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THE INFLUENCE OF MOLECULAR INTERACTIONS ON POLYMERIZATION—IV

COPOLYMERIZATION OF 2-NAPHTHYL METHACRYLATE AND METHYL METHACRYLATE IN SOLVENTS WITH DIFFERENT DIELECTRIC CONSTANTS

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Abstract—The copolymerization of 2-naphthyl methacrylate (2-NM) with methyl methacrylate (MMA) initiated by 2,2′-azoisobutyronitrile in carbon tetrachloride, chloroform, benzene, acetone and acetonitrile was investigated. The reactivity ratios determined by the methods of Fineman–Ross and Kelen–Tüdős are: in carbon tetrachloride—$r_{2\text{-NM}} = 2.46 \pm 0.25$, $r_{\text{MMA}} = 0.61 \pm 0.06$; chloroform—$r_{2\text{-NM}} = 2.71 \pm 0.30$, $r_{\text{MMA}} = 0.60 \pm 0.06$; benzene—$r_{2\text{-NM}} = 2.62 \pm 0.44$, $r_{\text{MMA}} = 0.63 \pm 0.11$; acetone—$r_{2\text{-NM}} = 4.13 \pm 0.45$, $r_{\text{MMA}} = 0.60 \pm 0.06$ and acetonitrile—$r_{2\text{-NM}} = 3.70 \pm 0.30$, $r_{\text{MMA}} = 0.62 \pm 0.05$.

The dependence of the reactivity ratios on the solvent is explained on the basis of formation of complexes between the electron-donating naphthalene rings and the electron-accepting methacrylic double bonds, as indicated by NMR studies.

INTRODUCTION

The polymerizations of 1-naphthyl methacrylate and 2-naphthyl methacrylate in various solvents have been investigated; it was established that the dielectric constant of the solvent influences the tacticity of the polymers [1, 2]. It was suggested that the behaviours of the naphthyl methacrylates are connected with the association of the monomer molecules in solvents with low dielectric constant and the dissociation of the complexes in solvents with high dielectric constants [3]. The interactions have been studied by ^{1}H NMR spectroscopy.

As recently observed, the copolymerization is governed by complex formation [4] and it is of interest to study the copolymerization of naphthyl methacrylate and methyl methacrylate in various solvents.

Copolymers of naphthyl methacrylate with methyl methacrylate and with styrene have been prepared by other authors [5–7] in order to obtain polymers exhibiting fluorescence emission and showing sensitivity to light. However, there are no data on the copolymerization parameters of naphthyl methacrylates.

The present paper deals with the copolymerization of 2-naphthyl methacrylate (2-NM) and methyl methacrylate (MMA) in solvents with various dielectric constants such as carbon tetrachloride, chloroform, benzene, acetone and acetonitrile and the determination of the monomer reactivity ratios in these solvents.

EXPERIMENTAL

Materials

2-Naphthyl methacrylate (2-NM) was synthesized and purified by the previously described method [2, 3]. Methyl methacrylate (MMA)—from Serra, BRD, was washed with 5 wt% sodium hydroxide water solution, dried and twice distilled. Other materials are specified as follows.

2,2′-Azoisobutyronitrile (AIBN)—purum, from Fluka, Switzerland. Carbon tetrachloride—purissimum, Laborchemie, Apolda, DDR. Chloroform—p.a. Factory for pure reagents, Vladaja, Bulgaria. Benzene—p.a. thiophene free, dried over sodium and distilled. Acetone—purum, aldehyde free, dried and distilled. Acetonitrile—purum, Laborchemie, Apolda, DDR.

Copolymerization

To 1 mol/l solution of the monomer mixtures in the solvent, 1 mol% (based on the monomers) AIBN was added. The solutions (10–12 ml) were put in ampoules. They were twice frozen with liquid nitrogen and degassed at 10^{-4}–10^{-5} Torr. The sealed ampoules were heated in a thermostat at 60°; for the acetone solutions, the temperature was 55°. The polymerization were homogeneous, except for acetonitrile where the polymers precipitate during the polymerization. The polymers were precipitated in methanol and filtered off. All polymers were dissolved in benzene, reprecipitated in methanol and dried at 25° under reduced pressure (1 Torr).

Measurements

The content of 2-NM units in the copolymers was determined by u.v. examination of solutions in chloroform. The spectra were recorded with spectrometer "Beckman—Model 24" at 277 nm. The calibration was made with poly(2-NM) assuming that the extinction coefficient does not vary with the content of 2-NM units in the copolymer. The compositions of some samples were determined by elemental analysis. The average difference between the methods does not exceed 4%. The intrinsic viscosities were determined in benzene at 25°.

RESULTS AND DISCUSSION

The compositions of the initial monomer mixtures and of the copolymers, and the conversions for the copolymerizations are summarized in Table 1. In solvents with low dielectric constants such as carbon tetrachloride, chloroform and benzene, the time

Table 1. Copolymerization of 2-naphthyl methacrylate (2-NM) and methyl methacrylate (MMA) in solvents with different dielectric constants

Solvent (dielectric constant)	Conversion (wt %)	Time of polymerization (min)	Content of 2-NM Initial mixture (wt %)	Content of 2-NM Copolymer (wt %)	Viscosity ($cm^3 \cdot g^{-1}$)
Carbon tetrachloride	3.5	53	84.97	91.90	4.11
(2.23)	5.9	49	78.59	90.76	
	7.8	58	71.76	85.47	
	13.3	47	63.58	79.18	
	10.4	50	54.96	68.48	
	7.2	51	31.96	46.06	
	7.2	48	17.71	27.43	
Chloroform	7.5	61	78.43	89.22	
(4.70)	6.1	61	63.81	82.77	3.65
	4.6	60	53.44	71.13	
	5.6	61	44.35	60.29	
	5.7	60	31.31	46.15	
	6.3	60	17.56	28.03	
Benzene	5.8	58	87.97	95.03	
(2.28)	4.3	57	78.50	91.98	
	2.6	55	71.80	81.97	
	2.7	65	63.73	76.67	
	2.7	70	55.06	71.81	
	4.6	83	44.09	62.13	
	7.1	91	31.65	42.00	4.80
	1.1	90	17.91	29.49	
Acetone	11.5	516	78.93	93.50	
(20.7)	11.5	517	71.66	88.62	
	1.6	518	63.73	86.10	3.61
	5.0	519	55.19	77.37	
	6.3	505	44.22	63.84	
	1.8	506	31.58	49.76	
	1.9	532	17.64	32.02	
Acetonitrile	3.6	115	84.89	95.20	
(36.2)	9.8	113	78.49	91.92	
	7.6	112	63.75	81.42	1.68
	8.4	107	55.02	78.11	
	5.2	104	44.37	64.24	
	6.5	142	31.70	46.85	
	10.8	112	17.52	29.22	

necessary to reach a convenient conversion is shorter than in acetone and acetonitrile. Consequently the rate of copolymerization in solvents with high dielectric constants is lower than in the solvents with low dielectric constants as previously observed for polymerization in the same solvents [1, 2].

A similar influence of the solvent on the copolymerization rate has been observed by other authors. According to Tsuchida *et al.* [8], the rates of polymerization of styrene with maleic anhydride at 70° in carbon tetrachloride and benzene initiated by AIBN are higher than those in acetone and tetrahydrofuran. In the copolymerization of maleic anhydride and phenanthrene [9], it was found that after 10 hr of irradiation in acetone, tetrahydrofuran and dimethylformamide the copolymerization does not proceed at all, whereas in chloroform, carbon tetrachloride and benzene conversions of about 5–7% were obtained.

The reactivity ratios of the copolymerization in all solvents were calculated from the results in Table 1. The experimental data treated by the Fineman–Ross (F–R) method are given in Figs 1 and 2, those treated by the Kelen–Tüdős (K–T) method are given in Figs 3 and 4. It is seen that the second method places the experimental points along the straight line determining the reactivity ratios more regularly thus providing better distribution of the errors than by the F–R method.

Table 2. Copolymerization reactivity ratios of 2-naphthyl methacrylate ($r_{2\text{-NM}}$) and methyl methacrylate (r_{MMA}) in various solvents calculated by the Fineman–Ross (F–R) and Kelen–Tüdős (K–T) method

Solvent	F–R $r_{2\text{-NM}}$	F–R r_{MMA}	K–T $r_{2\text{-NM}}$	K–T r_{MMA}	$r_{2\text{-NM}} \cdot r_{MMA}$ F–R	$r_{2\text{-NM}} \cdot r_{MMA}$ K–T
Carbon tetrachloride	2.13 ± 0.21	0.45 ± 0.28	2.46 ± 0.25	0.61 ± 0.06	0.95	1.50
Chloroform	2.43 ± 0.20	0.59 ± 0.15	2.71 ± 0.30	0.60 ± 0.06	1.43	1.63
Benzene	2.65 ± 0.27	0.81 ± 0.35	2.62 ± 0.44	0.63 ± 0.11	2.14	1.65
Acetone	4.11 ± 0.37	0.85 ± 0.21	4.13 ± 0.45	0.60 ± 0.06	3.48	2.48
Acetonitrile	3.78 ± 0.20	0.93 ± 0.16	3.70 ± 0.30	0.62 ± 0.05	3.50	2.29

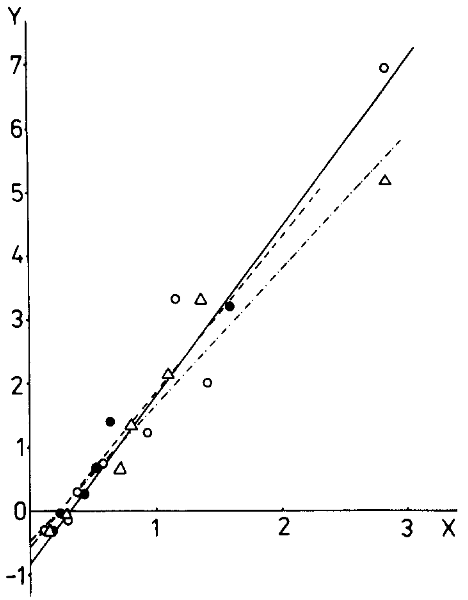


Fig. 1. Fineman–Ross plot for copolymerization of 2-NM and MMA in: carbon tetrachloride Δ–·–·–; chloroform ●– – –; benzene ○——.

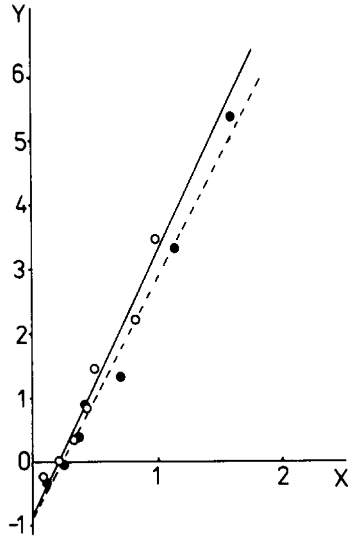


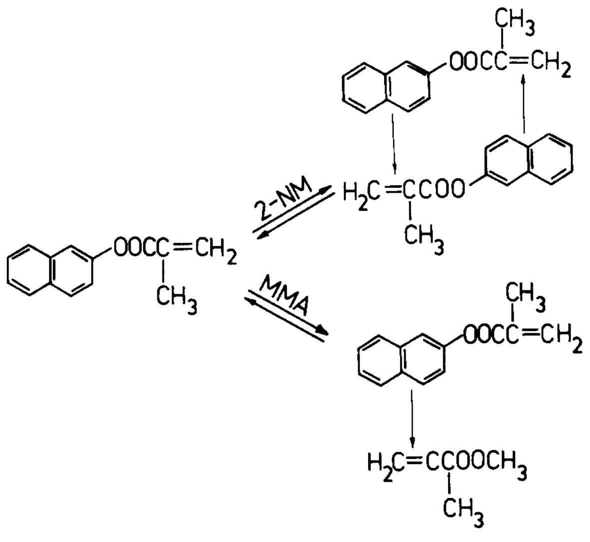
Fig. 2. Fineman–Ross plot for copolymerization of 2-NM and MMA in: acetone ○——; acetonitrile ●– – –.

The reactivity ratios for the 2-NM/MMA copolymerization systems in the solvents and the errors calculated by the least squares method are presented in Table 2. The $r_{2\text{-NM}}$ values are >1 in all solvents and those for r_{MMA} are <1 or close to 1. This result shows that 2-NM growing species react preferentially with 2-NM molecules. MMA growing ends exhibit a tendency to add 2-NM molecules independently of the dielectric constant of the solvent.

The $r_{2\text{-NM}} \cdot r_{\text{MMA}}$ value is near to 1 in chloroform and carbon tetrachloride showing that, in solvents with low dielectric constant, the monomers exhibit equal activity toward both kinds of growing species.

In acetone and acetonitrile, the values of $r_{2\text{-NM}}$ and r_{MMA} increase giving $r_{2\text{-NM}} \cdot r_{\text{MMA}} > 1$. In solvents with high dielectric constants, both growing radicals react preferentially the same monomer molecules and the copolymers might contain more blocks of both types.

As observed previously [3] by ^{1}H NMR study of solutions of naphthalene and methyl methacrylate and of 2-NM in solvents with low and high dielectric constants, in chloroform and carbon tetrachloride the following associations by donor–acceptor interaction take place:



The stability constant of the above complex formation is 0.22 M^{-1}.

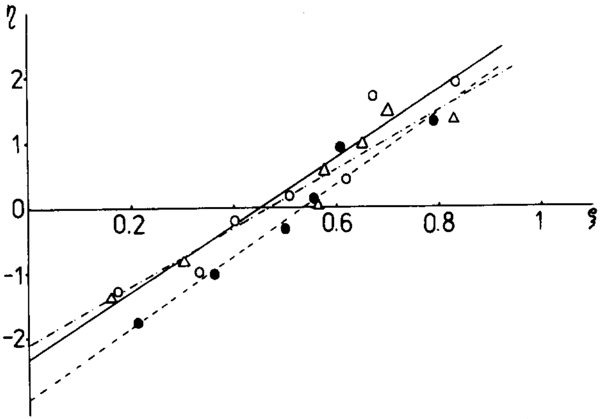


Fig. 3. Kelen–Tüdős plot for copolymerization of 2-NM and MMA in: carbon tetrachloride Δ–·–·–; chloroform ●– – –; benzene ○——.

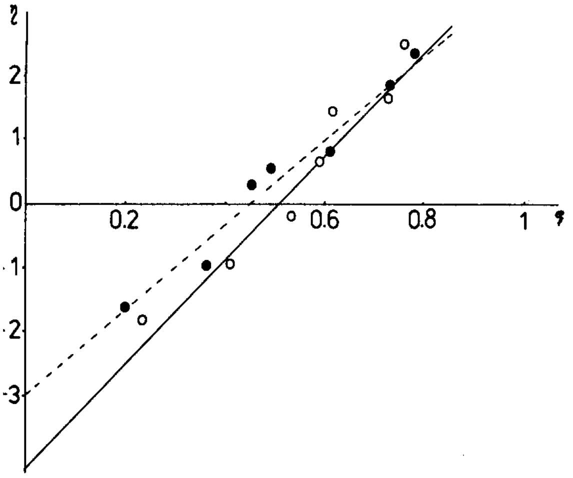


Fig. 4. Kelen–Tüdős plot for copolymerization of 2-NM and MMA in: acetone ○——; acetonitrile ●----.

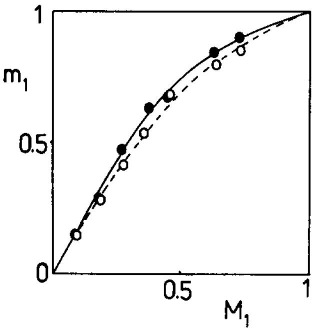


Fig. 5. Copolymerization of 2-NM and MMA; composition curves built up according to the r-values, obtained by Kelen–Tüdős method: in carbon tetrachloride ○----; in acetonitrile ●——. M_1—mol fraction of 2-NM in monomer feed; m_1—mol fraction of 2-NM in copolymer.

If complex formation influences the reactivity ratios as has been established for styrene with maleic anhydride [8], the copolymerization parameters must be lower in solvents with low dielectric constants as shown in Table 2 and Fig. 5. In acetonitrile and acetone where the monomer molecules are dissociated and surrounded by the molecules of the solvent, 2-NM radicals tend to react with 2-NM monomer molecules more than MMA radicals add MMA monomer molecules.

Our results agree with those of other authors investigating the influence of the reaction medium on the composition of styrene (S)/acrylic acid (A) copolymers [10]. The reactivity ratios change from $r_S = 0.30$ and $r_A = 0.13$ in benzene to $r_S = 1.6$ and $r_A = 0.05$ in dimethylformamide. Moreover the sequence distribution in the copolymers prepared in dimethylformamide differs from that in the corresponding copolymers prepared in benzene. The polystyrene blocks were longer in copolymers prepared in dimethylformamide. The authors did not explain the results on the basis of complex formation between the monomers.

A recent study of the copolymerization of maleic anhydride and stilbene [11] shows also that the copolymers obtained in chloroform correspond to lower reactivity ratios than those obtained in tetrahydrofuran.

CONCLUSION

Complex formation explains the change in the ^{1}H NMR spectra of the monomer molecules in different solvents. If complex formation does not completely govern the copolymerization, it can be assumed that it affects the behaviour of the monomers. Other interactions in different solvents between monomer and solvent molecules are also possible. The copolymerization process might be influenced by the solvent molecules also; they can react with the growing radicals in the different steps of the copolymerization.

It can be concluded that the investigation of the complex formation in different solvents might be important for prediction and regulation of the behaviours of monomer molecules in copolymerization. Moreover, the composition and the properties of the copolymers might be governed by changing the solvent.

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