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SOLID-STATE ^{15}N CPMAS NMR STUDY OF THE STRUCTURE OF POLYPYRROLE

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Abstract

The chemical structure of polypyrrole (PPy) has been studied by ^{15}N CPMAS NMR experiments on the ^{15}N-labeled material. Only one broad line is found at about 120 ppm (external reference $^{15}NH_4Cl$) which indicates that all nitrogen atoms of PPy are protonated. Thus, PPy is best described as a chain of linked pyrrole molecules. Two-dimensional NMR experiments show that the ^{15}N line is inhomogeneously broadened. The width of the line is substantially larger in positively charged PPy.

Introduction

In the past years the structure of polypyrrole (PPy, Fig. 1) has attracted considerable interest because of its potential use as a conducting material [1–3]. Unfortunately, the fact that this material is insoluble makes the elucidation of the molecular structure difficult. Generally, structural problems

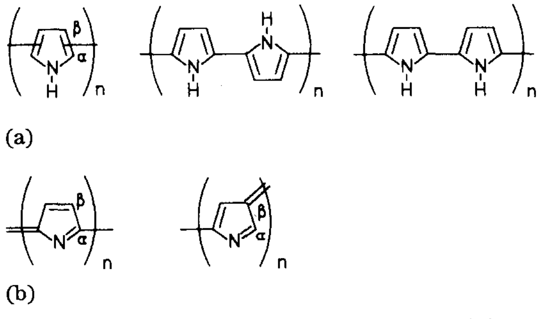

Fig. 1. Possible structures of polypyrrole (PPy).

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of polymers in the solid state [4] can conveniently be studied using high-resolution solid-state ^{13}C NMR spectroscopy under the conditions of cross polarization (CP) from protons, magic angle spinning (MAS) and proton decoupling [5–7]. Unfortunately, ^{13}C CPMAS NMR spectra of heterocyclic polymers often contain a manifold of different aromatic carbon atoms, which differ only slightly in their chemical shifts and yield unresolved featureless spectra [8, 9]. Thus, although interesting insights into the structure of PPy could be obtained using this technique the question of the chemical environment of the nitrogen atoms could not yet be unequivocally resolved; for example, the question remained open whether these polymers contain protonated or non-protonated sp^2 nitrogen atoms as shown in Fig. 1, and whether the relation between both types of nitrogen environments can be influenced by the preparation technique and by electrochemical oxidation.

Recently, it has been shown that the structure and dynamics of heterocyclic nitrogen-containing solids can conveniently be studied by using ^{15}N CPMAS spectroscopy of ^{15}N-enriched compounds [10–20]. This method is especially sensitive for distinguishing protonated and non-protonated sp^2 nitrogen atoms. Besides refs. 18–20, to our knowledge this method has not yet been applied to the problem of conjugated nitrogen-containing polymers. Thus, we have prepared various ^{15}N-enriched PPy phases and have performed ^{15}N CPMAS measurements on these materials which give novel insights into the structure of these materials as shown in the following.

Experimental

Our NMR experiments were performed on a Bruker CXP 100 spectrometer working at 90.02 MHz for protons. The CPMAS NMR experiments were performed with use of a 5 mm Doty MAS probe [21]. The rotation frequency of the 5 mm o.d. rotors was between 2.5 and 3.5 kHz. All spectra were referenced to external $^{15}NH_4Cl$.

Different PPy samples were electrochemically prepared from commercially available pyrrole-^{15}N (Alfred Hemplel GmbH, Düsseldorf) as described in the following. A 0.1 M solution of pyrrole-^{15}N in propylene carbonate containing 0.5 M of a supporting electrolyte was galvanostatically electrolyzed for 12 h at a current density of 1 mA/cm^2. The electrochemical equipment used has been described elsewhere [22]. The charged films were washed with highly purified acetonitrile and then dried *in vacuo*. Discharging of the PPy films was carried out potentiostatically in propylene carbonate in the presence of 0.1 M of a conducting salt, the same as that used for the electropolymerization process, at -1.0 V versus Ag/AgCl. The films were powdered for the NMR measurements. The following samples were prepared. Sample a: discharged PPy prepared with $LiClO_4$ as supporting electrolyte, prepared from sample b; sample b: charged PPy prepared with $LiClO_4$ as supporting electrolyte; sample c: discharged sample prepared with tetrabutylammonium-*p*-tolylsulfonate (TBATS) as supporting electrolyte, prepared from sample d; sample d: charged sample prepared with TBATS as supporting electrolyte.

These samples have the general constitution $(Py^{y+}X_y^-)_n$, where X is the counterion of the supporting electrolyte and y was found by elemental analysis to be of the order of 0.3 for the charged samples and close to zero for the discharged samples, in agreement with the literature [23].

Results

Figure 2 shows the ^{15}N CPMAS NMR spectra obtained for the various samples. The spectra contain only one broad nitrogen resonance at 120 ppm downfield from $^{15}NH_4Cl$. Whereas the line positions do not depend on sample preparation, the signal linewidths do. Figure 2(a) shows the spectrum of sample a which was electrochemically prepared using $LiClO_4$ as supporting electrolyte and then discharged. The signal linewidth is approximately 25 ppm. Without discharge (sample b) the linewidth is substantially larger, i.e. approximately 50 ppm, as shown in Fig. 2(b). In order to elucidate possible spectral changes because of the preparation method PPy was also prepared

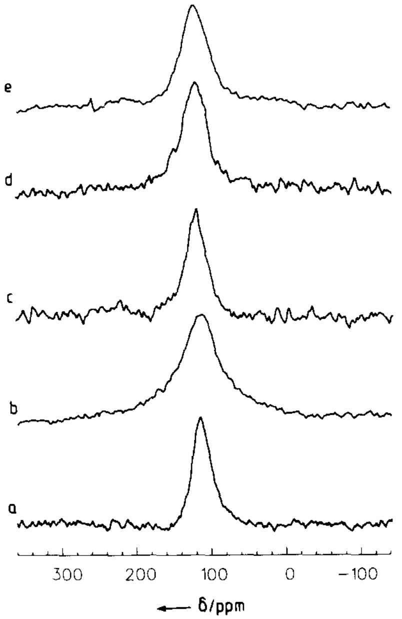

Fig. 2. ^{15}N CPMAS NMR spectra of 95% ^{15}N-enriched polypyrrole (PPy) at 9.12 MHz and 26 °C: (a) neutral PPy sample a prepared from sample b; (b) oxidized PPy sample b with ClO_4^- as counterion; (c) uncharged sample c prepared from sample d; (d) partly oxidized PPy sample d prepared with *p*-tolylsulfonate as counterion; (e) same as (d) but 800 Hz rotation frequency. Experimental conditions: ext. ref. $^{15}NH_4Cl$, 3 μs 90° pulses, 6 ms cross-polarization time, 51 ms acquisition time, 10 kHz sweep width, 2.18 s repetition time, 30 Hz line broadening; rotation frequencies app. 2.7 kHz, (a) 33 000 scans, (b) 36 000 scans, (c) 2458 scans, 2.77 s repetition rate, (d) 2640 scans.

with tetrabutylammonium-*p*-tolylsulfonate (TBATS) as supporting electrolyte. Whereas the spectrum of the discharged sample c closely resembles the spectrum of sample a the signal linewidth of the charged sample d is only slightly increased to 30 ppm. In order to check whether the PPy signal is characterized by a large anisotropy, a slow-spinning experiment at a rotation frequency of 800 Hz was performed on sample c as shown in Fig. 2(d). The sidebands are very weak indicating no significant chemical-shift anisotropy. Furthermore a dipolar dephasing experiment [24] indicated that the signal arises from protonated nitrogen atoms.

In order to determine the origin of the line broadening of the ^{15}N signals of PPy we performed variable-temperature experiments on different samples. The idea was that if the lines are homogeneously broadened because of the presence of fast T_2 processes arising from interaction with radical electrons some temperature dependence of the spectra should be observed. Unfortunately, when we started an experiment on sample b at 70 °C the high-power NMR pulse ignited the material resulting in an explosion which destroyed the whole sample and damaged the stator. Therefore, we did not attempt anymore to take spectra of charged PPy samples with the ClO_4^- as counterion. Variable-temperature experiments on the other samples did not give significantly different results from those shown in Fig. 2 indicating that a substantial part of the linewidth must result from an inhomogeneous broadening mechanism. This interpretation could be further supported by performing a two-dimensional exchange experiment as proposed by Szeverenyi *et al.* [25]. The result of this measurement on sample c is shown in Fig. 3. From the differences in lateral and longitudinal extension, it can be concluded that the line broadening is inhomogeneous. This signifies the presence of a distribution of slightly differing chemical shifts. The longitudinal-to-lateral signal width is approximately 2.6.

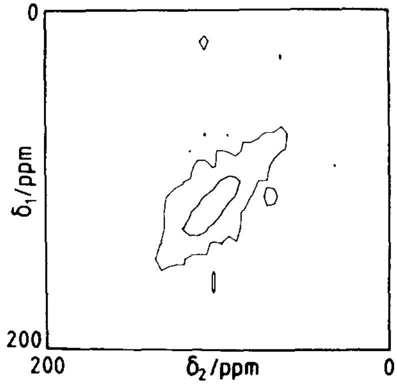

Fig. 3. Two-dimensional ^{15}N CPMAS NMR polarization-transfer experiment on ^{15}N-enriched neutral PPy at 9.12 MHz and 300 K with a mixing time of 100 ms. No attempts were made to monitor possible spin diffusion at larger mixing times. There were 32 by 256 points in the original data matrix, 512 scans per spectrum. Experimental conditions: 3 μs 90° pulses, 3.1 s repetition time. Other acquisition parameters as in Fig. 2(a).

Discussion

What do these spectra tell us about the structure of polypyrrole? The most important result is that only nitrogen atoms bounded to a hydrogen atom can be observed. It is well known that pyrrolic non-protonated nitrogen atoms in porphyrins appear above 200 ppm [10, 16, 26]. Even in the charged state the nitrogen atoms remain protonated. Note that the chemical shifts of pyrrole nitrogen atoms experience only a small high-field shift. Thus, only the structure shown in Fig. 1(a) can be observed and not those in Fig. 1(b). The observation of a dominant inhomogeneous line broadening indicates deviations from an ideal arrangement of polypyrrole [3] which assumes that the pyrrole rings of a given chain are linked in the α-positions and arranged in a plane with alternative *trans*-orientations (Fig. 1(a)) [3]. Evidence for the latter has been obtained from electron diffraction [3] and XPS [27, 28] studies of thin polypyrrole films. These deviations from an ideal chain might have different origins. First, there could be a conformational disorder when not only *trans*- but also *cis*-orientations of the pyrrole units are present. Secondly, a high degree of disorder is introduced by the presence of β-links between the different pyrrole rings. Thirdly, it may be that the pyrrole chains are cross-linked. Evidence for such cross-links has been obtained recently in a similar case [29].

Conclusion

^{15}N CPMAS NMR experiments on polypyrrole show that this material is best described as a polymer consisting of pyrrole units linked by C—C bonds. Moreover, ^{15}N CPMAS spectroscopy of PPy can be used as a tool in order to control whether a given material is chemically uniform or not.

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