An Alternate Approach to the Determination of Rate Parameters in Copolymerization*

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Synopsis

A new method which proposes the use of a steady state CSTR is presented for the determination of rate parameters in a copolymerization system. The approach does not limit the conversion levels in the reactor and allows precise estimation of reactivity ratios. In the presence of gel effect, the suggested approach additionally reveals the cumulative variations of termination rate processes with extent of conversion. Such an *a priori* method which enables estimation of rate parameters in the high conversion region has not been available in the literature previously. The method proposed is illustrated using copolymerization of styrene–methyl methacrylate as a model system.

INTRODUCTION

The overall rate of copolymerization depends on the relative rates of initiation, propagation, and termination of the monomer radicals. Dostal[1] was the first to devise a copolymerization reaction scheme by assuming that the rate of addition of a monomer to growing free radicals depends only on the nature of the radical chain end. Subsequently, the quasisteady state assumption was added to Dostal's reaction scheme (which implied that the initiation and termination rates be equal) and the overall polymerization rate was derived as[2]

$$R_p = \frac{(r_A C_A^2 + 2C_A C_B + r_B C_B^2) R_K^{1/2}}{[(r_A \delta_A C_A)^2 + 2\phi r_A r_B \delta_A \delta_B C_A C_B + (r_B \delta_B C_B)^2]^{1/2}} \quad (1)$$

where

$$r_A = k_{P_{AA}}/k_{P_{AB}}$$

$$r_B = k_{P_{BB}}/k_{P_{BA}}$$

$$\delta_A = (2k_{t_{AA}}/k_{P_{AA}}^2)^{1/2}$$

$$\delta_B = (2k_{t_{BB}}/k_{P_{BB}}^2)^{1/2}$$

$$\phi = k_{t_{AB}}/[2(k_{t_{AA}}k_{t_{BB}})^{1/2}]$$

$$R_k = 2fk_d C_k$$

Thus, in the classical terminal model described by eq. (1), the seven rate constants for chain growth and termination have been reduced to five rate parameters. r_A and r_B are the reactivity ratios, and they define the rate constant for a given chain end adding to its own monomer relative to that of the same chain end adding to the other monomer. δ_A and δ_B contain the rate constants of individual monomers

in homopolymerization, and ϕ is a measure of the cross-termination reaction, being the ratio of the rate constant for cross termination to the geometrical mean of the rate constants for symmetrical termination.

At low conversions, especially before the onset of the gel effect, the kinetic parameters are essentially independent of conversion. For a given initial composition of monomers and for a prescribed degree of conversion, the reactivity ratios are the key parameters in the production and control of a copolymer. The bulk of the literature in the area of copolymerization has been confined to the determination of reactivity ratios at low levels of conversion using batch reactors. Two recent reviews[3,4] have summarized the existing methods of determination of reactivity ratios, wherein a concise survey of the limitations of the known calculation procedures has been provided. Tidwell and Mortimer[5] have shown that considerable confusion exists as regards the experimentally determined values of reactivity ratios; indeed many workers, despite careful experimentation, have found difficulty in obtaining consistent results.

At high levels of conversions, the propagation and termination processes do not obey the classical model, and significant differences occur between the experimentally measured compositions and those calculated according to the copolymer composition equation [eq. (2)], using published reactivity ratios. The deviations begin with the start of the gel effect and increase with increasing conversion.[6] Presently no procedure that would allow the estimation of these deviations is available. The major concern of the present work is therefore to develop an alternative but self-consistent strategy to estimate the rate parameters for copolymerization at different levels of conversion.

ANOMALIES IN THE EXISTING PROCEDURES

In 1944, Mayo and Lewis[7] derived the simple copolymer equation

$$\frac{dC_A}{dC_B} = \frac{C_A}{C_B} \frac{r_A C_A + C_B}{r_B C_B + C_A} \tag{2}$$

This equation, which relates the polymer composition and initial monomer concentrations, is nonlinear in r_A and r_B, and, when there is a significant change in the relative monomer concentration, the use of eq. (2) results in biased estimates of the reactivity ratios. The magnitude of the differences between the biased r_A, r_B values and correctly computed values depends on
  (a) the conversion level reached in the formation of the polymer,
  (b) the actual reactivity ratios applicable to the system under study, and
  (c) the initial monomer compositions.
Evaluation of data by eq. (2) gives reactivity ratios measured under unsteady conditions. In general, analytical errors and reproducibility of the data cannot be checked for its adequacy in the use of unsteady reactors. Systematic errors, mainly occurring in physicochemical analytical procedures, are especially critical as they are latent mistakes and are revealed only in the change of r_A and r_B values.

The error in the reactivity ratios calculated using the differential form of the copolymer composition equation could be avoided at lower conversions by using any of the newly available estimation procedures:
  (1) integrated form of the copolymer equation,[8]
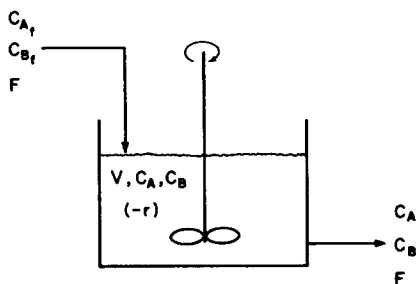 (2) analytical solution with weighting factor,[9]

Fig. 1. Continuous stirred tank reactor.

(3) method of grouping,[10]

(4) consideration of experimental errors in both variables,[3]

(5) quantitative gas chromatographic analysis and linear regression,[11] and

(6) nonlinear least square methods.[5,12]

All of the above methods, despite use of the integrated form of the copolymer equation, give biased estimates of the reactivity ratios when used at high conversion levels.

PROPOSED METHODOLOGY

We propose that the determination of the reactivity can be done by conducting the copolymerization in a continuous flow stirred tank reactor (CSTR). The use of CSTR to determine the kinetics of homogeneous reactions is well known in the chemical engineering literature.[13] In fact, under suitable conditions, the kinetics of even heterogeneous (viz., gas–solid catalytic) systems can be determined. Today specially designed CSTR such as a Berty reactor or a Carberry reactor is commercially available. It is indeed surprising that, despite its easy access and convenience, it has still not found wide use in copolymerization systems. To our knowledge, only a few experimental studies are reported in CSTR.[14,15] Bulk of the experimental systems are still carried out in batch reactors.

CSTR, as the name implies, is a reactor in which the contents are well stirred and uniform in composition throughout. The exit stream from this reactor has the same composition as the fluid within the reactor. The sketch of a typical CSTR is shown in Figure 1. With reference to this figure, the conservation equation for the reacting species can be written as

$$\text{accumulation} = \text{input} - \text{output} - \text{consumption due to reaction} \qquad (3)$$

In mathematical terms this can be rewritten as

$$V\frac{dC_A}{dt} = FC_{A_f} - FC_A - Vr \qquad (4)$$

where F represents the inflow per unit time (outflow assumed to be same), V is the volume of the reaction mixture, and r the reaction rate in appropriate units. At steady state the accumulation term in eq. (4) equals zero, rendering a simple algebraic equation

$$F\left(C_{A_f} - C_A\right) = Vr \qquad (5)$$

For a steady state copolymerization system involving two components A and B, eq. (5) can be written as

$$C_{A_f} - C_A = R_A\theta \quad \text{(for monomer A)} \tag{6}$$

$$C_{B_f} - C_B = R_B\theta \quad \text{(for monomer B)} \tag{7}$$

where θ represents the residence time V/F and R_A and R_B are the appropriate rates of polymerization defined as

$$R_A = k_A C_A C_k{}^{1/2} \tag{8}$$

$$R_B = k_B C_B C_k{}^{1/2} \tag{9}$$

with

$$C_k = C_{k_f}/(1 + k_d\theta)$$

The rate parameters k_A and k_B are functions of conversion and are defined as

$$k_A = [(r_A - 1)x + 1]/T_1^{1/2} \tag{10}$$

$$k_B = [(1 - r_B)x + r_B]/T_1^{1/2} \tag{11}$$

$$x = C_A/(C_A + C_B) \tag{12}$$

$$T_1 = T/(2fk_d) \tag{13}$$

and $T = (r_A\delta_A x)^2 + 2 \phi r_A r_B \delta_A \delta_B x(1 - x) + [r_B\delta_B(1 - x)]^2$.

The parameter T involves the constants corresponding to the termination rate processes. The combination of eqs. (10) and (11) eliminates the termination processes, and we obtain a single equation

$$\frac{k_A}{k_B} = \frac{(r_A - 1)x + 1}{(1 - r_B)x + r_B} \tag{14}$$

The equivalence of eq. (14) to the Mayo–Lewis equation [eq. (2)] is obvious. Indeed, eq. (14) may be rewritten as

$$\frac{k_A}{k_B} = \frac{(r_A - 1)x + 1}{(1 - r_B)x + r_B} = \frac{F_A}{F_B}\frac{C_B}{C_A} \tag{15}$$

Equation (15) may be regarded as the steady state version of the basic Mayo–Lewis equation and can be used to estimate the rate parameters for copolymerization at different levels of conversions.

Discussion of the Proposed Method

The proposed method offers several advantages. The advantages especially at low conversions are:

1. k_A and k_B in eq. (15) are the apparent rate constants and represent the ratio of propagation of individual monomers to the termination rate processes in copolymerization. The equation therefore embodies all the rate processes simultaneously occurring and is more appropriate for the estimation purposes.

2. In the Mayo–Lewis equation, one needs to determine the instantaneous values of the concentration of monomers in the polymer to determine the cumulative average composition of monomers (F_A and F_B) in the polymer. This difficulty is avoided in eq. (15), which requires only the concentration of the parent monomers in the reactor, which could be easily determined by the well-known experimental techniques. Once the concentrations of the monomers are

determined accurately, the rate of individual monomers are determined from eqs. (6) and (7) corresponding to different residence times in the reactor (i.e., at different conversions). k_A and k_B required in eq. (15) could then be evaluated directly from eqs. (8) and (9).

3. Since the copolymerization is conducted at steady state conditions, the reactivity ratios estimated are based on a large number of data points, collected at fixed levels of conversion. This is advantageous, since all errors arising from the analytical techniques could be reduced.

4. The use of eq. (15) does not restrict the conversion levels in the copolymerization experiments. At high levels of conversion, with the onset of gel effect, the reactivity ratios as also the other three rate parameters (δ_A, δ_B, and ϕ) start changing with the extent of conversion. Both k_t and k_p, which are incorporated in δ_A and δ_B [eq. (1)], are dependent on the extent of conversion of the monomer. The use of δ variations with conversion, as obtained from the homopolymerization, to copolymerization may be objectionable, since the transfer and gel effect processes may start affecting the δ values at different levels of conversion in the homo- and copolymerization systems. Hence in the absence of a feasible process to determine individually the variations of the rate parameters δ_A, δ_B, and ϕ with conversion, the variation of T_1, which embodies all the termination rate processes, is evaluated with conversion from eqs. (10) or (11).

5. It may be noted that the use of eq. (15) involves almost as much computation efforts as for the Mayo–Lewis equation. Further, many copolymerization systems may encounter a multiplicity region (see Balaraman et al.[16]) at high levels of conversion. Knowledge of the precise inlet and startup conditions of the re-
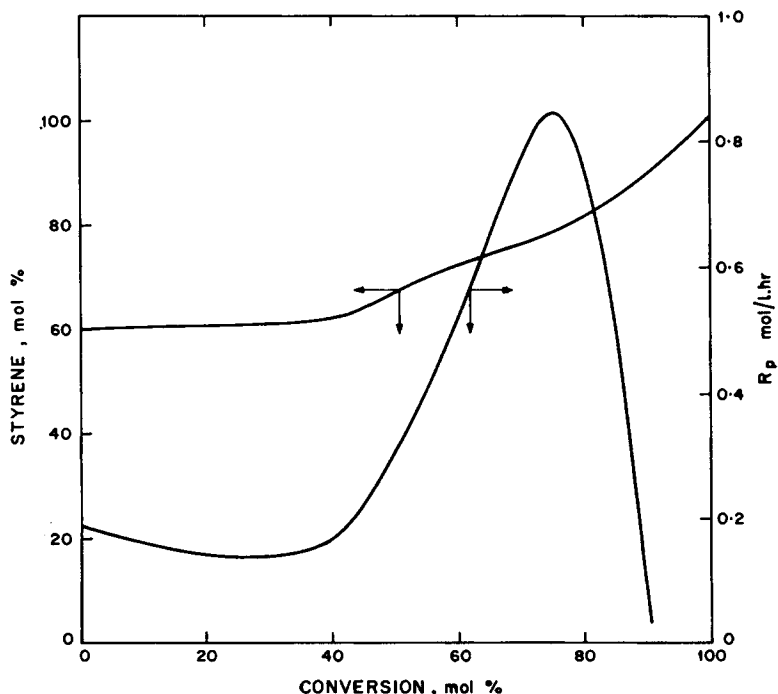

Fig. 2. Experimental data on styrene–methyl methacrylate system [redrawn from Dionisio and O'Driscoll (1979)].
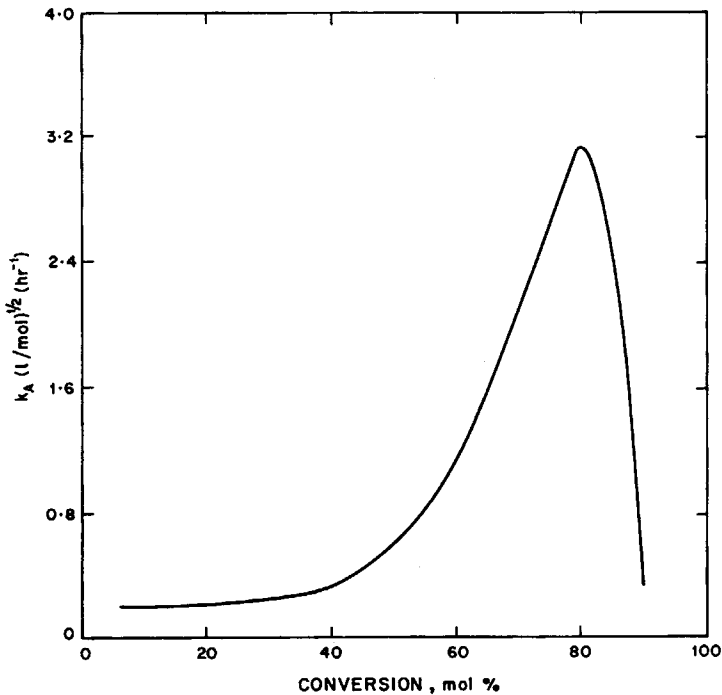
Fig. 3. Variation of k_A with conversion.

actor, therefore, will become essential to reach a steady conversion. While this is not a disadvantage, it certainly may require more information about the system. In spite of these minor deficiencies, eq. (15) still offers a unique and hitherto unreported method of *a priori* estimation of the rate parameters in copolymerization.

ILLUSTRATIVE EXAMPLE

In order to elucidate the methods proposed in this work, we analyze the data of Dionsio and O'Driscoll[17] for the styrene–methyl methacrylate system. Using benzoylperoxide as the initiator, the feed concentrations of monomers and initiator are given as

$$C_{A_f} = 5.35442 \text{ mol/L}, \quad C_{B_f} = 3.57464 \text{ mol/L}, \quad C_{K_f} = 0.00826 \text{ mol/L}.$$

The experimentally obtained rate of copolymerization, R_p, and the instantaneous mole fraction of styrene in the reacting monomer, x, at a conversion m are reproduced in Figure 2.

An Illustration of Estimation of Reactivity Ratios and T_1 with Extent of Conversion

The residence time θ required in a CSTR to achieve a given conversion is calculated from Figure 2 using the equation

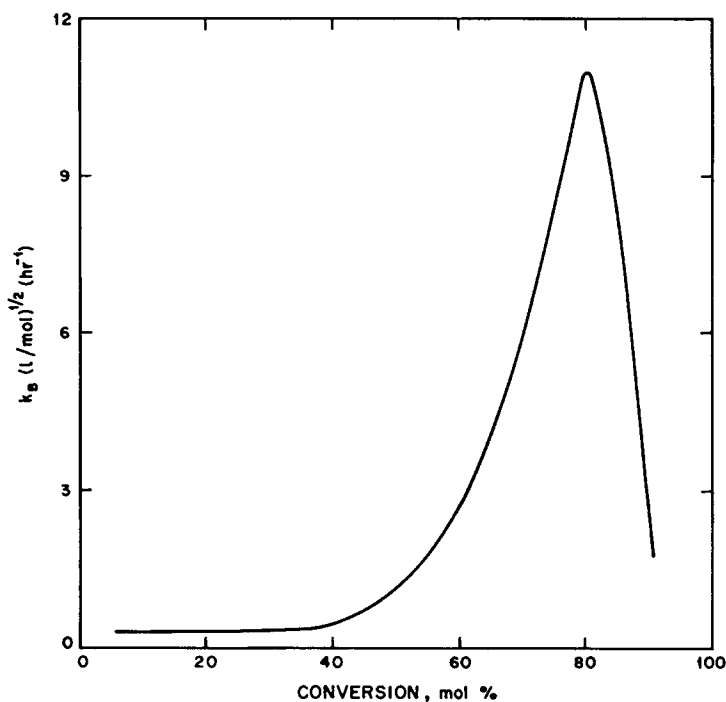$$\frac{m}{\theta} = \frac{R_p}{C_{A_f} + C_{B_f}} \tag{16}$$

Fig. 4. Variation of k_B with conversion.

The individual rates of polymerization (R_A and R_B) are calculated using eqs. (6) and (7) and the values of k_A and k_B are obtained using eqs. (8) and (9). k_A and k_B calculated at different levels of conversion are displayed in Figures 3 and 4. The reactivity ratios are calculated from eq. (15) using the computer program provided by Montgomery and Fry.[18] The reactivity ratios calculated are shown as a function of conversion in Figure 5. The reactivity ratios obtained at low levels of conversion (less than 20%) are $r_A = 0.5190$ and $r_B = 0.4732$, which compare well with the reported values in the literature. Once r_A and r_B are known, the parameter T_1 is calculated using eq. (10) or (11). The plot of $T_1^{1/2}$ as a function of conversion is illustrated in Figure 6 (curve A).

Comparison of Figures 5 and 6 reveals that rather drastic variations in r_A and r_B occur almost at about the same level of conversion ($\approx$ 20%) where the parameter T_1 also shows large variations. While the termination rate processes are known to be affected by the changes in the diffusion characteristics of the reaction system associated with the gel effect, the variations in r_A and r_B and hence of propagation rate constants appears surprising. A careful look at eq. (14), however, reveals that such a variation is theoretically possible. Figures 2–4 show the variation of x, k_A, and k_B with the extent of conversion. Examination of these figures indicate that k_B varies substantially in comparison with the variation of x and k_A for a given level of conversion. In order to compensate for the large variation of the ratio k_A/k_B [lhs of eq. (14)], it is apparent therefore that r_A and r_B should vary so as to satisfy eq. (14).
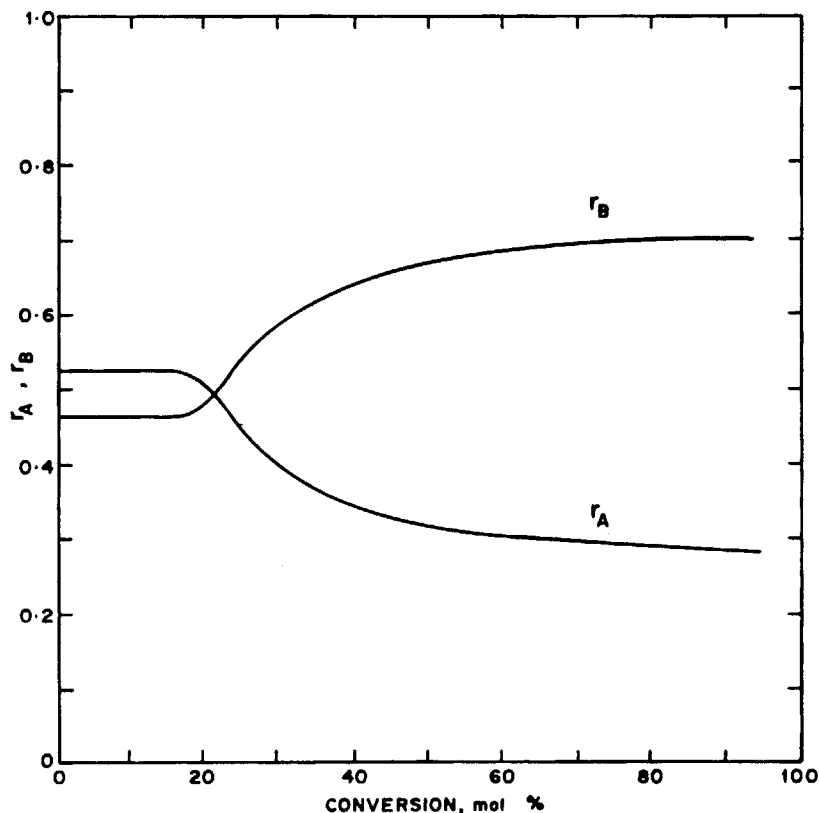
Fig. 5. Variation of r_A and r_B with conversion.

Cumulative Variation of Termination Rate Processes with Conversion

Let us examine the variation of T_1 with the extent of conversion (Fig. 6). T_1 contains the parameters r_A, r_B, and x besides the parameters δ_A, δ_B, and ϕ corresponding to the termination rate processes all of which are varying with the extent of conversion. In order to calculate the variation of T_1 due to the termination processes alone, we adopted the following procedure. Equation (13) is rewritten as follows:

$$T_1 = (r_A \delta'_A x)^2 + 2\phi r_A r_B \delta'_A \delta'_B x(1-x) + [r_B \delta'_B (1-x)]^2 \tag{17}$$

where

$$\delta'_A = \delta_A/(2fk_d)^{1/2} \quad \text{and} \quad \delta'_B = \delta_B/(2fk_d)^{1/2} \tag{18}$$

Evaluation of δ'_A and δ'_B requires the knowledge of fk_d, which can be estimated by making use of the propagation and termination constants for styrene and methyl methacrylate homopolymerizations reported in the literature at lower conversions.[19,20] At the temperature of operation (333°K), these constants are given as

$$k_{p_{AA}} = 0.145 \times 10^3 \text{ L/mol·s}$$
$$k_{p_{BB}} = 0.705 \times 10^3 \text{ L/mol·s}$$
$$k_{t_{AA}} = 2.9 \times 10^7 \text{ L/mol·s}$$
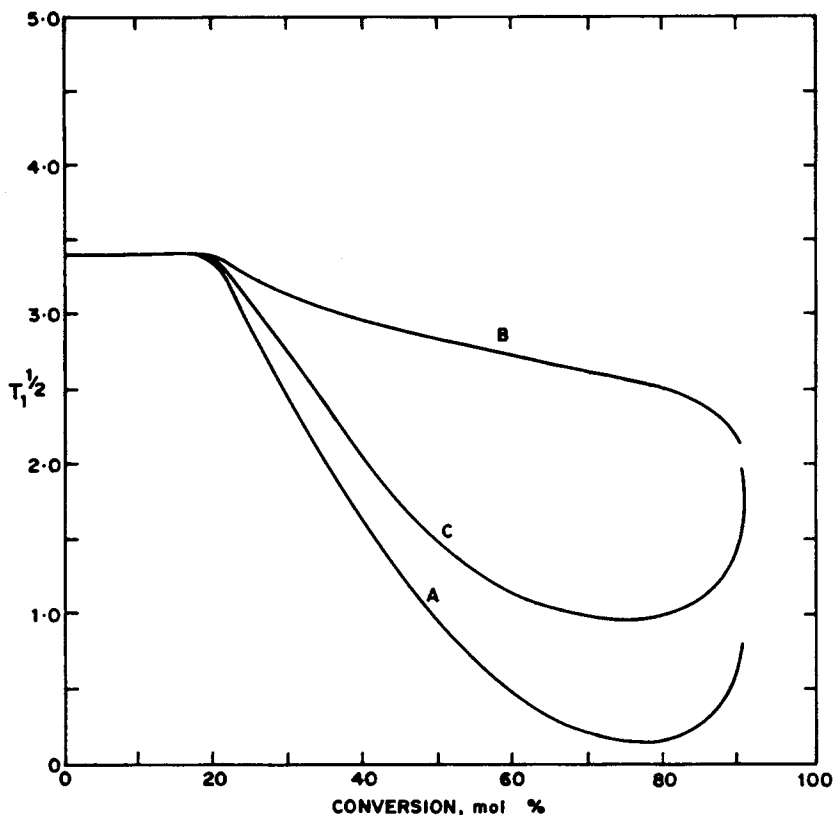$$k_{t_{BB}} = 2.55 \times 10^7 \text{ L/mol·s}$$

Fig. 6. Variation of T_1 with conversion.

$$\phi = 13$$

Knowing T_1 and T, it is possible to calculate fk_d from eq. (13) as

$$fk_d = 1.846 \times 10^{-6} \text{ s}^{-1}$$

Further, using $k_d = 2.6 \times 10^{-6}$ s^{-1} (see Ref. 20), we find $f = 0.71$.

We now assume δ'_A, δ'_B, and ϕ to be constants in eq. (17) and calculate $T_1^{1/2}$ due to the variation of r_A, r_B, and x with the extent of conversion. The plot is shown in Figure 6 (curve B). With reference to Figure 6, we note that curve A incorporates the variation of all the parameters (r_A, r_B, δ'_A, δ'_B, ϕ, x) with the extent of conversion, while curve B shows the influence of variation of r_A, r_B, and x only. The deviation between the two curves can therefore be attributed to the variations in the parameters δ'_A, δ'_B, and ϕ with the extent of conversion. This variation is shown in curve C. While it is not possible to obtain variations in the individual termination rate parameters with the extent of conversion, the total variations of the termination rate processes can be obtained easily.

CONCLUSIONS

1. The present work outlines an alternative and advantageous methodology for the determination of rate parameters in copolymerization at different levels of conversions.

2. The method employed does not limit the conversion levels in the reactor and allows precise estimation of reactivity ratios.

3. The method also permits the determination of the cumulative variation of termination rate processes with the extent of conversion explicitly.

4. The method proposed is illustrated for the important copolymerization system of styrene–methyl methacrylate.

NOMENCLATURE

C_A	concentration of monomer A
C_B	concentration of monomer B
C_K	concentration of initiator K
f	initiator efficiency for copolymerization
F	Flow rate of reactants
k_A, k_B	apparent rate constants defined by eqs. (10) and (11)
k_d	rate constant for initiator decomposition
$k_{P_{AA}}, k_{P_{AB}}, k_{P_{BA}}, k_{P_{BA}}, k_{P_{BB}}$	rate constants for propagation
$k_{t_{AA}}, k_{t_{AB}}, k_{t_{BA}}, k_{t_{BB}}$	rate constants for termination
m	conversion of monomers
R_A	rate of polymerization of monomer A
R_B	rate of polymerization of monomer B
R_k	rate of initiation
R_p	total rate of copolymerization
r	reaction rate in a CSTR defined by eq. (5)
r_A, r_B	monomer reactivity ratios
T, T_1	termination rate parameters defined by eq. (13)
V	volume of the reaction mixture
x	mole fraction of styrene in total monomer, defined by eq. (12)

Greek

δ_A, δ_B, ϕ	defined by eq. (1)
δ'_A, δ'_B	defined by eq. (18)
θ	residence time

Subscripts

A	monomer A
B	monomer B
K	initiator
f	feed

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