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Penultimate model in the study of the 'bootstrap' effect in the methyl methacrylate–acrylamide copolymerization system

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Methyl methacrylate (MMA)–acrylamide (AA) system was studied in radical conventionally and non-conventionally initiated polymerization reaction with respect to the 'bootstrap' effect using the penultimate model propagation kinetics of vinyl copolymerization. For this, two different methods, the Nelder–Mead simplex method and a scanning method have been adapted for the determination of r_1, r'_1, r_2, r'_2 parameters without constraints to the reactivities of the monomers used. Among the penultimate r-parameters the ranges of their statistically equivalent values have been determined. Good agreement of the calculated copolymer microstructure with results on the experimental basis for styrene–acrylonitrile monomer system proves the reliability of the calculation procedures. The triad fractions of the MMA–AA copolymer calculated on the basis of the penultimate model showed that the penultimate model does not provide any better representation of the copolymerization of MMA with AA than the previously discussed terminal model. Spectral analysis of the triads in copolymer is proposed to verify the right kinetic model as well as the applicability of the 'bootstrap' model for the monomer system. © 1997 Elsevier Science Ltd.

(Keywords: methyl methacrylate; acrylamide; copolymerization)

INTRODUCTION

Many studies done on solvent effects in copolymerization involving polar monomers indicated a great importance of the partitioning of the monomers between solvent and propagating polymer chains. In our previous paper[1] we have studied the methyl methacrylate (MMA)–acrylamide (AA) system in radical conventionally and non-conventionally initiated polymerization reaction with respect to the 'bootstrap' effect by Harwood[2]. Harwood applied successfully his method for several monomer pairs. Our previous study showed the non-applicability of the idea of the 'bootstrap' effect to the investigated monomer system under discussed conditions. It was assumed that one of the possible reasons for the deficiency can be the terminal kinetic model of the copolymerization reaction selected for the calculation of the monomer sequence distributions (triad fractions f). The main purpose of the present consideration is thus to apply penultimate model propagation kinetics of vinyl copolymerization to analyse the monomer sequence distribution of investigated copolymers from the point of view of the 'bootstrap' effect. The penultimate model was first introduced by Merz *et al.*[3] and since then it has been used extensively to explain the composition–conversion and sequence distribution data which did not fit the classical terminal model.

The authors describe a new approach for calculation of the reactivity ratios for the penultimate model of copolymerization reaction, calculate the corresponding reactivity ratios for methyl methacrylate and acrylamide, and finally, verify (by calculation of the monomer sequences distribution) the appearance of the 'bootstrap' effect in the copolymerization system pictured with the penultimate kinetic model of copolymerization.

EXPERIMENTAL

The methods used for purifying the monomers, conditions of polymerization, as well as the methods of the copolymer analysis of the copolymer composition data used for the present work have been given in detail previously[1].

RESULTS AND DISCUSSION

Calculation procedures of the reactivity ratios in the penultimate model

Different methods have been used to determine r_1, r'_1, r_2, r'_2 parameters using initial mole fractions of each monomer in monomer feed and in the polymer as input data. The most advanced one seems that used the Marquardt technique[4], discussed in detail by Pittman and D'Arcy Rounsefell[5]. We have found, however, that use of Marquardt's least squares method may result in wrong convergence in the vicinity of the 'true' solution. This is caused by particular behaviours of the most commonly used objective functions. To study this

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problem and to test alternative methods we have used a modified Nelder–Mead[6] simplex method and a scanning method. Both of them were applied without constraints to the values of the reactivities of the monomers used. Thus, the methods were not limited to some special cases, for example, for which $r_1 = r'_1 = 0$. For both methods the objective function given by

$$s = \sqrt{\sum_i^n (F_{1(i)}^{\text{exptl}} - F_{1(i)}^{\text{calc}})^2/(n-4)}$$

was optimized. $F_1 = f(r_1, r_2, r'_1, r'_2, f_1)$ follows from the penultimate copolymer equation

$$\frac{F_1}{F_2} = \frac{f_1(\bar{r}_1 f_1 + f_2)}{f_2(\bar{r}_2 f_2 + f_1)}$$

where F_1 and F_2 stand for the mole fractions of monomer 1 and 2 in copolymer, f_1 and f_2 are the mole fractions of monomer 1 and 2 in monomer feed and $\bar{r}_1$ and $\bar{r}_2$ are given by

$$\bar{r}_1 = \frac{r'_1(f_1 r_1 + f_2)}{f_1 r'_1 + f_2)} \qquad \bar{r}_2 = \frac{r'_2(f_2 r_2 + f_1)}{f_2 r'_2 + f_1)}$$

where the reactivity ratios are

$$r_1 = k_{111}/k_{112} \qquad r_2 = k_{222}/k_{221}$$

$$r'_1 = k_{211}/k_{212} \qquad r'_2 = k_{122}/k_{121}$$

and parameters k have the common meanings of the propagation rate coefficients. We believe that the simplex and scanning methods were not tested till now from the point of view of usefulness for calculation of r-parameters. The first method (simplex) needs initial mole fractions of each monomer in monomer feed and in the polymer as input data as well as some more or less reasonable first guess for the adjustable parameters, the four reactivity ratios. For the purpose of this work the r_1 and r_2 values for MMA and AA were taken from the terminal model and r'_1 and r'_2 were set as $r'_1 = r_1$ and $r'_2 = r_2$.

It has been proved that for all systems convergence of the simplex method is stable and rapid; the typical number of iterations does not exceed 200. This is a very good result as for the simplex method. In our calculation we used different starting points obtaining the same resulting parameters. As is evident from *Tables 1* and *2* as well as from *Figures 1* and *2* the calculated penultimate model reactivity ratios provide an excellent approximation of the mole fraction of methyl methacrylate in the copolymer with the mole fraction of methyl methacrylate in the feed.

Comparing the reactivity ratios obtained in the presence and absence of conventional initiator under otherwise quite similar conditions (*Tables 1* and *2*) the conclusion can be drawn that the mechanism of the initiation of the polymerization reaction can have some influence on the determined reactivity ratios. For example, the presence of AIBN in the system results in decreasing of the r_1 (MMA) and increasing of the r_2 values. The most probable interpretation is that the complexed MMA molecules (with the appropriate solvent or with another MMA molecule) relatively more often take part in the copolymerization reaction when compared with the conventional free radical initiation.

The scanning method needs, as the simplex, initial mole fractions of each monomer in monomer feed and in the polymer as input data; additionally instead of a first guess for the adjustable parameters, the limits for scanning must be selected as well as the scanning step for each adjustable parameter. As the limits are larger and the steps are smaller the computational time is longer.

We found, that for all systems for unconstrained fit we can find multiple results with the same standard error (*Tables 1* and *2*). There is not a 'sharp' minimum with unique parameters, instead we have a rather large multidimensional plateau of the objective function s. Therefore each particular point located in the vicinity of the main axis of the error hyperellipsoid (at the given confidence level) can be regarded as statistically proved solution.

Therefore, the best idea is to join these two methods. In a first step the approximate solution is estimated and then the neighbouring space is scanned. We thereby obtain, besides the final values of the parameters, the ranges of their statistically equivalent values.

For both the above methods, simplex and scanning, the covariance matrix can be calculated at final estimates.

Table 1 The calculated penultimate reactivity ratios of MMA (r_1, r'_1) and AA (r_2, r'_2) in various reaction media at 75°C in the absence of any conventional initiator

No.	Reaction medium[a]	Penultimate reactivity ratios[b] r_1	r_2	r'_1	r'_2	Standard error
1	Dioxane	5.53 (5.20–6.80)[c]	0.90 (0.84–0.90)	0.23 (0.20–0.25)	3.60 (2.92–6.82)	0.016
2	Cyclohexanone	8.75 (7.74–10.20)	0.65 (0.60–0.68)	0.27 (0.25–0.30)	1.64 (1.15–2.28)	0.015
3	Cyclohexanone /dioxane (1/1.16 in volume)	3.25 (2.72–3.96)	0.54 (0.48–0.66)	0.57 (0.36–0.76)	1.88 (0.92–2.24)	0.012
4	Cyclohexanone /benzene (1/1.16 in volume)	11.82 (10.80–11.06)	1.05 (1.06–1.10)	0.06 (0.06)	5.91 (4.00–4.50)	0.012

[a] The total monomers concentration 1 mol l^{-1}

[b] Reactivity ratios calculated by the simplex method

[c] Range of the penultimate reactivity ratio calculated by the scanning method

Table 2 The penultimate reactivity ratios of MMA (r_1, r'_1) and AA (r_2, r'_2) under various reaction conditions at 70°C calculated from the data of Saini *et al.*[8]

No.	Reaction medium	Penultimate reactivity ratios[c] r_1	 r_2	 r'_1	 r'_2	Standard error
1	Dioxane[a]	3.61 (3.22–3.68)[d]	1.73 (1.70–1.90)	0.50 (0.48–0.60)	1.54 (1.04–2.28)	0.018
2	Dioxane[b]	3.35 (2.60–3.86)	2.03 (1.84–2.24)	0.81 (0.40–0.90)	2.70 (2.34–3.08)	0.025
3	Dioxane/ ethanol (70/30 in volume)[a]	3.00 (2.48–3.18)	0.74 (0.66–0.90)	1.23 (1.00–1.40)	0.88 (0.50–1.00)	0.022
4	Ethanol[a]	2.44 (2.34–2.60)	1.03 (0.88–1.18)	4.73 (2.60–5.00)	0.25 (0.16–0.30)	0.007
5	Ethanol[b]	2.74 (2.50–2.90)	0.74 (0.64–0.90)	3.31 (3.20–7.20)	0.37 (0.30–0.60)	0.014

[a] The total monomers concentration 0.8 mol l^{-1}, the AIBN concentration 0.4 g l^{-1}
[b] The total monomers concentration 0.4 mol l^{-1}, the AIBN concentration 1 g l^{-1}
[c] Reactivity ratios calculated by the simplex method
[d] Range of the penultimate reactivity ratio calculated by the scanning method

Covariance matrix

Let us assume we use proper procedure for estimation of the reactivity ratios; this may be the non-linear least squares method (e.g. that of Marquardt), the simplex method, the scanning method of any other. If the objective function used is the sum of squared differences between experimental and calculated x_m then for the final estimation, regarded as the 'true' solution, we can write

$$\mathrm{Cov}(r) = \sigma(x_m)\ (J^T J)^{-1}$$

where $\sigma(x_m)$ is the standard deviation of mole fraction of monomer 'm' and J is the Jacobian of the objective function (matrix of partial derivatives of the ith term of objective function with respect to adjustable parameter). Upper index 'T' denotes transposed matrix (rows to columns) and '−1' denotes the inverse of the resulting matrix. In this expression equal weights for each experimental points are assumed.

Having the covariance matrix the standard errors and correlation coefficients for the pairs of adjustable parameters can be estimated. The correlation coefficient, q_{ij}, for the pair i–j of parameters (e.g. r_1–r'_1) is equal to $\mathrm{Cov}(ij)/[\mathrm{Cov}(ii) \times \mathrm{Cov}(jj)]^{-2}$; where $\mathrm{Cov}(ij)$, etc.

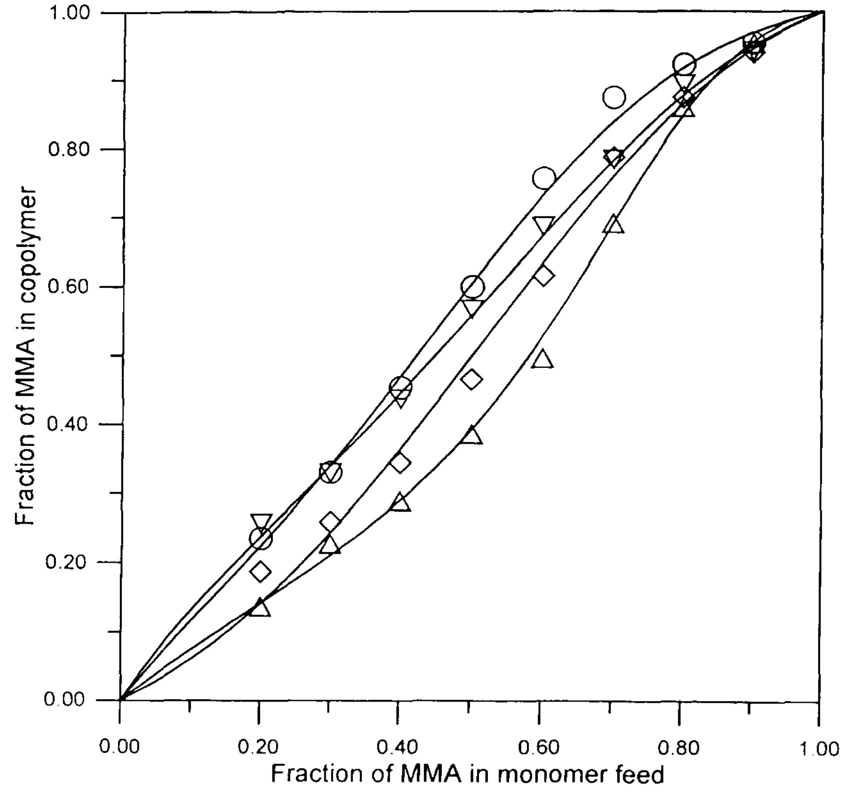

Figure 1 Fraction of MMA in copolymer vs fraction of MMA in feed. Experimental results are our results from ref. 1. Solid lines are fits of the penultimate model to the data with reactivity ratios calculated by the simplex method for different reaction medium given in *Table 1*: (◇) in dioxane: $r_1 = 5.53$, $r_2 = 0.90$, $r'_1 = 0.23$, $r'_2 = 3.60$; (○) in cyclohexanone: $r_1 = 8.75$, $r_2 = 0.65$, $r'_1 = 0.27$, $r'_2 = 1.64$; (△) in cyclohexanone/dioxane (1 : 1.16 in volume): $r_1 = 3.25$, $r_2 = 0.54$, $r'_1 = 0.57$, $r'_2 = 1.88$; (▽) in cyclohexanone/benzene (1 : 1.16 in volume): $r_1 = 11.82$, $r_2 = 1.05$, $r'_1 = 0.06$, $r'_2 = 5.91$

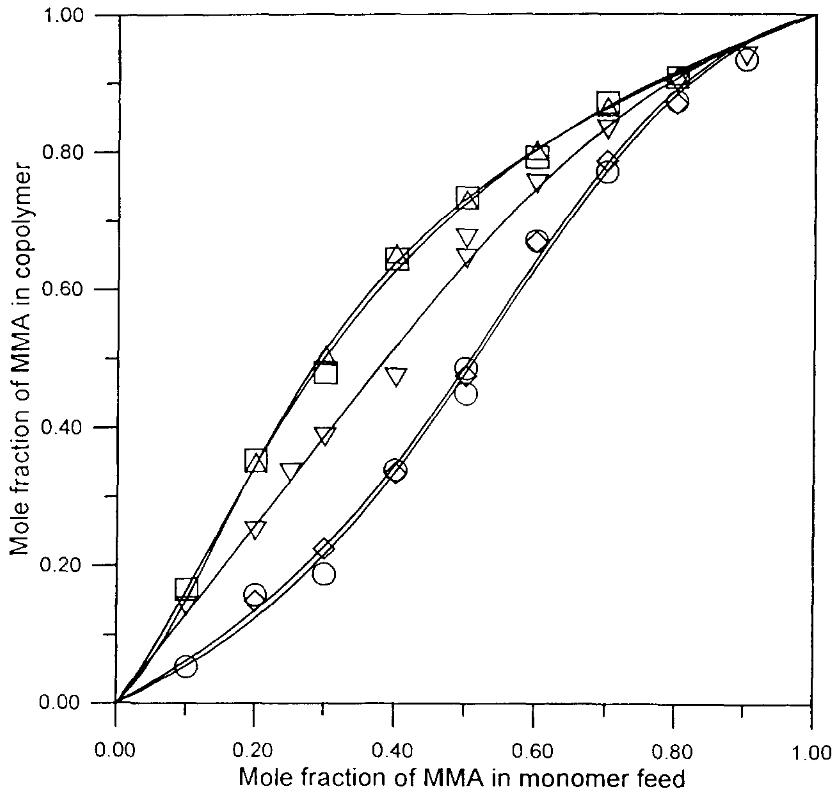

Figure 2 Fraction of MMA in copolymer vs fraction of MMA in feed. Experimental results of Saini *et al.*[8]. Solid lines are fits of the penultimate model to the data with reactivity ratios calculated by the simplex method for different reaction medium given in *Table 2*: (◇) in dioxane at the total monomers concentration 0.8 mol l^{-1} and the AIBN concentration 0.4 g l^{-1}: $r_1 = 3.61$, $r_2 = 1.73$, $r'_1 = 0.50$, $r'_2 = 1.54$; (○) in dioxane at the total monomers concentration 0.4 mol l^{-1}, the AIBN concentration 1 g l^{-1}: $r_1 = 3.61$, $r_2 = 1.73$, $r'_1 = 0.50$, $r'_2 = 1.54$; (△) in dioxane/ethanol (70/30 in volume) at the total monomers concentration 0.8 mol l^{-1} and the AIBN concentration 0.4 g l^{-1}: $r_1 = 3.25$, $r_2 = 0.54$, $r'_1 = 0.57$, $r'_2 = 1.88$; (▽) in ethanol at the total monomers concentration 0.8 mol l^{-1} and the AIBN concentration 0.4 g l^{-1}: $r_1 = 2.44$, $r_2 = 1.03$, $r'_1 = 4.73$, $r'_2 = 0.25$; (□) in ethanol at the total monomers concentration 0.4 mol l^{-1}, the AIBN concentration 1 g l^{-1}: $r_1 = 2.74$, $r_2 = 0.74$, $r'_1 = 3.31$, $r'_2 = 0.37$

should be read as corresponding elements of the Cov-matrix. The correlation coefficients can range from 0 to ±1. The value equal to 0 means that two adjusted parameters are independent of each other. The value ±1 means that parameters are linearly dependent; one of them can be, usually, excluded from consideration.

Calculated standard deviation of adjustable parameter is a statistical measure of the confidence range for this parameter; the larger the calculated standard error the less determinable the parameter; it means the 'true' solution can be within this range with the same probability for all points. From a statistical point of view the standard errors determined confidence limits for parameters; the larger the confidence limit the more undefined the parameter. This fact seems to be overlooked by other investigators.

Table 3 Penultimate model reactivity ratios for styrene (r_s) and acrylonitrile (r_a) calculated from the data of Hill *et al.*[9,10]

			Penultimate reactivity ratios				
Solvent	Source	Calculation method	r_s	r_a	r'_s	r'_a	Standard error
Bulk	Our results	Simplex scanning	0.23	0.04	0.65	0.10	0.005
			(0.22–0.24)	(0.00–0.08)	(0.59–0.73)	0.10	0.005
	Hill *et al.*	Weighted average[10]	0.232	0.036	0.566	0.087	0.022
		Composition[9]	0.23	0.04	0.66	0.10	
		Triad composition[9]	0.24	0.06	0.58	0.09	
Toluene	Our results	Simplex scanning	0.25	0.26	0.46	0.06	0.007
			(0.24–0.27)	(0.25–0.26)	(0.43–0.49)	0.06	0.007
	Hill *et al.*	Weighted average[10]	0.263	0.123	0.549	0.125	
		Triad composition[10]	0.242	0.133	0.566	0.109	0.023
Acetonitrile	Our results	Simplex scanning	0.43	0.06	0.60	0.08	0.005
			(0.40–0.46)	0.06	(0.55–0.68)	(0.07–0.08)	0.005
	Hill *et al.*	Weighted average[10]	0.311	0.073	0.637	0.104	
		Triad composition[10]	0.322	0.052	0.621	0.105	0.020

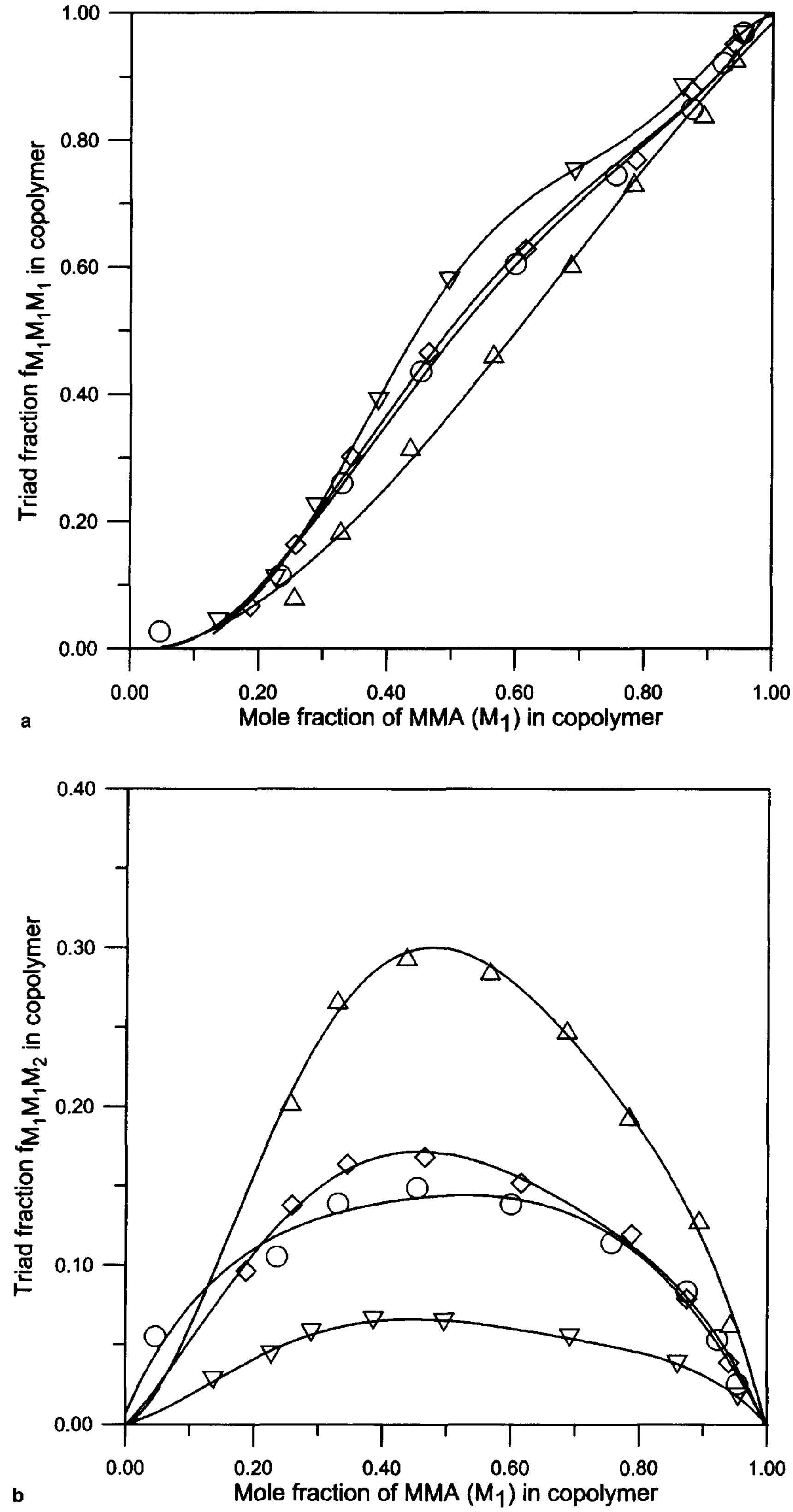

Figure 3 Methyl methacrylate (M_1)-centred triad fractions for methyl methacylate–acrylamide copolymer calculated from the penultimate model vs M_1 in monomer feed. Experimental results are our results from ref. 1: (◇) in dioxane, (○) in cyclohexanone, (△) in cyclohexanone/dioxane (1/1.16 in volume), (▽) in cyclohexanone/benzene (1/1.16 in volume): (a) $f_{M_1M_1M_1}$ triad fraction; (b) $f_{M_1M_1M_2}$ triad fraction; (c) $f_{M_2M_1M_2}$ triad fraction

For all nine investigated systems we could not find, however, any clear correlation between some characteristics of the investigated system and magnitude of correlation between the estimated reactivity ratios. For some investigated systems (system 1 in *Table 1* and systems 1, 3, 4 and 5 in *Table 2*) r'_1 and r'_2 are highly correlated (with correlation coefficient of 0.99). In addition, for all investigated systems standard errors calculated for estimated reactivity ratios are of order of these ratios or higher. As we said before, it means the 'true' solution can

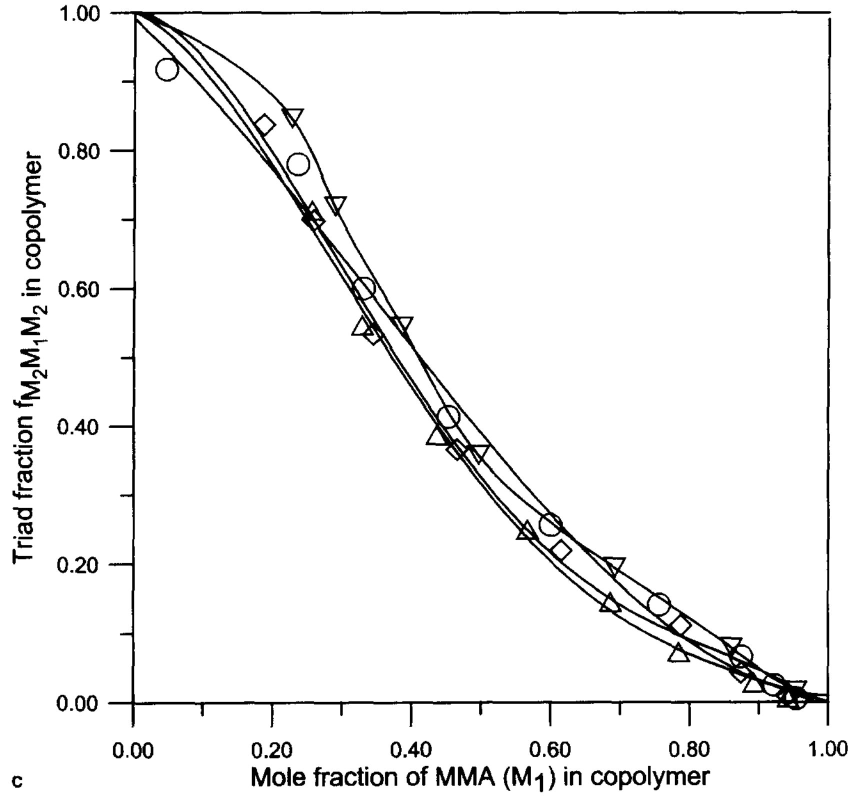

Figure 3 Continued

be within this range with the same probability for all values of the reactivity ratios obtained.

This conclusion is supported by the previous discussed results of the scanning method: for all discussed MMA–AA systems no 'sharp' minima with unique parameters were obtained.

Verification of the calculation procedures

In order to verify the calculation procedures the data for the monomer system which is believed to obey the penultimate kinetics has been treated with the same calculation procedures. One of the most successfully studied monomer systems from that point of view is a styrene (r_s)–acrylonitrile (r_a) system investigated in detail (among others) by Hill *et al.*[9,10]. They determined for styrene and acrylonitrile the corresponding penultimate reactivity ratios (r_s, r_a, r'_s, r'_a) for polymerization in bulk, toluene and acetonitrile in two independent ways, from the weight fractions of the monomers in copolymer and from experimental measured triad fractions in copolymer. Taking the monomer fractions in monomer feed and copolymer data of Hill *et al.*[9,10] we calculated the corresponding penultimate reactivity ratios (r_s, r_a, r'_s, r'_a) with the simplex and scanning method.

The results are given in *Table 3*. They are generally in good agreement with the results of Hill *et al.*[9,10] and in excellent agreement with the reactivity ratios estimated on the basis of the copolymer–monomer composition relationship for copolymerization in bulk. In toluene, reactivity of acrylonitrile departs most significantly from the data of Hill *et al.*[10] (enhancement of r_a and decreasing of r'_a). The departure of the copolymerization in toluene when compared with the data of Pichot *et al.*[11] was also discussed by Hill *et al.*[10] but the reason for the difference has not been firmly established. Not going into detailed discussion on the solvent effect of the particular monomer system it can be concluded that both simplex and scanning calculation procedures can give reliable estimates for the penultimate reactivity ratios.

Monomer sequence distributions

Monomer sequence distributions in the methyl methacrylate–acrylamide copolymers were calculated according to the method for the penultimate model described by Harwood[2]. Unconditional probabilities for the sequences (which are conditions in the conditional probability expressions used to calculate the copolymer structure) have been evaluated by the matrix multiplication method described earlier in detail by Harwood *et al.*[12].

As shown earlier[1], for the MMA–AA system no 'bootstrap' effect could have been observed when a terminal model was applied for calculation of the triad fractions neither in thermal initiated systems in dioxane, cyclohexanone, cyclohexanone/dioxane and cyclohexanone/benzene mixtures nor for conventional free radical initiated copolymerization by Saini *et al.*[8] in dioxane, ethanol and dioxane/ethanol solvent mixtures. Now, the triad fractions calculated on the basis of the penultimate model reactivity ratios do not provide any better proof for the 'bootstrap' effect for the MMA–AA monomer pair than it was in the case when the terminal model was used[1] (*Figures 3* and *4*). Thus, either both kinetic models, the terminal and the penultimate model, do not assure an adequate representation of the copolymerization reaction of MMA with AA or, the 'bootstrap' effect has not so general validity as seems to be expected by its author[2]. Not having adequate representation of the copolymerization reaction results in the calculated triad fractions distribution which

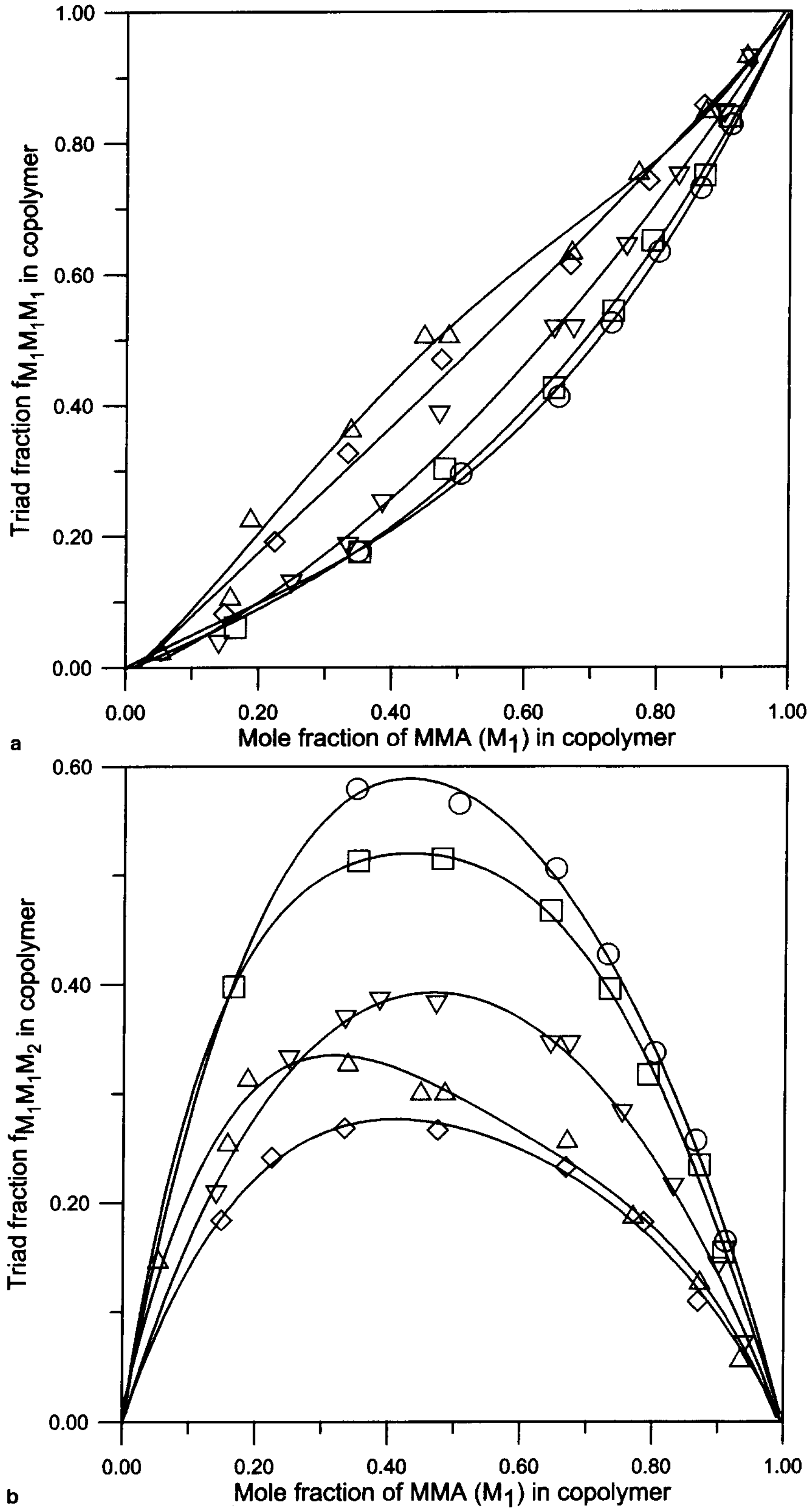

Figure 4 Methyl methacrylate (M_1)-centred triad fractions for methyl methacylate–acrylamide copolymer calculated from the penultimate model *versus* M_1 in monomer feed. Experimental results of Saini *et al.*[8]: (◇) in dioxane at the total monomers concentration 0.8 mol l^{-1} and the AIBN concentration 0.4 g l^{-1}; (○) in dioxane at the total monomers concentration 0.4 mol l^{-1}, the AIBN concentration 1 g l^{-1}; (△) in dioxane/ethanol (70/30 in volume) at the total monomers concentration 0.8 mol l^{-1} and the AIBN concentration 0.4 g l^{-1}; (▽) in ethanol at the total monomers concentration 0.8 mol l^{-1} and the AIBN concentration 0.4 g l^{-1}; (□) in ethanol at the total monomers concentration 0.4 mol l^{-1}, the AIBN concentration 1 g l^{-1}: (a) $f_{M_1M_1M_1}$ triad fraction; (b) $f_{M_1M_1M_2}$ triad fraction; (c) $f_{M_2M_1M_2}$ triad fraction

does not match the experimental determined microstructure of the copolymer. Thus, it can be that another appropriate kinetic model of the particular copolymerization reaction could explain more adequately the formation of the microstructure of the copolymer. However, so far as we know, no other kinetic model was proposed for the monomer system than that discussed here. It might not be easy to find

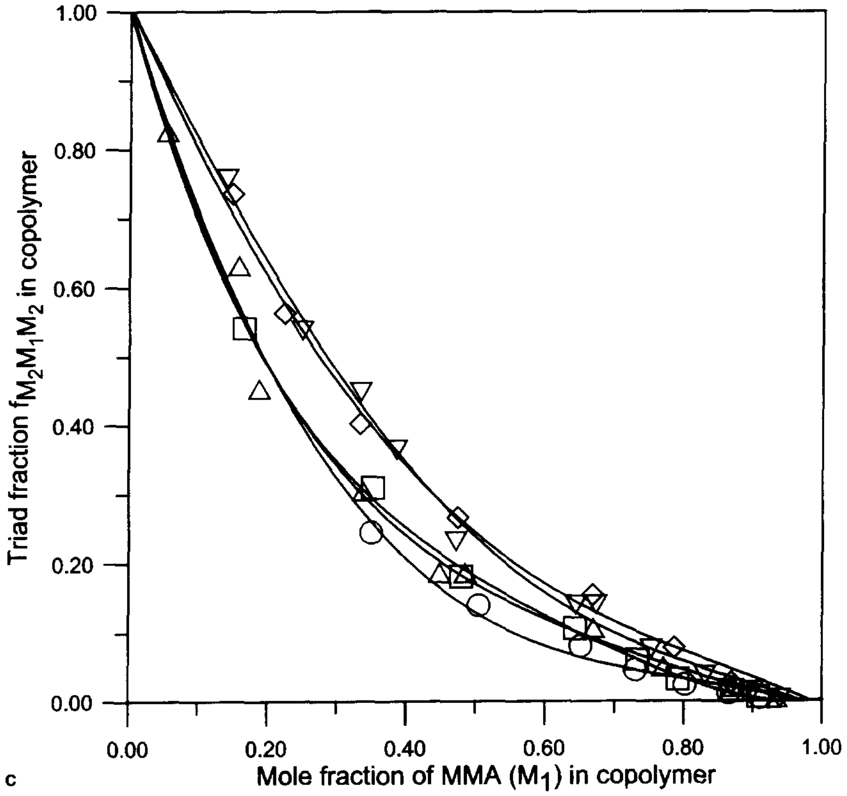

Figure 4 Continued

one as the AA molecules undergo in solution specific association that results in changes of the AA vinyl bond activity as discussed before[1].

The second possibility is, that the 'bootstrap' model does not apply to the investigated system. Recently, we have shown[13] that the same poor agreement between the postulated microstructure from the 'bootstrap' model and calculated triad distribution can be observed for another monomer pair. This result was obtained for the methyl methacrylate–styrene system in methyl cyanoacetate and phenol, a monomer pair considered[14] well described with the terminal model and incorporated 'bootstrap' model.

It seems that the spectral analysis of the triads in copolymer will verify the chosen kinetic model as well as the co-existence of the copolymer sequences obtained in different solvent plotted against the copolymer composition.

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