

Copolymerization at moderate to high conversion levels: 2. Estimation of relative reactivity ratios in terms of the penultimate model for systems $r_2 = 0$

Wojciech Krzysztof Czerwinski
 Silcherstrasse 22, D-22761 Hamburg, Germany
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The numerical integration method was developed to determine the relative reactivity ratios according to the simplified penultimate model (systems with $r_2 = 0$). It allows one to calculate the copolymer composition for zero conversion level. This procedure was used to verify the Walling–Briggs method. For this purpose literature data for the monomer system styrene/methyl α -cyanocinnamate were evaluated in terms of both methods. On increasing the mole fraction of M_2 in the feed ($[M_2] > 0.60$) the deviations of the Walling–Briggs method from the numerical procedure increased, reaching 1%–3% even at low conversion levels. This agrees with the theoretical considerations. The calculated copolymer composition for the zero conversion obtained from the numerical integration method was further used to determine the relative reactivity ratios by means of the linear Kelen–Tüdös method. Up to 23 wt.% conversion, no substantial differences were found between the obtained parameters using the copolymer compositions determined in terms of both integration methods. © 1997 Elsevier Science Ltd.

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INTRODUCTION

The increasing role of model discrimination in polymerization kinetics makes it necessary to improve our knowledge of methods for determining model increments. Among the models discussed the penultimate model finds growing interest^{1–12}. Within this model the reactivity of the growing radical (terminal monomeric unit) is considered to be affected by the constitution of the penultimate monomeric unit^{13–16}. When considering the copolymerization of two homopolymerizable monomers, four relative reactivity ratios (r_1, r_1' and r_2, r_2') are required. However, if for example the monomer M_2 does not homopolymerize, the copolymerization model reduces to a two-parameter equation (r_1, r_1')⁸.

The ability to estimate the relative reactivity ratios as model increments (for non-zero conversion), especially for moderate to high conversion levels, represents a practical aspect. It permits one to investigate the copolymerization of comonomer systems without any knowledge of the time–conversion relationships and without any loss of information about these systems.

Two methods are described in the literature applying to the penultimate model: numerical integration¹⁷ of the four-parameter model and the method by Walling and Briggs^{8,18}, the WB method, which is a two-parameter model. In terms of the last method a simple recalculation of the copolymer composition from non-zero to zero conversion is possible. This arrangement allows one to make use of the differential copolymerization equation for estimating the relative reactivity ratios (e.g. r_1 and r_1')⁸. As presented in⁸, the application of this method to the simplified penultimate model meets obstacles to a precise solution and is strictly valid for high $[M_1]:[M_2]$ or fairly high $m_1:m_2$ ratios ($[M_i]$ as

monomer concentrations in the feed, m_i as monomer fractions in the polymer).

In the present study a procedure for determining reactivity ratios based on the numerical integration of the simplified penultimate model was used to verify the approximate character of the Walling–Briggs (WB) method⁸. Such verification has practical importance because of potential wide application due to its simplicity. For this purpose literature data for the monomer system styrene (St $\equiv M_1$)/methyl α -cyanocinnamate (MCC $\equiv M_2$)¹⁰ are evaluated in terms of the numerical integration method and the results are compared with the results obtained in terms of the Walling–Briggs method.

CALCULATION PROCEDURES

Assuming that monomer M_2 does not homopropagate ($r_2 = 0$), the penultimate copolymerization equation takes the following form¹³:

$$\frac{m_1}{m_2} = 1 + r_1' \frac{[M_1] r_1 [M_1] + [M_2]}{[M_2] r_1' [M_1] + [M_2]} \quad (1)$$

where $[M_i]$ stands for monomer concentration or monomer mole fraction in the feed and m_i for monomer mole fraction in the polymer. The relative reactivity ratios r_1 and r_1' stand for

$$r_1 = \frac{k_{p111}}{k_{p112}} \quad \text{and} \quad r_1' = \frac{k_{p211}}{k_{p212}} \quad (2)$$

For a given data set of m_i as function of $[M_i]$ at non-zero conversion both parameters, r_1 and r_1' , were calculated using both the WB method combined with the Kelen–Tüdös (KT) linearization and the non-linear least squares

(NLLS) procedure according to the method of Tidwell and Mortimer (TM method)¹⁹.

Linear procedure

Equation (1) was linearized adopting the KT method⁸:

$$\eta = (r_1 + \frac{1}{\alpha r_1'}) \cdot \xi - \frac{1}{\alpha r_1'} \quad (3)$$

with η and ξ

$$\eta = \frac{G}{\alpha + F}, \quad \xi = \frac{F}{\alpha + F} \quad (4)$$

$$G = x \frac{y-2}{y-1}, \quad F = \frac{x^2}{y-1} \quad (5)$$

$$x = \frac{[M_1]}{[M_2]}, \quad y = \frac{m_1}{m_2} \quad (6)$$

Setting ζ_1 and ζ_2 as partial conversions of monomers M_1 and M_2 it was shown approximately that the composition change of the monomer mixture or of the polymer with the reaction progress can be calculated by means of the factor z :

$$z \approx \frac{\ln(1 - \zeta_1)}{\ln(1 - \zeta_2)} \quad (7)$$

in such a way that

$$y = zx \text{ (WB method)} \quad (8)$$

or

$$x = \frac{y}{z} \text{ (KT method)} \quad (9)$$

In the present paper the WB method was used to replace y in equations (3)–(5) from equation (8) so it follows that

$$G = x \frac{zx-2}{zx-1}, \quad F = \frac{x^2}{zx-1} \quad (10)$$

Non-linear procedure

In the NLLS method the numerical integration of equation (1) was applied in such a way that the copolymer composition m_i was recalculated to zero conversion under simultaneous approximation of r_1 and r_1' values.

The final r_1 and r_1' are therefore valid for zero conversion. The following presentation 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_1' values are estimated directly from experimental data (non-zero conversion) in terms of the NLLS procedure but appropriate arbitrary values can be chosen.
- (2) The aim of this point is to find such a copolymer composition $m_2^C=0$ respective to the starting monomer feed composition $[M_2]$ which after integration until the experimental conversion C and using the chosen r_1 and r_1' values yields a cumulative copolymer composition $m_2^{\text{calc}} = m_2^{\text{exper}}$. This is repeated for each point separately.

Remark. If the copolymerization curve calculated with r_1 and r_1' 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 (ML)²⁰ transformation method of the differential copolymerization equation was used as follows: for $[M_2] < \text{limit value}$ (usually 0.5) r_1' remains unchanged and

$$r_1^{\text{ML}} = \frac{y-1}{r_1'x^2} + \frac{y-2}{x}$$

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

$$r_1^{\text{ML}} = \frac{y-1}{x(r_1x - (y-2))}$$

The search for the best point fulfilling the condition $m_2^{\text{calc}} = m_2^{\text{exper}}$ was performed in the present study adopting the minimization by means of Fibonacci numbers. The search intervals were as follows: (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 1; (c) for $[M_2] = m_2$ no search. (Since M_2 does not homopolymerize, (b) and (c) were not used in this work.)

- (3) After $m_2^C=0$ values have been found for all M_2 feed compositions, points were selected (see point 7) and new r_1 and r_1' values were calculated by means of the NLLS method.
- (4) The search as described under 2 was repeated using new r_1 and r_1' values estimated under 3. The searching intervals were then 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 (first minimum + 0.01). (b) was not used in this work, see remark point 2.) This precaution was found necessary to avoid local minima and can be used once only (more than two local minima were not observed).
- (5) Points 3 and after 2 were repeated changing the searching intervals as follows: lower limit, last $m_2^C=0 - 0.1m_2^C=0$; upper limit, last $m_2^C=0 + 0.1m_2^C=0$. The factor 0.1 may be reduced stepwise until 0.02–0.03 when repeating point 5 (this measure accelerates calculations).
- (6) Point 5 was repeated until a stability in r_1 and r_1' was obtained. In this example, as finishing criterion we stipulated that the sum of differences of r_1 and r_1' between the two last NLLS runs should be less than or equal to 0.001. Higher accuracy in r_i values seems to be meaningless.
- (7) For each estimation of r_1 , r_1' and $m_2^C=0$ two successive convergency runs were applied²¹. During the first run points exceeding the total partial conversion of one of the monomers were eliminated²¹. For this purpose the total consumption of both monomers was monitored in the integration loop. During the second convergency run the selecting criterion was changed to the following: if $|m_2^{\text{calc}} - m_2^{\text{exper}}| \geq 0.0003$ and ($r_1^{\text{ML}} < 0.5r_1$ or $r_1^{\text{ML}} > 1.5r_1$) and ($r_1^{\text{ML}} < 0.5r_1$ or $r_1^{\text{ML}} > 1.5r_1$) then eliminate data point. As proposed in²¹, this criterion should help to eliminate improper experimental points containing inadequate information about the $[M_2] \rightarrow m_2$ relation from calculations.
- (8) The error in r_1 and r_1' was estimated according to¹⁹ 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.

Table 1 Copolymer composition as a function of the monomer feed composition for the system styrene (M_1)/methyl α -cyanocinnamate (M_2) for non-zero and zero conversion

Number	Mole fraction M_2 in the feed [M_2]	Mole fraction M_2 in copolymer m_2^{exper}	Conversion in wt.% C^{exper}	Calculated mole fraction M_2 in the copolymer at zero conversion	
				WB method $m_2^{C=0, \text{WB}}$	Numerical integration method ^a $m_2^{C=0, \text{num}}$
1	0.050	0.135	2.8	0.138	0.137
2	0.100	0.201	3.3	0.204	0.203
3	0.150	0.237	3.4	0.239	0.238
4	0.200	0.261	3.7	0.262	0.262
5	0.323	0.325	3.8	0.325	0.325
6	0.420	0.356	3.6	0.355	0.356
7	0.547	0.400	2.6	0.398	0.399
8	0.640	0.386	3.0	0.381	0.385
9	0.691	0.415	2.9	0.409	0.414
10	0.779	0.431	2.8	0.422	0.429
11	0.866	0.459	2.4	0.445	0.457
12	0.050	0.141	4.6	0.146	0.143
13	0.100	0.195	5.0	0.199	0.197
14	0.150	0.243	5.3	0.246	0.245
15	0.200	0.270	5.7	0.271	0.271
16	0.339	0.310	5.6	0.309	0.310
17	0.420	0.400	6.1	0.399	0.400
18	0.564	0.375	4.9	0.370	0.374
19	0.655	0.414	9.0	0.399	0.412
20	0.714	0.435	8.4	0.417	0.431
21	0.791	0.456	6.9	0.433	0.452
22	0.926	0.486	5.3	0.418	0.479
23	0.050	0.139	18.3	0.168	0.143
24	0.100	0.201	20.1	0.224	0.212
25	0.150	0.249	27.5	0.276	0.257
26	0.200	0.277	28.6	0.295	0.283
27	0.420	0.369	22.8	0.362	0.367
28	0.546	0.364	18.6	0.343	0.358

^a Calculated with relative reactivity ratios listed in Table 2, last column.

Table 2 Reactivity ratios for the system St/MCC (M_1/M_2) calculated for zero conversion level

Relative reactivity ratio	KT method		NLLS method
	from $m_2^{C=0, \text{WB}}$	from $m_2^{C=0, \text{num}}$	from $m_2^{C=0, \text{num}}$
r_1	0.195 ± 0.043	0.225 ± 0.046	0.222 ± 0.030
r_1	1.652 ± 0.384	1.273 ± 0.203	0.806 ± 0.365

EVALUATION OF THE SYSTEM STYRENE/METHYL α -CYANOCINNAMATE

Recently it was shown in¹⁰ that the copolymerization behaviour of the system styrene/methyl α -cyanocinnamate can be adequately described in terms of the penultimate model and the penultimate effect was shown to be relatively strong ($r_1'/r_1 \approx 3-6$). This was further evidenced by the linearization of the copolymerization data adopting the Kelen-Tüdös linearization of equation (1)⁸. The procedure proposed in the present paper was applied to the same data¹⁰ to allow a comparison of both calculation procedures: the Walling-Briggs method and the presented numerical integration. In Table 1 the copolymer composition experimentally measured at the given conversion level is presented as a function of the monomer feed composition¹⁰.

The copolymer composition data are compared with the copolymer composition values calculated for a differential

conversion at the zero conversion level in terms of both the Walling-Briggs method and the numerical integration. Some data points taken from¹⁰, especially when $m_2 = 0.5$, were omitted to allow calculations. It follows from the listed results that, as derived in⁸, there is good agreement between the methods under consideration for $[M_2] < 0.3-0.4$ at low conversion. In the interval $0.4 < [M_2] < 0.6$ only small differences were observed between both methods (5th and 6th column in Table 1).

For $[M_2] > 0.6$ more pronounced deviations ($< 2\%$) from the numerical method were observed (points 9-11, 19-22, 28) as a result of the non-fulfillment of the condition expressed in⁸ approximately as $[M_1]:[M_2] \gg 1$.

With the increasing conversion $m_2^{C=0, \text{WB}}$ becomes larger than $m_2^{C=0, \text{num}}$ for $[M_2] < 0.4$ and in the interval $0.4 < [M_2] < 0.6$ practically no changes were observed.

The calculated $m_2^{C=0, \text{WB}}$ and $m_2^{C=0, \text{num}}$ values were used

for estimating the relative reactivity ratios r_1 and r_1' . For this purpose the modified Kelen–Tüdös (KT) linearization⁸ was chosen and an additional estimation followed with the $m_2^{C=0, \text{num}}$ values in terms of the NLLS method. The calculated increments are listed in *Table 2*.

The parameters r_1 and r_1' were calculated for comparison in terms of the KT method⁸ (replacing x in equations (3)–(5) from equation (9)). We obtained $r_1 = 0.222 \pm 0.045$ and $r_1' = 1.248 \pm 0.207$. This result is very close to the values determined by the NLLS method even though both methods lack a common basis to be compared since the KT method approximates x and the presented NLLS method approximates y .

CONCLUSIONS

The Walling–Briggs method for the evaluation of copolymerization data obtained at non-zero conversion was used for the estimation of the relative reactivity ratios according to the penultimate model⁸. Conditions limiting this method were tested by means of the numerical integration method as reference. The examination was performed using experimental data for the system styrene/methyl α -cyanocinnamate, a comonomer couple showing a rather strong penultimate effect¹⁰. It was found that the WB method can be applied with success in the region $0 < [M_2] < 0.4$ – 0.6 , but it produces deviations at higher $[M_2]$ mole fractions even at low conversion. The use of this method should then be limited especially to low and medium mole fractions of M_2 in the comonomer feed.

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