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Solvent Effects in Radical Copolymerization

III. Methacrylamide^{*)}

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SUMMARY:

The free radical copolymerization of methacrylamide with styrene and methyl methacrylate has been investigated at 70°C in solvents having different dielectric constants. A strong influence of the solvent on the copolymerization parameters has been observed. Such behaviour is quite similar to that found by the same authors for acrylamide copolymerization and differs completely from that found for N,N-dialkyl acrylamide. The influence of the solvent properties (polarity, dielectric constant *etc.*) on the amide-enol equilibrium is discussed.

ZUSAMMENFASSUNG:

Die radikalische Copolymerisation von Methacrylsäureamid mit Styrol und Methylmethacrylat wurde bei 70°C in Lösungsmitteln verschiedener Dielektrizitätskonstante untersucht. Es wurde ein starker Einfluß des Lösungsmittels auf die Copolymerisationsparameter beobachtet. Dieses Verhalten ist dem bei der Copolymerisation von Acrylamid sehr ähnlich, aber ganz verschieden von dem der N,N-Dialkylacrylsäureamid-Copolymerisation. Der Einfluß der Natur des Lösungsmittels (Polarität, Dielektrizitätskonstante, usw.) auf das Amid-Enol-Gleichgewicht wird diskutiert.

A recent work¹⁾ has shown that the reactivity ratios are strongly influenced by the polymerization medium in the free radical copolymerization of acrylamide with styrene and methyl methacrylate. A similar investigation²⁾ has been carried out for the copolymerization of N,N-dimethyl acrylamide with the same monomers; in this case a completely different behaviour has been observed, *i.e.* no influence of the solvent on the copolymer compositions was evidenced. This suggested to investigate the copolymerization of methacrylamide in different solvents.

The copolymerization of methacrylamide with methyl methacrylate in ethanol^{3,4)} and more recently with 1.2-dimethyl-5-vinyl-pyridinium methylsulfate⁵⁾ has already been reported. The present paper deals with copolymerization of methacrylamide and non-ionizable monomers in different solvents.

^{*)} For the previous paper of this series, see G. SAINI, A. LEONI, and S. FRANCO, *Makromol. Chem.*, **146** (1971) 165.

Experimental

Monomers: Methacrylamide (MAM), styrene (ST), methyl methacrylate (MM), were trade products. MAM (Schuchard) was crystallized from chloroform before polymerization. ST and MM (Montedison) were purified by distn. prior to use.

Solvents: Dioxane, ethanol, were reagent grade products and were dried and purified by distn. before use according to the usual techniques.

Initiator: α,α' -Azobisisobutyronitrile (Fluka) was crystallized twice from ethyl ether.

Procedure: All experiments were performed in a glass tube which was filled with dry monomers, solvent, and initiator. The tube was then sealed in a nitrogen atmosphere and heated at 70°C. All the copolymerizations were stopped by pouring the tube content into an excess of a non-solvent; according to the copolymer compositions, methanol, acetone or ethyl ether were used. The conversions to polymer were in each case lower than 10%. The copolymers were dissolved again, reprecipitated, washed and accurately dried. For both the system MAM/ST and MAM/MM, the total concn. of monomers was kept constant at 0.8 mole/l. of solvent. The initiator was used in the amount of 0.4 g/l. of solvent (see Tables 1 and 2).

Copolymers analysis: The copolymer compositions were determined on the basis of their nitrogen content. The analyses were carried out by a Perkin-Elmer Model 240 elemental analyzer on products previously dried under reduced pressure to constant weight.

IR spectra: The IR absorptions were obtained using a Perkin-Elmer Model 125 spectrophotometer on KBr disks.

Results and Discussion

The copolymerization results are listed in Tables 1 and 2; the experimental points and the copolymerization curves are reported in Figs. 1 and 2 where monomer f_1 and copolymer F_1 compositions are expressed as molar ratios with respect to MAM. The r_1 and r_2 values (Table 3) have been obtained by the FINEMAN and ROSS method.

Table 1. Copolymerization of methacrylamide (1) with styrene (2) at 70°C in dioxane (a) and ethanol (b). The total monomer concentration was 0.8 mole/l. solvent, α,α' -azobisisobutyronitrile was used in the amount of 0.4 g/l. solvent

f_1	N in copolymer (%)		F_1	
	(a)	(b)	(a)	(b)
0.20	1.78	1.80	0.129	0.131
0.30	4.31	2.85	0.302	0.201
0.40	5.64	4.65	0.391	0.325
0.50	7.43	6.42	0.500	0.436
0.60	8.78	6.95	0.583	0.474
0.70	11.20	8.51	0.722	0.568
0.80	12.66	10.21	0.805	0.662

Table 2. Copolymerization of methacrylamide (1) and methylmethacrylate (2) at 70°C in dioxane (a) and ethanol (b). The total monomer concentration was held constant at 0.8 mole monomer/l. solvent. α,α' -azobisisobutyronitrile was used in the amount of 0.4 g/l. solvent

f_1	N in copolymer (%)		F_1	
	(a)	(b)	(a)	(b)
0.20	2.03	1.82	0.142	0.128
0.30	3.47	2.69	0.239	0.188
0.40	5.28	3.90	0.357	0.268
0.50	7.57	5.15	0.500	0.349
0.60	9.37	6.25	0.609	0.419
0.70	11.22	8.26	0.715	0.542
0.80	12.55	10.41	0.792	0.669

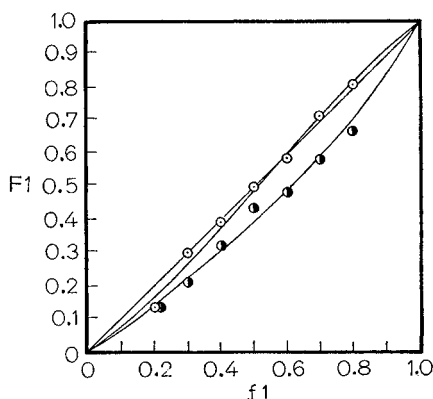


Fig. 1

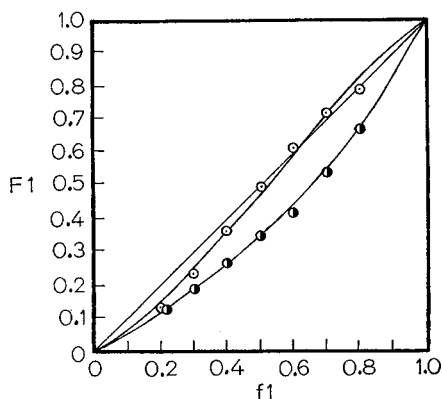


Fig. 2

Fig. 1. Copolymerization diagram for the system methacrylamide (1)/styrene (2) in dioxane (○) and ethanol (●) at 70°C. The lines were calculated for $r_1 = 1.29$ and $r_2 = 1.46$ (dioxane) and $r_1 = 0.54$ and $r_2 = 1.44$ (ethanol). The monomer f_1 and copolymer F_1 compositions are expressed as molar ratios with respect to MAM

Fig. 2. Copolymerization diagram for the system methacrylamide (1)/methylmethacrylate (2) in dioxane (○) and ethanol (●) at 70°C. The lines were calculated for $r_1 = 1.27$ and $r_2 = 1.55$ (dioxane) and $r_1 = 0.43$ and $r_2 = 1.68$ (methylmethacrylate). The monomer f_1 and copolymer F_1 compositions are expressed as molar ratios with respect to MAM

The experimental data clearly show a strong solvent influence on these copolymerizations. In particular, the copolymers obtained in dioxane were always richer in MAM than the copolymers obtained in ethanol. A similar behaviour was already observed in the copolymerization of acrylamide (AM) with the same comonomers¹⁾. The differences can be evidenced by examining the IR spectra of copolymers obtained from 0.5 MAM molar feed ratio. The IR spectra for the copolymerization systems

MAM/ST in different solvents are reported in Fig. 3 a,b; the intensity of absorptions of MAM (1660 cm^{-1}) and ST monomer units (1490 cm^{-1} ; 755 cm^{-1} ; 700 cm^{-1}) is influenced by the nature of the solvent used in copolymerization. Similar results are obtained for the copolymerization system MAM/MM (see Fig. 3 c,d).

Another point is the rather unusual behaviour for the copolymerizations in dioxane; in fact, both the calculated r_1 and r_2 values are higher than 1 for the MAM/ST and MAM/MM systems. These high values indicate a low tendency of the monomers to alternate. The same behaviour has already been reported for AM¹⁾.

These experimental results do not allow a complete explanation for such strong solvent effect. It should be remembered that ALFREY and

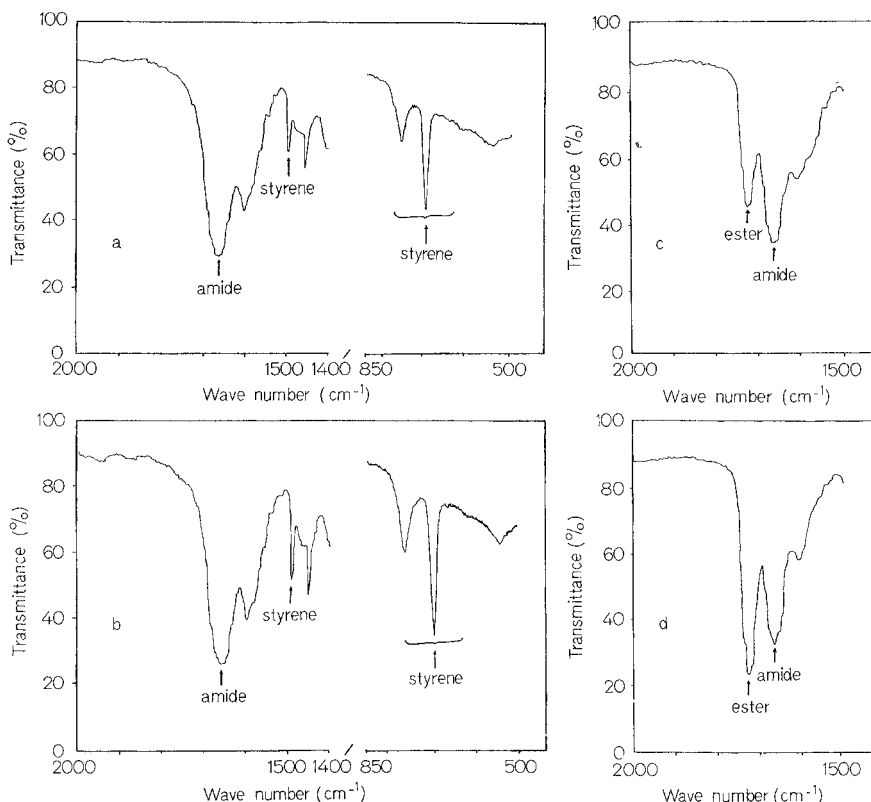


Fig. 3 a-d. IR spectra (KBr disk) of copolymers obtained from 0.5 MAM molar ratio of feeding: MAM/ST system (a) in dioxane, (b) in ethanol; MAM/MM system (c) in dioxane, (d) in ethanol. The conditions are reported in Tables 1 and 2

PRICE scheme predicts that the dielectric constant of the solvent should affect the copolymerization ratios; however until recently no evidence was presented for an appreciable influence of this particular parameter. For the AM copolymerizations¹⁾, it was assumed that the dielectric constant and polarity could be one of the possible reasons for the solvent dependence. The authors tried to correlate this influence with the enolization equilibrium of the amidic group. The same authors²⁾ in a following paper showed that there is no significant influence of the solvent in the copolymerization of dimethyl acrylamide (DMAM) under the same conditions. A tentative explanation of this behaviour was suggested by considering that in DMAM, the enolic form can not be present.

The results obtained in the present work seem to give further support to this suggestion; in fact for this monomer, there is again the possibility of enolization due to the presence of migrable hydrogen on the amidic group. Such amide-enol equilibrium could be influenced by solvents of different polarity and dielectric constants.

Other points which have to be considered for a complete evaluation of this phenomenon, can be different monomer solvations, different stabilities of the growing radicals, and hydrogen bond formation in the different solvents.

The MAM copolymerization with MM has been previously studied by other authors^{3,4)} in ethanol at 65°C and 70°C resp. A very good agreement has been observed for the r_1 and r_2 values reported by these authors and those obtained in the present work for the copolymerizations carried out in the same solvent (see Table 3).

More recently MONAGLE and MOSHER⁵⁾ reported the copolymerization of MAM with 1,2-dimethyl-5-vinyl-pyridinium methylsulfate (DMVPMS) in solvents having different dielectric constants. The authors attributed the observed effect of the solvent on copolymerization reactivity to differ-

Table 3. Reactivity ratios for methacrylamide (MAM) copolymerizations

Monomer 1 Monomer 2		Dioxane	Ethanol		
		this paper	this paper	ref. ³⁾	ref. ⁴⁾
MAM/ST	r_1	1.29 ± 0.08	0.54 ± 0.08	—	—
	r_2	1.46 ± 0.09	1.44 ± 0.15	—	—
MAM/MM	r_1	1.27 ± 0.19	0.43 ± 0.04	0.47 ± 0.04	0.49 ± 0.02
	r_2	1.55 ± 0.22	1.68 ± 0.07	1.5 ± 0.02	1.65 ± 0.05

ences in the degree of ionization of DMVPMS monomer as a result of differences in the dielectric constants of the solvent. In particular, these authors obtained copolymers richer in MAM in solvents of low dielectric constant (such as glacial acetic acid) than in solvents of high dielectric constant (such as water and dimethylsulfoxide). On the basis of the results obtained in the present work, it seems therefore reasonable to attribute the differences found by MONAGLE and MOSHER not only to the effect of the solvent on DMVPMS, but also on MAM.

- 1) G. SAINI, A. LEONI, and S. FRANCO, *Makromol. Chem.* **144** (1971) 235.
- 2) G. SAINI, A. LEONI, and S. FRANCO, *Makromol. Chem.* **146** (1971) 165.
- 3) K. CRAUWELS and G. SMETS, *Bull. Soc. Chim. Belges* **59** (1950) 443.
- 4) G. A. PETROVA, G. A. SHTRAIKHMAN, and A. A. VANSHEIDT, *Zh. Fiz. Khim.* **33** (1959) 1246.
- 5) D. J. MONAGLE and W. A. MOSHER, *Am. Chem. Soc., Div. Polymer Chem., Preprints* **10**, No. 2 (1969).