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RADICAL POLYMERIZATION OF DIETHYLAMINOETHYL METHACRYLATE AND ITS SALTS IN VARIOUS SOLVENTS

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Abstract—NMR-spectral data for diethylaminoethyl methacrylate and its salts in various solvents have been considered with the kinetics of polymerization of these monomers. The data on the interaction of a monomer with a solvent obtained using NMR-spectroscopy lead to ideas about the effect of the formation of hydrogen bond between solvent and monomer molecules, protonization and ionization of the monomer on its reactivity in the polymerization. The effect of various conformations of growing polymer chains upon the rate of polymerization is also very important.

INTRODUCTION

Recently much interest has been shown in polymers based on aminoalkyl(meth)acrylates and their salts. This interest is caused by the uses of such polymers in particular for water purification, in paper production, etc. A review of the polymerizations of these monomers has been published [1]. Investigation on the kinetics of radical polymerization of aminoalkylmethacrylates and their salts has shown that the total polymerization rate of these monomers increases on going from organic solvents to water, a particularly large effect of the nature of the solvent being found for aminoether salts [1, 2].

To understand the causes of the observed kinetic effects, we have determined the absolute values of the rate constants of propagation and termination in the polymerization of diethylaminoethyl methacrylate (DE) and some of its salts in various solvents [3]. According to the data in Table 1, increase of the total polymerization rate in an aqueous solution is due entirely to an increase of k_p. The value of k_t also increases on going from organic to aqueous media.

It should be noted that an increase of both k_p and k_t on going from an organic solvent to water is found also for other water-soluble monomers e.g. acrylamide, acrylic acid, *N*-vinylpyrrolidone [4].

The electronic states of monomers and macroradicals, determining the reactivity of these compounds, largely depend on the nature of the solvent. Indeed, the processes of ionization, of the formation of contact and free ion-pairs and intermolecular hydrogen bonds, affecting the electronic states of aminoethers and their salts, are associated with the proton–donor and polar characteristics of the solvent. Therefore, to throw light on the mechanism underlying the effect of the nature of the solvent on radical polymerizations of these monomers and of other water-soluble monomers, there is a need for further study in which examination of the kinetics of the process accompanies an investigation into the interaction of monomers and polymers with solvents of different nature and into the effect of the nature of the solvent on the electronic structures of monomers and polymers.

Evidence for changes of the electronic structures of the groups C═O and C═C in DE and in its salts with variation of the properties of the medium is furnished by u.v.- and i.r.-spectroscopic data [3]. Indeed, an increase in the polarity of the solvent, of its proton–donor properties and the replacement of an organic solvent by water account for a change in the conjugation of the C═O and C═C groups, as indicated by a long-wave shift of π–π^*-transition in these compounds, as well as displacement of the absorption band of the carbonyl group to lower frequencies.

More complete information on the change of the electronic state of all the functional groups of aminoethers and their salts under the effect of the medium can be obtained by using NMR-spectroscopy.

The ^{1}H- and ^{13}C-NMR-spectra of DE and its salts in various solvents have been studied by us [5]. In the present work the data have been considered with kinetics of polymerization of these monomers.

In solvents not forming hydrogen bonds with the oxygen of the carbonyl group of DE (dioxan, chloroform), the chemical shifts of the ^{13}C of this group in the protonated and nonprotonated forms of an aminoether are practically coincident. Comparison of the chemical shifts of ^{13}C of the C═O group in aminoether and in its protonated form in methanol indicates that protonation prevents the formation of intermolecular hydrogen bonds by the carbonyl group. This effect is indicated by a lower value of the chemical shift in the protonated form in methanol. At the same time, the chemical shifts of ^{13}C of the group CH_2═ in the protonated form are larger than in the nonprotonated aminoether. Thus, protonation of DE accounts for a decrease of the electron density of the β-carbon atom in the C═C bond, thereby increasing the reactivity of the monomer.

One should note the coincidence of the chemical shifts of ^{13}C of the C═O group in the protonated forms of DE and in DE quarternized by methyl

Table 1. The value of k_p and k_t in the polymerization of DE, DE·AA and DE·HCl in various solvents; 25° u.v.-light, 365 nm

Monomer	Solvent	$k_p \cdot 10^{-3}$ (mol/l·sec)	$k_t \cdot 10^{-7}$ (mol/l·sec)
DE	Dioxan	0.090 ± 0.027	0.060 ± 0.016
	Dioxan–water*	0.36 ± 0.070	0.33 ± 0.060
	Methanol	0.70 ± 0.15	1.3 ± 0.30
DE·AA	Dioxan	0.30 ± 0.080	0.10 ± 0.030
	Dioxan–water*	1.8 ± 0.63	1.2 ± 0.42
	Water	72 ± 16	65 ± 15
DE·HCl	Methanol	3.3 ± 0.70	0.90 ± 0.20
	Methanol–water*	11 ± 2.0	6.0 ± 1.2

*Water content 5 vol%.

bromide. Such a coincidence suggests that no intermolecular hydrogen bond is formed in the protonated form.

The protonated forms of aminoether in organic solvents exist as ionic pairs. The evidence is found in the spin–spin interaction of J (CH_2NH^+) observable in PMR-spectra. In aqueous solutions, because of rapid intermolecular proton exchange, this interaction is not observed. Consequently, in these solutions the protonated forms exist mainly as free ions.

Comparison of chemical shifts of ^{13}C and ^1H of the CH_3 group in the ethyl group on the nitrogen atom (atom C_8) in the acetic acid salt of DE (DE·AA) and in the protonated forms and quaternized DE permits us to determine the degree of ionization of this salt.

In all the studied solvents, which are not acids, the chemical shifts of ^1H associated with the atom C_8 of DE are practically the same (~ 1.03 ppm), thus indicating the existence of aminoether in these solvents in the nonprotonated form. In the presence of an equimolar quantity of hydrochloric or trifluoracetic (TFAA) acids, DE will be completely protonated, regardless of the nature of the solvent, and the chemical shift of ^1H in C_8 is 1.35–1.49 ppm.

The values of chemical shifts of the ^{13}C atom of C_8 in the DE spectra in acetic acid and TFAA likewise suggest the existence of an aminoether in a protonated form. Since the values of the chemical shifts of ^{13}C of the carbonyl group in DE and in DE·HCl and DE·TFAA salts in dioxan and chloroform solutions coincide whereas the chemical shifts of ^{13}C of atom C_8 in DE and its salts are significantly different, we may conclude that the protonation of DE occurs solely at the nitrogen atom.

Analysis of the NMR spectra (^1H and ^{13}C) of DE·AA salt in various solvents enables us to follow the transition from the nonprotonated to the protonated form of DE. If the position and multiplicity of signals in PMR spectra of aminoether and its acetic acid salt in dioxan solution are practically similar, the PMR spectrum of DE·AA in the aqueous solution already coincides with that of DE·HCl salt in which aminoether is present in a completely protonated form. An intermediate position for the chemical shifts of all the atoms of DE·AA salt in solution in chloroform and methanol indicates the presence of both the nonprotonated and protonated form of DE in these solvents. A similar conclusion is to be drawn from the analysis of ^{13}C-NMR spectra of DE·AA salt. Thus, the values of the chemical shifts of C_8 of DE·AA, which are sensitive to the protonation process, change on passing from dioxan to water by 2 ppm and in the aqueous solution coincide with the chemical shift for the protonated form of DE. There is, moreover, coincidence of the chemical shifts of ^{13}C of the other DE carbon atoms in DE·AA and DE·HCl salts in the aqueous solution.

In the sequence of solvents dioxan–chloroform–methanol–water for the DE·AA system, there is a gradual transition from the nonprotonated to the protonated form of aminoether. Making use of the value of 9.5 ppm for the chemical shift δ_{CH_3} for the protonated form (the mean value for the three studied salts) and a value 12.5 ppm for the nonprotonated form, we determined the content of the protonated form of aminoether in the DE·AA system in various solvents. The calculation has revealed that the mole fractions of the protonated form in dioxan, chloroform, methanol and water are 0.4, 0.6, 0.9 and 1.0 respectively. Thus, the quantity of the protonated form of aminoether in the DE·AA system increases with increase of the dielectric permeability and solvating capacity of the solvent.

With variation of the proton-donor capacity of the solvent molecules and the change of the chemical shift of ^{13}C of the C=O group, there is a change of the chemical shift of ^{13}C of the CH_2= also, the values of chemical shifts for these groups being related linearly for aminoether both in the nonprotonated and the protonated forms (Fig. 1). Such a dependence is evidence for the fact that a change of the electronic state of the C=O group because of the formation of a hydrogen bond with the solvent molecules will lead to a change in the electron density on the carbon atom of the CH_2= group as a result of the conjugation of the carbonyl group and the olefinic bond. The observed displacement of the ^1H and ^{13}C signals of C=O and CH_2= groups towards weaker field in passing from CCl_4 to methanol and water is evidence [6] for a certain decrease of the electron density on the carbon atoms on the C=O and CH_2= groups and, consequently, of a change in the reactivity of the monomer. Indeed, as follows from the data in Fig. 2, a variation of $\delta_{C=O}$ is accompanied by a variation of the polymerization rate both for DE and for DE·AA and DE·HCl.

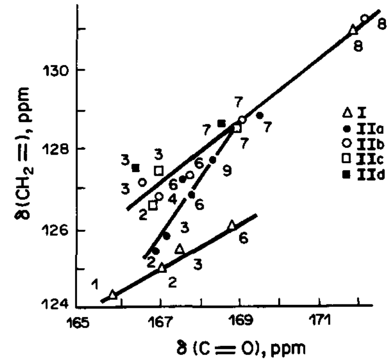

Fig. 1. Interdependence of the chemical shifts of ^{13}C of the groups C=O and CH_2= of DE (I), of the salts of DE·AA (IIa), DE·HCl (IIb), DE·TFAA (IIc), DE·CH_3I (IId) in various solvents: 1, CCl_4; 2, dioxan; 3, chloroform; 4, acetone; 5, acetic acid; 6, methanol; 7, water; 8, TFAA; 9, methanol–water, 50:50 mol%.

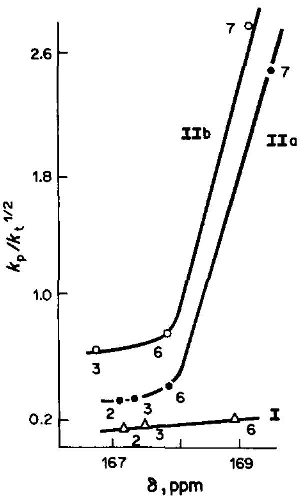

Fig. 2. Correlation between the polymerization rate and chemical shifts of ^{13}C of group C=O in DE (**I**), DE·AA (**IIa**) and DE·HCl (**IIb**). Numbering of solvents as in Fig. 1.

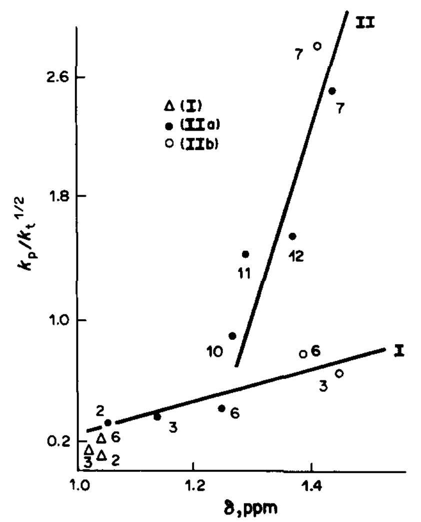

Fig. 3. Correlation between the polymerization rate and chemical shifts of ^1H of CH_3 group in DE (**I**), DE·AA (**IIa**), DE·HCl (**IIb**) in organic solvents (**I**) and in dioxan–water mixtures and in water (**II**). 10, Dioxan–water = 70:30; 11, dioxan:water = 50:50; 12, dioxan:water = 30:70 vol%. Numbering of other solvents as in Fig. 1.

In the DE·AA system, the degree of the protonation, as pointed out above, depends on the nature of the solvent; in some solvents (particularly in water–organic mixtures), the acetic acid salt of DE appears to exist in the form of an equilibrium mixture of molecular complexes with a hydrogen bond N ... HO and protonated forms: contact ion-pairs $NH^+ \ldots O^-$ and free ions.

Thus, a change in the nature of the solvent leads not only to protonation of aminoether but also to the formation of different forms of protonated salt, contact ion-pairs and free ions. Understandably, the kinetic parameters of polymerization of these compounds are markedly different.

Polymerization of DE in all cases is slower than the polymerization of its salts. In organic solvents where protonation mainly leads only to contact ion-pairs, the reaction rate increases comparatively little with increase of protonation (Fig. 3, curve 1). A more noticeable increase of the polyermization rate is found in the formation of free ions. Indeed, with increase of the water content in water–dioxan mixtures and particularly in passing to aqueous solution, i.e. increasing fraction of free ions, there is a sharp increase in the polymerization rates of DE and DE·HCl (Fig. 3, curve 2).

To explain these results, let us examine the effect of the nature of the solvent on the electronic state of DE and its salts. Such an effect is due both to the formation of a H-bond between the solvent and the carbonyl group of the monomer and also to the appearance of a positive charge at the nitrogen atom. If we use for estimating the "polarity" of the solvent an empirical scale E_T [7], we discover that the values of $\delta_{C=O}$ plotted against E_T satisfactorily fit a single straight line, regardless of whether they belong to the nonprotonated (DE) or protonated (DE salts) form [Fig. 4(a)]. A different picture is found for a similar dependence of $\delta_{CH_2=}$ upon E_T [Fig. 4(b)] where we distinctly see two lines one of which corresponds to the nonprotonated (line 1) and the other to the protonated (line 2) forms. The higher values of the chemical shift of the $CH_2=$ group for the protonated form of aminoether as compared to its nonprotonated form (by 2–3 ppm) are associated with an additional displacement of the electronic density from

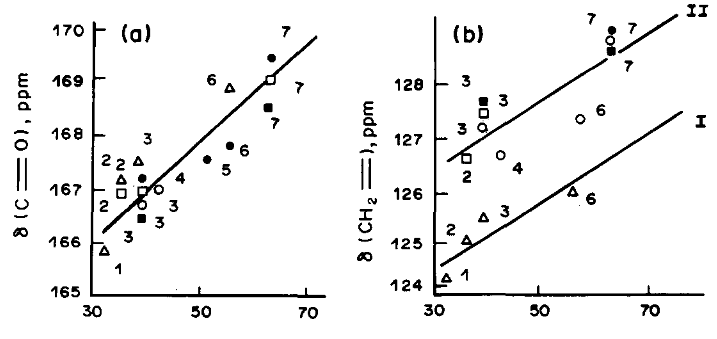

Fig. 4. Interdependence of E_T and the chemical shifts of ^{13}C of the groups C=O (a) and $CH_2=$ (b) for DE and its salts in various solvents. Numbering of solvents as in Fig. 1.

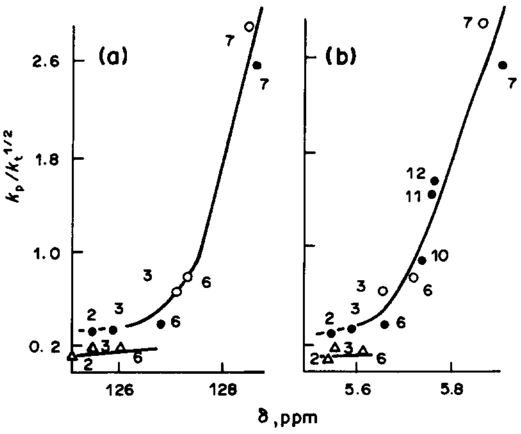

Fig. 5. Correlation between the polymerization rate and the chemical shifts of ^{13}C (a) and ^1H (b) of group $CH_2=$ in DE (I), DE·AA (**IIa**), DE·HCl (**IIb**). Numbering of solvents as in Figs 1 and 3.

$CH_2=$ to the positive-charged nitrogen atom. Such a change of the electron density on the C=C bond happens, in effect, to be one of the reasons for faster polymerization of aminoether salts as compared to nonprotonated DE.

Decrease of the electron density on the double bond of the monomer, because of the formation of a hydrogen bond with C=O and protonation on the nitrogen atom, leads possibly to a faster reaction of the monomer with the radical because of the nucleophillic properties of alkyl radicals [8]. This effect can explain the faster polymerization of aminoether monomers in going from inert (dioxan) to proton-donor (methanol) organic solvents. Indeed, from the data in Fig. 5, there is a practically linear dependence between the values of $\delta_{CH_2=}$ and $k_p/k_t^{1/2}$ in the polymerizations of DE, DE·AA and DE·HCl.

Quite a different picture is obtained by examining the polymerization of aminoether salts in aqueous–organic mixtures and in aqueous solution, i.e. in those systems where aminoether salts exist as free ions. Although the value of $\delta_{CH_2=}$ in such solvents various linearly with the E_T parameter (Fig. 4), the polymerization rate in these systems greatly increases compared to polymerization in organic solvents, a sharp departure from the linear dependence $k_p/k_t^{1/2}$ vs $\delta_{CH_2=}$ being observed (Fig. 5). To explain this kind of behaviour, apart from a variation of the reactivity of the monomer because of a variation of the electron density on the double bond, it is apparently necessary to take into account the effect of the solvent on the conformational state of macromolecules.

Earlier in studying acrylamide polymerization, it was found that an increase in the size of the polymer coil in going from solutions in DMSO to aqueous solutions accounts for a significant increase in polymerization rate [9]. In the case of aminoethers, change from an organic solvent to aqueous–organic mixtures and aqueous solutions must lead to a more significant variation of the size of the polymer coil since, apart from a variation of the thermodynamic property of the solvent, the degree of the ionization of the salts is likewise subject to change. The appearance of free ions in aqueous solutions contributes to a further increase in the size of the polymer coil, thus accounting for faster polymerization.

A change in the size of the polymer coil in the presence of water was established experimentally; the relative viscosity of solutions of DE·AA polymers increases with increase in the quantity of water in a mixed solvent dioxan–water.

A different conformation of growing macroradicals of aminoether and its salts in solution is also one of the causes of the faster polymerizations of the salts as compared to nonprotonated aminoether. The intrinsic viscosities of DE and DE·HCl polymers of the same molecular mass, as measured in solution in methanol in the presence of LiCl, differ by a factor of *ca* two, thus indicating a lower density of the macromolecular coil of the salt as compared to aminoether.

Thus, the results indicate that the effect of the nature of the solvent on the radical polymerization of aminoether monomers is mainly due to two factors:

(1) variation of the reactivity of the monomers because of the formation of hydrogen bonds with the solvent and protonation on the nitrogen atom; and
(2) variation of the conformational characteristics of polymer chains in various solvents.

The role of the latter factor is shown particularly in going from organic solvents to water. It can be assumed that, for radical polymerizations of other water-soluble monomers also, the effect of the nature of the solvent is due to the same factors.

EXPERIMENTAL PROCEDURES

Monomers and solvents for spectral measurements were prepared in the following manner: DE was kept over Al_2O_3 and was twice distilled *in vacuo* at 86°/9 mm Hg, n_D^{20} 1.4440; DE·HCl salt was recrystallized from acetone, m.p. 102°. Chloroform was dried over P_2O_5; the other solvents were dried over CaH_2 and then distilled.

The ^{13}C-NMR spectra were recorded on the spectrometer Bruker HX-90 (90 MHz) in the Fourier regime with broad band decoupling from spin–spin interaction with protons. The ^1H-NMR spectra were recorded on the spectrometer Tesla BS-437 at a frequency of 100 MHz. All the spectra were taken at 30° with HMDS as internal standard. To convert the chemical shifts to a standard scale relative to TMS, 1.95 and 0.05 ppm respectively were added to the values of the measured chemical shifts of Carbon-13 and protons.

Polymerization was carried under the action of u.v.-light (365 nm) in the presence of azobisisobutyronitile as a photosensitizer. The value of $k_p/k_t^{1/2}$ was calculated from the total polymerization rate and initiation rate. To determine the rate of initiation, we measured the length of the induction period of polymerization by conducting the process in the presence of known quantities of an effective inhibitor viz. 2,2,6,6-tetra-methyl-4-oxopiperidine-*N*-oxyl.

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