Non-classical free-radical polymerization: 3. Diffusion-control in degradative addition*

C. H. Bamford
Bioengineering and Medical Physics Unit, University of Liverpool, Liverpool L69 3BX, UK

and E. Schofield
Research Laboratories, Kodak Limited, Headstone Drive, Harrow, Middlesex, HA1 4TY, UK

(Received 5 July 1982)

The different kinetic features associated with polymerizations in which retardation arises through degradative transfer and degradative addition processes are considered. Reasons are given for believing that in reactions retarded by degradative transfer neglect of the interaction between 'inactive' radicals is justifiable, while with degradative addition this is not so. A kinetic treatment of the latter is developed in which all three termination reactions between propagating and inactive radicals are assumed to be diffusion-controlled with a single rate coefficient and equations are derived which permit from experimental data on rates of polymerization estimation of the definitive kinetic parameters $k_p/k_t^{\prime -1/2}$, $k_{pm}/k_t^{\prime -1/2}$ and $k_{fm}/k_t^{\prime -1/2}$ (k_p, k_t', k_{pm}, k_{fm} are the rate coefficients of propagation, termination, reinitiation and degradative additions, respectively). The kinetic equations are satisfactorily consistent with ew experimental data on the polymerization of 1-vinylimidazole in ethanol solution at 70°C, for which there is strong evidence for the occurrence of degradative addition. A modified procedure for processing data for polymerizations with degradative transfer is put forward which is convenient for estimating the kinetic parameters and reveals in a simple manner the importance of re-initiation. It is suggested that this treatment could be generally useful in the early stages of the study of a retarded polymerization.

Keywords Free-radical polymerization; degradative addition; degradative transfer; diffusion-control; treatment of data; 1-vinylimidazole; vinyl chloride

INTRODUCTION

The conventional mechanism for a retarded free-radical polymerization, in which a radical of low reactivity is produced by interaction of a propagating chain with some other species (which may be the monomer), has been recognized for many years[1]. It is reproduced with standard notation in scheme (1); S represents an added retarder which interacts with propagating chains according to reaction (1 iv) (rate coefficient k_f) giving rise to the 'inactive' radical S·. Alternatively, if monomer is the only retarder (S = M) we shall denote the rate coefficient of (1 iv) by k_{fm} and the derived inactive radical by X·.

$$\text{initiator} \rightarrow R\cdot_0 \qquad k_d \qquad (1\ \text{i})$$

$$R\cdot_0 + M \rightarrow R\cdot_1 \qquad k_i \qquad (1\ \text{ii})$$

$$R\cdot_r + M \rightarrow R\cdot_{r+1} \qquad k_p \qquad (1\ \text{iii})$$

$$R\cdot_r + S \rightarrow S\cdot \qquad k_f \qquad (1\ \text{iv})$$

$$S\cdot + M \rightarrow R\cdot_1 \qquad k_{pm} \qquad (1\ \text{v})$$

$$R\cdot_r + R\cdot_s \rightarrow \text{polymer} \qquad k_t \qquad (1\ \text{vi})$$

$$R\cdot_r + S\cdot \rightarrow \text{polymer} \qquad k_{trs} \qquad (1\ \text{vii})$$

$$S\cdot + S\cdot \rightarrow \begin{array}{c}\text{inactive}\\ \text{products}\end{array} \qquad k_{tss} \qquad (1\ \text{viii})$$

A rigorous kinetic treatment of equation (1), such as that first given by Kice[2] has several disadvantages in practice which have probably limited the application of this type of approach[3].

We have considered the application of equation (1) to the polymerization of vinyl chloride[3] and 1-vinylimidazole[4], in both cases omitting the termination reaction (1 viii) involving two S· radicals. This procedure leads to the relation (2), valid for long chains.

$$\frac{k_t k_{trs} \omega^3}{k_p{}^3 k_{pm} [\text{M}]^4} + \left\{1 + \frac{2k_{trs}k_f}{k_{pm}k_t} \cdot \frac{[\text{S}]}{[\text{M}]}\right\} \frac{k_t}{k_p{}^2} \frac{\omega^2}{[\text{M}]^2} - \frac{k_{trs}}{k_{pm}k_p} \cdot \frac{\mathscr{I}\omega}{[\text{M}]^2} - \mathscr{I} = 0 \qquad (2)$$

Here, $\omega (= -\text{d}[\text{M}]/\text{d}t)$ and $\mathscr{I}$ are the rates of polymerization and initiation, respectively. Neglect of

---

* Parts 1 and 2 are refs. 3 and 4, respectively.

0032-3861/83/040433-06$03.00

(1 viii) is justifiable if this reaction is relatively slow on account of the very small concentration of S· (i.e. $[\mathrm{S}\cdot] \ll [\mathrm{R}\cdot]$, where $[\mathrm{R}\cdot] = \sum_{1}^{\infty}[\mathrm{R}_r\cdot]$) or the extremely low reactivity of the radical. In many systems showing retardation acceptable explanations of such low reactivity are not obvious.

Consequently, it becomes necessary to examine to what extent the assumption $[\mathrm{S}\cdot] \ll [\mathrm{R}\cdot]$ may be justified *a posteriori* from the results obtained by the use of equation (2). For a stationary concentration of [S·] we have, if $k_{tss} = 0$,

$$k_f[\mathrm{R}\cdot][\mathrm{S}] - k_{pm}[\mathrm{S}\cdot][\mathrm{M}] - k_{trs}[\mathrm{R}\cdot][\mathrm{S}\cdot] = 0$$

so that

$$\frac{[\mathrm{S}\cdot]}{[\mathrm{R}\cdot]} = \frac{k_f[\mathrm{S}]}{k_{pm}[\mathrm{M}] + k_{trs}[\mathrm{R}\cdot]} \qquad (3)$$

The kinetic treatment leads to evaluation of the three parameters $k_p k_t^{-\frac{1}{2}}$, $k_p k_{trs}/(k_{pm}k_t)$ and k_f/k_p so that it is necessary to rewrite equation (3) in terms of these quantities. [R·] on the right side of equation (3) may be replaced by its equivalent (valid for long chains) $\omega/(k_p[\mathrm{M}])$. If we now define

$$\lambda = \frac{k_{trs}}{k_t} \qquad (4)$$

we obtain from equation (3)

$$\frac{[\mathrm{S}\cdot]}{[\mathrm{R}\cdot]} = \frac{1}{\lambda}\cdot\frac{k_f}{k_p}\cdot\frac{k_p k_{trs}}{k_{pm}k_t}[\mathrm{S}]\left\{[\mathrm{M}] + \frac{k_p k_{trs}}{k_{pm}k_t}\cdot\frac{k_t}{k_p{}^2}\frac{\omega}{[\mathrm{M}]}\right\}^{-1} \qquad (5)$$

Values of the parameters on the right side of equation (5) have been reported in two instances. (a) The polymerization of vinyl chloride in chlorobenzene (S) at 25°C; for a typical system from Figure 2 of ref. 3 ($[\mathrm{M}] = 4.32$ mol dm^{-3}, $[\mathrm{S}] = 6.83$ mol dm^{-3}, $\omega = 5 \times 10^{-5}$ mol dm^{-3} s^{-1}) we find, with the aid of the parameters given, that [S·]/[R·] may be expressed by equation (6a).

$$[\mathrm{S}\cdot]/[\mathrm{R}\cdot] = 3.8/\lambda \qquad (6a)$$

$$[\mathrm{X}\cdot]/[\mathrm{R}\cdot] = 5.1/\lambda \qquad (6b)$$

(b) The polymerization of 1-vinylimidazole in ethanol at 70°C. We have already described a study of this system[4]; certain features suggested the occurrence of significant re-initiation (1 v) and further examination was desirable. The results will be described later in this paper; here we note that treatment of the data with the aid of equation (2) gave the following parameters

$$k_p k_t^{-\frac{1}{2}} = 0.1\ \mathrm{mol}^{-\frac{1}{2}}\,\mathrm{dm}^{\frac{3}{2}}\,\mathrm{s}^{-\frac{1}{2}},$$

$$k_p k_{trs}/k_{pm}k_t = 4.44 \times 10^4, \qquad (7)$$

$$k_{fm}/k_p = 1.65 \times 10^{-3}.$$

For a typical system with $[\mathrm{M}] = 4$ mol dm^{-3}, $\omega = 5 \times 10^{-5}$ mol dm^{-3} s^{-1}, we find from equations (5) and (7) the expression for [X·]/[R·] in equation (6b). There are two cases of interest:

(i) If λ is not far from unity (i.e. $k_{trs} \sim k_t$), equations (6a, b) show that the concentration of inactive radicals is not negligible and neglect of (1 viii) can be justified only in terms of a sufficiently small k_{tss}.

(ii) On the other hand, for $\lambda \gg 1$, [S·] and [X·] are relatively small, and neglect of (1 viii) follows naturally unless k_{tss} is unexpectedly large.

Rates of interaction of two active radicals, or one active and one 'inactive' radical such as S· or X·, are likely to be diffusion-controlled. For the vinyl chloride polymerizations reported in ref. 3, we have given reasons for believing that the radical S· is generated by atom-abstraction from the solvent. Since this is a small species compared to the average propagating radical, diffusion-control would be expected to lead to the condition $\lambda \gg 1$. Consequently we believe that case (ii) above is appropriate to the polymerization of vinyl chloride under the conditions reported[3] so that the success of (2) in interpreting the experimental data is understandable. The situation with 1-vinylimidazole is quite different since reaction (1 iv) is an addition process, giving an inactive polymeric radical. (Evidence for this has already been adduced[4] and recently we have obtained additional confirmatory data[5].) Thus we should expect $\lambda \sim 1$, giving rise to case (i) above. It seems virtually impossible for the condition $\lambda \gg 1$ to hold with degradative addition.

Unless we believe that k_{tss} is abnormally small, the simplest assumption to make for retardation arising from degradative addition is that all three termination reactions are diffusion-controlled, so that $k_t = k_{trs} = k_{tss} = k_t'$. In the present paper, we examine the consequences of this assumption, which does not seem to have been discussed in this connection previously. We shall assume that k_t' is independent of monomer/solvent ratio. The latter is unlikely to affect k_t' significantly through its effect on viscosity, which is rather small[4], but could do so by virtue of its influence on radical conformations. Note that the situation is not analogous to a copolymerization[6], in which large changes in k_t' often accompany variations in monomer feed ratio, since in the present case the compositions of the interacting radicals do not vary.

The rate coefficient k_{pm} for the re-initiation reaction (1 v) is of chemical interest in retarded polymerization and we also explore the possibilities of evaluating parameters which include it.

EXPERIMENTAL

Rates of polymerization of 1-vinylimidazole in ethanol at 70°C, with initiation by azobis(isobutyronitrile), have been measured dilatometrically. Experimental techniques and procedures for purification of the materials were similar to those already described[4]. The purity of 1-vinylimidazole was checked by g.l.c. analysis with the aid of Hewlett Packard 5840A equipment having a 25 m fused silica capillary column and liquid phase SP2100. Only a single peak was observable.

RESULTS AND DISCUSSION

Rates of polymerization for a series of initiator and monomer concentrations are presented in *Figures 1* and *2*. In general, the ω–[M] dependence is similar in form to that already reported[4], although the slopes of the curves

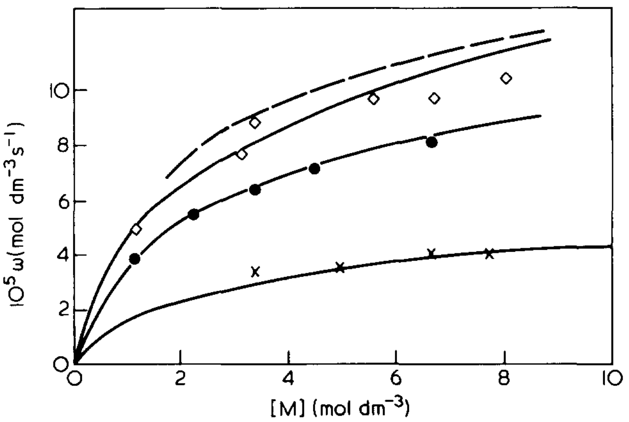

Figure 1 **Polymerization of 1-vinylimidazole (1-VIM) in ethanol at 70°C. Dependence of rate of polymerization ω on [1-VIM]. 10^3[azobis(isobutyronitrile)]/mol dm^{-3}: X, 2.77; ●, 7.32; ◇, 9.88. Full curves calculated from equation (11) with parameters in equations (14) and (16)**

at high [M] appear to be more pronounced according to the later determinations.

Diffusion-control in degradative addition polymerization

If termination between polymer radicals is diffusion-controlled the total rate of radical interaction[6] is $k_t'([\mathrm{R}\cdot]+[\mathrm{S}\cdot])^2$, hence under stationary conditions we have

$$\mathscr{I}=k_t'([\mathrm{R}\cdot]+[\mathrm{S}\cdot])^2 \text{ or } [\mathrm{R}\cdot]+[\mathrm{S}\cdot]=(\mathscr{I}/k_t')^{\frac{1}{2}} \qquad (8)$$

The individual stationary state equations for $[\mathrm{R}\cdot]$ and $[\mathrm{S}\cdot]$ are:

$$\begin{aligned}&\mathscr{I}-k_f[\mathrm{R}\cdot][\mathrm{S}]+k_{pm}[\mathrm{S}\cdot][\mathrm{M}]-k_t'[\mathrm{R}\cdot]^2-k_t'[\mathrm{R}\cdot][\mathrm{S}\cdot]=0,\\ &k_f[\mathrm{R}\cdot][\mathrm{S}]-k_{pm}[\mathrm{S}\cdot][\mathrm{M}]-k_t'[\mathrm{R}\cdot][\mathrm{S}\cdot]-k_t'[\mathrm{S}\cdot]^2=0.\end{aligned} \qquad (9)$$

From these equations we easily derive

$$\begin{aligned}[\mathrm{R}\cdot]&=\left(\frac{\mathscr{I}}{k_t'}\right)^{\frac{1}{2}}\frac{k_{pm}[\mathrm{M}]+(\mathscr{I}k_t')^{\frac{1}{2}}}{k_{pm}[\mathrm{M}]+k_f[\mathrm{S}]+(\mathscr{I}k_t')^{\frac{1}{2}}}\\ [\mathrm{S}\cdot]&=\left(\frac{\mathscr{I}}{k_t'}\right)^{\frac{1}{2}}\frac{k_f[\mathrm{S}]}{k_{pm}[\mathrm{M}]+k_f[\mathrm{S}]+(\mathscr{I}k_t')^{\frac{1}{2}}}\end{aligned} \qquad (10)$$

Thus, for long chains, the rate of polymerization $\omega=k_p\mathrm{M}[\mathrm{R}\cdot]$ is given by the simple relation

$$\omega=k_p[\mathrm{M}]\left(\frac{\mathscr{I}}{k_t'}\right)^{\frac{1}{2}}\frac{k_{pm}[\mathrm{M}]+(\mathscr{I}k_t')^{\frac{1}{2}},}{k_{pm}[\mathrm{M}]+k_f[\mathrm{S}]+(\mathscr{I}k_t')^{\frac{1}{2}}} \qquad (11)$$

According to equation (11), the apparent initiator exponent x will be in the range $0.5<x<1$. So long as reinitiation occurs significantly, $x=1$ is excluded. The classical relation is recovered from equation (11) if either initiation or reinitiation is sufficiently high. If S = M (i.e. monomer is the retarder), then at high [M] and/or low $\mathscr{I}$ (i.e. $(k_{pm}+k_{fm})[\mathrm{M}]\gg(\mathscr{I}k_t')^{\frac{1}{2}}$) the ω–[M] plot becomes linear, with slope and intercept given in equation (12).

$$\text{slope}=\left(\frac{\mathscr{I}}{k_t'}\right)^{\frac{1}{2}}\frac{k_pk_{pm}}{k_{pm}+k_{fm}} \qquad (12)$$

$$\text{intercept}=\frac{\mathscr{I}k_p}{k_{pm}+k_{fm}}$$

The slope is therefore that for the classical unretarded reaction multiplied by the factor $k_{pm}/(k_{pm}+k_{fm})$.

Determination of kinetic parameters

In the following the rate of initiation has been calculated from the initiator (I) concentration by taking the first-order rate coefficient for decomposition of I as $3.4\times10^{-5}\,\mathrm{s}^{-1}$ and the efficiency of initiation as 0.54[4]; thus $\mathscr{I}=3.67\times10^{-5}\,[\mathrm{I}]$.

(*i*) $k_pk_t'^{-\frac{1}{2}}$, $k_{fm}k_t'^{-\frac{1}{2}}$

When the retarder is an added species S, determination of $k_pk_t'^{-\frac{1}{2}}$ requires merely observations in the absence of S. when S = M, the rate equation (11), rewritten as in equation (13), may be employed (assuming $\mathscr{I}$ is known).

$$\frac{[\mathrm{M}]\mathscr{I}^{\frac{1}{2}}}{\omega}\left\{1+\frac{k_{pm}[\mathrm{M}]}{(\mathscr{I}k_t')^{-\frac{1}{2}}}\right\}=\frac{k_t'^{\frac{1}{2}}}{k_p}\left\{1+\frac{(k_{fm}+k_{pm})[\mathrm{M}]}{(\mathscr{I}k_t')^{-\frac{1}{2}}}\right\} \qquad (13)$$

From equation (13) it follows that a plot of $[\mathrm{M}]\mathscr{I}^{\frac{1}{2}}/\omega$ vs. $[\mathrm{M}]/\mathscr{I}^{\frac{1}{2}}$ has an intercept of $k_t'^{\frac{1}{2}}/k_p$ at $[\mathrm{M}]/\mathscr{I}^{\frac{1}{2}}=0$. If measurements of rates of polymerization for low values of $[\mathrm{M}]/\mathscr{I}^{\frac{1}{2}}$ are available, evaluation of the intercept does not present any difficulty, since k_{pm} is usually small and the second term on the left of equation (13) is negligible. In the absence of such measurements evaluation of $k_t'^{\frac{1}{2}}/k_p$ is only approximate unless $k_{pm}k_t'^{-\frac{1}{2}}$ (or equivalent) is known. The value of $k_t'^{\frac{1}{2}}/k_p$ so obtained may be refined by using it to evaluate $k_{pm}k_t'^{-\frac{1}{2}}$ (see (ii)) and then plotting the left side of equation (13) against $[\mathrm{M}]/\mathscr{I}^{\frac{1}{2}}$. $k_{fm}k_t'^{-\frac{1}{2}}$ or k_{fm}/k_p may be estimated from the slope of the line. Such a plot is presented in *Figure 3*. Although there is some scatter, the points for different [M] and $\mathscr{I}$ do not seem to show any systematic deviation from the straight line. The parameters resulting from *Figure 3* are:

$$k_pk_t'^{-\frac{1}{2}}=0.12\ \mathrm{mol}^{-\frac{1}{2}}\,\mathrm{dm}^{\frac{3}{2}}\,\mathrm{s}^{-\frac{1}{2}} \qquad (14)$$

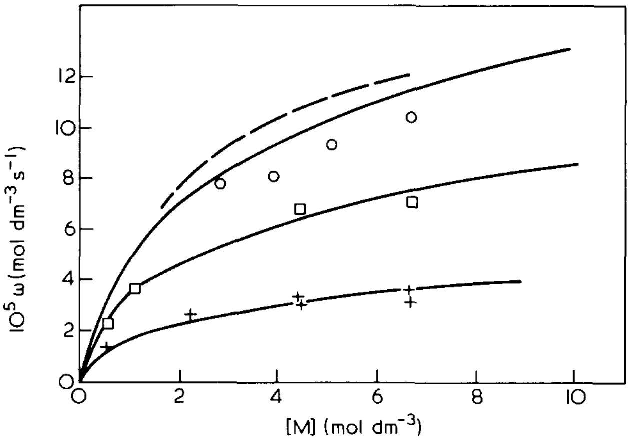

Figure 2 **Polymerization of 1-vinylimidazole (1-VIM) in ethanol at 70°C. Dependence of rate of polymerization ω on [1-VIM]. 10^3[azobis(isobutyronitrile)]/mol dm^{-3}: +, 2.60; □, 6.53; ○, 10.84. Full curves calculated from equation (11) with parameters in equations (14) and (16)**

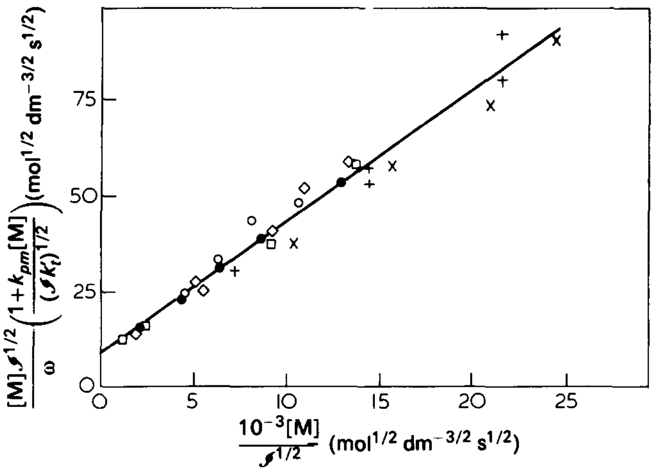

Figure 3 Plot of data in *Figures 1* and *2* according to equation (13); $k_{pm}k_t'^{-1/2}$ has been taken as 2×10^{-5} mol$^{-1/2}$ dm$^{3/2}$ s$^{-1/2}$ (equation (16)). Key to initiator concentrations in Figures 1 and *2*. Rates of initiation $\mathscr{I}$ were calculated as described in text

$$\frac{k_{fm}}{k_p}=3.3\times10^{-3};\ k_{fm}k_t'^{-\frac{1}{2}}=4.0\times10^{-4}\ \text{mol}^{-\frac{1}{2}}\ \text{dm}^{\frac{3}{2}}\ \text{s}^{-\frac{1}{2}}$$

In systems with an added retarder S the relation analogous to equation (13) is obtained by replacing $k_{fm}[\mathrm{M}]$ in equation (13) by $k_f[\mathrm{S}]$. The parameter k_f/k_p (or $k_fk_t'^{-\frac{1}{2}}$) may be determined from the slope of the plot of $\mathrm{M}\mathscr{I}^{\frac{1}{2}}/\omega$ vs. $\mathrm{S}/\mathscr{I}^{\frac{1}{2}}$ at constant $[\mathrm{M}]/\mathscr{I}^{\frac{1}{2}}$, and refined as described above.

(ii) $k_{pm}k_t'^{-\frac{1}{2}}$ (or equivalent)

When the monomer is the retarder we may proceed from equation (13) to derive expressions which permit, in principle, evaluation of kinetic parameters involving k_{pm}. A straightforward rearrangement of equation (13) gives equation (15):

$$\frac{[\mathrm{M}]\mathscr{I}^{\frac{1}{2}}}{\omega}=\frac{k_t'^{\frac{1}{2}}}{k_p}+\frac{k_{fm}}{k_p\left(\frac{\mathscr{I}^{\frac{1}{2}}}{[\mathrm{M}]}+\frac{k_{pm}}{k_t'^{\frac{1}{2}}}\right)} \qquad (15)$$

From this is follows that a plot of $\left(\frac{[\mathrm{M}]\mathscr{I}^{\frac{1}{2}}}{\omega}-\frac{k_t'^{\frac{1}{2}}}{k_p}\right)^{-1}$ vs. $\mathscr{I}^{\frac{1}{2}}/[\mathrm{M}]$ should be a straight line with

$$\text{slope}=k_p/k_{fm}$$

and

$$\text{intercept}=\frac{k_pk_{pm}}{k_{fm}k_t'^{\frac{1}{2}}}$$

Such a plot for the 1-vinylimidazole polymerization is presented in *Figure 4*. The line drawn, which is in acceptable agreement with the experimental data, corresponds to the values

$$\frac{k_{fm}}{k_p}=3.3\times10^{-3};\ \frac{k_pk_{pm}}{k_{fm}k_t'^{\frac{1}{2}}}=6\times10^{-3}\,\text{mol}^{-\frac{1}{2}}\text{dm}^{\frac{3}{2}}\text{s}^{-\frac{1}{2}}$$

i.e.

$$k_{pm}k_t'^{-\frac{1}{2}}=2\times10^{-5}\,\text{mol}^{-\frac{1}{2}}\text{dm}^{\frac{3}{2}}\text{s}^{-\frac{1}{2}} \qquad (16)$$

or

$$\frac{k_{pm}}{k_p}=1.6\times10^{-4}$$

It is satisfactory that the value of k_{fm}/k_p deduced in this way is in excellent agreement with that in equation (14). The plot in *Figure 3* was constructed with the aid of $k_{pm}k_t'^{-\frac{1}{2}}$ given in equation (16).

Note that if the retarder is an additive and not monomer, the relation corresponding to equation (15) is

$$\frac{[\mathrm{M}]\mathscr{I}^{\frac{1}{2}}}{\omega}=\frac{k_t'^{\frac{1}{2}}}{k_p}+\frac{k_f[\mathrm{S}]/[\mathrm{M}]}{k_p\left(\frac{\mathscr{I}^{\frac{1}{2}}}{[\mathrm{M}]}+\frac{k_{pm}}{k_t'^{\frac{1}{2}}}\right)}, \qquad (17)$$

so that a plot of the type described above may be constructed from data obtained at constant [S]/[M].

Relations may be deduced from equation (11) which allow parameters containing k_{pm} to be evaluated from slopes instead of intercepts. By solving equation (11) (S = M) for k_{pm} we obtain, after rearrangement

$$\frac{k_{fm}k_t'^{-\frac{1}{2}}\omega/\mathscr{I}}{k_pk_t'^{-\frac{1}{2}}-\frac{\omega}{[\mathrm{M}]\mathscr{I}^{\frac{1}{2}}}}-1=\frac{k_{pm}[\mathrm{M}]}{k_t'^{\frac{1}{2}}\ \mathscr{I}^{\frac{1}{2}}}. \qquad (18)$$

The left side may be evaluated with the aid of known parameters and plotted against $[\mathrm{M}]\mathscr{I}^{-\frac{1}{2}}$. Equation (18) is the most satisfactory relation we have found for deducing $k_{pm}k_t'^{-\frac{1}{2}}$ in this fashion, but our data give considerable scatter; the extreme values of $k_{pm}k_t'^{-\frac{1}{2}}$ obtained from equation (18) are 10^{-4} and 10^{-5} mol$^{-\frac{1}{2}}$ dm$^{\frac{3}{2}}$ s$^{-\frac{1}{2}}$, with a

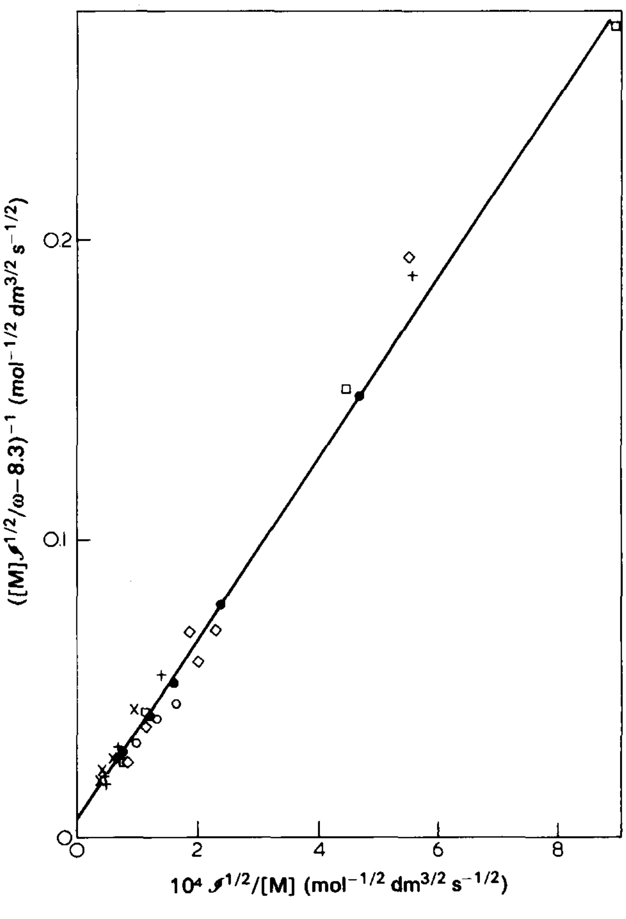

Figure 4 Plot of data in *Figures 1* and *2* according to equation (15); $k_t'^{1/2}/k_p=8.3$ mol$^{1/2}$ dm$^{-3/2}$ s$^{1/2}$ (equation (14)). Key to initiator concentrations in *Figures 1* and *2*

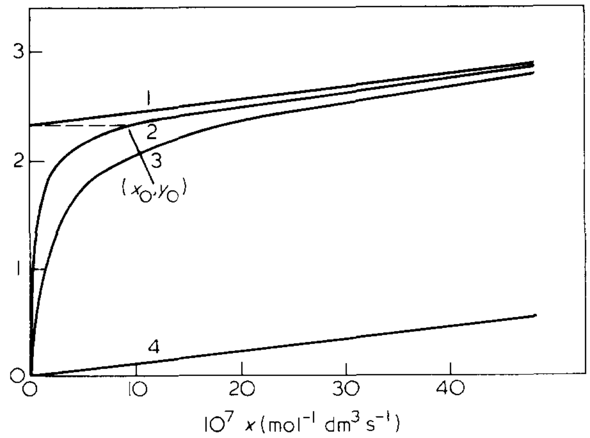

Figure 5 **Plot of equation (20). Curve 2 has been calculated with the aid of the parameters for the polymerization of vinyl chloride in chlorobenzene at 25°C given in ref 3. The straight line 1 is the asymptote at high x, intersecting the y axis at $(0, y_0)$. The same parameters are used for curves 3 and 4, except that for 3 k_{pm} is four times greater and for 4 $k_{pm}=\infty$**

most probable value close to that in equation (16). The tendency to exaggerate experimental scatter is likely to be a general feature of plots based on relations such as equation (18), in view of the small value of k_{pm}.

The parameters in equations (14) and (16) have been used together with equation (11) in calculating the dependence of the rate of polymerization on monomer and initiator concentrations, with results presented in *Figures 1* and *2*. We believe the calculated curves are a reasonably satisfactory representation of the experimental data. Unfortunately, the latter show an undesirable amount of scatter, but there do not seem to be any major systematic discrepancies attributable to inadequacies of equation (11).

Systems with degradative transfer

Equation (2) is applicable to systems of this type in which mutual termination reactions between inactive transfer radicals are negligible. This relation is less tractable than equation (11), referring to degradative addition; moreover it contains an additional unknown, viz. k_{trs}/k_t, which is assumed to be unity in the derivation of equation (11). We have already shown that if experimental data on rates of polymerization over a very **wide range of $\mathscr{I}$ are available the cubic equation (2) may be** fitted and the three appropriate kinetic parameters evaluated. We now describe an alternative treatment of equation (2) which provides information about the rate of reinitiation more directly.

By making the substitutions

$$x=\omega/[\mathrm{M}]^2, \quad y=\mathscr{I}/\omega \qquad (19)$$

we may reduce equation (2) to equation (20):

$$y+\frac{k_pk_{pm}}{k_{trs}}\frac{y}{x}-\frac{k_t}{k_p^2}x=\frac{k_tk_{pm}}{k_{trs}k_p}+\frac{2k_f}{k_p}\frac{[\mathrm{S}]}{[\mathrm{M}]} \qquad (20)$$

A plot of y vs. x according to equation (20) has the form shown in *Figure 5*. For sufficiently large x the curve is effectively linear (asymptote, curve 1); if $k_{pm}=0$ the whole plot is a straight line intersecting the y axis at a positive value. For $k_{pm}\neq 0$ the curve passes through the origin; the steepness of the descending portion near the origin is an inverse measure of the magnitude of k_{pm} (compare curves 2 and 3). As $k_{pm}\rightarrow\infty$ the reaction approaches a classical polymerization and the plot becomes a straight line through the origin (curve 4). This type of plot therefore provides a direct indication of the incidence of reinitiation.

Since degradative transfer is a common cause of retardation, we suggest that a useful early stage in the study of a retarded polymerization could be the construction of an $\mathscr{I}/\omega$ (or $[\mathrm{I}]/\omega$) vs. $\omega/[\mathrm{M}]^2$ plot of this type. If the kinetic scheme we have discussed (and therefore equation (2)) are appropriate all the experimental data, for different values of $\mathscr{I}$ and [M], should lie on a single curve.

The following relations, giving quantitative expression to the above, may be derived without difficulty.

$$\text{Slope at high } x=k_t/k_p^2 \qquad (21\,\mathrm{i})$$

Intercept (*int*) on y axis of straight line in equation (21 i) (asymptote)

$$int=\frac{k_{pm}k_t}{k_pk_{trs}}+\frac{2k_f[\mathrm{S}]}{k_p[\mathrm{M}]} \qquad (21\,\mathrm{ii})$$

$$\text{Slope at the origin}=\frac{k_t}{k_p^2}\left(1+\frac{2k_fk_{trs}[\mathrm{S}]}{k_{pm}k_t[\mathrm{M}]}\right)$$

$$=\frac{k_{trs}}{k_pk_{pm}}int \qquad (21\,\mathrm{iii})$$

Limiting relations. (21 iv)

$k_{pm}=0$. Slope and intercept of plot are given by equations (21 i), and (21 ii) with $k_{pm}=0$, respectively.

$k_{pm}=\infty$. The slope of the straight line passing through the origin is given by equation (21 i).

These relations are sufficient for evaluation of the definitive parameters $k_pk_t^{-\frac{1}{2}}$, $k_fk_p^{-1}$ and $k_fk_{trs}/(k_{pm}k_t)$. However, it is difficult to determine the slope of the curve at the origin at all precisely, since measurements down to extremely low x are required. Any appropriate point (not on the linear part of the curve) may, of course, be used to provide a relation alternative to equation (21 iii). A simple procedure is to choose a point (x_0,y_0) on the curve not too far from the origin; then if $\alpha=y_0/x_0$ we may show that

$$\frac{k_pk_{pm}}{k_{trs}}=\frac{1}{\alpha}\left\{int-y_0+y_0\frac{k_t}{\alpha k_p^2}\right\}. \qquad (21\,\mathrm{v})$$

A particularly simple situation therefore arises if $y_0=int$ (see *Figure 5*): from equation (21 iv) we see that in these circumstances

$$\frac{k_pk_{pm}}{k_{trs}}=y_0\frac{k_t}{\alpha^2k_p^2}, \qquad (21\,\mathrm{vi})$$

or

$$\frac{k_{pm}k_t}{k_pk_{trs}}=y_0\left(\frac{k_t}{\alpha k_p^2}\right)^2 \qquad (21\,\mathrm{vii})$$

Both these latter relations are convenient alternatives to equation (21 iii).

Returning to equation (2) (S = M) we may show that according to this relation the slope of ω vs. [M] curves as $[\mathrm{M}]\rightarrow\infty$ tends to the value given in equation (22) which also gives the intercept made by the asymptote on the ω-axis.

$$\text{slope: } k_p\left(\frac{\mathscr{I}}{k_t}\right)^{\frac{1}{2}}\left(\frac{k_{pm}k_t}{k_{pm}k_t+2k_{fm}k_{trs}}\right)^{\frac{1}{2}} \qquad (22)$$

$$\text{intercept: } \frac{\mathscr{I}k_pk_{fm}k_{trs}^2}{(k_{pm}k_t+2k_{fm}k_{trs})^2}$$

There are obvious similarities between these relations and those in equation (12) for the diffusion-control model. Thus, in both cases the slope at high [M] is zero if $k_{pm}=0$, increases with increasing k_{pm} and as $k_{pm}\rightarrow\infty$ (vanishing retardation) the slopes approach the classical value and the intercepts tend to zero. However, the slope of the ω vs. [M] curve does not generally decrease monotonically with increasing [M] so that, at intermediate values, slopes lower than that given in equation (22) are found.

Comparison of kinetic behaviour

We conclude by enquiring whether the types of kinetic behaviour of systems showing degradative addition and degradative transfer, summarized by equations (11) and (2) (or (20)), differ significantly in practice. It would appear that although general qualitative resemblances necessarily exist, for example, involving the dependence of rate of polymerization on initiator and monomer concentrations, there are significant quantitative differences. Thus the kinetics of the polymerization of vinyl chloride in chlorobenzene conform closely to equation (2), but are not compatible with the geometric mean assumption for the termination reactions[3] ($k_{trs}=(k_tk_{tss})^{\frac{1}{2}}$). The diffusion-control relations we have discussed are based on a special case of the latter, indeed equation (11) follows from the geometric-mean relation (equation (27) of an earlier paper[3]) on setting all three termination coefficients equal. The diffusion-control treatment is therefore unsatisfactory for the vinyl chloride system. Detailed examination shows that a much larger value of the parameter $k_{trs}/(k_{pm}k_t^{\frac{1}{2}})$ is required to fit the experimental data than is compatible with the former treatment. This observation is consistent with the views expressed earlier in the paper.

Conversely, we have investigated the compatibility of the data on 1-vinyl-imidazole polymerization with equation (20). A plot according to the latter equation has the form of *Figure 5*, although there is a great deal of scatter. The values of the parameters quoted in equation (7) were derived from this graph and were then used, in conjunction with equation (2) to construct ω vs. [M] diagrams. It seems to us that the agreement between experiment and calculation is significantly less satisfactory than in *Figures 1* and *2*. In particular, equation (2) does not, in this instance at least, allow adequately for the effects of changes in the initiator concentration. While a satisfactory fit may be obtained for low initiator concentrations, discrepancies increase as the initiator concentration increases, as illustrated by the broken curves in *Figures 1* and *2*. Although further more precise data are desirable to establish the point, we believe that the two types of system show observable differences in kinetic behaviour.

REFERENCES

1 See e.g. Bamford, C. H., Barb, W. G., Jenkins, A. D. and Onyon, P. F. 'Kinetics of Vinyl Polymerization by Radical Mechanisms', Butterworths, London, 1958, Ch. 6

2 Kice, J. L. *J. Am. Chem. Soc.* 1954, **76**, 6274; *J. Polym. Sci.* 1956, **19**, 123

3 Atkinson, W. H., Bamford, C. H. and Eastmond, G. C. *Trans. Faraday Soc.* 1970, **66**, 1446

4 Bamford, C. H. and Schofield, E. *Polymer* 1981, **22**, 1227

5 Bamford, C. H. and Schofield, E. *Polymer* 1983, **23** (*Commun*), 4

6 North, A. M. and Postlethwaite, D. *Polymer* 1964, **5**, 237; North, A. M. in 'Reactivity, Mechanism and Structure in Polymer Chemistry', (Eds. A. D. Jenkins and A. Ledwith), John Wiley, London, 1974, Ch. 5