

# Study of methyl methacrylate–acrylamide copolymerization system in cyclohexanone in the absence of conventional radical initiator

Mir Munsif Ali Talpur\*, Paweł Oracz and Andrzej Kaim†

University of Warsaw, Faculty of Chemistry, ul. Pasteura 1, 02-093 Warsaw, Poland

(Received 9 November 1993; revised 3 October 1995)

The copolymerization of a methyl methacrylate–acrylamide system has been studied at 75°C in the absence of any radical initiator, thermal in dioxane, and in pure cyclohexanone, cyclohexanone/dioxane mixture and cyclohexanone/benzene mixture. The *r*-parameter values are calculated by FR, YBR, KT and EVM methods. The calculation method considerably influences the reactivity ratio values. A comprehensive comparative study of *r*-parameters and ‘bootstrap’ effect for the investigated systems, and the same monomer system initiated by the free radical initiator described in the literature, is presented. Discrepancies between the results obtained and examples for the ‘bootstrap’ effect given in the literature are discussed. The kinetic data obtained confirm specific interactions of methyl methacrylate and cyclohexanone. Copyright © 1996 Elsevier Science Ltd.

(Keywords: methyl methacrylate; acrylamide; copolymerization)

## INTRODUCTION

The radical homopolymerization of several polar vinyl monomers in the presence of some active acidic hydrogen atom containing compounds has been the subject of many publications<sup>1–8</sup>. The mechanism of the reaction involving transfer of the hydrogen radical abstracted from these compounds to the monomer, originally proposed by Ouchi and co-workers<sup>3–5</sup> for the polymerization of methyl methacrylate (MMA) initiated with aldehydes and later discussed for the polymerization of MMA initiated by cyclohexanone, still remains uncertain for many reasons. For example, the so-called thermal polymerization of MMA, which is most probably always simultaneously present in all the investigated polymerization systems, with the presence of MMA being itself still under discussion<sup>9–11</sup>, very much complicates the kinetic and spectral analysis of the investigated reaction.

For this reason the proof of the mechanism obtained from electron paramagnetic resonance (e.p.r.) investigations performed by Sato *et al.*<sup>2</sup> and Ouchi *et al.*<sup>5</sup> seems to be indecisive<sup>12</sup>. Moreover, we suspect that the compounds with acidic hydrogen atoms can undergo some thermal transformations, liberating radicals which can initiate the polymerization, e.g. the thermal radical self-condensation of cyclohexanone<sup>13</sup>.

Recently, we have been studying the initiating activity of these acidic hydrogen containing compounds in the copolymerization system of MMA–styrene (St) in the absence of any conventional radical initiator<sup>14,15</sup>.

In the MMA–St copolymerization system, St was a monomer that did not homopolymerize in the presence of cyclohexanone in the absence of any conventional radical initiator, while MMA did polymerize. Acrylamide (AAM), like MMA, homopolymerized in the presence of cyclohexanone<sup>6</sup>. Therefore, it was interesting to investigate the MMA–St copolymerization system with St replaced by AAM in the absence of any conventional radical initiator. Thus, the main purpose of the present paper is to study the copolymerization reaction of MMA and AAM in the presence of cyclohexanone, without using any additional radical initiator, in comparison with the known free radically initiated copolymerization of the same monomer pair. The assumed mechanism of the initiation of the reaction involves transfer of the hydrogen radical between a complexed acidic hydrogen containing compound and the monomer. Thus, solvent effects in the copolymerization are crucial. They will be discussed in terms of the ‘bootstrap’ effect.

## EXPERIMENTAL

Acrylamide, a pure grade reagent (Fluka AG) was further purified<sup>16</sup> by recrystallizing from benzene. The crystals were filtered out and dried *in vacuo* over phosphorus pentoxide for two days. The melting point, which was the criterion of purity, was found to be 84.8°C.

Dioxane (Xenon, Łódź, Poland) was purified according to the procedure described in the literature<sup>17</sup>. The middle portion of dry dioxane distilled at 101°C under a dry oxygen-free nitrogen stream was taken for use.

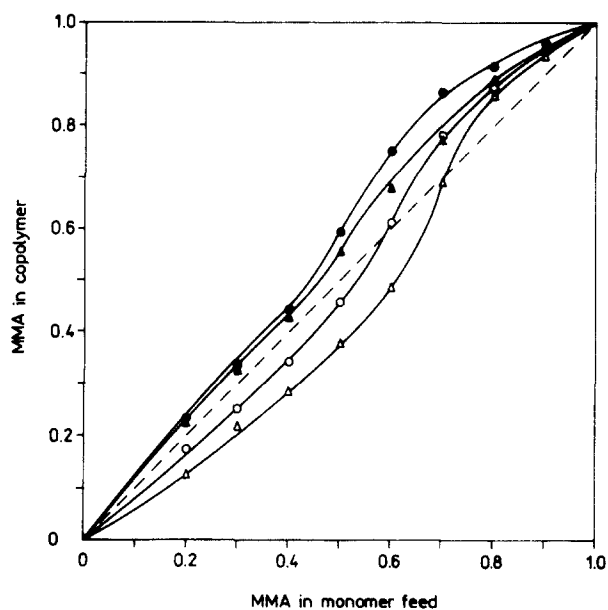
The purification of MMA, cyclohexanone and benzene, as well as the procedure for copolymerization, has been described previously<sup>14,15</sup>.

\*Permanent address: Department of Chemistry, Shah Abdul Latif University, Khaipur (Mir’s), Sindh, Pakistan

† To whom correspondence should be addressed

**Table 1** Copolymerization of methyl methacrylate ( $M_1$ ) and acrylamide ( $M_2$ ) at 75 °C

Thermal copolymerization of $M_1$ with $M_2$ in dioxane							Copolymerization of $M_1$ with $M_2$ in cyclohexanone						
Mole fract. in feed		React. time (min)	Conver. weight (%)	Results of elemental analysis of copolymer			Mole frac. $M_1$ in copol.	React. time (min)	Conver. weight (%)	Results of elemental analysis of copolymer			Mole frac. $M_1$ in copol.
$M_1$	$M_2$			N (%)	C (%)	H (%)				N (%)	C (%)	H (%)	
0.90	0.10	360	2.027	0.868	58.325	7.89	0.94	90	7.43	0.64	61.495	8.365	0.954
0.80	0.20	360	1.716	1.83	57.755	8.045	0.874	90	7.32	1.11	60.424	8.13	0.922
0.70	0.30	360	1.547	3.175	56.800	7.98	0.787	90	7.258	1.835	59.692	8.50	0.876
0.60	0.40	360	1.632	6.07	54.110	8.015	0.615	90	5.234	3.665	57.490	7.69	0.756
0.50	0.50	360	1.461	8.86	49.620	7.725	0.465	135	6.813	6.350	53.770	8.48	0.598
0.40	0.60	420	1.381	11.32	47.065	7.545	0.344	135	6.724	9.085	51.560	8.035	0.453
0.30	0.70	420	1.253	13.23	45.775	7.600	0.258	135	6.816	11.66	48.740	7.785	0.330
0.20	0.80	420	1.202	14.89	44.715	7.115	0.186	135	5.073	13.74	45.205	7.79	0.235
0.90	0.10	110	6.225	0.82	60.175	7.855	0.942	240	2.994	0.645	59.500	8.380	0.954
0.80	0.20	110	6.635	1.54	60.300	8.39	0.893	240	3.451	2.035	58.289	7.891	0.860
0.70	0.30	110	6.741	3.22	58.790	7.72	0.784	240	3.672	4.730	54.438	7.813	0.992
0.60	0.40	110	6.667	4.83	58.565	8.36	0.686	240	3.590	8.298	51.432	7.344	0.494
0.50	0.50	110	6.307	6.945	56.225	8.22	0.566	240	3.563	10.450	48.110	7.501	0.386
0.40	0.60	240	7.839	9.43	52.425	7.71	0.436	240	3.261	12.520	45.653	7.614	0.289
0.30	0.70	240	7.768	11.68	50.055	7.86	0.328	240	3.249	13.940	44.225	7.959	0.227
0.20	0.80	240	6.577	13.39	47.070	7.47	0.256	240	2.873	16.100	41.543	7.720	0.137

**Figure 1** Copolymerization of MMA ( $r_1$ ) and AAm ( $r_2$ ) at 75 °C. Reaction medium: (○) dioxane; (△) cyclohexanone/benzene (1/1.16, v/v) mixture; (●) cyclohexanone; (▲) cyclohexanone/dioxane (1/1.16, v/v)

All the copolymerization reactions were carried out at 75 °C. Ethyl ether was used as a copolymer precipitator. The copolymer composition was determined on the basis of its nitrogen content by using a Perkin-Elmer Micro Analyzer (CHN) model no. 240. For calculation purposes the average value of at least two experiments have been taken into account. For the reactivity ratios calculation the conversion was always kept below 8% of

the total monomer weight. The absence of any peroxide group in the cyclohexanone and dioxane was confirmed iodometrically<sup>18,19</sup>.

## RESULTS AND DISCUSSION

The copolymer composition data as mole fractions of MMA for the MMA–AAm system in different solvents are listed in *Table 1* with the corresponding weight percentage conversion. No thermal copolymerization of the monomer system in benzene was observed. The MMA–AAm copolymer composition curves as a function of monomer feed are reported in *Figure 1* and refer to the thermal copolymerization in dioxane, as well as to the copolymerization of monomers in cyclohexanone, in cyclohexanone/dioxane (1/1.16, v/v) and in cyclohexanone/benzene (1/1.16, v/v), respectively. The reactivity ratios for MMA ( $r_1$ ) and AAm ( $r_2$ ) for all the investigated copolymerization systems are calculated by the Finemann and Ross (FR) method<sup>20</sup>, the Yezerielev, Brokhina and Roskin (YBR) method<sup>21</sup>, the Kelen and Tüdös (KT) method<sup>22</sup> and by a method based on the Error-In-Variable Model (EVM)<sup>23</sup> (*Table 2*). By the EVM method the  $r$ -parameters are generated using random errors of 5 and 1% for monomer feed composition and copolymer composition, respectively.

As expected<sup>24,25</sup>, different calculation methods offer different  $r$ -parameter values for the same set of experimental data. For the present monomer pair the  $r$ -parameter data found in the literature are calculated by the FR method (*Table 3*), which, according to Joshi<sup>26</sup>, has become obsolete and most satisfactorily replaced by the YBR method. All the YBR, KT and EVM methods

**Table 2** The  $r_1$  (MMA) and  $r_2$  (AAM) values calculated by different methods in various reaction media at 75°C in the absence of any conventional initiator

Reaction medium	$r$ value	Calculation method			
		FR method	YBR method	KT method	EVM method
Dioxane	$r_1$	1.98 ± 0.66	1.93 ± 0.07	1.91 ± 0.26	1.99
	$r_2$	1.82 ± 0.66	1.69 ± 0.06	1.73 ± 0.26	1.84
Cyclohexanone	$r_1$	2.53 ± 1.13	2.52 ± 0.09	2.93 ± 0.55	2.72
	$r_2$	0.90 ± 1.13	0.85 ± 0.05	1.24 ± 0.55	1.05
Cyclohexanone/dioxane (1/1.16, v/v)	$r_1$	1.96 ± 0.84	1.82 ± 0.21	1.96 ± 0.30	1.88
	$r_2$	1.07 ± 0.84	0.95 ± 0.23	1.08 ± 0.30	1.05
Cyclohexanone/benzene (1/1.16, v/v)	$r_1$	2.57 ± 2.33	1.94 ± 0.08	1.87 ± 0.71	1.78
	$r_2$	3.64 ± 2.33	2.46 ± 0.10	2.46 ± 0.71	2.60

**Table 3** The  $r_1$  (MMA) and  $r_2$  (AAM) values for free radical initiated copolymerization given in the literature

Reaction medium	$r$ value	Calculation method	
		FR method	EVM method <sup>c</sup>
Dioxane <sup>27 a</sup>	$r_1$	2.55 ± 0.40	2.09
	$r_2$	2.45 ± 0.35	2.15
Dioxane <sup>27 b</sup>	$r_1$	2.44 ± 0.38	2.15
	$r_2$	2.39 ± 0.32	2.20
Dioxane <sup>28 c</sup>	$r_1$	3.050 ± 0.274	2.78
	$r_2$	0.982 ± 0.090	0.75
Dioxane/ethanol (7/3, v/v) <sup>27 a</sup>	$r_1$	2.53 ± 0.22	2.00
	$r_2$	0.82 ± 0.07	0.78
Ethanol <sup>27 a</sup>	$r_1$	2.60 ± 0.21	3.31
	$r_2$	0.44 ± 0.06	0.64
Ethanol <sup>27 b</sup>	$r_1$	2.65 ± 0.20	3.26
	$r_2$	0.47 ± 0.02	0.60
DMSO <sup>29 d</sup>	$r_1$	3–3.5	
	$r_2$	0.15–1	
Chloroform <sup>29 d</sup>	$r_1$	0.25–0.30	
	$r_2$	1.0–3.5	

<sup>a</sup> The total monomers' concentration constant at 0.8 mol l<sup>-1</sup> of solvent; the AIBN concentration constant at 0.4 g l<sup>-1</sup> of solvent; reaction at 70°C

<sup>b</sup> The total monomers' concentration constant at 0.4 mol l<sup>-1</sup> of solvent; the AIBN concentration constant at 1 g l<sup>-1</sup> of solvent; reaction at 70°C

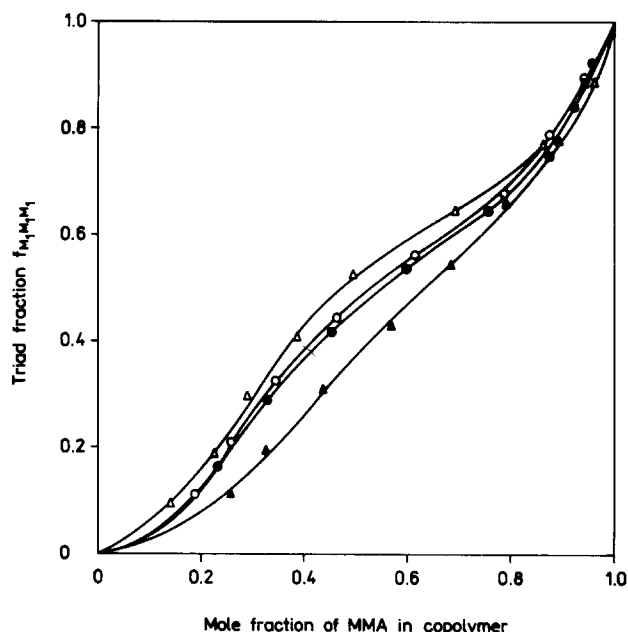
<sup>c</sup> The solvent/monomer ratio varying in the range 230–435 (in ml mol<sup>-1</sup>); the AIBN concentration constant at 0.261 mol%; reaction at 65°C; yield (in %) from 34.4 to 75

<sup>d</sup> The reactivity ratios varying up to the amounts of acetic acid and/or water added to the reaction mixture; reaction at 60°C

<sup>e</sup> Recalculated by the EVM method<sup>23</sup>. The  $r$ -parameters generated, assuming random errors of 5 and 1% for monomer feed composition and copolymer composition, respectively

are nowadays considered to be better and more reliable<sup>23,25,26</sup>. For comparison, the data found in the literature have been recalculated by the EVM method (Table 3). By comparing the  $r$ -parameters obtained by the same calculation method, significant solvent effects can be observed.

However, a comparison of the reactivity ratios, in order to study the solvent effect on the radical copolymerization, has to be done very carefully. Harwood<sup>30</sup> found that the origin of solvent effects on the copolymerization of some polar monomers, including the AAm–St system, was not on the chain end reactivity, but appeared to originate in a solvent partitioning phenomenon. Thus, as a result of the 'bootstrap' effect, most of the reactivity ratios that

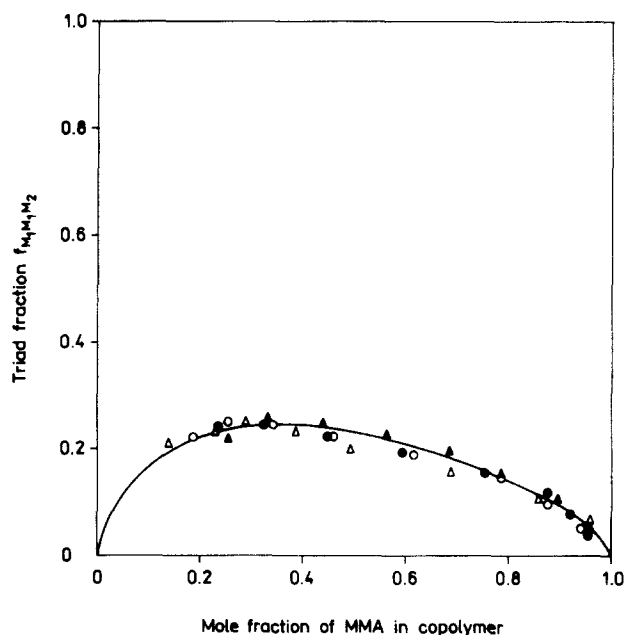


**Figure 2** Triad fractions  $f_{M_1M_1M_1}$  ( $M_1$  corresponds to MMA) for copolymer prepared at 75°C. Reaction medium: (○) dioxane; (△) cyclohexanone/benzene (1/1.16, v/v); (●) cyclohexanone; (▲) cyclohexanone/dioxane (1/1.16, v/v)

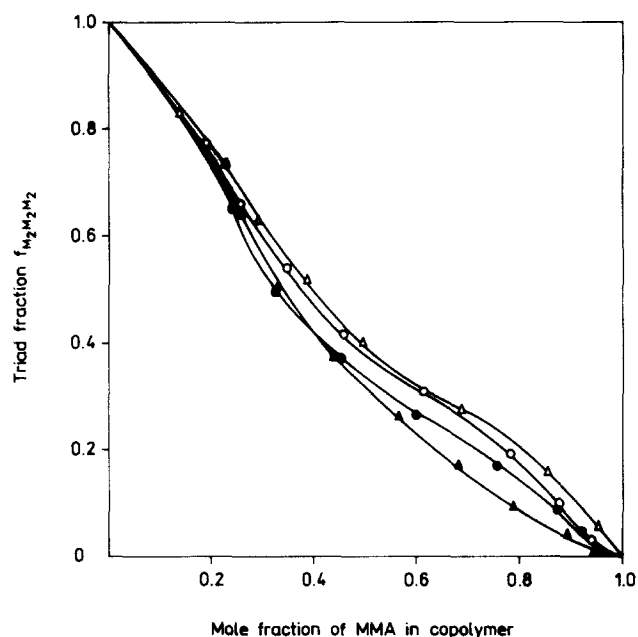
have been determined for polar monomers can be artefacts.

In order to test if the solvent effect observed is or not a partitioning effect the calculation procedure for the monomer sequence distributions (triad fractions  $f$ ), using the terminal model<sup>31,32</sup> for copolymerization described by Harwood<sup>30,33</sup> has been applied.

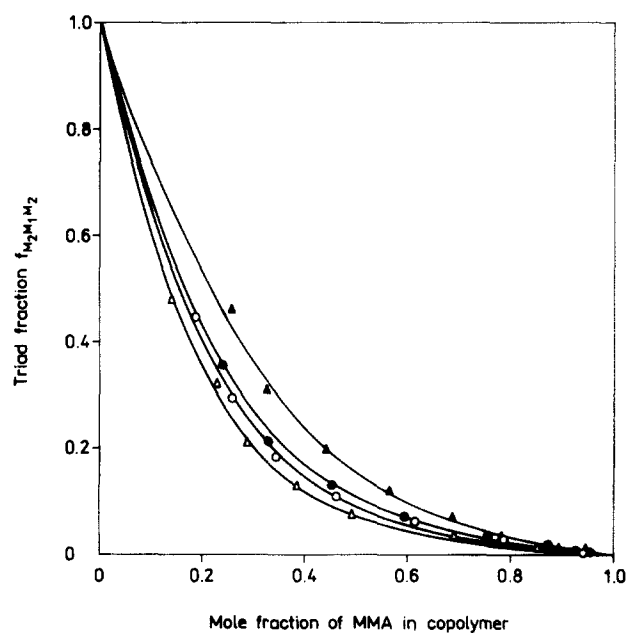
Figures 2–5, which are plots of triad functions calculated for the copolymers *versus* copolymer compositions, show that, except for  $f_{M_1M_1M_2}$  ( $M_1$  and  $M_2$  correspond to MMA and AAm, respectively) where the differences are small, the calculated triad fractions depend on the solvent used for copolymerization. All the curves have almost the same shape, but the curves for cyclohexanone/dioxane and cyclohexanone/benzene are always positional between the remaining two. The same picture can be seen when the results of Saini *et al.*<sup>27</sup> have been considered. The reactivity ratios for MMA and AAm of Saini *et al.*<sup>27</sup> have been recalculated using the EVM method and the above calculation procedure



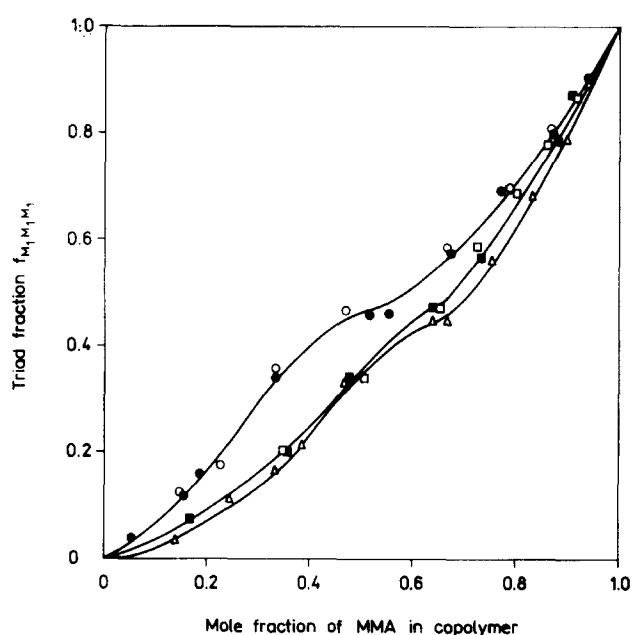
**Figure 3** Triad fractions  $f_{M_1 M_1 M_2}$  ( $M_1$  and  $M_2$  corresponds to MMA and AAm, respectively) for copolymer prepared at 75°C. Reaction medium: (○) dioxane; (△) cyclohexanone/benzene (1/1.16, v/v); (●) cyclohexanone; (▲) cyclohexanone/dioxane (1/1.16, v/v)



**Figure 5** Triad fractions  $f_{M_2 M_2 M_2}$  ( $M_2$  corresponds to AAm) for copolymer prepared at 75°C. Reaction medium: (○) dioxane; (△) cyclohexanone/benzene (1/1.16, v/v); (●) cyclohexanone; (▲) cyclohexanone/dioxane (1/1.16, v/v)



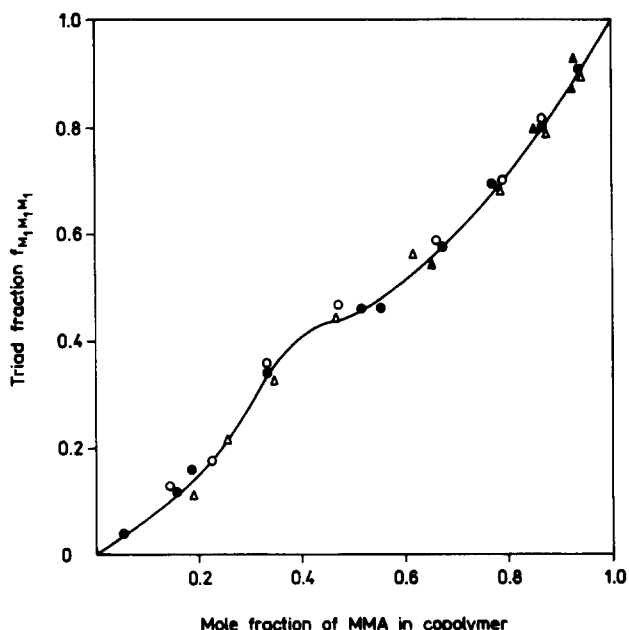
**Figure 4** Triad fractions  $f_{M_2 M_1 M_2}$  ( $M_1$  and  $M_2$  corresponds to MMA and AAm, respectively) for copolymer prepared at 75°C. Reaction medium: (○) dioxane; (△) cyclohexanone/benzene (1/1.16, v/v); (●) cyclohexanone; (▲) cyclohexanone/dioxane (1/1.16, v/v)



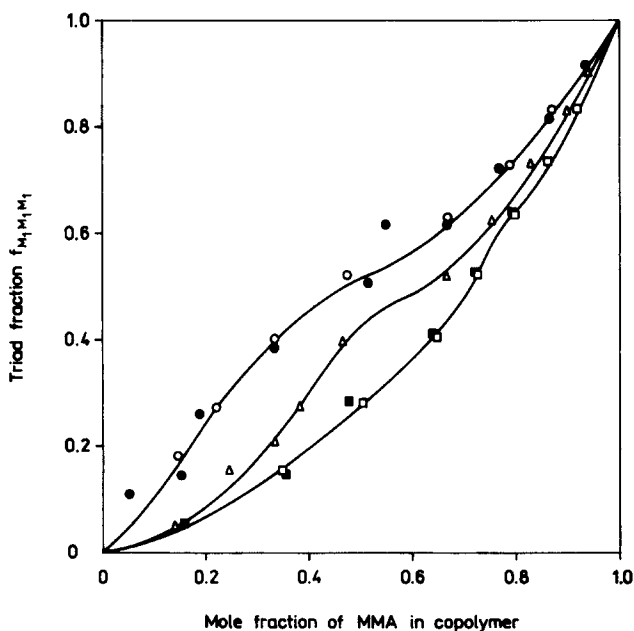
**Figure 6** Triad fractions  $f_{M_1 M_1 M_1}$  for the MMA–AAm free radical initiated copolymerization at 70°C under different conditions<sup>27</sup> ( $M_1$  corresponds to MMA) calculated from reactivity ratios obtained with the EVM method. (○) In dioxane, total monomer concentration 0.8 mol l<sup>-1</sup> of solvent, [AIBN] = 0.4 g l<sup>-1</sup> of solvent; (●) in dioxane, total monomer concentration 0.4 mol l<sup>-1</sup> of solvent, [AIBN] = 1 g l<sup>-1</sup> of solvent; (△) in dioxane/ethanol (7/3, v/v), total monomer concentration 0.4 mol l<sup>-1</sup> of solvent, [AIBN] = 1 g l<sup>-1</sup> of solvent; (□) in ethanol, total monomer concentration 0.8 mol l<sup>-1</sup> of solvent, [AIBN] = 0.4 g l<sup>-1</sup> of solvent; (■) in ethanol, total monomer concentration 0.4 mol l<sup>-1</sup> of solvent, [AIBN] = 1 g l<sup>-1</sup> of solvent

for the triad fractions evaluation applied. For example, *Figure 6* shows  $f_{M_1 M_1 M_1}$  for the MMA–AAm free radical initiated copolymerization system in different solvents. Thus, *Figures 2–6* suggest that the microstructure of MMA–AAm copolymers having the same composition depends on the solvent choice. It should be pointed out that for the same solvent (dioxane) particular triad fraction types calculated from the data of the mentioned authors agree very well. *Figure 7* shows  $f_{M_1 M_1 M_1}$  obtained for the thermal MMA–AAm radical copolymerization system in dioxane compared with the  $f_{M_1 M_1 M_1}$

calculated from the results for free radical initiated copolymerization of Saini *et al.*<sup>27</sup> and Orbay *et al.*<sup>28</sup>. As can be seen from the conditions of polymerization described in *Table 3* corresponding to those of *Figure 7*, the temperature and the high conversion



**Figure 7** Triad fractions  $f_{M_1 M_1 M_1}$  for the MMA-AAm copolymerization in dioxane under different conditions and by different authors ( $M_1$  corresponds to MMA). (○) At 70°C, total monomer concentration 0.8 mol l<sup>-1</sup> of solvent, [AIBN] = 0.4 g l<sup>-1</sup> of solvent<sup>27</sup>; (●) at 70°C, total monomer concentration 0.4 mol l<sup>-1</sup> of solvent, [AIBN] = 1 g l<sup>-1</sup> of solvent<sup>27</sup>; (△) at 75°C, total monomer concentration 1 mol l<sup>-1</sup> of reaction mixture, thermal in dioxane, our results; (▲) at 65°C, solvent/monomer ratio varying in the range 230–435 (in ml mol<sup>-1</sup>), [AIBN] = 0.261 mol%, yield (in %) from 34.4 to 75<sup>28</sup>



**Figure 8** Triad fractions  $f_{M_1 M_1 M_1}$  for the MMA-AAm free radical initiated copolymerization at 70°C under different conditions<sup>27</sup> ( $M_1$  corresponds to MMA) calculated from reactivity ratios obtained with the FR method. (○) In dioxane, total monomer concentration 0.8 mol l<sup>-1</sup> of solvent, [AIBN] = 0.4 g l<sup>-1</sup> of solvent; (●) in dioxane, total monomer concentration 0.4 mol l<sup>-1</sup> of solvent, [AIBN] = 1 g l<sup>-1</sup> of solvent; (△) in dioxane/ethanol mixture (7/3, v/v), total monomer concentration 0.4 mol l<sup>-1</sup> of solvent, [AIBN] = 1 g l<sup>-1</sup> of solvent; (□) in ethanol, total monomer concentration 0.8 mol l<sup>-1</sup> of solvent, [AIBN] = 0.4 g l<sup>-1</sup> of solvent; (■) in ethanol, total monomer concentration 0.4 mol l<sup>-1</sup> of solvent, [AIBN] = 1 g l<sup>-1</sup> of solvent

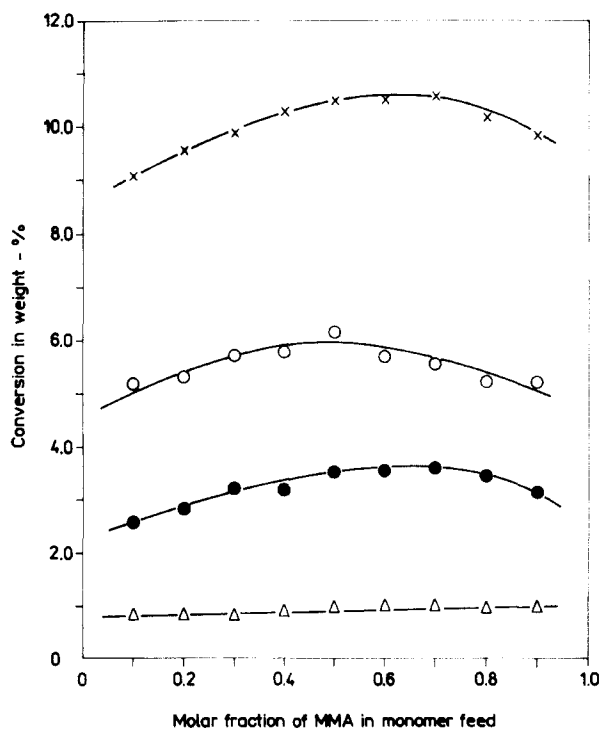
conditions used for copolymerization by Orbay *et al.*<sup>28</sup> seem not to have significant influence on the microstructure of MMA-AAm copolymers obtained. The reasons for the discrepancy between these data and examples for the 'bootstrap' effect given in the literature will be discussed.

One of them could be the selected model of copolymerization for evaluation of the propagation rates. We have chosen, as mentioned above, the most universally applicable terminal model for polymerization. All the models which could have been taken into consideration are discussed by Harwood<sup>30</sup>. For the MMA-AAm radical copolymerization system in dioxane one of the models considering complexed monomers should be of interest as the strong hydrogen bonding ability of dioxane to amide group of AAm<sup>16</sup> effects its association in solution<sup>29</sup> and disturbs the keto/enol equilibrium of acrylamide<sup>27</sup>, which in consequence changes the vinyl bond activity in the copolymerization reaction.

Additionally, introduction of the penultimate instead of the terminal model of copolymerization as well the selection of the calculation method for the penultimate model could also have some influence on the  $f$  parameters. Figure 8 shows the triad fractions calculated on the basis of the reactivity ratios originally calculated by Saini *et al.*<sup>27</sup> using the FR method. Comparing Figures 8 and 6 the quantitative influence of the calculation method for reactivity ratios on the  $f$  parameters is evident.

Finally, the system of monomers containing AAm, discussed by Harwood<sup>30</sup>, viz. St with AAm consists of polar and non-polar monomers.

As we have shown above, MMA-AAm copolymers prepared in the same solvent (dioxane) have the same microstructure (Figure 7), but the reactivity ratios of MMA and AAm initiated thermally in dioxane and in dioxane with use of free radical initiator (Tables 2 and 3) are quite different. The  $r$ -parameter data for thermal copolymerization of the MMA-AAm system in dioxane or in any other solvent could not be found in the literature. The absence of conventional free radical initiator leads to smaller  $r_1$  values. It is the more interesting as the thermal polymerization of MMA is well pronounced in dioxane<sup>19</sup> whereas the thermal polymerization of AAm in dioxane does not proceed<sup>6</sup>. The corresponding conditions of reactions in dioxane differ in the total monomer concentration, conversions to polymer obtained, the amount of the free radical initiator and the temperature of the reaction. All of these parameters (except for the amount of free radical initiator) have an influence on the internal structure of the reaction medium. Lately, we have found thermodynamic evidence for the dependence of the internal structure of the reaction medium on the monomer concentration<sup>34</sup>. In the very early stages of copolymerization an equilibrium may be established in which monomers are distributed between free solvent and the domains of growing polymer radicals<sup>30</sup>. The partition coefficient that characterizes the distribution of monomers between free solvent and the domains of growing polymer radicals might be quite complex<sup>30</sup> and, in our opinion, can be influenced by the internal structure of the reaction medium. Hence, it can be said that the differences in reactivity ratios reflect, to some extent, different internal structures of the reaction medium.



**Figure 9** Conversion of copolymerization of MMA and AAm versus mole fraction of MMA in monomer feed at 75°C. reaction time 4h, thermal in dioxane and in the presence of different concentrations of cyclohexanone (Chn): [Chn] 0 mol l<sup>-1</sup>; no copolymer: (●) [Chn] = 0.44 mol l<sup>-1</sup>; (○) [Chn] = 0.61 mol l<sup>-1</sup>; (×) [Chn] = 0.79 mol l<sup>-1</sup>; (Δ) thermal in dioxane

The copolymerization of the monomers carried out in cyclohexanone/benzene (1/1.16, v/v) mixture in the absence of any conventional radical initiator gives the highest  $r_2$  ratio for all systems investigated. The reason for so high an  $r_2$  value can be that, in solvents like benzene, monomeric AAm is believed to form extensive plurimolecular aggregates through which propagation may proceed rapidly to give AAm blocks<sup>35</sup>. Despite the above discussion on the discrepancy between our data and the theory of the 'bootstrap' effect, it is interesting to point out that the  $f_{M_2M_2M_2}$  values corresponding to the AAm triad fractions in the copolymer obtained in cyclohexanone/benzene are simultaneously the highest for all the systems and, moreover, the effect is stronger for a high AAm mole fraction in monomer feed. On the other hand, as dioxane has a very strong hydrogen bonding capability to the amide group of AAm<sup>16</sup>, and cyclohexanone is a strong polar solvent<sup>17</sup>, fewer AAm blocks in the copolymer are observed (Figures 1 and 5).

Other effects related to the cyclohexanone/monomer ratio, which can affect at least the quantitative picture of the solvent effects, should be also taken into account. As has already been shown, the concentration of cyclohexanone in the reaction medium has influenced the calculated reactivity ratios as well as the monomer sequence distributions in the monomer system. The rate of copolymerization increases when benzene is replaced by cyclohexanone, as illustrated in Figure 9. It is evident from the data in Figure 9 that only the presence of cyclohexanone (except the residual thermal copolymerization always present in the monomer systems containing MMA) initiates the copolymerization reaction. Moreover,

each concentration of cyclohexanone in the copolymerization system corresponds to an optimal molar fraction of MMA (in the range 0.5–0.8) in the monomer feed, giving a maximum monomer conversion.

This proof indicates that the initiating ability of cyclohexanone in the copolymerization reaction is connected not only to the concentration of cyclohexanone, but also to the ratio of cyclohexanone to the monomer concentration. It follows from the data in Figure 9 that a higher conversion is achieved when the molar ratios of both the monomers in the monomer feed composition approach equal levels, with the simultaneous presence of a higher concentration of cyclohexanone in the reaction mixture.

## REFERENCES

- 1 Kubushiro, K., Takemoto, K. and Imoto, M. *Makromol. Chem.* 1968, **120**, 39
- 2 Sato, T., Metsugi, M. and Otsu, T. *Makromol. Chem.* 1979, **180**, 1175
- 3 Imoto, M., Maeda, T. and Ouchi, T. *Chem. Lett.* 1978, 153
- 4 Imoto, M., Maeda, T. and Ouchi, T. *J. Polym. Sci., Polym. Chem. Edn* 1979, **17**, 385
- 5 Ouchi, T., Murayama, N. and Imoto, M. *Bull. Chem. Soc. Jpn* 1980, **53**, 748
- 6 Kaim, A. *J. Polym. Sci., Lett. Edn* 1984, **22**, 203
- 7 Kaim, A. *J. Polym. Sci., Polym. Chem. Edn* 1984, **22**, 189
- 8 Kaim, A. *J. Polym. Mater.* 1986, **3**, 73
- 9 Stickler, M. and Meyerhoff, G. *Makromol. Chem.* 1980, **181**, 1311
- 10 Lingnau, J. and Meyerhoff, G. *Polymer* 1983, **24**, 1473
- 11 Lehrle, Roy, S. and Shortland, A. *Eur. Polym. J.* 1988, **24**, 425
- 12 Kaim, A. and Kołodziejki, W. *Polym. Commun.* 1984, **25**, 308
- 13 Kaim, A., Kaminski, J. and Kołodziejki, W. *Acta Chim. Hung.* 1988, **125**, 141
- 14 Kaim, A. and Talpur, M. M. A. *J. Polym. Mater.* 1993, **10**, 95
- 15 Talpur, M. M. A. and Kaim, A. *J. Macromol. Sci.-Chem.* 1994, **A31**, 535
- 16 Minsk, L. M., Kotlarchick, C. and Darlak, R. S. *J. Polym. Sci., Polym. Chem. Edn* 1973, **11**, 355
- 17 Riddick, J. A., Bunger, W. B. and Sakano, T. K. 'Techniques of Chemistry', vol. 2, 'Organic Solvents', 4th Edn. Wiley-Interscience, New York, 1986
- 18 Imoto, M., Oishi, M. and Ouchi, T. *Makromol. Chem.* 1975, **176**, 3287
- 19 Kaim, A. *J. Polym. Mater.* 1992, **9**, 71
- 20 Finemann, M. and Ross, S. D. *J. Polym. Sci.* 1947, **5**, 259
- 21 Yezerielev, A. I., Brokhina, A. and Roskin, Y. S. *Vysokomol. Soedin.* 1969, **A11**, 1670
- 22 Kelen, T. and Tüdös, F. *J. Macromol. Sci.-Chem.* 1975, **A9**, 1
- 23 Dube, M., Amin Sanayei, R., Penlidis, A., O'Driscoll, K. F. and Reilly, P. M. *J. Polym. Sci., Part A: Polym. Chem.* 1991, **29**, 703
- 24 Greenly, R. Z. *J. Macromol. Sci.-Chem.* 1980, **A14**, 445
- 25 Leicht, R. and Fuhrmann, J. *J. Polym. Sci., Polym. Chem. Edn* 1983, **21**, 2215
- 26 Joshi, R. M. *J. Macromol. Sci.-Chem.* 1973, **A7**, 1231
- 27 Saini, G., Leoni, A. and Franco, S. *Makromol. Chem.* 1971, **144**, 235
- 28 Orbay, M., Laible, R. and Dulog, L. *Makromol. Chem.* 1982, **183**, 47
- 29 Jacob, M., Smets, G. and Deschryver, F. *J. Polym. Sci.* 1972, **B10**, 669
- 30 Harwood, H. J. *Makromol. Chem. Makromol. Symp.* 1987, **10/11**, 331
- 31 Mayo, F. R. and Lewis, F. M. *J. Am. Chem. Soc.* 1944, **66**, 1594
- 32 Alfrey, T. and Goldfinger, F. *J. Chem. Phys.* 1944, **12**, 205, 244, 322
- 33 Harwood, H. J. in 'Data Processing in Chemistry' (Ed. Z. Hippe), Elsevier, New York, 1981, pp. 133–148
- 34 Wilczura, H., Talpur, M. M. A., Kaim, A. and Kasprzycka-Guttman, T. *J. Chem. Eng. Data*, 1995, **40(6)**, 1233
- 35 Chapiro, A. and Perek-Spritzer, L. *Eur. Polym. J.* 1975, **11**, 59