A new linear method to calculate monomer reactivity ratios by using high conversion copolymerization data: terminal model

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A new linear method of calculation of monomer reactivity ratios is presented for copolymerizations up to very high conversion. It is a linear least-squares method involving several iterations. The basis of calculation is the differential copolymerization equation and the Kelen–Tüdős (K–T) method. The principle and the calculation of computer-simulated data indicate that this new method can correct completely the systematic errors due to high conversion. Calculation using data in the literature shows that this method can be applied in any real systems. The comparison of K–T and extended K–T methods is also discussed.

(Keywords: copolymerization; reactivity ratios; linear method; high conversion; terminal model)

INTRODUCTION

Most existing procedures for calculating reactivity ratios can be classified as linear least-squares (LLS), and non-linear least-squares (NLLS) methods. It is accepted that LLS methods, such as those proposed by Fineman and Ross (F–R)[1], and by Kelen and Tüdős (K–T)[2], can only be applied to experimental data at sufficiently low conversion, because the calculation is based on the differential copolymerization equation[3,4]. The only exception is the extended Kelen–Tüdős method (Ex.K–T)[5], which involves a rather more complex calculation, but is still a LLS method; it can be applied to medium-high conversion experimental data (in most situations conversion can be as high as 40%) without significant systematic error.

To date, if the copolymerizations are carried to high conversions, the exact calculation of reactivity ratios can only be achieved by a NLLS method based on the integrated copolymerization equation[6]. The NLLS procedure can be classified further to a non-weighted NLLS method, such as that proposed by Tidwell and Mortimer[7], and a weighted NLLS method, such as the various forms of 'error-in-variable model'[8–11]. Compared to the LLS method, the NLLS method requires many iterations and a fairly good initial estimation of variables is always needed to attain convergence results. Even so, the different criteria of convergence, and the different initial estimates of reactivity ratios r_1 and r_2 can very often lead to conflicting results. As pointed out by Tüdős *et al.*[5], application of NLLS methods may lead to severe conceptual errors. That is why a fairly good estimation of reactivity ratios as the initial input is always needed for any NLLS calculations.

Our purpose here is to introduce a completely new calculation method which can provide exact solution of reactivity ratios at very high conversion, but which still uses the LLS method without systematic error. As for a NLLS method, our new procedure also necessitates several iterations, but possesses the important and attractive feature that any initial values can be used to start the calculation procedure without affecting the end results.

PRINCIPLE

The differential copolymerization equation is[3,4]:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\left(\frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]}\right) \tag{1}$$

where $[M_1]/[M_2]$ is the ratio of the molar concentrations of monomers M_1 and M_2 in the feed or, equivalently, the ratio of their mole fractions f_1 and f_2. This ratio is usually denoted by f:

$$f = \frac{f_1}{f_2} = \frac{[M_1]}{[M_2]} \tag{2}$$

$d[M_1]/d[M_2]$ is the ratio of instantaneous rates of consumption of the monomers and also expresses the instantaneous composition of the copolymer produced. If the conversion is sufficiently low, the average copolymer composition (usually expressed by F) produced from $t = 0$ to $t = t$ is:

$$F = \frac{F_1}{F_2} = \frac{\Delta[M_1]}{\Delta[M_2]} \approx \frac{d[M_1]_0}{d[M_2]_0} \tag{3}$$

In equation (3), F_1 and F_2 are the average values of the mole fractions of the monomer units in the copolymer.

For convenience we define y as the instantaneous copolymer composition:

$$y \equiv \frac{d[M_1]}{d[M_2]} \tag{4}$$

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Thus equation (1) can be rewritten as:

$$y = \frac{r_1 f^2 + f}{r_2 + f} \tag{5}$$

which can be recast as:

$$f = \frac{(y-1) + \sqrt{(1-y)^2 + 4r_1 r_2 y}}{2r_1} \tag{6}$$

The negative sign before the square root in equation (6), which is also possible mathematically, has been neglected because it leads to the impossible solution wherein f is negative.

The only quantities that are accessible experimentally are the initial monomer feed composition f_0, the average copolymer composition F, and the monomer feed composition at the particular stage of copolymerization f_t. It is impossible to obtain the instantaneous copolymer composition y from experiment. Hence in the various linear methods based on equation (1), y is replaced by F or other accessible parameters, as shown in *Table 1*, where z is a conversion-dependent variable:

$$z = \frac{\log([M_1]/[M_1]_0)}{\log([M_2]/[M_2]_0)} \tag{7}$$

Method 2 is the usual LLS method of using equation (1) or the equivalent equation (5). It can only be applied to systems with sufficiently low conversion[11], normally lower than 5–8%. By replacing f_0 with F/z, method 6 (Ex.K–T) can correct much of the systematic error produced at medium-high conversion (see Figure 5 in ref. 5). Thus in most situations, the Ex.K–T method can be applied to systems with conversion not higher than about 40%. Detailed comments and explanation on methods 1–6 can be found in ref. 5.

It is well known that, apart from the special case of azeotropic copolymerization, for any real experiment, neither f_0 nor f_t can follow the relationship with F that is given by equation (5), i.e.

$$F \neq \frac{r_1 f_0^2 + f_0}{r_2 + f_0} \tag{8}$$

$$F \neq \frac{r_1 f_t^2 + f_t}{r_2 + f_t} \tag{9}$$

However, a definite quantity (which we denote by f^*) must exist such that equation (5) does hold exactly, namely:

$$F = \frac{r_1 f^{*2} + f^*}{r_2 + f^*} \tag{10}$$

Table 1 Various linear methods based on differential copolymerization equation

Method	f	y	Note
1	f_0	$y_0 = F_0$	Exact method, but experimentally impracticable
2	f_0	F	Usual method, applied to sufficiently low conversion, such as F–R, K–T
3	f	F	Not applied in practice
4	f_0	zf_0	Approximations by Walling and Briggs[20]
5	f	zf	A variation of method 3 (not applied in practice)
6	F/z	F	Ex.K–T method[5]
7	f^*	F	Our new method

This quantity f^* can be regarded as an average, integrated, monomer feed composition.

Our purpose (method 7) is to find this f^* to replace f_0. From the preceding discussion, we know that this f^* can correct completely the systematic error produced at any high conversion. If this f^* can be found successfully, our new method will be completely without systematic error. Unfortunately, this f^* cannot be measured experimentally. So the question is how to find f^*.

If it is assumed in the first instance that the true values of r_1 and r_2 are known, then according to the integrated copolymerization equation it follows that[6]:

$$\theta = 1 - \left[\left(\frac{f_1}{f_{1,0}}\right)^{\alpha}\left(\frac{1-f_1}{1-f_{1,0}}\right)^{\beta}\left(\frac{f_{1,0}-\delta}{f_1-\delta}\right)^{\gamma}\right] \tag{11}$$

where θ denotes the fractional conversion of total monomers on a mole basis, and:

$$\alpha = \frac{r_2}{1-r_2} \tag{12}$$

$$\beta = \frac{r_1}{1-r_1} \tag{13}$$

$$\gamma = \frac{1-r_1 r_2}{(1-r_1)(1-r_2)} \tag{14}$$

$$\delta = \frac{1-r_2}{2-r_1-r_2} \tag{15}$$

For the ith experimental point, the instantaneous monomer feed composition $f(i)$, the instantaneous copolymer composition $y(i)$, as well as the average copolymer composition $F^c(i)$ at any conversion $\theta(i)$ can be calculated, and this $F^c(i)$ should be equal to $F^e(i)$, if the latter experimental quantity can be measured without error.

Although it is not true, at this stage of the argument we consider deliberately that this calculated $F^c(i)$ is the same as the instantaneous copolymer composition y instead of average composition (because there are no simple equations linking monomer feed and average copolymer composition). In this situation the corresponding instantaneous monomer feed composition $f^c(i)$ may be calculated by replacing y in equation (6) with $F^c(i)$:

$$f^c(i) = \frac{[F^c(i)-1] + \sqrt{[1-F^c(i)]^2 + 4r_1 r_2 F^c(i)}}{2r_1} \tag{16}$$

The $f^c(i)$ calculated in this way will comply with the relationship of equation (5) with both $F^c(i)$ and the measured $F^e(i)$, that is:

$$F^c(i) = \frac{r_1[f^c(i)]^2 + f^c(i)}{r_2 + f^c(i)} \tag{17}$$

and

$$F^e(i) = \frac{r_1[f^c(i)]^2 + f^c(i)}{r_2 + f^c(i)} \tag{18}$$

Then by using a LLS method (F–R or K–T), a plot of the variable combinations of $f^c(i)$ and $F^e(i)$ will lead to the same true r_1, r_2. This means the $f^c(i)$ is exactly equal to the quantity $f^*(i)$ which is being sought.

Of course we cannot know initially the true values of r_1 and r_2. If the assumed r_1 and r_2 are not correct, the calculated values of $F^c(i)$ will be different from the measured $F^e(i)$. Also the values of $f^c(i)$ calculated from $F^c(i)$ via equation (6) can be valid in equation (5) only with $F^c(i)$, but not with measured $F^e(i)$. That is, equation (17) remains valid, but equation (18) does not. Thus the plot of the variable combination of $f^c(i)$ and $F^e(i)$ will lead to values of r_1 and r_2 that are different from the assumed ones. Only after several tests to find the true values of r_1 and r_2 can the correct $f^*(i)$ be found and then the new calculated r_1 and r_2 will not change. In other words, the criterion that recalculated values of r_1 and r_2 are equal to those assumed, means that both the true values of reactivity ratios and the correct f^* have been obtained.

The *modus operandi* is thus: for a series of experimental data points, $f_0(i)$, $F^e(i)$, $\theta(i)$, $i = 1, 2, \ldots n$, the reactivity ratios are calculated by the following iteration steps.

1. Assign initial values $r_1^{(0)}$, $r_2^{(0)}$.
2. Test their validity by:
    - 2.1. using $r_1^{(0)}$, $r_2^{(0)}$, $f_0(i)$, $\theta(i)$ to calculate $F^{c(0)}(i)$;
    - 2.2. using $F^{c(0)}(i)$ in conjunction with equation (16) to calculate $f^{c(0)}(i)$;
    - 2.3. using $f^{c(0)}(i)$, $F^e(i)$, adopt the K–T plot method to obtain new values of the reactivity ratios $r_1^{(1)}$, $r_2^{(1)}$.
3. If $r_1^{(1)} \neq r_1^{(0)}$ or $r_2^{(1)} \neq r_2^{(0)}$, then test $r_1^{(1)}$, $r_2^{(1)}$ by steps similar to 2.1–2.3 to obtain new values, $r_1^{(2)}$, $r_2^{(2)}$.

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At the kth iteration, test $r_1^{(k-1)}$, $r_2^{(k-1)}$ by:
using $r_1^{(k-1)}$, $r_2^{(k-1)}$, $f_0(i)$, $\theta(i)$ calculate $F^{c(k-1)}(i)$;
using $F^{c(k-1)}(i)$ and equation (16) calculate $f^{c(k-1)}(i)$;
using $f^{c(k-1)}(i)$, $F^e(i)$, adopt the K–T plot method to obtain $r_1^{(k)}$, $r_2^{(k)}$.

Repeat the above iteration until:

$$|r_1^{(k)} - r_1^{(k-1)}| < \varepsilon \quad \text{and} \quad |r_2^{(k)} - r_2^{(k-1)}| < \varepsilon \qquad (19)$$

where ε is a very small value. If the difference between two consecutive calculated reactivity ratios is smaller than ε, then the reactivity ratios may be considered to have attained constant values, so that the $f^c(i)$ calculated at the last iteration, $f^{c(k-1)}(i)$, is the $f^*(i)$ for the ith experiment point. In order to show the accuracy of our method, for all calculations we let $\varepsilon = 0.0001$, which is much more accurate than needed in practice.

In connection with the principles of the procedure described, it is necessary to elaborate on certain aspects. First, the integrated copolymerization equation, equation (11), is not employed in fact, because there are certain situations in which it cannot be applied, namely $r_1 = 1$, $r_2 = 1$, or $r_1 + r_2 = 2$ (see equations (12)–(15)). Instead we use another equivalent method, i.e. integrating the differential equation (1) numerically step by step. The step-by-step method divides the whole copolymerization process into many very small steps, during each of which the feed composition is assumed constant and the copolymer composition is calculated by equation (1). After each step, the feed composition is readjusted by allowing for the amount of both monomers that have entered the copolymer. The process is repeated to the given conversion (θ) for that experimental point (i). The copolymer composition is then averaged over all steps. Heatley *et al.*[12] pointed out that for such a step-by-step calculation, a step length of 0.2% of initial monomers is sufficiently small. By calculation we have verified their conclusion, but nonetheless we adopt an even smaller step length, 0.1% ($\theta = 0.001$), for all calculations.

Secondly, we use the K–T plot method because of its superiority to the F–R method. Thus, interchanging the subscripts of monomer 1 and monomer 2 leads to the same reactivity ratios by the K–T method, but not by the F–R method. This advantage remains in our new method. Moreover, although 'K–T plot' has been mentioned, no actual plot is needed, since all calculations are made with computer by the LLS method.

RESULTS AND DISCUSSION

Using computer-simulated data

To demonstrate the accuracy of our method, we use a computer to simulate a series of data points with medium–high conversion. The results are given in *Table 2*, where conversion has been expressed on a weight per cent basis instead of θ. This case is referred to as system 1. The results of calculations for all iteration steps from beginning to end are shown in *Table 3*. The 95% confidence intervals are calculated with the last iteration data according to the standard procedure given by Tüdős *et al.*[13].

Table 3 also includes the difference, S, between calculated and measured average copolymer composition:

$$S = \sum_{i=1}^{n} [F^e(i) - F^c(i)]^2 \qquad (20)$$

Table 2 Computer-simulated experimental data for medium–high conversion: system 1 ($MW_1 = 200$, $MW_2 = 100$, $r_1 = 10$, $r_2 = 0.2$, where MW_1 and MW_2 are the molecular weights of monomers M_1 and M_2, respectively)

f_0	F^e	Conversion (wt%)
0.1111	0.5188	19.96
0.2500	1.2188	29.95
0.4286	2.0950	39.95
0.6667	5.2467	10.01
1.0000	7.8574	20.00
1.5000	11.3457	29.99
2.3333	19.8333	19.98
4.0000	32.6700	29.99
9.0000	70.4286	40.03

Table 3 Iteration results of system 1

Iteration	r_1	r_2	S
0	1	1	5072.1915405
1	8.4511806	0.3096774	182.2368645
2	10.0619642	0.2287886	0.1199289
3	10.0260248	0.2057612	0.0104143
4	10.0080843	0.2015177	0.0002300
5	10.0032989	0.2004853	0.0001881
6	10.0021194	0.2002344	0.0003603
7	10.0018319	0.2001734	0.0004132
8	10.0017619 ±0.0027038	0.2001586 ±0.0002522	0.0004268

S can be used as a kind of objective function in the NLLS method, for which the only criterion for the advancing iteration is a decrease in S. However, for our method it is not necessary for S to be calculated in order for the iteration steps to proceed. For the end results, S may or may not reach a minimum value. The criterion to stop the calculation is attainment of constant values of r_1 and r_2.

From *Table 3* it can be seen that in our method the convergence is very rapid. For such a big difference between the initial estimation ($r_1^{(0)} = r_2^{(0)} = 1$) and end results ($r_1 = 10.00$, $r_2 = 0.20$), only eight iterations can lead to values of r_1, r_2 unchanged within four decimal places. Arbitrary initial values of $r_1^{(0)} = 1$, $r_2^{(0)} = 1$ were used in *Table 3*. We can also use any other initial values. Thus in *Table 4* two examples are given of widely differing initial values of $r_1^{(0)}$ and $r_2^{(0)}$. From *Tables 3* and *4* it can be seen that any initial values of r_1, r_2 can start the calculation, without affecting the end results. This is one of the advantages of our method compared to the NLLS method.

Table 4 Iteration results of system 1 by using different initial values

Iteration	r_1	r_2	S
0	0.1	100	6129.8819544
1	1.3264118	−0.3097455	4487.0528164
2	8.7720509	0.1755836	84.5842051
3	9.9669529	0.2004629	0.0842672
4	10.0018105	0.2004356	0.0005138
5	10.0020528	0.2002295	0.0003743
6	10.0018259	0.2001724	0.0004145
7	10.0017608	0.2001583	0.0004270
	±0.0027044	±0.0002523	
0	100	1	353931.8497277
1	10.0823445	0.1562285	2.1211249
2	9.9606192	0.1897397	0.0492936
3	9.9929683	0.1983092	0.0041796
4	9.9996156	0.1997041	0.0009669
5	10.0012232	0.2000443	0.0005397
6	10.0016139	0.2001272	0.0004563
7	10.0017089	0.2001473	0.0004372
8	10.001732	0.2001522	0.0004327
	±0.0027201	±0.0002538	

Table 5 Computer-simulated experimental data of very high conversion: system 2 ($MW_1 = 200, MW_2 = 100, r_1 = 0.01, r_2 = 0.05$)

f_0	F^e	C (wt%)
0.1111	0.3319	45.42
0.1111	0.2500	54.54
0.2500	0.4997	66.66
0.2500	0.4000	75.00
0.4286	0.7433	76.80
0.4286	0.6000	84.62
0.6667	0.8993	84.20
0.6667	0.7999	92.86
1.0000	0.9639	79.51
1.0000	0.9650	89.47
1.5000	0.9972	65.60
1.5000	1.1025	75.16
2.3333	1.0227	44.28
2.3333	1.0471	53.35
4.0000	1.0542	25.22
4.0000	1.0969	33.85
9.0000	1.1128	8.04
9.0000	1.2099	16.29

Table 6 Iteration results of system 2

Iteration	r_1	r_2	S
0	1	1	144.2167554
1	0.0527578	0.2310075	0.6545507
2	0.0226413	0.1462693	0.0927818
3	0.0174338	0.1131704	0.0368632
4	0.0156829	0.0958645	0.0213531
5	0.0146188	0.0851719	0.0135825
6	0.0138728	0.0778433	0.0091322
7	0.0132931	0.0726087	0.0066503
8	0.012788	0.0686223	0.0047072
9	0.0123806	0.0655005	0.0033877
10	0.0120496	0.0630178	0.0024565
11	0.0117727	0.0610124	0.0018141
12	0.0115287	0.0593506	0.0013150
13	0.0113201	0.0580284	0.0009725
14	0.0111497	0.0569063	0.0007454
15	0.0109902	0.0559466	0.0006161
16	0.0108406	0.0551287	0.0004518
17	0.0107274	0.0544236	0.0003419
18	0.0106304	0.053813	0.0002496
19	0.0105509	0.0533287	0.0001919
20	0.0104821	0.0529071	0.0001480
21	0.0104217	0.0525395	0.0001142
22	0.0103686	0.0522181	0.0000881
23	0.0103218	0.0519368	0.0000663
24	0.0102782	0.0517009	0.0000503
25	0.0102430	0.0514938	0.0000388
26	0.0102123	0.0513117	0.0000300
27	0.0101852	0.0511516	0.0000232
28	0.0101612	0.0510106	0.0000179
29	0.0101401	0.0508863	0.0000138
30	0.0101214	0.0507767	0.0000107
31	0.0101049	0.0506800	0.0000082
32	0.0100903	0.0505946	0.0000063
	±0.0001494	±0.0001020	

Table 7 K–T and Ex.K–T results of system 1 and system 2

System	Method	r_1	r_2
1	K–T	8.4512 ± 0.9828	0.3097 ± 0.1492
	Ex.K–T	10.0130 ± 0.0215	0.2022 ± 0.0020
2	K–T	0.0519 ± 0.0397	0.2231 ± 0.0605
	Ex.K–T	0.0082 ± 0.0050	0.0458 ± 0.0036

A computer is next used to simulate a series of data points with very high conversion for a copolymerization denoted by system 2 (see *Table 5*), the corresponding iteration results being shown in *Table 6*. It can be seen that our method is an exact calculation method without systematic error no matter how high the conversion. Very high conversion only requires a greater number of iterations, as seen in *Table 6*. Certainly if the copolymerization reaches 100% conversion then this data point will be useless because copolymer composition will always equal the initial monomer feed composition regardless of reactivity ratios.

For comparison, we also apply the K–T and Ex.K–T methods to calculate r_1 and r_2 for these same two systems. The results are shown in *Table 7*. By comparison of *Table 7* with *Table 3* it can be seen that, if the conversion is medium–high, the Ex.K–T method can also provide good results. However, if the conversion is very high, comparison of *Table 7* with *Table 6* shows that the Ex.K–T method yields a large error. Under these circumstances, the superiority of our new method over the Ex.K–T method is evident.

Using data from literature

Since our method has now been shown to apply very satisfactorily for computer-simulated data, it is necessary to consider real systems with unavoidable random experimental errors. In general, one method may work well with computer-simulated data but does not satisfy real experimental data containing random errors. Consequently, we now apply our method to data reported in the literature for several different copolymerizations up to different maximum conversion (low–medium). *Table 8* shows the results calculated by our method as well as the K–T and Ex.K–T procedures. The purpose of the comparison in *Table 8* is to show that, even with random error inherent in real systems, our method is reliable. Indeed our method and the Ex.K–T method yield almost identical values of r_1 and r_2.

Table 8 Results of calculations using literature data by various methods

Ref.	Maximum conversion (wt%)	Method[a]	r_1	r_2
15	7.2	Ours (4)	0.3707 ± 0.0933	0.1321 ± 0.0306
		K–T	0.3772 ± 0.0973	0.1371 ± 0.0322
		Ex.K–T	0.3696 ± 0.0948	0.1324 ± 0.0313
16	8.5	Ours (4)	0.6479 ± 0.2810	0.9062 ± 0.2557
		K–T	0.6578 ± 0.2837	0.9096 ± 0.2559
		Ex.K–T	0.6458 ± 0.2899	0.9048 ± 0.2644
17	9.49	Ours (5)	4.6506 ± 1.2837	0.0339 ± 0.0742
		K–T	4.4920 ± 1.2741	0.0503 ± 0.0913
		Ex.K–T	4.6485 ± 1.3345	0.0339 ± 0.0780
18	19.1	Ours (5)	4.2910 ± 0.4805	0.0190 ± 0.0457
		K–T	3.8753 ± 0.5094	0.0294 ± 0.0379
		Ex.K–T	4.2855 ± 0.4955	0.0034 ± 0.0177
19	9.2	Ours (4)	2.1539 ± 0.3375	0.3761 ± 0.1066
		K–T	2.1120 ± 0.3305	0.3932 ± 0.1102
		Ex.K–T	2.1540 ± 0.3517	0.3757 ± 0.1110
7	36.4	Ours (7)	0.5598 ± 0.0680	0.4755 ± 0.0611
		K–T	0.6256 ± 0.0747	0.5502 ± 0.0697
		Ex.K–T	0.5591 ± 0.0822	0.4734 ± 0.0744

[a] The number in parentheses following 'Ours' denotes the number of iterations; for all calculations, values were set at $\varepsilon = 0.0001$ and initial $r_1^{(0)} = r_2^{(0)} = 1$

Meyer[14] has published a series of conversion–composition data up to very high conversions for the styrene–methyl methacrylate system. From these data, he also derived reactivity ratios by the graphical intersection method. Although his data extended to very high conversion (the highest is $\theta = 0.95$), he only used experimental data below $\theta = 0.50$ to determine the reactivity ratios. Now we use our new method as well as the K–T and Ex.K–T methods to calculate r_1 and r_2 for his data. First the data points below $\theta = 0.50$ are employed in order to effect a comparison with the results of Meyer. Then all data up to all conversions are used for the calculations. The results are shown in *Tables 9* and *10*.

From *Tables 8* and *9* it can be seen that our method works very well with real systems, and also that the convergence is very quick. *Tables 8–10* show that for low conversion data[15,16], the three procedures (K–T, Ex.K–T and our new method) gave almost the same reactivity ratios. This finding is wholly reasonable because, although the K–T method makes no allowance for shift in monomer concentration, this accord among the three methods applies only to the region in which such a shift is very small. However, for medium–high conversion data[7,17–19], the K–T method resulted in appreciable error, whereas the other two methods still gave reactivity ratios which agreed very well with each other. For very high conversion data[14], the reactivity ratios from the K–T and Ex.K–T methods are different from each other; it is also seen that for some of the systems conducted to high conversion, there are differences afforded by our procedure and the Ex.K–T method. This is similar to the situation found for computer-simulated data (system 1 and system 2).

The differences between the results afforded by our method and the Ex.K–T method at high conversion (*Tables 9* and *10*) are not consistently great because the data used related to the particular case in which the

Table 9 Comparison of our new method with the graphical intersection method for results reported by Meyer[14]: M_1 = styrene, M_2 = methyl methacrylate

Experiment number[a]		Maximum conversion (mol%)	I[b]	New method		Graphics intersection[14]	
$f_0 = 4$	$f_0 = 0.25$			r_1	r_2	r_1	r_2
19–30	19–13	46.26	6	0.5344 ± 0.0312	0.5922 ± 0.0361	0.53 ± 0.02	0.56 ± 0.06
		95.00	9	0.5434 ± 0.0280	0.6399 ± 0.0367		
19–43	19–17	44.35	6	0.5429 ± 0.0267	0.5417 ± 0.0315	0.55 ± 0.02	0.53 ± 0.06
		86.30	8	0.5435 ± 0.0250	0.5450 ± 0.0233		
19–43	19–49	45.13	7	0.5397 ± 0.0246	0.5201 ± 0.0309	0.54 ± 0.02	0.53 ± 0.08
		67.73	8	0.5448 ± 0.0281	0.5508 ± 0.0309		
19–43	19–34	44.35	6	0.5374 ± 0.0291	0.5056 ± 0.0472	0.53 ± 0.02	0.46 ± 0.06
		70.40	7	0.5465 ± 0.0427	0.5616 ± 0.0661		
19–42	19–45	44.48	6	0.5548 ± 0.0697	0.5947 ± 0.1179	0.53 ± 0.03	0.42 ± 0.06
		91.07	8	0.5447 ± 0.0425	0.5208 ± 0.0654		
All experiments		46.26	6	0.5397 ± 0.0229	0.5457 ± 0.0223		
		95.00	7	0.5450 ± 0.0189	0.5715 ± 0.0190		

[a] For detailed conversion–composition data of each experiment, refer to Tables 2–3 and 5–10 in ref. 14

[b] I, number of iterations

Table 10 Results of calculation by the K–T and Ex.K–T methods using the data of Meyer[14]: M_1 = styrene, M_2 = methyl methacrylate

Experiment number		Maximum conversion (mol%)	K–T		Ex.K–T	
$f_0 = 4.0$	$f_0 = 0.25$		r_1	r_2	r_1	r_2
19–30	19–13	46.26	0.5793 ± 0.0392	0.6394 ± 0.0457	0.5340 ± 0.0364	0.5877 ± 0.0413
		95.00	0.6499 ± 0.0769	0.7330 ± 0.0910	0.5275 ± 0.0945	0.6911 ± 0.1495
19–43	19–17	44.35	0.5968 ± 0.0251	0.5981 ± 0.0304	0.5412 ± 0.0343	0.5361 ± 0.0392
		86.30	0.6107 ± 0.0362	0.6368 ± 0.0364	0.5386 ± 0.0431	0.5305 ± 0.0357
19–43	19–49	45.13	0.5945 ± 0.0304	0.5859 ± 0.0396	0.5387 ± 0.0316	0.5180 ± 0.0387
		67.73	0.6101 ± 0.0441	0.6355 ± 0.0488	0.5437 ± 0.0399	0.5528 ± 0.0424
19–43	19–34	44.35	0.5880 ± 0.0383	0.5515 ± 0.0618	0.5370 ± 0.0348	0.5069 ± 0.0559
		70.40	0.6083 ± 0.0724	0.6318 ± 0.1088	0.5480 ± 0.0712	0.5901 ± 0.1098
19–42	19–45	44.48	0.6037 ± 0.0757	0.6387 ± 0.1268	0.5525 ± 0.0831	0.5885 ± 0.1377
		91.07	0.6432 ± 0.0633	0.6213 ± 0.0962	0.5417 ± 0.0621	0.4937 ± 0.0837
All experiments		46.26	0.5901 ± 0.0250	0.5997 ± 0.0246	0.5383 ± 0.0279	0.5420 ± 0.0263
		95.00	0.6320 ± 0.0361	0.6593 ± 0.0346	0.5365 ± 0.0397	0.5808 ± 0.0422

reactivity ratios were not very small. Unfortunately we were unable to locate literature data extending to high conversion for systems in which both reactivity ratios were small or in which one of them was small and the other large. As indicated by Tüdős *et al.*, such types of reactivity ratio restrict the accurate applicability of the Ex.K–T method for medium–high conversion.

CONCLUSIONS

A new linear method of calculating monomer reactivity ratios can be applied to copolymerization systems with very high conversion without systematic error due to high conversion. It is an iterated LLS method based on the differential copolymerization equation and on the K–T plot method. Any initial estimation of reactivity ratios can start the calculation without any effect on the end results. The advantage of the K–T method, i.e. interchanging the subscripts of monomers can lead to the same results, is retained in this new method. All the calculations are carried out by computer, normally within 1 min excluding data input time, except for those systems with very high conversion for which the computing time is slightly longer. We believe that an important advantage of the new procedure is its freedom of restrictions with regard to feed composition, extent of conversion and values of reactivity ratios. Moreover, although details are not provided here, it is possible to calculate the joint confidence interval of the reactivity ratios in addition to the individual confidence intervals presented here.

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NOMENCLATURE

f	$f = f_1/f_2$, instantaneous monomer feed at $t = t$, if $t = 0$, then specified as f_0
f^c	Calculated by equation (16) at each iteration
f^*	Calculated by equation (16) at the last iteration (when reactivity ratios calculated from two concessive iterations are unchanged)
F	$F = F_1/F_2$, average copolymer composition produced from $t = 0$ to $t = t$
F^c	Calculated average copolymer composition from $t = 0$ to $t = t$ at each iteration
F^e	Experimental found average copolymer composition from $t = 0$ to $t = t$
$[M_j]$	$j = 1, 2$, molar concentration of monomer j at $t = t$
$d[M_j]$	$j = 1, 2$, monomer j consumed at $t = t$
$d[M_j]_0$	$j = 1, 2$, monomer j consumed at $t = 0$

$\Delta[M_j]$	$j = 1, 2$, monomer j consumed from $t = 0$ to $t = t$
$r_j^{(0)}$	$j = 1, 2$, initially assumed reactivity ratios
$r_j^{(k)}$	$j = 1, 2$, $k = 1, 2, \ldots$, recalculated reactivity ratios at each iteration
S	Defined by equation (20)
y	$y = \mathrm{d}[M_1]/\mathrm{d}[M_2]$, instantaneous copolymer composition produced at $t = t$
y_0	$y_0 = \mathrm{d}[M_1]_0/\mathrm{d}[M_2]_0$, instantaneous copolymer composition produced at $t = 0$
θ	Fractional conversion of total monomers on a mole basis