}] + [C_6H_5COO^{\cdot}])$ (in the absence of induced decomposition and transfer reactions) in the polymer should be close to unity. The degrees of incorporation of phenyl and benzoyloxy radicals for various initiator and monomer concentrations are shown in Tables 3–5.

The results show that the proportion of phenyl radicals in the polymer increases from about 50% at 3.5 M to nearly 70% at 0.56 M monomer. It is unlikely that, at such fairly high levels of phenyl radicals in the polymer, $[C_6H_5^{\cdot}] \ll [C_6H_5COO^{\cdot}]$. Since k'_{prt} is assumed to be very similar to k_{prt}, it would be expected that the termination of macroradicals by phenyl groups would be significant making kinetic analysis for PRT by the Deb and Gaba mechanism more complicated than shown in Eqn 3. Attempts have been made to estimate R_i/R_{prt} by the analysis of polymer samples for initiator fragments [9] using the method described by Bevington [10]; they will be reported separately.

Acknowledgements—The work reported here was carried out while the author was on study leave from the University of Benin. The suggestions, encouragement and guidance of Dr G. S. Park (UWIST) and Dr J. Lewis (UWIST) throughout the period of this work are acknowledged.

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