Reactions on Heteroaromatic Polymers with Amine Groups

A NMR study of chemical reactions and products of poly(*N*–vinylimidazole)

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Protonation, quaternization and addition reactions of poly(N-vinylimidazole) to the imidazole nitrogen atom in the position 3 to obtain the corresponding ionic derivatives were studied by NMR spectroscopy. Information and data on the reaction type and product microstructure are presented. The chain tacticity is a special structure aspect which was in detail studied by means of proton and carbon NMR spectra confirming that the chain configuration is not modified by any of the three polymer-analogous reactions.

Keywords: poly(N-vinylimidazole); polyelectrolytes; benzyl chloride; trifluoroacetic acid; acrylic acid; chain tacticity; polymer microstructure

Poly(*N*-vinylimidazole) (PNVI) is a polymer with numerous applications. It is a precursor for cationic polyelectrolytes used, for example, to retain metals by complexation [1,2].

The first synthesis of this ionizable polymer is rather old [3], but there are many recent publications on biomedical and pharmaceutical applications [4], antimicrobial properties of its hydrogels [5], as well as about catalytic applications [6-8], CO_2 separation [9], and medium protection [10]. In many cases PNVI has been functionalized by polymer-analogues reactions involving the imidazole nitrogen atom in the position 3 to obtain salts as well as quaternization and addition products [11-13]. It is the aim of the present article to expose how the NMR methodology can be used to investigate the reactions leading to such derivative products.

Experimental part

Materials

Poly(*N*-vinylimidazole) with M_w of 46000 Da was obtained by the radical polymerization of distilled monomer (Aldrich) in methanol at 50 °C. Trifluoroacetic acid (TFAA), benzyl chloride (BzCl) and solvents (deuterium oxide and deuterated methanol) from Aldrich or Fluka were used as received. Acrylic acid (AA) from Aldrich was distilled before use.

Instruments

The NMR spectra were obtained in D_2O at 300 K by using a Bruker Avance DRX 400 spectrometer equipped with 5 mm direct detection z-gradient QNP probe and operating at 400.1 and 100.6 MHz for ^1H and ^{13}C nuclei. The chemical shifts in β scale referred to sodium 3-(trimethylsilyl)-[2,2,3,3-d_4]-1-propionate (TSP) as internal standard are reported. Bruker TopSpin 1.3 PL10 and TopSpin 2.1 PL5 software were used for the spectrometer control and data processing. Deuterium oxide (D_2O) and deuterated methanol (CD_3OD) were used as NMR solvents.

Synthesis of PNVI derivatives

Protonated poly(*N*-vinylimidazole) (PNVI-TFAA): Reaction mixtures with 1:4, 1:2, 3:4 and 1:1 TFAA:PNVI molar ratios were prepared and monitored directly in 5 mm NMR tubes. Two solutions in deuterium oxide, one of 2% (0.21 M) PNVI and the other of 1% (0.07 M) TFAA, were used for the preparation of mixtures. Normally, this reaction is an equilibrium one (scheme 1). ^1H-NMR spectra for different reactant ratios are presented in figure 1.

Poly(3-benzyl-1-vinylimidazol-3-ium chloride) **(**PNVI-BzCl**)**: Two solutions in D_2O were prepared: 0.19 g (2 mM) of PNVI in 5 mL solvent, and 0.26 g (2 mM) of BzCl in 5 mL solvent. Combining these solutions, five reaction mixtures of 1:4, 1:2, 3:4, 1:1 and 1:2.5 PNVI:BzCl molar ratios were prepared in 5 mm NMR tubes. The reactions were performed at 60 °C for one week using an oil bath. The polymer conversion degree was determined from corresponding ^1H-NMR spectra by using the signals arising from the polymer chain methylene groups (2.0-3.0 ppm) and CH_2N^+ groups (4.9-5.5 ppm). The reaction product which resulted from the 1:2.5 PNVI:BzCl mixture was precipitated and washed with diethyl ether. After vacuum drying, its ^1H-NMR spectrum was recorded in D_2O at several temperatures and analyzed relative to PNVI (fig. 2).

^{1}H-NMR (D_2O, 300 K), δ (ppm): 2.0-3.0 (2H, chain-$\mathrm{C\mathbf{H}_2}$), 3.0-4.7 (1H, chain-$\mathrm{C\mathbf{H}}$), 5.0-5.5 (2H, broad, $\mathrm{C\mathbf{H}_2N^+}$), 6.5-8.0 (7H, broad, aromatic protons of chemical structures in scheme 2).

Poly (3-carboxyethyl 1-vinylimidazole) betaine (PNVI-AA): A solution containing 0.94 g (10 mM) PNVI in 5 mL methanol was heated at 50 °C for 15 min and then 0.89 mL (13 mM) AA was added. The reaction was performed at 50-55 °C for 24 hours. From the final reaction medium (dark yellow colored) the solvent and unreacted acrylic acid were removed and the resulted gel was dissolved in water and precipitated with acetone. A white powder was obtained after vacuum drying at 70 °C.

^{1}H-NMR (D_2O, 300 K), δ (ppm): 2.5-2.0 (2H, chain-$\mathrm{C\mathbf{H}_2}$), 2.68 (2H, s, $\mathrm{C\mathbf{H}_2COO^-}$), 4.2-3.6 (1H, broad, chain-$\mathrm{C\mathbf{H}}$), 4.36 (2H, s, $\mathrm{C\mathbf{H}_2N^+}$), 7.6-7.0 (2H, m, H4 and H5 of imidazole ring), 8.9 (1H, broad s, H2 of imidazole ring which exchanges with deuterium from solvent). **^{13}C-NMR** (D_2O, 300 K), δ (ppm): 39.59 (chain-$\mathrm{\mathbf{C}H_2}$, meso), 39.85 (chain-$\mathrm{\mathbf{C}H_2}$, racemic), 42.40 ($\mathrm{\mathbf{C}H_2COO^-}$), 50.21 ($\mathrm{\mathbf{C}H_2N^+}$), 56.36-59.46 (chain-$\mathrm{\mathbf{C}H}$: 56.36, 56.64, syndiotactic triads; 57.77,

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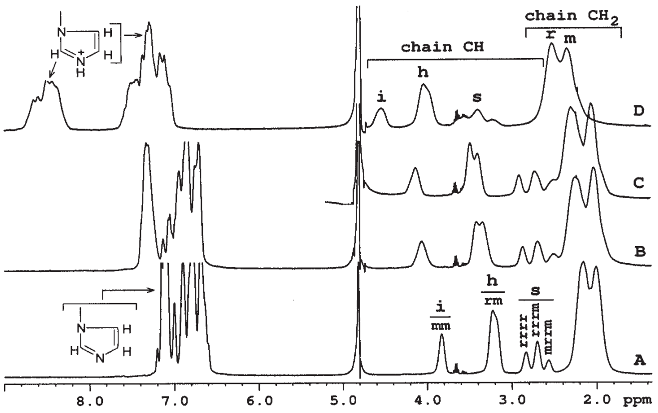


Fig.1. ^{1}H-NMR spectra of TFAA:PNVI mixtures in D_2O for several TFAA:PNVI molar ratios: 0.0 (A), 0.50 (B), 0.75 (C), and 1.0 (D).

heterotactic triads; 59.47, isotactic triads), 122.84 (C5), 126.33-126.96 (C4), 138.70 (C2), 179.75-180.05 (C=O).

Results and discussions

Tacticity of PNVI

Poly(*N*-vinylimidazole) shows tacticity sensitive ^{1}H-NMR spectra (fig. 1A). Thus, chain-methine signal is split due to triads: 3.75 ppm from isotactic (**i**) or meso-meso (**mm**), 3.16 ppm from heterotactic (**h**) or meso-racemic (**mr**), and 2.83-2.59 ppm from syndiotactic (**s**) or racemic-racemic (**rr**) triads, where **m** and **r** are abbreviations for the meso and racemic diades. In addition, the signal from syndiotactic triads is split due to pentads: 2.83 ppm from **mrrm**, 2.71 ppm from **mrrr**, and 2.59 ppm from **rrrr** pentads. This signal assignment is based on previous publications [13].

Table 1

MEASURED AND CALCULATED INTENSITIES OF THE CH SIGNAL COMPONENTS

Sequences	Intensity calculated with $P_m = 0.43$	Intensity measured from	
		*HC	*CH
Triads			
mm	0.185	0.215	0.188
mr	0.490	0.476	0.480
rr	0.325	0.308	0.332
Pentads **rr**			
mrrm	0.060	0.060	0.068
mrrr	0.159	0.151	0.157
rrrr	0.105	0.097	0.106
Pentads **mr**			
rmrr+mmrm	0.249	-	0.245
mmrr+rmrm	0.242	-	0.235

It is known that the theoretical ratios between the integrals of triad signals for a polymerization process with Bernoulli statistics are

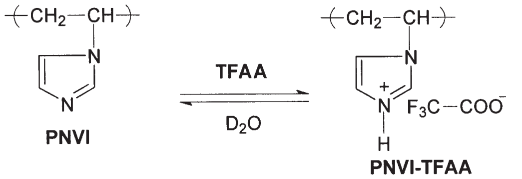
$$<mm>:<mr+rm>:<rr>=P_m^2:2P_m(1-P_m):(1-P_m)^2,$$

where P_m is the probability of meso addition [14]. Using the integrals of PNVI methine signals in figure 2A, it results $P_m = 0.43$. This means that the used polymer is nearly atactic because a pure atactic polymer has $P_m = 0.5$. The fact that 0.43 is a correct value is confirmed by similar values of the calculated and measured methine proton and carbon signal intensities presented in table 1.

The tacticity splitting of PNVI signals is even better visible in ^{13}C-NMR spectra (fig. 4B) than in ^{1}H-NMR spectra as follows: the syndiotactic methine signal is split due to pentads in the both types of spectra, but the carbon spectra shows in addition a pentad splitting in doublet for the heterotactic signal component. Also the methylene carbon signal is split due to tetrads (fig. 4A).

Protonation reaction of PNVI

Monitoring the modification of ^{1}H-NMR spectra when the molar ratio TFAA:PNVI is changed (fig. 1), it was observed that the chain methine signal shifts and widens with the protonation degree, but without additional splittings. This means that the protonation in protic solvents is an equilibrium reaction (scheme 1). The order of the low field shift is $^+$N=CH-N > CH (isotactic) ~ CH (heterotactic) > CH (syndiotactic) ~ CH_2.



Scheme 1. Protonation reaction of PNVI with trifluoroacetic acid

The relative intensities of the methine signals of PNVI-TFAA are similar to PNVI, meaning that the chain stereochemistry is not affected by protonation. The significant signal broadening is explained by the quadrupolar relaxation of the nitrogen-14 nucleus (I=1) [15,16], the rate of which increasing with density of ammonium groups.

Quaternization reaction of PNVI

The spectra of quaternization products of PNVI with benzyl chloride (PNVI-BzCl) are presented in figs. 2 and 3. Comparing the spectra of PNVI-BzCl (fig. 2B) and PNVI (fig. 2A), one observes the new signal at 5.3 ppm which arises from N^+CH_2Ph groups. The shape of unresolved multiplet indicates tacticity effects. Another interesting observation is that the splitting of the chain CH signal seems to remain similar to the case of PNVI, but low field shifted and broadened. As explained above, these differences, which are valid for all reaction products in this article, are explained by the positive charge and quadrupolar relaxation of the nitrogen-14 nucleus.

The isotactic component of the chain-methine signal of quaternized PNVI is masked at the room temperature by the non-deuterated water signal (fig. 2B), and to reveal it, the spectrum was also recorded at 90 °C (fig. 2C). Thus, the water signal shifts upfield and uncovers the isotactic signal at 4.6 ppm. Consequently, the spectra B and C in figure 2, clearly confirm that the chain configuration is not modified by quaternization.

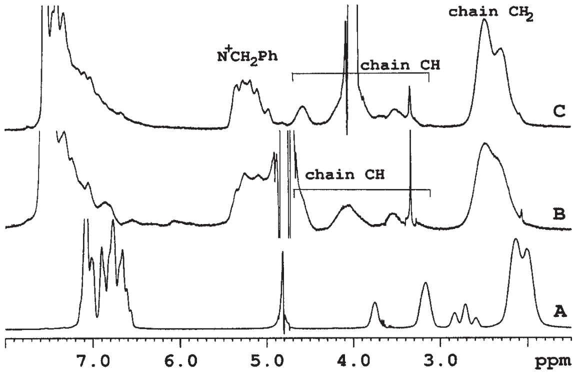
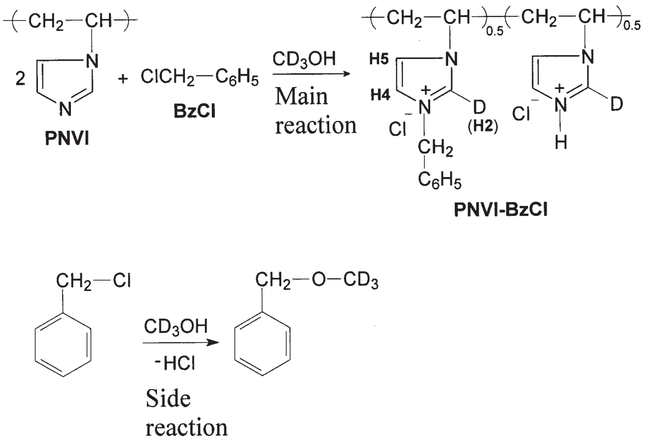
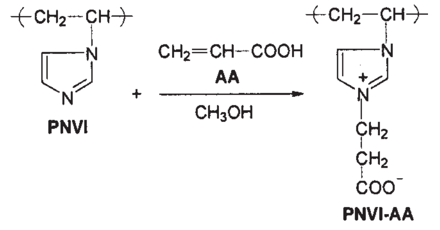


Fig. 2. ^{1}H-NMR spectra of PNVI (A) at 300 K and PNVI-BzCl at 300 K (B) and 363 K (C). The sharp signal at 3.3 ppm arises from a trace of methanol used for purification

The mechanism of quaternization in scheme 2 is supposed to explain the following additional observations made when the solvent is CD_3OH: (i) the deuteration of the imidazole ring in the position 2, (ii) the presence of salt units, and (iii) the formation of benzyl methyl ether.



Scheme 2. Quaternization reaction of PNVI with benzyl chloride and a secondary reaction with formation of methyl benzyl ether



Scheme 3. Addition reaction of PNVI with acrylic acid leading to poly(carboxybetaine) PNVI-AA

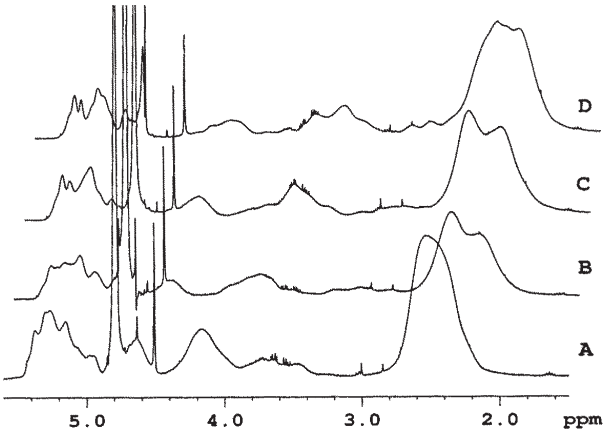


Fig. 3. ^{1}H-NMR spectra of the quaternization medium in D_2O for several PNVI:BzCl molar ratios: 0.25 (A), 0.5 (B), 0.75 (C), and 1.0 (D). The strong singlet at 4.75 ppm arises from methylene protons of BzCl. This figure does not contain the aromatic proton signals

The presence of benzyl methyl ether is supported by the sharp signal at 4.55 ppm in the reaction mixture, the intensity of which increases when the ratio PNVI:BzCl decreases (fig. 3).

Addition reaction of PNVI

The addition reaction between PNVI and acrylic acid (AA) is presented in scheme 3, the reaction product consisting of betaine units. This reaction was confirmed elsewhere from ^{1}H-NMR spectra [17].

The interest in the present study was to interpret the ^{13}C-NMR spectrum and to observe if the addition reaction affects the chain configuration. Such an observation is not so evident in proton NMR spectra due to the signal overlapping [17]. On the other hand it is known that the carbon chemical shifts are more sensitive to the polymer stereochemistry than the proton signals [18]. This later fact is confirmed by the extended signals from methylene and methine carbon nuclei of PNVI-AA and PNVI as shown in figure 4. Thus, for PNVI-AA (fig. 4A) that the chain $^*CH_2$ signal is split due to meso (**m**) and racemic (**r**) diads, while the chain *CH signal shows rather clear components for the three tacticity triads: syndio (s), hetero (h) and isotactic (i). Moreover, the signal of syndiotactic triads seems to be sensitive, but without separation, to pentads. A tendency of triade splitting is also visible for the signal CH_2COO^-. However, the methylene and methine carbon signals of PNVI (fig. 4B) are better split than those of the betaine product.

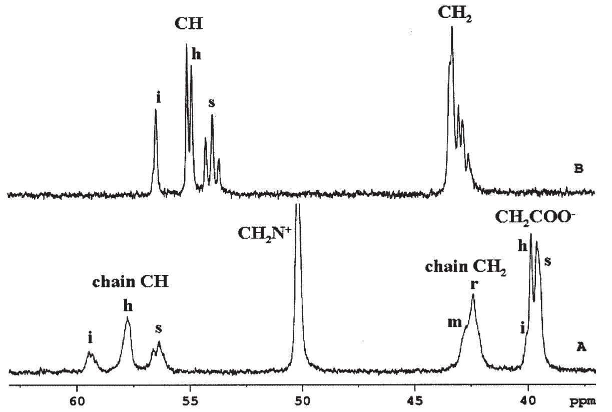


Fig. 4. ^{13}C-NMR signals of methylene and methine groups of PNVI-AA (A) and PNVI (B)

Table 2
MEASURED AND CALCULATED INTENSITIES OF THE COMPONENTS OF THE *CH CARBON SIGNAL

Sequences (triads)	Intensity calculated with Pm=0.42	Intensity measured from *CH
mm	0.177	0.176
mr	0.489	0.487
rr	0.333	0.336

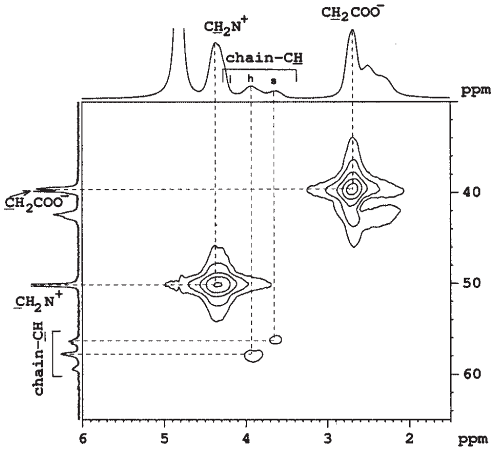


Fig. 5. HMQC spectrum of PNVI-AA showing the assignments of ^{13}C-NMR signals

Table 2 shows for comparison the carbon signal intensities calculated and measured for the triad components of the methine signal. One can observe that the correspondence is quite good. Unfortunately, there are not other carbon signals with measurable tacticity components.

The difference of only 0.01 (< 3%) between the values P_m determined from the proton and carbon spectra is not significant and is due to the experimental errors.

The assignment of the carbon signals is based on the HMQC 2D spectrum (fig. 5) which shows the correlations between the proton and corresponding carbon signals. An unexpected observation is that the methylene carbon signal of the $^*CH_2COO^-$ groups is electronically more shielded than that of the chain $^*CH_2$ groups.

Conclusions

It was proved that the NMR spectroscopy allows to obtain unique information about the three considered reactions by both *in situ* observation and product identification. Thus, the dependence of the signal position on the reactants ratio confirms (i) the equilibrium of the protonation reaction, and (ii) the parallelism of quaternization and neutralization reactions.

Unique data about the chain tacticity were obtained for PNVI and its three derivatives, proving that the chain configuration is not modified by the three polymer-analogous reactions, as expected.

As a final remark, it can be stated that the NMR spectroscopy cannot be surpassed by any other method in studies of *in situ* kinetics and secondary reactions, as well as for polymer microstructure.

Acknowledgement: This paper is dedicated to the 65th anniversary of "Petru Poni" Institute of Macromolecular Chemistry of Romanian Academy from Iasi, Romania.

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Manuscript received:21.05.2014