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The Influence of Intermolecular Interactions on the Polymerization, 1

^{1}H NMR Investigation of Solutions of Naphthalene and Methyl Methacrylate, of 2-Naphthyl Methacrylate, and of 1-Naphthyl Methacrylate

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SUMMARY:

The solutions of methyl methacrylate (MMA) and naphthalene (N), of 2-naphthyl methacrylate (2-NM) and of 1-naphthyl methacrylate (1-NM) in chloroform, acetone, acetonitrile and *N*,*N*-dimethylformamide are studied by ^{1}H NMR spectroscopy. In chloroform and in pure MMA, N causes a shift of the signal of the high field vinyl proton H_a of MMA to higher field, whereas in acetone and acetonitrile the signal of H_a has the τ-value for MMA in the absence of N. The H_a signals of 2-NM and 1-NM in acetone, acetonitrile and *N*,*N*-dimethylformamide shift downfield as compared with those in chloroform. The τ-value of the downfield vinyl proton H_b does not vary with a change of the solvent. The separation of the vinyl signals $\Delta = \tau(H_a) - \tau(H_b)$ becomes equal to that of pure MMA.

The formation of 1:1 complexes between the electron donating naphthalene ring and the electron accepting methacrylic double bond is assumed. The stability constant of the MMA-N complex is 0,22 $l \cdot mol^{-1}$. Some structures for the complexes are proposed on the basis of molecular models of the monomer molecules. The results confirm the known theories for the influence of the solvents in radical polymerization of MMA. They can explain the kinetic changes of polymerization of 2-NM and 1-NM.

Introduction

The kinetics of radical polymerization of the methacrylates and the stereospecificity of the corresponding polymers depend on the monomer structure and on the nature of the solvent. The well-known theory of Henrici-Olivé and Olivé explains the influence of the solvent on the kinetics of methyl methacrylate (MMA) polymerization on the basis of a formation of a charge transfer complex between the growing radical and the monomer or/and the solvent, where only the complex with monomer leads to propagation[1]. Bamford and Brunby suggested that besides the above complex formation the interaction between monomer and solvent can influence the chain propagation[2].

A change in the kinetics has been established by us in radical polymerization of methacrylic esters containing aromatic nuclei in the alcoholic units depending on their electron donating capacity. This change has been explained by the assumption of complex formation between the monomer molecules namely between the aromatic nuclei as donors and the methacrylic double bonds as acceptors[3–5].

The stereoregularity of the polymethacrylates obtained by radical polymerization depends also on the nature of the alcoholic substituent. Poly(methyl methacrylate) is built up predominantly from syndiotactic triads whilst polymethacrylates with bulky substituents investigated by Niezette and Desreux⁶⁾ contain a higher quantity of isotactic triads reaching 65% for radical polymerization of triphenylmethyl methacrylate⁷⁾. 2-Naphthyl methacrylate (2-NM) gives 16% isotactic triads⁶⁾. According to the results of Nishino et al.⁸⁾ the isotactic triads in poly(1-naphthyl methacrylate) and in poly(2-naphthyl methacrylate) are in the range of 41–58%. The explanations of these facts are obscure and contradictory. Some authors assign the tendency for the decrease of syndiotacticity mainly to the bulkiness of the substituent, others assign this tendency to the aromatic character of the substituents and to the interaction among them. Casals et al.⁹⁾ especially for this purpose synthesized a methacrylate with a very bulky alcoholic unit and they obtained by radical polymerization a polymer with 12% isotactic triads and 50% syndiotactic triads.

We suppose that the kinetic changes in the polymerization of methacrylates as well as the stereoregularity of the obtained polymethacrylates are due to complex formation of the monomer molecules through interaction between their electron donating aromatic rings and the electron accepting C=C double bonds. An evidence for the complex formation between MMA and benzene is given by Allen and Bateup¹⁰⁾ by an NMR study of MMA spectra in different aromatic solvents such as benzene, styrene and halogen substituted benzenes under non-polymerization conditions.

The present paper deals with ^1H NMR of the interaction of MMA with naphthalene (N) and of the interaction between the molecules of 1-naphthyl methacrylate (1-NM) as well as between those of 2-NM in solvents with different dielectric constants.

Experimental Part

Materials

Methyl methacrylate (MMA) from Serra, West Germany, purified from hydroquinone by stirring with sodium hydroxide and distillation at reduced pressure.

1-Naphthyl methacrylate (1-NM) synthesized by the method of Patai et al.¹¹⁾ from methacryloyl chloride and sodium 1-naphtholate. The reaction was carried out at 5°C, then stirred for 2 h at room temperature. The product was extracted with diethyl ether, washed with a 5 wt.-% aqueous NaOH solution and with water. After drying and removing the ether the product was twice fractionated under vacuum (1 mmHg) at 152–154°C; $n_D^{20} = 1{,}5955$.

2-Naphthyl methacrylate (2-NM) synthesized by the method of Patai et al.¹¹⁾. The obtained product was filtered and stirred for 1 h with a 5 wt.-% aqueous NaOH solution and then recrystallized from 60 wt.-% aqueous ethanol, from n-hexane and once again from 70 wt.-% aqueous ethanol; mp 66–67°C.

Naphthalene (N) from Fluka, Switzerland, purum, mp 79–80°C.

Deuterochloroform from Chemapol, Czechoslovakia, 99,95% D.

Perdeuteroacetone from Isocommerz, DDR, 99,7% D.

Perdeuteroacetonitrile from Isocommerz, DDR, 85% D.

N,N-Dimethylformamide from Laborchemie-Apolda, DDR, pure.

Measurements

^1H NMR spectra were recorded with a spectrophotometer NMR, Tesla BS 487C, 80 MHz with tetramethylsilane as internal reference at 25°C in unsealed tubes. The error of measurement was ±0,5 Hz.

10 Wt.-% solutions of 1-NM and of 2-NM were measured. N was added in a mole ratio 1:1 to the 10 wt.-% solutions of MMA. The spectra of MMA and N without solvent were recorded on saturated (at 25 °C) solution of N in MMA (30–35 wt.-%).

The stability constant of the complex between MMA and N in chloroform was determined by the method of Hanna and Ashbaugh[12] based on the following equation:

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

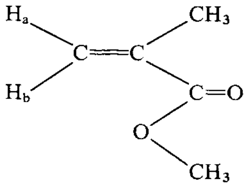
where $\Delta^{(A)} = \tau_{obs} - \tau_{MMA}$
τ_{obs}: chemical shift of H_a proton of MMA in chloroform solution of MMA and N.
τ_{MMA}: chemical shift of H_a proton of MMA in chloroform.
$\Delta_{AD}^{(A)} = \tau_{AD}^{(A)} - \tau_{MMA}$
$\tau_{AD}^{(A)}$: chemical shift of H_a of the pure complex.
m_D: amount-of-substance concentration of the donor N.
K: stability constant of the complex.

Solutions were made with constant concentration of MMA (0,6 mol/l) and concentration of N between 0,50 and 2,80 mol/l. Their ^1H NMR spectra were recorded at 25 °C with tetramethylsilane as internal reference.

Results and Discussion

Interaction between methyl methacrylate and naphthalene

The NMR spectra of MMA and its equimolar mixtures with N in chloroform and acetone in the range of $\tau = 1$–5 p.p.m. are shown in Fig. 1. The signals of the protons of the vinyl group are seen. If the vinyl protons H_a and H_b lie in the molecule of MMA as follows:



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H_b gives a signal at low field and H_a at high field.

When N is added its multiplet signal appears in the interval $\tau = 2{,}175$–$2{,}700$ p.p.m.

The chemical shifts of all protons in MMA as well as the separation of the vinyl protons $\Delta = \tau(H_a) - \tau(H_b)$ are given in Tab. 1. In chloroform in the presence of N all signals are shifted to high field. H_a is more sensitive than H_b to the presence of N. Thus, N causes an increase of the chemical shift of H_a to high field with 0,100 p.p.m. Because of the weaker increase of H_b Δ reaches 0,625 p.p.m. This value is near to that obtained by Allen and Bateup studying the interaction of MMA with benzene[10]. A greater increase of H_a τ-value agrees with the results found for the shift to higher field of *β-trans* proton (corresponding to H_a) in the interaction of α,β-unsaturated ketones with benzene[13].

The structures given in Fig. 2 can be assumed for the donor-acceptor complex formation between MMA and N in the mole ratio 1:1. MMA without any solvent (Tab. 1) gives signals

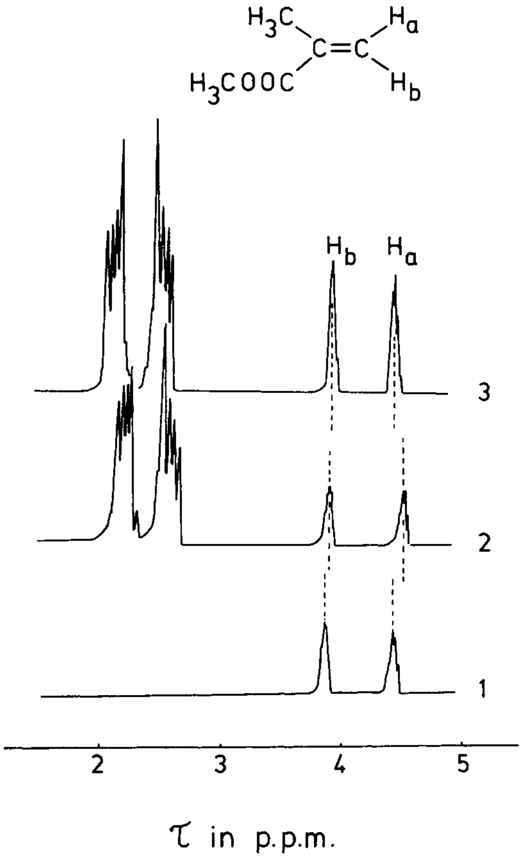

Fig. 1. ^1H NMR spectra at 80 MHz of methyl methacrylate (MMA) in $CDCl_3$ (spectrum 1), MMA and naphthalene (N) in $CDCl_3$ (spectrum 2) and MMA and N in $(CD_3)_2CO$ (spectrum 3)

slightly shifted to high field for all protons. This might be attributed to a kind of weak self-association among the MMA molecules. But the decrease of Δ shows that the effect can be neglected. The addition of N to MMA leads to the same changes as those obtained in chloroform solution. This result confirms the assumption for complex formation between N and MMA.

The association between donor and acceptor is a reversible process and it depends on the dielectric constant of the medium:

$$\mathrm{MMA} + \mathrm{N} \rightleftharpoons [\mathrm{MMA} \cdot \mathrm{N}]$$

In chloroform which has a small dielectric constant the equilibrium must be shifted to stronger association. In acetone which has the higher dielectric constant this equilibrium can be shifted to the left and might reach complete dissociation. As it is seen in Tab. 1 and Fig. 1 in acetone the chemical shift of H_b is not influenced by the presence of N. The τ-value of H_b differs only in the error limit from that of H_b of MMA without solvent. The most sensitive

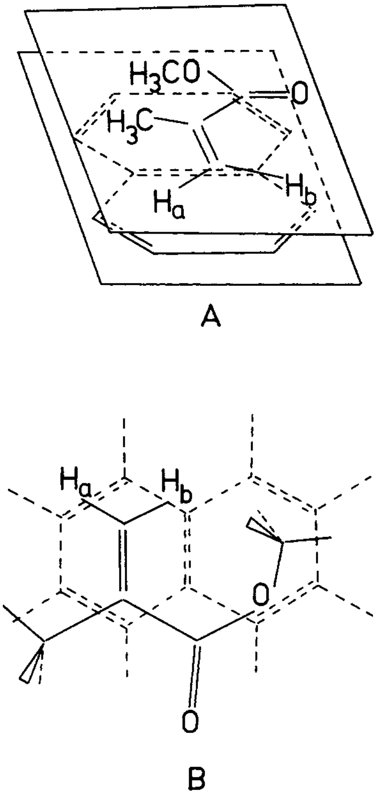

Fig. 2. Assumed models of the methyl methacrylate (MMA)-naphthalene (N) complex, mole ratio 1:1. A: according to Allen and Bateup representation of MMA-benzene 1:1 complex[10]. B: on the basis of the molecular models of MMA and N. The MMA molecule lies above the plane of the N molecule, according to the Komiyama and Hirai representation of MMA-styrene complex[14]

Tab. 1. Chemical shifts τ in p.p.m. and separation of the vinyls $\Delta = \tau(H_a) - \tau(H_b)$, (cf. **1**) in the NMR spectra of methyl methacrylate (MMA) and of the mixture of MMA and naphthalene (N) in chloroform, acetone and without solvent at 25 °C

Substances	Solvent	$\tau(H_b)$	$\tau(H_a)$	$\Delta = \tau(H_a) - \tau(H_b)$	$\tau(OCH_3)$	$\tau(\alpha\text{-}CH_3)$
MMA	$CDCl_3$	3,887	4,450	0,563	6,275	8,025
MMA+N	$CDCl_3$	3,925	4,550	0,625	6,375	8,075
MMA+N	$(CD_3)_2CO$	3,950	4,475	0,525	6,372	8,100
MMA	—	3,962	4,500	0,538	6,337	8,080
MMA+N	—	3,975	4,575	0,600	6,400	8,112

(to complex formation) H_a signal is shifted in acetone downfield and assumes a τ-value near to that of pure MMA. The separation of the vinyls has a value also near to that of MMA. It can be pointed out that the τ-values of the methoxy and α-methyl groups depend slightly on the dielectric constants of the solvents, and the small changes can be neglected. The interval of the N multiplet signal is shifted downfield ($\tau = 2{,}100$–$2{,}625$ p.p.m.).

All these results contribute to the assumption that the forces of interactions are concentrated namely in the electron donating N rings and the electron accepting C=C double bonds.

A quantitative measure for the strength of interaction between MMA and N is the stability constant of the complex. Assuming 1 : 1 complex formation the method of Hanna and Ashbaugh$^{12)}$ was used to obtain this constant. The method is based on the change in the τ-value of the most sensitive (to the interaction) proton for solutions with different mole ratios between the donor and the acceptor. From the slope of the straight line in Fig. 3 the stability constant of the complex was calculated. The value obtained $K = 0{,}22\,l\cdot mol^{-1}$ is slightly higher than that for the complex MMA-benzene$^{10)}$ and shows that the forces of interaction between aromatic donors and MMA are of the same order.

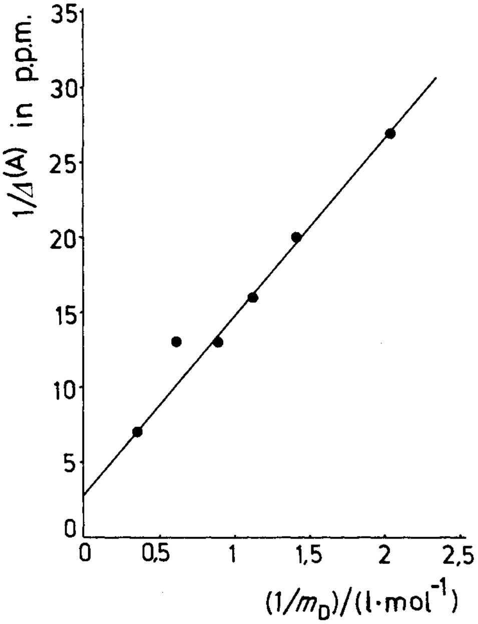

Fig. 3. Hanna-Ashbaugh plot for methyl methacrylate (MMA)-naphthalene (N) interaction in chloroform assuming 1 : 1 complex formation; concentration of MMA = 0,6 mol/l; concentration of N varying between 0,5 and 2,8 mol/l

Interaction in 2-naphthyl methacrylate

In order to study the interaction among the molecules of 2-NM, solvents with different dielectric constants, such as chloroform, acetone, acetonitrile and *N*,*N*-dimethylformamide are used. As it is seen in Fig. 4 the NMR spectrum of 2-NM in chloroform contains the signal of the naphthalene ring in the interval $\tau = 2{,}100\text{–}2{,}863$ p.p.m. and the signals of H_b and H_a vinyl protons. The τ-values of H_a and H_b are shifted to lower field in comparison with those of MMA. This shift can be explained with the influence of the aromatic ring of the alcoholic substituent in the methacrylic ester$^{15)}$. The τ-values of the signals of 2-NM in chloroform and in the other solvents are given in Tab. 2. The separation of the vinyls $\Delta = 0{,}650$ p.p.m. in chloroform is near to that of the mixture of MMA and N in the same solvent (Tab. 1).

An interaction similar to the complex formation between MMA and N can be assumed for 2-NM. The donor and the acceptor in this case are incorporated in one molecule. Due

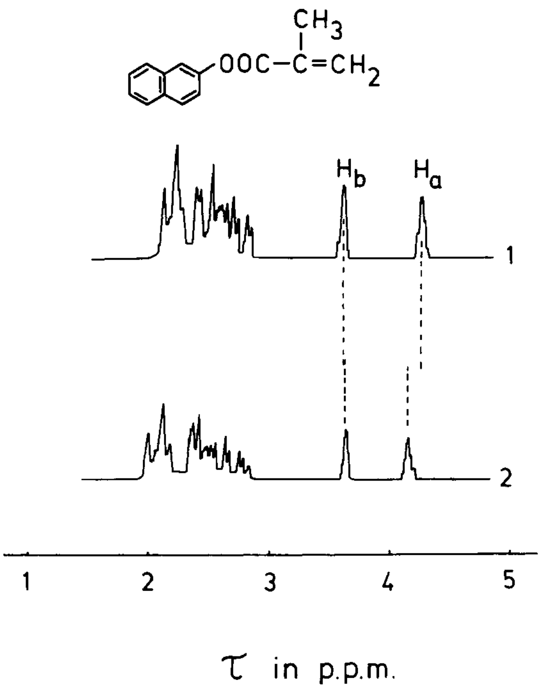

Fig. 4. ^{1}H NMR spectra at 80 MHz of 2-naphthyl methacrylate in $CDCl_3$ (spectrum 1) and in CD_3CN (spectrum 2)

Tab. 2. Chemical shifts τ in p.p.m. of the vinyl protons and H_b (cf. **1**), of the α-methyl group and the separation of the vinyls $\Delta = \tau(H_a) - \tau(H_b)$ in the NMR spectra of 2-naphthyl methacrylate in different solvents. The dielectric constants of the solvents ε are taken from[16)]

Solvent	ε	$\tau(H_b)$	$\tau(H_a)$	$\Delta = \tau(H_a) - \tau(H_b)$	$\tau(\alpha\text{-}CH_3)$
$CDCl_3$	4,7	3,625	4,275	0,650	7,900
$(CD_3)_2CO$	20,7	3,625	4,150	0,525	7,900
CD_3CN	36,2	3,637	4,150	0,513	7,900
$(CH_3)_2NCHO$	36,7	3,625	4,100	0,475	—

to the rigidity of the 2-NM molecule the interaction between the donor and the acceptor can be realized between two molecules in both ways given in Fig. 5. In chloroform the association must be more pronounced and well seen. In acetone the τ-value of H_b does not change while the signal of H_a shifts noticeably (with 0,125 p.p.m.) downfield. The Δ-value becomes equal to that of the mixture of MMA and N in acetone and very near to that of the pure MMA. This fact might be explained by a dissociation of the complex as in the case of MMA and N. In acetonitrile the signals of H_a and H_b have the same τ-values as in acetone although the former solvent has a higher dielectric constant. The interval of the N multiplet has the same τ-value of 1,975–2,850 p.p.m. in acetone as in acetonitrile, i.e. it is shifted downfield similarly to the mixture of MMA and N.

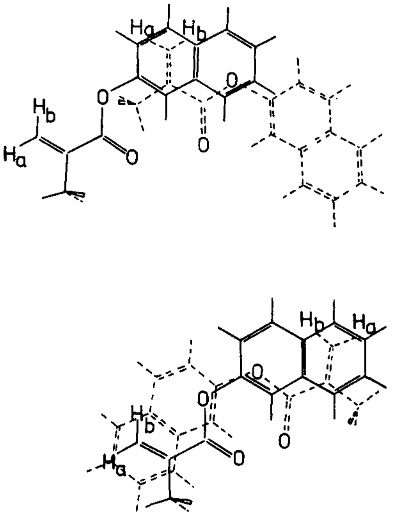

Fig. 5. Two possible models of the assumed complex between two 2-naphthyl methacrylate molecules on the basis of molecular models

Therefore, dissociation of the complex takes place in both solvents and it is complete already in acetone.

All results show that the changes in NMR signals are predominantly due to the assumed intermolecular interaction. *N*,*N*-dimethylformamide (its dielectric constant does not differ from that of acetonitrile) causes a more pronounced shift of the H_a signal to lower field than acetone and acetonitrile. The separation of the vinyls becomes lower than the Δ-value for the pure MMA. The same shift of 37 Hz (in our experiments it is 38 Hz) is observed by other authors[17] and it is explained with the formation of a complex between MMA and *N*,*N*-dimethylformamide, the influence of the latter being in the opposite direction i.e. shifting the H_a signal to lower field in comparison with the high field shift caused by N.

The signal of the α-methyl group in 2-NM does not depend on the change of the solvent. Its τ-value is unchanged in solvents of different dielectric constants and this confirms also the assumed complex formation.

Interaction in 1-naphthyl methacrylate

As it is seen in Fig. 6 the NMR spectrum of 1-NM shows chemical shifts of the N ring in an interval of $\tau = 2{,}000$–$2{,}838$ p.p.m. and signals of H_b and H_a protons similar to those in 2-NM. The vinyl protons of 1-NM are at lower field as compared with those of MMA because of the aromatic alcoholic unit. The τ-values of H_b, H_a and of the α-methyl group are smaller than the τ-values of the same protons in 2-NM (Tab. 2 and Tab. 3). The interval of the N multiplet signal is also shifted to lower field. These phenomena can be attributed to a stronger influence of the N ring as substituent in the 1-NM molecule. This ring is situated nearer to the H_a and H_b protons than in 2-NM comparing the molecular models of 1-NM (Fig. 7) and of 2-NM (Fig. 5). The Δ-value of 1-NM in chloroform (Tab. 3) is higher than in the other solvents as it is for 2-NM and this can be explained with complex

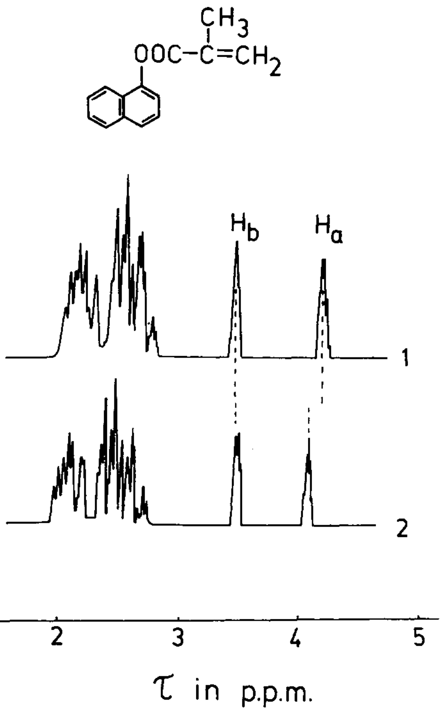

Fig. 6. ^1H NMR spectra at 80 MHz of 1-naphthyl methacrylate in $CDCl_3$ (spectrum 1) and in $(CD_3)_2CO$ (spectrum 2)

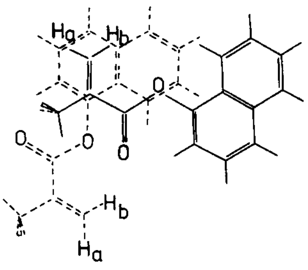

Fig. 7. Model of the assumed complex between two 1-naphthyl methacrylate molecules on the basis of the molecular models

Tab. 3. Chemical shifts τ in p.p.m. of the vinyl protons H_a and H_b (cf. **1**) and of the α-methyl group as well as the separation of the vinyls $\Delta = \tau(H_a) - \tau(H_b)$ in the NMR spectra of 1-naphthyl methacrylate in different solvents with different dielectric constants (cf. Tab. 2)

Solvent	$\tau(H_b)$	$\tau(H_a)$	$\Delta = \tau(H_a) - \tau(H_b)$	$\tau(\alpha\text{-}CH_3)$
$CDCl_3$	3,487	4,212	0,725	7,850
$(CD_3)_2CO$	3,500	4,100	0,600	7,850
CD_3CN	3,500	4,100	0,600	7,850
$(CH_3)_2NCHO$	3,525	4,100	0,575	—

formation. In acetone and in acetonitrile the signal of H_a in 1-NM is shifted downfield with 1,112 p.p.m., whereas the H_b signal does not change. The Δ-value decreases with 0,125 p.p.m. in comparison with that obtained in chloroform. As it is shown in Fig. 7 the complex formation in chloroform between the N ring and the methacrylic double bond influences mainly the H_a signal. The interaction forces in 1-NM are concentrated in the same place and they are as strong as those observed in 2-NM and in the mixture of MMA and N. In acetone the τ-value of the N multiplet signal is in the interval 1,950–2,750 p.p.m., i.e. it is shifted downfield similarly to the shifts in 2-NM and in the mixture of MMA and N. The α-methyl signal remains at the same τ-value in all solvents as it is with 2-NM, showing that the α-methyl group in both napthyl methacrylates does not take part in the complex formation. The α-methyl group lies far from the centre of the N ring in the assumed structure of the complexes (Figs. 5 and 7).

In solvents with high dielectric constants like acetone and acetonitrile the equilibrium of the complex formation process is shifted to the left to complete dissociation.

In *N,N*-dimethylformamide the τ-value of H_a does not differ from those obtained in the other solvents with high dielectric constants. The Δ-value decreases because of the slight shift of the H_b signal to high field, contrary to the observed shifts in 2-NM but it remains smaller in both 1-NM and 2-NM than the Δ-value in acetone and acetonitrile.

Conclusion

The ^{1}H NMR investigation of the mixture of MMA and N in solvents with different dielectric constants shows that by small values of the dielectric constant the electron donating N can interact with the electron accepting double bond of MMA, forming a complex as it has been established for MMA and benzene and its derivatives[10]. A similar interaction is observed also in the solutions of 2-NM and 1-NM that can be explained with the intermolecular interaction between the electron donating and the electron accepting units of these molecules.

In solvents with high dielectric constants the changes in the NMR spectra indicate that the interaction is disturbed and the complexes are dissociated.

The observed interactions confirm the theories for the influence of the solvents in radical polymerization of MMA. They can explain the established changes in polymerization kinetics of 2-NM and 1-NM[4,5] and probably the tendency of the latter to form stereoregular polymers.

The detailed study of the polymerization of these monomers in dependence upon the dielectric constant of the solvent as well as the structure of the obtained polymers will be the object of our future investigations.

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