

The influence of molecular interaction on polymerization, 8^{a)}

Copolymerization of monomethyl itaconate with 2-naphthyl methacrylate

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SUMMARY:

The copolymerization of monomethyl itaconate (monomethyl 2-methylenesuccinate, MMI) with 2-naphthyl methacrylate (2-NM) initiated with 2,2'-azoisobutyronitrile (AIBN) in solvents of different dielectric constants and capability to form hydrogen bonds was investigated. The reactivity ratios of the monomer pairs in the different solvents are as follows:

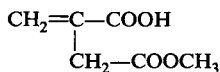
in chloroform: $r_{\text{MMI}} = 2,44 \pm 0,19$ and $r_{2\text{-NM}} = 1,20 \pm 0,28$
 in 1,4-dioxane: $r_{\text{MMI}} = 0,49 \pm 0,04$ and $r_{2\text{-NM}} = 0,97 \pm 0,29$
 in acetone: $r_{\text{MMI}} = 0,15 \pm 0,00$ and $r_{2\text{-NM}} = 0,28 \pm 0,03$
 in acetonitrile: $r_{\text{MMI}} = 0,10 \pm 0,01$ and $r_{2\text{-NM}} = 0,35 \pm 0,14$.

IR and ¹H NMR spectroscopy studies show the influence of the solvent on the capability of the monomers to form hydrogen bonds and donor-acceptor associates. The changes in the reactivity ratios of both monomers are attributed to the interaction observed between the monomer molecules as well as between the molecules of the monomers and the respective solvent.

Introduction

The copolymerization of 2-naphthyl methacrylate (2-NM) and 1-naphthyl methacrylate (1-NM) with methyl methacrylate (MMA) in solution exhibits changes of the monomer reactivity ratios depending on the solvent used^{1,2)}. We explained this phenomenon with a complex formation between the methacrylic double bond and the electron donating naphthalene nucleus, depending on the dielectric constant of the solvent³⁾.

Monomethyl itaconate (MMI)^{c)}



a) Part 7: cf. 4).

b) Unfortunately Dr. H. Boudevska has deceased on January 4, 1984.

c) Systematic IUPAC name for itaconic acid: 2-methylenesuccinic acid.

is a monomer containing both ester and carboxylic groups and an electron acceptor double bond. The latter therefore can interact with electron donating monomers. This is the case in the interaction of MMI and styrene (St), we have previously observed. The study of the polymerization of these monomers in different solvents shows that the reactivity ratios of the monomers depend both on the dielectric constants of the medium and on the possibility for hydrogen bond formation between the monomer molecules and the solvent⁴). MMI copolymerizes with MMA in a solution of ethyl acetate and the reactivity ratios found are $r_{\text{MMI}} = 0,03 \pm 0,04$ and $r_{\text{MMA}} = 0,64 \pm 0,37$ ⁵). So far MMI has not been copolymerized with methacrylic derivatives containing aromatic substituents in the alcoholic units.

The present paper deals with the study of the copolymerization of MMI and 2-NM in solvents of different dielectric constants and in solvents which are able to form hydrogen bonds such as chloroform, 1,4-dioxane, acetone and acetonitrile. The solvents cause a change of the relative reactivity ratios of the two monomers. An attempt was made to explain these changes by means of IR and ¹H NMR spectral measurements of the monomers and their mixtures in different solvents. Some properties of the polymers were also determined.

Experimental part

Reagents:

Monomethyl itaconate (MMI) was obtained by the esterification of itaconic acid (m.p. 168 – 168,5 °C) with methanol in the presence of acetyl chloride as catalyst⁶). Yield: 81%. It was recrystallized from a mixture of benzene/petroleum ether (volume ratio 1 : 2,5) leading to white needles, m. p. 66 – 67 °C.

2-Naphtyl methacrylate (2-NM) was obtained from methacryloyl chloride and the sodium salt of 2-naphtol⁷). The product was washed subsequently with 5 wt.-% aqueous NaOH and water till neutral reaction and was recrystallized from 70 vol.-% aqueous ethanol solution. Yield: 32%, m. p. 66 °C.

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

Chloroform, p. a., from the factory for pure reagents, Vladaja, Bulgaria, dried with CaCl₂, distilled and kept over molecular sieve (4 Å).

Acetonitrile, pure, from Laborchemie-Apolda, DDR, dried with CaCl₂, distilled and kept over molecular sieve (4 Å).

Acetone, purified from aldehydes by a treatment with silver nitrate and sodium hydroxide. The mixture was stirred for 10 min, the obtained precipitate was filtered and the filtrate dried with sodium carbonate. After filtration the acetone was distilled, b. p. 55 °C (710 mmHg), and kept over molecular sieve (4 Å).

1,4-Dioxane, p. a. from Reanal, Budapest, Hungary, dried over sodium and distilled.

Benzene, p. a. from Chemapol, Czechoslovakia, purified from thiophene and dried with sodium.

Petroleum ether, from Factory for pure reagents, Bourgas, Bulgaria, boiling range 40 – 80 °C.

Deuteriochloroform, 99,95% D, Chemapol, Czechoslovakia; *Perdeutero-1,4-dioxane*, 99,00% D, Merck, BRD; *Perdeuteroacetone*, 99,70% D, Izokomerz, DDR; *Perdeuteroacetonitrile*, 85,00% D, Isokomerz, DDR.

Copolymerization:

To 1 mol/l solutions of the mixtures with different mole ratios of the monomers 0,5 mol-% (with reference to both monomers) 2,2'-azoisobutyronitrile was added. The solutions were placed into glass ampoules, twice frozen and evacuated (10^{-4} mmHg). The sealed ampoules were heated in a thermostat at 60 °C for a definite time. The copolymers obtained in chloroform, 1,4-dioxane and acetone were precipitated with methanol (for mole ratios [MMI]/[2-NM] between 1:7 and 1:1) or in petroleum ether (for mole ratios [MMI]/[2-NM] between 3:1 and 7:1). The copolymers, obtained in acetonitrile, precipitated during the polymerization. The precipitate was separated from the solution, dissolved in 1,4-dioxane and precipitated with methanol or petroleum ether.

All copolymers were reprecipitated from 1,4-dioxane with methanol or petroleum ether depending on the ratio [MMI]/[2-NM], and dried under vacuum (1 mmHg) at 25 °C.

Analysis:

The content of MMI was determined as the copolymer was dissolved in tetrahydrofuran and titrated with 0,1 M solution of potassium hydroxide in ethanol in the presence of thymol blue as indicator.

The determination of the reactivity ratios of the monomers and the errors as calculated by the least squares method was made according to the method of Fineman and Ross with a computer type "Hewlett-Packard", model HP 85, USA and according to the Kelen-Tüdös method⁸⁾.

The ¹H NMR spectra were recorded at 60 MHz with a spectrometer Tesla BS 467 in the solvents deuteriochloroform and perdeuteroacetonitrile at 25 °C with tetramethylsilane as internal reference. For the determination of the stability constant of the complex between MMI and 2-NM in chloroform 10 wt.-% solutions of MMI and mixtures of MMI with 2-NM in mole ratios between 1:0,5 and 1:3 in deuteriochloroform were used. The results were treated by the Hanna-Ashbaugh method⁹⁾ based on the following equation:

$$\frac{1}{\Delta(A)} = \frac{1}{K \cdot \Delta(A)_{AD}} \cdot \frac{1}{m_D} + \frac{1}{\Delta(A)_{AD}}$$

where: $\Delta(A) = \delta_{MMI} - \delta_{obs}$

δ_{MMI} : chemical shift of the COOH proton of MMI in chloroform

δ_{obs} : chemical shift of the COOH proton of MMI in chloroform solution of MMI and 2-NM

$\Delta(A)_{AD} = \delta_{AD}^{(A)} - \delta_{MMI}$

$\delta_{AD}^{(A)}$: chemical shift of the COOH proton of MMI in the pure complex

m_D : amount-of-substance concentration of the donor 2-NM

K : stability constant of the complex

The IR spectra were recorded with a spectrophotometer "Karl Zeiss"-Jena, Model UR-20.

The reduced viscosities of the copolymers were determined in 0,5 wt.-% solution of 1,4-dioxane at 25 °C.

Results and discussion

The copolymerization of MMI and 2-NM was studied in solvents well dissolving both monomers and their mixtures in different mole ratios. The solvents used are different as to their dielectric constants and their ability to form hydrogen bonds. The results obtained for the copolymerizations in chloroform, 1,4-dioxane, acetone, and acetonitrile in the presence of equal quantities of the initiator AIBN with respect to the monomers are given in Tab. 1. It can be seen that the time for reaching nearly

equal conversions depends upon the nature of the solvent used. The longest time of heating was necessary for acetonitrile, the solvent with the highest dielectric constant. The duration of the heating depends also on the quantity of MMI in the reaction mixture. With increasing the fraction of MMI in the initial mixture the heating time increases too, independent of the solvent used. MMI does not only retard the process of copolymerization but also lowers the reduced viscosity of the resultant copolymers. In all solvents those copolymers with a high content of MMI were those with the low reduced viscosity values.

From the data for the copolymerizations of the initial monomer mixtures and those of the copolymers determined by the analysis of the MMI contents in the copolymers (Tab. 1), the relative reactivity ratios r of the monomers in the four solvents were

Tab. 1. Copolymerization of monomethyl itaconate (MMI) and 2-naphthyl methacrylate (2-NM) at 60°C in chloroform, 1,4-dioxane, acetone, and acetonitrile in the presence of 0,5 mol-% 2,2'-azoisobutyronitrile (AIBN)

Solvent (dielectric constant)	Time of copolymerization in min	Conversion in %	$\frac{\eta_{sp}}{c}$ ^{a)} cm ³ · g ⁻¹	Content of MMI in wt.-%	
				in initial mixture	in copoly- mer
Chloroform (4,70)	60	3,1	—	8,8	12,9
	150	14,2	—	11,9	15,0
	180	14,9	1,8	18,4	20,5
	180	14,9	—	40,4	44,2
	240	12,6	—	67,0	79,2
	240	15,3	1,1	77,2	58,5
	240	15,2	—	82,6	91,6
1,4-Dioxane (2,21)	25	15,9	3,1	8,8	13,7
	30	12,8	—	11,9	14,3
	35	15,2	—	18,4	15,0
	60	6,1	1,7	40,4	32,2
	150	15,4	—	67,0	51,9
	160	9,1	—	77,2	64,4
	170	7,1	—	82,6	74,4
Acetone (20,70)	15	5,3	—	8,8	21,1
	15	7,1	—	11,9	24,7
	20	10,5	0,7	18,4	20,0
	50	4,8	—	40,4	37,4
	105	3,5	—	67,0	46,7
	180	1,8	0,6	77,2	53,1
	300	6,3	—	82,6	57,7
Acetonitrile (36,20)	120	15,1	2,2	8,8	26,3
	120	11,3	—	11,9	25,9
	180	8,1	—	18,4	27,3
	240	11,0	—	40,4	32,9
	600	10,2	—	67,0	42,8
	860	10,2	1,0	77,2	46,7
	870	7,9	—	82,6	53,5

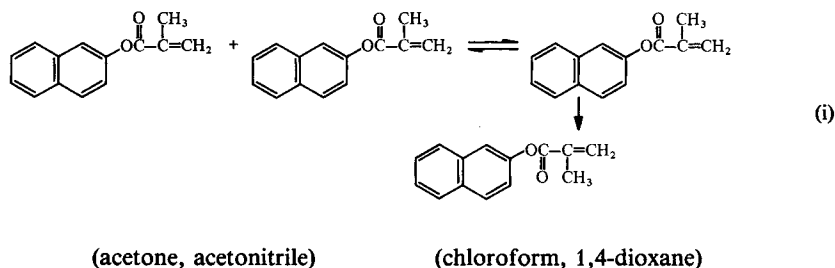
^{a)} Reduced viscosity in solution of 0,5 wt.-% copolymer in 1,4-dioxane.

Tab. 2. Copolymerization reactivity ratios of monomethyl itaconate (r_{MMI}) and 2-naphthyl methacrylate ($r_{2\text{-NM}}$) in chloroform, 1,4-dioxane, acetone, and acetonitrile, as determined by the Fineman-Ross (F-R) and Kelen-Tüdös (K-T) methods

Solvent	F-R method			K-T method		
	r_{MMI}	$r_{2\text{-NM}}$	$r_{\text{MMI}} \times r_{2\text{-NM}}$	r_{MMI}	$r_{2\text{-NM}}$	$r_{\text{MMI}} \times r_{2\text{-NM}}$
Chloroform	$2,44 \pm 0,19$	$1,20 \pm 0,28$	2,93	$2,31 \pm 0,77$	$0,87 \pm 0,14$	2,01
1,4-Dioxane	$0,49 \pm 0,04$	$0,97 \pm 0,29$	0,48	$0,31 \pm 0,10$	$0,75 \pm 0,12$	0,23
Acetone	$0,15 \pm 0,00$	$0,28 \pm 0,03$	0,04	$0,05 \pm 0,01$	$0,31 \pm 0,04$	0,02
Acetonitrile	$0,10 \pm 0,01$	$0,35 \pm 0,14$	0,04	$0,06 \pm 0,02$	$0,28 \pm 0,05$	0,02

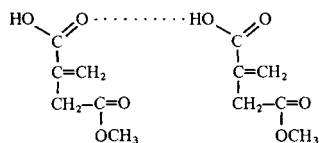
calculated. The results are shown in Tab. 2. In chloroform the r -values of both monomers are highest; in 1,4-dioxane they are lower and in acetone and acetonitrile they reach their lowest values. The r_{MMI} value varies in a wide range depending on the solvent, whereas $r_{2\text{-NM}}$ is less sensitive to a change of the solvent.

On the basis of our previous investigations on the copolymerization of MMI and styrene in the same solvents⁴⁾ it can be assumed that in chloroform, a solvent with a low dielectric constant which is incapable of interacting with MMI by hydrogen bond formation, MMI and 2-NM form an associate. This usually leads to lower r -values and a tendency of alternation. But, in the copolymerization of MMI and 2-NM the opposite phenomenon is observed. The monomers tend to react with their own radicals. This unexpected result could be attributed to a complex formation between the 2-NM molecules in the chloroform medium as we have previously observed³⁾:

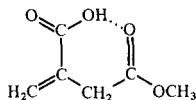


In media with a high dielectric constant the 2-NM molecules are surrounded by the polar molecules of the solvent and the equilibrium of complex formation according to Eq. (i) is shifted to the left.

Moreover, the association of MMI is influenced by the medium, too. In chloroform the formation of intermolecular (iia) and intramolecular (iib) hydrogen bonds between the MMI molecules was observed as follows:



(iia)



(iib)

This association via hydrogen bonds has been proven by IR spectroscopy and ^1H NMR ⁴⁾.

In the IR spectra of 2-NM (Tab. 3) the range $700 - 920\text{ cm}^{-1}$ is characteristic for the out-of-plane vibrations (δ_{CH}) of the aromatic nuclei. In acetonitrile and 1,4-dioxane the absorption maxima are intensive and are situated at 775 and 812 cm^{-1} , while in chloroform the intensities decrease strongly and the maxima are shifted to 815 and 840 cm^{-1} , respectively.

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

Solvents	Wave numbers in cm^{-1} of		
	C—H	$=\text{CH}_2$	C=O
Chloroform	815, 840	947	1 725
1,4-Dioxane	753, 812	950	1 733
Acetonitrile	775, 812	950	1 731

The range $1700 - 1800\text{ cm}^{-1}$ is characteristic for the stretching vibrations of the carbonyl group ($\nu_{\text{C=O}}$). In the solution of 2-NM in chloroform this absorption maximum is situated at 1725 cm^{-1} , while in acetonitrile and in 1,4-dioxane it appears at 1731 and 1733 cm^{-1} , respectively. The shift of the out-of-plane vibration of the aromatic nuclei towards higher wave numbers together with the shift of the stretching vibration of the CO-group towards lower ones, confirms the association of the 2-NM molecules previously observed by ^1H NMR spectroscopy³⁾.

The ^1H NMR spectra of MMI and of their mixtures in chloroform and acetonitrile are given in Figs. 1 and 2. The chemical shifts of the signals for the different protons are given in Tab. 4. Evidence for the interaction is presented by the signal of the $-\text{COOH}$ proton in MMI, which in chloroform appears at the lowest field and the differences $\Delta = \delta_{(\text{H}_b)} - \delta_{(\text{H}_a)}$ of the methylene protons in MMI and in 2-NM, respectively.

The 2-NM molecules associated between themselves and separately the associated MMI molecules tend to increase the values of the relative reactivity ratios observed in

Fig. 1. ^1H NMR spectra (60 MHz) of 2-naphtyl methacrylate (2-NM), (trace 1), of monomethyl itaconate (MMI), (2), and of the [2-NM]/[MMI] = 1:1 mixture, (3), in deuteriochloroform

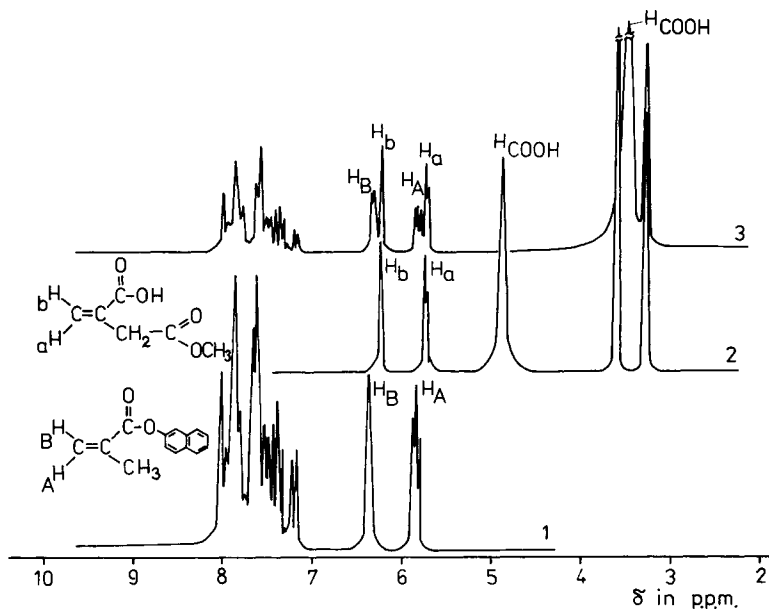
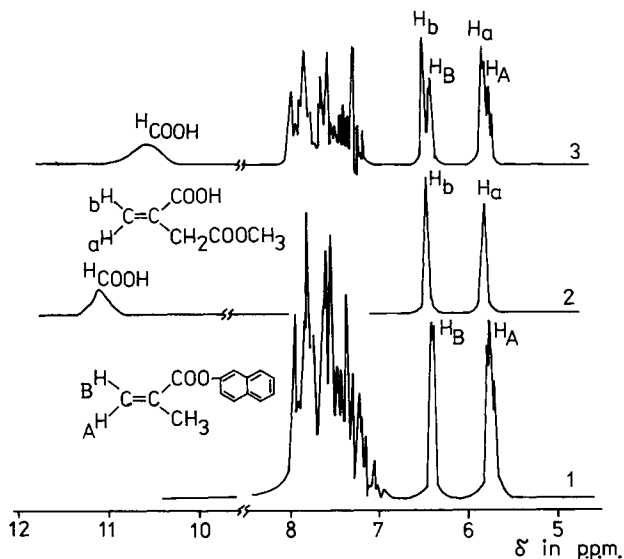


Fig. 2. ^1H NMR spectra (60 MHz) of 2-naphtyl methacrylate (2-NM), (trace 1), of monomethyl itaconate (MMI), (2), and of the [2-NM]/[MMI] = 1:1 mixture, (3), in perdeuteroacetonitrile

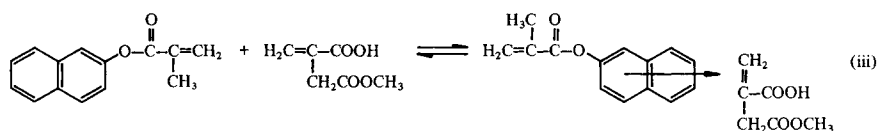
Tab. 4. Chemical shifts δ (in p. p. m.) in the ^1H NMR spectra of monomethyl itaconate (MMI) and 2-naphthyl methacrylate (2-NM) and their equimolar mixtures (values marked with asterisk*) in different solvents

Solvent	MMI ^{a)}				2-NM ^{b)}				
	$\delta_{(\text{H}_a)}$	$\delta_{(\text{H}_b)}$	Δ	$\delta_{(\text{COOH})}$	$\delta_{(\text{H}_A)}$	$\delta_{(\text{H}_B)}$	Δ'	$\delta_{(\alpha\text{CH}_3)}$	$\delta_{(\text{naph.nuc.})}$
Chloroform	5,816	6,450	0,634	11,133	5,633	6,266	0,633	1,966	6,766 – 7,890
	5,616*	6,266*	0,650*	10,050*	5,566*	6,183*	0,617*	1,900*	6,883 – 7,893*
1,4-Dioxane	5,700	6,233	0,533	8,061	—	—	—	—	—
Acetone	5,800	6,300	0,500	5,800	5,850	6,375	0,525	2,100	—
Acetonitrile	5,633	6,150	0,517	4,783	5,716	6,250	0,534	—	7,000 – 7,960
	5,716*	6,233*	0,517*	3,500*	5,816*	6,316*	0,500*	—	7,150 – 8,033*

a) Δ (in p. p. m.) = $\delta_{(\text{H}_b)} - \delta_{(\text{H}_a)}$.

b) Δ' (in p. p. m.) = $\delta_{(\text{H}_B)} - \delta_{(\text{H}_A)}$.

chloroform. A third possible interaction between MMI and 2-NM depending on the solvent can be expressed by the following scheme (Eq. (iii)):



The stability constant of this complex as calculated by the Hanna-Ashbaugh method on the basis of the shift of the most sensitive signal of the $-\text{COOH}$ proton in the ^1H NMR spectra of MMI/2-NM mixtures of different mole ratios (Tab. 5) is

Tab. 5. Determination of the stability constant of the complex between monomethyl itaconate (MMI) and 2-naphthyl methacrylate (2-NM) in deuteriochloroform^{a)}

N	Mole ratio MMI/2-NM	δ_{COOH}	$\Delta^{(A)}$	$\frac{m_D}{\text{mol} \cdot \text{l}^{-1}}$
1	1:0,5	10,966	0,167	0,2004
2	1:1,0	10,233	0,900	0,2747
3	1:1,5	10,266	0,867	0,3372
4	1:2,0	9,850	1,283	0,3490
5	1:2,5	9,533	1,600	0,3750
6	1:3,0	9,566	1,567	0,3750

a) Explanation of symbols, see Exptl. Part.

$0,18 \text{ l} \cdot \text{mol}^{-1}$. This numerical value is lower than the corresponding value for the complex between 2-NM and MMA being $0,22^3)$. This shows that probably in chloroform three kinds of complex formations take place. But, the complexes between 2-NM molecules and those between MMI molecules connected by hydrogen bonds predominate.

In 1,4-dioxane — a solvent with a low dielectric constant — the 2-NM molecules remain still associated. MMI forms hydrogen bonds with 1,4-dioxane. This leads to a slight decrease of the $r_{2\text{-NM}}$ value in comparison to the one in chloroform and to a strong decrease of r_{MMI} (Tab. 2). In acetone and acetonitrile — solvents with high dielectric constants — the association between monomer molecules is destroyed, leading to a decrease of the copolymerization reactivity ratio values r .

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