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# Terminal and Penultimate Reactivity Ratios in the Styrene-Acrylonitrile Free-Radical Copolymerization System in Bulk

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# TERMINAL AND PENULTIMATE REACTIVITY RATIOS IN THE STYRENE-ACRYLONITRILE FREE-RADICAL COPOLYMERIZATION SYSTEM IN BULK

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## ABSTRACT

The terminal and penultimate model reactivity ratios for the styrene -acrylonitrile monomer system in bulk have been investigated by the simplex and scanning method. It has been shown that Mayo-Lewis equation has an unique solution when determining the reactivity ratios according to the terminal model while for the penultimate model the non-uniqueness in determination of the reactivity ratios has been found. The numerical values of the penultimate $r$-parameters calculated with the simplex method depend on the initial guess for $r$-parameters.

Several sets of penultimate reactivity ratios for the styrene-acrylonitrile system in bulk have been found to be equal from mathematical point of view. The reactivity ratios with comparable standard deviation have an equivalent graphical representation on the copolymerization diagragm. It has been also confirmed that the penultimate model is a more appropriate of the models considered to describe the variation of the copolymer composition with the monomer feed. Taking into account previous results for the styrene-methyl methacrylate system in bulk it is thereby assumed that the occurrence non-uniqueness in determination of the penultimate model reactivity ratios does not depend on the monomer system.

## INTRODUCTION

In our previous paper [1], we described a new approach for the calculation of the reactivity ratios for both the terminal and penultimate models of copolymerization reaction. For this purpose, we used a modified Nelder-Mead [2] simplex and scanning method.

To verify the calculation procedures, we applied the data of Hill *et al.* [3, 4] for the styrene ($M_1$)-acrylonitrile ($M_2$) monomer system in bulk, toluene and acetonitrile as input data. Taking the monomer fractions in monomer feed and copolymer composition data of Hill *et al.* [3, 4] we recalculated the corresponding penultimate reactivity ratios with the simplex and scanning method.

For all investigated systems, it was found that within a reasonable accuracy (measured with standard deviation $\sigma$), more than one set of penultimate $r$-parameters describes the propagation kinetics of the free radical copolymerization of the styrene-acrylonitrile. For bulk copolymerization and = 0.005 the reactivity ratios for $r_{11}$, $r_{22}$, and $r_{21}$ were found to vary in the ranges of 0.22-0.24, 0.00-0.08, 0.59-0.73, respectively. The $r_{12}$ parameter was found to be 0.10. It should be noted that the monomer system displays [5, 6] a significant penultimate unit effect in copolymerization reaction proved by Cywar *et al.* [7] in the independent kinetic study.

On the other hand, our most recent results [8] on non-uniqueness in determination of terminal and penultimate model reactivity ratios for the styrene ($M_1$) - methyl methacrylate ($M_2$) free-radical copolymerization system, it means for a monomer system characterized by a much less pronounced [9] penultimate unit effect, proved that the final result of calculating the penultimate $r$-parameters using the non-linear least-squares (nlls) fits depends on the initial guess of the $r$-parameters. It was found, that two different sets of initial guess values for $r_{11}$, $r_{22}$, $r_{21}$ and $r_{12}$, set I: $r_{11} = r_{21} = r_1$ and $r_{22} = r_{12} = r_2$ and set II: $r_{11} = r_1$, $r_{21} = 1/r_2$, $r_{22} = r_2$, $r_{12} = 1/r_1$, resulted in two different sets of penultimate reactivity ratios, 0.664, 0.489, 0.366, 0.384 and 0.727, 0.490, 2.890, 4.583, respectively. Moreover, each of the reactivity ratios sets was surrounded by multiple sets of reactivity ratios with comparable standard errors. It should be noted that copolymerization curves for the styrene-methyl methacrylate system, calculated for the multiple sets of reactivity ratios with comparable standard errors were almost indistinguishable on the graphical scale.

Preliminary results on the reactivity ratios for the styrene-acrylonitrile monomer system given previously [1], and these for the styrene-methyl methacrylate system [8] described briefly above, suggest that the phenomenon of the non-uniqueness in determination of reactivity ratios, at least for penultimate model, is not associated with a type of monomer system. Therefore, it can be observed for any monomer system, irrespective of the existence or non-existence of the penultimate unit effect in the polymerization.

The extent of the non-uniqueness in determination of terminal and penultimate model reactivity ratios for the styrene-acrylonitrile monomer system in bulk is not yet well defined. Therefore, the aim of the present work is to study in detail, using the simplex method and scanning method, the non-uniqueness in determination of terminal and penultimate model reactivity ratios in the styrene-acrylonitrile free-radical copolymerization system in bulk.

## EXPERIMENTAL

For the purpose of the present work, experimental data published by Hill *et al.* [3, 4] were used for the styrene-acrylonitrile free-radical copolymerization system in bulk at 60°C.

Calculation procedures according to the simplex and scanning methods were described previously [1, 8].

## RESULTS AND DISCUSSION

### Terminal Model

The reactivity ratios for styrene ($M_1$), $r_1$, and acrylonitrile ($M_2$), $r_2$, for bulk free-radical copolymerization system at 60°C with the simplex procedure according to the terminal model were found to be 0.340 and 0.054, respectively. Initial guess values for $r_1$ and $r_2$ selected for calculation were chosen arbitrarily, $r_1 = 0.5$ and $r_2 = 0.1$. The corresponding standard deviation, $\sigma$, was calculated to be equal to 0.0151. These $r$-values are very similar to the results obtained by Hill *et al.* [3, 6] with a nonlinear least-squares procedure using the monomer feed and copolymer composition data (Table 1).

To study the ranges of the terminal $r$-parameters with a comparable standard deviation the scanning method was applied. The scanning experiment presented in Figure 1 was performed under the following conditions: ranges of $r_1$ and $r_2$ were 0.200-0.400 (step 0.002) and 0.02-0.100 (step 0.002), respectively. During the scanning experiments all sets of terminal $r$-parameters with $\sigma \leq 0.04$ were collected. It shows that, under the scanning conditions applied, the reactivity ratios

[a] Using $r_1 = 0.5$ and $r_2 = 0.1$ as initial guess for the non-linear least-squares (nlls) fit

[b] Using $r_{11} = r_{21} = r_1 = 0.340$ and $r_{22} = r_{12} = r_2 = 0.054$ as initial guess for the nlls fit

[c] Using $r_{11} = r_1 = 0.340$, $r_{21} = 1/r_2 = 18.518$, $r_{22} = r_2 = 0.054$, $r_{12} = 1/r_1 = 2.941$ as initial guess for the nlls fit

[d] Copolymer composition determined [6] by duplicate percent nitrogen analysis by the micro-Kjeldahl technique and from the relative intensities of the aromatic (styrene) and methylene and methine (acrylonitrile +styrene) resonances in the $^1$H NMR

[e] Copolymer composition determined [3] from copolymer analysis

[f] Copolymer composition determined [3] from triad fractions in copolymer

[g] Copolymer composition determined [9] as a average from % N elemental analysis, $^1$H-NMR spectra, and from the triad fractions.

[h] Value of $\sigma$ given in original work

[i] Value of $\sigma$ calculated by simplex method using the original $r$-parameters and copolymerization data

TABLE 1. Comparison of the Calculated Terminal and Penultimate Model *R*-Parameters using the Simplex Method for the Experimental Data of Hill *et al*. [3, 4] for the Bulk Styrene-Acrylonitrile Free-Radical Copolymerization System at 60°C with thoseof Hill *et al*. [3, 6] and Klumperman *et al*. [9].

| | Our results | | | Results of Hill et al. | | | | | | Results of Klumperman et al. |
|---|---|---|---|---|---|---|---|---|---|---|
| | Terminal model[a] | penultimate model | | terminal model | | | penultimate model | | | penultimate model |
| | | Set I[b] | Set II[c] | copolymer composition[d] | copolymer composition[e] | copolymer composition[f] | copolymer composition[d] | copolymer composition[e] | copolymer composition[f] | copolymer composition[g] |
| $r_1$ | 0.340 | | | 0.331 | 0.34 | 0.47 | | | | |
| $r_2$ | 0.054 | | | 0.053 | 0.05 | 0.08 | | | | |
| $r_{11}$ | | 0.223 | 0.222 | | | | 0.229 | 0.23 | 0.24 | 0.249 |
| $r_{22}$ | | 0.038 | 0.036 | | | | 0.039 | 0.04 | 0.06 | 0.063 |
| $r_{21}$ | | 0.652 | 6.916 | | | | 0.634 | 0.66 | 0.58 | 0.581 |
| $r_{12}$ | | 0.098 | 1.027 | | | | 0.091 | 0.10 | 0.09 | 0.122 |
| $\sigma^h$ | 0.0151 | 0.0048 | 0.0044 | 0.01 | | 0.12 | 0.005 | | 0.06 | |
| $\sigma^j$ | | | | 0.0153 | 0.0163 | 0.0386 | 0.0051 | 0.0054 | 0.0200 | 0.0179 |

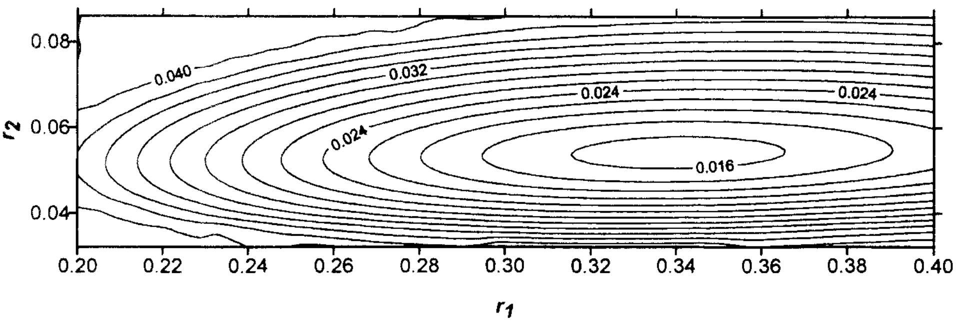

**Figure 1.** The terminal model reactivity ratios for styrene ($r_1$) and acrylonitrile ($r_2$) calculated using the scanning method. Contour lines correspond to the reactivity ratios of the same standard deviation $\sigma \times 10^3$.

for styrene ($r_1$) and acrylonitrile ($r_2$) for bulk free-radical copolymerization system at 60°C found to be 0.340 and 0.054, respectively, present an unique result with $\sigma = 0.0151$. The contour lines in Figure 1 corresponding to the reactivity ratios of the same standard deviation characterize a very sharp global minimum of the 3-dimensional ($r_1$, $r_2$, $\sigma$) space. Thus, they show the standard deviation for any pair of $r_1$ and $r_2$ parameters in bulk determined for the set of experimental data. It is interesting to point out that the correlation coefficient between the two parameters is very small and equals to 0.1071.

Thus, it can be concluded that the Lewis-Mayo [11] equation has a unique solution when describing the radical copolymerization in bulk of the styrene-acrylonitrile system according to the terminal model. Simultaneously however, as it is evident from the visual inspection of Figure 2 (see the (•) points), the terminal model, even with its best reactivity ratios, is not able to describe the variation of the copolymer composition with the monomer feed in a exact way. This fact has been known for a long time. Ham [5] was the first to interpret deviations from the terminal model on the basis of penultimate effects.

## Penultimate Model

The penultimate reactivity ratios for styrene ($M_1$) and acrylonitrile ($M_2$) $r_{11}$, $r_{22}$, $r_{21}$ and $r_{12}$ for bulk free-radical copolymerization system at 60°C, described by experimental data of Hill *et al.* [3, 4], were calculated with the simplex procedure using an initial guess values $r_{11} = r_{21} = r_1$ and $r_{22} = r_{12} = r_2$, where $r_1$ and $r_2$ come from the terminal model. The $r_{11}$, $r_{22}$, $r_{21}$, $r_{12}$ parameters were found to be 0.223,

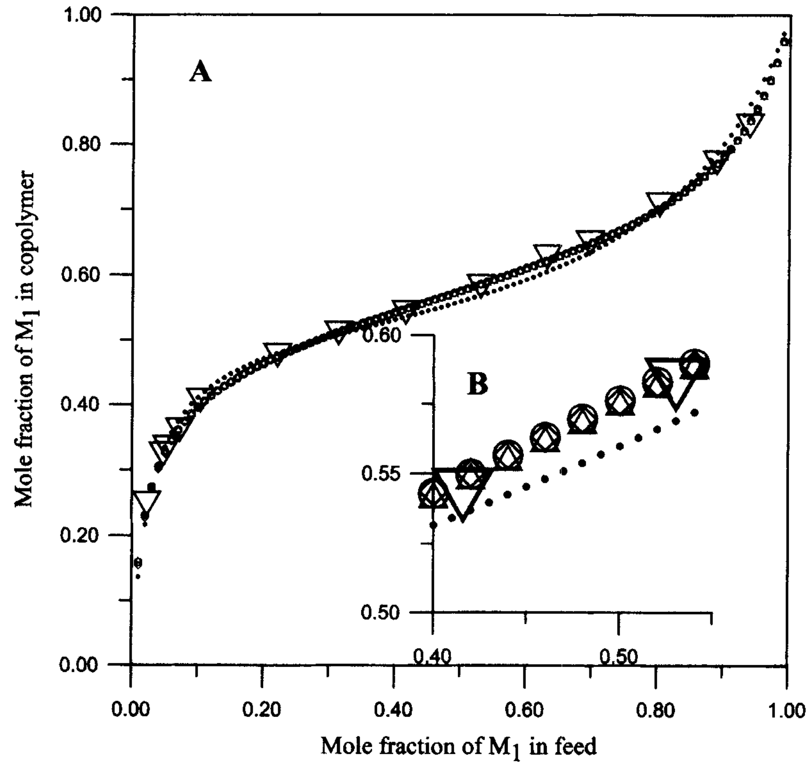

**Figure 2.** Copolymerization diagrams for the styrene-acrylonitrile free-radical copolymerization system in bulk at 60°C using reactivity ratios calculated by simplex method for the data of Hill *et al.* [3, 4]: (∇) experimental data of Hill *et al.* [3, 4]; (•) calculated points corresponding to terminal model reactivity ratios $r_1$ = 0.340 and $r_2$ = 0.054 with $\sigma$ = 0.0151; (0) calculated points corresponding to penultimate model reactivity ratios $r_{11}$= 0.223, $r_{22}$= 0.038, $r_{21}$ = 0.652 and $r_{12}$ = 0.098 with $\sigma$ = 0.0048 and with $r_{11} = r_{21} = r_1$ = 0.340 and $r_{22} = r_{12} = r_2$ = 0.054 as initial guess for the reactivity ratios calculation; (Δ) calculated points corresponding to penultimate model reactivity ratios $r_{11}$= 0.222, $r_{22}$= 0.036, $r_{21}$ = 6.916 and $r_{12}$ = 1.027 with $\sigma$ = 0.0044 and with $r_{11} = r_1$ = 0.340, $r_{21} = 1/r_2$ = 18.518, $r_{22} = r_2$ = 0.054, $r_{12} = 1/r_1$ = 2.941 as initial guess for the reactivity ratios calculation; (◊) calculated points corresponding to penultimate model reactivity ratios $r_{11}$= 0.23, $r_{22}$= 0.04, $r_{21}$ = 0.66 and $r_{12}$ = 0.10 given by Hill *et al.* [3] , calculated standard deviation $\sigma$ = 0.0054. Part A corresponds to general view; part B corresponds to an excerpt of A.

0.038, 0.652 and 0.098, respectively (Table 1, set I). The standard deviation, $\sigma$, was found to be 0.0048. These results match very well with those reported by Hill *et al.* [3] for copolymer composition determined by duplicate percent nitrogen analysis by the micro-Kjeldahl technique and from the relative intensities of the aromatic (styrene) and methylene and methine (acrylonitrile + styrene) resonances in the $^1$H-NMR (Table 1). It should be stressed that these data on copolymer composition were used by us for simplex calculation as input data.

The second set of the penultimate reactivity ratios was obtained (Table 1, set II) as a result of a simplex calculation when $r_{11} = r_1$, $r_{21} = 1/r_2$, $r_{22} = r_2$, $r_{12} = 1/r_1$ were used as initial guess values, where $r_1$ and $r_2$ were estimated terminal model parameters. The corresponding standard deviation was found to be $\sigma = 0.0044$. It should be noticed that both sets of results, sets I and II, are surrounded by different $r$-parameters sets and comparable standard deviation $\sigma$.

The two sets of penultimate reactivity ratios, sets I and II, differ very much in the $r_{21}$ and $r_{12}$ parameters. Both of them, however, present a substantial and equal improvement in graphical representation of experimental data (Figure 2, points (o) and ($\Delta$) for the set I and II, respectively) when compared with the terminal model.

In order to study the 4-dimensional space ($r_{11}$, $r_{22}$, $r_{21}$, $r_{12}$) enclosing the two sets of the penultimate reactivity ratios a scanning procedure was applied. Ranges of $r$-parameters $r_{11}$, $r_{22}$, $r_{21}$, $r_{12}$ taken for the final scanning experiment were 0.200-0.240 (step 0.004), 0.035-0.040, (step 0.001), 0.500-9.000 (step 0.004) and 0.048-1.100 (step 0.004), respectively.

During the scanning experiment all sets of penultimate $r$-parameters with $\sigma \leq 0.007$ were collected. 2-Dimensional projections of the 4-dimensional space ($r_{11}$, $r_{22}$, $r_{21}$, $r_{12}$) for penultimate model reactivity ratios with the standard deviation $\sigma \leq 0.007$ are presented in Figure 3. As the boundary value of the standard deviation was set arbitrarily to $\sigma \leq 0.007$, it is quite obvious that the area and shape of the marked surfaces created from the scanning results presented in Figure 3 depend on the chosen boundary standard deviation. It is demonstrated in Figure 4 how the number of the $r_{21}$ and $r_{12}$ reactivity ratios (measured by the area encircled by the contour lines) increases with the growing standard deviation. From Figure 3, it is also clear why numerical values of the penultimate $r$-parameters calculated with the simplex method depend on the initial guess for $r$-parameters. For the conditions applied in the scanning experiment, the 5-dimensional space ($r_{11}$, $r_{22}$, $r_{21}$, $r_{12}$, $\sigma$) is divided in the $r_{21}$-$r_{12}$ dimensions in two parts. The two sets of penultimate reactivity ratios, set I and set II, belong to the two different discrete local minimum placed in the scanned space. Set I is placed, however, in the local minimum surrounded by

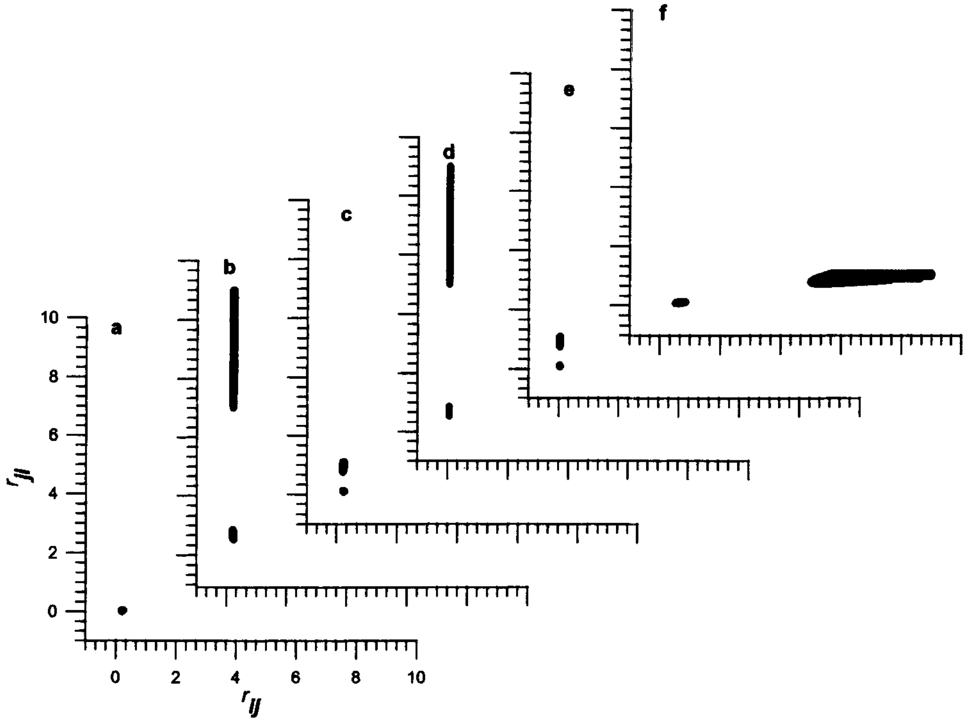

**Figure 3.** 2-Dimensional projections of the penultimate model reactivity ratios $r_{ji}$ vs. $r_{ij}$ ($i,j$=1,2) with the standard deviation ( $\sigma \leq 0.007$. Data were collected from scanning the following ranges of $r_{11}$, $r_{22}$, $r_{21}$, $r_{12}$: 0.200-0.240 (step 0.004), 0.035-0.040 (step 0.001), 0.500-9.000 (step 0.004) and 0.048-1.100 (step 0.004), respectively.

a) $r_{22}$ vs. $r_{11}$
b) $r_{21}$ vs. $r_{11}$
c) $r_{12}$ vs. $r_{11}$
d) $r_{21}$ vs. $r_{22}$
e) $r_{12}$ vs. $r_{22}$
f) $r_{12}$ vs. $r_{21}$

much declivous surfaces when compared with those of the local minimum associated with the set II of penultimate reactivity ratios.

It should be noticed that the sets I and II are not the only local minimum in the 5-dimensional space ($r_{11}$, $r_{22}$, $r_{21}$, $r_{12}$, $\sigma$) space, and another initial guess values would lead to the different local minimum. A detailed analysis of the data presented

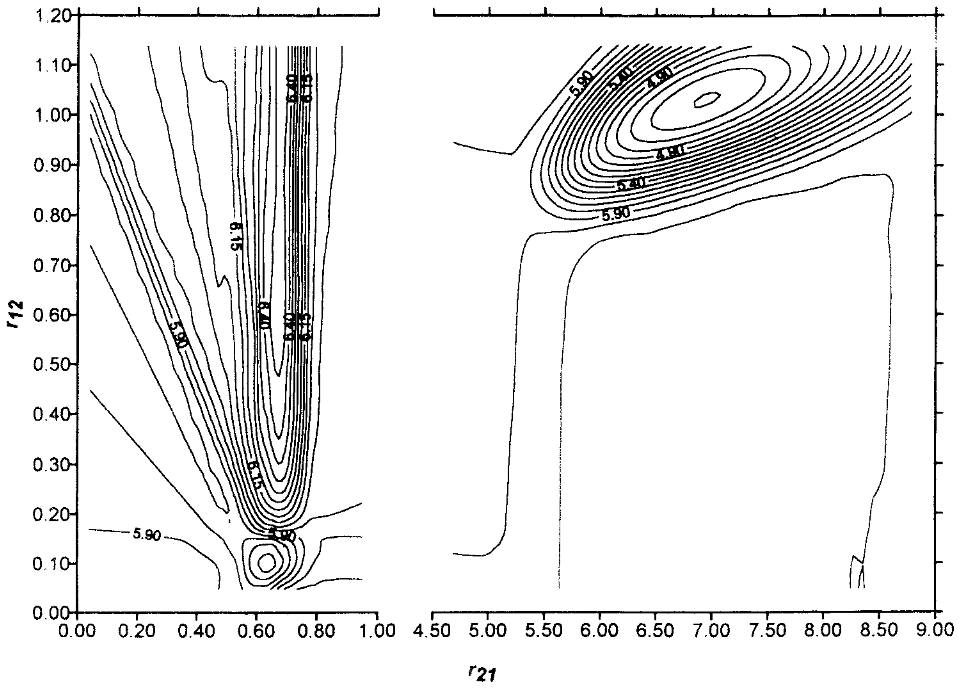

**Figure 4.** The penultimate model reactivity ratios for styrene ($r_{21}$) and acrylonitrile ($r_{12}$) from scanning as in Figure 2. Contour lines encircle the reactivity ratios with the same standard deviation $\sigma$ x $10^3$.

in Figure 3 shows that many different local minimums can be found in the investigated space with the comparable standard deviation. For example, the two following sets of the reactivity ratios $r_{11}$, $r_{22}$, $r_{21}$, $r_{12}$ with standard deviation $\sigma$ =0.0048, sets III and IV, were found to be present in the investigated space: 0.228, 0.038, 7.004, 1.044 and 0.232, 0.036, 6,580, 1,044, respectively.

## CONCLUSIONS

Similar to the previous studies on the styrene-methyl methacrylate system in bulk, in this work the uniqueness in determination of the terminal model reactivity ratios and non-uniqueness in determination of the terminal and penultimate model reactivity ratios in the styrene-acrylonitrile free-radical copolymerization in bulk is clearly demonstrated.

The occurrence of the "non-uniqueness phenomenon" is not associated with the type of the monomer pair. It seems that each comonomer pair can be described by many sets of reactivity ratios wıtn a similar standard deviation. In other words, the known copolymerization equation of Merz *et al.* [12] has, from a mathematical point of view, many equal solutions. The equal solutions are characterized by the comparable standard deviation of the calculated penultimate reactivity ratios. The similarity of the standard deviation is a condition for the equivalent graphical representation of the copolymerization.

Contrary however, the equation according to the terminal model has an unique solution when describing the radical copolymerization.

Our results also confirm the known fact that the penultimate model is the more appropriate of the models considered to describe the variation of the copolymer composition with the monomer feed.

It is worth mentioning, however, that the monomer sequences distribution calculated according to the procedure given by Harwood [13] for the "bootstrap model" was quite different for different sets of styrene and methyl methacrylate reactivity ratios with comparable standard deviation [14].

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