

The influence of molecular interaction on polymerization, 10^{a)} On the copolymerization of methacrylic acid with styrene

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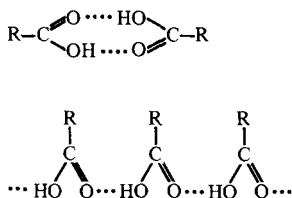
SUMMARY:

Free radical copolymerization of methacrylic acid (MA) with styrene (St) at 60 °C, initiated by 2,2'-azoisobutyronitrile (AIBN) is carried out in hydrogen-bond forming solvents and in solvents not capable of forming hydrogen bonds but exhibiting different dielectric constants. The influence of the solvent on copolymerization reactivity ratios, rate of polymerization, composition, molecular weight and polydispersity of the copolymers obtained is shown. The reactivity ratios of methacrylic acid r_{MA} and of styrene r_{St} are determined by two different methods with good agreement. The values obtained by the Kelen-Tüdös method are as follows: in carbon tetrachloride: $r_{MA} = 0,54 \pm 0,01$; $r_{St} = 0,06 \pm 0,03$; in chloroform: $r_{MA} = 0,51 \pm 0,01$; $r_{St} = 0,08 \pm 0,03$; in acetone: $r_{MA} = 0,43 \pm 0,00$; $r_{St} = 0,65 \pm 0,02$; in 1,4-dioxane: $r_{MA} = 0,41 \pm 0,02$; $r_{St} = 0,59 \pm 0,05$; in acetonitrile: $r_{MA} = 0,06 \pm 0,02$; $r_{St} = 0,29 \pm 0,00$.

Changes of reactivity ratios depending on the medium are explained on the basis of the results from IR and ¹H NMR spectroscopy and gel permeation chromatography (GPC).

Introduction

Many papers deal with the influence of the reaction medium on the rate of polymerization, the molecular weight, the structure and the reactivity ratios of unsaturated carboxylic acids^{1,2)}. It is known³⁾ that depending on the medium carboxylic acids can associate via hydrogen bonds to dimers or linear plurimolecular aggregates:



These associates exist in nonpolar (inert) solvents and decompose in solvents capable of hydrogen bond formation with the COOH group as well as in polar solvents not capable of hydrogen bond formation. Formation and decomposition of

a) Part 9: H. Boudevska, V. Sinigersky, Makromol. Chem. **185**, 531 (1984).

b) Deceased.

such aggregates may influence the rate of polymerization, the steric arrangement in the polymer and the behaviour of the monomers in the copolymerization process.

The effect of hydrogen bond formation on the reactivity of unsaturated carboxylic acids has been investigated first for the systems methacrylic acid/methyl methacrylate and methacrylic acid/styrene following their copolymerization in bulk and in *N,N*-dimethylformamide (DMF)⁴. Later, the copolymerization of methacrylic acid (MA) and acrylamide with styrene (St) and methyl methacrylate in various solvents have been studied⁵⁻⁸. So far, there are no detailed data describing the influence of solvents differing in their chemical nature on the reactivity of MA in its copolymerization with St.

The present paper is an attempt to cover this gap. The copolymerization of MA with St was carried out in hydrogen bonding solvents (acetone, 1,4-dioxane) and in others, not possessing this feature, but exhibiting different dielectric constants (carbon tetrachloride, chloroform, acetonitrile).

Experimental Part

Reagents: *Methacrylic acid* from Fluka, distilled i. vac., b. p. (5 mmHg) = 51,5°C. *Styrene* from SE "Neftochim" Bourgas, free of stabilizers, twice distilled i. vac. 2,2'-Azoisobutyronitrile from Fluka, recrystallized from ethanol, m. p. = 102–103°C. *Carbon tetrachloride* purum, from Laborchemie Apolda DDR, dried with CaCl₂, distilled and kept with molecular sieve (4 Å). *Chloroform*, p. a. from Factory for pure reagents, Vladaja, Bulgaria, dried with CaCl₂, distilled and kept with molecular sieve (4 Å). *Acetone*, purified from aldehydes by treatment with silver nitrate and sodium hydroxide. The mixture is stirred for 10 min, the obtained precipitate filtered off and dried with sodium carbonate. After filtration the acetone is distilled, b. p. = 55°C, and kept with molecular sieve (4 Å). *1,4-Dioxane*, p. a. from Fluka, dried over sodium and distilled. *Acetonitrile*, purum from Fluka. *Deuteriochloroform*, 99,95% D, from Chemapol, Czechoslovakia; *perdeuteroacetonitrile*, 85,00% D, from Isokomerz, DDR; *perdeuteroacetone*, 99,70% D, from Isokomerz, DDR; *perdeutero-1,4-dioxane*, 99,00% D, from Merck, BRD.

Copolymerization: To 1 mol/l solutions of mixtures with different mole ratios of monomers 0,5 mol-% (with reference to both monomers) of 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 fixed time. In carbon tetrachloride, chloroform and acetonitrile the copolymers fell out as white precipitates, which were filtered, dissolved in methanol or 1,4-dioxane and reprecipitated in petroleum ether. In acetone and 1,4-dioxane the polymerization in the ampoules, containing up to 50 mol-% MA was homogeneous and in those with over 50 mol-% MA it was heterogeneous. In the first case the polymers obtained were precipitated in ethanol and in the second — after filtration — the products were dissolved in methanol and precipitated in diethyl ether.

All polymers were purified by reprecipitation from a suitable solvent and dried i. vac. (1 mmHg) at 25°C.

Analyses: The polymers were analysed for the content of MA. The samples were dissolved in tetrahydrofuran (THF) or a mixed solvent THF/methanol 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 conducted according to the method of Fineman and Ross⁹ with a "Hewlett-Packard" calculator, model HP 85, USA, and according to the Kelen-Tüdös method¹⁰.

The ^1H NMR spectra were recorded at 80 MHz with a spectrometer Tesla BS 487 C of solutions in the deuterated analogs of the solvents used for the copolymerization and tetramethylsilane as internal reference. For the determination of the stability constant of the complex between MA and St in chloroform 10 wt.-% solutions of MA and mixtures of MA and St in mole ratios between 1:0,5 and 1:3 in deuteriochloroform were used. The results were treated according to the Hanna-Ashbaugh method¹¹⁾, based on the following equation:

$$\frac{1}{\Delta(A)} = \frac{1}{K \cdot \Delta_{AD}^{(A)}} \cdot \frac{1}{m_D} = \frac{1}{\Delta_{AD}^{(A)}}$$

where:

$\Delta^{(A)}$: $\delta_{MA} - \delta_{obs}$

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

δ_{obs} : chemical shift of the COOH proton of MA in chloroform solution of MA and St

$\Delta_{AD}^{(A)}$: $\delta_{AD}^{(A)} - \delta_{MA}$

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

m_D : amount of substance concentration of the donor St

K : stability constant of the complex

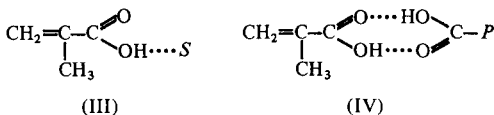
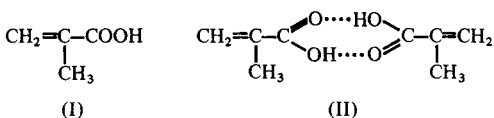
The IR spectra were recorded with a spectrophotometer "Karl Zeiss"-Jena, Model UR-20.

For GPC we used a gel permeation chromatograph type "Waters Associates 244" with Ultra-styragel columns, pore sizes according to producer's specification of 10^5 , 10^4 , 10^3 , 500 and 100 Å, with THF as mobile phase, a flow rate of 1 ml/min, temperature 35 °C and a refractive index detector.

GPC-calibration is performed by polystyrene standards of different molecular weights. The values of number-average molecular weight, \bar{M}_n , weight-average molecular weight, \bar{M}_w , and \bar{M}_w/\bar{M}_n are calculated using M 730 Data Module (Waters Ass.).

Results and discussion

As already known¹²⁾, depending on the solvent, methacrylic acid (MA) can exist in the following forms: monomer (I), dimer (II), associated with a molecule of the solvent S (III) and associated with a carboxylic group of the growing chain of the polymer P (IV):

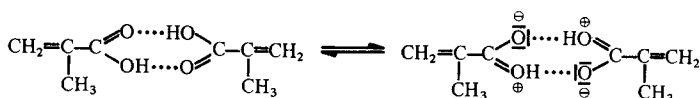


The following scheme shows the equilibria between these forms:





Forms (II) and (IV), existing in bulk and in nonpolar solvents (benzene, chloroform, carbon tetrachloride, exhibit a higher reactivity as compared with form (III) which predominates in polar and hydrogen-bonding solvents. This is due to the complementary resonance stabilisation of the carboxylic dimer, allowing a π -electron cloud transfer through the H-bridge and causing partial delocalization of the π -electrons. The unpaired electron of the corresponding radical is considerably delocalized, too. This way of resonance stabilization is not possible for the solvated carboxylic acid (III) and the corresponding radical.



It is supposed, therefore, that the nature of the solvent influences the reactivity of the unsaturated carboxylic acids by shifting the association equilibria Eqs. (1) – (5) according to the ability of the solvent to form H-bonds with the acid.

That is why for the copolymerization of MA with St we have chosen hydrogen bonding solvents (acetone, 1,4-dioxane) and solvents not possessing this feature but having different polarities (carbon tetrachloride), chloroform, acetonitrile). As ^1H NMR and IR spectroscopy are the most suitable methods for studying hydrogen bonds, we have taken the spectra of MA in the solvents used. The ^1H NMR spectra of MA in chloroform and acetonitrile (Fig. 1) and in 1,4-dioxane and acetone (Fig. 2) show convincingly the influence of the solvent. As already found in our previous papers¹³⁾, it is the carboxylic proton H^{C} which is most sensitive to the change of the solvent. It can be seen from Figs. 1 and 2 that in chloroform the signal of the H^{C} proton appears at lower field, which agrees with other observations on hydrogen bonds¹⁴⁾.

In acetonitrile this signal is shifted to higher field by 7,125 p.p.m. In hydrogen bonding solvents the H^{C} peak is positioned between those in chloroform and acetonitrile. 1,4-Dioxane forms hydrogen bonds but the signal of the H^{C} proton is situated at stronger field compared to chloroform where MA exists in its most reactive form (II). This shows that in 1,4-dioxane the less active form (III) predominates. The H^{C} peak in acetone (forming H-bonds and having a relatively high dielectric constant) is

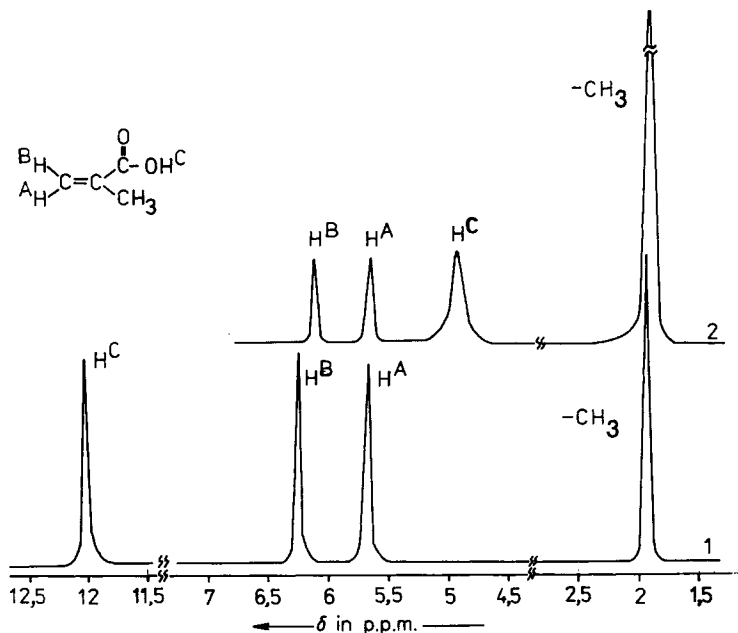


Fig. 1. ^1H NMR spectra (80 MHz) of methacrylic acid (MA) in deuteriochloroform (trace 1) and perdeuteroacetonitrile (2)

strongly shifted to higher field and is positioned near to the signal in acetonitrile. In these two solvents the associates MA/solvent predominate, which are formed either through hydrogen bonds or by polar interactions. This may cause the different reactivity of MA in its copolymerization with St in different solvents.

The chemical shifts of $-\text{CH}_2-$ and $-\text{CH}_3$ protons (Tab. 1) are only slightly affected by the solvent.

The data from the IR spectra fully agree with the results obtained by the ^1H NMR study (Tab. 2). The absorption band of the stretching vibration of the CC double bond is slightly affected by the solvent, whereas that of the COOH group is shifted toward higher wave number by $29 - 31 \text{ cm}^{-1}$ on replacing chloroform by 1,4-dioxane or acetonitrile. This shift is in agreement with the changes observed in the absorption maxima upon hydrogen bond formation¹⁵⁾. The alteration in the position of the absorption band for the OH group confirms the data obtained by the ^1H NMR study. These shifts express the changes in the association equilibria Eqs. (1) – (3) due to the transition from nonpolar to hydrogen-bonding solvents. These results show that depending on the capability of the solvent to form hydrogen bonds the differences in the reactivity of the monomers are to be expected.

The data for the copolymerization of MA with St in various solvents, shown in Tab. 3, prove the changes observed in the ^1H NMR and IR spectra. It is seen from Tab. 3 that the rate up to 10% conversion depends on the nature of the solvent used.

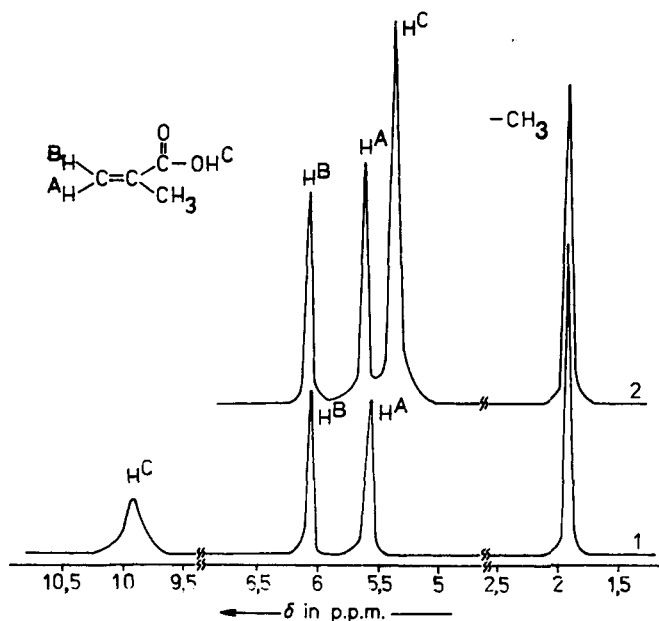


Fig. 2. ^1H NMR spectra (80 MHz) of methacrylic acid (MA) in perdeutero-1,4-dioxane (trace 1) and perdeuteroacetone (2)

Tab. 1. Chemical shifts δ (in p.p.m.) in the ^1H NMR spectra of methacrylic acid (MA) in different solvents. (For notations $\delta(\)$ see Fig. 1; $\delta(\text{COOH}) = \delta(\text{H}^C)$)

| Solvent | $\delta(\text{COOH})$ | $\delta(\text{CH}_3)$ | $\delta(\text{H}^A)$ | $\delta(\text{H}^B)$ | $\Delta = \delta(\text{H}^B) - \delta(\text{H}^A)$ |
|--------------|-----------------------|-----------------------|----------------------|----------------------|--|
| Chloroform | 12,000 | 1,925 | 5,650 | 6,225 | 0,575 |
| Acetone | 5,325 | 1,900 | 5,575 | 6,050 | 0,475 |
| 1,4-Dioxane | 9,925 | 1,900 | 5,550 | 6,050 | 0,500 |
| Acetonitrile | 4,875 | 1,900 | 5,600 | 6,050 | 0,450 |

Tab. 2. Characteristic IR absorption maxima of methacrylic acid (MA) in different solvents

| Solvents | Wave numbers in cm^{-1} of | | |
|--------------|-------------------------------------|----------------|--------------|
| | $=\text{CH}_2$ | $-\text{COOH}$ | $-\text{OH}$ |
| Chloroform | 1 630 | 1 690 | 2 800–3 400 |
| Acetone | — | — | 3 030–3 500 |
| 1,4-Dioxane | 1 634 | 1 719 | 3 000–3 400 |
| Acetonitrile | 1 634 | 1 721 | 3 030–3 500 |

Tab. 3. Copolymerization of methacrylic acid (MA) and styrene (St) at 60 °C in different solvents in the presence of 0,5 mol-% 2,2'-azoisobutyronitrile (AIBN)

| Solvent (dielectric constant) | Time of copolymeris. in min | Conversion in % | Content of MA in wt.-% | |
|-------------------------------------|-----------------------------------|--------------------|------------------------|--------------|
| | | | in monomer mixture | in copolymer |
| Carbon tetra- chloride (2,23) | 240 | 6,4 | 8,4 | 30,6 |
| | 150 | 6,5 | 10,5 | 33,6 |
| | 120 | 1,7 | 14,4 | 46,7 |
| | 60 | 4,8 | 21,6 | 50,6 |
| | 60 | 3,2 | 45,2 | 61,5 |
| | 60 | 8,1 | 71,3 | 69,8 |
| | 60 | 9,6 | 80,5 | 74,0 |
| | 60 | 9,4 | 85,2 | 82,1 |
| | 60 | 8,8 | 88,2 | 85,3 |
| | 270 | 9,8 | 8,4 | 25,4 |
| Chloroform (4,70) | 150 | 4,1 | 10,5 | 36,8 |
| | 120 | 10,9 | 14,4 | 38,2 |
| | 60 | 8,9 | 21,6 | 46,9 |
| | 60 | 9,9 | 45,2 | 62,0 |
| | 60 | 9,5 | 80,5 | 75,3 |
| | 60 | 5,8 | 88,2 | 83,1 |
| | 60 | 10,2 | 8,4 | 11,5 |
| Acetone (20,70) | 1 200 | 11,4 | 10,5 | 13,0 |
| | 960 | 11,4 | 14,4 | 17,8 |
| | 840 | 10,5 | 21,6 | 24,3 |
| | 600 | 10,1 | 45,2 | 45,3 |
| | 200 | 4,7 | 80,5 | 69,7 |
| | 180 | 4,0 | 85,3 | 75,0 |
| | 600 | 12,1 | 8,4 | 12,2 |
| 1,4-Dioxane (2,21) | 480 | 10,5 | 10,5 | 14,1 |
| | 480 | 8,4 | 14,4 | 19,6 |
| | 420 | 9,4 | 21,6 | 25,9 |
| | 280 | 5,7 | 45,2 | 46,4 |
| | 300 | 11,9 | 71,3 | 61,5 |
| | 180 | 10,5 | 80,5 | 66,8 |
| | 720 | 7,3 | 8,4 | 16,9 |
| Acetonitrile (36,20) | 900 | 11,5 | 10,5 | 25,4 |
| | 540 | 8,9 | 14,4 | 29,6 |
| | 300 | 7,2 | 21,6 | 31,6 |
| | 100 | 3,8 | 45,3 | 39,9 |
| | 90 | 10,6 | 71,3 | 48,6 |
| | 60 | 3,7 | 80,5 | 55,0 |
| | 50 | 4,2 | 85,3 | 59,7 |

The highest copolymerization rate is observed in chloroform and in carbon tetrachloride, the lowest in acetone. The contents of MA in the initial mixture also affect the copolymerization rate. Regardless of the solvent used, an increase of the MA concentration in the initial mixture leads to an increase of the copolymerization rate.

The nature of the solvent does not only affect the rate of copolymerization, but also affects the composition of the polymers obtained. Hydrogen bond formation between monomeric MA and solvent (1,4-dioxane or acetone), connected with a decrease in MA reactivity, leads to a decrease of the MA content in the copolymers. The same influence has been found in DMF, pyridine¹⁶⁾ and quinoline¹⁷⁾.

From the data in Tab. 3 the reactivity ratios r of the monomers in the five solvents used have been calculated by two different methods with good agreement (Tab. 4). In chloroform and carbon tetrachloride where the reactive dimer (II) of MA predominates, r_{MA} has the highest value and r_{St} the lowest one. These results are close to the r -values for copolymerization in bulk⁴⁾ ($r_{MA} = 0,66$; $r_{St} = 0,2$). When going from chloroform or carbon tetrachloride to hydrogen-bonding solvents (acetone, 1,4-dioxane) r_{MA} decreases. In acetonitrile (having the highest dielectric constant) r_{MA} reaches its lowest value. The alteration of r_{MA} is accompanied by an alteration of the r_{St} values. With a decrease of k_{21} ($r_{MA} = k_{11}/k_{12}$, $r_{St} = k_{22}/k_{21}$) the r_{St} -values increase.

Tab. 4. Copolymerization reactivity ratios of methacrylic acid (r_{MA}) and styrene (r_{St}) in different solvents calculated according to Fineman-Ross (F-R) and Kelen-Tüdös (K-T)

| Solvent | r_{MA} | | r_{St} | | $r_{MA} \cdot r_{St}$ | |
|----------------------|-------------|-------------|-------------|-------------|-----------------------|------|
| | F-R | K-T | F-R | K-T | F-R | K-T |
| Carbon tetrachloride | 0,50 ± 0,01 | 0,54 ± 0,01 | 0,05 ± 0,03 | 0,06 ± 0,03 | 0,02 | 0,03 |
| Chloroform | 0,55 ± 0,01 | 0,51 ± 0,01 | 0,04 ± 0,06 | 0,08 ± 0,03 | 0,02 | 0,04 |
| Acetone | 0,42 ± 0,01 | 0,43 ± 0,00 | 0,61 ± 0,04 | 0,65 ± 0,02 | 0,26 | 0,27 |
| 1,4-Dioxane | 0,35 ± 0,02 | 0,41 ± 0,02 | 0,48 ± 0,08 | 0,59 ± 0,05 | 0,16 | 0,24 |
| Acetonitrile | 0,12 ± 0,00 | 0,06 ± 0,02 | 0,35 ± 0,06 | 0,29 ± 0,00 | 0,04 | 0,02 |

MA could associate except with its own molecules or with the solvent with St molecules via donor-acceptor interactions:

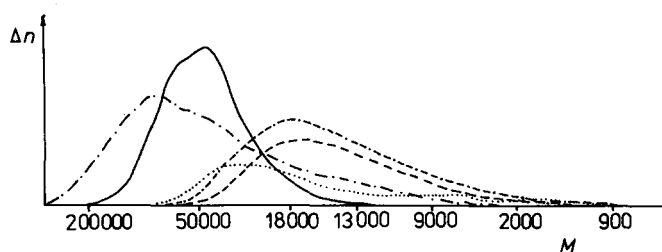


The stability constant of this complex, as calculated by the Hanna-Ashbaugh method on the basis of the H^C -proton shifts in the 1H NMR spectra of MA/St mixtures of different mole ratios in deuteriochloroform (Tab. 5), exhibits the not very high value of $0,11 \text{ l} \cdot \text{mol}^{-1}$. This shows that in chloroform the complexes of hydrogen-bonded MA molecules predominate.

It was interesting to see how far the nature of the solvent influences the molecular weight and the polydispersity of the obtained polymers. That is why we investigated the MA-St copolymers by means of gel permeation chromatography (GPC). The elution curves are given in Fig. 3 and the numerical data for the polydispersity and the

Tab. 5. Data for the determination of the stability constant of the complex between methacrylic acid (MA) and styrene (St) in deuteriochloroform (see Exptl. part)

| No. | Mole ratio MA/St | $\delta(\text{COOH})$ | $\Delta(\text{\AA})$ | $\frac{m_D}{\text{mol} \cdot \text{l}^{-1}}$ |
|-----|---------------------|-----------------------|----------------------|--|
| 1 | 1:0,5 | 11,712 | 0,288 | 0,374 |
| 2 | 1:1,0 | 11,325 | 0,675 | 0,526 |
| 3 | 1:1,5 | 11,275 | 0,725 | 0,638 |
| 4 | 1:2,0 | 11,075 | 0,925 | 0,698 |
| 5 | 1:2,5 | 11,012 | 0,988 | 0,749 |
| 6 | 1:3,0 | 10,700 | 1,300 | 0,787 |

Fig. 3. DPC curves of methacrylic acid/styrene (MA/St) copolymers obtained in carbon tetrachloride (---), chloroform (—), acetone (---), 1,4-dioxane (·····) and acetonitrile (-·-·-); calibration of abscissa with polystyrene standards of different molecular weights; Δn : refractive index differenceTab. 6. Number-average molecular weights (\bar{M}_n) — (polystyrene) — and polydispersity index (\bar{M}_w/\bar{M}_n) of methacrylic acid/styrene copolymers (MA/St), obtained in different solvents at 60°C (see Exptl. part)

| Solvent | Content of MA in copolymer in wt.-% | \bar{M}_n | \bar{M}_w/\bar{M}_n |
|----------------------|---|-------------|-----------------------|
| Carbon tetrachloride | 33,60 | 6 770 | 1,34 |
| Chloroform | 36,82 | 37 650 | 1,51 |
| Acetone | 24,34 | 6 520 | 1,72 |
| 1,4-Dioxane | 25,88 | 6 980 | 3,03 |
| Acetonitrile | 31,56 | 13 630 | 5,26 |

molecular weights in Tab. 6. Comparing these results with the r values obtained (Tab. 4), we found a correlation between the r_{MA} alteration and polydispersity. The copolymers with the highest molecular weight and low polydispersity were obtained by copolymerization of MA with St in chloroform.

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