Non-classical free-radical polymerization: 7. Kinetic analysis of some polymerizations by the group-termination coefficient procedure

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The group-termination coefficient procedure previously described has been used to analyse the kinetics of some free-radical polymerizations, with the aid of experimental data in the literature. It is shown that early interpretations of observations on the polymerization of styrene at high rates of initiation probably led to considerable overestimates of the significance of primary radical termination. Further extended experimental studies in this field are desirable. Three other types of system considered are polymerizations with simple chain-transfer, those with degradative addition and those with ideal retardation. In each case the derivation of kinetic parameters is discussed.

(Keywords: non-classical polymerization; size-dependent termination; group-termination coefficient; primary radical termination; degradative addition; retarded polymerization)

INTRODUCTION

One manifestation of the diffusion control of bimolecular termination in free-radical polymerization is a dependence of the termination coefficient k_t on the sizes of the participating radicals. Generally this is small except for small radicals, when it becomes significant and leads to departures from 'ideal' kinetic behaviour[1]. Theoretical studies[2] of the size dependence of k_t have not produced a functional form suitable for use in a kinetic scheme, so that recourse has been made to empirical relations. Of these, the geometric mean approximation gives the simplest calculations and has received most attention; this originated from reports by Yasukawa *et al.*[3,4] that the agreement between observed and calculated molecular weights of polystyrene fractions was improved by assuming that k_t shows a slow variation with radical size as expressed by the following equation, in which r, s are sizes of the participating radicals:

$$k_t \propto r^{-0.1} s^{-0.1} \tag{1}$$

Olaj *et al.*[5] have published extensive calculations on the geometric mean approximation. Although the harmonic mean is theoretically preferable to the geometric[6,7], it appears that many calculated quantities (e.g. $\bar{P}_w/\bar{P}_n$) are insensitive to the type of mean used[8].

In a recent paper[9] the present author has introduced the concept of a 'group-termination coefficient' and shown how it may be used in deriving explicit expressions suitable for incorporation into kinetic schemes. The general procedure is to replace sums of the type $\sum_r r^{-\beta} R_r^{\cdot}$ in geometric mean calculations by expressions containing the familiar quantities $\bar{r}$ and $R^{\cdot}$ $(=\sum_r R_r^{\cdot})$, i.e. the mean radical size and the total radical concentration, respectively. (In the above $R_r^{\cdot}$ is a radical of size r, and for simplicity concentration brackets are omitted; β is a small positive exponent, $\approx$0.1.) This replacement is achieved by use of the ratio Z defined by

$$Z = \sum_r r^{-\beta} R_r^{\cdot} / \bar{r}^{-\beta} R^{\cdot} \tag{2}$$

Z is a function of radical size distribution; in our problems it is generally greater than unity. In this way, with the aid of an approximation described in the earlier paper[9], which is necessary for many systems other than the simplest (e.g. those in which there is chain transfer), explicit expressions have been derived which were not previously available. Polymerizations so treated were reactions without and with chain transfer, those in which there is a degradative addition to monomer[10] and those with 'ideal' retardation.

In this paper these treatments are extended and applied to existing experimental data.

GENERAL TREATMENT AND DISCUSSION

The nomenclature of the earlier paper[9] is used throughout*.

Polymerizations without chain transfer; primary radical termination

The (instantaneous) rate of polymerization ω obtained with a monomer concentration M and rate of initiation $\mathscr{I}$ is

$$\omega = \mathscr{I} \frac{(1-\beta)^{\beta/(1-\beta)}}{a^{1/(1-\beta)}} \Gamma 1/(1-\beta) \tag{3}$$

which may be recast in the form

$$\omega = k_p M \left(\frac{\mathscr{I}}{k_{to}} \right)^{1/2} F_0 \tag{4}$$

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* See Nomenclature

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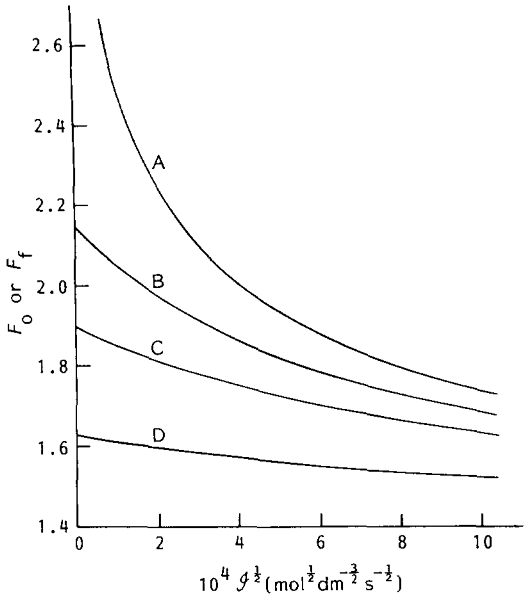

Figure 1 Comparison of non-classical and classical rates of polymerization: dependence on chain transfer. F_0 and F_f are calculated from equations (5) and (13) ($r_0 = 1$) with the parameters in equation (7) for polymerization of styrene with the following values of l: curve A (F_0), 0; curve B, 2×10^{-3}; curve C, 5×10^{-3}; curve D, 15×10^{-3}. $M = 5$ mol dm^{-3}

where

$$F_0 = \frac{1}{r_0^{\beta}} \left(\frac{1-\beta}{a} \right)^{\beta/(1-\beta)} \Gamma 1/(1-\beta) \qquad (5)$$

Here r_0 is a standard, arbitrarily chosen, radical size and k_{t0} the termination coefficient for radicals of this size. (Many workers take $r_0 = 1$ for simplicity.) F_0, a function of monomer concentration and rate of initiation, is the factor required to 'correct' the classical rate expression (in parenthesis in equation (4)) to obtain the rate of polymerization with size-dependent k_t. Some values of F_0 are presented in *Figure 1*. According to equations (4) and (5) the exponent of $\mathscr{I}$ in ω is $(1-2\beta)/2(1-\beta)$, which is < 0.5 if $\beta \neq 0$. Results outlined later (see *Figure 2*) show that for styrene polymerization in *N*,*N*-dimethylformamide at 60°C $\beta = 0.139$, so that the exponent of $\mathscr{I}$ is 0.42. This is consistent with the views of Yasukawa and Murakami[11]. The monomer exponent in ω is $1/(1-\beta)$. Note that the effective (mean) termination coefficient is k_{t0}/F_0^2.

It is well known that under conditions of high rates of initiation and low monomer concentrations deviations from ideal kinetic relations appear, the initiator exponent falling below 0.5 and the monomer exponent increasing above 1.0. These results are readily explained in terms of primary radical termination and early studies by Bamford *et al.*[12] and Okamura *et al.*[13,14] were directed towards quantifying this effect. Since the experimental conditions would necessarily favour small mean radical sizes, a size-dependent k_t would today be anticipated but was not considered in the early work. This aspect will now be explored, with the aid of the rate data of Bamford *et al.*[12] on the polymerization of styrene in *N*,*N*-dimethylformamide solution at 60°C for a range of azobisisobutyronitrile concentrations. By the use of ferric chloride as retarder it was shown that for the concentrations studied $\mathscr{I}$ was independent of M and proportional to the initiator concentration.

When written in logarithmic form equation (3) becomes:

$$\log \omega = \frac{1-2\beta}{2(1-\beta)} \log \mathscr{I} + \frac{1}{1-\beta} \log M + \frac{1}{1-\beta} \log \frac{k_p r_0^{-\beta}}{k_{t0}^{1/2}} + \log\{(1-\beta)^{\beta/(1-\beta)} \Gamma 1/(1-\beta)\} \qquad (6)$$

so that a plot of log ω *versus* log $\mathscr{I}$ for constant M enables β and $k_p r_0^{-\beta}/k_{t0}^{1/2}$ to be evaluated from the slope and intercept, respectively. The ω–$\mathscr{I}$ data[12] are plotted according to equation (6) in *Figure 2*, in which the dashed line has a slope of 0.5, corresponding to the classical case ($\beta = 0$). Clearly, the polymerization deviates significantly from classical kinetics. The linear regression line in *Figure 1* has a correlation coefficient 0.997 and leads to the following values:

$$\beta = 0.139; \quad \frac{k_p r_0^{-\beta}}{k_{t0}^{1/2}} = 0.011 \text{ mol}^{-1/2} \text{dm}^{3/2} \text{s}^{-1/2} \qquad (7)$$

Mahabadi[15] reported $\beta = 0.12$ for the polymerization of bulk styrene at 30°C. The value of the parameter $k_p r_0^{-\beta}/k_{t0}^{1/2}$ may be compared with that of its classical analogue[12] $k_p/k_t^{1/2} = 0.021$ mol$^{-1/2}$ dm$^{3/2}$ s$^{-1/2}$.

From equation (6) and the data in equation (7) the ω *versus* M curves (constant $\mathscr{I}$) in *Figures 3* and *4* have been calculated. The mean propagating radical sizes shown have been calculated from equation (22) of Reference 9. The general agreement between the observed and calculated rate data is reasonably good and suggests that a good deal, if not all, of the reported departure from classical kinetics in this system may be accounted for by size dependence of k_t, without a specific primary radical effect.

Equation (6) may also be used to evaluate β and $k_p r_0^{-\beta}/k_{t0}^{1/2}$ from a plot of log ω *versus* log M at constant and known $\mathscr{I}$, and in suitable circumstances this procedure can have advantages over that described above. In the present system both the thermodynamic quality of the solvent and the viscosity change as M is varied and both influence k_t and hence ω. No allowance for these factors was made in the data reported. A similar detailed study of a system as free as possible from these disadvantages could give valuable information about the incidence of

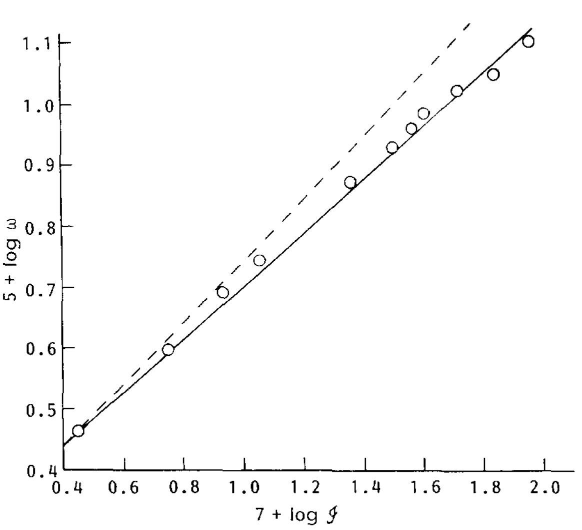

Figure 2 Polymerization of styrene (2.90 mol dm^{-3}) in *N*,*N*-dimethylformamide at 60°C with initiation by azobisisobutyronitrile. Plot of experimental data[12] according to equation (6)

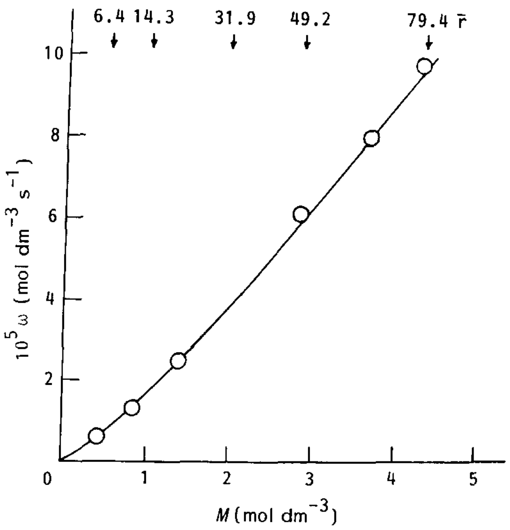

Figure 3 Dependence of rate of polymerization on monomer concentration for the polymerization of styrene in *N*,*N*-dimethylformamide at 60°C: ——, calculated from equation (6) for $\mathscr{I} = 1.42 \times 10^{-6}$ mol dm^{-3} s^{-1} using the parameters in equation (7); ○, from Reference 12. Some values of the mean radical size are shown

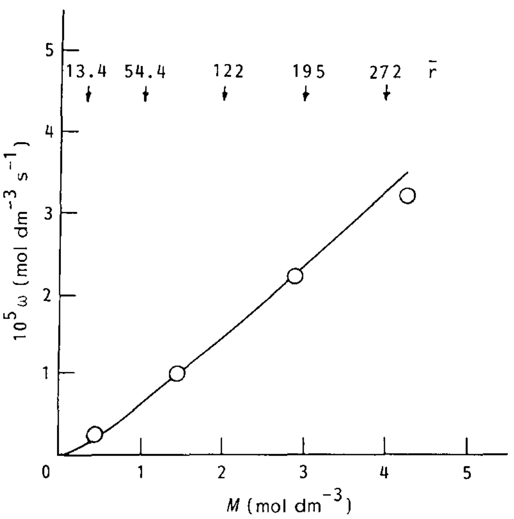

Figure 4 Dependence of rate of polymerization on monomer concentration for the polymerization of styrene in *N*,*N*-dimethylacetamide at 60°C: ——, calculated from equation (6) for $\mathscr{I} = 1.42 \times 10^{-7}$ mol dm^{-3} s^{-1} using the parameters in equation (7); ○, from Reference 12. Some values of the mean radical size are shown

primary radical termination. At present it seems certain that the original workers[12] made a considerable overestimate of its incidence.

Polymerizations with simple chain transfer

The occurrence of chain transfer introduces complications into the calculation of many kinetic quantities in systems of the type under discussion. An expression for the radical-size distribution (equation (8))

$$R_r^{\cdot} = V \exp\left(-lr - \frac{b}{1-\beta} r^{1-\beta}\right) \tag{8}$$

may be deduced by the procedure described without difficulty, but approximation becomes necessary when deriving explicit relations for $\sum R_r^{\cdot}$ and related quantities. We follow the method of Reference 9.

The most accurate expression for the rate of polymerization is readily shown to be

$$\omega = \mathscr{I} \frac{\overline{r^{\beta}}}{aZ_{\mathrm{f}}} \tag{9}$$

where Z_{f}, the value of Z (equation (2)) for the transfer distribution (8), is given by[9]

$$Z_{\mathrm{f}} = \frac{\{\Gamma(1-\beta)/(1-\alpha)\}\{\Gamma 2/(1-\alpha)\}^{\beta}}{\{\Gamma 1/(1-\alpha)\}^{1+\beta}} \tag{10}$$

Substitution of Z_{f} from equation (10) and $\bar{r}$ from equation (41) of Reference 9 into equation (9) leads to the relation

$$\omega = \frac{\mathscr{I}}{a}\left\{\left(\frac{1-\alpha}{b+l}\right)^{\beta/(1-\alpha)} \frac{\Gamma 1/(1-\alpha)}{\Gamma(1-\beta)/(1-\alpha)}\right\} \tag{11}$$

This expression may be written in the following form, analogous to equation (4), to illustrate the departure from classical kinetics:

$$\omega = k_{\mathrm{p}} M \left(\frac{\mathscr{I}}{k_{\mathrm{to}}}\right)^{1/2} F_{\mathrm{f}} \tag{12}$$

where the 'correction factor' F_{f} is

$$F_{\mathrm{f}} = \frac{1}{r_0^{\beta}} \left(\frac{1-\alpha}{l+b}\right)^{\beta/(1-\alpha)} \frac{\Gamma 1/(1-\alpha)}{\Gamma(1-\beta)/(1-\alpha)} \tag{13}$$

If $l=0$, F_{f} and F_0 are identical and if $\beta=0$, $F_{\mathrm{f}}=F_0=1$. The effective termination coefficient is $k_{\mathrm{t0}}/F_{\mathrm{f}}^2$.

These equations show that if $\beta \neq 0$ the rate of polymerization is reduced by the occurrence of ('non-retarding') chain transfer, an effect attributable to the reduction in mean radical size and the consequent increase in k_{t} (see Reference 5). Values of F_{f} calculated from equation (13) ($r_0 = 1$) for different extents of transfer l, using the parameters for styrene polymerization already given, are presented in *Figure 1* as a function of $\mathscr{I}^{1/2}$. As might be anticipated, F_{f} decreases sharply with increasing $\mathscr{I}^{1/2}$ when l is small, but changes relatively little when transfer predominates.

Systems with degradative addition

In these systems a propagating chain may add to a component (e.g. the monomer) to produce a radical of low reactivity in reinitiation but which may terminate by inter-radical reactions[16–18]. Degradative addition is therefore analogous to degradative transfer. It is assumed here that degradative addition to monomer occurs, but this does not reduce the generality of the treatment.

The component processes are summarized in equation (14) in which equation (14d) represents the degradative step, producing the relatively unreactive S$^{\cdot}$-type radical. Reinitiation is shown in equation (14e) and all three possible terminations in equation (14h). The latter are supposed to have equal rate coefficients[18] which are, of course size-dependent.

$$\text{initiator} \xrightarrow{\text{(a)}} R_0^{\cdot} \xrightarrow[\text{M}]{\text{(b)}} R_1^{\cdot} \ \text{rate of initiation } \mathscr{I}$$

$$\begin{array}{lll}
R_r^{\cdot} + \mathrm{M} \xrightarrow{\text{(c)}} R_{r+1}^{\cdot} & k_{\mathrm{p}} & \\
R_r^{\cdot} + \mathrm{M} \xrightarrow{\text{(d)}} S_{r+1}^{\cdot} & k_{\mathrm{fm}} & \\
S_r^{\cdot} + \mathrm{M} \xrightarrow{\text{(e)}} R_{r+1}^{\cdot} & k_{\mathrm{pm}} & (14)
\end{array}$$

$$\mathrm{R}_r^{\cdot}+\mathrm{L}\xrightarrow{\text{(f)}}\mathrm{L}^{\cdot}\qquad k_{\mathrm{fL}}$$

$$\mathrm{L}^{\cdot}+\mathrm{M}\xrightarrow{\text{(g)}}\mathrm{R}_1^{\cdot}$$

$$\left.\begin{array}{l}\mathrm{R}_r^{\cdot}+\mathrm{R}_s^{\cdot}\\ \mathrm{R}_r^{\cdot}+\mathrm{S}_s^{\cdot}\\ \mathrm{S}_r^{\cdot}+\mathrm{S}_s^{\cdot}\end{array}\right\}\xrightarrow{\text{(h)}}\text{polymer}\qquad k_{\mathrm{t}}$$

In the following the products of reactions (14d,e) are taken as $\mathrm{S}_r^{\cdot}$ and $\mathrm{R}_r^{\cdot}$ respectively, instead of $\mathrm{S}_{r+1}^{\cdot}$ and $\mathrm{R}_{r+1}^{\cdot}$ as written; this greatly simplifies the treatment without introducing significant error into the conventional long-chain approximation. Non-degradative chain transfer to species L is included (equations (14f,g)).

In the earlier paper[9] expressions were deduced for the following: the radical size distributions $\mathrm{R}_r^{\cdot}$ and $\mathrm{S}_r^{\cdot}$, $\mathrm{R}^{\cdot}$, $\mathrm{S}^{\cdot}$, $\bar{r}$ and $\bar{s}$ (the number-average size of $\mathrm{S}^{\cdot}$ radicals). The rate of polymerization was also evaluated, but in a form which loses precision in some circumstances. A preferable type of expression, analogous to equation (9), is developed below.

The rate of reaction of radicals of size r with the group $\mathrm{R}^{\cdot}$ is[9]

$$k_{\mathrm{t0}}\left(\frac{\bar{r}}{r_0}\right)^{-\beta}Z_{\mathrm{R}}\mathrm{R}^{\cdot}\left(\frac{r}{r_0}\right)^{-\beta}\mathrm{R}_r^{\cdot}\tag{15}$$

Z_{R} referring to the $\mathrm{R}^{\cdot}$ group (equation (2)), so that the total rate of reaction for all $\mathrm{R}^{\cdot}$ with the group (i.e. $k_{\mathrm{t}}\mathrm{R}^{\cdot 2}$) is

$$k_{\mathrm{t0}}\left(\frac{\bar{r}}{r_0}\right)^{-\beta}Z_{\mathrm{R}}\mathrm{R}^{\cdot}\sum_r\left(\frac{r}{r_0}\right)^{-\beta}\mathrm{R}_r^{\cdot}=k_{\mathrm{t0}}\left(\frac{\bar{r}}{r_0}\right)^{-2\beta}Z_{\mathrm{R}}^2\mathrm{R}^{\cdot 2}\tag{16}$$

Similarly, the total rate of reaction between all $\mathrm{R}^{\cdot}$ radicals and those of the $\mathrm{S}^{\cdot}$ group is

$$k_{\mathrm{t0}}\left(\frac{\bar{s}}{r_0}\right)^{-\beta}Z_{\mathrm{S}}\mathrm{S}^{\cdot}\sum_r\left(\frac{r}{r_0}\right)^{-\beta}\mathrm{R}_r^{\cdot}=k_{\mathrm{t0}}\left(\frac{\bar{r}}{r_0}\right)^{-\beta}\left(\frac{\bar{s}}{r_0}\right)^{-\beta}Z_{\mathrm{R}}Z_{\mathrm{S}}\mathrm{R}^{\cdot}\mathrm{S}^{\cdot}\tag{17}$$

Z_{S} referring to the $\mathrm{S}^{\cdot}$ group (equation (2)). The two corresponding expressions for reactions of the $\mathrm{S}^{\cdot}$ radicals may be written down immediately:

$$k_{\mathrm{t0}}\left(\frac{\bar{s}}{r_0}\right)^{-\beta}\left(\frac{\bar{r}}{r_0}\right)^{-\beta}Z_{\mathrm{S}}Z_{\mathrm{R}}\mathrm{S}^{\cdot}\mathrm{R}^{\cdot}\tag{18a}$$

$$k_{\mathrm{t0}}\left(\frac{\bar{s}}{r_0}\right)^{-2\beta}Z_{\mathrm{S}}^2\mathrm{S}^{\cdot 2}\tag{18b}$$

The sum of all four terms is the total rate of bimolecular termination and so is equal to the rate of initiation:

$$\frac{k_{\mathrm{t0}}}{r_0^{-2\beta}}(\bar{r}^{-\beta}Z_{\mathrm{R}}\mathrm{R}^{\cdot}+\bar{s}^{-\beta}Z_{\mathrm{S}}\mathrm{S}^{\cdot})^2=\mathscr{I}\tag{19}$$

Thus

$$\mathrm{R}^{\cdot}\left(\bar{r}^{-\beta}Z_{\mathrm{R}}+\bar{s}^{-\beta}Z_{\mathrm{S}}\frac{\mathrm{S}^{\cdot}}{\mathrm{R}^{\cdot}}\right)=\left(\frac{\mathscr{I}}{k_{\mathrm{t0}}}\right)^{1/2}r_0^{-\beta}$$

so that

$$\omega=k_{\mathrm{p}}M\mathrm{R}^{\cdot}=\frac{\mathscr{I}}{a}\left(\bar{r}^{-\beta}Z_{\mathrm{R}}+\bar{s}^{-\beta}Z_{\mathrm{S}}\frac{\mathrm{S}^{\cdot}}{\mathrm{R}^{\cdot}}\right)^{-1}\tag{20}$$

for long chains. Values of Z_{R} and Z_{S} calculated from the appropriate distributions are given in equations (21) and $\bar{r}$, $\bar{s}$, $\mathrm{S}^{\cdot}/\mathrm{R}^{\cdot}$ are known from the earlier paper[9]. Equation (20) is therefore suitable for computing ω. The full expression for ω is set out in equation (22).

$$\begin{aligned}Z_{\mathrm{R}}&=\frac{\{\Gamma(1-\beta)/(1-\zeta)\}\{\Gamma2/(1-\zeta)\}^{\beta}}{\{\Gamma1/(1-\beta)\}^{1+\beta}}\\ Z_{\mathrm{S}}&=\frac{\{\Gamma(1-\beta+\gamma)/(1-\zeta)\}\{\Gamma(2+\gamma)/(1-\zeta)\}^{\beta}}{\{\Gamma(1+\gamma)/(1-\zeta)\}^{1+\beta}}\end{aligned}\tag{21}$$

$$\omega=\frac{\mathscr{I}}{a}\times\left\{\frac{\left(\frac{1-\zeta}{k}\right)^{\beta/(1-\zeta)}\Gamma1/(1-\zeta)}{\Gamma(1-\beta)/(1-\zeta)+\frac{mc}{a(1+c)}\left(\frac{1-\zeta}{k}\right)^{\gamma/(1-\zeta)}\Gamma(1-\beta+\gamma)/(1-\zeta)}\right\}\tag{22}$$

Note that as the reinitiation process (14e) becomes faster, the degradative aspect of the polymerization decreases. As $k_{\mathrm{pm}}\to\infty$, $c\to0$, $k\to b+l$ and $\zeta\to\alpha$; under these conditions the expression (22) becomes identical with equation (11).

An alternative approach involves modification of the classical kinetic equation to accommodate size-dependent k_{t}, as described in the examples in the preceding subsections. The classical relation with constant k_{t} derived from scheme (14) is[18]

$$\omega=k_{\mathrm{p}}M\left(\frac{\mathscr{I}}{k_{\mathrm{t}}}\right)^{1/2}\frac{k_{\mathrm{pm}}M+(\mathscr{I}k_{\mathrm{t}})^{1/2}}{k_{\mathrm{pm}}M+k_{\mathrm{fm}}M+(\mathscr{I}k_{\mathrm{t}})^{1/2}}\tag{23}$$

Derivation of the modified version is effected by replacing the termination terms $k_{\mathrm{t}}\mathrm{R}^{\cdot 2}$, $k_{\mathrm{t}}\mathrm{R}^{\cdot}\mathrm{S}^{\cdot}$ and $k_{\mathrm{t}}\mathrm{S}^{\cdot 2}$ in the stationary state equations for $\mathrm{R}^{\cdot}$ and $\mathrm{S}^{\cdot}$ by their non-classical analogues in equations (16)–(18) and making use of equation (19). In this way we obtain

$$\omega=k_{\mathrm{p}}F_{\mathrm{R}}M\left(\frac{\mathscr{I}}{k_{\mathrm{t0}}}\right)^{1/2}\frac{k_{\mathrm{pm}}F_{\mathrm{S}}M+(\mathscr{I}k_{\mathrm{t0}})^{1/2}}{k_{\mathrm{pm}}F_{\mathrm{S}}M+k_{\mathrm{fm}}F_{\mathrm{R}}M+(\mathscr{I}k_{\mathrm{t0}})^{1/2}}\tag{24}$$

for long chains in which the corresponding factors F_{R}, F_{S} are

$$F_{\mathrm{R}}=\left(\frac{\bar{r}}{r_0}\right)^{\beta}Z_{\mathrm{R}}^{-1};\qquad F_{\mathrm{S}}=\left(\frac{\bar{s}}{r_0}\right)^{\beta}Z_{\mathrm{S}}^{-1}\tag{25}$$

In spite of their different appearance, expressions (22) and (24) are equivalent and computation of ω from them gives virtually identical values.

Note that the classical rate equation (23) does not contain a chain transfer term since the calculated rate is, of course, independent of this process. With size-dependent k_{t} the rate is influenced by chain transfer; this enters into equation (24) through F_{R} and F_{S}, which are in turn dependent on $\bar{r}$, Z_{R} and $\bar{s}$, Z_{S}, all of which are affected by transfer.

In the simpler treatment of Reference 10 a relation similar to equation (24) was used, being based on the assumption that $\bar{r}=\bar{s}$; under these conditions $Z_{\mathrm{R}}=Z_{\mathrm{S}}$ and $F_{\mathrm{R}}=F_{\mathrm{S}}$.

Equation (24) offers the simplest approach to evaluation of the kinetic parameters of the system from measured value of $\mathscr{I}$ and ω. The relation (27) derived in Reference 9 may be used:

$$\bar{r}=\frac{\omega}{\mathscr{I}+l\omega}\left\{(1-\zeta)\frac{\Gamma2/(1-\zeta)}{[\Gamma1/(1-\zeta)]^2}\right\}\tag{26}$$

ζ is not known but $\bar{r}$ is not very sensitive to this quantity in the range of interest and a first approximation may be made by taking $\zeta=\beta$ (actually $\zeta \leqslant \beta$). The expression in braces in equation (26) has values unity and 1.216 for $\zeta=0$ and $\zeta=0.16$, respectively. In the experiments on the polymerization of acenaphthylene in Reference 10 the error in $\bar{r}$ involved in replacing ζ by β ($\beta=0.16$) is always <9%; this would appear as a maximum error in F_r of 1.4% (equation (25)). Although a useful estimate of $\bar{r}$ may be made in this way, unfortunately $\bar{s}$ cannot be so treated. The procedure used in Reference 10 (i.e. the assumptions $\bar{r}=\bar{s}$, $F_R=F_S$ referred to above) may be adopted to determine first approximations to the parameters $k_p/k_{t0}^{1/2}$, k_{fm}/k_p and k_{pm}/k_p, which are subsequently refined with the aid of the exact equations. Experimental[19] and derived data for the acenaphthylene polymerization are presented in *Tables 1* and *2*; the former contains the calculated kinetic parameters and the latter typical values of calculated quantities and a comparison of observed and calculated rates of polymerization, which are seen to agree within experimental error. The value of $k_p/k_{t0}^{1/2}$ differs a little from that obtained by Bamford *et al.*[10] ($0.02\,\mathrm{mol}^{-1/2}\,\mathrm{dm}^{3/2}\,\mathrm{s}^{-1/2}$), who used the approximate treatment without refinement. Reference to *Table 2* shows that in these experiments F_R and F_S differ by a few per cent, so that $F_R=F_S$ is reasonable as a first approximation.

Systems with ideal retardation

The product(s) of interaction of a propagating chain and an ideal retarder do not enter into subsequent processes which influence the rate of polymerization. Bamford *et al.*[20] examined the polymerization of methacrylonitrile in DMF solution at 60°C in the presence of ferric chloride as retarder with initiation by azobisisobutyronitrile, and reported rates of polymerization for a series of ferric chloride concentrations.

Table 1 Values of kinetic parameters (equation (24)) for polymerization of acenaphthylene in toluene at 60°C; initiation by azobisisobutyronitrile. $\beta=0.16$, $r_0=50$

$k_p/k_{t0}^{1/2}$	$2.32\times10^{-2}\,\mathrm{mol}^{-1/2}\,\mathrm{dm}^{3/2}\,\mathrm{s}^{-1/2}$
k_{fm}/k_p	10.1×10^{-3}
k_{pm}/k_p	3.60×10^{-3}

The treatment of this type of polymerization with size-dependent k_t was described in Reference 9. Mean radical sizes in retarded systems may well be small so that size dependence in k_t may be significant, but nevertheless it may not play a major role since radical termination by the retarder can predominate. In the theoretical treatment[9] the long-chain assumption ($\bar{r} \gg 1$) was retained and direct reaction between initiator radicals and retarder was neglected.

The required value of a was calculated from equation (3) assuming $\beta=0.1$, and using values of ω and $\mathscr{I}$ reported for the unretarded polymerization: 1.34×10^{-5} and $4.78\times10^{-7}\,\mathrm{mol\,dm^{-3}\,s^{-1}}$, respectively. The result is $a=4.69\times10^{-2}$ for $M=2.79\,\mathrm{mol\,dm^{-3}}$, so that $k_p/k_{t0}^{1/2}=5.28\times10^{-3}\,\mathrm{mol}^{-1/2}\,\mathrm{dm}^{3/2}\,\mathrm{s}^{-1/2}$ (with $r_0=1$). Bamford *et al.*[20], assuming constant k_t, gave $k_p/k_t^{1/2}=6.97\times10^{-3}\,\mathrm{mol}^{-1/2}\,\mathrm{dm}^{3/2}\,\mathrm{s}^{-1/2}$. The retardation curve was calculated by the iterative procedure outlined[9] and, as may be seen from *Figure 5*, agrees satisfactorily with the

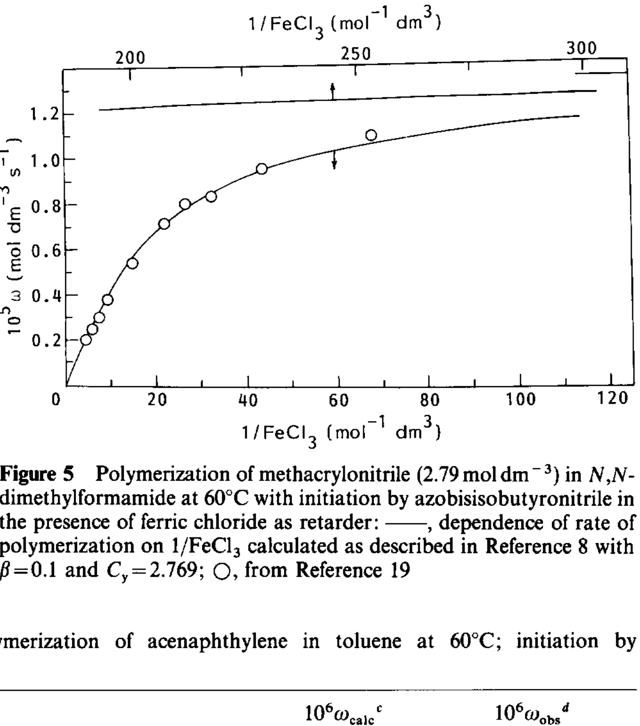

Figure 5 Polymerization of methacrylonitrile ($2.79\,\mathrm{mol\,dm^{-3}}$) in *N*,*N*-dimethylformamide at 60°C with initiation by azobisisobutyronitrile in the presence of ferric chloride as retarder: ——, dependence of rate of polymerization on 1/FeCl$_3$ calculated as described in Reference 8 with $\beta=0.1$ and $C_y=2.769$; ○, from Reference 19

Table 2 Experimental and derived quantities (equation (24)) for polymerization of acenaphthylene in toluene at 60°C; initiation by azobisisobutyronitrile. $\beta=0.16$

M (mol dm^{-3})	$10^7\mathscr{I}$ (mol dm^{-3} s^{-1})	$10^3 l$	$\bar{r}^a$	$\bar{s}^a$	$S^\cdot/R^{\cdot\,b}$	F_R	F_S	$10^6\omega_{calc}{}^c$ (mol dm^{-3} s^{-1})	$10^6\omega_{obs}{}^d$ (mol dm^{-3} s^{-1})
0.50	1.814	11.7	16.42	18.07	0.1959	0.7388	0.7701	3.07	2.99
0.75	1.814	7.446	24.56	28.37	0.2995	0.7880	0.8208	4.53	4.54
1.00	1.814	5.311	32.39	37.22	0.3990	0.8238	0.8569	5.86	5.48
1.20	1.814	4.243	38.44	44.01	0.4750	0.8467	0.8798	6.86	7.33
1.50	1.814	3.182	47.20	53.76	0.5826	0.8750	0.9079	8.26	7.98
2.00	1.814	2.115	61.24	69.21	0.7458	0.9122	0.9445	10.41	10.40
2.50	1.814	1.476	74.81	83.97	0.8905	0.9418	0.9733	12.40	12.80
3.00	1.814	1.047	88.19	98.40	1.0192	0.9668	0.9975	14.29	14.50
2.00	0.241	2.115	113.24	123.40	1.4517	1.0079	1.0331	2.97	2.91
2.00	0.482	2.115	92.50	102.15	1.1925	0.9754	1.0035	4.56	4.55
2.00	0.723	2.115	81.91	91.15	1.0462	0.9563	0.9860	5.87	5.80
2.00	0.964	2.115	74.99	83.87	0.9469	0.9427	0.9733	7.02	6.93
2.00	1.203	2.115	69.96	78.54	0.8735	0.9321	0.9634	8.06	7.94
2.00	1.685	2.115	62.75	70.83	0.7679	0.9158	0.9479	9.94	9.89
2.00	2.411	2.115	55.64	63.14	0.6642	0.8981	0.9309	12.39	12.30

[a] Calculated from equation (75), Reference 9
[b] Calculated from equations (73a, 74a), Reference 9
[c] Calculated from equation (24) (this paper)
[d] From Reference 19

experimental data[20]. However, the mean radical sizes for $1/\mathrm{FeCl_3} = 5\,\mathrm{mol^{-1}\,dm^3}$ and $1/\mathrm{FeCl_3} = 10\,\mathrm{mol^{-1}\,dm^3}$ are only about 4.9 and 9.0, respectively, so there may be appreciable error in the lower part of the calculated curve. The only adjustable parameter (excluding β which has been arbitrarily chosen above, but for which there are no independent experimental data) is the retardation constant C_y; a value $C_y = 2.769$ appeared to give the most satisfactory agreement with experiment (*Figure* 5). This corresponds to $k_p/k_y = 0.361$; the value found from the classical treatment is 0.325[20].

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NOMENCLATURE

a	$(\mathscr{I}k_{t0})^{1/2}/(k_pMr_0^{-\beta})$ $(=1/\bar{v}$ if $\beta=0)$
b	$a/(1+l)$
c	ak_p/k_{pm}
k	$b+l+mc/(1+l)(1+c)$
l	C_LL/M, $(C_L=k_{fL}/k_p)$
m	degradative addition constant to monomer $(=k_{fm}/k_p)$
C_y	retardation constant $(=k_y/k_p$, $k_y=$ rate coefficient for radical-retarder reaction)

Exponents

α	$\phi(b/l)\beta$
γ	$\phi(c)\beta$
ε	$\phi\{mc/(1+l)(1+c)b\}\gamma$
ζ	$\phi[\{b+mc/(1+l)(1+c)\}/l](\beta-\varepsilon)$

Here

$$\phi(x)=\frac{x}{1+x}\left(\frac{x}{6.125+3x}+0.667\right)$$

$$\phi(\infty)=1$$