A new linear method to calculate monomer reactivity ratios by using high-conversion copolymerization data: penultimate model with $r_2=0$

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The new iterative linear least-squares method for calculation of monomer reactivity ratios for the terminal model, proposed by Mao and Huglin, is applied to the penultimate model system with $r_2=0$. The principle and the calculation procedure are similar for the two different models. All advantages of the new method when applied to the terminal model, i.e. fast convergence, exact calculation and the fact that any initial estimation of reactivity ratios always leads to the same correct results, remain valid when applied to the penultimate model. The superiority of the new method over the Kelen–Tüdös and extended Kelen–Tüdös procedures is even more evident for the penultimate model than for the terminal model.

(Keywords: monomer reactivity ratios; modelling; high conversion)

INTRODUCTION

Recently, Kelen, Tüdös, Braun and Czerwinski[1] proposed a linear method to calculate monomer reactivity ratios with simplified penultimate model, i.e. $r_2=0$, which was intended to be applicable to systems not limited to low-conversion copolymerization data. However, because one monomer (monomer 1) reacts much faster than the other one, their method is not as good as the well known terminal model extended Kelen–Tüdös method[2], which in most situations can be applied to copolymerization data up to 40% conversion.

In our previous paper[3], a new iterative linear least-squares method, which can be used for copolymerization data obtained at any conversion, was presented to calculate monomer reactivity ratios with the terminal model. This procedure is especially useful for very high conversion. In the present paper, this method is applied to the penultimate model with $r_2=0$.

THE PENULTIMATE MODEL AND THE SIMPLIFIED PENULTIMATE MODEL

The copolymer composition equation for the penultimate model is:

$$\frac{d[M_1]}{d[M_2]}=\frac{1+\dfrac{r'_1[M_1]}{[M_2]}\dfrac{r_1[M_1]+[M_2]}{r'_1[M_1]+[M_2]}}{1+\dfrac{r'_2[M_2]}{[M_1]}\dfrac{r_2[M_2]+[M_1]}{r'_2[M_2]+[M_1]}} \tag{1}$$

where

$$r_1=k_{111}/k_{112} \qquad r'_1=k_{211}/k_{212}$$
$$r_2=k_{222}/k_{221} \qquad r'_2=k_{122}/k_{121} \tag{2}$$

In this general form of the penultimate model, there are four reactivity ratios to be estimated and it is impossible to transfer equation (1) to a linear form.

However, if monomer 2 cannot homopolymerize, i.e. $r_2=r'_2=0$, equation (1) simplifies to:

$$\frac{d[M_1]}{d[M_2]}=1+\frac{r'_1[M_1]}{[M_2]}\frac{r_1[M_1]+[M_2]}{r'_1[M_1]+[M_2]} \tag{3}$$

This simplified form contains only two reactivity ratios to be estimated, and it can be transferred to a linear form. Consequently, in the following text, only this simplified penultimate model will be employed.

In practice, $d[M_1]/d[M_2]$ is usually approximated to $\Delta[M_1]/\Delta[M_2]$, provided the conversion is low enough. By this approximation, equation (3) becomes:

$$\frac{\Delta[M_1]}{\Delta[M_2]}=1+\frac{r'_1[M_1]}{[M_2]}\frac{r_1[M_1]+[M_2]}{r'_1[M_1]+[M_2]} \tag{4}$$

and equation (4) can be rewritten as:

$$F=1+\frac{r'_1f(1+r_1f)}{1+r'_1f} \tag{5}$$

In equation (5), $f=f_1/f_2=[M_1]/[M_2]$, where f_1 and f_2 are respectively the mole fractions of monomers 1 and 2 in the feed, and $F=F_1/F_2=\Delta[M_1]/\Delta[M_2]$, i.e. the cumulative copolymer composition.

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KELEN–TÜDŐS LINEAR METHOD

As in the terminal model, our new method in the penultimate model is based on Kelen–Tüdős linear transformation[1]. Therefore, it is necessary to give the main features of the Kelen–Tüdős linear method before presenting our new method.

Kelen and Tüdős *et al.*[1] proposed transforming equation (5) to:

$$\eta = \left(r_1 + \frac{1}{\alpha r'_1}\right)\xi - \frac{1}{\alpha r'_1} \qquad (6)$$

where

$$\eta = G/(\alpha + H) \qquad \xi = H/(\alpha + H) \qquad (7)$$

$$G = f(F-2)/(F-1) \qquad H = f^2/(F-1) \qquad (8)$$

and

$$\alpha = (H_{\min} H_{\max})^{1/2} \qquad (9)$$

Hence, from a linear plot of η vs. ξ, r_1 and r'_1 can be calculated from the slope and intercept.

In a similar way to their treatment of conversion data in the terminal model, Kelen and Tüdős *et al.* suggested replacing f with F/z, where z is a conversion-dependent variable having the same meaning as z in the terminal model:

$$z = \frac{\ln([M_1]/[M_1]_0)}{\ln([M_2]/[M_2]_0)} \qquad (10)$$

Subscript 0 means the initial value. Hence G and H are calculated from equation (11) instead of equation (8):

$$G = \frac{F(F-2)}{z(F-1)} \qquad H = \frac{F^2}{(F-1)z^2} \qquad (11)$$

Although Kelen and Tüdős themselves always give the same name (KT) to their method regardless of whether conversion data are used or not, for convenience we assign their methods two different names, as was also done by others[4]. That is, if the conversion data are not considered, i.e. G and H are calculated by equation (8), we call this procedure the Kelen–Tüdős method (KT); but, if the conversion data are considered in the calculation, i.e. G and H are calculated by equations (10) and (11), then we term this procedure the extended Kelen–Tüdős method (Ex. KT).

NEW LINEAR METHOD OF MAO AND HUGLIN

The basic principle and the iterative procedure for calculating reactivity ratios by using any high-conversion data of the terminal model have been described previously[3] and this Mao and Huglin (MH) method has been used successfully for some new copolymerization systems[5]. Here we indicate how the MH procedure can be applied to the penultimate model with $r_2 = 0$.

Let the instantaneously produced copolymer composition be defined as y:

$$y \equiv d[M_1]/d[M_2] \qquad (12)$$

Thus equation (3) can be rewritten (without approximation) as:

$$y = 1 + \frac{r'_1 f(1 + r_1 f)}{1 + r'_1 f} \qquad (13)$$

The difference between equations (4) and (13) is that equation (4) is an approximate equation, which can only be used for low-conversion data, whereas equation (13) is an exact equation without the limitation of conversion.

Equation (13) can be recast as:

$$f = \frac{y - 2 + [(2-y)^2 - 4r_1(1-y)/r'_1]^{1/2}}{2r_1} \qquad (14)$$

The mathematically possible negative sign before the square root in equation (14) has been neglected because it always leads to the impossible situation wherein f is negative.

In the following treatment, superscript c means the calculated value, superscript e denotes the experimentally found value, and the iteration step relating to any quantity is denoted by a number (0, 1, 2, etc.) within parentheses in the superscript position.

Equation (14) is the basic equation that is used to calculate f^c in the penultimate model, i.e.

$$f^c(i) = \frac{F^c(i) - 2 + \{[2 - F^c(i)]^2 - 4r_1[1 - F^c(i)]/r'_1\}^{1/2}}{2r_1} \qquad (15)$$

For a series of n experimental data points at conversion θ:

$$f_0(i),\ F^e(i),\ \theta(i),\ i = 1, 2, \ldots, n$$

the new linear method applied to the penultimate model with $r_2 = 0$ contains the following iteration steps:

(1) Assign initially any arbitrary non-negative values to $r_1^{(0)}$, $r_1'^{(0)}$.

(2) Test their validity by:

  (2.1) Using $r_1^{(0)}$, $r_1'^{(0)}$, $f_0(i)$, $\theta(i)$ to calculate $F^{c(0)}(i)$ by integrating equation (3) numerically.

  (2.2) Using $F^{c(0)}(i)$ in conjunction with equation (15) to calculate $f^{c(0)}(i)$.

  (2.3) Using $f^{c(0)}(i)$, $F^e(i)$, adopt the KT method (equations (6)–(9)) to obtain new values of the reactivity ratios: $r_1^{(1)}$, $r_1'^{(1)}$.

(3) If $r_1^{(1)} \neq r_1^{(0)}$ or $r_1'^{(1)} \neq r_1'^{(0)}$ then test $r_1^{(1)}$, $r_1'^{(1)}$ by steps similar to (2.1)–(2.3), to obtain new values: $r_1^{(2)}$, $r_1'^{(2)}$.

. . .

(4) Repeat the above iteration until

$$|r_1^{(k)} - r_1^{(k-1)}| < \varepsilon \quad \text{and} \quad |r_1'^{(k)} - r_1'^{(k-1)}| < \varepsilon \qquad (16)$$

In all calculations shown in this paper, the step length of numerical integration was set as $\Delta\theta = 0.001$, and the convergence criterion was set as $\varepsilon = 0.0001$. All calculations were completed by computer automatically.

RESULTS AND DISCUSSION

Using computer simulated data

To check the validity of our new method, a series of data points with medium-high conversion was generated by a computer, as shown in *Table 1*. It should be noted that, owing to the inability of monomer 2 to homopolymerize, copolymerizations in which there is a low initial content of monomer 1 (e.g. $f_{1,0} = 0.1$) cannot proceed to high conversion. The iteration results from very different initial values of $r_1^{(0)}$, $r_1'^{(0)}$ are shown in *Table 2*. The 95% confidence intervals are calculated with the last iteration data according to the method given by Kelen and Tüdős *et al.*[6]. SQDIFF is the sum of squares of differences between calculated and experimental values of copolymer composition, as defined by Kelen and Tüdős *et al.*[1]:

Table 1 Computer simulated experimental data at medium-high conversion (MW_1 and MW_2 are arbitrarily selected molecular weights of monomers 1 and 2)

System 1: $MW_1 = 100$, $MW_2 = 150$, $r_1 = 0.1$, $r'_1 = 0.5$

$f_{1,0}$	F^c_1	Conversion (wt%)
0.1	0.5069	16.9
0.2	0.5152	34.4
0.3	0.5338	32.0
0.4	0.5527	33.0
0.5	0.5741	34.0
0.6	0.5989	35.1
0.7	0.6296	36.1
0.8	0.6735	37.0
0.9	0.7652	37.3

Table 2 Iteration results of System 1 from very different initial values of r_1 and r'_1

Iteration	r_1	r'_1	SQDIFF
0	1.0000000	1.0000000	0.8174159E−01
1	0.1700295	0.5116907	0.1548301E−02
2	0.1109903	0.4981427	0.4306003E−04
3	0.1019036	0.4995887	0.1589985E−05
4	0.1001854	0.5000897	0.6742174E−07
5	0.0998468	0.5001994	0.7410396E−08
End	0.0997791	0.5002204	0.4908550E−08
±	0.0007338	0.0005715	

Iteration	r_1	r'_1	SQDIFF
0	100.0000000	0.0100000	0.1669368
1	0.2791529	0.4328592	0.5556595E−02
2	0.1226489	0.4909260	0.1631585E−03
3	0.1041774	0.4979937	0.6308659E−05
4	0.1006150	0.4999118	0.2542967E−06
5	0.0999304	0.5001698	0.1487281E−07
6	0.0997952	0.5002163	0.5230326E−08
End	0.0997688	0.5002247	0.4810886E−08
±	0.0007326	0.0005705	

Iteration	r_1	r'_1	SQDIFF
0	0.0010000	100.0000000	0.4692238E−01
1	−0.2050036	2.2785046	0.2172922E−01
2	0.0758727	0.5707505	0.2180211E−03
3	0.0952771	0.5047083	0.7126835E−05
4	0.0989994	0.5006276	0.3829047E−06
5	0.0997239	0.5002528	0.4524943E−07
6	0.0998684	0.5001941	0.8905282E−08
7	0.0997832	0.5002198	0.4987346E−08
End	0.0997663	0.5002253	0.4802718E−08
±	0.0007355	0.0005728	

Table 3 Computer simulated experimental data up to very high conversion

System 2: $MW_1 = 100$, $MW_2 = 150$, $r_1 = 0.2$, $r'_1 = 4$

$f_{1,0}$	F^c_1	Conversion (wt%)
0.1	0.5400	15.7
0.2	0.5770	26.0
0.3	0.6057	35.5
0.4	0.6284	45.7
0.5	0.6487	56.5
0.6	0.6722	58.2
0.7	0.6994	80.1
0.8	0.7605	81.4
0.9	0.8754	81.0

Table 4 Iteration results of System 2

Iteration	r_1	r'_1	SQDIFF
0	1.0000000	1.0000000	0.1108351E−01
1	0.4075869	3.0930340	0.1534566E−02
2	0.2938091	3.6368911	0.3819171E−03
3	0.2490058	3.8037913	0.1117942E−03
4	0.2273165	3.8826296	0.3566101E−04
5	0.2157526	3.9286199	0.1179568E−04
6	0.2092916	3.9562809	0.4156396E−05
7	0.2055194	3.9733222	0.1490337E−05
8	0.2032790	3.9837754	0.5416834E−06
9	0.2019345	3.9901774	0.2016336E−06
10	0.2011221	3.9940875	0.7956127E−07
11	0.2006298	3.9964595	0.3648188E−07
12	0.2003298	3.9979208	0.2145011E−07
13	0.2001475	3.9988184	0.1655621E−07
14	0.2000368	3.9993551	0.1512372E−07
15	0.1999688	3.9996846	0.1487033E−07
16	0.1999273	3.9998901	0.1487893E−07
17	0.1999023	4.0000186	0.1498990E−07
End	0.1998870	4.0000892	0.1511090E−07
±	0.0002739	0.0047150	

Table 5 Computer simulated experimental data by terminal model

System 3: $MW_1 = 100$, $MW_2 = 150$, $r_1 = 0.5$, $r_2 = 0$

$f_{1,0}$	F^c_1	Conversion (wt%)
0.1	0.5075	15.9
0.2	0.5197	26.5
0.3	0.5357	36.5
0.4	0.5570	46.9
0.5	0.5860	57.8
0.6	0.6296	59.3
0.7	0.6881	60.3
0.8	0.7670	60.9
0.9	0.8709	60.8

$$\mathrm{SQDIFF} = \sum_{i=1}^{n} [F^c_1(i) - F^e_1(i)]^2 \tag{17}$$

From *Table 2* it can be seen that our new method applied to the penultimate model ($r_2 = 0$) retains all the advantages of its application to the terminal model, viz. rapid convergence, exact calculation and the finding that any initial assigned values lead to the same correct result. Now we use a computer to simulate a series of data points up to very high conversion, denoted by System 2 (see *Table 3*), the corresponding iteration results being shown in *Table 4*. From *Table 4* it can be seen that the new method is an exact calculation procedure without systematic error no matter how high the conversion.

If the copolymerization system can be described well by the terminal model for the case in which one monomer is not able to homopolymerize, i.e. $r_2 = 0$, it should follow automatically that the penultimate model describes the system equally well. This is because the former is a special case of the more general latter.

To verify this, another series of data points was generated with a computer by employing the terminal model, denoted by System 3 (see *Table 5*), and the corresponding iteration results are shown in *Table 6*. The findings are exactly as anticipated, viz. the penultimate model treatment results in r_1 and r'_1 having the same values, thus suggesting that the terminal model is applicable.

For comparison, we also apply the penultimate model KT and Ex. KT methods to calculate r_1 and r'_1 for these same three systems. The results are shown in *Table 7*. From *Table 7* it can be seen that neither the KT nor the Ex. KT method gives good results, if the copolymerizations are carried to medium-high conversions (30–40%). Although in the terminal model the Ex. KT method can be applied normally to copolymerization data up to 40% conversions with negligible systematic error[2], in the penultimate model with $r_2 = 0$, it is evident that 30–40% conversion data are too high to be used with the Ex. KT method. The superiority of the MH procedure to the Ex. KT method is much clearer in the penultimate model with $r_2 = 0$ than in the terminal model. This is because, in systems with $r_2 = 0$, the shift in monomer composition with conversion is always very fast, owing to the inability of monomer 2 to homopolymerize. The Ex. KT method can only partly correct the systematic error associated with the monomer composition shift with conversion, whereas the MH method can correct completely such systematic error, as indicated previously[3].

Table 6 Iteration results of System 3 by penultimate model with $r_2 = 0$

Iteration	r_1	r'_1	SQDIFF
0	100.0000000	0.0100000	0.4298904E−01
1	1.1260448	0.4097105	0.4891552E−02
2	0.6485773	0.4786142	0.4996738E−03
3	0.5458549	0.4929910	0.5441983E−04
4	0.5153012	0.4974997	0.6124839E−05
5	0.5054016	0.4990284	0.7576853E−06
6	0.5020028	0.4995618	0.1029934E−06
7	0.5008413	0.4997407	0.2211130E−07
8	0.5004376	0.4998065	0.1133613E−07
9	0.5003002	0.4998266	0.9635581E−08
End	0.5002540	0.4998340	0.9300074E−08
±	0.0016667	0.0007031	

Table 7 Penultimate model KT and Ex. KT results of computer simulated data: Systems 1–3

System	Method	r_1	r'_1
1	KT	0.3048 ± 0.1857	0.2928 ± 0.0564
	Ex. KT	−0.0942 ± 0.3006	1.0212 ± 0.4952
2	KT	0.4016 ± 0.1306	1.8087 ± 0.4496
	Ex. KT	0.1531 ± 0.1301	5.9159 ± 2.1513
3	KT	0.8519 ± 0.1159	0.2811 ± 0.0216
	Ex. KT	0.3850 ± 0.1795	0.6414 ± 0.0940

Using data from the literature

The procedure presented here has been checked by using real experimental data with unavoidable random errors. The systems examined were restricted to those data reported in the literature for copolymerizations in which the value of r_2 is exactly zero. In this connection it is important to note that, for several copolymerizations involving *N*-vinyl-2-pyrrolidone or maleic anhydride as monomer 2, the value of r_2 is very small, but not zero. This is apparent, for example, in the system ferrocenylmethyl methacrylate (M_1)/maleic anhydride (M_2)[7], for which $r_2 = 0.10$, despite the fact that maleic anhydride is generally considered to be a monomer that does not homopolymerize. In the selection from the literature, data points with $F_2 > 0.50$ were excluded.

Of several series of data[8–11] examined, three of them have been selected and the results are summarized in *Table 8*. It is apparent that the values of r_1 and r'_1 calculated by the KT method are out of line with those obtained via the other two procedures. This is because the KT method does not take the drift in composition with conversion into account. Extremely close accord is exhibited between the Ex. KT and MH methods for those systems in which the conversion extends to 24 wt%. We have been unable to locate primary copolymerization data in the literature for higher conversions. Nonetheless, as already stated, the calculations for the computer simulated data, i.e. Systems 1–3, demonstrate clearly the inadequacy of the Ex. KT method for high-conversion data. Thus in *Table 7* the values of r_1 and r'_1 afforded by both the KT and Ex. KT methods are markedly different from the true (i.e. assigned) values quoted in *Tables 1, 3* and *5*.

Although application of the penultimate model to copolymerizations with $r_2 = 0$ is a special case, we believe that the procedure described is useful because (i) correction for systematic error due to drift in composition is an inherent part of the iteration, (ii) the final result does not rely on a reasonable initial estimate of the

Table 8 Results of calculations by various methods using data in the literature

	System		Conversion (wt%)	Method	r_1	r'_1	Ref.
	M_1	M_2					
a	ST	MCC	21	KT	0.2807 ± 0.2825	0.5165 ± 0.4916	8
				Ex. KT	0.2287 ± 0.1969	0.6276 ± 0.5584	
				MH	0.2345 ± 0.1950	0.6115 ± 0.5264	
b	ST	FP	24	KT	0.1881 ± 0.0910	0.2344 ± 0.0613	8
				Ex. KT	0.1185 ± 0.0654	0.2706 ± 0.0745	
				MH	0.1172 ± 0.0600	0.2681 ± 0.0692	
c	ST	TolCI	21	KT	0.1309 ± 0.0780	0.1033 ± 0.0345	9
				Ex. KT	0.0592 ± 0.0380	0.1124 ± 0.0370	
				MH	0.0658 ± 0.0402	0.1095 ± 0.0330	

[a] Styrene with methyl cyanocinnamate, 60°C in toluene, from table 1 of ref. 8, No. 25–33

[b] Styrene with fumaroyldipyrrolidone, 60°C in dimethylsulfoxide, from table 3 of ref. 8, No. 1–12

[c] Styrene with tolylcitraconimide, 60°C in toluene, from table 1 of ref. 9, No. 13–20

reactivity ratios, being quite independent of their initial, arbitrarily assigned values, and (iii) from the practical standpoint it is not necessary to ascertain preliminary conditions needed to obtain low conversion. Such preliminary experiments can be wasteful of expensive monomers.

Computer programs in standard FORTRAN77 language of MH method (both terminal model and penultimate model) will be sent free of charge to anyone who can be reached by E-mail. Please contact us at the following E-mail address: R.Mao@chemistry.salford.ac.uk

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REFERENCES

1 Kelen, T., Tüdős, F., Braun, D. and Czerwinski, W. K. *Makromol. Chem.* 1990, **191**, 1853

2 Tüdös, F., Kelen, T., Foldes-Berezsnich, T. and Turcsanyi, B. *J. Macromol. Sci.-Chem* (*A*) 1976, **10**, 1513

3 Mao, R. and Huglin, M. B. *Polymer* 1993 **34**, 1709

4 Soundararajan, S. and Reddy, B. S. R. *J. Appl. Polym. Sci.* 1991, **43**, 251

5 Mao, R., Huglin, M. B., Davis, T. P. and Overend, A. S. *Polym. Int.* 1993, **31**, 375

6 Kelen, T., Tüdös, F., Braun, D. and Czerwinski, W. K. *Makromol. Chem.* 1990, **191**, 1863

7 Ayers, O. E., McManus, S. P. and Pittman, C. U. *J. Polym. Sci., Polym. Chem. Edn.* 1973, **11**, 1201

8 Braun, D., Czerwinski, W. K., Bednarski, R., Kelen, T. and Tüdős, F. *Makromol. Chem.* 1992, **193**, 465

9 Braun, D., Czerwinski, W. K., Bednarski, R., Tüdős, F. and Kelen, T. *Makromol. Chem.* 1992, **193**, 477

10 Bednarski, R., Braun, D., Borbely, J. and Kelen, T. *Makromol. Chem.* 1990, **191**, 773

11 Fordyce, R. G. and Ham, G. E. *J. Am. Chem. Soc.* 1951, **73**, 1186