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THE INFLUENCE OF MOLECULAR INTERACTION ON POLYMERIZATION—11*

A STUDY OF THE INFLUENCE OF THE SOLVENT ON THE TACTICITIES OF POLY(2-NAPHTHYL METHACRYLATE) AND POLY(CUMYLPHENYL METHACRYLATE) OBTAINED IN VARIOUS SOLVENTS

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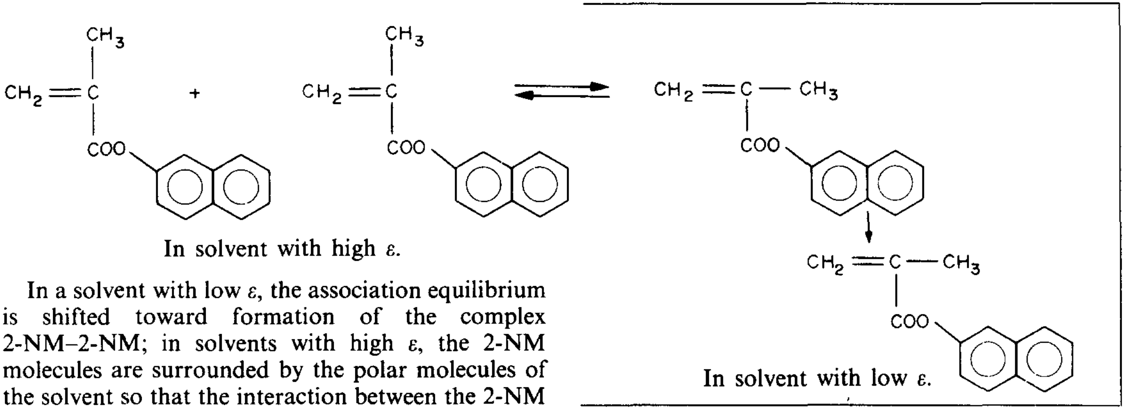
Abstract—Polymerizations of 2-naphthyl methacrylate and 4(1-methylphenethyl)phenyl methacrylate (cumylphenyl methacrylate) have been carried out in solvents with different dielectric constants and donor numbers (DN). By means of ^{1}H-NMR and fluorescence spectroscopy, the tacticities of the polymers were studied. It was found that the structures of the polymers depend on the dielectric constant of the solvent and not on its donor number. In solvents with high dielectric constant, the contents of isotactic triads are higher than for solvents with low dielectric constants.

INTRODUCTION

In a previous paper [1] we investigated the free radical polymerization of 2-naphthyl methacrylate (2-NM) in hexane, cyclohexane, benzene, acetone and acetonitrile. We found a correlation between the tacticity of the poly(2-naphthyl methacrylate) (P-2-NM) obtained and the polarity of the solvent, given by the dielectric constant (ε). We explained this phenomenon by the possibility of donor–acceptor interaction between the 2-NM molecules, dependent on the dielectric constant of the solvent [2].


In solvent with high ε.

In solvent with low ε.

In a solvent with low ε, the association equilibrium is shifted toward formation of the complex 2-NM–2-NM; in solvents with high ε, the 2-NM molecules are surrounded by the polar molecules of the solvent so that the interaction between the 2-NM molecules is strongly hindered and the equilibrium is shifted to the left. Thus we found two kinds of interaction *viz.* donor–acceptor on the one hand and dipole–dipole on the other. Many solvents possess an electron-donating ability given by the donor number (DN) [3]. If the solvent has a high donor ability, the formation of complexes 2-NM–solvent may be expected. Thus there are two quantities (ε and DN) which may influence the behaviour of monomer during polymerization.

We consider again the radical polymerization of 2-NM in various solvents, selected so that the influence of the DN as well as that of the dielectric constant may be followed. We wished to find out which of these two characteristics of the solvent determines the behaviour of the monomer during polymerization. A similar investigation was carried out also with 4(1-methylphenethyl)phenyl methacrylate (trivial name, cumylphenyl methacrylate, CPhM) the molecules of which also could form donor–acceptor associates between themselves [4].

EXPERIMENTAL

Materials

2-NM was synthesized by the Patai method [5] and CPhM by a published method [6]. The solvents used are given in

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*Part 10: H. Boudevska and O. Todorova, On the copolymerization of methacrylic acid with styrene *Makromolek. Chem.* In press.

Table 1. Solvents used for polymerization

Solvent	Drying agent‡	Dielectric constant (ε*)	Donor number (DN†)
DMSO	NaOH	49.0	29.8
Acetonitrile	$CaCl_2$	36.2	14.1
Methanol	$CaCl_2$	32.0	19.0
Acetone	$CaCl_2$	20.7	17.0
Nitrobenzene	$CaCl_2$	34.8	4.4
Nitromethane	$CaCl_2$	38.6	2.7
THF	KOH	7.3	20.0
1,4-Dioxane	$CaCl_2$	2.2	14.8
Chloroform	$CaCl_2$	4.7	—

*According to Ref. 7. †According to Ref. 8. ‡After drying, solvents pumped by distillation.

Table 1 as well as the ways of purification and the values of ε and DN.

Polymerization

Polymerization was carried out as previously described [1]. The concentration of the monomer was 1 mol/l with 1 mol% 2,2′-azoisobutyronitrile as initiator. The temperature was 60° and duration was 30–48 hr; yields were 60–80%. In most solvents, the polymerizations of 2-NM and CPhM were homogeneous. In methanol, acetonitrile and nitromethane, P-2-NM precipitated during polymerization. In methanol, acetonitrile/nitromethane and dimethylsulphoxide (DMSO) the polymerizations of CPhM were heterogeneous. The conversions of P-2-NM and poly(cumylphenyl methacrylate) (PCPhM) to poly(methyl methacrylate) (PMMA) were carried out as already described [1].

Measurements

The ^{1}H-NMR spectra were recorded on a spectrometer Bruker-250 WM-FT, 250 MHz at room temperature with TMS as internal reference. The spectra of all samples of PMMA were recorded in $CDCl_3$. The tacticities of these polymers were measured from the signals of the α-CH_3 protons at $\delta = 0.85$, 1.03 and 1.26 ppm, corresponding to s, h, and i-tactic triads [9]. The fluorescence spectra were taken on a fluorescent spectrometer Perkin–Elmer MPF 44 A at λ of excitation 290 nm. The concentration of the polymer solutions was 2×10^{-3} mol/l.

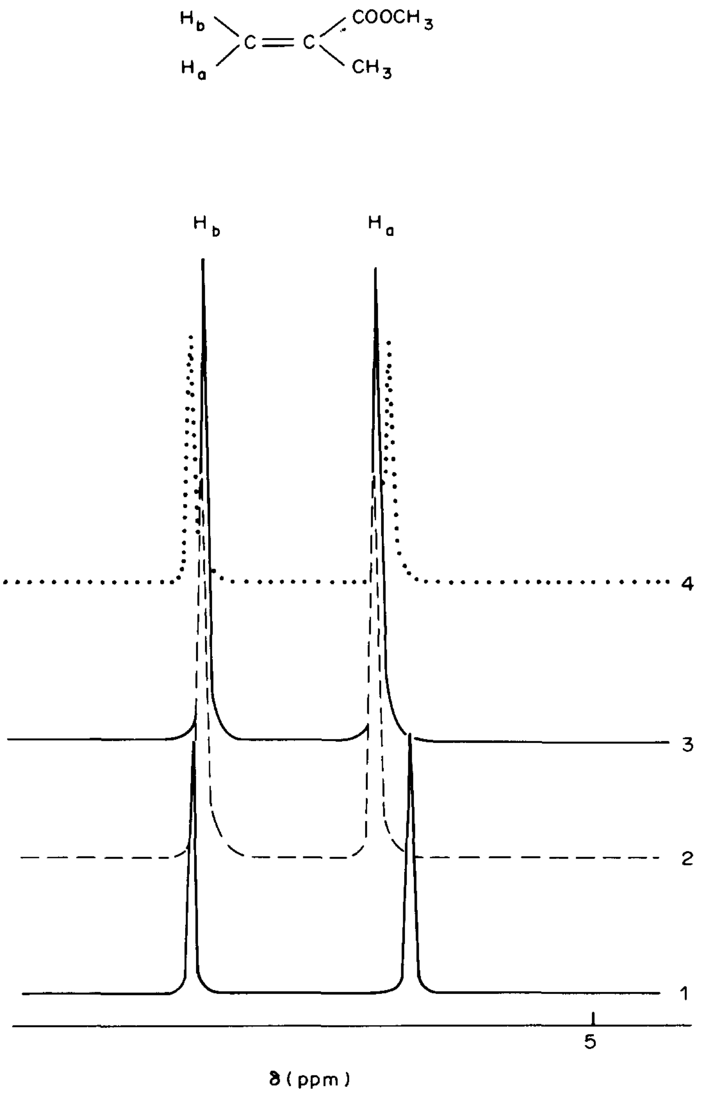

Fig. 1. ^{1}H-NMR spectra (at 250 MHz) of methyl methacrylate (MMA) in its equimolar mixtures with naphthalene (N), taken in the solvents: (1) deuterochloroform; (2) perdeuteroacetonitrile; (3) perdeuteronitromethane; (4) perdeuterotetrahydrofuran.

Table 2. Chemical shifts (δ in ppm) of the vinyl protons H_a and H_b of methyl methacrylate (MMA) in its equimolar mixtures with naphthalene (N) in various solvents

Solvent	δ_{H_b}	δ_{H_a}	$\Delta = \delta_{H_b} - \delta_{H_a}$
Chloroform	6.08	5.49	0.59
Acetonitrile	6.05	5.59	0.46
Nitromethane	6.05	5.58	0.47
THF	6.08	5.55	0.53

RESULTS AND DISCUSSION

In a previous paper [2] on the behaviour of the 2-NM molecules in solution, we used the model system methyl methacrylate (MMA)–naphthalene (N). It was shown that there may be donor–acceptor interaction where N plays the role of an electron donor and the vinyl double bond from MMA that of an electron acceptor. The resulting donor–acceptor complex MMA–N may exist in solvents with low dielectric constant. In a solvent with high ε where the MMA molecules are surrounded by the highly polar molecules of the solvent, this dipole–dipole interaction strongly hinders the formation of the complex MMA–N. The shifting of this donor–acceptor equilibrium to the left or to the right is observed via the shifting of the vinyl protons H_a and H_b in the ^{1}H-NMR spectrum of MMA.

We used the same system again. Figure 1 shows the signals of the vinyl protons H_a and H_b of MMA in the ^{1}H-NMR spectra of equimolar mixtures MMA–N in various solvents. Table 2 shows the chemical shifts of these protons as well as the differences Δ between them. In chloroform, a solvent with $\varepsilon = 4.7$ and no DN, where we have proved the existence of the complex MMA–N [2], the peak of the H_a proton appears at the strongest magnetic field ($\delta = 5.49$ ppm, $\Delta = 0.59$ ppm). With acetonitrile ($\varepsilon = 36.2$; DN $= 14.1$), the signal for the same proton is shifted 0.1 ppm downfield ($\delta = 5.59$ ppm and Δ decreases becoming 0.46 ppm). As acetonitrile is a solvent with both high ε and DN, it cannot be decided for certain which of these characteristics of the solvent is responsible for this shifting, i.e. for the decomposition of the complex MMA–N. It is not clear whether new complexes MMA–solvent are formed (due to the electron-donating ability of the solvent S) or we have only MMA molecules surrounded by the molecules of the solvent (dipole–dipole interaction due to the polarity of the solvent). With nitromethane [a solvent with high polarity ($\varepsilon = 38.6$) but low DN (DN $= 2.7$)] instead of acetonitrile, the pattern of the ^{1}H-NMR spectrum is the same as in acetonitrile; the H_a proton peak appears at $\delta = 5.58$ ppm and $\Delta = 0.47$ ppm. Therefore the high polarity of nitromethane hinders the interaction MMA–N. It could be assumed that the decomposition of the complex MMA–N in acetonitrile is also due to its polarity and not to its electron-donating properties. In the spectrum of the model system taken in tetrahydrofuran (THF; a solvent with low polarity, $\varepsilon = 7.3$ and high donor ability, DN $= 20.0$), the signal of the H_a proton is again shifted downfield compared to its position in chloroform ($\delta = 5.49$ ppm), but not to such an extent as in acetonitrile and nitromethane. The δ-value of this proton in THF is higher than that in chloroform but lower than in acetonitrile and nitromethane (Table 2). So we may conclude that for weak dipole–dipole interaction MMA–S, the solvent molecules, due to their high electron-donating ability, may compete to some extent with the donor N in its interaction with MMA, i.e. in the system there should exist at the same time the complexes MMA–N and MMA–S.

This ^{1}H-NMR study confirms the previously found relationship between the ability for donor–acceptor interaction between the 2-NM molecules and the dielectric constant of the solvent. Unfortunately we could not find such a relationship with the electron-donating ability of the solvent, as expressed by the donor number.

Bearing this in mind, we have carried out radical polymerization of 2-NM and CPhM in 9 solvents. For reasons discussed previously [1, 6], the polymers were converted by hydrolysis and methylation to PMMA, for which we determined the tacticity (i, h and s triads). Previously we found [10] that the ratio eximer intensity/monomer intensity (I_E/E_M) in the fluorescence spectra of P-2-NM depends on its structure so, in order to complete the data from the ^{1}H-NMR analysis, we recorded also the fluorescence spectra of these polymers. We found that PCPhM does not possess eximer emission.

Table 3 gives the results from the ^{1}H-NMR and fluorescence analysis of P-2-NM, obtained in various solvents. The obtained P-2-NM polymers are given in order of decreasing ratio I_E/I_M which is in agreement with the contents of isotactic triads. This ratio varies in the range 0.79–0.69. The lowest values 0.71 and 0.69 refer to polymers obtained in chloroform, THF and dioxane. The contents of isotactic triads, determined by ^{1}H-NMR, range from 0.15 to 0.06 and the

Table 3. Tacticity of poly(2-naphthyl methacrylate) obtained in various solvents

Solvent	Dielectric constant (ε)	Donor number (DN)	Fluorescence analysis (I_E/I_M)	Tacticity in triad fractions		
				mm	mr	rr
Acetonitrile	36.2	14.1	0.79	0.14	0.33	0.53
Methanol	32.0	19.0	0.79	0.12	0.38	0.50
DMSO	49.0	29.8	0.77	0.15	0.33	0.52
Nitromethane	38.6	2.7	0.76	0.11	0.37	0.52
Nitrobenzene	34.8	4.4	0.75	0.14	0.32	0.54
Acetone	20.7	17.0	0.74	0.10	0.37	0.53
1,4-Dioxane	2.2	14.8	0.71	0.09	0.36	0.55
THF	7.3	20.0	0.69	0.09	0.35	0.56
Chloroform	4.7	—	0.69	0.06	0.36	0.58

Table 4. Tacticity of poly(cumylphenyl methacrylate) obtained in various solvents

Solvent	Dielectric constant (ε)	Donor number (DN)	Tacticity in triad fractions		
			mm	mr	rr
DMSO	49.0	29.8	0.15	0.31	0.54
Methanol	32.0	19.0	0.15	0.37	0.48
Nitromethane	38.6	2.7	0.11	0.32	0.57
Acetonitrile	36.2	14.1	0.09	0.41	0.50
Nitrobenzene	34.8	4.4	0.09	0.32	0.59
THF	7.3	20.0	0.08	0.35	0.57
Acetone	20.7	17.0	0.07	0.37	0.56
1,4-Dioxane	2.2	14.8	0.06	0.37	0.57
Chloroform	4.7	—	0.06	0.31	0.63

lowest values are in the same solvents. These are the solvents with lowest values of ε and at the same time with different donor abilities, i.e. here again we find good correlation between the tacticity of the polymers and the dielectric constant of the solvent. No such correlation may be found with the DN.

The following example supports this conclusion. If we take two solvents with nearly the same DN but with different values of ε, say methanol and THF, the polymers have evident differences in their stereoregularity. If the DN was the determining factor, these polymers should have similar structures.

Table 4 shows the data from the ^{1}H-NMR analysis of samples of PCPhM. The polymers are given in order of decreasing content of isotactic fraction. It may be seen that the order is almost the same as for P-2-NMs. At the top of the Table are the polymers obtained in solvents with high ε; at the bottom are those obtained in solvents with low ε. The last two places are again occupied by the polymers obtained in chloroform and dioxane. Some differences in the arrangement of the solvents may be explained by the statistical character of the radical process, where effective control is hard to achieve.

From the obtained PCPhMs, we may again choose suitable pairs to prove the relation between tacticity and ε, e.g. chloroform and nitromethane. They have similar DNs but different ε. The tacticities of the polymers obtained in these solvents are also different and correlate with the change of ε.

CONCLUSIONS

In solution the molecules of 2-NM and CPhM may interact with themselves, forming donor–acceptor associates. The interactions depend on the solvent polarity; they occur in nonpolar solvents but not in polar solvents. If the nonpolar solvent has a strong electron-donating ability, it may compete with the donor, but it does not decompose the complex to such a degree, as in a solvent with a high dielectric constant. The presence of associates between the monomer molecules determines the stereoregularity of the polymers, i.e. there is a correlation between the dielectric constant of the solvent and the tacticity of the obtained samples of P-2-NM and PCPhM.

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