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### Solvent Effect on 3-Methylstyrene Radical Copolymerization with Methacrylic Acid and Methyl Methacrylate

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## **SOLVENT EFFECT ON 3-METHYLSTYRENE RADICAL COPOLYMERIZATION WITH METHACRYLIC ACID AND METHYL METHACRYLATE**

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### **ABSTRACT**

Radical copolymerization of 3-methylstyrene with methacrylic acid and methyl methacrylate in toluene, acetone, and isopropyl alcohol is studied. The calculated copolymerization reactivity ratios are smaller than unity. The established, well-defined alternating tendency in this case can be reasonably explained by the polar effect of comonomer-solvent H-bond formation on comonomer reactivity. The significant effect of methacrylic acid dimerization in toluene (again by H-bond formation) and dimer participation in chain propagation on the copolymerization of this monomer with 3-methylstyrene and methyl methacrylate is also shown.

## INTRODUCTION

Although the copolymers of 3-methylstyrene (3MS) with methacrylic acid (MA) and methyl methacrylate (MMA) find application in the production of paints and varnishes [1, 2], there is no information about the radical copolymerization characteristics of these monomers and the solvent effect on the copolymer composition. The situation with the 3MS isomer—4-methylstyrene (4MS)—is more favorable since its radical copolymerization with MMA in benzene ( $r_{4MS} = 0.44$ ,  $r_{MMA} = 0.34$ ) [3] and in water suspension [4] is studied. For this reason the radical copolymerizations of 3MS with MA or MMA in toluene (T), isopropyl alcohol (IPA), and acetone (A) are studied in this work. The solvents set chosen offers a variety of polarities, proton donor, and proton acceptor abilities. Thus the influence of these factors on the 3MS, MA, and MMA reactivities in radical copolymerization can be followed. The effect of the specific dimerization of MA in T as well as of the H-bond formation between MA, MMA, and IPA on copolymer composition is also investigated. Deviations of the experimental comonomer reactivities from their mean values as calculated by the ideal reactivity theory [5] by several methods in different solvents for the 3MS-MA, 3MS-MMA, and MA-MMA copolymerizations are reasonably explained as well.

## EXPERIMENTAL

### Materials

3MS, MMA (Fluka), and MA (Janssen) as well as the solvents used were purified by additional vacuum distillation. Azobisisobutyronitrile (1.0% based on the total weight of comonomers) was used as initiator.

### Copolymerization

Copolymerization was carried out in a three-necked flask at a temperature of 70°C with efficient stirring under argon. The conversion was smaller than 10% by weight. The 3MS-MA copolymers obtained were separated by precipitation in *n*-hexane or diethyl ether, 3MS-MMA copolymers were precipitated in *n*-hexane or ethyl alcohol, while diethyl ether was used for the MA-MMA copolymers. Purification was carried out by dissolution of the 3MS-MA copolymers in ethyl alcohol and of the other copolymers in acetone with a further precipitation in the above-mentioned precipitants. The purified copolymers were dried under vacuum at a temperature of 50°C.

The copolymer composition was determined by elementary C, H analysis of the 3MS-MMA copolymers and by titration of the MA-3MS and MA-MMA copolymer solutions with 0.1 M sodium hydroxide. The values of the copolymerization constants were calculated by the Kelen-Tüdös (KT) [6], modified Kelen-Tüdös (MKT) [7], Joshi-Joshi (JJ) [8], Ezrielev-Brochina-Roskin (EBR) [9], and Tidwell-Mortimer (TM) [10] methods. MKT accounts for copolymerization conversion by determination of the copolymerization reactivity ratios.

### Spectroscopic Analysis

$^{13}\text{C}$ -NMR spectra were recorded at 75.47 MHz (Bruker AC 300 spectrometer) using a sample concentration of 10% (w/v) in  $\text{DMSO}-d_6$  for a 3MS-MA copolymer and in  $\text{CD}_3\text{Cl}$  for a 3MS-MMA copolymer at 25 and 21°C, respectively. Typical  $^{13}\text{C}$ -NMR spectra are displayed in Figs. 1 and 6.

IR spectra were recorded on a Perkin-Elmer 983 G spectrometer at 22°C in a condensed state. UV spectra were recorded on a Specord UV-VIS (Carl Zeiss Jena) using spectroscopic grade purity solvents.

## RESULTS AND DISCUSSION

### 3MS-MA Copolymerization

The  $^{13}\text{C}$ -NMR spectrum of the copolymer produced a monomer feed composition of  $M_{\text{MA}} = 0.50$  is shown in Fig. 1. Its lines were compared in part with those of poly(3-methylstyrene) as identified by Evans et al. [11] and another part with the MA-MMA copolymer  $^{13}\text{C}$ -NMR spectrum identified by Johnsen et al. [12].

The dependence of the 3MS mole fraction ( $m_{3\text{MS}}$ ) in the 3MS-MA copolymers synthesized in T, IPA, and A on the 3MS mole fraction in the monomer feed ( $M_{3\text{MS}}$ ) is presented in Table 1. These results are linearized in the Kelen-Tüdös coordinates (Fig. 2).

$$\eta = \left( r_{3\text{MS}} + \frac{r_{\text{MA}}}{\alpha} \right) \xi - \frac{r_{\text{MA}}}{\alpha} \quad (1)$$

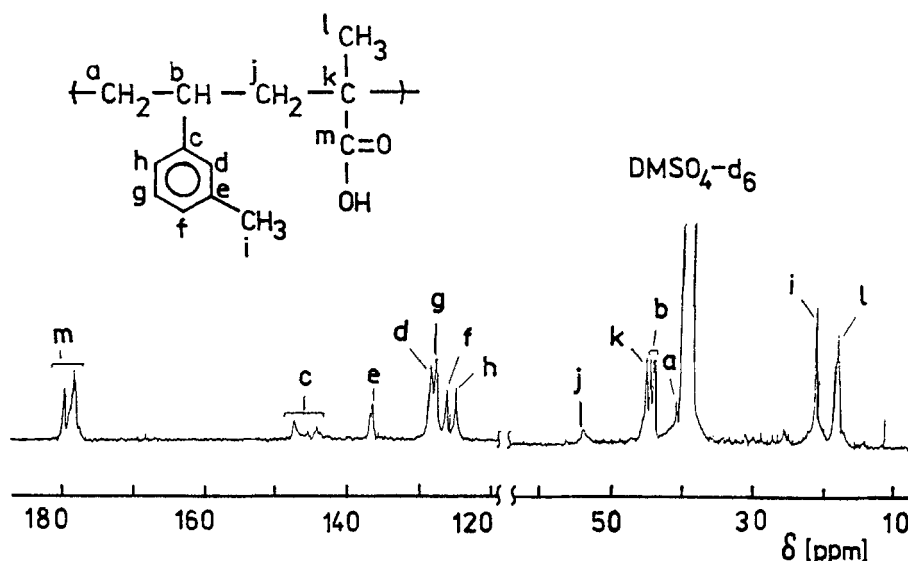


FIG. 1. 75.47-MHz  $^{13}\text{C}$ -NMR spectrum of 3MS-MA copolymer in  $\text{DMSO}-d_6$  at 25°C.

TABLE 1. Copolymerization Conversion and Composition of the 3MS-MA Copolymers ( $m_{3MS}$ ) Obtained in T, IPA, and A Depending on the Monomer Feed ( $M_{3MS}$ ). Temperature, 70°C; 1% (w/w) AIBN

No.	Solvent	$M_{3MS}$	$m_{3MS}$	Conversion, %
1	T	0.20	0.32	9.5
2	T	0.30	0.38	8.8
3	T	0.40	0.40	9.2
4	T	0.50	0.43	10.1
5	T	0.60	0.44	9.3
6	T	0.70	0.47	8.7
7	T	0.80	0.48	8.9
8	T	0.90	0.72	9.1
9	IPA	0.10	0.28	8.3
10	IPA	0.20	0.37	8.4
11	IPA	0.30	0.46	9.2
12	IPA	0.40	0.50	8.9
13	IPA	0.50	0.53	8.5
14	IPA	0.80	0.70	9.3
15	IPA	0.90	0.78	9.3
16	A	0.20	0.27	9.8
17	A	0.30	0.35	9.2
18	A	0.40	0.42	9.7
19	A	0.50	0.49	8.5
20	A	0.60	0.54	8.9
21	A	0.80	0.71	9.1
22	A	0.90	0.82	9.0

where

$$\eta = \frac{x(y-1)}{\alpha y + x^2}, \quad \xi = \frac{x^2}{\alpha y + x^2}, \quad x = \frac{M_{3MS}}{M_{MA}}, \quad y = \frac{m_{3MS}}{m_{MA}}$$

The  $r_{3MS}$  and  $r_{MA}$  values thus calculated are in agreement with those determined by the MKT, EBR, JJ, and TM methods (Table 2). They are used for the calculation of the  $m_{3MS}$  dependences on  $M_{3MS}$  which are compared in Fig. 3 with the experimental ones.

As it is seen from the data presented in Table 2 and Fig. 2, the calculated  $r_{3MS}$  and  $r_{MA}$  values are considerably smaller than unity. This can be attributed to the significant difference in the polarities of both comonomers ( $e_{3MS} = -0.03$  [13] and  $e_{MA} = 0.62$  [14]). This difference is favorable for a donor-acceptor interaction between the two comonomers and between the propagating chain ends  $\sim 3MS\cdot$  and  $\sim MA\cdot$  with MA and 3MS, respectively. The formation of the comonomer complex is possible in the first case, while in the second one the rise of the cross-propagation

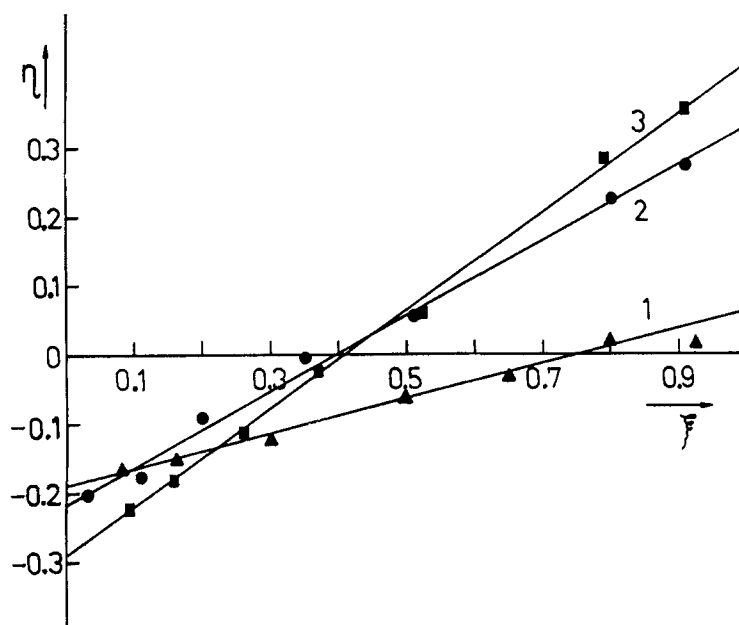


FIG. 2. Kelen-Tüdös plots of the 3MS-MA radical copolymerization in T (1), IPA (2), and A (3). Temperature: 70°C.  $\alpha = 1.524$  (1),  $\alpha = 0.842$  (2), and  $\alpha = 1.738$  (3).

rate constants  $k_{MA,3MS}$  and  $k_{3MS,MA}$  is an expected result. The participation of the comonomer complex in the propagation reaction and the increase of  $k_{MA,3MS}$  and  $k_{3MS,MA}$  lead to the same result—a decrease of the copolymerization constants values. Attempts to identify the comonomer donor-acceptor complexes by IR (Fig. 4) and UV (Fig. 5) spectroscopy did not confirm their formation. The observed shift of the band assigned to the C=C group (about  $1640\text{ cm}^{-1}$ ) of the IR spectrum of the monomers (Fig. 4a and Fig. 4c) and their mixture (Fig. 4b) is about  $2\text{ cm}^{-1}$ . It is rather insufficient to support the formation of such complexes. The same conclusion follows from the 1.5-nm shift of the UV maximum (around 253 nm) in passing from the MA UV spectrum (Fig. 5a) to the MA-3MS UV spectrum (Fig. 5b). Thus, the increase of  $k_{MA,3MS}$  and  $k_{3MS,MA}$  seems to be a more acceptable explanation for the alternating tendency when only spectroscopic results are considered.

The mean values of the reactivity ratios presented in Table 2 are  $r_{3MS,av} = 0.28$ ,  $r_{MA,av} = 0.33$ . These values are higher or equal to some of the experimental values when copolymerization is carried out in T or IPA but smaller than the respective experimental values when A is used as a solvent. The established solvent effect can be attributed to the influence of H-complex formation on the comonomer  $\pi$ -electron polarization and reactivity. It contributes additionally to the alternating tendency discussed above.

In the case of copolymerization in T, the formation of H-complex is possible only between two MA molecules (MA dimerization) [15] due to the low solvent polarity and the lack of proton donor and proton acceptor ability. Two H-bonds are formed between the carbonyl and hydroxyl groups of two MA molecules.

TABLE 2. Copolymerization Reactivity Ratios ( $r_{3MS}$ ,  $r_{MMA}$ ) of 3MS-MA Copolymerization in T, IPA, and A, Calculated by Kelen-Tüdös (KT), modified Kelen-Tüdös (MKT), Ezrielev-Brochina-Roskin (EBR), Joshi-Joshi (JJ), and Tidwell-Mortimer (TM) Methods. Temperature, 70°C; Initiator, AIBN (1% w/w)

Solvent	KT		MKT		EBR		JJ		TM	
	$r_{3MS}$	$r_{MA}$	$r_{3MS}$	$r_{MA}$	$r_{3MS}$	$r_{MA}$	$r_{3MS}$	$r_{MA}$	$r_{3MS}$	$r_{MA}$
T	0.06 ± 0.03	0.35 ± 0.08	0.05 ± 0.08	0.34 ± 0.19	0.09 ± 0.04	0.33 ± 0.08	0.03 ± 0.04	0.32 ± 0.05	0.08	0.36
IPA	0.33 ± 0.02	0.18 ± 0.02	0.31 ± 0.06	0.16 ± 0.04	0.31 ± 0.02	0.18 ± 0.08	0.33 ± 0.02	0.17 ± 0.02	0.31	0.16
A	0.42 ± 0.01	0.51 ± 0.01	0.41 ± 0.03	0.49 ± 0.04	0.42 ± 0.01	0.51 ± 0.01	0.42 ± 0.01	0.51 ± 0.01	0.40	0.49



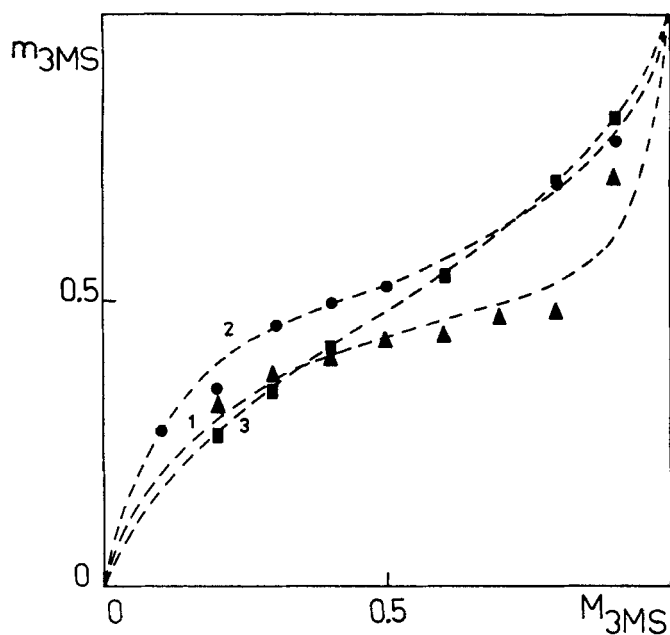


FIG. 3. Dependence of the mole fraction of 3MS ( $m_{3MS}$ ) in the 3MS-MA copolymers obtained in T (1), IPA (2), and A (3) on the mole fraction of 3MS in the monomer feed ( $M_{3MS}$ ). ( $\blacktriangle$ ,  $\bullet$ ,  $\blacksquare$ ) Experimental data, (---) calculated by the terminal model curves using the following copolymerization constant values:  $r_{3MS} = 0.06$ ,  $r_{MA} = 0.35$ , copolymerization in T;  $r_{3MS} = 0.33$ ,  $r_{MA} = 0.18$ , copolymerization in IPA;  $r_{3MS} = 0.42$ ,  $r_{MA} = 0.51$ , copolymerization in A.

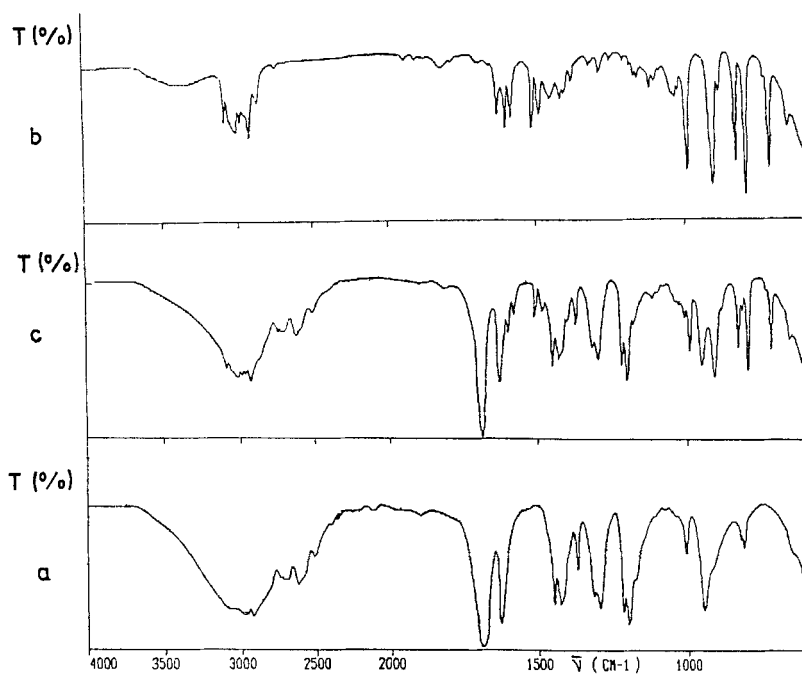


FIG. 4. IR spectra of MA (a), 3MS (b), and their equimolar mixture (c) in the condensed state in the  $3500\text{--}850\text{ cm}^{-1}$  region at  $22^\circ\text{C}$ .

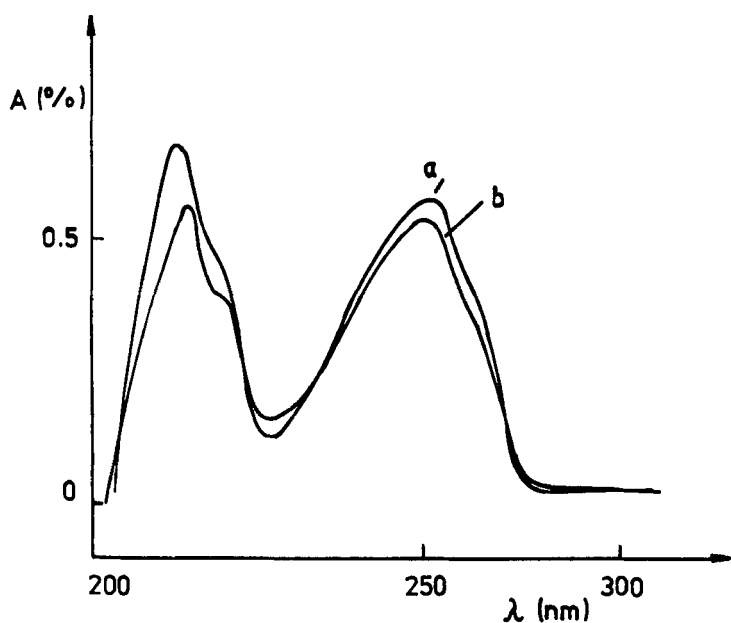


FIG. 5. UV spectra of  $4 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  3MS in IPA (a) and  $4 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  equimolar 3MS-MA mixture in IPA (b) at 22°C.

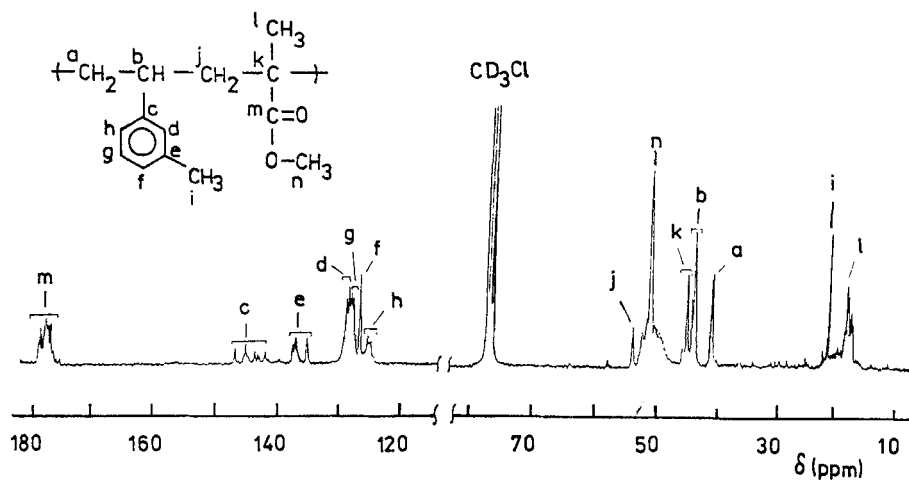
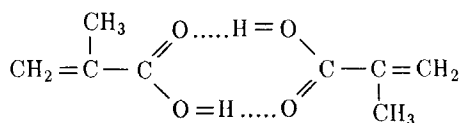


FIG. 6. 75.47-MHz  $^{13}\text{C}$ -NMR spectrum of 3MS-MMA copolymer in  $\text{CD}_3\text{Cl}$  at 21°C.

TABLE 3. Copolymerization Conversion and 3MS-MMA Copolymer Composition ( $m_{3MS}$ ) as Dependent on the Monomer Feed ( $M_{3MS}$ ). Temperature, 70°C; AIBN (1% w/w)

No.	Solvent	$M_{3MS}$	$m_{3MS}$	Conversion, %
1	T	0.10	0.32	8.5
2	T	0.20	0.38	7.7
3	T	0.30	0.40	9.2
4	T	0.50	0.43	9.8
5	T	0.80	0.44	8.6
6	T	0.90	0.47	9.1
7	IPA	0.10	0.19	9.5
8	IPA	0.20	0.33	8.7
9	IPA	0.30	0.38	8.6
10	IPA	0.40	0.47	7.3
11	IPA	0.50	0.51	9.2
12	IPA	0.60	0.56	9.1
13	IPA	0.80	0.66	8.9
14	A	0.10	0.18	8.4
15	A	0.20	0.29	8.9
16	A	0.30	0.39	7.9
17	A	0.40	0.46	9.2
18	A	0.70	0.65	7.8
19	A	0.80	0.72	8.1
20	A	0.90	0.84	8.4



$(MA)_2$

As a result of hydroxyl group participation in MA dimerization, the  $\pi$ -electron density of the monomer molecule increases. Carbonyl group participation in the same H-bond formation leads to a  $\pi$ -electron density decrease. Thus the two H-bonds in the MA dimer  $(MA)_2$  have an opposite influence on the MA electron acceptor ability with respect to 3MS. The fact that the experimentally determined  $r_{3MS}$  and  $r_{MA}$  values are smaller or equal to the average one proves the predominant electron acceptor effect of the H-bond at the MA carbonyl group in this case.

The MA dimerization in T has another influence on MA reactivity. The addition of the first dimer component to the propagating chain end offers an entropy profit at the addition of the second dimer component to the same end, as compared to the addition of the other monomer molecules. Thus the established unequation  $r_{MA} > r_{3MS}$  can be explained for the case of copolymerization carried out in T. In

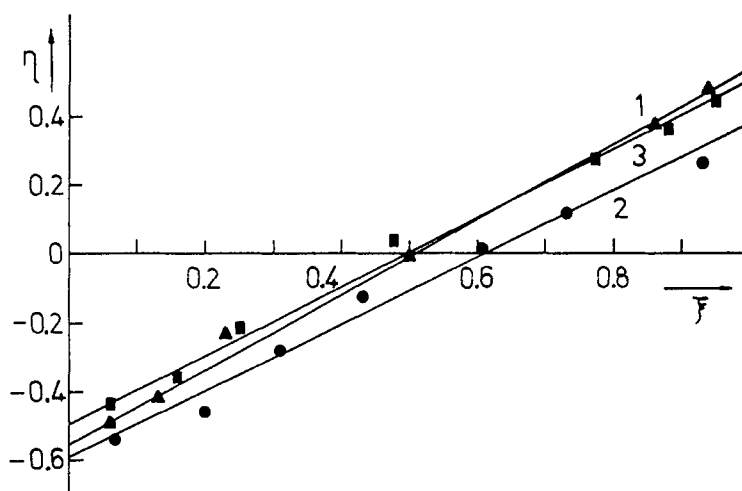


FIG. 7. Kelen-Tüdös plots of radical 3MS-MMA copolymerization in T (1), IPA (2), and A (3). Temperature: 70°C.  $\alpha = 0.986$  (1),  $\alpha = 0.654$  (2), and  $\alpha = 0.849$  (3).

the other solvents used,  $r_{MA} \leq r_{3MS}$ , i.e., in these more polar proton acceptor solvents (A, IPA), dimerizations are not probable.

In IPA each MA molecule forms two H-bonds with the solvent molecules. The above-mentioned predominant effect on the H-bond between the MA carbonyl group and IPA is a reason for the increase of the MA electron acceptor ability with respect to 3MS. For this reason, the  $r_{MA}$  and  $r_{3MS}$  values of IPA are smaller or equal to the average one.

There is no possibility of H-bond formation with the participation of the MA carbonyl group as well as of MA dimerization in A. H-bond formation is possible only between the MA hydroxyl group and the carbonyl group of A. However, as mentioned above, the formation of this type of H-bond leads to a decrease of MA electron acceptor ability with respect to 3MS. Thus the experimental  $r_{MA}$  and  $r_{3MS}$  values should be larger or equal to the mean values. This expectation is confirmed by the data included in Table 2 and Fig. 2.

It is interesting to study the influence of the solvents used on the 3MS-MMA copolymerization since MMA is a comonomer differing from MA in that it does not dimerize and it forms H-bond with its carbonyl group only.

### 3MS-MMA Copolymerization

The  $^{13}\text{C}$ -NMR spectrum of the copolymer obtained at a monomer feed composition of  $M_{MMA} = 0.50$  is shown in Fig. 6. As in the previous section, some of its lines coincide with those of poly(3-methylstyrene) [11] and others with a part of the MMA-MA copolymer  $^{13}\text{C}$ -NMR spectrum [12]. In contrast to the earlier case (Fig. 1), the  $\text{OCH}_3$  resonance at around 51 ppm appears in this spectrum (n band in Fig. 6). This fact as well as the discussed coincidence prove the 3MS-MMA copolymer structure.

TABLE 4. Copolymerization Reactivity Ratios ( $r_{3MS}$ ,  $r_{MMA}$ ) of 3MS-MMA Copolymerization in T, IPA, and A, Temperature, 70°C; Initiator, AIBN (1% w/w)

Solvent	KT		MKT		EBR		JJ		TM	
	$r_{3MS}$	$r_{MMA}$	$r_{3MS}$	$r_{MMA}$	$r_{3MS}$	$r_{MMA}$	$r_{3MS}$	$r_{MMA}$	$r_{3MS}$	$r_{MMA}$
T	$0.53 \pm 0.04$	$0.48 \pm 0.04$	$0.52 \pm 0.11$	$0.49 \pm 0.09$	$0.54 \pm 0.04$	$0.50 \pm 0.04$	$0.52 \pm 0.04$	$0.47 \pm 0.03$	$0.51$	$0.44$
IPA	$0.36 \pm 0.06$	$0.38 \pm 0.03$	$0.32 \pm 0.11$	$0.32 \pm 0.07$	$0.32 \pm 0.04$	$0.38 \pm 0.03$	$0.36 \pm 0.05$	$0.36 \pm 0.04$	$0.32$	$0.35$
A	$0.51 \pm 0.05$	$0.41 \pm 0.04$	$0.45 \pm 0.11$	$0.42 \pm 0.11$	$0.50 \pm 0.03$	$0.42 \pm 0.03$	$0.51 \pm 0.05$	$0.39 \pm 0.05$	$0.51$	$0.39$

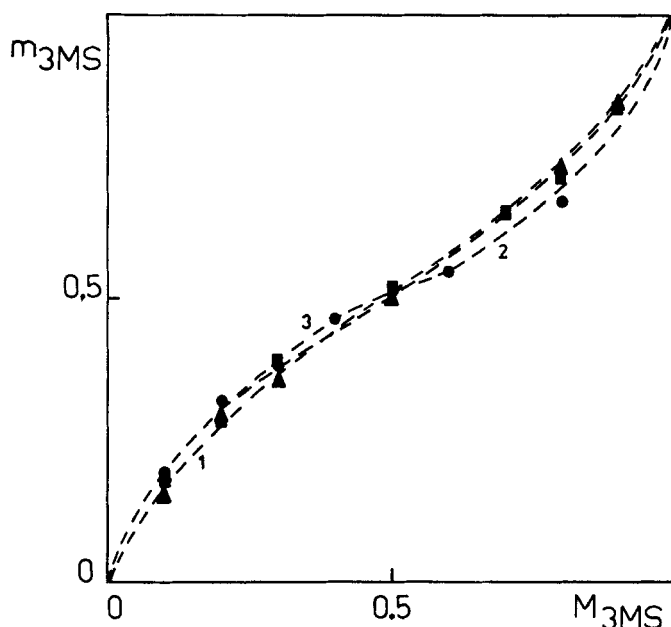


FIG. 8. Dependence of 3MS mole fraction ( $m_{3MS}$ ) in 3MS-MMA copolymers obtained in T (1), IPA (2), and A (3) on the 3MS mole fraction in the monomer feed ( $M_{3MS}$ ). ( $\Delta$ ,  $\bullet$ ,  $\blacksquare$ ) Experimental data, (---) calculated by the terminal model curves using the following copolymerization constant values:  $r_{3MS} = 0.53$ ,  $r_{MMA} = 0.48$ , solvent is T;  $r_{3MS} = 0.36$ ,  $r_{MMA} = 0.38$ , solvent is IPA;  $r_{3MS} = 0.51$ ,  $r_{MMA} = 0.41$ , solvent is A.

$m_{3MS}$  dependences of the 3MS-MMA copolymers obtained in T, IPA, and A on  $M_{3MS}$  are shown in Table 3. These results are linearized again in Kelen-Tüdös coordinates (1) where  $x = M_{3MS}/M_{MMA}$  and  $y = m_{3MS}/m_{MMA}$  (Fig. 7). The values calculated by all five methods are included in Table 4. Again, a good coincidence is observed and the values are used for the calculation of  $m_{3MS}$  as dependent on  $M_{3MS}$ . These calculated curves are compared to the experimental ones in Fig. 8.

The calculated  $r_{3MS}$  and  $r_{MMA}$  values are again smaller than unity (Fig. 7, Table 4). The reason is the same as in the case of 3MS-MA copolymerization—there is a considerable polarity difference between the two comonomers ( $e_{3MS} = -0.03$  [13] and  $e_{MMA} = 0.40$  [14]). Although not as large a difference as for the 3MS-MA comonomer pair, this difference is sufficient to make the alternating tendency strong in this case also.

The mean values of the reactivity ratios presented in Table 4 are  $r_{3MS,av} = 0.43$  and  $r_{MMA,av} = 0.41$ . These values are quite close to the experimental ones when copolymerization is carried out in T and A and considerably larger in IPA. It is clear that the restricted possibilities of H-bond formation between the comonomers and solvents in the discussed copolymerization mixture decrease the solvent effect on comonomer reactivity. The formation of only one H-complex between IPA and the carbonyl group of the MMA molecule is possible in this case. It was already shown that the formation of this type of H-bond increases the electron acceptor ability of the MMA molecules with respect to the 3MS one. For this reason the

TABLE 5. Copolymerization Conversion and Composition of the MA-MMA Copolymers ( $m_{MA}$ ) Obtained in T, IPA, and A as Dependent on the Monomer Feed Composition ( $M_{MA}$ ). Temperature, 70°C; Initiator, AIBN (1% w/w)

No.	Solvent	$M_{3MS}$	$m_{3MS}$	Conversion, %
1	T	0.10	0.36	9.9
2	T	0.20	0.49	9.2
3	T	0.30	0.53	8.5
4	T	0.40	0.61	9.1
5	T	0.60	0.71	9.4
6	T	0.70	0.77	8.1
7	T	0.80	0.84	8.6
8	T	0.90	0.91	9.0
9	IPA	0.10	0.12	8.9
10	IPA	0.20	0.21	8.5
11	IPA	0.40	0.34	8.8
12	IPA	0.60	0.49	9.2
13	IPA	0.70	0.58	9.3
14	IPA	0.80	0.66	9.3
15	IPA	0.90	0.79	8.8
16	A	0.10	0.21	7.2
17	A	0.20	0.34	8.1
18	A	0.40	0.50	8.3
19	A	0.70	0.69	8.3
20	A	0.80	0.77	9.2
21	A	0.90	0.86	8.6

experimentally established alternating tendency in IPA as a solvent is stronger than those estimated by mean values of the reactivity ratios as well as those for the copolymers obtained in T and A where H-bond formation between the solvents and comonomers is not possible.

The above results suggest that for these two copolymerizations the effect of the comonomer-solvent interaction on comonomer reactivity is of a second order of magnitude as compared to the effect of the initial comonomer polarity differences. Thus a study of the influence of solvents on MA-MMA copolymerization is of special interest because the comonomer  $\pi$ -electron polarities are close in this case ( $e_{MA} = 0.62$ ;  $e_{MMA} = 0.40$  [14]) but the two comonomers have quite different abilities for H-bond formation with the solvents.

### MA-MMA Copolymerization

The dependences of the MA mole fraction in the copolymers ( $m_{MA}$ ) obtained in T, IPA, and A on the MA mole fraction in the monomer feed ( $M_{MA}$ ) are given in Table 5. These results are linearized in Kelen-Tüdös coordinates (1) in Fig. 9 where

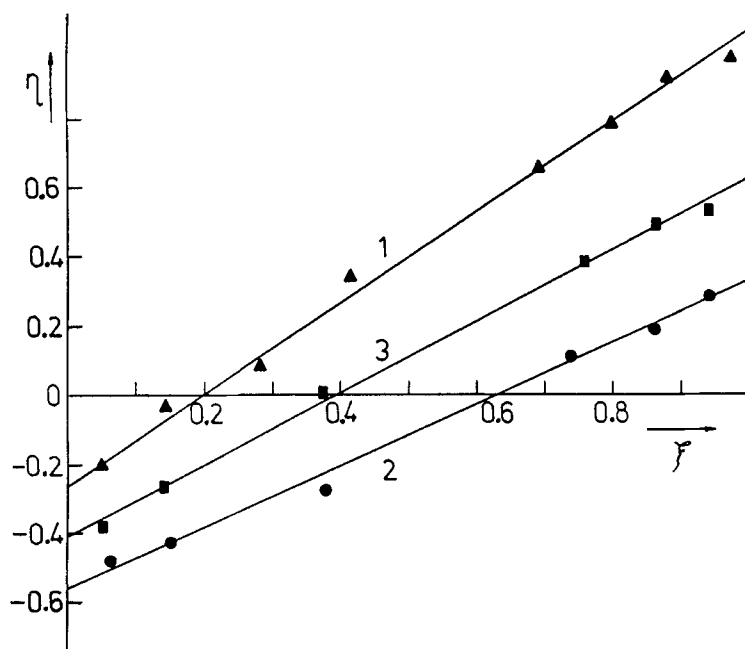


FIG. 9. Kelen-Tüdös plots of radical MA-MMA copolymerization in T (1), IPA (2), and A (3). Temperature: 70°C.  $\alpha = 0.410$  (1),  $\alpha = 1.376$  (2), and  $\alpha = 0.770$  (3).

$x = M_{\text{MA}}/M_{\text{MMA}}$  and  $y = m_{\text{MA}}/m_{\text{MMA}}$ . The copolymerization constant values ( $r_{\text{MA}}$  and  $r_{\text{MMA}}$ ) calculated by this method and by the four other methods are presented in Table 6. The values calculated by the different methods coincide again. They are used for the calculation of the  $m_{\text{MA}}$  dependences on  $M_{\text{MA}}$ , which are compared with the experimental ones in Fig. 10.

It is seen (Fig. 9 and Table 6) that again almost all  $r_{\text{MA}}$  and  $r_{\text{MMA}}$  values are smaller than unity despite the identity of the  $\pi$ -electron systems of both comonomers. Since the  $r_{\text{MA}}$  value in T is an exception to this rule, the MA-MMA copolymerization in T will be discussed below.

At first it is useful to calculate the  $r_{\text{MA}}$  and  $r_{\text{MMA}}$  values by the  $Q$ - $e$  scheme ( $Q_{\text{MA}} = 0.98$ ,  $e_{\text{MA}} = 0.62$  [14],  $Q_{\text{MMA}} = 0.78$ ,  $e_{\text{MMA}} = 0.40$  [14]):  $r_{\text{MA}} = 1.10$  and  $r_{\text{MMA}} = 0.89$ . They are quite close to unity. For this reason the deviations of these values from the experimental ones for MA-MMA copolymerization in IPA and A (Fig. 9, Table 6) confirm the alternating tendency. The latter can also be related to the induced difference between the  $\pi$ -electron polarities of the two comonomers. This difference arises from the H-bond between the MA hydroxyl group and the two solvents. This H-bond is possible only in A while in IPA this H-bond is in addition to the H-bonds between the carbonyl groups of the two comonomers and IPA. The interesting result that  $r_{\text{MA}} < r_{\text{MMA}}$  in IPA while  $r_{\text{MA}} > r_{\text{MMA}}$  in A (Table 6, Fig. 9) can be explained by the fact that the comonomer carbonyl groups form H-bonds only in IPA.

In T as a copolymerization solvent, the probable consequence of H-bond formation in the reaction medium is MA dimerization [15]. As already noted in the



TABLE 6. Copolymerization Reactivity Ratios ( $r_{MA}$ ,  $r_{MMA}$ ) of MA-MMA Copolymerization in T, IPA, and A, Temperature, 70°C; Initiator, AIBN (1% w/w)

Solvent	KT		MKT		EBR		JJ		TM	
	$r_{MA}$	$r_{MMA}$	$r_{MA}$	$r_{MMA}$	$r_{MA}$	$r_{MMA}$	$r_{MA}$	$r_{MMA}$	$r_{MA}$	$r_{MMA}$
T	1.06 ± 0.02	0.10 ± 0.01	1.07 ± 0.06	0.08 ± 0.02	1.05 ± 0.02	0.10 ± 0.01	1.06 ± 0.02	0.09 ± 0.01	1.09 ± 0.09	
IPA	0.33 ± 0.02	0.78 ± 0.03	0.31 ± 0.05	0.77 ± 0.08	0.33 ± 0.02	0.76 ± 0.02	0.32 ± 0.03	0.78 ± 0.03	0.32 ± 0.81	
A	0.63 ± 0.02	0.32 ± 0.02	0.62 ± 0.05	0.30 ± 0.04	0.62 ± 0.02	0.32 ± 0.01	0.64 ± 0.02	0.31 ± 0.02	0.64 ± 0.30	

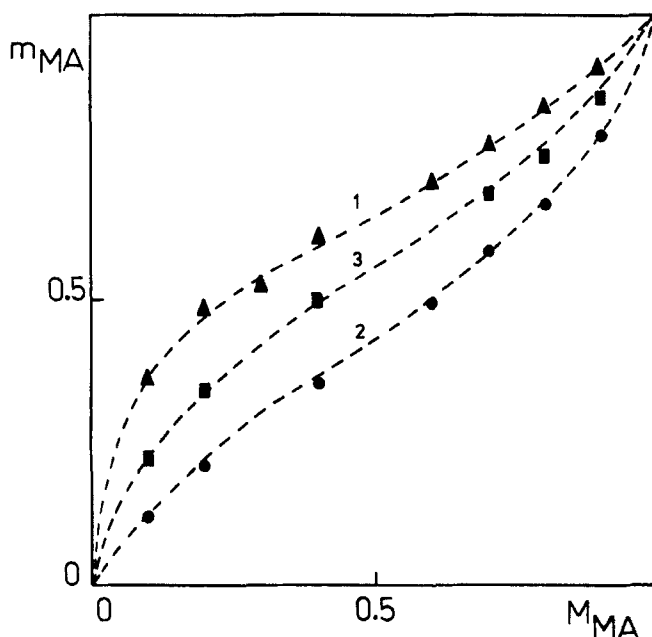


FIG. 10. Dependence of MA mole fraction ( $m_{MA}$ ) in the MA-MMA copolymers obtained in T (1), IPA (2), and A (3) on the MA mole fraction in the monomer feed ( $M_{MA}$ ). ( $\Delta$ ,  $\bullet$ ,  $\blacksquare$ ) Experimental data, (---) calculated by the terminal model curves using the following  $r_{MA}$  and  $r_{MMA}$  values:  $r_{MA} = 1.05$ ,  $r_{MMA} = 0.09$ , solvent is T;  $r_{MA} = 0.29$ ,  $r_{MMA} = 0.58$ , solvent is IPA;  $r_{MA} = 0.55$ ,  $r_{MMA} = 0.25$ , solvent is A.

discussion of 3MS-MA copolymerization in T, the dimer  $(MA)_2$  formation has a dual influence on comonomer reactivity. First, it increases the electron acceptor ability of MA with respect to MMA due to the predominant effect of MA carbonyl group participation in H-bond formation. This is one of the reasons for the very low  $m_{MMA}$  value (Table 5, Fig. 9) in this copolymerization. The entropy profit of the second dimer component addition to the propagating chain ends should also be taken into account since the propagation rate constants  $k_{MA,MA}$  and  $k_{MMA,MA}$  increase as compared to the MA addition in the monomer form. However, the increase of  $k_{MMA,MA}$  is a reason for an additional decrease of  $r_{MMA}$ , while the result of the  $k_{MA,MA}$  increase is a rise in  $r_{MA}$  to a value close to unity. The above-mentioned exception can be reasonably explained in this way.

## CONCLUSIONS

The well-defined alternating tendency of 3MS copolymerization with MA or MMA is a consequence of the substantial difference in the polarities of these comonomers. The experimentally determined copolymerization reactivity ratios in T, IPA, and A show that in addition to the predominant effect of the comonomer polarity differences, they depend considerably on the comonomer-comonomer and comonomer-solvent H-bond interactions. This effect is strongest in 3MS-MA copo-

lymerization since MA can participate in the formation of a larger number of H-bonds. When copolymerization is carried out in T, this effect is a consequence of MA dimerization by H-bonding. In IPA or A as solvent, the MA molecule takes part in H-bond formation by its hydroxyl and/or carbonyl groups. Because of the lower ability of MMA to form H-bonds, the solvent effect on the 3MS-MMA copolymerization characteristics is weaker. The assumption of the considerable influence of H-bond formation between the comonomers and solvents is experimentally confirmed by analysis of the influence of these solvents on the copolymerization of MA and MMA—two comonomers with almost identical  $\pi$ -electron systems. This influence does not exclude other propagation mechanisms [16–20] which lead to deviations from the characteristics of the terminal (Mayo–Lewis) model [21] relationships. However, the H-complex influence on the propagation reaction of these copolymerizations would account for all the deviations. The large amount of research experience for the styrene–MMA radical copolymerization [22, 23] can be used to this end in spite of the controversies [24] which exist.

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