The Influence of Molecular Interaction on Polymerization, 5[a]

Copolymerization of Benzyl Methacrylate with Maleic Anhydride

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SUMMARY:
Copolymerizations of benzyl methacrylate (BMA) with maleic anhydride (MA), initiated by 2,2'-azoisobutyronitrile at 70 °C in chloroform or acetonitrile, were investigated. The complex formation between the two monomers in chloroform was studied by ^{1}H NMR spectroscopy. The stability constant of the complex was found to be $0,25\ \mathrm{l \cdot mol^{-1}}$. The following copolymerization reactivity ratios were found: in chloroform: $r_{BMA} = 0,188 \pm 0,035$ and $r_{MA} = 0,003 \pm 0,005$, in acetonitrile: $r_{BMA} = 0,116 \pm 0,093$ and $r_{MA} = 0,231 \pm 0,027$. By ^{1}H NMR investigations it could be shown that the results correlate with the changes of the reactivity ratios depending on the solvent used.

Introduction

The formation of an alternating copolymer from maleic anhydride (MA) and both styrene and α-methylstyrene is explained in most cases with the participation of a donor-acceptor complex between the monomers during the polymerization process[1,2]. The complex between the strong electron acceptor (MA) and the donors (styrene and α-methylstyrene) has recently been confirmed by ^{1}H NMR spectroscopy.

One of the possibilities to control the complex formation is to carry out the polymerization in solvents with different dielectric constants, establishing weaker or stronger interactions between the monomers. The polymerization in different solvents gives information about the influence of complex formation on the polymerization itself as well as on the structure and properties of the polymers. Tsuchida et al.[1] have observed that in solvents such as carbon tetrachloride or benzene the rate of copolymerization between MA and styrene is higher than in acetone and tetrahydrofuran. The higher rate of copolymerization shows a maximum at a MA mole fraction of 0,5, whereas in acetone or acetonitrile a maximum does not appear. In the copolymerization of phenanthrene with MA, which also form a complex with a stability constant $K = 0,16\ \mathrm{l \cdot mol^{-1}}$, it has been established that the solvent strongly influences the copolymerization. At equal conditions, γ-irradiation and heating at 65 °C, copolymerization between MA and phenanthrene takes place in carbon tetrachloride, chloroform, or benzene, whereas in solvents like acetone, tetrahydrofuran, or dimethylformamide, no polymer was isolated[3].

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[a] Part 4: H. Boudevska, C. Brutchkov, V. Veltchev, Eur. Polym. J. **15**, 907 (1979).

It has been established that MA and methyl methacrylate (MMA) have very different reactivity ratios (r_{MA} = 0,02 and r_{MMA} = 6,7)[4]. The lack of interaction between these monomers, being both electron acceptors, probably hinders the copolymerization. A possibility to create better conditions for the interaction between methacrylate and MA is to include an electron donating substituent in the methacrylate molecule. Then, if the donor acceptor interaction defines the monomer reactivity ratios, a change in their values should be expected. A suitable model for this purpose is benzyl methacrylate (BMA), in which the aromatic ring, lying in the alcohol part of the methacrylic ester, may form a complex with MA. Therefore, we investigated the complex formation between BMA and MA in solvents with low and high dielectric constants using ¹H NMR spectroscopy. In the same solvents we carried out the copolymerizations and we determined the reactivity ratios of the monomers.

Experimental Part

Reagents: Maleic Anhydride (technical grade) was purified by distillation i. vac.; b.p. 86 − 87 °C at 10 − 12 Torr (13 − 16 mbar); m.p. 53 − 53,5 °C. Benzyl methacrylate was prepared by esterification of methacrylic acid (from Röhm & Haas, 99,5%, purified by distillation; b.p. (7 − 10 mbar) 55 − 63 °C) with benzyl alcohol (p.a., Reachim, Sojuzchimexport) in the presence of 2-hydroxy-5-sulfobenzoic acid (p.a., Reachim, USSR) as catalyst[5], b.p. (4 − 7 mbar) 105 − 130 °C; n_D^{20} = 1,5140. Deuterochloroform (from Chemapol, Czechoslovakia; 99,95% D), perdeuteroacetonitrile (from Isocommerz, DDR; 85,00% D), chloroform (from Factory for pure reagents, Vladaja, Bulgaria, p.a.), acetonitrile (from Laborchemie-Apolda, DDR, pure), and 1,4-dioxane (from Reanal, Budapest, Hungary, p.a.) were used without further purification.

¹H NMR Measurements and determination of the stability constant of the complex: ¹H NMR spectra were recorded with a spectrophotometer NMR, Tesla BS 457, 80 MHz, with TMS as internal reference at 25 °C in deuterochloroform and perdeuteroacetonitrile. For the determination of the stability constant, 10 wt.-% solutions of MA and of mixtures of MA with BMA in mole ratios of 1 : 0,5 to 1 : 2,5 in deuterochloroform were applied. The results were exploited by the method of Hanna and Ashbaugh[6], based on the following equation:

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

where $\Delta^{(A)}$ = $\tau_{MA\,obs} - \tau_{MA}$, and $\tau_{MA\,obs}$ = chemical shift of the MA protons in chloroform solutions of BMA and MA. τ_{MA} = chemical shift of the MA protons in chloroform. m_D = concentration (in mol · l⁻¹) of the donor BMA; $\Delta_{AD}^{(A)}$ = $\tau_{AD}^{(A)} - \tau_{MA}$ and $\tau_{AD}^{(A)}$ = chemical shift of the MA proton of the pure complex. K = stability constant of the complex.

Copolymerization: Solutions of the monomer mixtures (10 wt.-%) in different mole ratios, in the presence of 0,5 mole-% (related to the monomer) 2,2′-azoisobutyronitrile (AIBN), were put into ampoules. They were twice frozen and degassed at $10^{-4} - 10^{-5}$ mbar. The sealed ampoules were heated in a fixed thermostat at 70 °C for a certain time. The solutions were precipitated in methanol. The polymers were dissolved in benzene, reprecipitated in methanol, and dried at 40 °C i. vac. (4 − 5 mbar).

Analyses: The content of monomeric units of BMA in the copolymers was determined by UV analysis. The spectra were recorded with a spectrometer Beckman, model 24. The calibration was made with poly(benzyl methacrylate). The wave length at which its solution in 1,4-dioxane ($c = 5 \cdot 10^{-3}$ mol · l⁻¹) exhibits its highest extinction (258 nm) was used for all measurements.

The content of monomeric units of MA in the copolymers was determined by potentiometric titration, the samples being first hydrolysed by heating their 1,4-dioxane/water solutions

(volume ratio 10 : 1) for 2 h. The titration was carried out with 0,1 M KOH in ethanol, using the pH-meter Radelkis, TYP OP-204/1.

Results and Discussion

The ^{1}H NMR spectra of BMA, MA, and their mixtures in deuterochloroform are given in Fig. 1. A high field shift of $\Delta^{(A)} = 0{,}112$ p.p.m. of the MA proton signal after mixing it with BMA can be seen. A similar high field shift of the MA proton
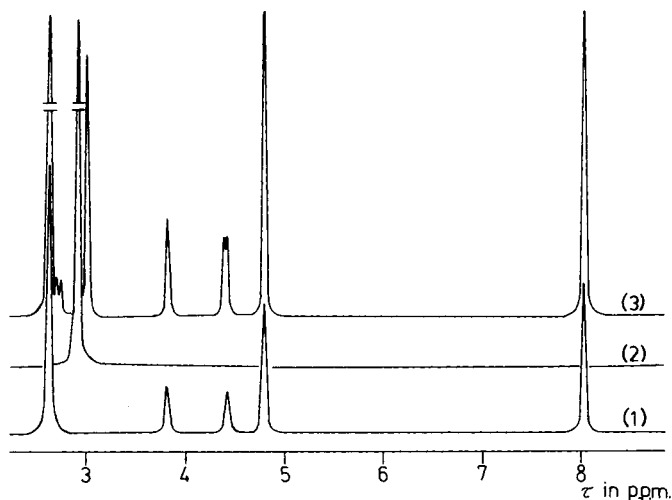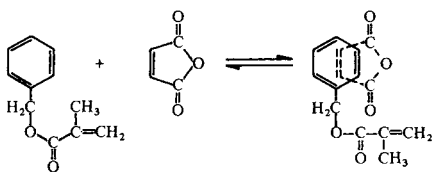

Fig. 1. ^{1}H NMR spectra (at 80 MHz) of benzyl methacrylate (BMA) (1), of maleic anhydride (MA) (2), and of the mixture of BMA and MA (mole ratio 1 : 1) (3), in deuterochloroform

after mixing with styrene has been also observed by Tsuchida et al.[1]. The difference between the MA signals $\Delta^{(A)}$ in absence and in presence of BMA is of the same order as in the complex formation between MA and α-methylstyrene[2]. As seen from Tab. 1, the chemical shifts of the protons of BMA are not influenced noticeably by the addition of MA. The same results have been observed for α-methylstyrene[2]. It can be concluded that in chloroform an interaction between BMA and MA takes place. The latter leads to the formation of a complex between MA and the aromatic ring of the ester according to the following scheme.

Tab. 1. Chemical shifts τ in p. p. m. in the ^{1}H NMR spectra of benzyl methacrylate (BMA), of maleic anhydride (MA), and of their mixtures in deuterochloroform and in perdeuteroacetonitrile

Substances (mole ratio)	Solvent	$\tau_{(CH=CH)}$	$\tau_{(C_6H_5)}$	$\tau_{(H_A)}$	$\tau_{(H_B)}$	$\tau_{(CH_2)}$	$\tau_{(CH_3)}$
BMA	CDCl$_3$	—	2,650	3,825	4,425	4,813	8,050
MA	CDCl$_3$	2,925	—	—	—	—	—
BMA/MA (1 : 1)	CDCl$_3$	3,037	2,663	3,838	4,425	4,825	8,050
BMA	CD$_3$CN	—	2,625	3,900	4,363	4,825	8,075
MA	CD$_3$CN	2,875	—	—	—	—	—
BMA/MA (1 : 1)	CD$_3$CN	2,900	2,625	3,900	4,365	4,825	8,075

The chemical shifts of the protons of BMA and MA in perdeuteroacetonitrile are given in Tab. 1. The τ-values of BMA do not change in equimolar mixtures of MA and BMA. The signal of the MA protons in the mixture is shifted to high field only with $\Delta^{(A)}$ = 0,025 p. p. m. This indicates that there is a weak interaction between BMA and MA even in a solvent with high dielectric constant like acetonitrile.

The results show that in chloroform the equilibrium of complex formation is shifted to association, whereas in acetonitrile it is drawn to a great extent to free molecules. The stability constant of the complex in chloroform was determined by ^{1}H NMR investigations according to the Hanna-Ashbaugh method[6]. The latter is based on the change in the τ-values of the proton most sensitive to complex formation for
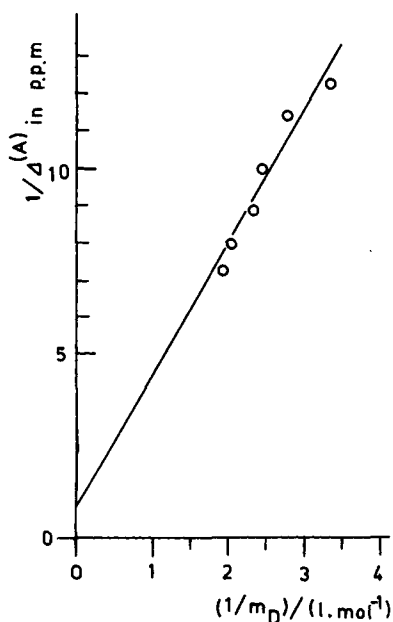

Fig. 2. Hanna-Ashbaugh plot for benzyl methacrylate (BMA)-maleic anhydride (MA) interaction in deuterochloroform assuming 1 : 1 complex formation

solutions with different mole ratios between donor and acceptor. This is the MA proton. The experimental data, treated by this method are given in Fig. 2. The value obtained from the slope of the straight line for the stability constant K is 0,25 $l \cdot mol^{-1}$.

The weak chemical shift of the MA proton in acetonitrile shows that the equilibrium is drawn to dissociation. This shift cannot be used for the determination of the stability constant, as the differences in the experimental measurements are rather near to the allowed errors.

The copolymerization of the two monomers was carried out in chloroform and acetonitrile. In order to determine the reactivity ratios, different mole ratios of BMA and MA were copolymerized to low conversions. The BMA content in the copolymers was determined by UV-analysis. Some of the copolymers were analysed for their content of monomeric units of MA, hydrolysing the anhydride group followed by potentiometric titration. It is seen from Tab. 2 that the results of both analyses are in acceptable agreement.

Tab. 2.   Contents of monomeric units of benzyl methacrylate (BMA) and maleic anhydride (MA) in the copolymers determined by UV-analysis and potentiometric titration, respectively

Mole ratio in the initial mixture BMA/MA	Content of monomeric units in the copolymers	
	BMA in wt.-%	MA in wt.-%
1 : 7	34,08	69,80
1 : 5	36,89	61,20
1 : 1	43,28	41,06
5 : 1	42,94	51,20
7 : 1	44,85	55,20

The copolymerization conditions in chloroform and acetonitrile as well as the co-polymer compositions are given in Tab. 3. The time necessary to reach 10% conversion depends on the solvent. In chloroform the reaction is faster than in acetonitrile. This correlates with the observations of Tsuchida et al.[1] in the copolymerization of MA with styrene.

The relative reactivity ratios were determined using the Fineman-Ross method. The errors were calculated by the least-square method. The values obtained are given in Tab. 4. In the copolymerization of BMA with MA the values of the reactivity ratios are low, which indicates that each radical exhibits a tendency to react with the other monomer. The product $r_{BMA} \cdot r_{MA}$ is an indication for alternating copolymerization. The reactivity ratio of BMA differs considerably from that of methyl methacrylate with $r_{MMA} = 6,7 \pm 0,2$, found for its copolymerization with MA at 75 °C[4,7], whereas the reactivity ratio of MA in both cases tends to zero.

The decrease of the values of the reactivity ratios of BMA is in agreement with the complex formation between BMA and MA in chloroform observed by ^1H NMR spectroscopy. This result confirms the ideas developed recently by many authors for the participation of donor acceptor complexes in copolymerization processes[8].

Tab. 3. Copolymerization of benzyl methacrylate (BMA) and maleic anhydride (MA) in chloroform and in acetonitrile

Solvent (dielectric constant)	Time of polymerization in min	Conversion in wt.-%	Content of BMA in wt.-%	
			initial mixture	copolymer[a]
Chloroform (4,70)	55	12,7	20,43	51,69
	45	8,2	26,44	51,45
	47	13,0	37,46	51,74
	45	12,6	54,50	55,22
	45	8,9	64,25	61,22
	45	8,3	72,94	62,43
	50	10,1	84,35	66,86
	45	9,5	92,64	68,56
Acetonitrile (36,2)	90	3,9	20,43	34,74
	120	13,9	26,44	37,70
	105	11,8	37,46	48,60
	65	6,7	54,50	54,30
	65	5,9	64,25	46,30
	80	11,0	84,35	46,68
	55	9,0	84,35	58,40
	50	10,8	92,64	59,70

[a] Content of monomeric units.

Tab. 4. Copolymerization reactivity ratios of benzyl methacrylate (BMA) and maleic anhydride (MA) in chloroform and in acetonitrile

Solvent	r_{BMA}	r_{MA}	$r_{BMA} \cdot r_{MA}$
Chloroform	$0,188 \pm 0,035$	$0,003 \pm 0,005$	0,0006
Acetonitrile	$0,116 \pm 0,093$	$0,231 \pm 0,027$	0,027

The reactivity ratio of BMA is slightly influenced by the solvent. In chloroform MA radicals exhibit a more pronounced tendency to join BMA monomeric molecules. In acetonitrile their relative reactivity increase, i.e., they tend to react more strongly with their own radicals. This change corresponds to the weaker complex formation in acetonitrile observed by NMR spectroscopy, i.e. with the shifting of the equilibrium of free molecules.

The changes in the reactivity ratios are small, but they coincide with those found recently by other authors in the copolymerization of MA with trans-stilbene[9] in chloroform and tetrahydrofuran. According to them, the r-value for stilbene remains zero for both solvents, whereas the r-values for MA increases from 0,04 in chloroform to 0,13 in tetrahydrofuran.

The results obtained indicate that there exists a correlation in the complex formation between BMA and MA, observed by ^{1}H NMR spectroscopy, and the low values of the reactivity ratios. The relative reactivity of MA depends on the dielectric constant of the solvent used.

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