Non-ideal kinetics in vinyl polymerization primary radical termination and chain transfer to solvent in benzoyl peroxide initiated polymerization of vinyl acetate in benzene

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The kinetics of vinyl acetate polymerization initiated by benzoyl peroxide in benzene at 60°C have been studied. Deviation of the rate of polymerization from kinetic orders of 0.5 in initiator and 1.0 in monomer is discussed in terms of primary radical termination and chain transfer to solvent.

INTRODUCTION

It is now widely accepted that primary radical termination and chain transfer to solvent are the two most important causes of non-ideality in free-radical initiated solution polymerization of vinyl monomers. The polymerization of vinyl acetate in benzene solution has been a subject of intensive study[1–6]. Deviation from ideal polymerization behaviour observed for the vinylacetate–benzene system has been explained in terms of transfer to solvent and copolymerization[4]; but recently Deb and Ray[7] claimed that primary radical termination is an important kinetic feature in the polymerization. This communication is part of a continuing study to assess the contribution of primary radical termination and transfer to solvent to non-ideality in vinyl polymerization. This study is based on the kinetic scheme:

$\mathrm{I} \xrightarrow{K_d} 2\mathrm{R}\cdot$ production of primary radicals

$\mathrm{R}\cdot + \mathrm{M} \xrightarrow{K_i} \mathrm{P_I}\cdot$ initiation of polymer chains

$\mathrm{P_I}\cdot + \mathrm{M} \xrightarrow{K_p} \mathrm{P}_n\cdot$ propagation

$\mathrm{P}_n\cdot + \mathrm{P}_m\cdot \xrightarrow{K_t} \mathrm{P}_n + \mathrm{P}_m,\ \mathrm{P}_n + \mathrm{P}_m$ mutual termination of growing polymer chains

$\mathrm{P}_n\cdot + \mathrm{R}\cdot \xrightarrow{K_{prt}}$ polymer primary radical termination

$\mathrm{P}_n\cdot + \mathrm{SH} \xrightarrow{K_{trs}}$ polymer $+ \mathrm{S}\cdot$ chain transfer to solvent

$\mathrm{S}\cdot + \mathrm{M} \xrightarrow{K_{is}} \mathrm{P_I}\cdot$ initiation by solvent radical

$\mathrm{P}_n\cdot + \mathrm{S}\cdot \xrightarrow{K_{ts}}$ polymer termination by solvent radical

EXPERIMENTAL

Materials

Vinyl acetate monomer obtained from BDH Ltd., was extracted with aqueous sodium hydroxide/sodium chloride solution (5% NaOH NaCl) to remove the hydroquinone stabiliser. The hydroquinone-free monomer was dried over calcium chloride and distilled through a vigreux column. The reaction boiling at 71°–72°C was collected and prepolymerized[8] to remove the inhibitors and retarders. The unreacted monomer was distilled off on a vacuum line into glass phials and stored at 7°C until required.

Benzoyl peroxide initiator was purified by precipitation from acetone solution using methanol and dried in a vacuum desicator. Analar benzene was used as the solvent for polymerization.

Polymerization

Polymerization rates were measured dilatometrically using vinyl acetate concentrations of 1.3–6.6 mol l^{-1} and initiator concentrations of 0.013–0.114 mol l^{-1} at 60°C in benzene solution. Polymerization was allowed to proceed to 3% conversion.

RESULTS AND DISCUSSION

The variations of the rate of polymerization as a function of initiator and monomer concentrations are shown in *Figure 1*. The kinetic orders in initiator and in monomer (*Table 1*) are significantly different from the 0.5 and 1.0 predicted for ideal polymerization. These deviations are discussed in terms of primary radical termination and chain transfer to solvent.

Primary radical termination

Bamford *et al.*[9] examined the kinetics of vinyl polymerization in which termination by primary radicals is considered as the main alternative reaction to initiation. They developed relationships between the rate of polymerization and the initiator concentration by considering the three different radical combination reactions: (a) recombination of primary radicals; (b) primary radical termination; and (c) combination of growing polymer radicals. In one treatment they assumed that the rate constant for primary radical termination is the geometric mean of the rate constant for primary radical combination and the rate constant for mutual

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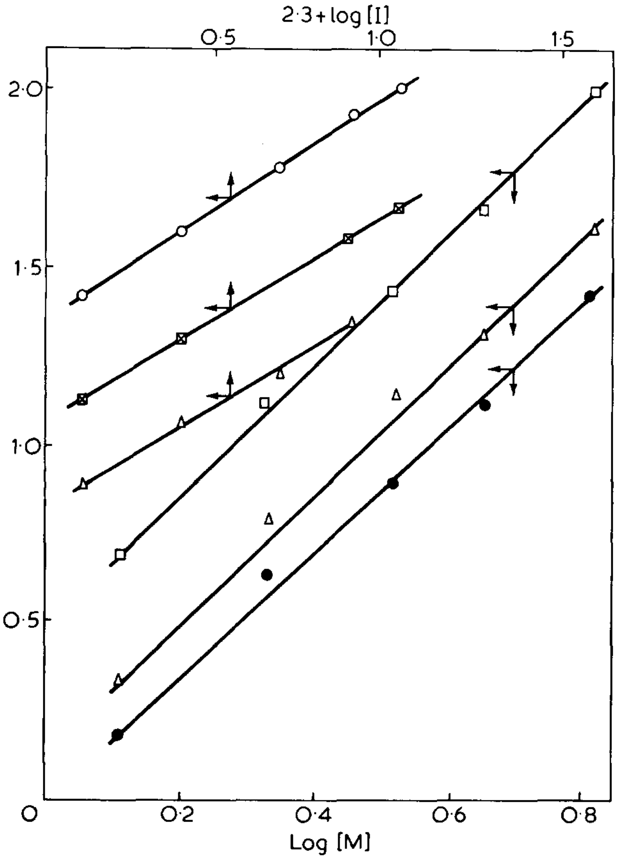

Figure 1 Dependence of rate of polymerization, R_p, on initiator concentration, [I], at (○), 6.6 M; (☒), 4.6 M; and (△), 1.3 M monomer and on monomer concentration, [M], at (□) 0.114 M; (△) 0.025 M; and (●) 0.013 M initiator at 60°C in benzene

termination of growing polymer chains. They also assumed that the kinetic chain length is large and obtained the relationship:

$$\frac{\mathrm{I}}{R_p}=\frac{K_t^{1/2}}{K_p\Sigma[M]^2}+\frac{K_t^{1/2}}{K_p(2K_d)^{1/2}}\cdot\frac{\mathrm{I}}{[M][I]^{1/2}} \tag{1}$$

where $\Sigma=K_i/(\sigma K_{prt})^{1/2}$ and σ is the geometric mean constant. *Figure 2* shows the data from this study presented as plots of I/R_p against $I/[I]^{1/2}$. It will be seen that the straight line plots intercept at negative values of I/R_p indicating the absence of primary radical termination in this system.

More recently, Deb and Meyeroff[10] developed a kinetic analysis for primary radical termination in initiator systems (like benzoyl peroxide) where the decomposition of primary radicals is in competition with initiation.

$$C_6H_5COO\cdot\xrightarrow{K'_d}C_6H_5\cdot+CO_2$$

$$C_6H_5\cdot+M\xrightarrow{K'_i}P_I\cdot$$

$$C_6H_5\cdot+P_n^{\cdot}\xrightarrow{K'_{prt}}\text{polymer}$$

By assuming that the termination by secondary radicals will be small compared to termination of primary radicals, the authors obtained a relationship:

$$\log\frac{R_p{}^2}{[I][M]^2}=\log\frac{2fK_dK_p{}^2}{K_t}-0.8684\frac{K_{prt}/K_iK_p}{\mathrm{I}+K'_d(K_i[M])}\cdot\frac{R_p}{[M]^2} \tag{2}$$

which enables the extent of primary radical termination, K_{prt}/K_iK_p, and primary radical decomposition, K'_d/K_i, to be determined. *Figure 3* shows that the plots of log $R_p^2/[I][M]^2$ against $R_p/[M]^2$ do not give the negative slopes predicted from equation (2). The positive slopes obtained indicate a predominant influence of chain transfer (and the absence of PRT) on the polymerization kinetics[11].

Degradative chain transfer to solvent

Until recently, the assessment of chain transfer constant to solvent (and to other additives) has relied on the use of the Mayo relationship between the degree of polymerization and the concentration of the solvent or additive. Deb[12] proposed a mechanism for assessing the extent of chain transfer to solvent from rate measurements. The proposed relationship

$$\frac{[I][M]^2}{R_p{}^2}=\frac{K_t}{2fK_dK_p{}^2}+\frac{C_s[SH]K_{ts}}{[M]fK_dK_{is}K_p}\cdot\left(1+\frac{K_{ts}}{K_{is}K_p}\frac{R_p}{[M]^2}\right)^{-1} \tag{3}$$

predicts a linear relationship between $[I]^2/R_p{}^2$ and $R_p/[M]^2$ at low values of $R_p/[M]^2$. Here, $[SH]$ represents the solvent concentration and C_s the chain transfer

Table 1 Kinetic orders in monomer and in initiator for benzoyl peroxide initiated polymerization of vinyl acetate in benzene at 60°C

[M] (mol l^{-1})	$\frac{d\log R}{d\log[I]}$	[I] (mol l^{-1})	$\frac{d\log R}{d\log[M]}$
1.3	0.54	0.013	1.77
2.3	0.52	0.025	1.81
3.3	0.58	0.050	1.80
4.6	0.59	0.087	1.84
6.6	0.61	0.14	1.87

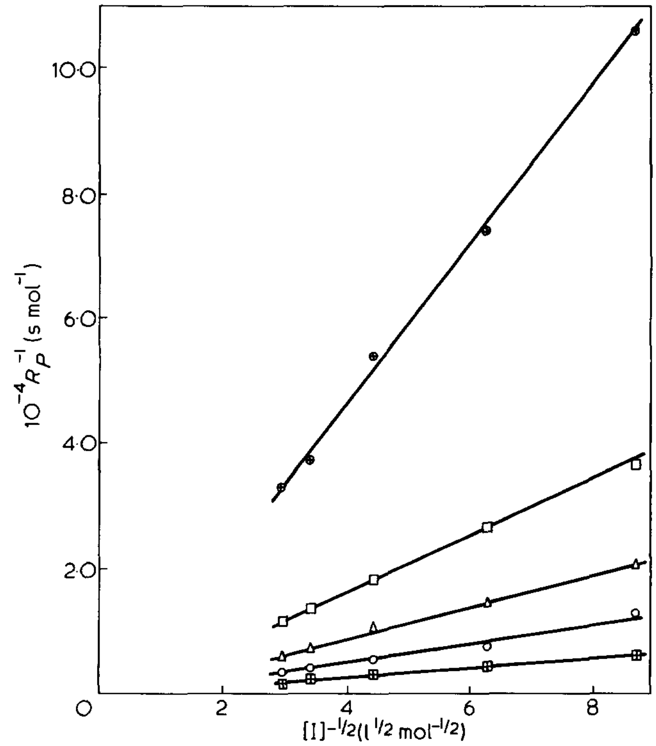

Figure 2 Primary radical termination: plots of R_p^{-1} against $[I]^{-1/2}$ for the polymerization of (⊗) 6.6 M; (□) 4.6 M; (△) 3.3 M; (○) 2.3 M and (⊞) 1.3 M monomer in benzene at 60°C

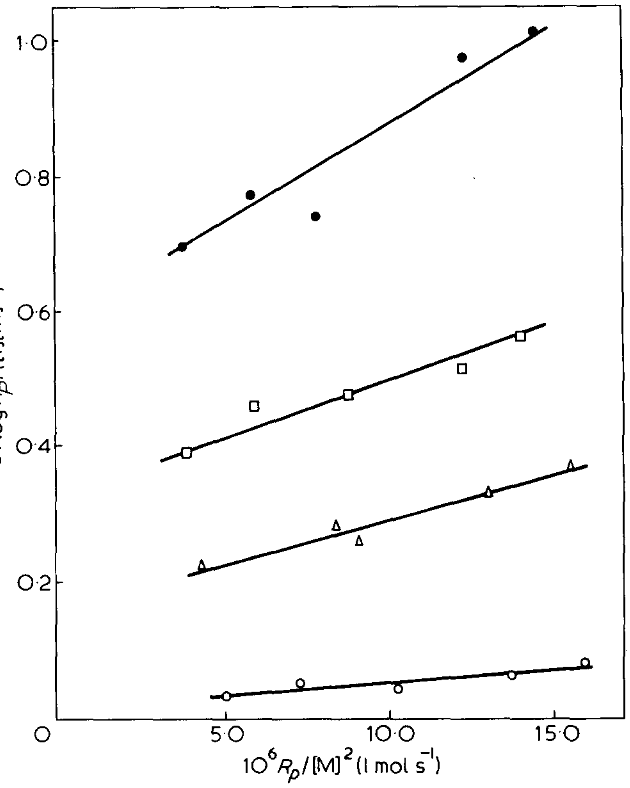

Figure 3 Primary radical termination: Semilogarithmic plots of $R_p^2/([I][M]^2)$ against $R_p/[M]^2$ for the polymerization of (●) 6.6 M; (□) 4.6 M; (△) 3.3 M; and (○) 2.3 M monomer in benzene at 60°C

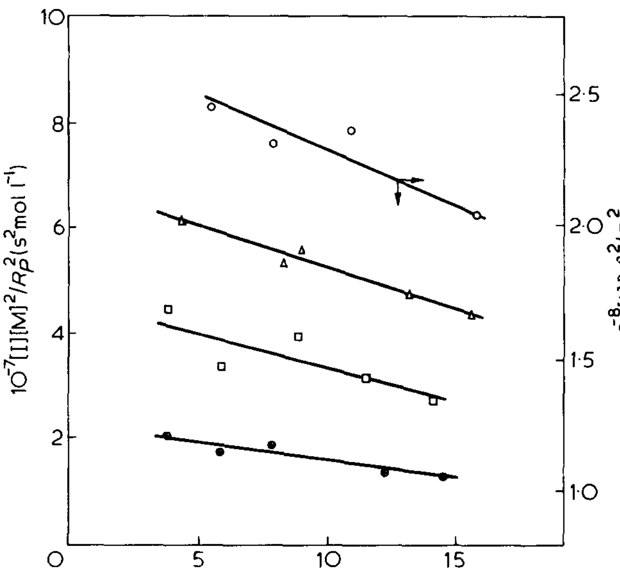

Figure 4 Degradative chain transfer to solvent: plots of $[I][M]^2/R_p^2$ against $R_p/[M]^2$ for the polymerization of (○) 6.6 M; (□) 4.6 M; (△) 3.3 M and (⊙) 1.3 M monomer in benzene at 60°C

Table 2 Values of intercepts and slopes of plots according to equation (3) and of $K_{ts}/K_{is}K_p$ at 60°C

[M] (mol l^{-1})	Intercept	Slope	K_{ts}/K_iK_p (mol s l^{-1})
1.3	2.79×10^8	3.89×10^{12}	1.39×10^4
3.3	6.76×10^7	1.56×10^{12}	2.31×10^4
4.6	4.57×10^7	1.41×10^{12}	3.09×10^4
6.6	2.23×10^7	7.01×10^{11}	3.14×10^4

constant to solvent. *Figure 4* shows that the plots of the data from this study according to equation (3) are linear throughout the entire range of $R_p/[M]^2$. From the values of the slopes and intercepts, an average value for $K_{ts}/K_{is}K_p$ of 2.4×10^4 mol l^{-1} s is obtained (*Table 2*).

The implications of the $K_{ts}/K_{is}K_p$ obtained can be assessed by comparing the rate of termination by solvent radicals with the rate of initiation by solvent radicals:

$$\frac{\text{Rate or termination by S}\cdot}{\text{Rate of initiation by S}\cdot} = \frac{R_{ts}}{R_{is}} = \frac{K_{ts}[P\cdot][S\cdot]}{K_{is}[M][S\cdot]} = \frac{K_{ts}[P\cdot]}{K_{is}[M]} \tag{4}$$

The rate of polymerization, $R_p = [P\cdot]K_p[M]$ (5)

so that:

$$\frac{R_{ts}}{R_{is}} = \frac{K_{ts}}{K_iK_p} = \frac{R_p}{[M]^2}$$

Substitution of the value for K_{rts}/K_iK_p and of the polymerization data from this study in equation (6) leads to values of R_{ts}/R_{is} of 0.3 at 1.3 mol l^{-1} monomer and 0.2 at 6.6 mol l^{-1} monomer. These results suggest that R_{ts} is about 23% of R_{is}.

This is in agreement with the idea of retardation by copolymerization put forward by Peebles *et al.*[6] which has also been demonstrated in the polymerization of vinyl chloride in the presence of allyl chloride[13]. However, Deb and Ray[7] have argued that a low ratio of R_{ts}/R_{is} would not explain the retardation in the polymerization rate of vinyl acetate in benzene. It is difficult at this stage to come to a conclusion about retardation by copolymerization involving benzene without a knowledge of molecular weights. Evaluation of molecular data should prove useful to the analysis of the polymerization kinetics and this will be communicated shortly.

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