Chain length dependence of termination rate constant: Computer experiment of effects on the kinetics of radical polymerization of styrene

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The kinetics of the radical polymerization of styrene, initiated by AIBN, have been studied by computer experiments. The models adopted assume a termination rate constant for polystyryl radicals with degrees of polymerization m and n, given by:

$$k_{t,mn} = k_\alpha m^{-\alpha} n^{-\alpha}$$

Deviations from simple kinetic rules have been found for $\alpha \neq 0.0$. For example, the rate of polymerization is roughly proportional to the 0.45 power of initiator concentration for $\alpha = 0.1$. Conventional methods for the kinetic study of radical polymerizations are shown to come to erroneous conclusions if the effects of the chain length dependence of termination rate constant are not taken into account.

INTRODUCTION

Studies of polymerization kinetics usually assume that the reactivities of polymeric chains are independent of their lengths. In diffusion-controlled reactions, however, this assumption may not be correct. Several workers have reported that the rate constant for termination in radical polymerizations is not always independent of chain length[1,2]; Horie and Mita[3] studied the rate constant for the quenching of the phosphorescence of poly(styryl benzil) by poly(styryl anthracene), k_q, as a model for the termination reaction. They observed that k_q is inversely proportional to the degree of polymerization, *DP* raised to the power 0.29 in benzene at 20°–40°C for a wide range of *DP*. Although the phosphorescence quenching process is not exactly identical to the radical–radical reaction, Horie and Mita's results affords clear evidence for the chain length-dependence of termination reaction rate constants.

Conflicting results in kinetic studies of radical polymerizations have recently been reported. Berger and Meyerhoff[4] discussed the radical termintion process in styrene by plotting $1/\overline{DP}$, the reciprocal of the average degree of polymerization, against kinetic chain length and concluded that disproportionation and combination compete each other with $k_{td}/k_{tc} = 0.25$ at 52°C. Their conclusion conflicts with that generally accepted[5]: the termination mechanism had previously been studied by measuring the average number of incorporated initiator fragments per polymer chain; it is concluded that polystyryl radicals exclusively terminate by combination at 25°–80°C[6–8].

We previously noted that the chain length dependence of the termination rate constant affects not only the molecular weight distribution of the polymer but also the polymerization kinetics[9]. To investigate this problem we adopted computer modelling of the radical polymerization of styrene at 60°C initiated by low concentrations of AIBN where complications due to primary radical termination and chain transfers can practically be neglected.

There is no universal agreement on the values of the rate constants or on notation. Here, we use those employed by Pryor and Coco[10]: $k_p = 145$, $k_t = 1.7 \times 10^7$, $fk_d = 6 \times 10^{-6}$, $k_i = 3 \times 10^2$, $k_{trM} = 1 \times 10^{-3}$, $k_{trI} = 5$, in $M^{-1}\,s^{-1}$ or s^{-1}.

COMPUTER EXPERIMENTS

We assume that the rate constant for termination between P_m and P_n (polystyryl radicals with m and n as their degrees of polymerization) is given by:

$$k_{t,mn} = k_\alpha m^{-\alpha} n^{-\alpha} \tag{1}$$

where $\alpha = 0.0$, 0.1 and 0.2. The rate constant for primary radical termination was assumed to be chain length-dependent and given by:

$$k_{prt,n} = k'_\alpha n^{-\alpha} \tag{2}$$

At steady state, the following simultaneous equations hold for $[P_n]$

$$[\mathrm{IBN}] = \frac{2fk_d[\mathrm{I}] + k_{trI}[\mathrm{I}]\sum [P_n]}{k_i[\mathrm{M}] + \sum\limits_n k_{prt,n}[P_n]} \tag{3a}$$

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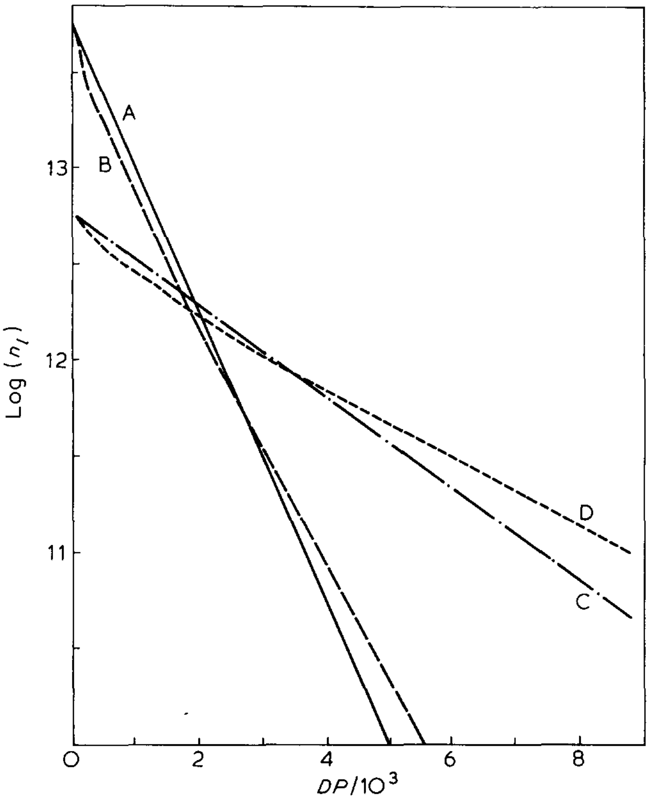

Figure 1 Semilog plots of the number of polystyryl radicals per litre N_l in the steady state against chain length *DP*. A, α = 0.0, [I] = 0.01 M; B, α = 0.2, [I] = 0.01 M; C, α = 0.0, [I] = 0.001 M; D, α = 0.2, [I] = 0.001 M

$$[P_1] = (k_i[\mathrm{IBN}][\mathrm{M}] + k_{trM}[\mathrm{M}]\sum_n [P_n])\Delta t \quad (3b)$$

$$[P_{n+1}] = [P_n]\,(1.0 - p_{t,n} - p_{prt,n} - p_{tr}) \quad (3c)$$

where $p_{t,n}$, $p_{prt,n}$ and p_{tr} represent the probabilities of deactivation of P_n by termination, primary radical termination and transfer, respectively, during a time Δt in which each polystyryl radical grows by one monomer unit.

These probabilities are given by:

$$p_{t,n} = 2k_\alpha n^{-\alpha}\sum_m m^{-\alpha}[P_m]\,\Delta t \quad (4a)$$

$$p_{prt,n} = k'_\alpha n^{-\alpha}[\mathrm{IBN}]\,\Delta t \quad (4b)$$

$$p_{tr} = (k_{trM}[\mathrm{M}] + k_{trI}[\mathrm{I}])\Delta t \quad (4c)$$

with

$$k_\alpha = k_t\left(\sum [P_n]\right)^2 \Big/ \left(\sum n^{-\alpha}[P_n]\right)^2 \quad (4d)$$

Transfer to polymer and other minor components, as well as the time variation of [M], were neglected.

The $[P_n]$ distribution in the steady state was calculated by the iterative method: i.e. starting from a tentative $[P_n]$ distribution, provisional k_α and $[P_n]$ distributions were iteratively calculated using equations (3) and (4) until they attained stationary values. The k_α values obtained with [I] = 0.001 M were 1.1×10^8 and 7.1×10^8 in M^{-1} sec^{-1} for α = 0.1 and 0.2, respectively. In these calcualtions, k'_α was tentatively equated to k_{prt}. The final results were scarcely influenced by the values assigned to k'_α and/or k_{trI} when [I] was less than 0.01 M.

The $[P_n]$ distributions for other initiator concentrations were calculated by employing these values for k_α, instead of those given by equation (4d). The $[P_n]$ distributions in steady state obtained with [I] = 0.001 and 0.01 *M* for α = 0.0 and 0.2 are given in *Figure 1*.

The apparent termination rate constant is given by

$$k_t(\mathrm{app}) = \sum_m \sum_n k_{t,mn}[P_m][P_n] \Big/ \left(\sum [P_n]\right)^2 \quad (8)$$

i.e. the weight average of $k_{t,mn}$; it is influenced by the $[P_n]$ distribution and, consequently, by [I]. Log–log plots of k_t(app) against [I] (*Figure 2*) for α = 0.0, 0.1 and 0.2 indicate that k_t(app) can be expressed approximately as follows:

$$k_t(\mathrm{app}) = C_\alpha[\mathrm{I}]^\alpha \quad (9)$$

with $C_\alpha = 3.4 \times 10^7$ and 6.8×10^7 in $M^{-(1+\alpha)}s^{-1}$ for α = 0.1 and 0.2, respectively.

At steady state and with low [I], the contribution of primary radical termination is negligibly small and the rate of chain initiation is practically equal to the rate of termination:

$$2f \cdot k_d[\mathrm{I}] = 2k_t(\mathrm{app})\left(\sum [P_n]\right)^2 \quad (10)$$

When the rate constant for termination is independent of chain length, this reduces to the square root rule:

$$R_p \propto [\mathrm{I}]^{1/2}$$

However, for systems in which the rate constant for termination varies with chain length, k_t(app) can be approximately represented by equation (9), and log–log plots of R_p against [I] give a slope of 0.45 for α = 0.1 and 0.40 for α = 0.2. The detection of these small deviations from the square root rule may not be easy for low [I] where contributions from

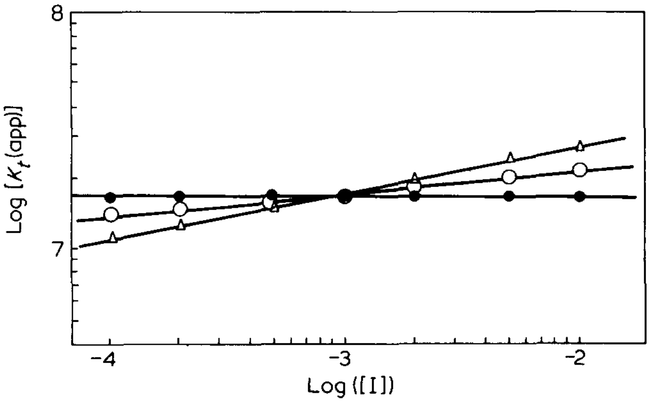

Figure 2 Log–log plots of apparent termination rate constant k_t (app) against [I]. ●, α = 0.0, ○, α = 0.1; △, α = 0.2

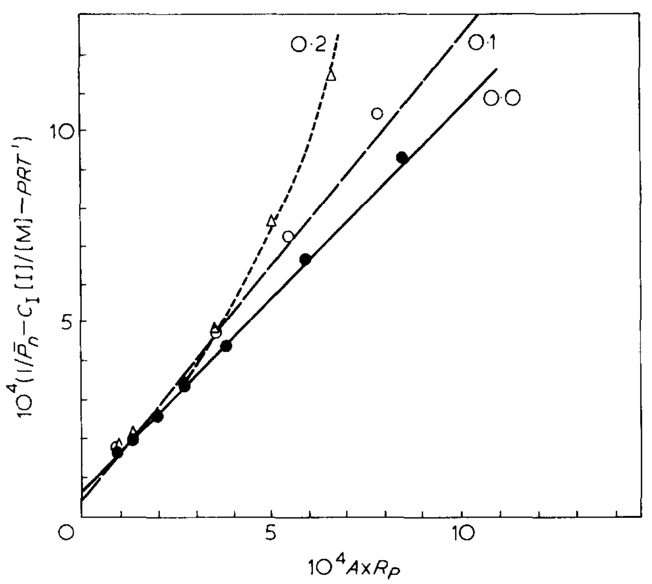

Figure 3 Plots of $1/\bar{P}_n - C_I\,[I]/[M] - PRT'$ against $A\cdot R_p$. ●, $\alpha = 0.0$; ○, $\alpha = 0.1$; △, $\alpha = 0.2$

thermal polymerization and side reactions with minor components influence the kinetics considerably.

If all the rate constants are independent of chain length the following equation holds:

$$1/\bar{P}_n - C_I[I]/[M] - PRT' = (1 + x)A\cdot R_p + C_M \qquad (11)$$

with

$$x = k_{td}/(k_{td} + k_{tc})$$

and

$$A = k_t/(k_p\,[M])^2$$

x may be estimated from the slope of a plot of the right hand side of equation (11) against $A\cdot R_p$. This plot may not give a correct value for x for $\alpha \neq 0.0$. To examine the kind of error introduced in the estimate of x by conventional plots of equation (11), $1/\bar{P}_n$ were calculated for various [I], assuming that polystyryl radicals are terminated exclusively by combination (i.e. $x = 0.0$) for $\alpha = 0.0$, 0.1 and 0.2; these values were used for plots of equation (11) where R_p and PRT' were given by $k_p[M]\,\Sigma[P_n]$ and $[IBN]\,\Sigma k_{prt,n}[P_n]/R_p$, respectively. The slope in *Figure 3* gives a correct value of 1.0 for $\alpha = 0.0$; however, the slope for $\alpha = 0.1$ is approximately 1.2 and an appreciable deviation from a straight line is observed for $\alpha = 0.2$. Thus, we can conclude that a conventional plot of equation (11) gives an erroneous value for k_{td} for a system where the rate constant for termination is not independent of chain length. The apparent value of x of 0.2 obtained for $\alpha = 0.1$, is practically equal to the value assigned as an actual value of x by Berger and Meyerhoff[4] from a plot of experimental data for styrene polymerization at 52°C.

Various modifications of equation (11) have been proposed for kinetic studies. For example a plot of $1/\bar{P}_n - A\cdot R_p$ against [I]/[M] under appropriate conditions has a slope which corresponds to k_{trI} and the deviation from linearity of a plot of $1/\bar{P}_n - C_I[I]/[M]$ against $A\cdot R_p$ can be employed to estimate k_{prt}. The present study, however, indicates that these plots may not give correct values for k_{trI}, k_{prt}, etc., if the rate constants for termination and/or primary radical termination vary appreciably with chain length.

DISCUSSION

Several workers have assigned different values for k_{prt}, k_{trI}, etc. In particular, the k_{trI} value of 5.0 employed in the present work is larger by several orders of magnitude than that accepted by most workers[5]. Even with this value, the contribution of chain transfer to AIBN is negligibly small at $[I] < 0.01$ M: several supplimentary studies with $k_{prt} = 7 \times 10^7$ and/or $k_{trI} = 0.0$ showed that the $[P_n]$ distributions in the steady states are hardly influenced by the choice of these values at $[I] < 0.01$ M where polystyryl radicals are deactivated mostly by termination. In *Figure 4* are shown the contributions of the respective mechanisms to the deactivation of polystyryl radicals in the model with $\alpha = 0.1$. Thus, we can consider that the deviation from the square root rule and the variation of k_t(app) with [I] are caused by an intrinsic effect of the chain length dependence of the termination rate constant as exemplified by equation (1), and not, for example, by the combined effects of chain transfers and primary radical termination.

The average number of incorporated initiator fragments per polymer chain gives a direct estimate of the disproportionation contribution, x, free from the ambiguity originat-

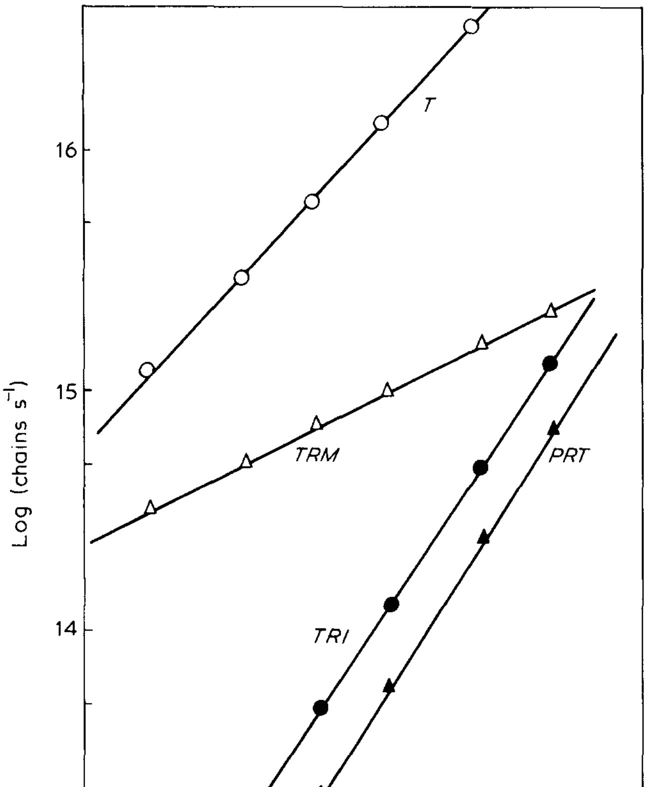

Figure 4 Contribution of various mechanisms to the deactivation of polystyryl radicals at various [I] for $\alpha = 0.1$. ○, Termination; △, transfer to monomer; ●, transfer to AIBN; ▲, primary radical termination

ing from some of the assumptions of polymerization kinetics, if experimental conditions are chosen carefully. A plot of equation (11) in *Figure 3* leads to an erroneous value of x if the termination rate constant is not independent of chain length. Thus, experimental results reported by Berger and Meyerhoff[4] indicate that polystyryl radicals are terminated essentially by combination for which the rate constant is slightly dependent on chain length, rather than a large contribution from disproportionation.

The rate-determining step in termination reactions is considered to be the segmental diffusion of active ends. Basic problems in diffusion-controlled reactions have been discussed by Wilemski and Fixman[11] and several other workers discussed the segmental diffusion of chain molecules in terms of inter- and intrachain reactions[12]. Satisfactory theories, however, have not yet been presented for the elucidation of polymer–polymer reactions.

Here the termination rate constant was assumed to be given by equation (1). Evidently, both k_α and α reflect the dynamical properties of polymeric chains and are influenced by many factors, e.g. an increase in the concentration of concomitant polymeric chains would disturb translational and segmental motions of polymer radicals and consequently affect these values. Further, more detailed experimental and theoretical data are required for discussion of the validity of equation (1).

At higher initiator concentrations, the kinetics may be much more complicated because the combined effects of chain-length dependence of termination, and primary radical termination, influence the chain length distribution of polystyryl radicals. Hence, exact knowledge of the chain-length dependence of $k_{prt,n}$ is needed for the complete analysis of kinetics at higher initiator concentrations.

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