Termination Rates in Free Radical Copolymerizations

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ABSTRACT

The rates of free radical copolymerizations at given rates of initiation can be analyzed ideally in terms of monomer feed concentrations and reactivity ratios, propagation rate constants for homopolymerizations of the particular monomers, and an overall rate constant for termination during copolymerization. This model, which is due to Atherton and North, can account for the effects of initiator concentration and viscosity of the polymerization medium on copolymerization rates.

This article reports an empirical formulation for the overall termination rate constant in terms of monomer concentrations and reactivity ratios and a cross-termination factor. The new model accounts for experimental data in the styrene-methyl methacrylate system in which polarity differences between unlike radicals may result in enhanced termination rates. It also predicts observed copolymerization rates of methyl methacrylate-vinyl acetate and styrene—α-methylstyrene mixtures in which polarity effects are absent. The cross-termination factor may be approximated from reactivity ratio data for predictive purposes.

INTRODUCTION

The rate of copolymerization of two monomers, A and B, can be expressed generally as [1]

$$
-\frac{d([A]+[B])}{dt} = \frac{R_i^{1/2}(r_1[A]^2 + 2[A][B] + r_2[B]^2)}{k_{to}^{1/2}\left[\dfrac{r_1[A]}{k_{pAA}} + \dfrac{r_2[B]}{k_{pBB}}\right]}
\tag{1}
$$

Here R_i is the rate of initiation, r_1 and r_2 are the monomer reactivity ratios given by the propagation rate constant ratios k_{pAA}/k_{pAB} and k_{pBB}/k_{pBA}, respectively, k_{pij} is the specific rate constant for addition of monomer j to a radical ending in monomer unit i [2], and the polymerization rate is defined as usual as the sum of the time changes in monomer concentrations, [A] and [B]. Here, also, k_{to} is an overall termination rate constant.

If the simple copolymer kinetic model [3, 4] is adopted, only the terminal monomer unit in the polymeric radical is considered to have any influence on the rates of propagation and termination of the kinetic chain. The rate of termination, R_t, is easily shown to be

$$
R_t = 2(k_{tAA}[A\cdot]^2 + k_{tAB}[A\cdot][B\cdot] + k_{tBB}[B\cdot]^2)
\tag{2}
$$

where the subscripts refer to reactions of radicals with radicals with the same (AA and BB) or opposite (AB and BA) terminal units. The mole fractions $\dot{X}_A$ and $\dot{X}_B$ of A- and B-ended radicals in the system are given by

$$
\dot{X}_A = \frac{[A\cdot]}{[A\cdot]+[B\cdot]}
$$

$$
\dot{X}_B = \frac{[B\cdot]}{[A\cdot]+[B\cdot]}
\tag{3}
$$

and

$$
R_t/([A\cdot]+[B\cdot])^2 = 2(k_{tAA}\dot{X}_A^2 + k_{tAB}\dot{X}_A\dot{X}_B + k_{tBB}\dot{X}_B^2) = 2k_{to}
\tag{4}
$$

where the overall termination rate constant is defined as

$$k_{to} = k_{tAA}\dot{X}_A{}^2 + k_{tAB}\dot{X}_A\dot{X}_B + k_{tBB}\dot{X}_B{}^2 \tag{5}$$

If Expression (6) is now invoked to define the cross-termination factor, ϕ:

$$\phi = \frac{k_{tAB}}{2(k_{tAA} \cdot k_{tBB})^{1/2}} \tag{6}$$

the following familiar form of the so-called "chemical control" model for copolymerization rate [5, 6] results:

$$-\frac{d([A] + [B])}{dt} = \frac{(r_1[A]^2 + 2[A][B] + r_2[B]^2) R_i^{1/2}}{(r_1^2\delta_A{}^2[A]^2 + 2\phi r_1 r_2 \delta_A \delta_B[A][B] + r_2^2\delta_B{}^2[B]^2)^{1/2}} \tag{7}$$

where δ_A and δ_B represent the termination-propagation rate constant ratios $k_{tAA}{}^{1/2}/k_{pAA}$ and $k_{tBB}{}^{1/2}/k_{pBB}$, respectively.

This is a one-parameter (ϕ) model in which polarity effects are implicitly assumed responsible for any tendency for mutual termination of polymer radicals with dissimilar ends. The cross-termination factor ϕ is expected to be unity on purely statistical grounds, since encounters between unlike radicals are twice as likely as those between similar radicals, at equal radical concentrations. In practice, ϕ can be calculated by inserting experimental copolymerization rates into Eq. (7). Deviations of ϕ from unity are ascribed to polar effects which favor cross-termination. The computed values of ϕ are not always unambiguous, however, since the apparent cross-termination factor may vary with monomer feed composition in a given system [5, 7].

It is clear, also, that termination reactions in radical homopolymerizations and copolymerizations are at least partially diffusion controlled [1, 8-10]. Atherton and North have proposed the formulation in Eq. (8) as an empirical expression for the overall termination rate constant, k_{to}, which appears in Eq. (1):

$$k_{to} = X_A k_{tAA} + X_B k_{tBB} \tag{8}$$

In this form, k_{to} is the average of homotermination rate constants weighted on the basis of the mole fractions X_A and X_B of the respective monomers in the copolymer.

Equations (1) and (8) provide a model for diffusion-controlled reactions with no adjustable parameters. This model is more realistic than the classical chemical control theory (Eq. 7) in some copolymerizations such as that of methyl methacrylate and vinyl acetate [1]. It cannot account, however, for the behavior of the methyl methacrylate-styrene system. In the latter case k_t values in the individual homo-polymerizations are similar, but the rate of copolymerization is relatively depressed when the reacting mixture contains more than about 0.2 mole fraction of styrene.

Russo and co-workers [11] have noted that diffusion control of the termination reaction is related to segmental rearrangement of the radical ends and adjacent few carbon atoms in the chain [9, 12]. Russo's ingenious mechanism postulates for calculation purposes that the length of the mobile radical-carrying segment is given by the last four carbon atoms in the chain [11]. There can then be 10 possible termination rate constants if allowance is made for the terminal and penultimate monomer residues in the two radicals which are involved in the termination reaction. The six so-called cross-termination rate constants are assumed to be equal to the geometric means of the corresponding self-terminations. The resulting equation, which contains two adjustable parameters, has been shown to produce useful and consistent rationalizations of results in copolymerizations of styrene with methyl methacrylate [11, 13] and butyl acrylate [11].

O'Driscoll and co-workers have suggested an equation based on terminal diad concentrations and a single adjustable parameter which produces a better fit to the styrene-methyl methacrylate data of Walling [5] than Eq. (7) with a single ϕ value [10].

Dependence of the overall copolymerization rate on copolymer composition seems reasonable since the nature of the terminal regions of the polymeric radicals should influence segmental mobility and termination reaction rates. The extent of these terminal regions and the functional relation between polymer composition and observed polymerization rates are unfortunately not clear. Russo's [11, 13] model is the only current approach which is not basically empirical. This theory requires fitting of the experimental data to two adjustable parameters, and when allowance is made for possible variation of initiation rate with comonomer feed composition, there exists an unfortunate possibility of saturating the experimental data (which are generally not plentiful) with adjustable variables.

This article reports on empirical approach to formulation of k_{to} which seems to fit the available data better than any of the alternative

methods cited above. It uses a parameter available from previous studies of the chemical control model (Eq. 7) and so can be employed for predictive purposes with current information. This appears to be an important advantage for practical purposes, although the connection between the model and the actual polymerization mechanism remains obscure.

POLYMERIZATION MODEL

Equation (5), which expresses k_{to} in terms of mole fractions of terminal radical units, does not account for observed termination rates because the termination reaction appears to depend on composition of the polymeric radical. In the absence of a rigorous functional relation it is tempting to substitute mole fractions of each monomer for the radical mole fractions, $\dot{X}_A$ and $\dot{X}_B$, in this equation.

The empirical formulation for k_{to} is now

$$k_{to} = k_{tAA}X_A^2 + k_{tAB}X_AX_B + k_{tBB}X_B^2 \tag{9}$$

The mole fractions X_A and X_B of monomer units in the polymer formed are given by [3, 4]

$$X_A = \frac{[A]([B] + r_1[A])}{r_1[A]^2 + 2[A][B] + r_2[B]^2} \tag{10}$$

and

$$X_B = 1 - X_A \tag{11}$$

Equation (6) is still used to define the rate constant k_{tAB} in terms of a cross-termination factor ϕ. This permits incorporation of previous experience with the chemical control model for predictive purposes.

The final expression for k_{to} is then

$$k_{to} = k_{tAA}X_A^2 + 2\phi(k_{tAA}k_{tBB})^{0.5}X_AX_B + k_{tBB}X_B^2 \tag{12}$$

Rates of polymerization can be predicted with Eqs. (1) and (12) from monomer feed concentrations and the rate of initiation. Input data required are the reactivity ratios and individual rate constants for propagation and termination in the homopolymerizations of the particular monomers. A value for the cross-termination factor, ϕ, is also needed.

The initiation rate in a series of copolymerizations can be accounted for by allowing for the proportionality of rate of polymerization, R_p, to $[I]^{1/2}$, where $[I]$ is the initiator concentration. This assumes no influence of monomer concentrations or mole ratios on initiator efficiency or rate of initiation. The influence of viscosity of the medium is likewise handled through the approximately inverse relation between rate of termination and $\eta^{-1/2}$, where η is the viscosity of the solvent-monomer mixture [14, 15]. Thus, using the terminology of a previous article [14], the rates of copolymerization in two experiments i and j may be compared by:

$$\frac{(R_p)_i}{(R_p)_j} = \frac{[I]_i^{1/2}(r_1[A]^2 + 2[A][B] + r_2[B]^2)_i}{[I]_j^{1/2}(r_1[A]^2 + 2[A][B] + r_2[B]^2)_j}$$

$$\frac{(r_1[A]/k_{pAA} + r_2[B]/k_{pBB})_j}{(r_1[A]/k_{pAA} + r_2[B]/k_{pBB})_i}\left(\frac{\eta_i}{\eta_j}\right)^{1/2}\left[\frac{k_{toj}}{k_{toi}}\right]^{1/2} \qquad (13)$$

The subscripts refer to copolymerizing systems i and j, in which monomer concentrations [A] and [B] and initiator concentrations and solvent viscosities may differ. The termination rate constant, k_{to}, for each experiment is given by Eq. (12), with appropriate values of X_A and X_B from Eqs. (10) and (11).

The value of ϕ for use in Eq. (12) can be approximated for predictive purposes from the $r_1 r_2$ product as described later in this article. Direct use of the model involves the estimation of ϕ from copolymerization rates, in parallel with the applications which have been made heretofore of the chemically controlled model in Eq. (7). If the present model is applicable, a constant value of ϕ should be obtained for a particular comonomer system, regardless of monomer feed ratios.

RESULTS

A previous report [14] from this laboratory has shown that the polymerization rates and molecular weight of styrene—α-methylstyrene

copolymers formed at $60°C$ are accounted for quantitatively by the present model (Eqs. 1 and 12). In this case ϕ is taken to be unity since polar effects are not expected in termination reactions in this system.

The styrene-methyl methacrylate system is generally considered to be an example of a chemically-controlled copolymerization. The cross-termination factor ϕ has been found to be about 13, by fitting R_p data to equation (7) [5, 7].

The styrene-methyl methacrylate data of Walling [5] are analyzed below according to the chemical control theory (Eq. 7), the model of Atherton and North (Eqs. 1 and 8), and the present model (Eqs. 1 and 12). The chemical control and present models each contain one adjustable parameter (ϕ), while the equations of Atherton and North have no such parameters. In this case sytrene is monomer A and the reactivity ratios are 0.52 and 0.46, respectively [5]. The styrene rate constants k_{pAA} and k_{tAA} are 176 Ms^{-1} and 2.7×10^7 Ms^{-1}, respectively [14, 16]. The methyl methacrylate rate constants k_{pBB} and k_{tBB} are 515 Ms^{-1} and 22.5×10^6 Ms^{-1}, respectively [17]. As shown below, these four rate constants account fairly well for the homopolymerization rates measured in the series of experiments which yielded the copolymerization rates of particular interest in this context.

The styrene-methyl methacrylate data of Walling [5] were normalized on R_i by using the reported rate of homopolymerization of styrene as a calibration value. The initial steady-state rates of polymerization of styrene (R_{pA}) and of a styrene-comonomer mixture $(R_p)_i$ are comparable through

$$\frac{R_{pA}}{(R_p)_i} = \frac{[I]_A^{1/2} k_{pAA}[A]}{[I]_i^{1/2} k_{tAA}^{1/2}} \frac{\left[\dfrac{r_1[A]}{k_{pAA}} + \dfrac{r_2[B]}{k_{pBB}}\right]_i}{[r_1[A]^2 + 2[A][B] + r_2[B]^2]_i} \frac{(k_{to})^{1/2}}{(\eta_A)^{1/2}} \frac{(\eta_A)^{1/2}}{(\eta_i)^{1/2}} \quad (14)$$

In Eq. (14) the subscript i refers to the copolymerizing mixture in which the comonomer concentrations are [A] and [B], respectively. Symbols which are subscripted A or are without subscript refer to the homopolymerizing system in which the initial monomer concentration is [A]. The concentration [A] of styrene differs in the two experiments compared in this equation. The initiator concentrations [I] and the solvent viscosities η are assumed to be equal in the homopolymerizing and copolymerizing experiments, for present purposes.

Similarly, the relative rates of styrene (R_{pA}) and methyl methacrylate (R_{pB}) homopolymerizations will be given by

TABLE 1. Copolymerization of Styrene and Methyl Methacrylate, 60 °C

Rate of polymerization, $Ms^{-1} \times 10^5$

Mole fraction styrene in feed	Experimental [1]			Chemical control [5, 7] Eq. (7), $\phi = 13$	Diffusion control [1], Eqs. (1) and (8)	Present model, Eqs. (1) and (12)		
	Trial 1	Trial 2	Mean			$\phi = 5$	$\phi = 10$	$\phi = 13$
1.000[a]			5.34	5.34	5.34	5.34	5.34	5.34
0.758	4.61	4.43	4.5	5.9	10.1	6.2	4.6	4.1
0.579	4.82	4.75	4.8	6.0	12.7	7.5	5.5	4.8
0.378	5.67	5.38	5.5	6.2	13.4	9.0	6.6	5.9
0.1906	7.78	7.95	7.9	6.7	17.6	11.1	8.4	7.5
0.0913	11.60	10.20	10.9	7.8	18.4	12.7	9.9	8.9
0.000	19.8	19.4	19.6	18.7	18.7	18.7	18.7	18.7

[a]Reaction with 1.000 mole fraction styrene taken as calibration value to normalize R_i.

$$\frac{R_{pA}}{R_{pB}} = \frac{[I]_A}{[I]_B^{1/2}} \frac{k_{pAA}[A]}{(k_{tAA})^{1/2}} \frac{(k_{tBB})^{1/2}}{k_{pBB}[B]} \frac{(\eta_A)^{1/2}}{(\eta_B)^{1/2}} \tag{15}$$

with the same assumptions.

Table 1 compares the experimental values of Walling [5] with predictions of the three models mentioned above. ϕ is given as approximately equal to 13 from fitting of the data to Eq. (7) [5, 7]. The rate constants chosen for homopolymerizations predict the methyl methacrylate polymerization rate fairly well, from Eq. (15), with R_i normalized on the reaction of pure styrene.

The rates of termination in polymerizations of the monomers alone do not differ much, but the copolymerization rate is lower than either homopolymerization value in styrene-rich feeds. The model using Eq. (8) cannot anticipate this trend. The chemical control theory, with ϕ taken as 13 from application of Eq. (7) [5, 7], simulates the observed trend of copolymerization rates but the general coincidence of figures seems to be better with the present model. Table 1 lists calculations with different ϕ values in the new model. Estimates with $\phi = 1$ in Eq. (12) are not listed as these yield results which are identical with those with k_{to} given by Eq. (8). This agreement is not general. It is an artifact of coincidence that $k_{tAA} = k_{tBB}$ for the two monomers of interest. In that case Eqs. (8) and (12) yield approximately equal values for the overall termination rate, k_{to}.

Melville and Valentine [7] have also reported copolymerization rates of styrene and methyl methacrylate. Initiation in this case was by photosensitized decomposition of benzoyl peroxide with light of wavelength greater than 3150 Å, at 30°C. The homopolymerization rate constants for styrene are $k_{pAA} = 46$ Ms^{-1} and $k_{tAA} = 8.0 \times 10^6$ Ms^{-1} [7]. The methyl methacrylate homopolymerization rate constants used in our calculations are $k_{pBB} = 286$ Ms^{-1} and $k_{tBB} = 2.44 \times 10^7$ Ms^{-1}, as reported by Matheson and co-workers [18]. These values differ from those employed in the original reference [7], but seem to be preferred because they account better for the relative rates of homopolymerization of the two monomers at equal initiation rates. The reactivity ratios at 30°C are $r_1 = 0.485$ and $r_2 = 0.422$ [7], in essential agreement with the 60°C values used above. As before, the rate of polymerization of pure styrene was taken as a calibration value to standardize R_i in Eqs. (1) and (7). Table 2 compares experimental rates of polymerization with values calculated using the chemical control model and the present theory. The cross-termination factor, ϕ, was taken as 13, in parallel with the preceding calculations. The tabulated results show that the predictions of the new model follow the trend of measured values somewhat better than those of the chemical control model.

TABLE 2. Copolymerization of Styrene and Methyl Methacrylate, 30°C

Mole fraction styrene in feed	Rate of polymerization, $Ms^{-1} \times 10^5$		
	Experimental [7]	Chemical control[a] [5, 7] Eq. (7), $\phi = 13$	Present model,[a] Eqs. (1) and (12), $\phi = 13$
0	4.60 4.70	3.92	3.92
0.052	1.88	1.78	2.27
0.195	1.13	1.33	1.35
0.418	0.82	1.23	0.92
0.804	0.80	1.14	0.55
1.0	1.05 1.15	1.10	1.10

[a]Reaction with 1.0 mole fraction styrene in feed taken as calibration value to normalize on R_i.

TABLE 3. Copolymerization of Styrene and Methyl Methacrylate, 30°C

Mole fraction styrene in feed	Experimental [7]	Chemical control, Eq. (7)		Present model, Eqs. (1) and (12)	
		$\phi = 10$	$\phi = 13$	$\phi = 10$	$\phi = 13$
0	–	10.75	10.75	10.75	10.75
0.031	7.11	6.30	5.71	7.85	7.28
0.131	4.67	4.39	3.90	4.86	4.39
0.338	2.60	3.86	3.43	3.20	2.85
0.622	2.42	3.60	3.25	2.17	1.92
0.888	2.24	3.23	3.06	1.67	1.48
1.000	3.02	3.02	3.02	3.02	3.02

Rate of polymerization, $Ms^{-1} \times 10^5$ [a]

[a]Predicted reaction rates were based on the experimental value with unit mole fraction styrene.

It must be noted that the experimental results in Table 2 are not unequivocal. The original authors [7] concluded that methyl methacrylate initiated faster than styrene in their photosensitized reaction and corrected the observed rate of polymerization using an argument involving measured values of copolymer chain lengths. The polymerization rates recalculated by Melville and Valentine are given in Table 3. (These data appear to be from a different set of experiments than those quoted in Table 2). Table 3 also includes predictions based on the present model and chemical control theory, both of which employ the cross-termination factor, ϕ. The rate constants used with the Table 2 calculations were also used here and the rate of styrene homopolymerization was again taken as a standard value to compensate for R_i. The data in Table 3 show that the present theory predicts the monomer feed composition more accurately than the unmodified chemical control model.

Russo and co-workers [11] have proposed a copolymerization model which includes effects of chain end flexibility. This involves the fitting of experimental data to two parameters. New experimental results for styrene-methyl methacrylate copolymerization have been presented in support of this model [13]. Figure 1 compares these data, for 60°C copolymerization, with the line predicted by our model with R_i normalized on styrene homopolymerization and the reactivity ratios and rate constants used earlier to account for the results of Walling [5]. Copolymerization rates from the present model, with $\phi = 10$ in this instance, tend to be lower than corresponding experimental values. In large measure, this results from the deviation between experimental and predicted values for the rate of polymerization of pure methyl methacrylate. The original authors [13] adjusted R_i for monomer feed composition. The present model would probably fit the experimental points closely if this adjustment were made, but this step has not been taken here since it did not seem to be necessary with the styrene-methyl methacrylate data of other workers which were considered above.

We have shown in an earlier article [14] that the present model applies to the copolymerization of styrene and α-methylstyrene in which the nature of polyradical ends has no discernable effect on the overall rate of termination (i.e., $\phi = 1$). Methyl methacrylate and vinyl acetate constitute another such system. This copolymerization was used as the basis for the diffusion control model of Atherton and North [1]. The data of the latter authors are compared in Table 4 to predictions of the original diffusion control model (Eqs. 1 and 8) and the present model (Eqs. 1 and 12). In this case methyl methacrylate is taken to be monomer A, r_1 and 20, and $r_2 = 0.015$ [19]. The homopolymerization rate constants (Ms^{-1}) are [1]: $k_{pAA} = 229$, $k_{tAA} = 1.66 \times 10^7$, $k_{pBB} = 988$ and $k_{tBB} = 17.7 \times 10^7$. Predictions were normalized on the
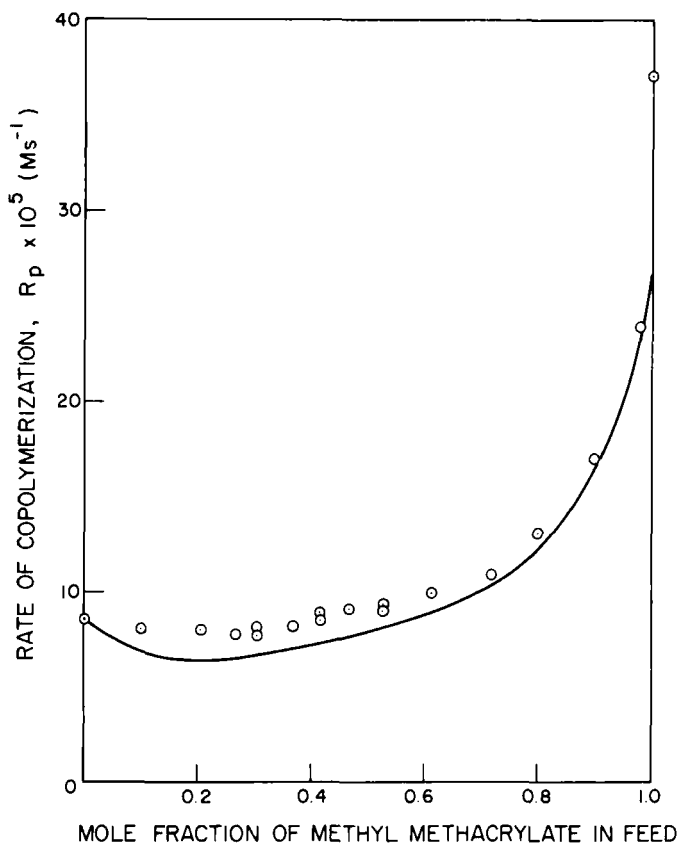
FIG. 1. Copolymerization of styrene and methyl methacrylate at 60°C. Data points are from Bonta and co-workers [13] and the curve is predicted from the present theory (Eq. 1, Eq. 12, ϕ = 10).

experimental polymerization rate with 0.54 mole fraction vinyl acetate in the feed to account for initiation rates. The tabulated data are given in terms of $R_p/R_i^{1/2}$ (R_p = rate of copolymerization) as in the original reference [1]. The two models seem to be about equally effective in predicting reaction rates in this case.

Similar conclusions are indicated by the comparison in Table 5 of the 60°C vinyl acetate-methyl methacrylate copolymerization rate data of Burnett and Gersmann [20]. The cross-termination factor, ϕ, was

TABLE 4 Copolymerization of Methyl Methacrylate and Vinyl Acetate, 30°C

Mole fraction vinyl acetate in feed	Ratio of rates, $(R_p/R_i^{1/2}) (M^{1/2} s^{-1/2}) \times 10^a$		
	Experimental [1]	Present model, Eqs. (1) and (12), $\phi = 1$	Diffusion control [1], Eqs. (1) and (8)
0.19	1.29	1.79	1.91
0.37	1.18	1.43	1.50
0.54	1.05	1.05	1.05
0.70	0.73, 0.93	0.71	0.69
0.86	0.64	0.38	0.35
0.97	0.13	0.15	0.15

[a]Reaction with 0.54 mole fraction vinyl acetate in feed taken as calibration value to normalize R_i.

TABLE 5. Copolymerization of Methyl Methacrylate and Vinyl Acetate, 60°C

Mole fraction vinyl acetate in feed	Rate of polymerization, $Ms^{-1} \times 10^4$ [a]		
	Experimental [20]	Present model, Eqs. (1) and (12), $\phi = 1$	Diffusion control [1], Eqs. (1) and (8)
0.976	37.2	18.0	17.7
0.915	28.0	22.2	21.3
0.756	29.1	31.5	30.8
0.645	42.4	42.4	42.4
0.548	60.7	59.2	60.1
0.453	78.7	80.1	82.5
0.325	103.9	108.3	113.4

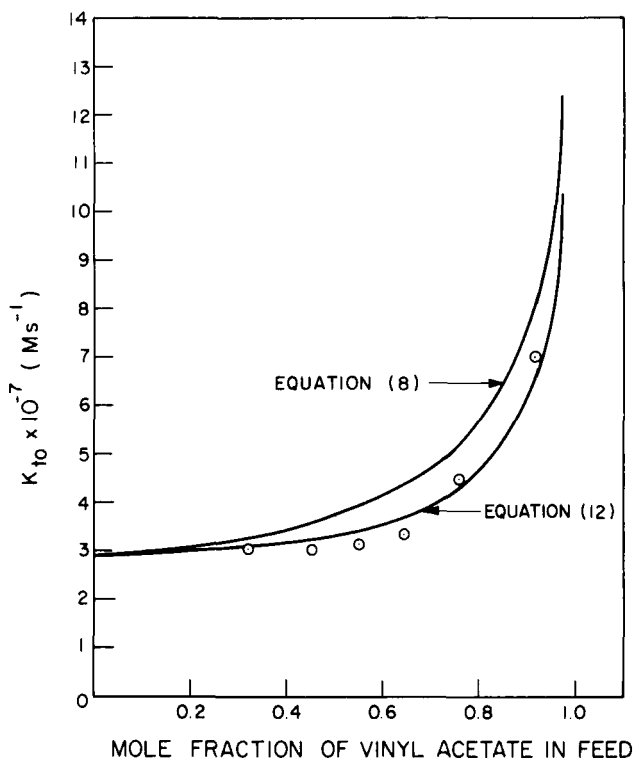[a]Reaction with 0.645 mole fraction vinyl acetate in feed taken as calibration value to normalize on R_i.

FIG. 2. Overall termination rate constant, k_{to}, for methyl methacrylate-vinyl acetate copolymerization. Circles are from data of Burnett and Gersmann [20] at 60°C. Curves are as predicted by Atherton and North [1] (Eq. 8) and the present (Eq. 12, $\phi = 1$) models.

again taken to be equal to 1 in the present model. The other kinetic parameters, from Atherton and North [1], are: r_1 28.6, r_2 0.035, k_{pAA} 589 Ms^{-1}, k_{tAA} 2.9×10^7 Ms^{-1}, k_{pBB} 3600 Ms^{-1}, and k_{tBB} 2.1×10^8 Ms^{-1}.

The comparisons in Tables 4 and 5 are inconclusive. It is useful, however, to take the analysis of the two models further in terms of the overall termination rate constant, k_{to}. Since Eq. (1) is common to both models, the experimental data can be inserted into this equation to estimate k_{to}. Figure 2 shows the k_{to} values calculated from the data of
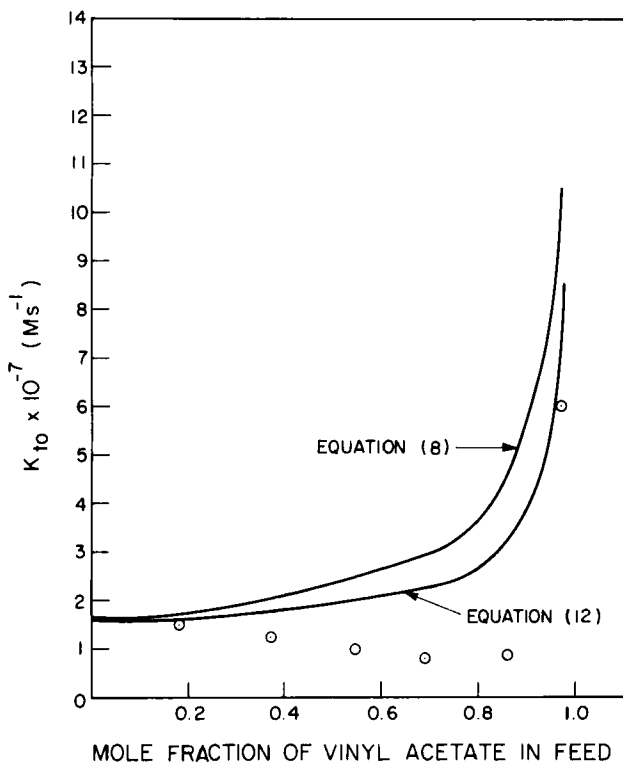
FIG. 3. Overall termination rate constant, k_{to}, for methyl methacrylate-vinyl acetate copolymerization. Circles are from data of Atherton and North [1] at 30°C. The curves are as predicted by Eqs. (8) and (12) with $\phi = 1$.

Burnett and Gersmann [20], which are listed in Table 5. The data curve predicted by the formulation in Eq. (8) is close to the experimental k_{to} data points, but Eq. (12) with $\phi = 1$ evidently produces an exact match within experimental uncertainty.

Figure 3 depicts the results of similar calculations based on the 30°C data of Atherton and North [1], which are compared in Table 4. Neither model follows the trend of k_{to} values with monomer feed composition as well as in the preceding figure. The predictions of Eq. (12) with $\phi = 1$ (present model) are again closer to the data points than the curve based on Eq. (8).

There seems to be some discrepancy between the conclusions indicated by the methyl methacrylate-vinyl acetate copolymerizations at 30 and 60°C. As shown in Fig. 2, Eq. (12) predicts the overall termination rate constant almost exactly, with ϕ taken as unity. The data points in Fig. 3 would suggest a value of $\phi < 1$ (homotermination favored over cross-termination). It seems unlikely that ϕ would vary markedly over such a small temperature range. Also, since no reason for a fractional ϕ is readily apparent, we are inclined to conclude that the situation suggested by Fig. 2 is the more general one.

DISCUSSION

Our model is evidently similar to that of Atherton and North [1]. It differs in the formulation of the overall termination rate constant and contains an adjustable parameter (ϕ) which is not present in the former model. The present model is able to account for copolymerization rates in the styrene-methyl methacrylate system which are not consistent with the formulation of k_{to} in Eq. (8). It fits the data in this case with a single value of ϕ, in contrast to Eq. (7) in which ϕ has been noted to depend on monomer feed composition [5, 6].

The predictive character of the present model can be enhanced by the following expedient.

An appropriate value of ϕ can be approximated for use in Eq. (12) from experimental r_1 and r_2 figures. Since a large value of ϕ indicates that cross-termination is a preferred reaction, polar effects may be expected to result in a tendency for alternating copolymerization and a low $r_1 r_2$ product in the particular system. An inverse relation is expected between ϕ and $r_1 r_2$ [21, 22]. An analytical relation is not anticipated since the model leading to Eq. (7) does not always yield ϕ values which are independent of monomer feed composition. An empirical plot can nevertheless be of some value in this context even though the ϕ values which are currently available were obtained by fitting data to the chemical control theory rather than to the present model.

Figure 4 shows a graph of the ϕ and $r_1 r_2$ data listed in this connection by Odian [23]. This representation is based on a few results from application of Eq. (7) and is meant for use only when each reactivity ratio is less than unity. The curve in Fig. 4 indicates a ϕ value of 3 for the styrene—α-methylstyrene system at 60°C, whereas the experimental data in this case are in fact fitted nicely with $\phi = 1$ [14]. This error is probably not very serious compared to the uncertainties in present absolute values of reactivity ratios and homopolymerization rate constants.

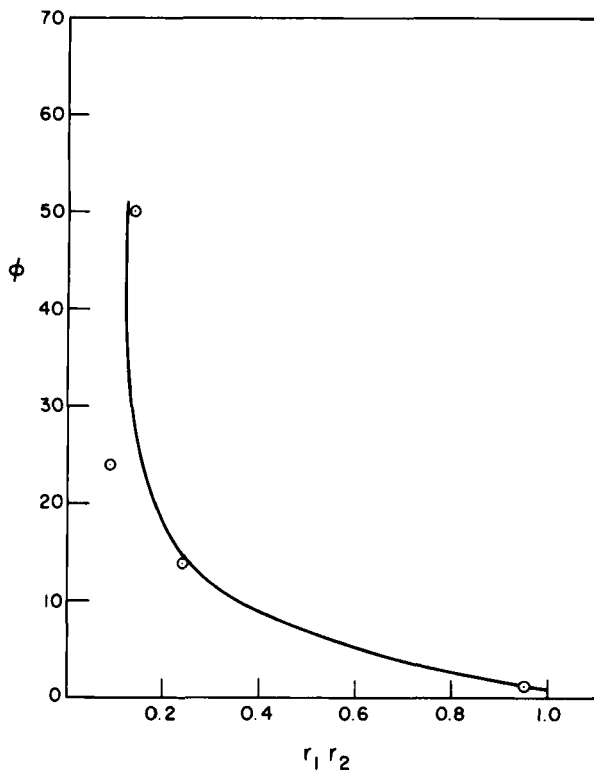This method of estimation of ϕ with Eqs. (1) and (12) results in a

FIG. 4. Cross-termination factor, ϕ, as a function of the reactivity ratio product, $r_1 r_2$, for $r_1 < 1$, $r_2 < 1$.

model with no adjustable parameters. As shown above, the formulation fits the rather limited experimental data very well. It is hoped that the model presented may be useful for practical predictive purposes although its empirical nature makes it unlikely that it will afford insights into the mechanism of radical copolymerizations.

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