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Copolymerization at moderate to high conversion levels: 1. New evaluation procedure of the relative reactivity ratios in terms of the terminal model

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For moderate or high conversion copolymerization data three sorts of peculiar data points are discussed which are disadvantageous in determining the relative reactivity ratios: (a) copolymer contains an unknown quantity of homopolymer because the comonomer was fully consumed before the end of the reaction, (b) estimation error of the conversion is relatively high, (c) estimation error of the copolymer composition is very high. For the numerical integration procedure according to the terminal model a selection is proposed to eliminate such data points from calculations which are suspected of being uncertain. Furthermore, a separate interpolative procedure is proposed which permits a final separation of points of type (a) from points of type (b) and (c).

(Keywords: copolymerisation; relative reactivity ratios; high conversion)

INTRODUCTION

The availability of an evaluation method for high conversion copolymerization data for the determination of the relative reactivity ratios is advantageous for several practical reasons. Comonomer systems may exhibit unexpected substituent or solvent effects on the reaction making it difficult to control. In such cases, normally, time conversion relations are required to keep conversion as low as possible. Only under such conditions is the differential copolymerization equation[1–4] for determining the relative reactivity ratios r_1 and r_2 applicable. In contrast, the number of new monomers still increases. Some of them are available only in low quantities or are unstable. Under these conditions the number of experiments must often be limited and/or low quantities of monomers are available. It is often necessary to convert them to such a degree that copolymers can be isolated, purified and analysed. Further, model discriminations require as reliable an estimation as possible for r_1 and r_2 values even from data obtained at higher conversions. Considering these facts, it follows that time may be saved if an evaluation method of r_1 and r_2 parameters directly from high conversion data is available.

For this purpose three methods may be applied.

(1) The Walling–Briggs treatment[5].

unconsumed comonomer); (b) point (a) does not hold, but the estimation error for conversion is above average; (c) partial conversions of comonomers are not exceeded and accurate conversion is available, but the measured composition of the copolymer is less accurate than for other data points.

The deviations under consideration are understood to be significantly high, i.e. erroneous conversion or copolymer composition exceeds the mean error still present in each data set. In this study the 2–3-fold error above average error was considered for testing the sensitivity of the proposed method. The origin of such errors may be experimental in nature (considerable inclusions of involatile solvents or, polymer loss during isolation) or may emerge during data transfer (reading, typing, etc.).

Data points under (a) are unappropriate to be used in the computation of the reactivity increments r_1 and r_2. Further, removal of points (a)–(c) considerably accelerates especially the numerical procedures and raises the accuracy of parameters being estimated.

In this connection the need for controlling elements in such computational technique should be emphasised. The aim of this work is to propose such elements as examples taking both chemical and computational aspects into account. They do not constitute a fully error-tolerant for the estimation of r_1 and r_2. Of course, data points of types (b) + (c) or even (a) + (b) + (c) etc. (more than one type of inaccuracy) can happen. They are not discussed here and, generally, such experiments should preferably be examined more closely.

Evaluation methods 1 and 2 mentioned previously allow investigations of the polymer composition as a function of the monomer feed composition at very different conversion levels. In contrast, in method 3 the polymer composition is followed by the progress of the reaction for a few monomer feed compositions only. In this case a much better control of the reaction conversion and of the copolymer composition is given. So far there is no need to discuss this method here. Additionally, the predetermination of points of type (a) in this case is not possible without any knowledge of r_1 and r_2. They cannot be separated out during computations and they may unfortunately be involved in the calculations.

CALCULATION METHODS

Method by Walling and Briggs[5]

This is the simplest and very reliable method of copolymer composition calculation for zero conversion from non-zero conversion data. It allows the use of the differential copolymerization equation for such experimental data (as a function of the monomer feed composition).

The differential copolymerization equation may be written as[18]

$$y_0 = \left(\frac{m1}{m2}\right)o = z.\frac{M_1{}^{\circ}}{M_2{}^{\circ}} = z.x_0 \qquad (1)$$

with m_i as mole ratio of monomer i in copolymer and M_i in monomer feed. The factor z is defined as:

$$z = \frac{\log\dfrac{M_1}{M_1{}^{\circ}}}{\log\dfrac{M_2}{M_2{}^{\circ}}} \qquad (2)$$

and can be calculated from measured data as follows.

$$z = \frac{\log(1-\zeta_1)}{\log(1-\zeta_2)} \qquad (3)$$

where ζ_1 and ζ_2 are partial conversions of the individual monomers:

$$\zeta_2 = \frac{C\left(\dfrac{MWM_2}{MWM_1} + x_o\right)}{\left(\dfrac{MWM_2}{MWM_1} + y\right)} \qquad (4)$$

$$\zeta_1 = \frac{y}{x_o}.\zeta_2 \qquad (5)$$

C denotes the total weight conversion, MWM_i molecular weight of the monomer i, y_0, in equation (1) is related to zero conversion, y corresponds to the given conversion and is known from the experiment as $y = m_1/m_2$, similar to x_o (s.equation (1)).

When computing y_0 one should first examine wether $\zeta_i < 1$. Otherwise points have to be removed from calculations, since equation (3) cannot be computed for $\zeta_i \geqslant 1$ and there is no physical meaning for such points. No criteria exist to eliminate points of type (b) or (c), so they will increase the inaccuracy of the estimation of r_1 and r_2.

Numerical integration of the differential copolymerization equation

The calculation procedure used in this article is briefly presented in Appendix A and is called here the 'main procedure' in contrast to the 'interpolation procedure' discussed in the next paragraph.

It is obvious that the elimination of points of type (a) and type (b) or (c) plays an essential role in the convergency of runs. While points of type (a) were very easily detected and could be effectively eliminated, the selection of points of type (b) and (c) caused instability or divergency of program runs. This was the case because the criterial values for finding points of type (b) and (c) changed considerably during computations. Then the calculation was divided into two stages: until the preliminary first convergency was reached, only the search for points of type (a) was performed. During the second stage (final convergency run) criteria for finding points of type (b) and (c) after elimination of points of typ (a) were applied using r_1 and r_2 estimated during the preliminary convergency run.

Search for points of type (a). The consumption of monomers during the reaction progress was monitored in the integration loop for each of the monomer mixture compositions under investigation. In given cases, the reaction conversion at which one of the comonomers was entirely consumed was noted, but the integration was continued until it reached the value 1 (end of reaction). That point (monomer mixture) was eliminated (appendix, points 3 and 7) and the remaining data points were resequenced to continue calculations.

Search for points of type (b) and (c). Points of these types showed one or both of the two following indications: the calculated cumulative copolymer composition was not equal to the measured value and/or the pair of individual copolymerization parameters r_1^{ML} and r_2^{ML} (see point 2 in the appendix) deviated from the values observed for all other points (r_1 and r_2). Depending on the individual r_1^{ML} and r_2^{ML} values the overall r_1 and r_2 values were updated after each approximation loop (appendix, point 3 and 6) and served as reference in the following elimination expression: if $|m_2^{calc} - m_2^{exper}| \geqslant 0.0003$ and($r_1^{ML} < 0.5r_1$ or $r_1^{ML} > 1.5r_1$) and($r_2^{ML} < 0.5r_2$ or $r_2^{ML} > 1.5r_2$)then eliminate the data point.

These limits were chosen arbitrarily and were found to be effective if the computed conversion differed by more than ± 5% from the measured value or the calculated copolymer composition deviated by more than ± 2% from the measured copolymer composition (see the Appendix, point 7).

Experiences with the search procedures. Procedures described above were tested on four simulated data sets. Assuming one pair of r_1 and r_2 values the cumulative copolymer composition was calculated for a set of different monomer feed compositions varying the global conversion in the range between 15% and 85% within the set of monomer feed compositions. Starting with this data set (data set 1) three other data sets were derived:

(1) data set 1: data points without any deviation from the classical copolymerization model — generated by means of known r_1 and r_2 values;
(2) data set 2: data taken from data set 1, but for two points the conversion was chosen high enough to exceed the total partial conversion of one of the comonomers;

Table 1 Copolymer composition as function of the monomer feed composition for the system methyl methacrylate (MMA = M_1)/ N-vinyl pyrrolid-2-one (NVP = M_2) for non-zero and zero conversion (polymerization at 60°C with AIBN as initiator, at 0.4 mol l^{-1} global monomer concentration)[a]

				Calc. mole fraction $m2$ in the copolymer at zero conversion		
No.	Mole fraction M_2 in the feed (M_2)	Mole fraction M_2 in coplymer (m_2^{exper}) 1st/2nd	conv. in wt% C^{exper}	WB method $m_2^{C=0, WB}$ 1st/2nd	Numerical integr. method [b] $m_2^{C=0, num}$ 1st/2nd	max. convers. $C^{exper,max}$ 1st/2nd
Solvent DMSO						
1	0.200	0.058/0.065	16.3	0.054/0.061	0.053/0.061	
2	0.400	0.159/0.167	63.2	0.085/0.094	0.076/0.085	
3	0.550	0.186/0.191	18.9	0.166/0.171	0.161/0.166	
4	0.650	0.276/0.230	24.2	0.240/0.190	0.224/0.190	
5	0.750	0.406/0.404	41.1	[c]/[c]	[c]/[c]	0.280/0.296
6	0.850	0.650/0.603	43.5	[c]/[c]	[c]/[c]	0.390/0.311
7	0.900	0.688/0.664	22.9	[c]/[c]	0.579/0.540	
8	0.940	0.758/0.763	40.6	[c]/[c]	[c]/[c]	0.155/0.166
9	0.980	0.852/0.835	38.5	[c]/[c]	[c]/[c]	10.001/0.001
Solvent methanol						
1	0.200	0.078/0.076	5.4	0.076/0.075	0.076/0.075	
2	0.400	0.139/0.140	3.3	0.137/0.138	0.137/0.138	
3	0.550	0.200/0.188	3.6	0.197/0.184	0.197/0.185	
4	0.650	0.239/0.239	5.0	0.233/0.232	0.234/0.234	
5	0.750	0.343/0.341	10.6	0.328/325	0.325/0.323	
6	0.850	0.664/0.610	53.2	[c]/[c]	[c]/[c]	0.437/0.375
7	0.900	0.692/0.646	27.4	[c]/[c]	0.569/0.467	
8	0.940	0.756/0.750	42.7	[c]/[c]	[c]/[c]	0.241/0.236
9	0.980	0.725/0.660	3,8	[c]/[c]	0.677/[c]	0.001/0.001

[a] The copolymer composition was determined (both 1st and 2nd anlysis) by means of the elemental analysis. [b] Calculated with relative reactivity ratios listed in Table 2, last column. [c] Method indicates that NVP (IM_2) was fully consumed before the end of reaction.

(3) data set 3: in the data set 1 the conversion of two points was altered (+5 and −10%) keeping the polymer composition unchanged;

(4) data set 4: in the data set 1 the composition of two copolymers was altered (+2 and −4% respectively);

The following general observations were made.

I. For data set 2 points polymerized above the total partial conversion of one of the monomers were eliminated during the first and mostly during the second convergency run.

II. Data points with altered conversion or copolymer composition have an effect on r_i – values being estimated. As result the behavior of type (a) was observed in the case of different points. The first run never led to r_i-values adopted originally preparing data sets 1–4. The second convergency run yielded correct r_i-values because a verified data sequence was in use.

III. It follows from I and II that during the first convergency run the first selection can eliminate data points of all types (a) to (c) and sometimes even additional points which often only slightly exceed the selection limits. However, the selected data points cannot be removed from the calculation during the second convergency run because they may contain points of type (b) and (c). As mentioned under I, points of type (a) are mostly found during the second convergency run, but it can happen that this is not the case.

At this stage tests made by changing the selection criteria between both convergency runs give the first indication of the origin of deviation of selected points. However the behavior of points of type (b) and (c) is very similar and it is, furthermore, not completely certain which points belong to type (a). It is then necessary to examine all selected data points by means of an independent procedure taking into account the relative reactivity ratios found in the main procedure. Such a procedure is presented in the following paragraph.

Interpolation procedure for examining selected data points

This separate procedure was used for each eliminated data point applying the values for r_1 and r_2 obtained in the main procedure.

(1) In the first step the copolymerization equation was integrated until the conversion $C=C^{exper}$, was reached. Simultaneously, the cumulative copolymer composition m_2^{calc} and the total consumption of both monomers are monitored in the integration loop.

(2) m_2^{calc} and m_2^{exper} were compared; for points m_2^{calc} belonging to the interval $m_2^{exper} \pm 0.05$. m_2^{exper} it was assumed that there is an agreement between the model calculation and the experimental result and no further calculations were performed (even data points of type (a) were included).

(3) In cases where the condition under 2 was not fulfilled and there was a degree of certainty that the copolymer composition was erroneous, the cumulative copolymer composition m_2^{calc} calculated under 1 was concidered as an interpolated approximate value replacing m_2^{exper} e.g. in the planning of experiments etc.

(4) The other cause of not fulfilling the condition under 2 can be an error in the conversion measurement. If there was such evidence, the copolymerization equation was reintegrated until $m_2^{calc} = m_2^{exper}$ instead of the condition $C=C^{exper}$. For this purpose the cumulative copolymer composition m_2^{calc} and the consumption of both monomers m_1, and m_2 was controlled in the integration loop. The conversion level C last reached indicated what the conversion should be if no other error were contained in the data.

Without any knowledge of the exact error source (inaccuracy of type (b) or (c)) no differentiation can be made concerning its origin.

Table 2 Reactivity ratio for the system MMA (M_1)/NVP (M_2) calculated for a differential conversion around zero conversion

Relative reactivity ratio	KT method	NLLS method
	from $m_2^{C=0,WB}$	from $m_2^{C=0,num}$
Solvent DMSO		
r_1	3.694 ± 0.356	6.184 ± 0.235
r_2	− 0.138 ± 0.003	0.127 ± 0.057
Solvent methanol		
r_1	2.708 ± 0.168	3.584 ± 0.370
r_2	− 0.145 ± 0.002	0.025 ± 0.005

This calculation procedure helps to distinguish points of type (a) from other selected points. Now they should be removed from the data set and the main procedure (the second convergency run) has to be repeated to calculate the final r_1 and r_2 values.

APPLICATION EXAMPLE: EVALUATION OF COPOLYMERIZATION DATA FOR THE SYSTEM METHYL METHACRYLATE (MMA = M_1)IN-VINYL PYRROLID-2-ONE (NVP = M_2)

The system MMA/NVP was polymerized at high dilution in two solvents: DMSO and methanol. The experimental conditions, the polymer composition as a function of the monomer feed composition and its recalculation results in zero conversion in terms of both methods: WB and numerical procedure are summarized in *Table 1*.

It can be seen from this presentation that the performance of both methods is very similar and almost identical at lower conversion levels. But, as expected, the numerical method allows a more precise description of the polymerizing system.

The relative reactivity ratios obtained in terms of both methods are shown in *Table 2*. For this calculation experiments which stopped already after NVP was fully consumed (indicated in table by [c]) were not considered.

The negative r_2-values resulting from the WB/KT method mean merely that the true (positive) values are very small. In this regard the results yielded by the numerical method are more useful.

It is noticeable that values presented in *Table 2* are distinctly dependent on solvent quality.

Examination procedure for eliminated points

Data points eliminated in the main procedure ([c] in *Table 1*) were examined in terms of the interpolation procedure described above. In this way the maximum weight conversion was found at which NVP should be still present in the monomer mixture, i.e. the maximum conversion which allowed interpretable results when repeating experiments. This maximum conversion $C^{\text{exper,max}}$ is listed in *Table 1*, last column.

APPENDIX A: MAIN PROCEDURE FOR CALCULATING THE RELATIVE REACTIVITY RATIOS R_1 AND R_2FROM NON-ZERO CONVERSION COPOLYMERIZATION DATA (COPOLYMER COMPOSITION AS A FUNCTION OF THE MONOMER FEED COMPOSITION DATA)

For the estimation of the relative reactivity ratios the non-linear least squares (NLLS) procedure according to Tidwell and Mortimer[19] (TM-method) was used. Simultaneously the numerical integration of the classical copolymerization equation was applied in such a way that the copolymer composition m_i was recalculated to zero conversion using r_1 and r_2 under approximation. The final r_1 and r_2 are therefore valid for zero conversion. The following computational procedure is related to the monomer m_2 and its content in polymer m_2^{exper} measured experimentally at the given non-zero conversion.

(1) The starting r_1 and r_2 values are estimated directly from experimental data (non- zero conversion) in terms of the NLLS procedure or they can be arbitrarily chosen.

(2) The aim of this point is to find the copolymer composition $m_2^{C=0}$ corresponding to the starting monomer feed composition $[M_2]$ which after integration until the experimental conversion C using the chosen r_1 and r_2 values yields a cumulative copolymer composition $m_2^{\text{calc}} = m_2^{\text{exper}}$. This is repeated for each experimental point separately.

REMARK

If the copolymerization curve calculated with r_1 and r_2 were used, copolymer composition points would almost never lie on it and no exact integration could run. To overcome this problem a new pair of parameters has to be adopted. In this procedure the Mayo-Lewis[2] (ML) transformation method of the differential copolymerization equation was used as follows: for $[M_2] <$ limit value (mostly 0.5)r_2 remains unchanged and

$$r_1^{ML} = \frac{y.r_2}{x^2} + \frac{(y+1)}{x}$$

with $x = (1 - [M_2])/[M_2]$ and $y = (1 - m_2^{\text{calc}})/m_2^{\text{calc}}$ and for $[M_2] \geq$ limit value r_1 remains unchanged

$$r_2^{ML} = \frac{x^2.r_1}{y} + \frac{x(y+1)}{x}$$

The search for the best point fulfilling the condition $m_2^{\text{calc}} = m_2^{\text{exper}}$ is performed adopting the minimization for $m_2^{C=0}$ (by means of Fibonacci numbers e.g.). The search intervals are:(a) for $[M_2] > m_2^{\text{exper}}$: from 0.0 to m_2^{exper}(b) for $[M_2] < m_2^{\text{exper}}$ from m_2^{exper} to l and(c) for $[M_2) = m_2$no search

(3) After $m_2^{c=0}$ values have been found for all m_2 feed compositions, points are (re)selected (s.point 7) and new r_1 and r_2 values are calculated by means of the NLLS method.

(4) The search as described under 2 is repeated using new r_1 and r_2 values estimated under 3. The searching intervals are now changed as follows.(a) for $[M_2] > m_2^{\text{exper}}$ from (first minimum − 0.01) to m_2^{exper}(b) for $[M_2] < m_2^{\text{exper}}$ from m_2^{exper} to the (first minimum + 0.01)This precaution was found necessary to avoid local minima and has to be used once only (more than two local minima were not observed).

(5) Points 3 and then 2 are repeated changing the searching intervals as follows: lower limit: last $m_2^{c=0}$ − 0. 1.last $m_2^{c=0}$, upper limit: last $m_2^{c=0}$ + 0. 1. last $m_2^{c=0}$ whereby the factor 0.1 may by reduced stepwise to 0.02–0.03 when repeating point 5 (accelerating precautions).

(6) Point 5 is repeated until a stability in r_1 and r_2 is obtained. In this example as finishing criterion was used: the sum of differences of r_1 and r_2 between two last NLLS runs should be less than or equal to 0.001. Higher accuracy in r_i values is meaningless in practice.

(7) For each estimation of r_1, r_2 and $m_2^{c=0}$ two successive convergency runs were used. During the first convergency run points exceeding the total partial conversion of one of the monomers were eliminated. For this purpose the total consumption of both monomers must be monitored in the integration loop. During the second convergency run the selection criterion of points of type (b) and (c)was changed as shown in the previous discussion.

(8) The error in r_1 and r_2 was estimated according to[19] during the last run of the optimization (points 5 and 6).

For the whole procedure double precision was used to reduce the numerical error cumulation.

REFERENCES

1. Alfrey, T. and Goldfinger, G., *J. Chem. Phys.*, 1944, **12**, 205.
2. Mayo, F.R. and Lewis, F.M., *J. Am. Chem. Soc.*, 1944, **66**, 1594.
3. Wall, F.T., *J.Am. Chem. Soc.*, 1944, **66**, 2050.
4. I. Sakurada, in *Kojugo-Hanno*, Society of Polymer Chemistry, Japan, Tokyo, 1944,.
5. Walling, C. and Briggs, E.A., *J.Am.Chem.Soc.*, 1945, **67**, 1774.
6. Kahn, D.J. and Horovitz, H.H., *J.Polym. Sci.*, 1961, **54**, 363.
7. H.J.Harwood, J.Polym. Sci. C, 25. 37 (1968).
8. Francis, A.P., Solomon, D.H. and Spurling, T.H., *J.Macromol. Sci., Chem.*, 1974, **A8**, 469.
9. Tomescu, M. and Simionescu, C., *Rev. Roum. Chim.*, 1975, **20**, 831.
10. Heublein, G., Wondraczek, R., Toparkus, H. and Berndt, H., *Faserforsch. Textiltechn.*, 1976, **27**, 57.
11. I.Agherghinei, Rev.Roum.Chim., 23. 445 (1978).
12. Meyer, V.E. and Lowry, G.G., *J.Polym. Sci. A1*, 1965, **3**, 2843.
13. Meyer, V.E., *J.Polym. Sci. A1*, 1966, **4**, 2819.
14. Ring, W., *Makromol. Chem.*, 1967, **101**, 145.
15. Kruse, R.L., *J.Polym.Sci. B*, 1967, **5**, 437.
16. H.J.Harwood, N.W.Johnston, H.Piotrowski, J. Polym. Sci. C, 25. 23 (1968).
17. D.R. Montgomery, C.E.Fry, J.Polym. Sci. C, 25. 59 (1968).
18. Tüdös, F., Kelen, T., Földes-Berezsnich, T. and Turcsányi, B., *J. Macromol. Sci., Chem. A*, 1976, **10**, 1513.
19. Tidwell, P. W. and Mortimer, G. A., *J. Polym. Sci., A*, 1965, **3**, 369.