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Non-uniqueness of penultimate model reactivity ratios and treatment of kinetic data

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Abstract

Non-linear curve-fitting regression method using parametric equation as 'user model' has been utilized to determine reactivity ratios signifying effects of terminal and penultimate groups in copolymerization. Residuals, standard errors and correlation coefficients have been compared with those of terminal model using Fukuda's data on styrene–methyl methacrylate copolymerization. Non-uniqueness and occurrence of two sets of values for the penultimate model reactivity ratios have been explained on the basis of specified feed composition calculations. The two sets of reactivity ratios corresponding to explicit penultimate model have been used for treatment of kinetic data and consistent and acceptable values of various kinetic constants have been obtained with only one set. The value of ϕ obtained corresponds very closely to theoretically predicted value.
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1. Introduction

It is generally accepted that compositions of most free-radically derived copolymers conform to two-reactivity ratios concept of terminal model [1]. One does not usually carry out rigorous analysis of polymer composition data in the feed composition range of interest and is inclined to tolerate considerable scatter as experimental uncertainties. Other models such as penultimate [2–4], complex-participation [5] and complex-dissociation [6] have been enunciated and tested for some copolymerizations. The situation is, however, overwhelmingly complex when one considers rates of copolymerizations even though Fukuda et al. [7,8] have attempted mathematical solutions for the rate equation based on penultimate model using adjustable parameters which seem to be related to the reactivity ratios and their products. The pioneering works of Fukuda et al. [7,8] have opened up possibilities of explaining the apparently anomalous behavior of copolymerization systems as

have been recently discussed [9]. However, it is accepted that both powerful experiments and uniqueness of methods of analysis are important to accept the validity or otherwise of particular model for a copolymerization system [10,11].

There has been a number of publications on determination of reactivity ratios mostly based on statistical and computational methods [10–21] and it is accepted that non-linear least square and other computational methods give more reliable results than the linearization methods or graphical methods [22–24]. However, there are unresolved issues such as choice of initial guess values [20,21], their influence on the computed values and the ability of more than one set of reactivity ratios to reasonably explain copolymer compositions [11,12,21] having comparable standard deviation.

In this communication, we use non-linear regression curve fitting to appropriate compositional equation containing the four reactivity ratios and address the issue of existence of two sets of reactivity ratios, particularly those representing the effect of penultimate groups. These two sets of reactivity ratios that explain compositional data are then applied to kinetic data of Fukuda et al. [7]. Values of various kinetic constants are determined using NLLS method [25] and compared with values available in

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literature. This allows one to identify the acceptable set of reactivity ratios and examine the applicability of explicit/implicit penultimate model in copolymerization.

2. Theoretical expressions

We would begin with the compositional equation containing four possible reactivity ratios r_1, r_2, r_1' and r_2' for low conversion.

$$y = \frac{\left\{1 + \dfrac{r_1'x(r_1x + 1)}{r_1'x + 1}\right\}}{\left\{1 + \dfrac{r_2'(r_2 + x)}{x(r_2' + x)}\right\}} \tag{1}$$

where $y = F_1/F_2 =$ molar ration of monomers in copolymer and $x = f_1/f_2 =$ molar ratio of monomers in feed; $r_1 = k_{111}/k_{112}$, $r_2 = k_{222}/k_{221}$, $r_1' = k_{211}/k_{212}$, $r_2' = k_{122}/k_{121}$ k_{ijl}'s are the specific rate constants of propagation of radical centre j preceded by monomer unit i and reacting with monomer l (i, j and l may each be monomer type 1 or 2).

Mole fraction F_1 of monomer-1 in copolymer is related to x as follows:

$$F_1 =$$

$$\frac{r_1r_1'x^4 + (r_1r_1'r_2' + 2r_1')x^3 + (2r_1'r_2' + 1)x^2 + r_2'x}{r_1r_1'x^4 + (r_1r_1'r_2' + 3r_1')x^3 + (4r_1'r_2' + 2)x^2 + (3r_2' + r_1'r_2r_2')x + r_2r_2'} \tag{2}$$

F_1 will be used in our analysis in preference to y due to inherent experimental error in determining copolymer compositions, whereas x is used to represent monomer-feed, as the experimental error in f_1 is considered negligible. Also, the coefficients in the expression relating F_1 and f_1 in power series form are somewhat more complicated.

In non-linear curve-fitting regression method [25] using the parametric equation as 'user model', we initially assume $r_1 = r_1'$ and $r_2 = r_2'$ as guess values to obtain values of the four reactivity ratios as near acceptable values through multiple iterations. Values so obtained are used as guess values to obtain the final values of reactivity ratios. Subsequently, we determine the sum of squared residuals, standard deviation and correlation coefficient. These are then compared with the values calculated for the purely terminal model ($r_1 = r_1'$, $r_2 = r_2'$). Strictly speaking, comparison of fit of experimental and derived copolymer composition values does not appear appropriate as the reactivity ratios r_1 and r_2 determined using two-parameter equation contain contribution of penultimate effect, however, small, and hence of r_1' and r_2'. The fact that two-parameter model explains copolymer compositions of styrene–methyl methacrylate system is an exceptional case probably because of nearness in the values of r_i and r_i' and of r_1 and r_2.

An important aspect of the present communication as will be explained below relates to more than one set of values for the reactivity ratios [11,12,21]. Once a curve-fit is obtained with reasonably good standard error of estimate and correlation coefficient, one can apply the following to the computed F_1–x curve:

at $y = 1$, $F_1 = 0.5$, $x = x_1$ (say) and

at $y = 2$, $F_1 = 0.66\ldots$, $x = x_2$ (say)

(in fact this choice is not restricted to $y = 1$ and $y = 2$ and can include any set of two values depending on the nature of the curves and availability of F_1 values at various x).

Using expression for F_1 as in Eq. (2), one obtains for r_1' and r_2' equations as follows:

$$Ar_1'^2 + Br_1' + C = 0 \tag{3}$$

and

$$r_2' = \frac{r_1'(r_1x_1^4 + x_1^3)}{(r_2 + x_1) + r_1'(r_2x_1 - r_1x_1^3)} \tag{4}$$

where

$$A = r_1x_2^4(r_2x_1 - r_1x_1^3) - (r_1x_1^4 + x_1^3)(2x_2^2 + 2r_2x_2 - r_1x_2^3)$$

$$B = r_1x_2^4(r_2 + x_1) - x_2^2(r_2x_1 - r_1x_1^3) - (r_1x_1^4 + x_1^3)$$
$$\times(2r_2 + 3x_2)$$

$$C = -x_2^2(r_2 + x_1)$$

As is evident from Eq. (3), r_1' is expected to give two values, real or imaginary depending on values of A, B and C. Accordingly, r_2' will also have same number of values. This information lends support to published conclusion that multiple pair of r_1' and r_2' values very different from each other seem to fit compositional data quite convincingly even for the system styrene–methyl methacrylate copolymerization which is considered to be a classical case when penultimate unit effect is negligible. Though penultimate unit effect has been elaborately described and identified in propagation by Fukuda et al. [7,8,26], to the best of our knowledge no comprehensive treatment has been made so far to test rate data directly and determine radical reactivity ratios and cross termination constant. It would be useful if method could be developed to determine these parameters and test the agreement between experimental and theoretical values of rate of copolymerization and specific rate constant of propagation.

Using R_i and R_p as the rates of initiation and copolymerization and $x = [M_1]/[M_2]$, the ratio of monomer concentrations in the feed at low conversions, we obtain under steady state conditions, appropriate relationship connecting these quantities with r_1, r_2, r_1', r_2', s_1, s_2, δ_1 ($= k_{111}/k_{t1}^{0.5}$), δ_2 ($= k_{222}/k_{t2}^{0.5}$) and $2\Phi(= k_{t12}/k_{t1}^{0.5}k_{t2}^{0.5})$, r_i and s_i being the monomer and radical reactivity ratios [7–9].
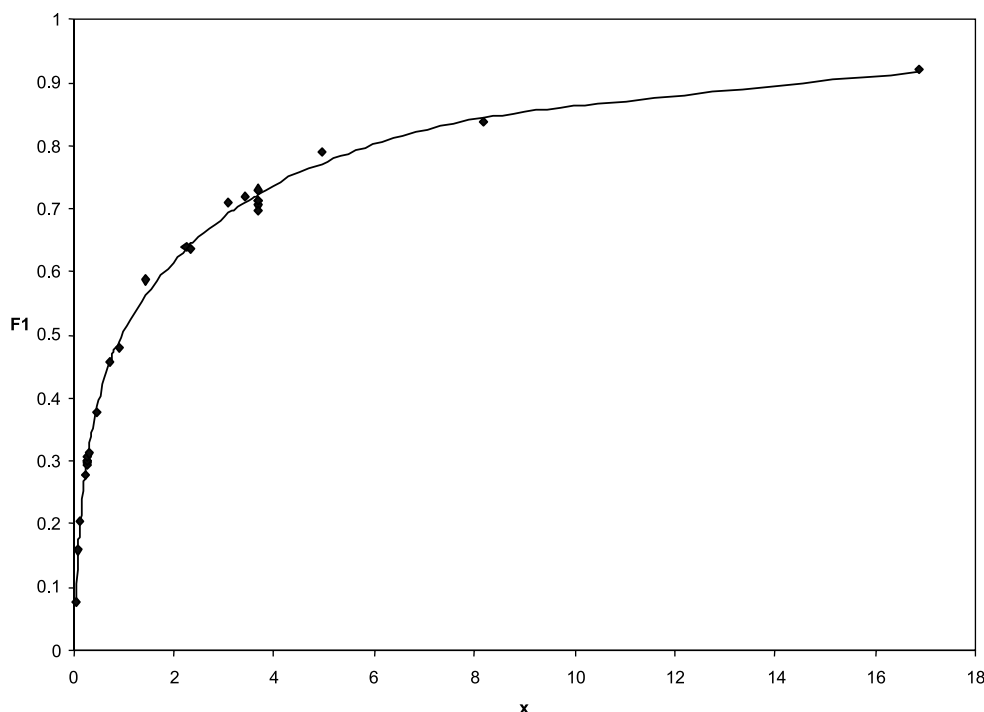
Fig. 1. Plot of F_1 vs. x for styrene–methyl methacrylate copolymerization [7] obtained through non-linear curve-fitting regression. (guess values: $r_1 = r_1' = 0.523$, $r_2 = r_2' = 0.46$). Values obtained: $r_1 = 0.6676$, $r_2 = 0.5048$, $r_1' = 0.3102$, $r_2' = 0.3220$ (—), computed curve; ($\bullet$), experimental data.

$$\frac{R_\mathrm{p}}{R_\mathrm{i}^{1/2}[\mathrm{M}_2]} =$$

$$\frac{r_1 r_1' x^4 + (3r_1' + r_1 r_1' r_2') x^3 + (4r_1' r_2' + 2)x^2 + (3r_2' + r_1' r_2 r_2')x + r_2 r_2'}{(A_1 x^6 + B_1 x^5 + C_1 x^4 + D_1 x^3 + E_1 x^2 + F_1 x + G_1)^{1/2}}$$

$$(5)$$

where

$$A_1 = r_1^2 r_1'^2 \delta_1^2,$$

$$B_1 = r_1 r_1'^2 \delta_1^2 / s_1 + 2r_1 r_1'^2 r_2' \delta_1 \delta_2 \Phi / s_2 + 2r_1^2 r_1'^2 r_2' \delta_1^2$$

$$C_1 = r_1^2 r_1'^2 r_2'^2 \delta_1^2 + r_1'^2 \delta_1^2 / s_1^2 + 2r_1 r_2 r_2' r_1'^2 \delta_1 \delta_2 \Phi$$

$$+2(r_1' + r_2' r_1'^2) r_1 r_2' \delta_1 \delta_2 \Phi / s_2 + 2r_1 r_2' r_1'^2 \delta_1^2 / s_1$$

$$+ r_1'^2 r_2'^2 \delta_2^2 / s_2^2 + 2r_1'^2 r_2' \delta_1 \delta_2 \Phi / (s_1 s_2),$$

$$D_1 = r_1 r_1'^2 r_2'^2 \delta_1^2 / s_1 + 2r_1 r_1' r_2'^2 \delta_1 \delta_2 \Phi / s_2 + 2r_1 r_2 (r_1'^2 r_2'^2$$

$$+ r_1' r_2') \delta_1 \delta_2 \Phi + 2r_2 r_2' r_1'^2 \delta_1 \delta_2 \Phi / s_1 + r_2 r_1'^2 r_2'^2 \delta_2^2 / s_2$$

$$+ 2r_1' r_2'^2 \delta_2^2 / s_2^2 + 2r_2' r_1'^2 \delta_1^2 / s_1^2 + 2r_1' r_2' (r_1' r_2'$$

$$+ 1) \delta_1 \delta_2 \Phi / (s_1 s_2),$$

$$E_1 = 2r_1 r_2 r_1' r_2'^2 \delta_1 \delta_2 \Phi + r_2^2 r_1'^2 r_2'^2 \delta_2^2 + 2r_1' r_2 (r_1' r_1'^2$$

$$+ r_2') \delta_1 \delta_2 \Phi / s_1 + r_1'^2 r_2'^2 \delta_1^2 / s_1^2 + 2r_2 r_1' r_2'^2 \delta_2^2 / s_2 + r_2'^2 \delta_2^2 / s_2^2$$

$$+ 2r_1' r_2'^2 \delta_1 \delta_2 \Phi / (s_1 s_2),$$

$$F_1 = 2r_1' r_2^2 r_2'^2 \delta_2^2 + 2r_1' r_2 r_2'^2 \delta_1 \delta_2 \Phi / s_1 + r_2 r_2'^2 \delta_2^2 / s_2,$$

$$G_1 = r_2^2 r_2'^2 \delta_2^2.$$

Since r_1, r_2, r_1' and r_2' are determinable from composition analysis and R_p and R_i are available from experiments, the above relationship can be used as a user model and treated by non-linear curve-fitting regression method [23] to determine s_1, s_2, δ_1, δ_2 and Φ. This will enable us to finally calculate the values of $k_{\mathrm{p}\_}$, the overall propagation rate constant as a function of monomer feed composition and verify one of the main premises on which Fukuda's analysis is based. The calculated value of ϕ will also indicate the extent of success of experimental data to justify theoretical prediction.

3. Results and discussion

Fig. 1 shows plot of F_1 vs. x_1, which is used to calculate values of x_1 and x_2 for determining the second set of reactivity ratio values. The values of r_1, r_2, r_1' and r_2' obtained through non-linear regression are 0.6676, 0.5048, 0.3102, and 0.3220, respectively. Further use of these values

Table 1
Reactivity ratios, sum of square of residuals (SSR), standard error (SE) and correlation coefficient (R) for copolymerization of styrene and methyl methacrylate [7]

Reactivity ratios	$SSR \times 10^4$	$SE \times 10^2$	R	Remarks
$r_1 = 0.523$ $r_2 = 0.460$	36.1180	1.2280	0.9987	Ref. [7]
$r_1 = 0.6676$ $r_1' = 0.3102$ $r_2 = 0.5048$ $r_2' = 0.3220$	32.2821	1.2113	0.9989	Through non-linear curve fitting—data Ref. [7]
$r_1 = 0.6676$ $r_1' = 3.2793$ $r_2 = 0.5048$ $r_2' = 4.4821$	32.7737	1.2205	0.9989	Through x_1, x_2 computation $x_1 = 0.967589$; $x_2 = 2.663010$—data Ref. [7]
$r_1 = 0.6676$ $r_2 = 0.5048$	146.0726	2.4670	0.9980	Considering effect of terminal units only

as guess values does not significantly alter the values of the reactivity ratios as well as the values of correlation coefficient and standard deviation. Values of x_1 (at $F_1 = 0.5$) and x_2 (at $F_1 = 0.667$) computed from the curve are 0.9676 and 2.6630, respectively. Two sets of real values of r_1' and r_2' obtained using $r_1 = 0.6676$ and $r_2 = 0.5048$ are $r_1' = 0.3103$ and 3.2793 and $r_2' = 0.3220$ and 4.4821, respectively. One set of values for r_1' and r_2' corresponds exactly to the values obtained through non-linear curve fitting while the other set, i.e. $r_1' = 3.2793$ and $r_2' = 4.4821$ represents substantially higher values. To examine the reliability of the sets of values obtained, we computed the sum of square of residuals (SSR) of copolymer compositions using the following two sets of the reactivity ratios:

$r_1 = 0.6676$	$r_1 = 0.6676$
$r_2 = 0.5048$	$r_2 = 0.5048$
$r_1' = 0.3102$	$r_1' = 3.2793$
$r_2' = 0.3220$	$r_2' = 4.4821$

For reference, we have also calculated the SSR neglecting effect of penultimate unit ($r_1 = r_1'$ and $r_2 = r_2'$) and using $r_1 = 0.523$ and $r_2 = 0.460$ and are shown in Table 1. As is seen, the sum of the square of residuals indicate a slightly better fit and interpretation of the copolymer composition data of styrene–methyl methacrylate by the reactivity ratios determined by the non-linear curve-fitting method and two-point method (x_1, x_2) compared to terminal model values. The values of reactivity ratios obtained from the non-linear curve-fitting corresponds very closely to the values obtained by Moad et al. [10] and both the sets of values show considerable effect of penultimate groups, which can not be neglected.

The present work brings out that copolymer composition of styrene–methyl methacrylate monomer pair can be adequately explained in terms of the effect of penultimate units in addition to terminal units. Clearly identifiable and distinguishable values of r_1' and r_2' signifying the effect of penultimate unit do exist and need to be considered to explain the system meaningfully. The values of r_1 and r_2

computed are quite different from the values generally used [7] and indicate that neglect of penultimate effect may give only apparent and not real values of r_1 and r_2. Since styrene–methyl methacrylate system is generally considered a representative of terminal model it appears logical to conclude that penultimate unit effect deserves to be considered as general.

Even though two values each of r_1' and r_2' appear chemically unrealistic, in view of their ability to convincingly explain the compositional data, it may be necessary to consider both sets of values for analysis of rate data before discarding any one set. Kaim and Oracz [11,12] pointed out that penultimate model would probably always give multiple sets of reactivity ratios with comparable standard deviations while analyzing the two sets of values determined by Schweer [21]. This was based on purely statistical analysis without reference to theoretical possibility of existence of two sets of reactivity ratios signifying penultimate group effect. While the authors did not indicate a reason, the present analysis shows that there will be always two sets [21] of r_1' and r_2' values for each set of r_1 and r_2 as embodied in the basic equation of polymer composition which includes the effect of penultimate group on the radical-monomer reactivity [27]. It is pertinent to mention here that the transformation of Eqs. (2)–(3) is not restricted to $F_1 = 0.50$ and 0.667 but is general for any value of $F_1 = p$ ($p < 1$). Thus, the quadratic form of Eq. (3) is a theoretical outcome indicating existence of two values for r_1' and hence of r_2'. However, the two sets of values determined here may belong to the series of statistically adequate solutions.

To ascertain that the two sets of values of r_1' and r_2' give only one set of values of r_1 and r_2, expressions for r_1 and r_2 were derived involving r_1', r_2', x_1 and x_2. Values of r_1 and r_2 obtained are $r_1 = 0.6676$, 0.6676 and $r_2 = 0.5049$, 0.5048, respectively. This indicates the uniqueness of the values of r_1 and r_2 determined by the present method. The present method is thus essentially different from purely statistical

Table 2
Kinetic parameters of styrene–methyl methacrylate copolymerization [7] obtained through non-linear curve-fitting regression using Eq. (5)

Reactivity ratios	Values of parameters
Set-1	
$r_1 = 0.6676$, $r_2 = 0.5048$	$\delta_1 = 80.9063$, $\delta_2 = 16.5497$, $\Phi = 1.2845$
$r_1' = 0.3102$, $r_2' = 0.3220$	$s_1 = 0.2547$, $s_2 = 0.3597$ (SS = 1.50×10^{-4}, $R = 0.99993$)
Set-2	
$r_1 = 0.6676$, $r_2 = 0.5048$	$\delta_1 = 73.310$, $\delta_2 = 15.6409$, $\Phi = 0.4617$
$r_1' = 3.2793$, $r_2' = 4.4821$	$s_1 = 0.4760$, $s_2 = 0.3402$ (SS = 2.21×10^{-4}, $R = 0.99984$)
Set-3	
$r_1 = r_1' = 0.5230$, $r_2 = r_2' = 0.4600$	$\delta_1 = 83.9988$, $\delta_2 = 6.9491$, $\Phi = 3.1040$
	$s_1 = 0.2358$, $s_2 = -0.3284$ (SS = 1.93×10^{-4}, $R = 099988$)

Guess values used [7]: $\delta_1 = 76.83$, $\delta_2 = 14.53$, $\Phi = 1.00$, $s_1 = 0.30$, $s_2 = 0.53$.

analysis where r_1 or r_2 or both are also different for different sets of reactivity ratios signifying penultimate group effect.

For comparison, we have also used $r_1 = 0.6676$ and $r_2 = 0.5048$ as guess values to fit the two parameter terminal model. It is interesting to note that the fitted curve shows $r_1 = 0.526$ and $r_2 = 0.460$ as the best values. This suggests that as far as application of two-parameter model to this system is considered, Fukuda's values appear most convincing and do not warrant more accurate determination of r_1 and r_2. Use of presently determined values of reactivity ratios as the terminal model values leads to a hopeless situation (standard error of estimate = 2.4670×10^{-2}) thereby indicating that they do not represent values of an exclusively terminal model.

Recent studies [9,11,18] show that there are distinctly identifiable and significant values of reactivity ratios indicating effect of penultimate units in controlling both compositions of copolymers and rates of copolymerization. The effect of penultimate units appears to operate through both the monomers (r_{ij}) and radicals (s_i) reactivity ratios rather than only through the latter as proposed by Fukuda et al. [7] in styrene–methyl methacrylate copolymerization. Moreover, it can be easily seen that $s_1 = k_{211}/k_{111} = (r_1'/r_1)$. k_{212}/k_{112}, so that when $r_1 = r_1'$, $k_{211}/k_{111} = k_{212}/k_{112}$. This means that the ratio of propagation rate constants of a radical is same for both the monomers. Similar conclusion applies for s_2. This is hard to comprehend and it seems that concept of radical reactivity ratios are meaningful only in presence of r_1' and r_2'.

Non-linear curve fitting regression as per Curve-Expert 1.3 [25] with Eq. (5) in square form as user model and using reactivity ratios determined here was performed on the rate of copolymerization data of Fukuda et al. [7]. Guess-values used in all the three cases (sets of reactivity ratios)
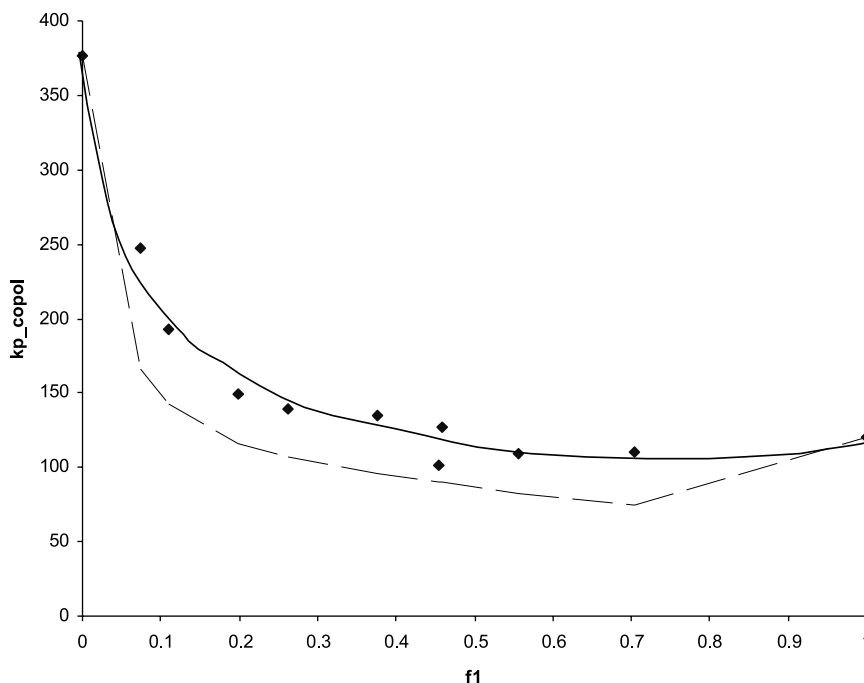

Fig. 2. Variation of k_{p_-}, the overall rate constant of propagation of styrene–methyl methacrylate copolymerization with f_1, mole fraction of styrene (♦), experimental data of Fukuda et al. [7]; (—), calculated curve using $r_1 = 0.6676$, $r_2 = 0.5048$, $r_1' = 0.3102$, $r_2' = 0.3220$, $s_1 = 0.2547$, $s_2 = 0.3597$; (- - -), calculated curve using $r_1 = 0.6676$, $r_2 = 0.5048$, $r_1' = 3.2793$, $r_2' = 4.4821$, $s_1 = 0.4760$, $s_2 = 0.3402$.
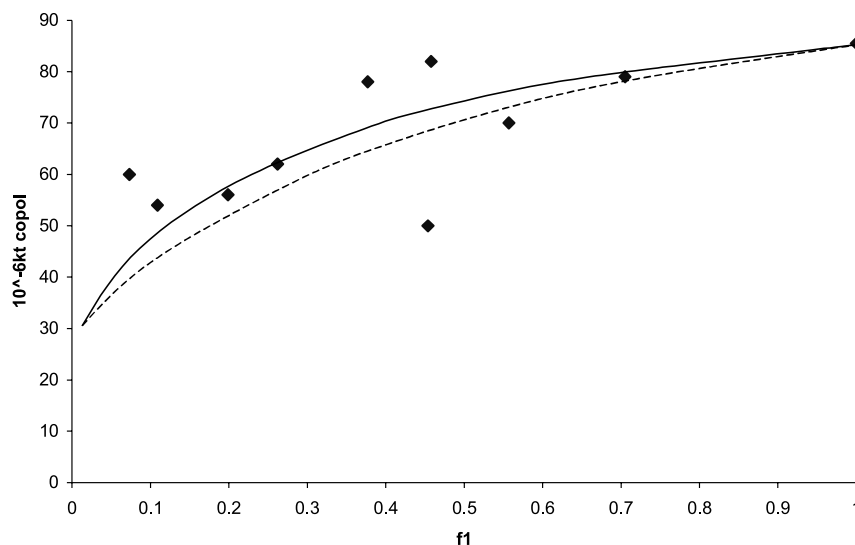
Fig. 3. Variation of k_t, the overall rate constant of termination for styrene–methyl methacrylate copolymerization with f_1, mole fraction of styrene in monomer feed. ($\blacklozenge$), experimental curve [7]; (- - -), calculated values using $r_1 = 0.6676$, $r_2 = 0.5048$, $r'_1 = 3.2793$, $r'_2 = 4.4821$, $\Phi = 0.4617$, $k_{t1} = 85 \times 10^6$, $k_{t2} = 30 \times 10^6$; (—), calculated curve using $r_1 = 0.6676$, $r_2 = 0.5048$, $r'_1 = 0.310$, $r'_2 = 0.3220$, $\Phi = 1.2845$, $k_{t1} = 85 \times 10^6$, $k_{t2} = 30 \times 10^6$.

are: $\delta_1 = 76.83$, $\delta_2 = 14.53$, $s_1 = 0.30$, $s_2 = 0.53$ and $\Phi = 1$. Values of these constants obtained from non-linear regression are presented in Table 2 for two sets of reactivity ratios obtained along with implicit penultimate model reactivity ratios of Fukuda et al. [7]. It appears that the set of reactivity ratios viz., $r_1 = 0.6676$, $r_2 = 0.5048$, $r'_1 = 0.3102$ and $r'_2 = 0.3220$ gives a better fit to rate data compared to the other set of reactivity ratios considering the standard error and the correlation coefficient. However, in the case of implicit penultimate model, negative value of s_2 is obtained indicating apparent failure (without assuming $\Phi = 1$). Applicability of the computation program is reflected in reasonable values of δ_1 and δ_2, which vary within 73–81 and 15–17, respectively. These values are very near to values reported in literature [3,28]. Value of Φ is not far removed from unity as required on theoretical ground and as obtained from small radical–radical reactions. This is probably the first attempt to obtain Φ from rate data incorporating effect of penultimate group in propagation steps.

We have used the values of various constants computed using non-linear curve-fitting regression to determine the $k_{p\_}$ (overall copolymerization propagation constant) as a function of monomer feed compositions using relationships given by Fukuda et al. [7] and compare these with the experimentally determined values. Fig. 2 shows variation of $k_{p\_}$ with mole fraction of styrene in the feed. We have used k_p values as 377 and 120 for MMA and styrene as average values of Fukuda et al. [7] in preference to 500 and 160 [29] for a realistic comparison with the experimental values. It is observed that the ratio of calculated and experimental values lie between 1.3 and 1.5 as with the values for the pure monomers when recent and improved values are considered. It is evident that the set of reactivity ratios representing higher r'_1 and r'_2 does not explain the experimental data

while the set of reactivity ratios with lower r'_1 and r'_2 represent the experimental data very well.

We have also calculated the rate constant of termination for copolymerization for styrene–methyl methacrylate using the computed values of the various constants and compared with the experimental values of Fukuda et al. [7]. In using the explicit model, however, the radical population expression will include the radical and monomer reactivity ratios in addition to rate constants of propagation for homo-polymerization. Assuming stationary-state copolymerization, we have,

$$(k_{112} + k_{212})p_1f_2 = (k_{121} + k_{221})p_2f_1$$

Introducing the reactivity ratios, we have,

$$p_1 = \frac{f_1}{f_1 + (k_{p1}/k_{p2})(1/r_1 + s_1/r'_1)/(1/r_2 + s_2/r'_2)} \quad (6)$$

where, p_1 is the radical population fraction of chain radicals ending in styrene, k_{pi} is the rate constant of propagation of monomer i, f_1 being the mole fraction of monomer-1, other symbols having their usual meaning.

The termination rate constant of copolymerization k_t is given [30] as $k_t = k_{t11}p_1^2 + 2k_{t12}p_1p_2 + k_{t2}p_2^2$ and $p_1(=1-p_2)$ being as given by Eq. (6). Fig. 3 shows variation of k_t, overall rate constant of termination in styrene–methyl methacrylate copolymerization with f_1, mole fraction of styrene. While the experimental data are quite scattered, the calculated curves appear to represent them reasonably well, particularly with the following set of parameters: $r_1 = 0.6676$, $r_2 = 0.5048$, $r'_1 = 0.3102$, $r'_2 = 0.3220$, $s_1 = 0.2547$, $s_2 = 0.3597$ and $\Phi = 1.2840$. The set of reactivity ratios representing higher values of r'_1 and r'_2 gives relatively lower values of k_t as was also seen in the case of $k_{p\_}$ indicating that they do not sufficiently explain the experimental data.
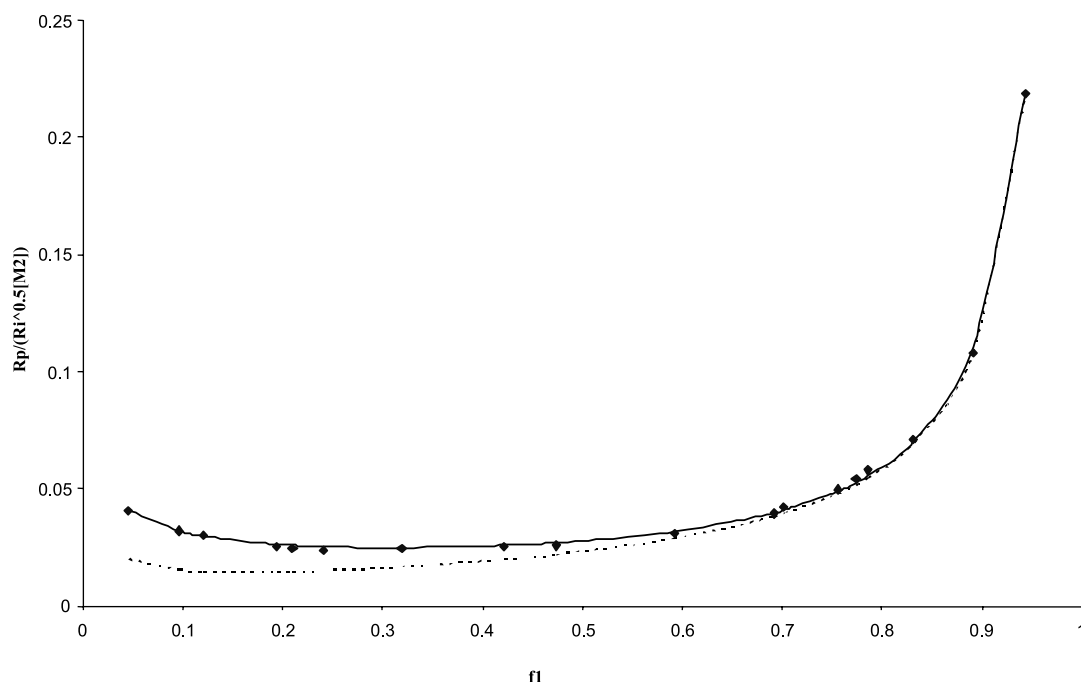
Fig. 4. Variation of $R_p/(R_i^{0.5}[M_2])$ with f_1 for styrene–methyl methacrylate copolymerization (♦), Fukuda's data [7]; (—), calculated curve using $r_1 = 0.6676$, $r_2 = 0.5048$, $r_1' = 0.3102$, $r_2' = 0.3220$, $s_1 = 0.2547$, $s_2 = 0.3597$, $\delta_1 = 80.9064$, $\delta_2 = 16.5497$, $\Phi = 1.2845$; (- - -), calculated curve using $r_1 = 0.6676$, $r_2 = 0.5048$, $r_1' = 3.2793$, $r_2' = 4.4821$, $s_1 = 0.4760$, $s_2 = 0.3402$, $\delta_1 = 73.3910$, $\delta_2 = 15.6409$, $\Phi = 0.4617$.

The non-linear curve fitting regression method as applied here in user-defined model for the copolymerization data thus affords reasonable values of various parameters signifying the effects of both terminal and penultimate groups in styrene–methyl methacrylate copolymerization. Distinct values of r_1' and r_2' in addition to r_1 and r_2 as determined earlier seem to explain most features of copolymerization of the monomers. The value of Φ is close to unity as required on theoretical grounds. The present method of regression does not necessitate assumption of $\Phi = 1$. The other set of data with higher penultimate effect fail to explain the rate of copolymerization data and other rate constants. It thus appears reasonable to conclude that a set of reactivity ratios should not only fit composition data but also the rate data to examine the acceptability or otherwise. Reactivity ratios as given by Fukuda et al. [7] and the assumption that the effect of penultimate units operate through radical reactivity ratios in styrene–methyl methacrylate copolymerization do not appear to explain important features of the system. Recent studies [9,27] also indicate that penultimate model and specifically, explicit penultimate model seems to be of general applicability and the present system is considered no exception.

Finally, we tried to construct the calculated $R_p/(R_i^{0.5}[M_2])$ vs. $f1$ curve with the values of various constants determined. Fig. 4 shows plot of this variation for the two sets of parameters. It is obvious that the following set of parameters determined in this communication covers all experimental points very accurately and substantiates the authenticity of

the method of analysis: $r_1 = 0.6676$, $r_2 = 0.5048$, $r_1' = 0.3102$, $r_2' = 0.3220$, $s_1 = 0.2547$, $s_2 = 0.3597$, $\delta_1 = 80.9063$, $\delta_2 = 16.5497$ and $\Phi = 1.2845$. Calculated curve with higher values of penultimate effect reactivity ratios shows only the trend but lies well below the experimental points. Thus it is seen that a correct and realistic set of reactivity ratios can be ascertained only through joint analysis of both compositional and kinetic data of copolymerization. Explicit penultimate model rather than implicit or terminal model appears to better explain styrene–methyl methacrylate copolymerization.

4. Conclusion

Non-uniqueness of penultimate model reactivity ratios is an inherent feature of compositional relationship of copolymerization. Two sets of reactivity ratios are determinable through simple NLLS method and copolymer compositions at two feed-ratios. Use of both sets of reactivity ratios to kinetic data can identify the correct set of values. This method has been applied to available literature data on styrene–methyl methacrylate copolymerization. Reliable values of radical reactivity ratios and cross termination constant have been obtained without any assumption, which conform to theoretical predictions. The analysis shows that for a correct assessment of reactivity ratios and applicability of any model for copolymerization, it is essential to carry out joint analysis of compositional and rate data.

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