Primary Radical Termination in Vinyl Chloride Polymerization

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ABSTRACT

The rate of vinyl chloride polymerization initiated by doubly labeled benzoyl peroxide (^{3}H in the phenyl ring and ^{14}C in the carboxyl group) in dichloroethane solution was measured by a dilatometric method. The relative significance of primary radical termination in polymerization is examined by kinetic analysis of the polymerization rate data and analysis of the polymer samples recovered at 10% conversion for combined initiator fragments.

INTRODUCTION

The ideal kinetic relationship describing the rate of free radical polymerization with respect to monomer and to initiator concentrations is expressed by

$$R_p = (fk_d k_p^2 /k_t)^{1/2} [M][I]^{1/2} \tag{1}$$

Deviations from this relationship are generally discussed in terms of 1) diffusion effects, 2) formation of electron donor-acceptor complexes, 3) chain transfer reactions, 4) hot radical theory, and 5) primary radical termination. Although the interaction of growing polymer radicals

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is generally considered important in emulsion polymerization, the process is often ignored or considered insignificant in the kinetic schemes of solution polymerizations. It is, however, widely recognized that primary radical termination is an important cause of nonideal kinetics in vinyl polymerization [1-7]. Several methods are available for estimating the relative extents of primary radical termination [1-4] and for distinguishing its influence on vinyl polymerization from that of chain transfer to solvents [5-7]. This communication examines the application of these methods and discusses their limitations to the polymerization of vinyl chloride in dichloroethane.

EXPERIMENTAL

The experimental procedures for the purification vinyl chloride monomer and the solvent, the preparation and purification of doubly labeled benzoyl peroxide initiator and of the polymer samples, and the assay of the polymer samples were reported in details in previous communications [8, 9].

RESULTS AND DISCUSSION

The rates of polymerization of vinyl chloride in dichloroethane solution at 60°C were measured by a dilatometric method at 0.56, 2.7, and 3.5 mol/L vinyl chloride using a wide range of initiator concentration. The dependence of the rate of polymerization on initiator concentration (Fig. 1) suggests that primary radical termination is important in the polymerization.

The reaction scheme of a free-radical-initiated polymerization of a vinyl monomer in which primary radical termination is considered the major cause of deviation from the ideal kinetic relationship between the rate of polymerization and initiator concentration can be represented as follows:

Decomposition of initiator:

$$I \longrightarrow 2R°$$
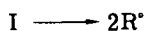
Initiation by primary radical:

$$R° + CH_2=CHX \xrightarrow{k_i} RCH_2-\overset{\centerdot}{C}HX$$
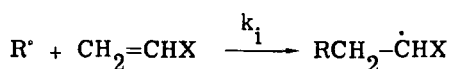
Decomposition of primary radical:

$$R° \xrightarrow{k_d'} R°' + y$$
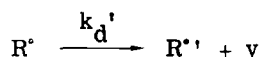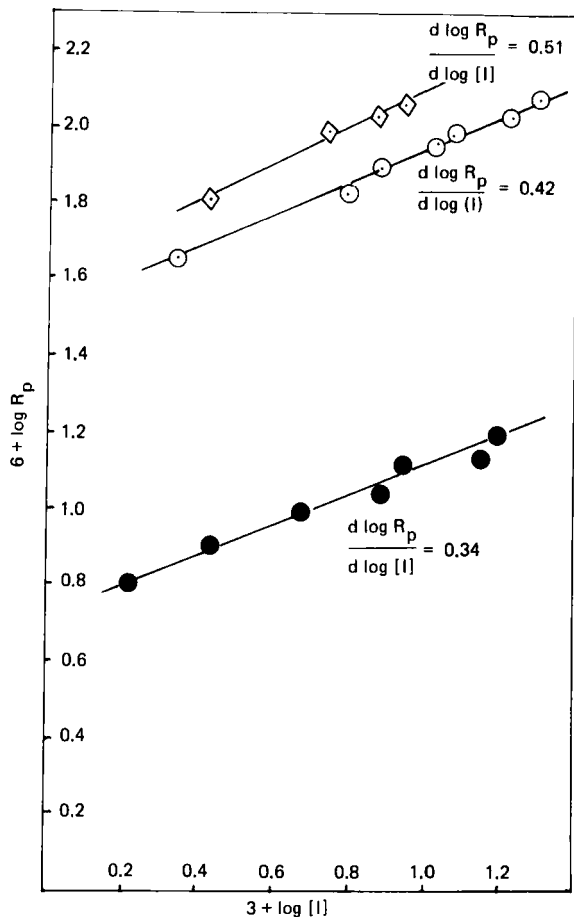
FIG. 1. Dependence of rate of polymerization on the initiator concentration (◇) 3.5, (◉) 2.7, and (●) 0.56 mol/L vinyl chloride in dichloroethane solution at 60°C.

Initiation by secondary radical:

$$R^{\cdot\,\prime} + CH_2=CHX \xrightarrow{k_i{}^\prime} R^\prime CH_2-\dot{C}HX$$

Propagation:

$$R(CH_2-CHX)_n CH_2-\dot{C}HX + CH_2=CHX \xrightarrow{k_p} R(CH_2-CHX)_{n+1}CH_2-\dot{C}HX$$

Mutual termination of growing polymer chain:

$$R(CH_2-CHX)_m CH_2-\dot{C}HX + \dot{C}HX-CH_2(CHX-CH_2)_n R \xrightarrow{k_t} polymer$$

Primary radical termination:

$$R(CH_2-CHX)_m CH_2-\dot{C}HX + R^\cdot \xrightarrow{k_{prt}} R(CH_2-CHX)_m CH_2-CHXR$$

Termination by secondary radicals:

$$R(CH_2-CHX)_n CH_2-\dot{C}HX + R^{\cdot\,\prime} \xrightarrow{k'_{prt}} R(CH_2-CHX)_n CH_2-CHXR'$$

One of the earliest methods used to estimate the extent of the in-
fluence of primary radical termination on vinyl polymerization was
developed by Bamford et al. [1] for azoisobutyronitrile-initiated
polymerization of styrene. The relationship proposed by the authors
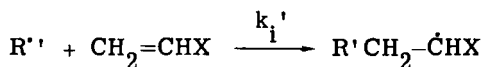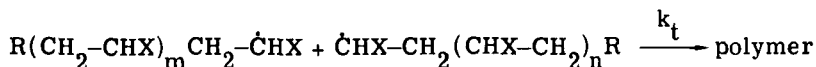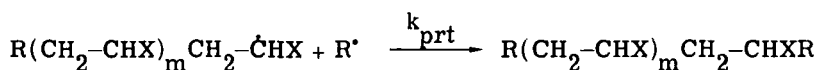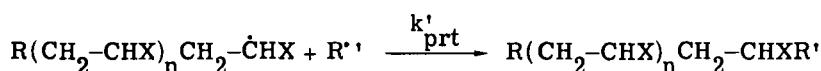
$$1/R_p = k_t^{1/2}/[M]^2 k_i/(k_{prt} \sigma)^{1/2}] + k_t^{1/2}/\{k_p(2k_d[I]^{1/2}[M])\} \quad (2)$$

was obtained by considering the three radical termination reactions:
(a) recombination of primary radicals, (b) primary radical termina-
tion, and (c) mutual termination of growing polymer chains; and on
the assumption that the rate constant for reaction (b) is a geometric
mean of the rate constants for reactions (a) and (c). The intercept
of the plot of $1/R_p$ against $1/[I]^{1/2}$ on the vertical axis gives a mea-
sure of the extent of primary radical termination. The intercepts of
the plots in Fig. 2 give values of 9.0×10^3, 7.44×10^3, 2.45×10^3
mol^{-1} L·s for the polymerization of 0.56, 2.7, and 3.5 mol/L vinyl
chloride, respectively, for the primary radical termination term
$\{k_t/[k_p^2 k_i^2/(\sigma k_{prt})]\}^{1/2}$, where σ is the geometric mean constant
for the rate constants for the recombination of primary radicals and
mutual termination of growing polymer chains.
    This method of assessing the extent of the influence of primary
radical termination on vinyl polymerization is limited to initiator
systems which produce primary radicals that have relatively long
half-lives and so do not readily decompose to give secondary radicals.
Besides, it has been suggested that since termination processes are
diffusion controlled even at low conversions to polymer, the rates of
the termination processes would be influenced by both the radical size
and the viscosity of the medium, and that an arithmetic mean relation-
ship between the radical termination reactions would be more appro-
priate [10].
    Deb and Meyerhoff [2] proposed a method for examining the influ-
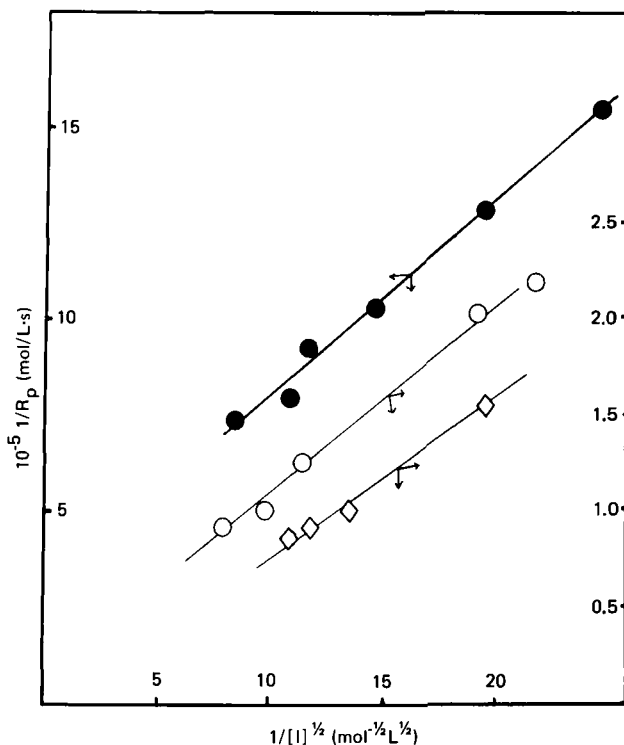
FIG. 2. Primary radical termination in vinyl chloride polymerization. plots of $1/R_p$ against $1/[I]^{1/2}$ for the polymerization of (◈) 3.5, (◉) 2.7, and (●) 0.56 mol/L vinyl chloride in dichloroethane solution at 60°C.

ence of primary radical termination on vinyl polymerization for initiator systems where the decomposition of the primary radicals is in competition with the initiation reaction. The authors considered the stationary state for $[R^{\cdot}]$, $[R^{\cdot \prime}]$ and $[-CH_2-\dot{C}HX]$, and by assuming that (a) mutual termination of $R^{\cdot}$ and $R^{\cdot \prime}$, (b) primary radical transfer, and (c) termination of growing polymer chains by $R^{\cdot \prime}$ are negligibly small, obtained

$$\log \frac{R_p^2}{[I][M]^2} = \log \frac{2fk_dk_p^2}{k_t} - 0.8684 \frac{R_p}{[M]^2} \left\{ \frac{k_{prt}/k_1k_p}{1 + k_d'/k_1[M]} \right\} \quad (3)$$

TABLE 1. Influence of Solvent, Monomer, and Initiator Types on the Extent of Primary Radical Termination in Vinyl Polymerization at 60°C

Polymerization system	$k_{prt}/k_i k_p$	$(mol \cdot L^{-1} \cdot s)$
Styrene-benzene-benzoyl peroxide	0.97×10^5	(1)
Styrene-benzene-benzoyl peroxide	1.5×10^5	(3)
Styrene-benzene-azoisobutyronitrile	3.4×10^5	(3)
Styrene-DMF-azoisobutyronitrile	2.04×10^4	([a])
Methyl methacrylate-benzene-azoisobutyronitrile	1.45×10^4	(4)
Vinyl chloride-dichloroethane-benzoyl peroxide	4.47×10^4	(8)
Vinyl chloride-dichloroethane-benzoyl peroxide	2.84×10^5	(12)
Vinyl chloride-dichloroethane-benzoyl peroxide	3.21×10^5	([b])

[a]Values worked out from the polymerization data of (1) by (4).
[b]Value obtained from the initiator fragment method.

the extent of primary radical termination, $k_{prt}/k_i k_p$, can be obtained from the slope of the plot of log $R_p/[I][M]^2$ against $R_p/[M]^2$ [2, 3, 6, 8, 11] (Table 1).

The Deb-Meyerhoff analysis considered that $[C_6H_5^{\cdot}] \ll [C_6H_5COO^{\cdot}]$ and that k_{prt} was approximately equal to k'_{prt} and so assumed that termination of growing polymer chains by phenyl radical would be negligible. These assumptions would not be valid at low monomer concentration. The assay of the polymer samples for initiator fragments (Tables 2A and 2B) indicates that between 50 and 70% of the initiator fragments incorporated in the polymer are phenyl radicals, suggesting that termination of growing polymer chains by phenyl radicals may be significant. The significance of the value of $k_{prt}/k_i k_p$ obtained can be assessed by comparing the rates of initiation and termination by the primary radicals:

$$R_i/R_{prt} = k_i[R^{\cdot}][M]/k_{prt}[R^{\cdot}][P^{\cdot}] = k_i k_p[M]^2/k_{prt}R_p \qquad (4)$$

TABLE 2A. Incorporation of Initiator Fragments in the Polymer at 60°C; [M] = 0.56 mol/L

10^3 [I] (mol/L)	$10^4 \dfrac{C_6H_5COO^. + C_6H_5^.}{[-CH_2-CHCl-]}$	$10^4 \dfrac{C_6H_5COO^.}{[-CH_2-CHCl-]}$	$\dfrac{C_6H_5COO^.}{C_6H_5COO^. + C_6H_5^.} = w$
1.61	1.71	0.64	0.37
2.67	2.19	0.71	0.32
4.62	3.08	1.08	0.35
7.51	2.51	0.89	0.36
8.42	2.85	0.92	0.32
9.70	3.51	1.32	0.35

TABLE 2B. Incorporation of Initiator Fragments in the Polymer at 60 C; [M] = 2.7 mol/L

10^3 [I] (mol/L)	$10^5 \dfrac{C_6H_5COO^. + C_6H_5^.}{[-CH_2-CHCl-]}$	$10^5 \dfrac{C_6H_5COO^.}{[-CH_2-CHCl-]}$	$\dfrac{H_6H_5COO^.}{C_6H_5COO^. + C_6H_5^.}$
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	9.26	4.63	0.50
11.56	12.96	6.13	0.47
15.98	11.71	5.63	0.48

TABLE 3. Variation of the R_i/R_{prt} Ratio with the Method of Assessing the Extent of Primary Radical Termination in the Polymerization of Vinyl Chloride in Dichloroethane Solution at 60°C

[M] (mol/L)	[I] × 10³ (mol/L)	R_i/R_{prt} (%)		
		Deb and Meyerhoff kinetic analysis	Extended kinetic analysis	Initiator fragment method
0.56	1.61	11	17	15
0.56	7.51	6	10	8
0.56	13.66	5	8	7
2.7	2.15	35	57	50
2.7	7.8	19	32	28
2.7	15.98	15	24	21
3.5	2.64	42	68	60
3.5	4.41	27	44	38
3.5	8.5	23	37	33

The low values of R_i/R_{prt} obtained (Table 3) indicate that the extent of primary radical termination deduced from the Deb and Meyerhoff analysis may be unreliable.

More recently, Deb [12] proposed an extended mathematical analysis in which the initiation and termination reactions of both primary and secondary radicals are considered.

$$
\log \frac{R_p{}^2}{[I][M]^2} = \log \frac{2fk_d k_p{}^2}{k_t} - 0.8684 \left\{ \frac{\dfrac{k_{prt}}{k_i k_p} + \dfrac{k_d{}'}{k_i[M]} \cdot \dfrac{k_{prt}}{k_i{}' k_p}}{1 + \dfrac{k_d{}'}{k_i[M]}} \right\} \frac{R_p}{[M]^2} \qquad (5)
$$

The slope of the plot of log $R_p{}^2/[I][M]^2$ against $R_p/[M]^2$ would represent the expression $(k_{prt}/k_i k_p)/(1 + k_d{}'/k_i[M])$ for a system in which termination and initiation reactions of the secondary radicals are considered negligible (Eq. 2), and $[k_{prt}/k_i k_p + (k_d{}' k_{prt}/k_i[M]k_i{}' k_p)]/(1 + /k_d{}'/k_i[M])$ where the initiation and termination reactions of the secondary radicals are considered important (Eq. 4). Values of 9.89 $\times$ 10^4 and 1.59 $\times$ 10^5 mol·L^{-1}·s for 0.56 and 2.7 mol/L vinyl chloride obtained from the slopes of the plots in Fig. 3 gave a value of 2.84 $\times$ 10^5 mol·L^{-1}·s for $k_{prt}/k_i k_p$ [12]. This value is much lower than the value of 4.47 $\times$ 10^4 mol·L^{-1}·s obtained without considering termination by phenyl radicals. The new value $k_{prt}/k_i k_p$ has been used to calculate the R_i/R_{prt} ratios. The results (Table 3) show considerable increase in the R_i/R_{prt} ratios and indicate that the extended mathematical analysis gives a more reliable assessment of the extent of primary radical termination in vinyl polymerization.

Although the mathematical formulations developed by Deb and coworkers have proved useful in quantifying the extent of PRT in vinyl polymerization, it could be argued that many of the assumptions made in the development of the relationships (Eqs. 3 and 5) may only be valid for a limited set of experimental data. The extended mathematical analysis, for instance, considers the initiation and termination reactions of both the primary and secondary radicals, and therefore could account for termination of macroradicals by phenyl radicals at low monomer concentration. It seems reasonable to expect that at low monomer concentrations (where primary radical termination would be more significant), that abstraction of hydrogen atom by both the primary and secondary radicals would become significant:
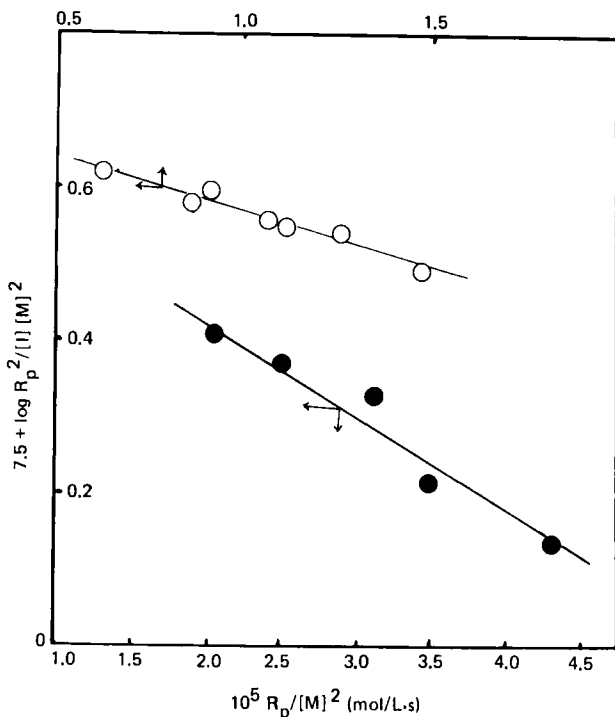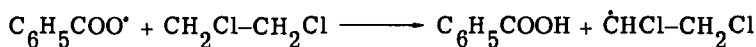
FIG. 3. Primary radical termination in vinyl chloride polymerization. Plots of log $R_p/[I][M]^2$ against $R_p/[M]^2$ for the polymerization of (⊙) 2.7 and (●) 0.56 mol/L vinyl chloride in dichloroethane solution at 60°C.

$$C_6H_5COO^{\cdot} + CH_2Cl-CH_2Cl \longrightarrow C_6H_5COOH + \overset{\cdot}{C}HCl-CH_2Cl$$

$$C_6H_5^{\cdot} + CH_2Cl-CH_2Cl \longrightarrow C_6H_5H + \overset{\cdot}{C}HCl-CH_2Cl$$

It then follows that for any mathematical treatment of PRT based only on kinetic data to adequately assess the extent of its influence at low monomer concentrations, it should consider the hydrogen abstraction reactions from the solvent by initiator radicals.

Bevington [13] described an initiator-fragment method for assessing the influence of primary radical termination in vinyl polymerization. The relationship

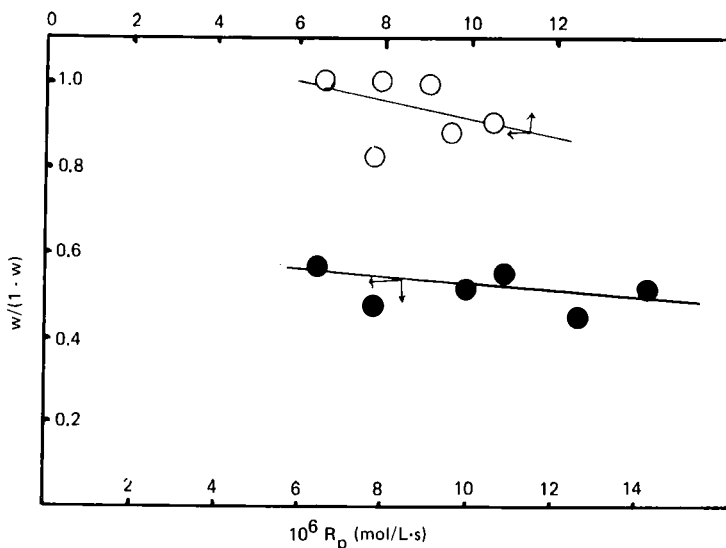$$w/(1 - w) = k_i[M]/k_d' + k_{prt}R_p/k_d k_p[M] \tag{6}$$

FIG. 4. Primary radical termination in vinyl chloride polymeriza-
tion plots of $w/(1 - w)$ against R_p for the polymerization of ($\circ$) 2.7 and
($\bullet$) 0.56 mol/L vinyl chloride in dichloroethane solution at 60°C.

where w is the fraction of benzoyloxy radicals which enter the polymer,
was obtained on the assumption that the ratio of the total rate of incor-
poration of initiator fragments in the polymer to the initiator concentra-
tion is constant throughout the whole range of $[I]$, and that all the phenyl
radicals produced by the decomposition of the primary radicals are cap-
tured by the monomer the slope of the plot of $w/(1 - w)$ against R_p at
constant monomer concentration would give a value for $k_{prt}/k_i k_d'$. The
levels of incorporation of initiator fragments in the polymer (Tables
2A and 2B) are presented in Fig. 4 as plots of $w/(1 - w)$ against R_p. The
figure shows a lot of scatter of experimental points for the polymeriza-
tion of 2.7 mol/L vinyl chloride; the slope of the plot for the polymeri-
zation of 0.56 mol/L vinyl chloride gives a value of 8.23×10^4 s for
$k_{prt}/k_p k_d'$, which can be combined with the values of $k_d'/k_i = 3.9$ [8]
to obtain a value of 3.21×10^5 mol·L^{-1}·s for $k_{prt}/k_i k_p$. This value lies
between those obtained from Eqs. (3) and (5), and leads to a higher
value for the ratio R_i/R_{prt} than is obtained from the Deb and Meyerhoff
method (Table 3).
    It therefore seems that analysis of primary radical termination
based on kinetic data alone would lead to an unreliable assessment of

the extent of its influence on vinyl polymerization. It is thought that other factors, such as the production of hot radicals, the formation of electron donor-acceptor complexes, and radical size–viscosity of polymerization medium–extent of conversion effects, acting together or independently, may very well produce the characteristic kinetic features (kinetic orders in monomer greater than 1.0, and in initiator less than 0.5) of primary radical termination.

The initiator-fragment method allows for a corroboration of kinetic data with analysis of the polymer samples for initiator fragments, and should therefore lead to a more reliable assessment of the extent of the influence of primary radical termination vinyl polymerization.

ACKNOWLEDGMENTS

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