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The use of Solver in Excel to solve copolymer composition equation in terminal and penultimate models of copolymerization

Summary — The standard Solver in Excel 97 was applied in order to solve the copolymer composition equation in terminal and penultimate models of copolymerization. An unquestionable advantage of this software is easy access standard because Solver is a part of Microsoft Office package. The radical copolymerization of styrene with acrylonitrile in bulk was chosen to prove the usefulness of the calculation procedure of Solver. These monomers system displays a significant penultimate effect.

For comparison the classical methods such as curve-fitting, Mayo-Lewis, Fineman-Ross, Kelen-Tüdős and Ezrielev-Brokhina-Roskin for the terminal model were also applied. The solutions obtained by Solver for penultimate model were compared with those obtained earlier by non-linear least squares minimizing method and Nelder-Mead simplex method. It was found that the precision of Solver is comparable with those obtained by above methods. The influences of started values, precision and convergence on the values of minimized function and so on the values of set of reactivity ratios have been also studied.

Key words: reactivity ratios, terminal model, penultimate model, styrene/acrylonitrile system.

The question about the copolymerization mechanism of many monomers remains open till now. Most often it is necessary to choose between the terminal model and the penultimate model, rarely the complex participation model should be taken into account. The discrimination among models bases on the choice of the equation fitting the variation of the copolymer composition with the monomer feed. In the terminal model there is Mayo-Lewis equation [1]:

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

and in the penultimate model Merz-Alfrey-Goldfinger equation [2]

$$n = \frac{d[M_1]}{d[M_2]} = \frac{1+\dfrac{r_{21}\dfrac{[M_1]}{[M_2]}\left(r_{11}\dfrac{[M_1]}{[M_2]}+1\right)}{r_{21}\dfrac{[M_1]}{[M_2]}+1}}{1+\dfrac{r_{12}}{\dfrac{[M_1]}{[M_2]}}\left(\dfrac{r_{22}+\dfrac{[M_1]}{[M_2]}}{r_{12}+\dfrac{[M_1]}{[M_2]}}\right)} \quad (2)$$

where: *n represents the ratio of monomers residues in copolymer, and [M1] and [M2] are the mole fractions of monomers M1 and M2 in feed, respectively; the parameters r1, r2, r11, r21, r22, r12 stand for the reactivity ratios of the monomers M1 and M2 in the terminal and penultimate model, respectively.*

The equation successfully describes the experiment if the differences between experimental and calculated copolymer compositions are minimal. The several methods of the reactivity ratio calculations from the terminal model equation were described. There were curve fitting [3, 4], Mayo-Lewis [1, 3], Fineman-Ross [5], Ezrielev-Brokhina-Roskin [6], Kelen-Tüdős [7, 8] methods. To solve equation (1) the simplex procedure [9] and the non-linear least squares (NLLS) method [10] were also applied. The calculation of four reactivity ratios from the second equation is more difficult. To minimize the differences between the experimental and calculated data the computer program must be used. For this purpose the non-linear least squares (NLLS) minimizing method [10, 11] and modified Nelder-Mead simplex method and a scanning method [9, 12] were used. In this work the use of Solver in Excel 97 to this purpose is presented. This program is a part of Microsoft Office 97, so it is easy available. To demonstrate the usefulness of Solver to solve the copolymer composition equation the data of Hill *et al.* [10] for styrene (M_1) and acrylonitrile (M_2) monomer system in bulk were used.

TERMINAL MODEL

In order to find the reactivity ratios the sum of squares of differences between the experimental and calculated mole fraction of styrene in copolymer was minimized according to following equation:

$$\sum_{i=1}^{15}(d[M_1]^{exp} - d[M_1]^{cal})^2 = \min \quad (3)$$

$d[M_1]^{cal}$ was obtained from the following equation:

$$d[M_1]^{cal} = \frac{n^{cal}}{n^{cal}+1} \quad (4)$$

where $n^{cal} = \frac{d[M_1]^{cal}}{d[M_2]^{cal}}$

Table 1 is the spreadsheet used in this procedure. The mole fractions of styrene $[M_1]$ and acrylonitrile $[M_2]$ in feed are given in first two columns, the experimental mole fractions of styrene $d[M_1]^{exp}$ and acrylonitrile $d[M_2]^{exp}$ in the copolymer — in the next two ones, column E contains the ratios of the experimental values of mole fractions of styrene and acrylonitrile in the copolymer. In cells F3 and G3 the started values of r_1 and r_2, respectively, are given. The values of n^{cal} calculated according to (1) are presented in the column H and column I consists values of $d[M_1]^{cal}$ calculated according to (2) The column J includes the squares of differences between experimental and calculated values of mole fractions of styrene in the copolymer. Finally the cell K3 contains the sum of squares from column J. That is an objective function (target cell). Its value depends on decision variables — reactivity ratios. The task of the Solver is to find some combination of values for the decision variables, which minimizes the target cell value. The standard Solver solves such problem with the GRG (Generalized Reduced Gradient) method. In order to start this procedure the Solver command from Tools menu should be chosen. As a consequence of this the Solver Parameters dialog appears. The cell K3 must be chosen as the target cell. Solver ought to minimize the target cell, so the option Min must be selected in the dialog box. The variable cells are F3 and G3. The non-negative values of variables should be chosen, because the negative values of reactivity ratios have no physical meaning. It can stipulate time limits or numbers of iterations, which Solver is allowed to reach before it finds an optimal solution. It can also specify the precision, the tolerance and the convergence of solution; in this work these values are equal to $1 \cdot 10^{-7}$, 1%, and $1 \cdot 10^{-7}$, respectively. Finally, the non-linear model must be defined. When Solver stops, one of the three kinds of Solver Completion Messages appears:

Table 1. The input values in spreadsheet in the terminal model (explanation in the text)

1	A	B	C	D	E[a]	F	G	H[b]	I[b]	J[c]	K[c]
2	$[M_1]$	$[M_2]$	$d[M_1]^{exp}$	$d[M_2]^{exp}$	$n = \frac{d[M_1]^{exp}}{d[M_2]^{exp}}$	r_1	r_2	n^{cal}	$\frac{n^{cal}}{n^{cal}+1}$	$(d[M_1]^{exp} - d[M_1]^{cal})^2$	$\sum_{i=1}^{15}(d[M_1]^{exp} - d[M_1]^{cal})^2$
3	0.021	0.979	0.234	0.766	0.305	1	1	0.021	0.021	0.0454	0.584162
4	0.023	0.977	0.248	0.752	0.330			0.024	0.023	0.0506	
5	0.047	0.953	0.323	0.677	0.477			0.049	0.047	0.0762	
6	0.053	0.947	0.333	0.667	0.499			0.056	0.053	0.0784	
7	0.072	0.928	0.360	0.640	0.563			0.078	0.072	0.0829	
8	0.104	0.896	0.406	0.594	0.684			0.116	0.104	0.0912	
9	0.221	0.779	0.476	0.524	0.908			0.284	0.221	0.0650	
10	0.314	0.686	0.510	0.490	1.041			0.458	0.314	0.0384	
11	0.416	0.584	0.542	0.458	1.183			0.712	0.416	0.0159	
12	0.530	0.470	0.582	0.418	1.392			1.128	0.53	0.0027	
13	0.631	0.369	0.627	0.373	1.681			1.710	0.631	0.0000	
14	0.696	0.304	0.649	0.351	1.849			2.289	0.696	0.0022	
15	0.802	0.198	0.705	0.295	2.390			4.051	0.802	0.0094	
16	0.889	0.111	0.772	0.228	3.386			8.009	0.889	0.0137	
17	0.939	0.061	0.829	0.171	4.848			15.393	0.939	0.0121	

[a] *cf.* Equation (1), [b] *cf.* Equation (4), [c] *cf.* Equation (3)

— "Solver found a solution"
— "Solver has converged to the current solution"
— "Solver cannot improve the current solution".

The first message means that the Solver found a locally optimal solution, there is no other set of values for the decision variables close to the current values, which yields a smallest value of the target cell. The second message appears when the value of the target cell is changing very slowly for the last few iterations. In this work the third message has never occurred. Such obtained solution is only a locally optimal solution not the global solution. In order to check if the local solution is the best possible "optimal solution" the Solver was started from different sets of initial values ranging from 0 to 20. It was found that independently of starting values of reactivity ratios the value of objective function remained un-

Table 2. The final values in spreadsheet in the terminal model (for symbols see Table 1, explanation in the text)

1	A	B	C	D	E	F	G	H	I	J	K
2	$[M_1]$	$[M_2]$	$d[M_1]^{exp}$	$d[M_2]^{exp}$	$n=\frac{d[M_1]^{exp}}{d[M_2]^{exp}}$	r_1	r_2	n^{cal}	$\frac{n^{cal}}{n^{cal}+1}$	$(d[M_1]^{exp}-d[M_1]^{cal})^2$	$\sum_{i=1}^{15}(d[M_1]^{exp}-d[M_1]^{cal})^2$
3	0.021	0.979	0.234	0.766	0.305	1	1	0.286	0.222	0.00014	0.00296
4	0.023	0.977	0.248	0.752	0.330			0.306	0.234	0.00020	
5	0.047	0.953	0.323	0.677	0.477			0.485	0.326	0.00001	
6	0.053	0.947	0.333	0.667	0.499			0.518	0.341	0.00007	
7	0.072	0.928	0.360	0.640	0.563			0.605	0.377	0.00028	
8	0.104	0.896	0.406	0.594	0.684			0.709	0.415	0.00008	
9	0.221	0.779	0.476	0.524	0.908			0.920	0.479	0.00001	
10	0.314	0.686	0.510	0.490	1.041			1.033	0.508	0.00000	
11	0.416	0.584	0.542	0.458	1.183			1.153	0.536	0.00004	
12	0.530	0.470	0.582	0.418	1.392			1.318	0.569	0.00018	
13	0.631	0.369	0.627	0.373	1.681			1.530	0.605	0.00049	
14	0.696	0.304	0.649	0.351	1.849			1.734	0.634	0.00022	
15	0.802	0.198	0.705	0.295	2.390			2.340	0.701	0.00002	
16	0.889	0.111	0.772	0.228	3.386			3.686	0.787	0.00021	
17	0.939	0.061	0.829	0.171	4.848			6.188	0.860	0.00102	

Table 3. The reactivity ratios in the terminal model of copolymerization for styrene (M_1) and acrylonitrile (M_2) system

Results of this work				Results of other works			
Method	r_1	r_2	$\delta^{a)}$		r_1	r_2	$\delta^{a)}$
curve-fitting	0.340	0.045	0.020	Hill *et al.* [15]	0.331	0.054	0.0153
Mayo-Lewis	0.365	0.060	0.017	Hill *et al.* [10]	0.340	0.050	0.0163
Fineman-Ross	0.256	0.049	0.017	Kaim [9]	0.340	0.054	0.0151
Kelen-Tudos	0.349	0.055	0.015				
E.-B.-R	0.282	0.051	0.019				
Solver	0.338	0.054	0.014				

[a)] Standard deviation

changed. That means that the obtained solution is the global solution. The reactivity ratios which give this solution are $r_1 = 0.338$ and $r_2 = 0.054$. The spreadsheet with report of solution is presented in Table 2.

To calculate the reactivity ratios of the studied system the classical methods such as fitting curve, Mayo-Lewis, Fineman-Ross, Kelen-Tüdõs and Ezrielev-Brokhina-Roskin were also applied. In the first two methods reactivity ratios were estimated graphically, in the rest of them — analytically using computer programs. The detailed descriptions of applied procedure are done in [13, 14]. Such calculated values of reactivity ratios are shown in Table 3. In the same table the standard deviations calculated from the following equation are also presented.

$$\delta = \sqrt{\frac{\sum_{i=1}^{k}\left(d[M_1]^{exp} - d[M_1]^{cal}\right)^2}{k-1}}$$

where *k is the number of experimental points.*

It is seen that the methods of Finemen-Ross and Ezrielev-Brokhina-Roskin gave the lower values of r_1 in comparison with the other methods. The comparison of standard deviations indicates that the Solver is the most precision method among all applied in this work. In the same table the values of reactivity ratios obtained by Hill *et al.* [10, 15] and Kaim [9] are also shown. It is seen that simplex method and NLLS method gave the same values of reactivity ratios and a comparable precision as Solver in the terminal model of copolymerization.

PENULTIMATE MODEL

In this model just as in the previous model the sum of squares of differences between the experimental and calculated mole fractions of styrene in copolymer was minimized. The spreadsheet on starting of Solver is seen in Table 4. Columns A—E are the same as described in the terminal model. The variable cells are F3, G3, H3 and I3. As their initial values the reactivity ratios calculated for the terminal model were accepted. The next columns are the same as in terminal model; only the algebraic formula from which the values of n^{cal} in column K were calculated is different. In this model the values of n^{cal} were calculated according to (2). The target cell is M3. All the options in the dialog box were the same as in the terminal model. In Table 5 the spreadsheet with results obtained by Solver is presented. The comparison of results of this work with those presented in literature is done in Table 6. It is seen that the results

Table 4. The input values in spreadsheet in the penultimate model (explanation in the text)

1	A	B	C	D	E[a]	F	G	H	I	J[b]	K[b]	L[c]	M[c]
2	$[M_1]$	$[M_2]$	$d[M_1]^{exp}$	$d[M_2]^{exp}$	$n=\frac{d[M_1]}{d[M_2]}$	r_{11}	r_{21}	r_{22}	r_{12}	n^{cal}	$\frac{n^{cal}}{n^{cal}+1}$	$(d[M_1]^{exp}-d[M_1]^{cal})^2$	$\sum_{i=1}^{15}(d[M_1]^{exp}-d[M_1]^{cal})^2$
3	0.021	0.979	0.234	0.766	0.305	0.34	0.34	0.05	0.05	0.302	0.232	0.0000	0.003421435
4	0.023	0.977	0.248	0.752	0.330					0.323	0.244	0.0000	
5	0.047	0.953	0.323	0.677	0.477					0.505	0.336	0.0002	
6	0.053	0.947	0.333	0.667	0.499					0.538	0.350	0.0003	
7	0.072	0.928	0.360	0.640	0.562					0.624	0.384	0.0006	
8	0.104	0.896	0.406	0.594	0.683					0.726	0.421	0.0002	
9	0.221	0.779	0.476	0.524	0.908					0.932	0.482	0.0000	
10	0.314	0.686	0.510	0.490	1.041					1.042	0.510	0.0000	
11	0.416	0.584	0.542	0.458	1.183					1.161	0.537	0.0000	
12	0.530	0.470	0.582	0.418	1.392					1.325	0.570	0.0001	
13	0.631	0.369	0.627	0.373	1.681					1.536	0.606	0.0005	
14	0.696	0.304	0.649	0.351	1.849					1.740	0.635	0.0002	
15	0.802	0.198	0.705	0.295	2.390					2.348	0.701	0.0000	
16	0.889	0.111	0.772	0.228	3.386					3.700	0.787	0.0002	
17	0.939	0.061	0.829	0.171	4.848					6.214	0.861	0.0010	

[a] *cf.* Equation (2). [b] *cf.* Equation (4). [c] *cf.* Equation (3).

Table 5. The final values in spreadsheet in penultimate model (for symbols see Table 4)

1	A	B	C	D	E	F	G	H	I	J	K	L	M
2	$[M_1]$	$[M_2]$	$d[M_1]^{exp}$	$d[M_2]^{exp}$	$n=\frac{d[M_1]}{d[M_2]}$	r_{11}	r_{21}	r_{22}	r_{12}	n^{cal}	$\frac{n^{cal}}{n^{cal}+1}$	$(d[M_1]^{exp}-d[M_1]^{cal})^2$	$\sum_{i=1}^{15}(d[M_1]^{exp}-d[M_1]^{cal})^2$
3	0.021	0.979	0.234	0.766	0.305	0.229	0.650	0.038	0.098	0.310	0.236	0.0000057	0.000231141
4	0.023	0.977	0.248	0.752	0.330					0.326	0.246	0.0000034	
5	0.047	0.953	0.323	0.677	0.477					0.473	0.321	0.0000028	
6	0.053	0.947	0.333	0.667	0.499					0.500	0.334	0.0000003	
7	0.072	0.928	0.360	0.640	0.562					0.572	0.364	0.0000166	
8	0.104	0.896	0.406	0.594	0.683					0.667	0.400	0.0000361	
9	0.221	0.779	0.476	0.524	0.908					0.903	0.474	0.0000024	
10	0.314	0.686	0.510	0.490	1.041					1.052	0.513	0.0000073	
11	0.416	0.584	0.542	0.458	1.183					1.213	0.548	0.0000382	
12	0.530	0.470	0.582	0.418	1.392					1.415	0.586	0.0000153	
13	0.631	0.369	0.627	0.373	1.681					1.641	0.621	0.0000314	
14	0.696	0.304	0.649	0.351	1.849					1.835	0.647	0.0000031	
15	0.802	0.198	0.705	0.295	2.390					2.340	0.701	0.0000190	
16	0.889	0.111	0.772	0.228	3.386					3.336	0.769	0.0000070	
17	0.939	0.061	0.829	0.171	4.848					5.079	0.836	0.0000423	

Table 6. The reactivity ratios in the penultimate model of copolymerization for styrene (M_1) and acrylonitrile (M_2)

	Results of this work			Results of Hill *et al.* [10, 15]		Results of Kaim [9]	
	Set I[a]	Set II[b]	I[c]	II[d]	III[e]	Set I[f]	Set II[g]
r_{11}	0.23	0.22	0.229	0.23	0.24	0.223	0.222
r_{21}	0.65	6.94	0.634	0.66	0.58	0.652	6.916
r_{11}	0.038	0.036	0.039	0.04	0.06	0.038	0.036
r_{21}	0.098	1.03	0.091	0.054	0.09	0.098	1.027
δ[h]	0.0042	0.0039					

[a], [b] different sets of started values of reactivity ratios, see the Table 7.
[c],[d] the reactivity ratios were calculated from copolymer compositions determined by different methods.
[e] the reactivity ratios were calculated from the copolymer compositions calculated from triad fractions.
[f] using $r_{11}=r_{21}=r_1=0.340$ and $r_{22}=r_{12}=0.054$ as initial guess for NLLS method.
[g] using $r_{11}=r_{21}=r_1=0.340$, $r_{22}=1/r_2=18.518$, $r_{22}=r_2=0.054$, $r_{12}=1/r_1=2.941$ as initial guess for NLLS fit.
[h] standard deviations.

Table 7. The influence of values of decision variables on a final value of the target cell

	Initial values					Final values				
	r_{11}	r_{21}	r_{22}	r_{21}	target cell	r_{11}	r_{21}	r_{22}	r_{12}	target cell
1	0	0	0	0	0.4937	0.22	6.94	0.036	1.03	0.0001953
2	**0.2**	**0.2**	**0.2**	**0.2**	**0.1752**	**0.23**	**0.65**	**0.038**	**0.098**	**0.0002311**
3	0.2	0.4	0.2	0.4	0.1946	0.22	6.94	0.036	1.03	0.0001953
4	**0.4**	**0.2**	**0.4**	**0.2**	**0.2877**	**0.23**	**0.65**	**0.038**	**0.098**	**0.0002311**
5	**0.5**	**0.5**	**0.5**	**0.5**	**0.3836**	**0.23**	**0.65**	**0.038**	**0.098**	**0.0002311**
6	0.6	0.6	0.6	0.6	0.4353	0.22	6.94	0.036	0.098	0.0001953
7	1	1	1	1	0.5842	0.22	6.94	0.036	0.098	0.0001953
8	0	1	0	1	0.1209	0.22	6.94	0.036	0.098	0.0001953
9	**1**	**0**	**1**	**0**	**0.4937**	**0.23**	**0.65**	**0.038**	**0.098**	**0.0002311**
10	2	1	2	1	0.7869	0.22	6.94	0.036	1.03	0.0001953
11	1	2	1	2	0.5702	0.22	6.94	0.036	1.03	0.0001953
12	2	2	2	2	0.7888	0.22	6.94	0.036	1.03	0.0001953
13	5	5	5	5	0.9411	0.22	6.94	0.036	1.03	0.0001953
14	9	9	9	9	1.0073	0.22	6.94	0.036	1.03	0.0001953
15	0	2	5	9	1.6000	0.22	6.94	0.036	1.03	0.0001953
16	2	4	6	8	1.0840	0.22	6.94	0.036	1.03	0.0001953
17	**9**	**5**	**2**	**0**	**1.1164**	**0.23**	**0.65**	**0.038**	**0.098**	**0.0002311**
18	8	6	4	2	0.9137	0.22	6.94	0.036	1.03	0.0001953

Table 8. The influence of precision and convergence on the target cell and reactivity ratios

	Precision	Convergence	Final values					Solver Result Dialog
			r_{11}	r_{21}	r_{22}	r_{12}	Target cell	
1	$1\cdot10^{-1}$	$1\cdot10^{-1}$	0.46	10.1	0.092	4.71	0.02938	Solver found a solution
2	$1\cdot10^{-2}$	$1\cdot10^{-2}$	0.41	10.0	0.040	4.68	0.004314	Solver found a solution
3	$1\cdot10^{-3}$	$1\cdot10^{-3}$	0.40	13.85	0.046	4.68	0.004056	Solver has converged to the current solution
4	$1\cdot10^{-4}$	$1\cdot10^{-4}$	0.22	6.94	0.036	1.03	0.0001953	Solver found a solution
5	$1\cdot10^{-5}$	$1\cdot10^{-5}$	0.22	6.94	0.036	1.03	0.0001953	Solver found a solution
6	$1\cdot10^{-6}$	$1\cdot10^{-6}$	0.22	6.94	0.036	1.03	0.0001953	Solver has converged to the current solution
7	$1\cdot10^{-7}$	$1\cdot10^{-7}$	0.22	6.94	0.036	1.03	0.0001953	Solver has converged to the current solution
8	$1\cdot10^{-1}$	$1\cdot10^{-7}$	0.46	10.1	0.092	4.71	0.02938	Solver found a solution
9	$1\cdot10^{-7}$	$1\cdot10^{-1}$	0.40	13.13	0.046	4.68	0.004074	Solver has converged to the current solution

of this work correspond with those of Hill *et al.* [10, 15] and Kaim [9].

As in the terminal model it was checked if the obtained solution was the "best possible" solution. In this purpose the objective function was minimized with different sets of initial values of reactivity ratios in the range of 0—9. The initial values of decision variables as well as the obtained solutions are shown in Table 7. It is seen that there are the two local minima in the studied range. The similar values of reactivity ratios were obtained by Kaim [9]. However Kaim informed of many local minima in investigated space with comparable standard deviations.

The influences of precision and convergence on the value of minimum of the objective function and so on the values of reactivity ratios were also studied. As started values of reactivity ratios r_{11}, r_{21}, r_{22} and r_{12} quite optionally the values 6, 8, 2 and 4, respectively, were accepted. The initial value of objective function with such values of reactivity ratios was equal to 0.7569. The precision and the convergence were changed in the range of $1\cdot10^{-1}$—$1\cdot10^{-7}$. The results obtained as well as Solver Results dialog are presented in Table 8. It is seen that the final values of the target cell and so reactivity ratios depend on both precision and convergence. The objective function attains minimum at the values of precision and convergence smaller than or equal to $1\cdot10^{-4}$. All the solutions in Tables 6 and 7 were found at precision and convergence equal to $1\cdot10^{-6}$. It is evident that at higher values of these parameters many sets of reactivity ratios can be obtained. However they are not the best possible "optimal solution". It was also found that the number in the option dialog Tolerance did not influence the value of target cell.

CONCLUSIONS

The styrene/acrylonitrile system, which is believed to obey the penultimate kinetics, has been treated with the Solver in order to verify the calculation procedure of this software. Solver as well as the earlier used methods confirmed that the penultimate model was more appropriate to describe the variation of the copolymer composition with the monomer feed than the terminal model. The reactivity ratios calculated by Solver for both models are in very good agreement with those obtained earlier. Solver has also confirmed that the Mayo-Lewis equation has a unique solution while for the penultimate model a non-uniqueness in determination of reactivity ratios takes place.

In accordance with above-mentioned achievements of Solver it seems to be valid the use of this software to determine the reactivity ratios for monomers systems which were little studied or not studied at all. Such monomers system is styrene/citraconic acid for which the reactivity ratios were calculated using Solver procedure [16].

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