

Polymer Communication

# Determination of penultimate model reactivity ratios and their non-uniqueness

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## Abstract

Nine copolymerization systems reported in literature have been analyzed for determining the terminal and penultimate model reactivity ratios and their non-uniqueness. A universal relationship covering the reactivity ratios and independent of monomer pair type has been developed and successfully verified for the copolymer systems.

A new method for determining the reactivity ratios has been developed using monomer feed concentrations at two specific copolymer compositions and is found to give reliable and accurate values.

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## 1. Introduction

Non-uniqueness of reactivity ratios [1–3] of penultimate model for copolymerization has recently been shown to be inherent in the equation of copolymer composition [4] derived through introduction of the effect of penultimate units in addition to terminal units. While  $r_1$  and  $r_2$ , signifying the reactivity ratios of terminal model or penultimate model having the same penultimate unit as the radical are unique,  $r_1'$  and  $r_2'$  representing true penultimate unit effect appear to have two sets of values satisfying data of copolymer compositions quite satisfactorily. This has been shown to apply for styrene-methyl methacrylate in a number of publications and is in contradiction of basic principles on which the composition equation is based and appears chemically unrealistic. Analysis of copolymerization rate data using the two sets of reactivity ratios seems to support only one set of values for styrene-methyl methacrylate system.

Fukuda's work on copolymerizations [5,6] of styrene-methyl methacrylate and *p*-chlorostyrene-methyl acrylate initiated a strong foundation for the acceptance of penultimate group effect in copolymerization. Critical examination by others [7,8] has further strengthened this concept in recent years. It would be interesting to see whether other systems also follow this pattern and also to examine if non-uniqueness of penultimate model reactivity ratios can be a general phenomenon.

In this communication we present analysis of compositional data of a few systems published in literature to find the penultimate model reactivity ratios and non-uniqueness thereof. We also present a universal general relationship covering the reactivity ratios of free-radical copolymerization which is independent of the monomer pair type. In addition, a method for determining the penultimate model reactivity ratios is presented and tested with literature data.

## 2. Determination of reactivity ratios

The penultimate model of copolymerization takes into account the influence of unit adjacent to the end radical on the reactivity of the radical with a reacting monomer. Appropriate

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specific rates are introduced into the reaction scheme thereby giving rise to four monomer reactivity ratios,  $r_1$ ,  $r_2$ ,  $r'_1$  and  $r'_2$  and two radical reactivity ratios [5,6],  $s_1$  and  $s_2$ . While the monomer reactivity ratios control copolymer compositions and rate of copolymerization, the radical reactivity ratios influence the rate of copolymerization only. The basic equation covering the penultimate model reactivity ratios is as follows:

$$F_1 = \frac{r_1 r'_1 x^4 + (r_1 r'_1 r'_2 + 2r'_1) x^3 + (2r'_1 r'_2 + 1) x^2 + r'_2 x}{r_1 r'_1 x^4 + (r_1 r'_1 r'_2 + 3r'_1) x^3 + (4r'_1 r'_2 + 2) x^2 + (3r'_2 + r'_1 r'_2 r'_2) x + r_2 r'_2} \quad (1)$$

where  $F_1$  is the mole fraction of monomer-1 in copolymer and  $x = (f_1/f_2)$ , the ratio of mole fractions of monomers in feed.

The advantage of using this relationship, which is of general applicability except for alternating copolymerization systems has been described earlier [4].

In evaluating the reactivity ratios, non-linear regression with Eq. (1) as user model [9] has been performed. Using  $F_1-x$  curve,  $x_1$  and  $x_2$  values corresponding to  $F_1 = 0.5$  and 0.6666... are computed. These parameters are related to  $r'_1$  and  $r'_2$  through  $r_1$  and  $r_2$  as follows [1]:

$$Ar'_1 + Br'_1 + C = 0 \quad (2)$$

where

$$\begin{aligned} A &= r_1 x_2^4 (r_2 x_1 - r_1 x_1^3) - (r_1 x_1^4 + x_1^3) (2x_2^2 + 2r_2 x_2 - r_1 x_2^3), \\ B &= r_1 x_2^4 (r_2 + x_1) - x_2^2 (r_2 x_1 - r_1 x_1^3) - (r_1 x_1^4 + x_1^3) (2r_2 + 3x_2), \\ C &= -x_2^2 (r_2 + x_1) \text{ and} \end{aligned}$$

$$r'_2 = \frac{r'_1 (r_1 x_1^4 + x_1^3)}{(r_2 + x_1) + r'_1 (r_2 x_1 - r_1 x_1^3)} \quad (3)$$

Evidently,  $r'_1$  and  $r'_2$  should have two sets of values for each set of values of  $r_1$  and  $r_2$  indicating the non-uniqueness of the penultimate model reactivity ratios. The method of determination of penultimate model reactivity ratios thus involves the following steps:

- (a) determine  $r_1$  and  $r_2$  through non-linear regression using Mayo–Lewis equation, i.e.

$$F_1 = (r_1 x^2 + x) / (r_1 x^2 + 2x + r_2) \quad (4)$$

- (b) determine  $r_1$ ,  $r_2$ ,  $r'_1$  and  $r'_2$  through non-linear regression using  $r_1 = r'_1$  and  $r_2 = r'_2$  as guess values. Further regression may be necessary in some cases using new set of values as guess values to get near constant values.
- (c) determine  $x_1$  and  $x_2$  from the regression curve ( $F_1$  vs.  $x$ ) at  $F_1 = 0.5$  and 0.6666..., respectively, and determine two sets of values for  $r'_1$  and  $r'_2$  through Eq. (2).

### 3. Monomer-pair independent relationship

It can be easily shown from Eq. (1) that the four reactivity ratios are related through either of the following equations:

$$\begin{aligned} (r'_1/r'_2)(r_1 x_1^4 + x_1^3) / (r_2 + x_1) + r'_1 (r_1 x_1^3 - r_2 x_1) / (r_2 + x_1) \\ = f_1(r, x) = 1 \end{aligned} \quad (5a)$$

or,

$$(r'_1/r'_2)(r_1 x_1^3 + x_1^2) + r'_1 (r_1 x_1^2 - r_2) = f_2(r, x) = 1 + r_2/x_1 \quad (5)$$

and,

$$\begin{aligned} r'_1 (r_1 x_2^2) + r'_1 r'_2 (r_1 x_2^3 - 2x_2^2 - 2r_2 x_2) / x_2^2 - r'_2 (2r_2 + 3x_2) / x_2^2 \\ = f_1(r, x) = 1 \end{aligned} \quad (6)$$

Such relationships can be obtained for any set of two specific  $F_1$  values. An interesting aspect of these equations is that they are general and not monomer pair specific. Thus all free-radical copolymerization systems which follow penultimate model can have a master plot embodied in Eq. (5a), (5) or (6). It will be interesting to verify the equation using data for a number of copolymer systems.

Corresponding equations for the terminal model represented by  $F_1 = (r_1 x^2 + x) / (r_1 x^2 + 2x + r_2)$  can be written as:

$$r_2 = r_1 x_1^2, \quad (7a)$$

$$r_1 x_2 - 2r_2/x_2 = 1 \quad (7b)$$

and finally

$$r_1 x_2 - 2r_1 x_1^2/x_2 = f_3(r, x) = 1 \quad (7)$$

These equations can also be tested and their applicability can be an indication of the applicability of models and selection.

### 4. Results and discussion

In the present communication we have analyzed nine binary copolymerization systems from literature that have been treated by respective authors [5,6,10–16] for determining reactivity ratios for the terminal model. In most cases the ratios have been determined by Fineman–Ross [17] and Kelen–Tüdös [18] linearization methods and statistical analysis showed reliability of the latter method. We have redetermined the values of  $r_1$  and  $r_2$  by non-linear regression [9] using Mayo–Lewis equation. Table 1 shows the presently determined values vis-à-vis the reported values and the similarity between the reported and the present values is evident. This indicates the reliability of the present NLLS method and the overall correctness of terminal model reactivity ratio values generally reported based on Kelen–Tüdös and other statistical methods.

$r_1$  and  $r_2$  thus determined were used to compute the penultimate model reactivity ratios through NLLS using  $r_1 = r'_1$  and  $r_2 = r'_2$  as guess values. Since subsequent computation using newly determined values as guess values did not indicate

Table 1  
Terminal model reactivity ratios

System	Reported values		NLLS values		SSR $\times 10^4$
	$r_1$	$r_2$	$r'_1$	$r'_2$	
St-BA [10]	0.88	0.20	0.881	0.207	3.4
St-MMA [5]	0.523	0.46	0.523	0.460	36.12
<i>p</i> -cSt-MA [6]	1.21	0.144	1.133	0.140	298.7
HEMA- <i>t</i> BA [13]	1.792	0.51	1.792	0.511	13.7
HEMA-BMA [12]	0.982	0.841	0.983	0.852	19.4
MMA-acrNMP [11]	0.98	0.466	1.034	0.508	7.9
MMA-acrNEP [16]	1.08	0.72	1.020	0.642	12.2
MMA-MVE [14]	0.92	1.00	0.920	1.004	32.4
St-2/EHA [15]	0.979	0.292	0.962	0.284	12.78

Abbreviations used: MA – methyl acrylate, HEMA – 2-hydroxyethyl methacrylate, *t*BA – *t*-butyl acrylate, BMA – butyl methacrylate, acrNMP – *N*-acryloyl-*N'*-methyl piperazine, acrNEP – *N*-acryloyl-*N'*-ethyl piperazine, MVE – *a*-tocopheryl methacrylate, MMA – methyl methacrylate, St – styrene, 2-EHA – 2-ethylhexyl acrylate *p*-cSt – *p*-chlorostyrene.

noticeable change, the first set of values of four ratios are generally constant and taken as reliable. Only in the case of HEMA-butyl methacrylate and MMA-*N*-acryloyl-*N'*-methyl piperazine (MMA-acrNMP), the values did show appreciable change and iteration was continued till reasonably constant values are obtained.

Table 2 shows the computed values of four reactivity ratios corresponding to penultimate model. A comparison of the sum of square of residuals (SSR) in Tables 1 and 2 brings out the better fit of copolymer compositional data to the penultimate model except for MMA-acrNMP where  $r_1$  values by both models are close to each other and the SSR values are same. It is evident that in all cases distinctly identifiable values of penultimate model reactivity ratios exist. It thus appears that penultimate model is of general applicability [4,6–8] and possibly cannot be dispensed with. Table 2 also includes two sets of reactivity ratios obtained using Eqs. (2) and (3). As was mentioned earlier [4], it is important to note that while  $r_1$  and  $r_2$  have unique values for both sets,  $r'_1$  and  $r'_2$  are distinctly different, one set coinciding with that obtained through NLLS method. This corroborates the earlier finding and tends to confirm the non-uniqueness of penultimate model reactivity ratios which has attracted attention in recent years. SSR values in all cases with the second set of values of reactivity ratios are

Table 2  
Penultimate model reactivity ratios

System	NLLS				SSR $\times 10^4$	$x_1, x_2$ method		SSR $\times 10^4$
	$r_1$	$r_2$	$r'_1$	$r'_2$		$r'_1(x)$	$r'_2(x)$	
St-BA [10]	0.865	0.187	0.998	0.25	2.67	2.391	0.611	2.68
St-MMA [5]	0.668	0.505	0.310	0.322	32.28	3.279	4.482	32.77
<i>p</i> -cSt-MA [6]	0.841 (0.92) <sup>a</sup>	0.149 (0.18) <sup>a</sup>	3.081 (2.3) <sup>a</sup>	0.251 (0.18) <sup>a</sup>	50.6 (63.03) <sup>a</sup>	3.271	0.260	52.6
HEMA- <i>t</i> BA [13]	1.875	0.470	1.813	0.605	13.47	1.620	0.536	13.47
HEMA-BMA [12]	2.036	0.771	0.224	0.435	7.14	1.341	25.821	16.88
MMA-acrNMP [11]	0.997	0.792	0.720	0.218	7.9	15.581	1.054	5.61
MMA-acrNEP [16]	1.072	0.581	1.132	0.849	0.59	<sup>b</sup>	<sup>b</sup>	–
MMA-MVE [14]	0.795	1.285	1.349	0.897	28.9	1.192	0.812	29
St-2/EHA [15]	1.011	0.635	0.636	0.108	11.33	<sup>b</sup>	<sup>b</sup>	–

<sup>a</sup> Values used by Ma et al. [6].

<sup>b</sup> No +ve value obtained.

better than those with terminal model values and are very close to the other set of penultimate model reactivity ratios obtained through NLLS method. Thus the existence of two sets of penultimate model reactivity ratios appears to be general rather than an exception. It is to be mentioned here that in one case, viz., St-2/EHA and MMA-acrNEP system positive values for  $r'_1$  and  $r'_2$  could not be obtained through  $x_1$ – $x_2$  method. This is due to high positive value of  $A$  of Eq. (2) for the first monomer pair in contrast to negative values for all other monomer pair and high sensitivity of  $(B^2 - 4AC)$  in the second case. A detailed analysis of conditions of  $(B^2 - 4AC)$  greater than or equal to 1 and extensive data on the above two systems are needed for finding the reason for the failure to obtain the other set of penultimate model reactivity ratios. *p*-Chlorostyrene-methyl acrylate copolymerization system is seen to follow the penultimate model. Use of  $r_2 = r'_2$  though more appropriate than the terminal model, is not as good as the penultimate model values.

#### 4.1. Monomer-pair independent relationship

We now try to examine the applicability of Eqs. (5), (5a) and (7) to the nine systems analyzed. Fig. 1 shows the plot of left-hand side of Eq. (5) against  $r_2/x_1$ . All the points corresponding to the systems give a unique fit (regression line is represented by  $f_2(r,x) = 0.9998r_2/x_1 + 1$ ) showing general applicability of Eq. (5) to all the copolymerization systems analyzed here which is as expected. Reliability of reactivity ratio values determined through  $x_1$ – $x_2$  method is evident as they are indistinguishable in the plot from the values computed for NLLS reactivity ratios. Similar conclusion is reached with Eq. (6) (figure not shown). A general and universal relationship among the four reactivity ratios based on copolymer composition corresponding to  $F_1 = 0.5$  and/or  $F_1 = 0.6666\dots$  at  $x_1$  and  $x_2$  of monomer feed compositions has therefore been obtained for free-radical copolymerization independent of the monomer pair. Compliance or otherwise to this relationship should also be a test for accuracy and authenticity of the monomer reactivity ratios determined.

Fig. 2 shows the plot of left-hand side of Eq. (5a) against  $r_2/x_1$  (it can be any function of  $r_i$  and  $x_i$  or combination –  $r_2/x_1$  is chosen to keep parity with the earlier plot). All the

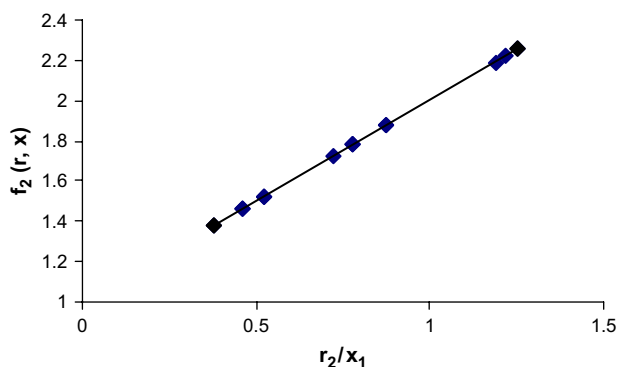


Fig. 1. Universal plot of  $f_2(r, x)$  vs.  $r_2/x_1$  for nine copolymerization systems according to Eq. (5) for penultimate model reactivity ratios.

computed points practically lie on the expected line. Maximum deviation was found to be of the order of  $4.58 \times 10^{-4}$ . This can also therefore be considered as a universal plot connecting the penultimate model reactivity ratios and  $x_1$  and to be a tool to authenticate the reliability of the determined parameters.

We now attempt to test the applicability of the reactivity ratios obtained for the terminal model from Eq. (7) and using the same  $x_1$  and  $x_2$  values and reactivity ratios determined by NLLS method. A plot of the left-hand side of Eq. (7) against  $r_2/x_1$  (can be any function of  $r_i$  and  $x_1$  or  $x_2$ ) is shown in the same figure. It is at once evident that the computed points are quite scattered implying that the terminal model reactivity ratios, even though very stringently determined, are not truly representing the systems (deviation as high as  $6.8 \times 10^{-2}$ ). Only in two cases, viz., styrene-butyl acrylate and HEMA-*t*-butyl acrylate, the agreement is good. This is expected as being due to the nearness of the  $r_1$  and  $r'_1$  and/or of  $r_2$  and  $r'_2$  (Table 2) showing moderate effect of penultimate unit towards radical–monomer reactivity. It thus appears that penultimate model needs to be considered in general for free-radical copolymerization which can also bring out those specific cases where penultimate units may not play very important role.

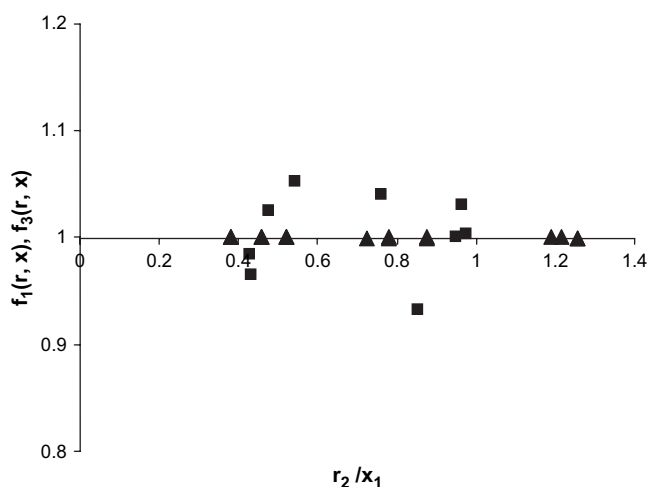


Fig. 2. Universal plot of  $f_1(r, x)$  – ▲ and  $f_3(r, x)$  – ■ according to Eq. (5a) and (7) for penultimate and terminal model reactivity ratios ( $r_2/x_1$  is taken as  $x$  axis to keep parity with plot in Fig. 1).

#### 4.2. New method for determination of penultimate model reactivity ratios

Eqs. (1) and (7) offer a possibility of determining all the four penultimate model reactivity ratios.  $F_1-x$  plots are in most cases approximately the growth rate saturation type expressed by  $F_1 = ax/(b+x)$ , particularly at low to moderately low  $x$  values. A plot of this type with  $a = b = 1$  as guess values can give a fairly good estimate of  $x_1$  and  $x_2$  corresponding to  $F_1 = 0.5$  and  $0.6666\dots$ , respectively. Eqs. (7) and (7a) are then used for calculating  $r_1$  and  $r_2$  which are used as guess values along with  $r_1 = r'_1$  and  $r_2 = r'_2$  for computing the four reactivity ratios by NLLS as has been already shown. This exercise has been carried out for the nine systems examined in the present communication. Table 3 shows the values of the reactivity ratios along with the sum of the square of residuals determined by this method. It is at once evident that the values so obtained are very close to those obtained earlier and in some cases exactly match them resulting in almost identical SSR values. It is to be mentioned here that the  $x_1$  and  $x_2$  values used here were obtained applying growth rate saturation model to the compositional data and hence are approximate only.  $r_1$  and  $r_2$  values obtained from Eqs. (7) and (7a) used as guess values for determining the four reactivity ratios are also thus very approximate. But the values of the reactivity ratios finally obtained lend credence to the method suggested here. The method is simple, convenient to use and is accurate as any other statistical method and deserves to be exploited.

#### 5. Conclusion

Terminal and penultimate model reactivity ratios of copolymerization for nine monomer pairs have been determined by NLLS method. It is observed that in all cases the copolymer compositions could be described better by the penultimate model rather than terminal model reactivity ratios. Distinctly identifiable  $r'_1$  and  $r'_2$  values for all the systems indicated general applicability of penultimate model. Non-uniqueness of penultimate model reactivity ratios could be ascertained in seven cases using  $x_1-x_2$  method developed earlier.

Universal relationships connecting all the four reactivity ratios have been developed and tested for the nine systems analyzed here with success. These relationships are independent of monomer pair and can be considered as general for

Table 3  
Reactivity ratios determined by the new method

System	$r_1$	$r_2$	$r'_1$	$r'_2$	SSR $\times 10^4$
St-BA [10]	0.865	0.187	0.998	0.250	2.67
St-MMA [5]	0.647	0.499	0.326	0.332	32.20
<i>p</i> -cSt-MA [6]	0.841	0.150	3.446	0.275	50.29
HEMA- <i>t</i> BA [13]	1.875	0.471	1.736	0.577	13.47
HEMA-BMA [12]	2.036	0.771	0.224	0.435	7.13
MMA-acrNMP [11]	0.997	0.792	0.720	0.218	7.90
MMA-acrNEP [16]	1.070	0.580	1.138	0.854	0.59
MMA-MVE [14]	0.795	1.285	1.348	0.896	28.94
St-2/EHA [15]	1.011	0.635	0.636	0.109	11.33

free-radical copolymerization. A fit to this relationship should give authenticity to the values of reactivity ratios determined by any method. While applying this method to the general expression for the terminal model, most of the studied systems do not follow. This also shows the more appropriateness of the applicability of penultimate model to free-radical copolymerization.

A new method has been proposed for determination of the four reactivity ratios based on  $F_1-x$  relationship and use of monomer feed compositions  $x_1$  and  $x_2$  for copolymer compositions corresponding to  $F_1$  equal to 0.5 and 0.6666..., respectively. This has been tested with the nine copolymerization systems and is found to give values similar to those determined by NLLS method with same degree of reliability as reflected in low SSR values. This method is also simple and convenient to use.

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