# The Copolymerization of Unsaturated Carboxylic Acids with Styrene and an Unsaturated Tertiary Amine in Benzene

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SUMMARY:
   The copolymerization parameters of 2-acryloyloxybenzoic (AOB) and 2-methacryloyloxy-benzoic (MOB) acids, methyl 2-methacryloyloxybenzoate (MMOB), and N-methyl-N-phenyl-2-aminoethyl methacrylate (MPAM) with styrene in benzene solution were determined and used in the calculation of the Alfrey-Price copolymerization constants *e* and *Q* for AOB, MOB, MMOB, and MPAM. Using *e* and *Q* thus determined and the corresponding tabulated values for methacrylic acid (MAA), the copolymerization parameters of pairs AOB-MPAM, MOB-MPAM, MMOB-MPAM, and MAA-MPAM were calculated. They are compared with those determined by the copolymerization of these pairs in which the interaction of functional groups on comonomers plays a role.

## Introduction

The effect of interaction between the organic components of the polymerization system (unsaturated carboxylic acids, unsaturated tertiary amines, vinylpyridines, some polar monomers, and donor and acceptor monomers) on the radical homopoly-merization and copolymerization was demonstrated in a number of papers. Inter-actions may cause changes in the a) reactivity of the monomer and the radical (i. e. the reacting particles), b) mobility of the reacting particles, c) concentration of the reacting particles at the reaction site, d) spatial orientation of the reacting particles.

A change in the reactivity of protophilic monomers in the presence of protogenic compounds[1–8] or protogenic monomers in the presence of protophilic com-pounds[1,9–14] is explained by the formation of a salt of the monomer or its associate with a protogenic or protophilic compound; in special cases such an interaction leads to the formation of initiation sites of polymerization[15]. Also electron-donor-acceptor complexes may be formed from comonomers[16,17], or from the monomer or the polymer radical and another component of the reaction system[18–22]. In the case of acrylamide (AAm), the solvent is also assumed to affect the equilibrium between the basic state of AAm and its more polar mesomeric form[23,24].

In thermodynamically good solvents the motion of polymer radicals, especially segmental diffusion, is reduced[25]. Polymer radical mobility may also be reduced by solvation of the propagating chains[4], and in poor solvents by enclosure of the radical in a densely packed polymer coil[26–28] or in aggregated macromolecules[29–31].

An enhanced fraction of the more polar comonomer in copolymers of acrylic acid (AA) with methyl methacrylate (MMA), of acrylonitrile (AN) with MMA[30], of MAA with styrene (St)[32], and MMA with N-vinylcarbazole[33] was explained by the higher local concentration of this comonomer at the reaction site. The acceleration of the

polymerization of 2-vinylpyridine (2-VP) in the presence of carboxylic acids has been explained by the formation of ordered associates of 2-VP-acid[34]. The formation of multimolecular associates of the monomer or of its adduct with the solvent was also used in the interpretation of the effect of solvents on the copolymerization of AA with St and of AAm with AN[14].

The favourable orientation of the propagating chain probably is responsible for the acceleration of the copolymerization of $N,N$-diethyl-2-aminoethyl methacrylate with $N$-vinyl-2-pyrrolidone in aqueous acetic acid[7]. The increased rates of polymerization of AA and AAm in some solvents were explained by an appropriate order of double bonds in multimolecular aggregates of these monomers[13,14]. A pronounced effect results from the association of monomer molecules with the polymer, called the matrix effect; it may lead to the initiation of polymerization of the sorbed monomer[35], to the acceleration of the propagation reaction, and sometimes also to stereoregulation of the basic units in the polymer chain[31,36-40].

One interesting interpretation of the different course of copolymerization in two solvents is that the microheterogeneity of the system is responsible, while the reactivity of the comonomers and the mechanism of the reaction remain unchanged in both solvents[32,33]. According to these authors the often accepted "penultimate effect" in fact reflects anomalies due to the microheterogeneity of the system.

The effect of molecular interaction might be markedly reflected also in the copolymerization of unsaturated carboxylic acids prepared by us earlier[41,42] with unsaturated tertiary amines. In order to evaluate the effect of mutual interaction between carboxylic and tertiary amine groups of comonomers on the composition of the copolymer, we determined the copolymerization parameters of AOB, MOB, MMOB and MPAM with St. These were used in the calculation of the Alfrey-Price constants $e$ and $Q$ of the particular comonomers, which in turn were employed in the calculation of the copolymerization parameters of pairs AOB-MPAM, MOB-MPAM, MMOB-MPAM and MAA-MPAM. The calculated copolymerization parameters were compared with the experimentally determined copolymerization parameters of the same pairs.
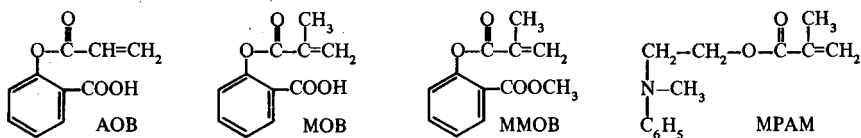


## Experimental Part

*Materials:* Acids AOB[41] and MOB[41], MPAM[42] (b. p. 106 °C/13 Pa, $d_4^{20}$ 1,0582 g · cm$^{-3}$) were prepared as described. MMOB was prepared by reacting methacryloyl chloride (0,14 mol) with methyl salicylate (0,1 mol) in benzene solution (30 ml) in the presence of triethylamine (0,14 mol) and hydroquinone (0,1 g) at 40 °C. After one hour the triethylamine hydrochloride thus formed was filtered off, the filtrate was shaken with a solution of 15 g NaHCO$_3$ in 80 ml H$_2$O, the organic layer was separated and dried with anhydrous sodium sulfate. By distillation in vacuum of the oil pump, the main fraction of MMOB, b. p. 90 – 92 °C/13 Pa, $n_D^{20}$ 1,5232, yield 54%, was obtained from the filtrate. MAA was recrystallized from ethanol and redistilled

twice at reduced pressure in nitrogen atmosphere (m. p. $16\,°C$, b. p. $60\,°C/$ $1,596$ kPA, $d_4^{20}$ $1,0153$ g $\cdot$ cm$^{-3}$). Styrene (St) and $2,2'$-azodiisobutyronitrile (AIBN) were purified by the usual procedures[15]. Thiophene-free benzene was dried over sodium and rectified on a Bruun column. The other solvents were redistilled.

*Methods:* The purity of liquid compounds was checked with a gas chromatograph Chrom 3, Laboratory Instruments, Prague. The copolymerizations were carried out at $50\,°C$ in glass dilatometers, ca. 8 cm$^3$ in volume, and in sealed glass ampoules, ca. 30 cm$^3$ in volume, in an inert atmosphere. In all cases, AIBN at a concentration of $0,02$ mol $\cdot$ dm$^{-3}$ was used as initiator and benzene was the solvent. Each pair of monomers was polymerized at $7-10$ different initial ratios given in Tab. 1. In the cases of pairs AOB-MPAM, MOB-MPAM, MAA-MPAM and MMOB-MPAM, the sum of the initial molar concentrations was $[M_1] + [M_2] = 1$ mol $\cdot$ dm$^{-3}$; for pairs St-AOB, St-MOB and St-MMOB it was $1,5$ mol $\cdot$ dm$^{-3}$, and for St-MPAM the sum was 3 mol $\cdot$ dm$^{-3}$. Times needed for reaching a conversion between 6 and 12% in the ampoules were determined using the observed rates of preliminary copolymerizations.

The copolymers with the highest AOB and MOB contents were precipitated from benzene solutions with a mixture of benzene and cyclohexane. The copolymers with a lower content of AOB and MOB were precipitated with cyclohexane, and the copolymers of MPAM with St and MMOB were precipitated with methanol. From the polymerization mixtures with MAA, liquid components were removed by distillation at room temperature, and the remaining copolymer was reprecipitated from THF solution with benzene or cyclohexane. The polymers separated by filtration were dried to constant mass in an evacuated desiccator.

The composition of copolymers AOB, MOB and MMOB with styrene was calculated from the carbon content and in the case of copolymers MPAM from the nitrogen content in the copolymers. The copolymerization parameters were calculated employing the Joshi-Joshi[43] and Fineman-Ross[44] methods. From the copolymerization parameters of styrene with the new comonomers, e and Q constants[45] of the latter were calculated using Eqs. (1) and (2):

$$e_2 = e_1 \pm (-\ln r_1 r_2)^{0,5} \tag{1}$$

$$Q_2 = \frac{Q_1}{r_1} e^{-e_1(e_1 - e_2)} \tag{2}$$

The e and Q values of the individual comonomers were used to calculate the copolymerization parameters for pairs of these comonomers by means of Eqs. (2) and (3).

$$r_2 = \frac{Q_2}{Q_1} e^{-e_2(e_2 - e_1)} \tag{3}$$

## Results

Tabs. 1 and 2 presents data on the composition of the initial mixtures of monomers and of the resulting copolymers in the copolymerization of styrene with the new comonomers and of AOB, MOB, MMOB and MMA with MPAM, and the copoly- merization parameters $r_1$, $r_2$ calculated with these data. Using the Fineman-Ross relation[44], $r_1$ and $r_2$ were calculated from Eq. (4)

$$\phi_0 - (\phi_0/\varphi) = r_1 (\phi_0^2/\varphi) - r_2 \tag{4}$$

after substitution of the initial mole ratio of both comonomers $[M_1]_0/[M_2]_0$ for $\phi_0$, and of the ratio of the repeating units in the increment of the copolymer $(-d[M_1]/[M_2] = m_1/m_2)$ for $\varphi$. After an interchange of the symbols $M_1$, $M_2$ for the given pair of comonomers, the same procedure was used to obtain the parameters $r_1'$, $r_2'$, given in brackets in Tabs. 1 and 2. The largest difference between these so-

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Tab. 1.  Monomer reactivity ratios $(r_1, r_2)$ of AOB, MOB, MPAM, and MMOB with styrene (St, monomer 1) in benzene solution at 50 °C[a]

| | St-AOB | | St-MOB | | St-MPAM | | St-MMOB | |
|---|---|---|---|---|---|---|---|---|
| | $F_0$ | $f$ | $F_0$ | $f$ | $F_0$ | $f$ | $F_0$ | $f$ |
| | 0,309 | 0,293 | 0,255 | 0,187 | 0,288 | 0,334 | 0,102 | 0,165 |
| | 0,358 | 0,327 | 0,324 | 0,238 | 0,347 | 0,370 | 0,202 | 0,261 |
| | 0,399 | 0,353 | 0,396 | 0,295 | 0,410 | 0,403 | 0,303 | 0,344 |
| | 0,506 | 0,383 | 0,517 | 0,353 | 0,451 | 0,443 | 0,398 | 0,396 |
| | 0,664 | 0,461 | 0,607 | 0,413 | 0,602 | 0,539 | 0,497 | 0,471 |
| | 0,716 | 0,472 | 0,680 | 0,446 | 0,637 | 0,577 | 0,497 | 0,482 |
| | 0,751 | 0,495 | 0,720 | 0,505 | 0,675 | 0,602 | 0,602 | 0,528 |
| | | | 0,752 | 0,513 | 0,718 | 0,632 | 0,675 | 0,565 |
| | | | | | | | 0,802 | 0,636 |
| | | | | | | | 0,880 | 0,727 |
| $r_1$ [b] | 0,068 (0,055) | | 0,155 (0,172) | | 0,445 (0,412) | | 0,245 (0,248) | |
| $r_2$ [b] | 0,661 (0,643) | | 1,175 (1,204) | | 0,592 (0,557) | | 0,433 (0,480) | |
| $r_1$ [c] | 0,053 ± 0,017 | | 0,158 ± 0,27 | | 0,438 ± 0,017 | | 0,282 ± 0,028 | |
| $r_2$ [c] | 0,639 ± 0,014 | | 1,178 ± 0,023 | | 0,584 ± 0,021 | | 0,479 ± 0,026 | |
| $r_1$ [d] | 0,06 ± 0,02 | | 0,16 ± 0,03 | | 0,44 ± 0,02 | | 0,27 ± 0,03 | |
| $r_2$ [d] | 0,64 ± 0,02 | | 1,18 ± 0,03 | | 0,58 ± 0,02 | | 0,47 ± 0,03 | |

[a]  $F_0$ and $f$ are mole fractions of the first comonomer in the starting polymerization mixture and in the copolymer, respectively; $F_0 = \dfrac{[M_1]_0}{[M_1]_0 + [M_2]_0}$, $f = \dfrac{m_1}{m_1 + m_2}$.

[b]  and [c] According to Fineman-Ross and Joshi-Joshi methods, respectively.

[d]  Average from [b] and [c].

called "inversion" values of the copolymerization parameters $(r_1 - r_1'$ or $r_2 - r_2')$ has been observed for the pair AOB-MPAM (0,19), while for most of the other pairs the differences are below 0,10.

The values $r_1, r_2$ calculated by the Joshi-Joshi method[43] remained unchanged after the symbols $M_1, M_2$ were interchanged. For most of the monomeric pairs, the average values of $r_1, r_2$ calculated from Eq. (4) differ from $r_1, r_2$ according to Joshi-Joshi by less than 0,02, and only for the pair MAA-MPAM the difference is 0,04. The average values of the copolymerization parameters are given in Tabs. 1 and 2 with an average deviation $(\Delta r)$ according to the Joshi-Joshi method.

In the calculation of the constant $e$ according to Eq. (1), the pair $r_1 + \Delta r_1, r_2 + \Delta r_2$ led to the highest and the pair $r_1 - \Delta r_1, r_2 - \Delta r_2$ to the lowest $e_2$ values. The average from these two extreme values for $e_2$ and the differences $(\pm \Delta e_2)$ between the average and the extreme $e_2$ values are shown in Tab. 3. After substitution of the extreme $e_2$ in Eq. (2), two extreme $Q_2$ values of the given comonomer were obtained. Tab. 3 gives the average of these two extreme values for $Q_2$ and the differences $(\pm \Delta Q_2)$ between the average and the extreme $Q_2$ values.

Using the $e$ and $Q$ values thus determined for the monomers newly prepared and the values published[46] for MAA (Tab. 3), the copolymerization parameters of pairs

Tab. 2. Monomer reactivity ratios of AOB, MOB, MAA, and MMOB with MPAM (monomer 2) in benzene solution at 50 °C[a]

| | AOB-MPAM | | MOB-MPAM | | MAA-MPAM | | MMOB-MPAM | |
|---|---|---|---|---|---|---|---|---|
| | $F_0$ | $f$ | $F_0$ | $f$ | $F_0$ | $f$ | $F_0$ | $f$ |
| | 0,244 | 0,490 | 0,294 | 0,588 | 0,205 | 0,466 | 0,101 | 0,165 |
| | 0,282 | 0,513 | 0,313 | 0,597 | 0,238 | 0,484 | 0,215 | 0,306 |
| | 0,330 | 0,557 | 0,333 | 0,614 | 0,263 | 0,518 | 0,425 | 0,500 |
| | 0,411 | 0,629 | 0,357 | 0,643 | 0,294 | 0,562 | 0,515 | 0,565 |
| | 0,489 | 0,706 | 0,385 | 0,656 | 0,333 | 0,624 | 0,502 | 0,542 |
| | 0,609 | 0,778 | 0,417 | 0,690 | 0,385 | 0,654 | 0,598 | 0,670 |
| | 0,662 | 0,817 | 0,455 | 0,725 | 0,455 | 0,699 | 0,700 | 0,768 |
| | 0,719 | 0,823 | 0,500 | 0,755 | 0,556 | 0,765 | 0,802 | 0,832 |
| | | | 0,556 | 0,787 | 0,714 | 0,850 | | |
| | | | 0,625 | 0,822 | | | | |
| $r_1$ [b] | 1,670 (1,860) | | 2,544 (2,607) | | 2,051 (2,205) | | 1,183 (1,075) | |
| $r_2$ [b] | 0,152 (0,230) | | 0,190 (0,206) | | 0,170 (0,220) | | 0,611 (0,528) | |
| $r_1$ [c] | 1,765 ± 0,061 | | 2,559 ± 0,008 | | 2,080 ± 0,013 | | 1,156 ± 0,070 | |
| $r_2$ [c] | 0,190 ± 0,066 | | 0,194 ± 0,026 | | 0,177 ± 0,040 | | 0,599 ± 0,070 | |
| $r_1$ [d] | 1,76 ± 0,06 | | 2,56 ± 0,04 | | 2,08 ± 0,07 | | 1,15 ± 0,07 | |
| $r_2$ [d] | 0,19 ± 0,07 | | 0,19 ± 0,02 | | 0,18 ± 0,04 | | 0,59 ± 0,07 | |

[a–d] For footnotes cf. Tab. 1.

Tab. 3. Determined $e_2, Q_2$ and calculated $r_1, r_2$ from $e_2, Q_2$

| $M_1 - M_2$ | $e_2$ | $Q_2$ |
|---|---|---|
| St-AOB | 1,02 ± 0,10 | 3,90 ± 0,32 |
| St-MOB | 0,50 ± 0,08 | 2,22 ± 0,15 |
| St-MAA [a] | 0,65 | 2,34 |
| St-MPAM | 0,37 ± 0,04 | 0,90 ± 0,04 |
| St-MMOB | 0,63 ± 0,04 | 1,18 ± 0,05 |
| | $r_1$ [b] | $r_2$ [b] |
| AOB-MPAM | 2,25 ± 0,37 | 0,29 ± 0,03 |
| MOB-MPAM | 2,31 ± 0,12 | 0,42 ± 0,02 |
| MAA-MPAM | 2,17 ± 0,17 | 0,43 ± 0,03 |
| MMOB-MPAM | 1,11 ± 0,02 | 0,84 ± 0,02 |

[a] St-MMA[46]: $r_1 = 0,13$, $r_2 = 0,91$.
[b] Calculated from $e_2, Q_2$.

AOB-MPAM, MOB-MPAM, MMOB-MPAM, and MAA-MPAM were calculated. The extreme $r_1$ and $r_2$ values, respectively, were obtained by the substitution of the data $e_1 - \Delta e_1$, $e_2 - \Delta e_2$, $Q_1 + \Delta Q_1$, $Q_2 + \Delta Q_2$ or $e_1 + \Delta e_1$, $e_2 + \Delta e_2$, $Q_1 - \Delta Q_1$,

$Q_2 - \Delta Q_2$ into Eqs. (2) and (3). Tab. 3 presents the average values of the calculated extreme $r_1, r_2$ values and the differences ($\pm \Delta r$) between the average and extreme $r_1$, $r_2$ values.

Solid lines in Figs. 1 and 2 represent the copolymerization diagrams of the monomer pairs under investigation, which were constructed using the differential copoly-
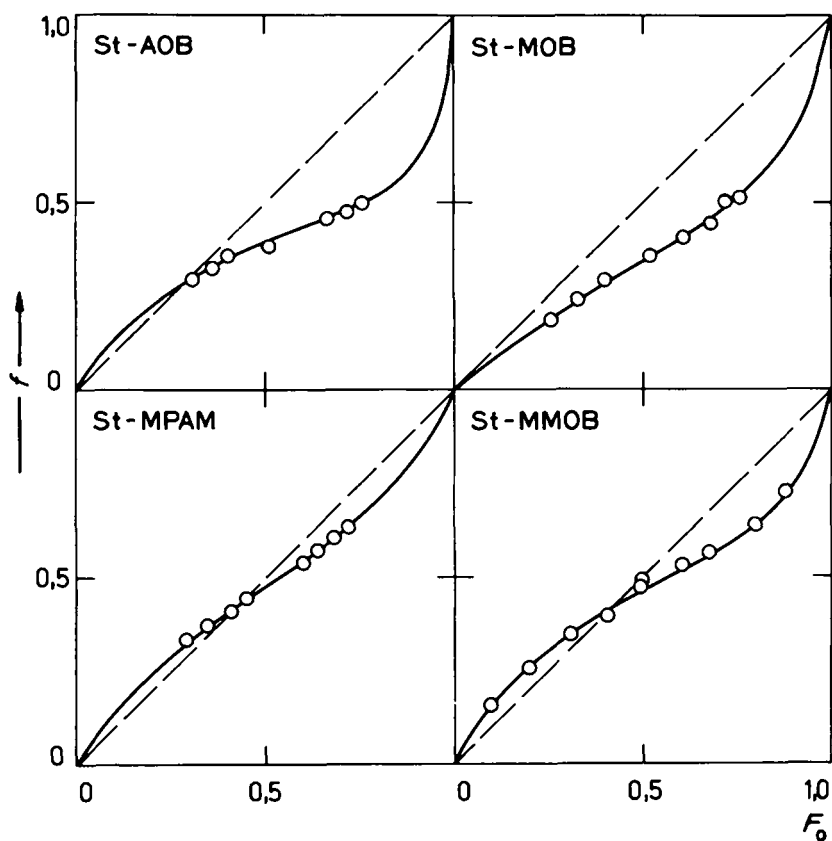


Fig. 1. Copolymerization diagrams of pairs St-AOB, St-MOB, St-MPAM, and St-MMOB calculated using the determined copolymerization parameters (———); (○): experimentally determined composition of the copolymer; $F_0$ and $f$: mole fractions of the first comonomer of the given pair in the starting polymerization mixture and in the copolymer, respectively

merization equation and the copolymerization parameters determined in this study. Experimental points, i.e. the determined composition of the copolymer ($f$) obtained from the initial monomeric mixture ($F_0$) are marked with circles.
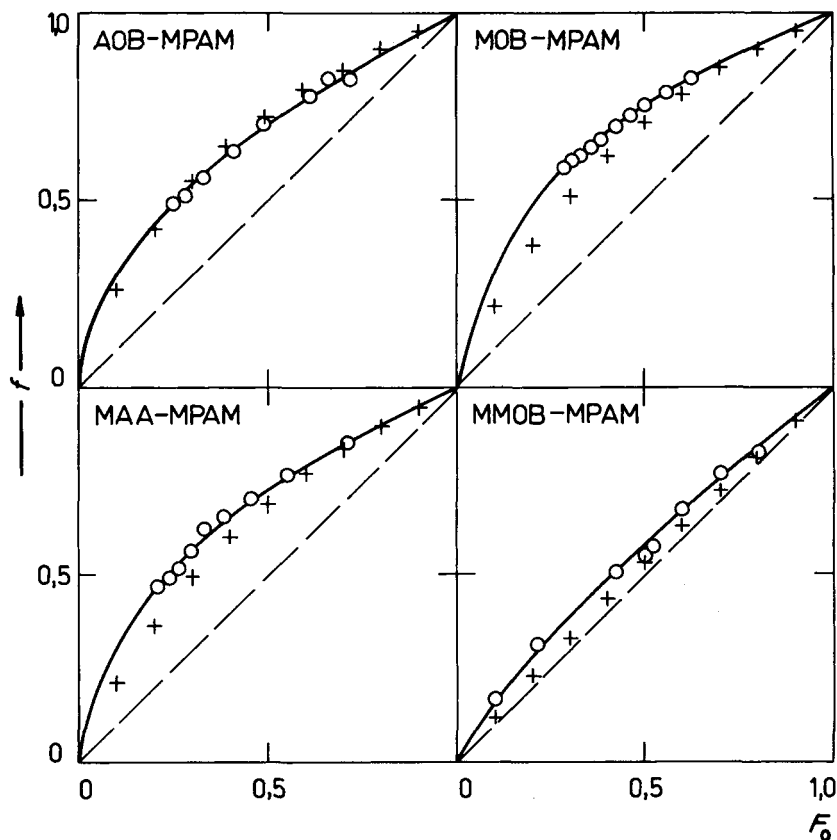
Fig. 2.  Copolymerization diagrams of pairs AOB-MPAM, MOB-MPAM, MAA-MPAM, and MMOB-MPAM calculated using copolymerization parameters determined (———) and calculated ( + ) from the $e$ and $Q$ constants of comonomers (symbols as in Fig. 1)

For the sake of comparison, the copolymerization diagrams of pairs AOB-MPAM, MOB-MPAM, MMOB-MPAM, and MAA-MPAM were calculated using the copolymerization parameters evaluated from $e$ and $Q$ constants of these comonomers. Their course is marked with crosses in Fig. 2. For the pair AOB-MPAM, the calculated copolymerization diagram coincides with the determined composition of the copolymer. For the pairs MOB-MPAM, MMOB-MPAM, and MAA-MPAM the calculated diagrams are close to the determined composition of the copolymers.

The rates of polymerization ($R_p$) calculated from the amount of the polymer obtained within a certain time are only approximate because of polymer losses during precipitation. The ratio $R_p/([M_1] + [M_2])$ was of the order $10^{-5} \cdot s^{-1}$ and decreased in the order of pairs St-AOB, St-MOB, St-MPAM, St-MMOB and with increasing mole fraction of St in the mixture. The $R_p/([M_1] + [M_2])$ obtained in the copolymerization

of carboxylic acids with MPAM (at an equimolar ratio of comonomers) are two to three times higher than in the copolymerization of acids with St. The limiting viscosity numbers (in THF, 20 °C) of copolymers St-AOB (0,59 to 0,70 cm$^3 \cdot$ g$^{-1}$) were somewhat higher than those of copolymers St-MOB (0,35 to 0,45 cm$^3 \cdot$ g$^{-1}$) and slightly decreased with increasing styrene content in the initial polymerization mixtures.

## Discussion

AOB and MOB are analogs of phenyl acrylate and phenyl methacrylate. The tabulated values of the Alfrey-Price constants $e$ and $Q$ for phenyl methacrylate[46] are 0,73 and 1,49, respectively. The $e$ and $Q$ values of phenyl acrylate could not be found, but for alkyl acrylates (from methyl to octyl) the $e$ values lie in the range 0,6 to 0,9 and the $Q$ values in the range 0,35 to 0,66; for methacrylic acid[46], $e$ and $Q$ are 0,65 and 2,34 and for acrylic acid 0,77 and 1,15, respectively. Tab. 3 shows that AOB and MOB have $e$ values close to acrylates and methacrylates, but their $Q$ values are considerably higher. According to the Alfrey-Price relation[45], $Q$ is a function of the difference between the mesomeric energies of the monomer and the radical obtained therefrom. Hence, the stability of C-radicals from AOB and MOB should be much higher than of C-radicals from phenyl esters of AA and MAA. On the grounds of close values of the Taft induction constants[47] for the groups —COOH (2,1) and —COOCH$_3$ (2,0), it was possible to assume that the electron density on the vinyl group or radical centre of phenyl ester of MAA would be affected by the introduction of —COOH or —COOCH$_3$ groups into the phenyl ring virtually in the same way. If, consequently, the content of a certain comonomer in the copolymer were determined only by the reactivity of its double bond and of its free radical, the copolymerization parameters of pairs St-MOB and St-MMOB should be the same. Tabs. 1 and 3 and Fig. 1 show, however, that the copolymerization characteristics and copolymerization diagrams of both pairs are distinctly different. For MOB, the constant $Q$ calculated from the determined composition of copolymers with St is close to MAA, while for MMOB it is closer to the value for MPAM (Tab. 3) or for phenyl methacrylate (cf. above). The analysis indicates that the faster enrichment of the copolymer St-MOB with the acid MOB than of the copolymer St-MMOB with the ester MMOB is not a consequence of the higher reactivity of the vinyl bond and radical centre in the acid compared to the ester. A cause being more likely is the different participation of MOB and MMOB in the molecular interaction which may produce alterations in the system leading to a change in the polymer composition (cf. introduction). The fact that the acid MOB enters the copolymer with St more quickly than the ester MMOB may be a result of the association of —COOH groups from the monomer and from the polymer chain; it might lead to an increased MOB concentration near the radical centre, to a preferred orientation of the associated MOB with respect to the radical, and possibly also to an impeded termination of the polymer radical enveloped with MOB[4, 7, 26, 40].

The $Q$ value of the amine calculated from the composition of copolymers St-MPAM is lower than that of AOB and MOB; the values of the $e$ and $Q$ constants of the amine are close to those found for ethyl methacrylate (0,52 and 0,73)[46].

It can be seen from the copolymerization parameters of AOB, MOB, MAA, and MMOB with MPAM (Tab. 2) that molecules of acids are added much more quickly to both radicals, i. e. to the own and to the foreign radical, than the molecule of MMOB. At the same time, the copolymerization parameters of AOB and MOB, i. e. of analogs of phenyl acrylate and phenyl methacrylate, with MPAM are closer to the parameters of the pair MAA-MPAM than of MMOB-MPAM. This is also revealed by the copolymerization diagrams the courses of which are closer for the pairs MOB-MPAM and MAA-MPAM than for the pairs MOB-MPAM and MMOB-MPAM. For the same reasons, as in the copolymerization with St, it is not very likely that the faster enrichment of the copolymer MOB-MPAM with the acid than of the copolymer MMOB-MPAM with the ester MMOB is due to the different effects of the —COOH and —COOCH$_3$ groups on the reactivity of the vinyl group and of the radical centre in the phenyl ester of MAA. A cause may rather be seen in the association of carboxylic groups from the monomer and from the polymer radical leading to changes in the polymerization system as mentioned above.

The copolymerization parameters of pairs AOB-MPAM, MOB-MPAM, MAA-MPAM, and MMOB-MPAM calculated from $e$ and $Q$ of monomers (Tab. 3) do not include the effect of the interaction between amino groups and —COOH groups on the relative reactivity of the comonomers. The copolymerization diagrams were calculated using these parameters (crosses in Fig. 2). The first of them, for the pair AOB-MPAM, is in good accordance with the determined composition of copolymers (circles), while the other ones are close to this compositon. The accordance between the calculated and experimentally determined composition of the copolymer suggests that the interaction between the carboxylic group of one comonomer and the amino group of the other comonomer had no essential effect on the relative reactivity of comonomers in benzene solution.

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