Brief Communications

^{1}H NMR spectra of water contained in solutions of poly(*N*-vinylpyrrolidone) and its modification products in $CDCl_3$

T. P. Klimova,[a] T. A. Babushkina,[a]* and V. Yu. Khvostova[b]

[a]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 119991 Moscow, Russian Federation.
E-mail: tab@ineos.ac.ru
[b]*All-Russia Research Institute of Gas and Gas Technology,*
142717 pos. Razvilka, Moscow Region, Russian Federation

^{1}H NMR spectra in $CDCl_3$ of poly(*N*-vinylpyrrolidone), epoxidized poly(*N*-vinylpyrrolidone), and products derived from the latter by modification with amino acids (glycine, β-alanine, γ-aminobutyric acid, and ε-aminocaproic acid) were examined. The ^{1}H NMR spectra of the modified polymers contain signals for water protons due to different centers of water sorption. These signals differ in chemical shift and integral intensity and indicate a changed spatial packing of the polymer as the result of its modification.

Key words: NMR spectroscopy, poly(*N*-vinylpyrrolidone), epoxidized poly(*N*-vinylpyrrolidone), modified polymers.

Water-soluble poly(*N*-vinyl amides), in particular, poly(*N*-vinylpyrrolidone) (PVP), are being extensively studied as models of natural polymers with the carbamoyl group.[1] Homo- and copolymers of *N*-vinylpyrrolidone are found in a large number of drugs and medicinal preparations and serve as carriers of biologically active substances, as well as sorbents and coagulants. The area of application of PVP is now constantly extending since even slight modification of PVP gives rise to polymers with new functional properties. The changed functional properties of a modified polymer can be attributed to a change in its spatial packing upon the modification.

According to the literature data,[1] the dissolution of PVP in aqueous or aqueous-organic media is accompanied by hydrogen bonding between the C=O groups and water molecules. Moreover, water molecules associated with the carbonyl groups of the pyrrole rings are bound to each other by hydrogen bonds. In a hydrophobic solvent (*e.g.*, chloroform), the spatial arrangement of the monomer units of a polymer relative to each other will substantially differ from that in an aqueous solution: the hydrophilic groups (C=O for PVP) will be shielded from the solvent to the largest possible extent. However, the surface of such "convoluted" macromolecules can bear cavities (folds and pockets) that contain C=O groups interacting with water molecules.

Modification of PVP with molecules containing acetamido or amino groups can favor the formation of a par-

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tially cross-linked polymer with new cavities containing water molecules or water associates differing from water in PVP.[1] These water molecules can produce new signals in ^{1}H NMR spectra, thus indicating a changed spatial packing of the modified polymer.

^{1}H NMR data for polymers in hydrophobic solvents can be more informative than those in aqueous solutions. First of all, this relates to the number and capacity of water sorption centers and changes in the spatial packing of the modified polymer molecule.

To verify this assumption, we examined the ^{1}H NMR spectra of solutions of PVP and its modified derivatives in $CDCl_3$ (in this solvent, signals for water bound to polymers can be observed).

Experimental

Deuterated chloroform (Merck, water content 0.007%) and PVP (molecular weight 12 600±2700 (FS 42-1194-78)) were used. Epoxidized poly(*N*-vinylpyrrolidone) (EPVP) and polymers modified with amino acids (glycine (Gly), β-alanine (Ala), γ-aminobutyric acid (ABA), and ε-aminocaproic acid (ACA)) were prepared according to known procedures.[2,3] The polymer chain length in a PVP was estimated at 110 to 130 units from its molecular weight and the molecular weight of each monomer unit. Since the yields of modified polymers are low (~1%), one can believe that for every polymer chain there is on average a molecule of amino acid.

The concentrations of the polymers in chloroform were 6 mg mL^{-1}. ^{1}H NMR spectra were recorded on a Bruker WM-250 spectrometer at 295 K (unless otherwise specified). The chemical shift of signals for the residual chloroform protons in $CDCl_3$ was taken to be δ 7.25.

Results and Discussion

Apart from the signals of the residual chloroform protons, the ^{1}H NMR spectrum of pure $CDCl_3$ contains a signal of water protons (δ 1.55, line width at half-length ≤3 Hz), which is shifted upfield upon heating (δ 1.43, 320 K). Apparently, the acid proton of chloroform interacts with the O atom of water.

When water is added to this chloroform (500 μL of $CDCl_3$ + 4 μL of D_2O), another, broader signal for its protons appears at δ 4.82 (line width at half-length ≥9 Hz, 288 K), which is also shifted upfield upon heating (δ 4.51, 310 K). This low-field signal can be assigned to water, which is immiscible with chloroform (block water) and forms hydrogen bonded associates.

The ^{1}H NMR spectrum of a solution of PVP in chloroform shows two sets of signals. The first set includes signals of the NCH_α protons in the polymer chain and of the $-CH_2C=O$ fragments of pyrrolidone at δ 2.8—4.0; the second set includes signals of the CH_2 protons in the polymer chain and of the $C-CH_2-C$ and NCH_2 fragments of pyrrolidone at δ 1.0—2.4. The recorded spectrum agrees with the literature data.[4]

Apart from the aforementioned signals, the ^{1}H NMR spectrum contains a signal of water (δ 5.64, line width at half-length 25 Hz). Upon heating, this line becomes noticeably broader and shifted upfield to δ 5.27 at 338 K. The integral intensity of this signal approaches the intensity of the signal for water in $CDCl_3$ and the amount of water corresponds approximately to one molecule per ten monomer units in the polymer chain. The signal at δ 5.64 was assigned to the protons of water associated with C=O groups in hydrophilic cavities of the polymer, where the water O atom is not involved in hydrogen bonding.

The studied samples of PVP polymers in chloroform contained different amounts of water in the hydrophilic areas of the polymer (type I). For this reason, the chemical shifts of the water signals ranged from δ 5.6 to 4.7.

The ^{1}H NMR spectrum of a PVP sample containing more water in chloroform shows a signal for the water protons at δ 4.8 (line width at half-length ~20 Hz), which is close to the chemical shift of the block water; the spectrum is shown in Fig. 1, *a* (the distortion of that line and other narrow signals in the spectrum are due to monomer residues upon dialysis). Association of water molecule is characteristic of the latter. The integral intensity of this line corresponds to one water molecule per four monomer units. Upon heating, this line becomes noticeably broader and shifted upfield.

The ^{1}H NMR spectrum of EPVP differs only slightly from the spectrum of PVP, which agrees with chemical analysis data indicating a low degree of epoxidation.

The ^{1}H NMR spectrum of EPVP in chloroform shows a broad peak for water (δ 4.70, line width at half-length ~70 Hz) with an integral intensity corresponding to one water molecule per six monomer units (Fig. 1, *b*). This indicates a similar spatial packing of the PVP and EPVP chains in chloroform.

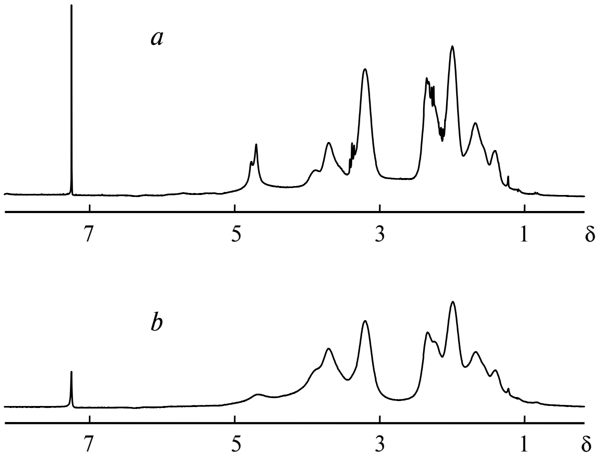

Fig. 1. ^{1}H NMR spectra of PVP (*a*) and EPVP (*b*) in $CDCl_3$.

Modification of EPVP with amino acids attached to its side chain can sufficiently strongly change the spatial packing of the polymer chain and give rise to new cavities (type II) containing water molecules that differ from water in the hydrophilic areas of the polymer (type I). For instance, the ^{1}H NMR spectra of EPVP modified with various amino acids in $CDCl_3$ show, along with signals for the polymer and water at δ 4.7—5.6, another higher-field signal of the water protons (δ 2.70—3.05). Its integral intensity approaches the intensity of a signal for one water molecule per monomer unit. Much water in cavities of the type II indicates a substantial increase in the number of water sorption centers, *i.e.*, a less compact (loosened) spatial packing of the monomer units in the polymer molecule. The upfield shift of the signals of the protons of this water suggests that the O atoms of water whose protons are associated with the C=O groups can additionally interact with the acid proton of chloroform also contained in newly formed cavities.

The ^{1}H chemical shifts of the signals of water in cavities of the types I and II in the polymers studied are given in Table 1.

For instance, the ^{1}H NMR spectrum of EPVP modified with Gly in $CDCl_3$ shows two signals of water protons: a broad signal at δ 5.30 and a narrower one at δ 2.80 (Fig. 2, *a*); upon heating, they are shifted upfield (to δ 5.06 and 2.62, respectively). The intensity of the higher-field signal of the structural water protons equals the intensity of a signal of one water molecule per monomer unit. With an increase in the relative water content of the solution (as the result of chloroform evaporation), the signals in cavities of the types I and II are shifted upfield. In this case, the signal at δ 5.30 becomes still broader and is of low intensity, while the signal at δ 2.80 is superimposed on the signal of the polymer (δ 2.30), thus increasing its intensity (Fig. 2, *b*).

The ^{1}H NMR spectrum of EPVP modified with Ala in $CDCl_3$ shows a signal for water in a cavity of the type II (δ 2.77); its intensity corresponds to one water molecule per monomer unit (Fig. 3, *b*).

Table 1. Chemical shifts δ of the water protons in the ^{1}H NMR spectra of the polymers studied and the number *N* of their monomer units per water molecule in cavities of the types I and II

Polymer	I		II	
	δ	*N*	δ	*N*
PVP	5.64, 4.80	10 4	—	—
EPVP	4.70	6	—	—
EPVP + Gly	5.30	8	2.80	1
EPVP + Ala	4.60	6	2.77	1
EPVP + ABA	5.00	4	3.10	1
EPVP + ACA	5.45	6	2.80	1

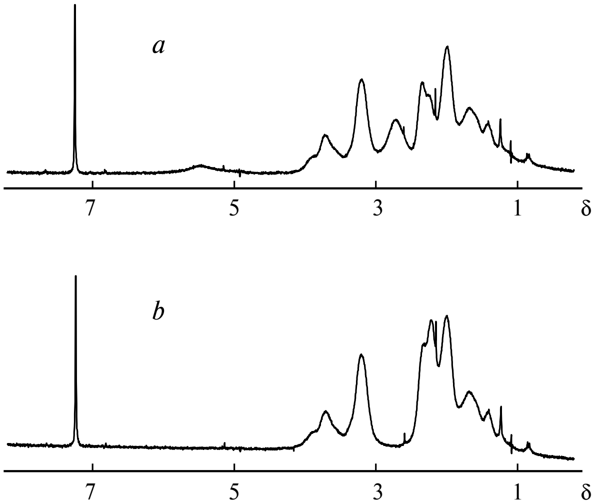

Fig. 2. ^{1}H NMR spectra of Gly-modified EPVP (*a*) and of the same sample with an increased relative water content (*b*) (in $CDCl_3$).

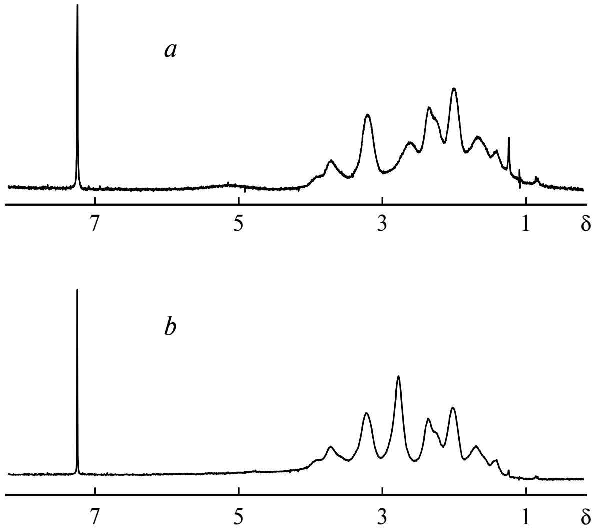

Fig. 3. ^{1}H NMR spectra of EPVP modified with ACA (*a*) and Ala (*b*) in $CDCl_3$.

A signal of water at δ 2.80 was also observed in the spectrum of EPVP modified with ACA (Fig. 3, *a*). This spectrum contains a broad signal for water at δ 5.40. Upon heating, both the signals are shifted upfield and the higher-field signal appears as a doublet (δ 2.70 and 2.65) at 305 K.

It is also worth noting that the intensity ratio of the signals of NCH_α and $CH_2C=O$ protons of pyrrolidone changed upon modification. A nearly doubled relative intensity of the signal at δ 3.70 in the spectra of the modified polymers suggests the respective increase in the isotactic configuration compared to the dominant syndiotactic one.

Thus, the ^{1}H NMR spectra of EPVP modified with amino-containing acids in chloroform show two types of signals for water corresponding to two types of hydrophilic cavities in the polymer. Much water in sorption centers of the type II indicates a less compact spatial packing of monomer units in the polymer chain containing an amino acid as a side substituent. Appearance in the ^{1}H NMR spectra of polymers in chloroform of signals for water in cavities of the type II can be indicative of a changed spatial packing of the modified polymer. These changes are not detected by ^{1}H NMR spectroscopy in aqueous solutions of the polymers, but they are clearly pronounced in the ^{1}H NMR spectra of polymers in chloroform.

The positions of the signals for water in chloroform are determined by a set of possible hydrogen bonds in its molecule: (1) withdrawing interaction of the water O atoms with the acid proton of $CHCl_3$ (δ 1.55), (2) acceptor-donor interaction during the formation of water associates (δ 4.8), (3) donating interaction of the water protons with the C=O groups of the polymer (δ 5.6), and (4) acceptor-donor interactions of the water O atoms with the acid proton of chloroform and of the protons of the same water molecule with the C=O group of the polymer (δ 2.8).

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