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Generalized method for determination of penultimate model reactivity ratios and analysis of data

Pramil C. Deb

Defence Institute of Advanced Technology, Girinagar, Pune 421025, Maharashtra, India

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Abstract

Method of determination of penultimate model reactivity ratios has been generalized to take care of specific systems where copolymer composition data are available only in narrow ranges. A number of copolymerization systems reported in literature have been analyzed and applicability of generalized relationship was tested. Most systems are seen to follow penultimate model better than the terminal model. Monomer independent universal relationship of penultimate model reactivity ratios has similarly been generalized and successfully tested.

Keywords: Terminal model; Penultimate model; Reactivity ratios

1. Introduction

In recent years there has been a renewed interest in model selection to explain various features of free radical copolymerization [1–3] subsequent to the critical analysis of a few copolymerization systems by Fukuda et al. [4,5]. A number of models [5–8] have been proposed and examined with copolymer composition data and methods for determination of reactivity ratios [9–13] have been developed from time to time. In an earlier communication [13], a method was described for determination of penultimate model reactivity ratios based on initial guess values for the two reactivity ratios r_1 and r_2. Growth rate saturation model represented by $y = ax/(x + b)$ where a and b are constants was applied to F_1–x data (representing mole fraction of monomer-1 in copolymer and mole ratio of monomer-1 and monomer-2, respectively). Two monomer feed compositions x_1 and x_2 corresponding to copolymer compositions at $F_1 = 1/2$ and $F_1 = 2/3$ were determined from the F_1–x curve and approximate reactivity ratios of the terminal model were calculated from appropriate relationship. These values were used as guess values for determination of correct values of terminal and penultimate models' reactivity ratios by NLLS method as described earlier [13,14]. It is, however, observed in many copolymerization systems that irrespective of monomer feed compositions copolymer compositions are biased towards particular monomer resulting in F_1 values far removed from 1/2 and/or 2/3. Corresponding x_1 and x_2 values of monomer feed compositions may not, therefore, be available for determining the initial guess values from the relationships $r_2 = r_1x_1^2$ and $r_1x_2 - 2r_1x_1^2/x_2$ [13]. It is therefore necessary to develop general relationship covering F_1, r_i and x_i. The universal relationship of penultimate model reactivity ratios [13] similarly needs generalization rather than only for F_1=1/2. In this communication the relationships are generalized to cater for normal as well as unusual copolymerization systems having biased copolymer compositions. The relationships will be tested for various systems reported in the literature.

2. General relationships

Let F_{11} and F_{12} represent the mole fractions of monomer-1 in copolymers at monomer feed ratios x_{11} and x_{12} of $x(=f_1/f_2)$. Using Mayo–Lewis equation for the terminal model,

$$F_1 = \left(r_1x^2 + x\right)/\left(r_1x^2 + 2x + r_2\right),$$

E-mail address: pramil_cd@yahoo.co.in

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we have

$$F_{11} = \left(r_1 x_{11}^2 + x_{11}\right) / \left(r_1 x_{11}^2 + 2x_{11} + r_2\right) \text{ and}$$
$$F_{12} = \left(r_1 x_{12}^2 + x_{12}\right) / \left(r_1 x_{12}^2 + 2x_{12} + r_2\right).$$

Combination and simplification of the above equations finally lead to

$$r_1 = \frac{(a-1)x_{11} - (b-1)x_{12}}{bx_{12}^2 - ax_{11}^2} \tag{1}$$

and

$$r_2 = ar_1 x_{11}^2 + (a-1)x_{11} \tag{2}$$

where $a = (1/F_{11}) - 1$ and $b = (1/F_{12}) - 1$.

For $F_{11} = 1/2$ and $F_{12} = 2/3$, these equations transform to $r_1 x_2 - 2r_1 x_1^2 / x_2 = 1$ and $r_2 = r_1 x_1^2$ which were derived earlier [13] (x_{11} was changed to x_1 for convenience of comparison). Eqs. (1) and (2) can be used for any pair of copolymer compositions selected along $F_1 - x$ curve represented by the growth rate saturation model for determination of x_{11} and x_{12} corresponding to F_{11} and F_{12}. The monomer-pair independent general equation relating the four penultimate model reactivity ratios, a and x_{11} likewise is represented by

$$\begin{aligned}&\left(r_1'/r_2'\right)\left\{ar_1 x_{11}^3 + (2a-1)x_{11}^2\right\} + r_1'\left\{ar_1 x_{11}^2 + (a-1)\right.\\ &\quad \left.\left(2 + 1/r_1' r_2'\right)x_{11} - r_2 + (a-1)/r_1'\right\}\\ &\quad = f(r, a, x) = 1 + r_2/x_{11}.\end{aligned} \tag{3}$$

When $a = 1$, i.e., at $F_{11} = 0.5$, this equation changes to

$$\left(r_1'/r_2'\right)\left(r_1 x_1^3 + x_1^2\right) + r_1'\left(r_1 x_1^2 - r_2\right) = 1 + r_2/x_1 \tag{4}$$

which was derived earlier [13] (x_{11} written as x_1 for convenience).

3. Results and discussion

In the present communication 11 binary copolymerization systems reported in the literature [15–23] have been analyzed with special emphasis on rather unusual systems having widely different terminal model reactivity ratios, one of them being very low. These systems are generally treated by the terminal model and then semi-quantitatively compared with the applicability of penultimate model. In some cases, other models are also tried for comparison [21–23]. Terminal model is mainly intended towards determination of reactivity ratios by various linear and non-linear methods [16–19] and determining the superiority based on deviation and confidence intervals. It has been emphasized recently [1–5,13,14] that penultimate rather than terminal model should be of general applicability and that this model includes the effect of terminal model reactivity ratios r_1 and r_2. In an earlier communication, nine copolymerization systems were analyzed [13] and it was shown that most systems follow penultimate model and a new method was proposed to determine the reactivity ratios. This necessitated finding of monomer feed at copolymer compositions F_1=1/2 and 2/3. It was presumed that systems biased towards higher content of one monomer in the copolymer and leading to preferentially alternating copolymer may not follow penultimate model. These systems generally comprise a not-too polar/non polar monomer and a polar monomer.

We have selected a few systems which form copolymers with almost equal content of both monomers at various feed ratios and hence existence of $F_1 = 2/3$ is not certain. This will not allow determination of x_1 and x_2 and hence of r_1 and r_2 as initial guess values using growth rate saturation model. There is thus a necessity for generalization and Eqs. (1) and (2) should eliminate this limitation. The guess values of r_1 and r_2 along with the assumption $r_1 = r_1'$ and $r_2 = r_2'$ are then used to determine the reactivity ratios of terminal and penultimate models from the $F_1 - x$ equation as user model by non-linear least square method (NLLS) [24]. Table 1 shows values of terminal and penultimate model reactivity ratios along with the values of F_{11} and F_{12} used to obtain x_{11} and x_{12} from $F_1 - x$ curve constructed through growth rate saturation model as a first approximation [13]. The sum of the square of residuals generally shows a better fit for the penultimate model except for NIPA–MAA system. In fact for this system a very small negative value (−0.028 with SSR=19.41×10^{-4}) is obtained for r_2 for the penultimate model

Table 1
Values of terminal model and penultimate model reactivity ratios determined by the generalized method

System	F_{11}	F_{12}	r_{1t}	r_{2t}	$SSR_t \times 10^4$	r_{1p}	r_{2p}	r_1'	r_2'	$SSR_p \times 10^4$
OA–ST	0.5	0.667	0.303	0.676	1.14	0.324	0.689	0.264	0.613	1.03
NIPA–AA	0.7	0.9	19.465	0.78	11.26	13.248	0.948	5.972	0.105	6.48
NIPA–MAA	0.55	0.9	7.349	0	84.23	12.422	0	3.218	0.014	181.48
MmA–MA	0.5	0.9	136.244	3.572	194.42	20.166	10.936	14.187	0.007	92.62
PAMA–GMA	0.5	0.667	1.556	1.446	7.21	1.389	1.557	1.094	0.788	6.26
CIAN–ST	0.333	0.45	0.01	0.347	17.68	2.673	0.374	0.0007	0.315	16.21
BzMA–EMA	0.5	0.667	0.602	0.987	33.49	1.901	0.866	0.083	0.509	4.59
AA–VAc	0.5	0.667	2.476	0.041	21.68	1.902	0.054	2.927	0.032	12.81
FA–ST	0.4	0.65	0.095	0.468	35.55	0.059	0.168	0.339	1.952	25.41
CIAC–ST	0.25	0.45	0.012	0.711	35.92	0.654	0.661	0.002	0.760	31.39
NIPA–AMPS	0.55	0.8	1.555	0.072	127.22	1.174	0.0751	3.078	0.096	119.01

Abbreviations used: OA, *n*-octyl acrylate; ST, styrene; NIPA, *N*-isopropylacrylamide; AA, acrylic acid; MAA, methacrylic acid; MmA, methyl 2-acetamidoacrylate; MA, methyl acrylate; PAMA, phenacyl methacrylate; GMA, glycidyl methacrylate; CIAN, citraconic anhydride; BzMA, 3,4-dichlorobenzyl methacrylates; EMA, ethyl methacrylate; VAc, vinyl acetate; FA, fumaric acid; CIAC, citraconic acid; AMPS, 2-methyl-2-acrylamidopropane sulfonic acid.

which has been taken as 0. This aspect will be taken up while discussing the individual systems. For convenience of understanding, we would henceforth use r_{1t} and r_{2t} for the terminal model reactivity ratios and r_{1p} and r_{2p} for r_1 and r_2 of the penultimate model.

Systems such as *n*-octyl acrylate–styrene [15], 3,4-dichlorobenzyl methacrylate–ethyl methacrylate [16] and phenacyl methacrylate–glycidyl methacrylate [17] are characterized by well-defined terminal model reactivity ratios. While for the first system both terminal and penultimate models predict similar reactivity of radicals and copolymer compositions, for the other two there is a distinct bias of reactivity of radicals towards monomer depending on the penultimate unit. In the second system, r_{1p} is almost 23 times of r_1' indicating the preponderance of $M_1M_1M_1$ triads compared to $M_2M_1M_1$ sequences along the chain and may be due to phenyl ring interactions between dichlorobenzyl fragments. SSR values also indicate a better fit for the penultimate model. Comparison of r_{2p} and r_2' indicates higher reactivity of $M_1{-}M_2^{\bullet}$ radical towards M_2 monomer compared to $M_2M_2^{\bullet}$ radical in phenacyl methacrylate–glycidyl methacrylate system [17]. Penultimate model thus not only seems to give generally a better fit, but also appears to give a better insight into the reactivity of various radicals for these systems.

The monomer pair methyl 2-acetamidoacrylate–methyl acrylate [18] giving a potential thermosensitive copolymer at specific composition is characterized by a very high value of r_{1t} compared to r_{2t} indicating monomer-1 rich copolymers even at moderately low concentration of the monomer. Penultimate model, however, indicates a reasonably high value for r_{2p} and a negligible value for r_2'. This implies a good tendency for the formation of sequences of methyl acrylate along the chain, particularly at high methyl acrylate concentrations making the polymer more hydrophobic and water insoluble. Balanced hydrophobicity at 77 mol% of methyl acrylate leading to thermosensitivity is probably because of optimum content of sequences of this monomer rather than its mere random presence in the copolymer chain. Sudden and unexpected increase of methyl acrylate in the copolymer chain above 80 mol% of this monomer also seems to justify this explanation. It is imperative to mention here that copolymerization for this system has been carried out to rather high conversions. However, considering the wide difference in the reactivity ratios and the Q values [18], the present analysis may not be very inappropriate.

Copolymerization systems involving *N*-isopropylacrylamide and unsaturated acids have been critically analyzed by Xue et al. [19] and importance of conversion and purification has been highlighted. Reported data have been analyzed here and the reactivity ratios are presented in Table 1. In the case of amide–methacrylic acid, penultimate model SSR value is substantially higher than the terminal model value due to the reason mentioned earlier (though lower than the SSR (222.9×10^{-4}) based on an average terminal model reactivity ratio values given by the authors). Reactivity ratio values for both models presented here do not indicate higher reactivity of methacrylic acid as was also brought out by the authors [19] though the presence of the acid as penultimate unit appears to reduce the reactivity of amide radical as reflected in the relatively low value of r_1' compared to r_{1p}. Reactivity ratios pertaining to both models could be conveniently determined for *N*-isopropylacrylamide–acrylic acid and 2-methyl-2-acrylamidopropane sulfonic acid (AMPS). Acrylic acid radical seems to be equally reactive to both acrylic acid and amide monomers when adjacent to an acid unit as reflected in appreciable value of r_{2p} and formation of triads and higher order sequences of acrylic acid is not ruled out. *N*-Isopropylacrylamide–AMPS is characterized by the fact that in contrast to other two amide–acid systems, in this case r_1' is almost three times higher than r_{1p} indicating higher reactivity of the amide radical to its own monomer when the penultimate unit is the sulfonic acid rather than the amide itself. This fact coupled with $r_{1p}\approx1$ makes this pair prone to form alternating copolymer as has also been brought out by Xue et al. [19].

Acrylic acid–vinyl acetate [20] is known for biased content of the acid in the copolymer compositions due to higher reactivity of the acid. Penultimate model reactivity ratios also support generally the high reactivity of acrylic acid radical towards its own monomer. However, $r_1' > r_1$ suggests that this reactivity is further enhanced when the radical is preceded by a vinyl acetate unit in ethanol–water azeotrope. Fumaric acid–styrene pair does not show the tendency to form charge-transfer complex in dimethyl formamide and it has been concluded that the copolymerization process is best described by the terminal model [21]. Values of reactivity ratios and SSR indicate a better fit by the penultimate model (the present values of reactivity ratios give slightly better fit than by the values reported). They also indicate an enhanced reactivity of the acid radical to its own monomer having styrene as penultimate unit and some sequence lengths of fumaric acid can be formed.

Citraconic anhydride–styrene system is characterized by formation of 1:1 charge-transfer complex [22] in contrast to citraconic acid–styrene system which does not show tendency for complex formation [23]. SSR values for the systems indicate equally good fit by both terminal and penultimate models. However, citraconic anhydride radical shows appreciable tendency of sequencing with the anhydride once its adjacent unit is its own monomer. Thus in addition to alteration tendency, some sequences of anhydride units are possible along the copolymer chain. This may explain higher content of anhydride in copolymer than in monomer feed at low concentrations of the anhydride. Citraconic acid–styrene is characterized by having negligible r_1' value while the other three ratios are nearly equal to each other. Thus this analysis does not allow a choice between terminal and penultimate models.

The aforesaid discussion suggests that while a number of copolymerization systems can be described by both terminal and penultimate models, the latter model appears to give generally better fit to copolymer compositional data. Penultimate model also appears to give a better understanding of the possibility of sequence formation even in systems having a tendency to alteration. This, however, is only suggestive and not conclusive. Fractionation and experimental sequence determination may lead to interesting and new aspects. The new method of determination of reactivity ratios based on

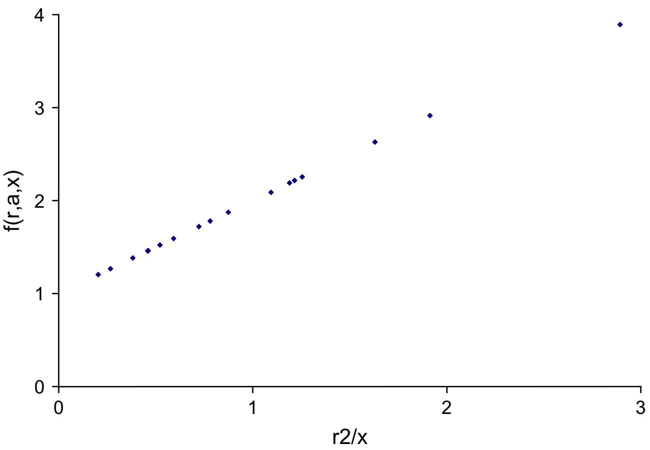

Fig. 1. Universal plot $f\ (r,a,x)$ vs. r_2/x for penultimate model reactivity ratios according to Eq. (3) for the 19 copolymerization systems including those of Ref. 13.

initial guess values applying growth rate saturation model to compositional data gives reliable values for both models.

The applicability of the universal penultimate model relationship represented by Eq. (3) is shown in Fig. 1. Also included are the values for the nine systems reported earlier [13]; 19 out of 20 points (some are overlapped) are covered by a straight line represented by $f\ (r,a,x) = 0.9980 + 1.0021r_2/x_{11}$. Graphical point for MmA–MA (68.58, 69.72) for x and y axes has not been included as this compresses other points. The system *N*-isopropylacrylamide–methacrylic acid for which a value of 0 is assumed for r_{2p}, reason for which has been explained earlier does not fit in the universal plot. Thus it can be emphasized that the universal relationship is valid for most systems (except for system having $r_{2p} = 0$) analyzed here and can be taken as an indication of applicability of the method proposed earlier and generalized here. It is to be mentioned here that the values of x_{11} used for Eq. (3) are values at F_{11} obtained from NLLS curve corresponding to user model for final determination of reactivity ratios and not from the growth rate saturation model which is used only for the selection of initial guess values and are only tentative and approximate.

4. Conclusion

Method of determination of terminal and penultimate model reactivity ratios based on initial guess values obtained using growth rate saturation model to F_1–x data and NLLS has been used for 11 copolymerization systems. The generalized method gives reliable and consistent values compared to terminal model values obtained by other methods. It is observed that penultimate model explains most features of radical copolymerization including systems where reactivity ratios are widely different and one of the monomers has very low tendency of homopolymerization.

The generalized and monomer pair independent relationship of penultimate model reactivity ratios could cover most systems studied here and thus appears to be truly universal for free radical copolymerization.

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