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Solvent Effects in Radical Copolymerization

1. Acrylamide

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SUMMARY:

Acrylamide has been free radical copolymerized with styrene and methyl methacrylate at 70 °C in different solvents (dioxane, dioxane/ethanol mixture, ethanol). A strong influence of the solvent on the copolymer compositions has been observed; particularly copolymers richer in acrylamide have always been obtained in dioxane.

These results indicate that the nature of the solvent (polarity, dielectric constant *etc.*) could affect the polarity and the reactivity of the acrylamide double bond as well as the stability of the growing radical. Other factors are also discussed.

ZUSAMMENFASSUNG:

Acrylamid wurde mit Styrol und Methylmethacrylat in verschiedenen Lösungsmitteln (Dioxan, Dioxan/Äthanol und Äthanol) bei 70 °C radikalisch copolymerisiert. Das Lösungsmittel hat einen starken Einfluß auf die Zusammensetzung der Copolymeren. Bei der Copolymerisation in Dioxan wurden Copolymere mit höherem Acrylamid-Gehalt gefunden. Es wird angenommen, daß die Natur des Lösungsmittels (Polarität, Dielektrizitätskonstante usw.) die Polarität und die Reaktionsfähigkeit der Acrylamid-Doppelbindung beeinflussen kann ebenso wie die Stabilität des wachsenden Radikals. Andere mögliche Ursachen werden diskutiert.

Introduction

Previous work on the free radical copolymerization showed that there is no influence of the solvent on the monomer reactivity ratios[1,2]. More recently Ito and Otsu[3] found small solvent effects for the system styrene/methyl methacrylate. Solvent effects on copolymer compositions have been found only in special cases as copolymerization of acid or basic monomers in aqueous solutions depending on the pH value[4-7]; other similar cases are related to ionizable monomers (sodium styrene sulfonate[8], acrylic and methacrylic acid[9,10]) or to heterogeneous copolymerizations in which the ratio of the monomers concentration in the polymerization phase differs from the ratio of feed[11-15].

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In the present work the authors give experimental evidence that in the free radical copolymerization of a non-ionizable monomer such as acrylamide with styrene and methyl methacrylate, the reactivity ratios are strongly influenced by the solvent medium.

Experimental

Monomers

Acrylamide (AM), styrene (ST) and methyl methacrylate (MM) were commercial products. AM (Nymco) was crystallized from chloroform and accurately dried before polymerization. ST (Montedison) was purified by distillation under reduced pressure (30 mm Hg) before polymerization; the fraction boiling in the range 73−75 °C was collected and used. MM (Montedison) was purified by distn. before polymerization; the fraction boiling in the range 100−102 °C (760 mm Hg) was collected and used.

Solvents

Dioxane and ethanol were reagent grade products and were dried and distd. according to the usual techniques.

Initiator

$\alpha.\alpha'$-azobisisobutyronitrile (Fluka) was crystallized twice from ethyl ether.

Procedure

All experiments were performed in glass tubes which were 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; the conversions to polymer were in each case lower than 10 %.

The total concn. of monomers was kept constant at 0.4 mole/l. of solvent; dioxane, a mixture of dioxane/ethanol (70/30 in volume) and pure ethanol were used as solvents. The initiator was used in the amount of 1 g/l. of solvent (see Tables 1 and 2). A comparative experimental series was carried out for the system AM/MM at a total monomer concentration of 0.8 mole/l. of solvent; dioxane and ethanol were used as solvents. The initiator was used in the amount of 0.4 g/l. of solvent (see Table 3).

The copolymers were precipitated in methanol, acetone or ethyl ether; they were dissolved again, reprecipitated, washed and dried accurately.

Copolymers analysis

The copolymer compositions were determined on the basis of their nitrogen contents. The analyses were carried out by the semi-micro Kjeldahl method on products previously dried under reduced pressure to constant weight.

A number of authors[16, 17] reported that the radical homopolymers of AM, under some polymerization conditions, exhibit nitrogen contents lower than calculated; this fact was

correlated with evolution of ammonia due to the formation of inter- and intra-molecular imide groups. In order to check the reliability of the nitrogen content determination, a series of AM homopolymerizations was carried out under the same conditions (initiator, solvent and temp.). The nitrogen contents were found to range between 19.40 and 19.80% (calcd. 19.70%). Therefore it can be concluded that the copolymer compositions can be determined with reasonable accuracy from nitrogen analysis.

IR Spectra

The IR spectra have been obtained using a Perkin Elmer Model 125 spectrophotometer. The copolymers were examined in KBr disk; the AM spectra in different solvents were obtained in KBr cells using a compensating cell.

Results and Discussion

The copolymerization results are listed in Tables 1, 2, and 3. The experimental points and the copolymerization curves for each system are reported in Figs. 1, 2, and 3, respectively; monomer f_1 and copolymer F_1 compositions indicate molar ratios with respect to AM. The experimental data show a strong influence of the solvents on these copolymerizations.

Table 1. Results of the free radical copolymerisation of acrylamide (M1) and styrene (M2) at 70°C

Monomer feed f_1	% N in copolymer			Copolymer composition F_1		
	(a)	(b)	(c)	(a)	(b)	(c)
0.10	1.34	1.28	–	0.096	0.092	–
0.20	2.44	2.06	2.26	0.171	0.146	0.159
0.30	–	–	2.73	–	–	0.191
0.40	6.17	5.24	3.26	0.400	0.346	0.225
0.50	8.24	6.68	5.73	0.513	0.429	0.375
0.50	8.36	6.79	–	0.518	0.435	–
0.60	10.39	8.36	7.44	0.621	0.519	0.470
0.70	12.63	9.95	8.67	0.724	0.599	0.535
0.75	–	–	9.25	–	–	0.564
0.80	–	12.83	10.09	–	0.732	0.606
0.90	17.36	15.58	14.45	0.922	0.847	0.801

The copolymerizations have been carried out at 70°C (a) in dioxane, (b) in a dioxane/ethanol mixture (70/30 in volume), (c) in ethanol.

The total monomers concentration has been maintained constant at 0.4 mole/l. of solvent.

The initiator $\alpha.\alpha'$-azobisisobutyronitrile has been used in the amount of 1 g per liter of solvent.

Table 2. Results of the free radical copolymerization of acrylamide (M 1) and methylmeth-acrylate (M 2) at 70°C

Monomer feed	% N in copolymer			Copolymer composition F_1		
f_1	(a)	(b)	(c)	(a)	(b)	(c)
0.10	0.94	0.86	—	0.066	0.061	—
0.20	1.86	1.44	1.33	0.128	0.100	0.092
0.30	3.45	2.48	1.87	0.230	0.169	0.129
0.40	5.10	3.73	3.08	0.330	0.247	0.208
0.50	9.20	5.04	4.03	0.552	0.327	0.267
0.50	8.48	5.56	—	0.515	0.356	—
0.60	11.45	8.75	5.58	0.662	0.529	0.357
0.70	14.90	10.48	8.60	0.813	0.615	0.521
0.75	—	11.55	—	—	0.666	—
0.80	15.64	13.43	11.16	0.843	0.751	0.648
0.90	18.28	16.02	15.40	0.947	0.860	0.835

The copolymerizations have been carried out at 70°C (a) in dioxane, (b) in a dioxane/ethanol mixture (70/30 in volume) (c) in ethanol.

The total monomers concentration has been maintained constant at 0.4 mole/l. of solvent.

The initiator $\alpha.\alpha'$-azobisisobutyronitrile has been used in the amount of 1 g/l. of solvent.
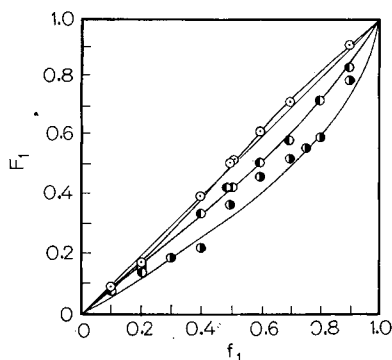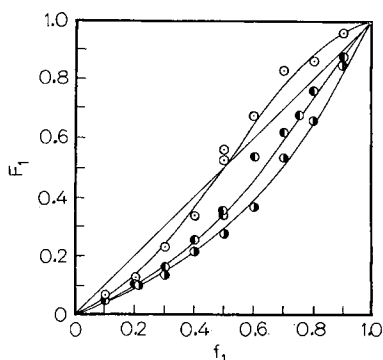

Fig. 1   Fig. 2

Fig. 1. Copolymerization diagram for the system acrylamide (M_1)/styrene at 70°C. ○ Di-oxane. Line calculated for $r_1 = 1.38$, $r_2 = 1.27$. ◑ Dioxane/ethanol (mixture 70/30 in Vol.). Line calculated for $r_1 = 0.59$, $r_2 = 1.13$. ◑ Ethanol. Line calculated for $r_1 = 0.30$, $r_2 = 1.44$. Reference Table 1

Fig. 2. Copolymerization diagram for the system acrylamide (M_1)/methyl methacrylate at 70°C. ○ Dioxane. Line calculated for $r_1 = 2.45$, $r_2 = 2.55$. ◑ Dioxane/ethanol (mixture 70/30 in vol.). Line calculated for $r_1 = 0.82$, $r_2 = 2.53$. ◑ Ethanol. Line calculated for $r_1 = 0.44$, $r_2 = 2.60$. Reference Table 2

Table 3. Results of the free radical copolymerization of acrylamide (M 1) and methylmethacrylate (M 2) at 70 °C

Monomer feed f_1	% N in copolymer		Copolymer composition F_1	
	(a)	(b)	(a)	(b)
0.10	–	–	–	–
0.20	1.90	1.15	0.131	0.081
0.30	3.20	1.95	0.214	0.135
0.40	5.15	2.90	0.332	0.198
0.50	8.75	4.10	0.526	0.270
0.60	11.59	5.42	0.667	0.349
0.70	14.02	8.10	0.776	0.496
0.80	15.85	11.26	0.852	0.651
0.90	–	–	–	–

The copolymerizations have been carried out at 70 °C (a) in dioxane, (b) in ethanol.
The total monomers concentration has been maintained constant at 0.8 mole/l. of solvent.
The initiator α.α′-azobisisobutyronitrile has been used in the amount of 0.4 g/l. of solvent.

The data show that in each copolymerization system, the copolymers obtained in dioxane are always richer in AM than the copolymers obtained in the other solvents. These differences can be evidenced by examining the IR spectra of copolymers obtained from 0.5 AM molar ratio of feeding. The IR spectra for the system AM/ST in different solvents are reported in Fig. 4; they show that the intensity of absorptions characteristic of AM (1660 cm^{-1}) and ST (1490, 755, 700 cm^{-1}) is influenced by the nature of the solvent. Similar results are obtained for the system AM/MM (see Fig. 5). It can be noticed that such peculiar behaviour remains constant also by changing monomers and initiator concentrations (see Table 3 and Fig. 3); a comparison between the results obtained for
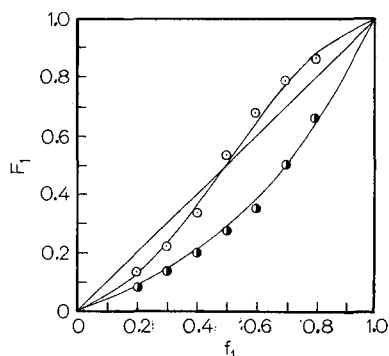

Fig. 3. Copolymerization diagram for the system acrylamide (M_1)/methyl methacrylate at 70 °C. ○ Dioxane. Line calculated for $r_1 = 2.39$, $r_2 = 2.44$. ◑ Ethanol. Line calculated for $r_1 = 0.47$, $r_2 = 2.65$. Reference Table 3
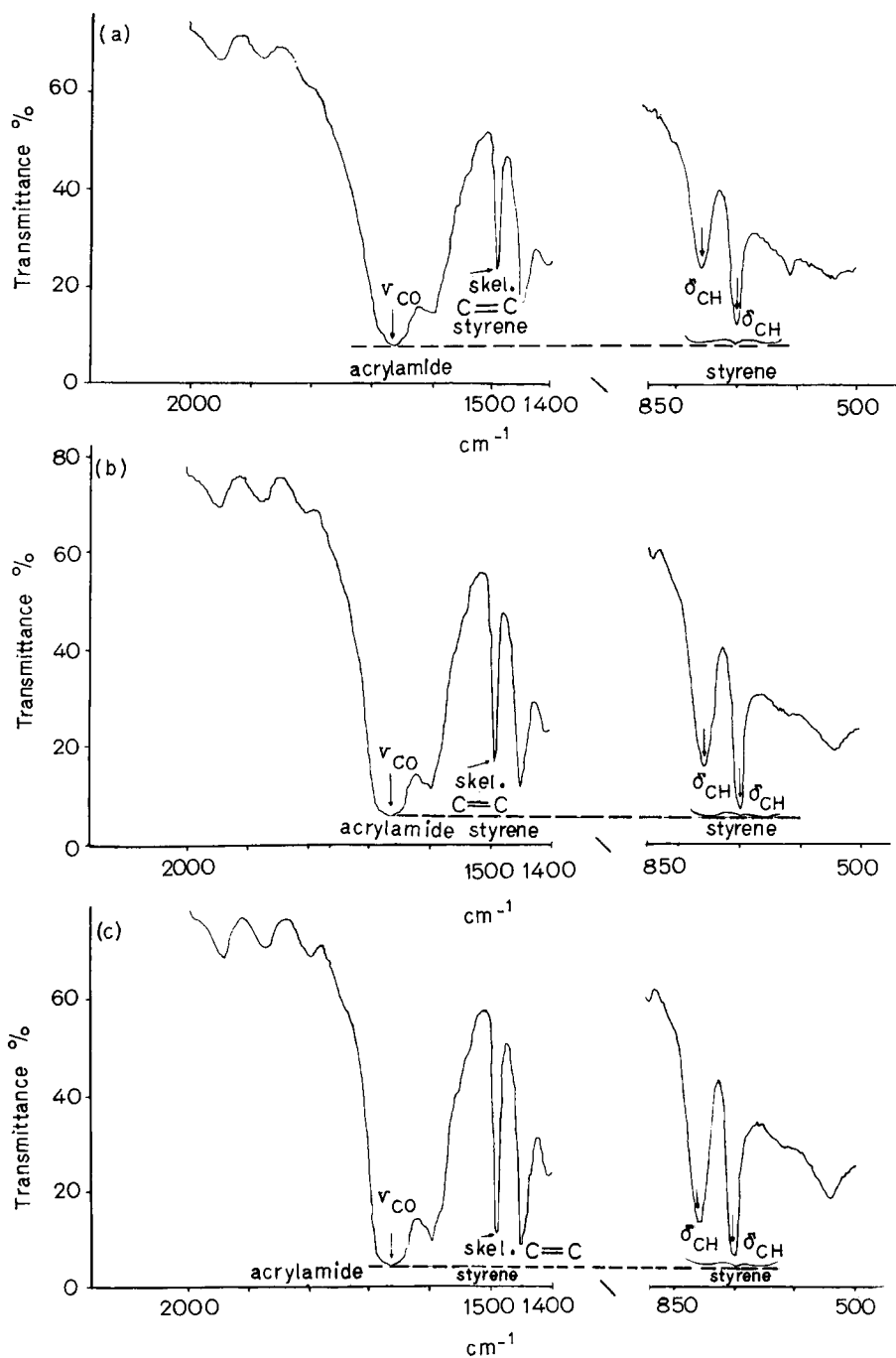
Fig. 4. Acrylamide/styrene system. IR spectra (KBr disk) of copolymers obtained from 0.5 acrylamide molar ratio of feeding: (a) in dioxane, (b) in a dioxane/ethanol mixture (70/30 in volume), (c) in ethanol. The conditions are reported in Table 1
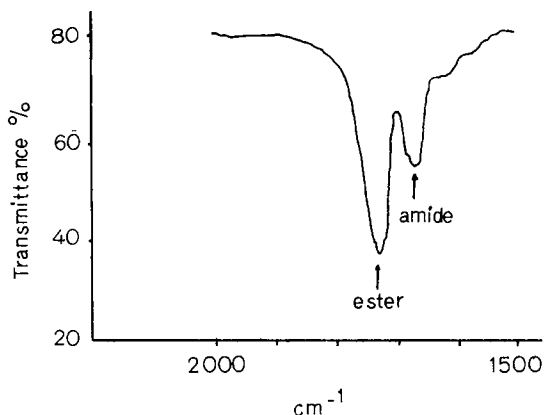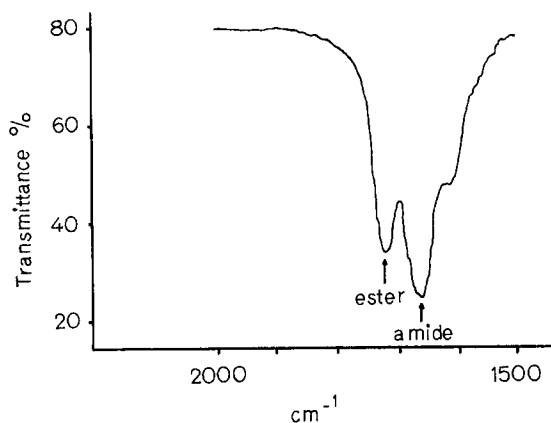
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Fig. 5a

Fig. 5b

Fig. 5. Acrylamide/methyl methacrylate system. IR spectra (KBr disk) of copolymers obtained from 0.5 acrylamide molar ratio of feeding: (a) in ethanol, (b) in dioxane. The conditions are reported in Table 2

the AM/MM system according to the experimental conditions of Tables 2 and 3 does not show practically significant differences.

Another point worth mentioning is the rather unusual behaviour in the copolymerization of AM both with ST and MM; in some cases in fact, the calculated copolymerization curves correspond to values of r_1r_2 higher than 1 (see Table 4). The r_1 and r_2 values have been obtained by the FINE-MAN and ROSS method and checked by the intersection method according to MAYO and WALLING. Results of this kind were found for some other copolymerizations but not frequently; these high values of r_1r_2 indicate a low tendency of the monomers to alternate: the copolymer should be composed mainly of small sequences of monomeric units of the same type[18].

It is not easy to find a satisfactory explanation of such strong solvent effect on radical copolymerization of AM. It can be recalled that the

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Table 4. Copolymerization parameters in different solvents at 70 °C (1 = acrylamide, 2 = styrene or methylmethacrylate)
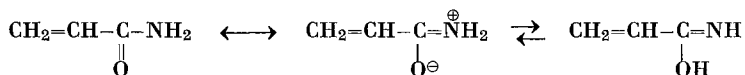
	Dioxane	Dioxane/ethanol (mixture, 70/30 in volume)	Ethanol
	AM/ST system[a]		
r_1	1.38 ± 0.09	0.59 ± 0.10	0.30 ± 0.09
r_2	1.27 ± 0.17	1.13 ± 0.05	1.44 ± 0.22
	AM/MM system[b]		
r_1	2.45 ± 0.35	0.82 ± 0.07	0.44 ± 0.06
r_2	2.55 ± 0.40	2.53 ± 0.22	2.60 ± 0.21
	AM/MM system[c]		
r_1	2.39 ± 0.32	–	0.47 ± 0.02
r_2	2.44 ± 0.38	–	2.65 ± 0.20

[a] Ref. Table 1, Fig. 1.   [b] Ref. Table 2, Fig. 2.   [c] Ref. Table 3, Fig. 3.

ALFREY and PRICE scheme takes into account the dielectric constant of the copolymerization medium. Experimental work of LEWIS and coworkers[1] as well as of PRICE and WALSH[2] on the copolymerization of ST and MM in solvents of different dielectric constants showed that the copolymerization parameters do not depend on the dielectric constant of the medium. These data suggested to the authors mentioned that the competition of two monomers for a growing free radical is not appreciably dependent on the nature of the medium in which the reaction takes place.

More recently ITO and OTSU[3] re-examined the same system in different solvents and reported that the copolymerization parameters should depend on the polar nature of the solvents. However the effect on copolymer compositions is small as shown by Fig. 6 obtained by plotting the experimental data obtained by these authors, as compared with the effect found in the AM copolymerization.

The peculiar behaviour of AM when copolymerized in different solvents could arise from a displacement of the following equilibria:

$$CH_2=CH-\underset{\underset{O}{\|}}{C}-NH_2 \longleftrightarrow CH_2=CH-\underset{\underset{O^\ominus}{|}}{C}=\overset{\oplus}{N}H_2 \rightleftarrows CH_2=CH-\underset{\underset{OH}{|}}{C}=NH$$

brought about by solvents of different dielectric constant and polarity. These equilibria have been taken into account to explain the base-catalyzed hydrogen migration of AM[19-20].
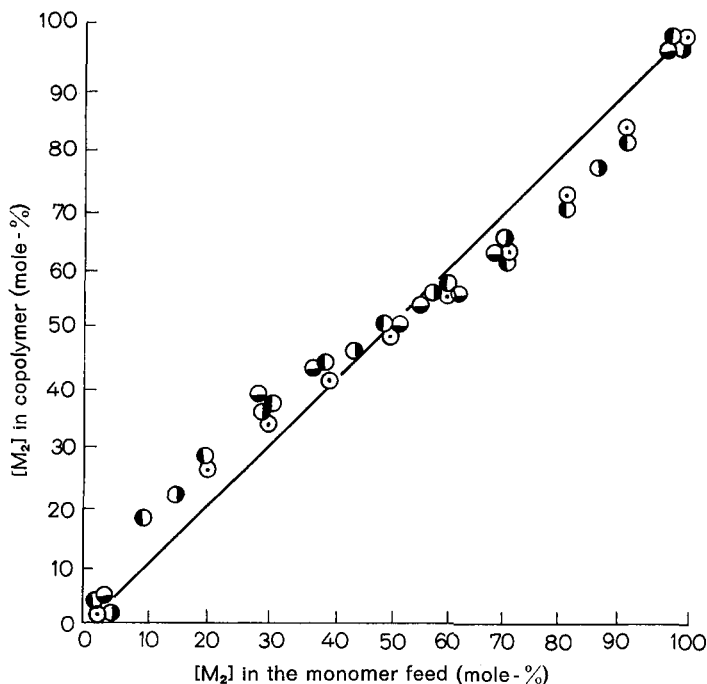
Fig. 6. Copolymerization diagram for the system styrene (M_1)/methylmethacrylate (M_2). Figure obtained by plotting the experimental data obtained by T. ITO and T. OTSU (see ref.[3]).

$r_1 = 0.57 \pm 0.032$	$r_2 = 0.46 \pm 0.032$	⊙ Benzene
$r_1 = 0.48 \pm 0.045$	$r_2 = 0.49 \pm 0.045$	◑ Benzonitrile
$r_1 = 0.44 \pm 0.054$	$r_2 = 0.39 \pm 0.054$	◖ Benzyl alcohol
$r_1 = 0.35 \pm 0.024$	$r_2 = 0.35 \pm 0.024$	◒ Phenol

The displacement of these equilibria could affect the polarity of the double bond and its reactivity. In fact the IR spectra of AM in dioxane and in ethanol show a shift of the absorptions of C=O and vinyl groups (see Table 5). It is also worth mentioning that the copolymers are richer

Table 5. IR spectra of the acrylamide in various solvents

Characteristic absorption	Dioxane cm^{-1}	Ethanol cm^{-1}
C=O	1690	1679
C=C	1642	1633
NH_2	1617	1607

in AM when obtained in dioxane, that is in the solvent of lowest dielectric constant (2.2 at 25 °C).

Other effects related to the different nature of the solvents (e.g. monomer solvation, hydrogen bonding ability, influence on the growing radical stability etc.) which can affect the behaviour in the AM copolymerization should be taken also into account.

Additional informations will be given by investigating the role of the solvent in the copolymerizations of methacrylamide and N-substituted acrylamides; work is now in progress in our laboratories.

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