

## The influence of molecular interaction on polymerization, 9<sup>a)</sup>

### Copolymerization of 2-naphthyl methacrylate with acrylonitrile

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#### SUMMARY:

The copolymerization of 2-naphthyl methacrylate (2-NM) with acrylonitrile (AN) initiated by 2,2'-azoisobutyronitrile (AIBN) was carried out in solvents with different dielectric constants. The relative reactivity ratios of the monomers determined by the Fineman-Ross method in the solvents used are as follows:

in chloroform:  $r_{2\text{-NM}} = 0,96 \pm 0,05$ ;  $r_{\text{AN}} = 0,00 \pm 0,02$

in benzene:  $r_{2\text{-NM}} = 0,84 \pm 0,09$ ;  $r_{\text{AN}} = 0,01 \pm 0,04$

in acetone:  $r_{2\text{-NM}} = 0,52 \pm 0,09$ ;  $r_{\text{AN}} = 0,00 \pm 0,02$

in acetonitrile:  $r_{2\text{-NM}} = 0,51 \pm 0,06$ ;  $r_{\text{AN}} = 0,00 \pm 0,03$

The capability of the monomers to form donor-acceptor associates was shown by means of <sup>1</sup>H NMR spectroscopy. The observed interactions between the monomer molecules on one side and between the molecules of the monomers and the solvent on the other side were used to explain the changes in the reactivity ratios of both monomers obtained in different solvents.

#### Introduction

Differences in the relative reactivity ratios have been observed in dependence of the solvent used as a medium for copolymerization of 2-naphthyl methacrylate (2-NM) and methyl methacrylate (MMA) initiated with 2,2'-azoisobutyronitrile (AIBN)<sup>1,2)</sup>. We explained these results with the possibility of complex formation between the electron accepting double bond and the electron donating naphthalene nucleus which depends on the dielectric constant of the solvent. An influence of the solvent on the reactivity ratios of the monomers has been observed in the system acrylonitrile-styrene, too<sup>3)</sup>, which might be connected with the participation of AN in the formation of different associates.

The present paper contains the results of the copolymerization of 2-NM and AN carried out in solvents with different dielectric constants. The relative reactivity ratios of the monomers in chloroform, benzene, acetone, and acetonitrile were determined. The IR and <sup>1</sup>H NMR spectra of the monomers and their mixtures in the different solvents were also studied. The results obtained can be connected with the changes of the monomer reactivity ratios.

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<sup>b)</sup> Unfortunately Dr. H. Boudevska has deceased on January 4, 1984.

## Experimental part

### Reagents

*2-Naphthyl methacrylate (2-NM)* — obtained from methacryloyl chloride and the Na salt of 2-naphthol<sup>4</sup>). The product was washed with 5% water solution of NaOH and with water till neutral reaction. Recrystallized from 70% ethanol. Yield 32%, m. p. 66°C.

*Acrylonitrile (AN)* — from "Neftochim", Bourgas, Bulgaria, distilled, b. p. 76–77°C.

*2,2'-Azobisisobutyronitrile (AIBN)* — from Fluka, recrystallized from ethanol, m. p. 102–103°C.

*Chloroform* — p. a., from factory for pure reagents, Vladaja, Bulgaria, dried with calcium chloride, distilled, and kept under molecular sieve 4 Å.

*Acetonitrile* — pure, from Laborchemie-Apolda, DDR, dried with calcium chloride, distilled, and kept under molecular sieve 4 Å.

*Acetone* — p. a., from factory for pure reagents, Vladaja, Bulgaria. Purified from aldehydes by treatment with silver nitrate and sodium hydroxide. The mixture was stirred for 10 min, the obtained precipitate was filtered off, and the filtrate was dried with potassium carbonate. After filtration, acetone was distilled, b. p. 55°C, and kept under molecular sieve 4 Å.

*Benzene* — p. a., from Chemapol, Czechoslovakia. Purified from thiophene and dried with sodium.

*Deuteriochloroform* — 99,95% D, Chemapol, Czechoslovakia; *Perdeuteroacetonitrile* — 85% D, Isokomerz, DDR; *Perdeuteroacetone* — 99,70% D, Isokomerz, DDR; *Perdeutero-benzene* — 99,60% D, Merck, BRD; *Perdeuterotetrachloroethane* — 99,0% D, Merck, BRD.

### Copolymerization

Mixtures of the monomers with different mole ratios (concentration 2 mol/l) were prepared and 1 mol-% AIBN related to each monomer was added. The mixtures were put into glass ampoules, twice frozen, and degassed under vacuum,  $10^{-3}$ – $10^{-4}$  mm Hg (0,14 Pa–0,014 Pa). The sealed ampoules were put in a thermostat at 60°C for a fixed time. The polymerization in chloroform, benzene, and acetone was homogeneous and the obtained solutions of the copolymers were precipitated in methanol. In acetonitrile the copolymers fell down as a white precipitate. The solvent was decanted and the precipitate dissolved in benzene. To the copolymers with high contents of AN some dimethylformamide was added in order to get full dissolution. The solutions were precipitated with methanol.

All copolymers were purified by dissolving in benzene and precipitating with a tenfold excess of methanol.

In all experiments the conversion was about 10%.

### Analysis and apparatus

The content of acrylonitrile units in the copolymers obtained was determined on the basis of the elemental analysis for nitrogen. The composition of some copolymers was determined from their <sup>1</sup>H NMR spectra by a known method<sup>5</sup>).

The determination of the relative reactivity ratios of the monomers and of their errors was carried out with a computer type "Wang-2200 B" using a known program<sup>6</sup>).

The <sup>1</sup>H NMR spectra of the copolymers were recorded on the spectrometers "Varian" at 100 MHz and "Tesla-BS 467" at 80 MHz. Perdeuterotetrachloroethane was used as a solvent for the copolymers and the apparatus was adjusted according to the signal of the solvent at 110°C. The <sup>1</sup>H NMR spectra of the mixtures 2-NM/AN in deuteriochloroform were recorded on a spectrometer "Tesla-BS 467" with tetramethylsilane (TMS) as internal reference.

The IR spectra were recorded on a spectrometer "Karl Zeiss — Jena", model UR 20.

The viscometric measurements were carried out on 0,4 wt.-% THF solutions at 25°C.

## Results and discussion

The results from the experiments on copolymerization of 2-naphthyl methacrylate (2-NM) and acrylonitrile (AN) in chloroform, benzene, acetone, and acetonitrile are given in Tab. 1. It is seen that the time of heating necessary for a conversion of about 10% increases with the increase of the quantity of AN in the initial monomer mixture. The AN quantity influences also the process of copolymerization decreasing the viscosity number of the obtained copolymers. In all solvents used the copolymers with high contents of AN exhibit low values of viscosity.

Tab. 1. Copolymerization of 2-naphthyl methacrylate (2-NM) and acrylonitrile (AN) at  $T = 60^\circ\text{C}$  in chloroform, benzene, acetone, and acetonitrile in presence of 1 mol-% AIBN

Solvent (dielectric constant)	Time of polymerization in min	Conversion in wt.-%	$\eta_{sp}/c$ $\text{cm}^3 \cdot \text{g}^{-1}$	Content of AN in wt.-%		
				Initial mixture	Copolymer	
					det. by elemental analysis	det. by $^1\text{H}$ NMR
Chloroform (4,7)	30	12,8		3,4	3,1	3,1
	35	17,8	0,334	4,8	4,0	
	50	15,4	0,285	7,7	5,0	
	55	10,3		20,0	9,6	10,0
	90	9,2		44,2	14,8	
	90	6,0		63,6	29,1	28,0
	120	7,0		69,2	27,4	
Benzene (2,28)	30	6,3	0,374	4,8	4,7	
	25	4,8		7,7	6,0	
	35	5,2	0,249	20,0	9,9	
	80	9,1		42,8	16,2	
	90	5,4		55,5	22,7	
	90	5,6		63,6	30,7	32,1
	100	8,0		69,2	37,4	
Acetone (20,70)	20	7,1		4,8	6,8	
	18	4,8	0,309	7,7	6,6	
	45	8,2		20,0	10,3	11,1
	70	3,9		42,8	19,7	
	120	12,2		55,5	22,9	
	120	9,7	0,154	63,6	26,7	
	140	10,3		69,2	31,3	
Acetonitrile (36,20)	15	5,0		3,4	5,1	5,7
	25	5,0		4,8	6,2	5,2
	50	10,3		20,0	8,4	9,5
	65	6,5	0,211	42,9	14,5	
	90	9,2		55,5	18,2	19,7
	100	11,2		63,6	24,1	
	100	7,4	0,162	69,2	30,9	30,4

On the basis of the data in Tab. 1 the relative reactivity ratios  $r_{2\text{-NM}}$  and  $r_{\text{AN}}$  of the two monomers were calculated by the methods of Fineman-Ross (F-R), Kelen-Tüdös (K-T)<sup>7)</sup>, and Joshi-Joshi (J-J)<sup>8)</sup> (Tab. 2). It is seen that the  $r$ -values obtained by all three methods are in good agreement. The J-J and K-T methods give slightly higher results than F-R. The higher  $r$ -values by K-T are accompanied by larger errors compared with the other methods. This may be due to the nonlinear distribution of the points obtained by the K-T plot (Fig. 1). Such a nonlinear distribution has been observed by other authors, calculating the  $r$ -values of copolymerization systems of monomers forming charge-transfer complexes<sup>9, 10)</sup>.

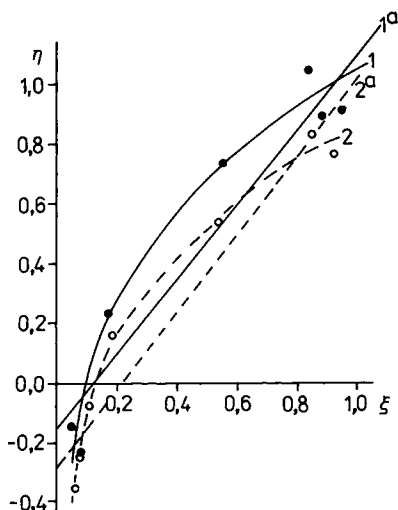


Fig. 1. Kelen-Tüdös plot<sup>7)</sup> for copolymerization of 2-naphthyl methacrylate and acrylonitrile in (1): chloroform ((1<sup>a</sup>): straight line obtained by the least squares method), (2): benzene ((2<sup>a</sup>): straight line obtained by the least squares method)

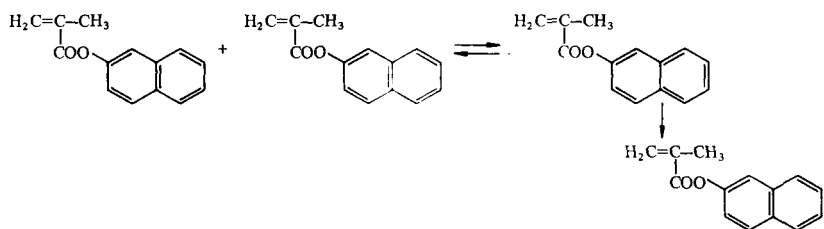
In chloroform and benzene (solvents with low dielectric constants)  $r_{2\text{-NM}}$  have relatively high values,  $r_{2\text{-NM}}$  in benzene being a little bit lower than in chloroform. In acetone and acetonitrile (solvents with high dielectric constants) the  $r_{2\text{-NM}}$  values decrease considerably. This result does not agree with the changes of  $r_{2\text{-NM}}$  observed previously by studying the copolymerization of 2-NM with methyl methacrylate (MMA), where  $r_{2\text{-NM}}$  increases in the solvents with high dielectric constants<sup>1, 2)</sup>.  $r_{\text{AN}}$  is practically unaffected by the solvent and its values are close to 0 which means they are lower than  $r_{\text{AN}}$  in the copolymerization MMA-AN ( $r_{\text{AN}} = 0,15$ ;  $r_{\text{MMA}} = 1,20$ )<sup>11)</sup>. The lower values of  $r_{2\text{-NM}}$  and  $r_{\text{AN}}$  show that 2-NM tends to copolymerize with AN more readily than MMA does.

However, in the copolymerization of 2-NM and AN an increased tendency of the 2-NM molecules to react with their own radicals in chloroform and benzene is observed. This fact may be explained by the association between 2-NM molecules previously observed by us in chloroform<sup>12)</sup>. In a medium with a high dielectric constant, as in acetone and acetonitrile, the molecules of 2-NM are surrounded by the

Tab. 2. Copolymerization reactivity ratios of 2-naphthyl methacrylate ( $r_{2\text{NM}}$ ) and acrylonitrile ( $r_{\text{AN}}$ ) in various solvents calculated by the Fineman-Ross (F-R), Joshi-Joshi (J-J), and Kelen-Tüdös (K-T) methods

Solvent	F-R		J-J		K-T	
	$r_{2\text{NM}}$	$r_{\text{AN}}$	$r_{2\text{NM}}$	$r_{\text{AN}}$	$r_{2\text{NM}}$	$r_{\text{AN}}$
Chloroform	$0,96 \pm 0,05$	$0,00 \pm 0,02$	$1,04 \pm 0,07$	$0,02 \pm 0,07$	$1,10 \pm 0,20$	$0,05 \pm 0,03$
Benzene	$0,84 \pm 0,09$	$0,01 \pm 0,04$	$0,94 \pm 0,07$	$0,06 \pm 0,10$	$0,98 \pm 0,26$	$0,09 \pm 0,04$
Acetonitrile	$0,52 \pm 0,09$	$0,00 \pm 0,02$	$0,58 \pm 0,05$	$0,00 \pm 0,18$	$0,63 \pm 0,26$	$0,00 \pm 0,03$
Acetone	$0,51 \pm 0,06$	$0,00 \pm 0,03$	$0,66 \pm 0,09$	$0,08 \pm 0,03$	$0,77 \pm 0,27$	$0,07 \pm 0,05$

polar molecules of the solvent. The formation of associates between the 2-NM molecules is strongly hindered and the equilibrium is drawn to the left. This leads to a decrease in the value of  $r_{2\text{-NM}}$ .



(acetone, acetonitrile)

(chloroform, benzene)

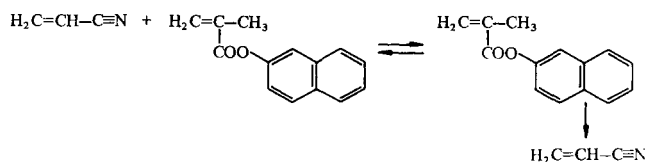
In the IR spectra of 2-NM, recorded in the four solvents (Tab. 3), changes in the positions of the absorption maxima in dependence of the medium were observed. In chloroform the out-of-plane vibrations of the aromatic nucleus are shifted to higher

Tab. 3. Characteristic IR absorption maxima of 2-naphthyl methacrylate in different solvents

Solvent	Wave number in $\text{cm}^{-1}$		
	C—H	$=\text{CH}_2$	C=O
Chloroform	825, 840	947	1 725
Benzene	— —	947	1 733
Acetone	753, 812	950	—
Acetonitrile	775, 812	950	1 731

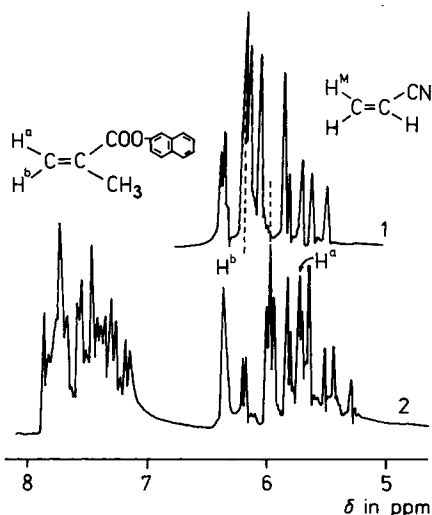
wave number and the stretching vibration of the carbonyl group,  $\nu_{\text{CO}}$ , to lower wave number compared with its position in acetonitrile. This confirms the association between the molecules of 2-NM observed by  $^1\text{H}$  NMR<sup>12)</sup>. In benzene  $\nu_{\text{CO}}$  appears at  $1733\text{ cm}^{-1}$ , so that a partial interaction of 2-NM with the solvent benzene can be assumed.

AN and 2-NM may form associates according to the scheme:



An evidence for the existence of this type of complex is given by the  $^1\text{H}$  NMR spectra of AN in deuteriochloroform and of an equimolar mixture of 2-NM and AN in the same solvent (Fig. 2). It can be seen that in the spectrum of the mixture the signals of AN are shifted toward higher magnetic field. The strongest signal of  $\text{H}^{\text{M}}$  in the multiplet of AN protons is shifted by 0,17 p.p.m. Comparing the  $^1\text{H}$  NMR spectra of AN taken in perdeuteroacetone and perdeuteroacetonitrile with those of mixtures of 2-NM and AN in the same solvents the shift of the signals for the AN protons is quite insignificant (0,01 – 0,05 p.p.m.). This shows that in these solvents the equilibrium of complex formation is shifted to dissociation.

Fig. 2.  $^1\text{H}$  NMR spectra (at 80 MHz) of acrylonitrile (1) and of an equimolar mixture of acrylonitrile and 2-naphthyl methacrylate (2) in deuteriochloroform



In order to determine the stability constant of the complex between 2-NM and AN in chloroform the  $^1\text{H}$  NMR spectra of several mixtures of 2-NM and AN having mole ratios in the interval from 1:2 to 5:1 were recorded. The chemical shifts of the most intensive signal in the spectrum of AN in its mixtures were used for the calculation by

Tab. 4. Determination of the stability constant of the complex 2-NM/AN in deuteriochloroform

No.	Mole ratio 2-NM/AN	$\delta$ (AN obs.)	$\Delta^{\text{A}}$ <sup>a)</sup>	$1/\Delta^{\text{A}}$	$\frac{m_{\text{D}}}{\text{mol} \cdot \text{l}^{-1}}$ <sup>b)</sup>	$1/m_{\text{D}}$ $\text{l} \cdot \text{mol}^{-1}$
1	0,5:1	6,03	0,11	9,09	0,51	1,96
2	1,0:1	5,97	0,17	5,88	0,80	1,25
3	1,5:1	6,02	0,11	8,69	0,56	1,79
4	3,0:1	6,02	0,12	8,33	0,60	1,67
5	5,0:1	6,00	0,13	7,69	0,62	1,61

<sup>a)</sup>  $\Delta^{\text{A}} = \delta_{\text{AN}} - \delta_{\text{AN obs.}}$

<sup>b)</sup>  $m_{\text{D}}$ : donor concentration.

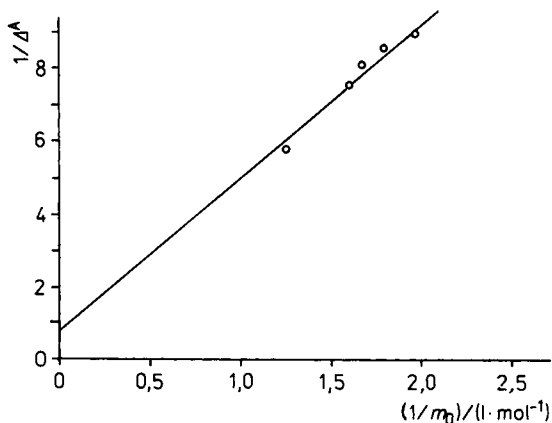


Fig. 3. Hanna-Ashbaugh plot for 2-naphthyl methacrylate (2-NM)-acrylonitrile (AN) in deuteriochloroform;  $m_D$ : donor conc.;  $\Delta^A = \delta_{AN} - \delta_{AN}^{obs.}$  ( $\delta_{AN}^{obs.}$ : chemical shift of AN protons in  $CDCl_3$  solutions of AN + 2-NM)

the Hanna-Ashbaugh method<sup>13)</sup>. The value of  $K$  is  $0,18 \text{ l} \cdot \text{mol}^{-1}$  (Tab. 3, Fig. 3). This value is lower than the value of the stability constant of the complex between MMA and naphthalene which is  $K = 0,22 \text{ l} \cdot \text{mol}^{-1}$ <sup>12)</sup>. This shows that in chloroform and benzene (solvents with low dielectric constants) complexes between 2-NM molecules as well as complexes between 2-NM and AN exist simultaneously.

The existence of a complex between 2-NM and AN can explain the decrease of  $r_{2-NM}$  (Tab. 2) in comparison to the relative reactivity ratio of MMA in its copolymerization with AN. The  $r_{2-NM}$  value in benzene and chloroform is similar to the value of  $r_{BMA}$  in the copolymerization of benzyl methacrylate (BMA) with AN ( $r_{AN} = 0,28$ ;  $r_{BMA} = 0,82$ )<sup>14)</sup>.

The unexpected decrease of  $r_{2-NM}$  in the polar solvents is difficult to be explained, but it correlates with the results obtained by other authors studying the copolymerization of MMA and St in dioxane, acetone, and dimethylformamide. They found that with the increase of solvent polarity  $r_{MMA}$  decreases<sup>15)</sup>.

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