^{15}N CPMAS NMR study of the structure and reactions of polypyrrylenemethine and polyfurylenepyrrylenemethine

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Abstract

The chemical structure and reactions of the recently prepared conducting polymers polypyrrylenemethine (PPM) (H. Bräunling and R. Becker, *Ger. Offen. Patent Applic. No. 3 710 657* (Mar. 31, 1987)) and polyfurylenepyrrylenemethine (PFPM) have been studied using high-resolution solid-state ^{15}N CPMAS NMR spectroscopy of the ^{15}N-labeled compounds. The results show the presence of azomethine nitrogen atoms which can be protonated with acids and deprotonated again with bases as free base porphyrins. Thus, these polymers have to be regarded, at least partially, as polymer analogs of the corresponding free base porphyrins.

Introduction

Of the conducting polymers with pyrrole monomer units, polypyrrole (PPy) has attracted most attention [1, 2]. Recently, two novel polymers, polypyrrylenemethine (PPM) [3] and polyfurylenepyrrylenemethine (PFPM) [4] (Fig. 1) have been synthesized. These polymers may be formally regarded as the polymer analogs of the cyclic free base porphyrins and can, therefore, exist in protonated, oxidized and reduced forms as shown in Fig. 2. Since heterocyclic conducting polymers are generally insoluble, the elucidation of their structure and their solid-state reactivity constitutes a challenging problem. Structural problems of polymers in the solid state can often be conveniently studied using high-resolution solid-state ^{13}C CPMAS NMR spectroscopy of spin $\frac{1}{2}$ nuclei under the conditions of cross polarization (CP) from protons, magic angle spinning (MAS) and proton decoupling [5–7]. In the case of PPy the ^{13}C CPMAS spectra contain a manifold of different aromatic carbon atoms leading to broad structureless lines which are difficult to interpret [8]. The situation is similar for PPM and PFPM. Thus, it was not possible to determine by ^{13}C CPMAS NMR spectroscopy whether both polymers contain

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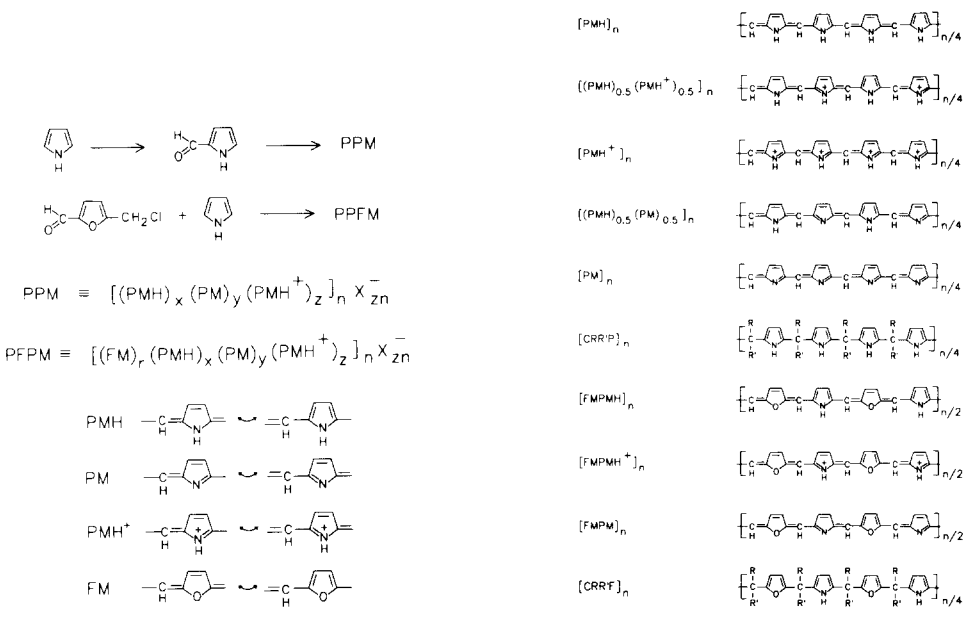

Fig. 1. Synthesis [4] and general structures of polypyrrylenemethine (PPM) and polyfurylenepyrrylenemethine (PFPM). FM ≡ furylenemethine, PM ≡ pyrrylenemethine. X: counteranion.

Fig. 2. Special structures of PPM and PFPM which demonstrate the analogy to the class of free base porphyrins.

protonated imino nitrogen rings (PMH) and (PMH^+) as well as azomethine nitrogen rings (PM) as proposed in Fig. 1. These units are both found in the case of porphyrins.

In a series of papers it has been shown that solid-state proton transfer reactions of the latter can be easily followed by ^{15}N CPMAS NMR spectroscopy of the ^{15}N-labeled compounds [9–16]. Also, in the case of nitrogen-containing conducting polymers, such as PPy [17], polyaniline (PANI) [18, 19] and polyphthalocyaninatosiloxanes [20], interesting insights into the molecular structure have been obtained using this method. Therefore, we have prepared ^{15}N-labeled PPM and PFPM and have performed ^{15}N CPMAS NMR experiments on these materials in order to investigate further the molecular structure and the reactivity of this material. In this paper the results are reported and discussed.

Experimental

The ^{15}N CPMAS NMR spectra were obtained with a Bruker CXP 100 NMR spectrometer working at 2.1 T (proton frequency 90 MHz) and a Bruker MSL 300 spectrometer working at 7.1 T (proton frequency 300.13 MHz). Both spectrometers were equipped with Doty-MAS probes [21].

^{15}N-labeled PPM and PPDM were synthesized using commercially available pyrrole-^{15}N as a starting material (AH-Hempel GmbH, Düsseldorf). The latter was first converted into 2-pyrrolealdehyde-^{15}N using a procedure described in ref. 22. The crude reaction product, which (in contrast to the procedure described in the literature) was already crystalline, was purified by twofold sublimation at 40 °C and 10^{-3} mbar. ^{15}N-labeled PPM and PFPM were then prepared from 2-pyrrolealdehyde-^{15}N by reaction with $POCl_3$ as dehydrating agent using slightly modified procedures described in the literature (example 5 [3] and method 2 [4], respectively).

Several samples of PPM and PFPM were prepared as shown in Table 1. The structures of the different samples were derived from the mode of preparation and elementary analysis. The phosphate stems from the $POCl_3$ used in the reaction. Sample I corresponds to raw PPM. Sample II was obtained from Sample I by extraction with water. This process eliminates chlorine quantitatively but phosphate only partly. Although the product was dried at 100 °C and 10^{-3} mbar the structure calculated from the elementary analysis shows an additional content of water and oxygen. Sample III was prepared from Sample I by extraction with 10% aqueous ammonia. This procedure led to a substantial decrease in the conductivity of the material. The elementary analysis again shows the addition of water and oxygen, but also ammonia has been added. Sample IV was obtained by extracting the phosphate from Sample II with concentrated aqueous HCl (67 h, 20 °C).

Two different ^{15}N-labeled PFPM samples were prepared. Sample V corresponds to the raw product. Sample VI was obtained by the doping of Sample V with iodine. Since these samples have been previously described in detail [4] no further details concerning their structure and conductivity are given here.

Results and discussion

The ^{15}N CPMAS NMR spectrum of raw PPM (Sample I) is shown in Fig. 3(a). The spectrum is not very different from the spectrum of neutral polypyrrole PPy [18] since only one broad line is observed around 120 ppm which is

TABLE 1

Samples of PPM and PFPM prepared in this study

Type	Sample	Structure	Conductivity (S cm^{-1})
PPM	I	$(PMH)_n(HCl)_{0.5n}(HPO_3)_{0.5n}$	2.4×10^{-8}
PPM	II	$(PM)_n(H_3PO_4)_{0.38n}(H_2O)_{0.47n}O_{0.16n}$	1.5×10^{-5}
PPM	III	$(PM)_n(NH_3)_{0.20n}(H_2O)_{0.43n}O_{0.37n}$	$<10^{-10}$
PPM	IV	$(PM)(HCl)_{0.41}(H_2O)_{0.18}O_{0.52}$	
PFMM	V		
PFMM	VI		

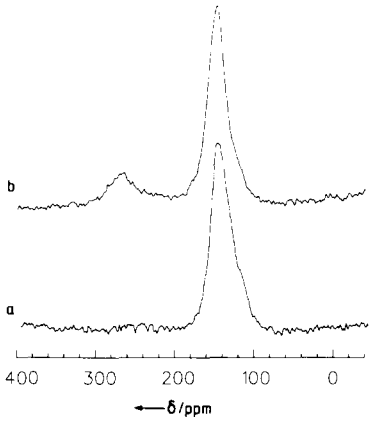

Fig. 3. 9.12 MHz ^{15}N CPMAS NMR spectra of polypyrrylenemethine (PPM) at 2.1 T (OL 131/5): (a) raw PPM; (b) after treatment of the raw material with excess NH_3/H_2O. Experimental conditions: (a) 4000 scans, 7 kHz sweep width, 10 Hz line broadening; 3.17 s repetition rate, 3 μs 90° pulses, 6 ms cross-polarization time; (b) 10 000 scans, otherwise same conditions as (a).

typical for protonated imino nitrogen atoms in pyrrole rings. This means that no azomethine nitrogen atoms, i.e. PM units (see Figs. 1 and 2) are present in the sample. Note that the ^{13}C CPMAS spectrum of this sample consists of only one broad line at ~ 130 ppm. These results would be consistent with a PPM structure with x, $z > 0$ and $y = 0$ in Fig. 1. Note, however, that we cannot exclude the presence of additional structural units labeled in Fig. 2 as CRR'P. CRR' could correspond to CH_2, CHOH and CO groups. Note also that crosslinking could occur during the polymerization process which is not considered in Fig. 2.

The ^{15}N and ^{13}C CPMAS NMR spectra of sample II are very similar to those of sample I. Note that in the ^{13}C CPMAS NMR spectrum of this material no signal could be assigned to a carbon atom originating from the addition of water or oxygen to a double bond as one could have anticipated from the structure of this sample given in Table 1.

Since it is difficult to distinguish between PMH and PMH^+ units by ^{15}N CPMAS NMR spectroscopy the material was treated with aqueous NH_3 in order to convert the PMH^+ units into PM units. The ^{13}C spectra of Sample III obtained in this way were not very informative of whether this treatment was successful. Besides the broad line at 130 ppm two very weak and broad ^{13}C signals could be detected at 170 and 210 ppm. These signals might be attributed to imino and carbonyl groups originating from oxygenation process.

In contrast, the ^{15}N CPMAS spectra were more instructive. In fact, as shown in Fig. 3(b), we observed a novel low field line at 220 ppm for Sample III. This line has a chemical shift corresponding to the nonprotonated azomethine nitrogen atoms of porphyrins [10, 16, 17, 23], i.e. it must arise from the PM units. The question then arose of whether it was possible to quantify the amount of these units in Sample II and, as a consequence, the

amount of PMH^+ in Sample I. A problem with CPMAS NMR spectroscopy is that the line intensities do not generally correspond to the real concentrations of the different chemical environments monitored because the latter may be subject to different cross-polarization dynamics. This is especially true for protonated and nonprotonated nitrogen atoms. We estimate, however, that this uncertainty does not introduce a large error because an increase of the cross-polarization time did not really affect the line intensities in Fig. 3(b), in contrast to a decrease. Therefore, we estimate from the line-intensity ratio that the mole fraction of PM units is approximately 20%. Attempts to further deprotonate the material were unsuccessful.

There are several possibilities why the fraction y of PM units seems to be smaller than expected for the ideal porphyrin-type structure $[(PMH)_x(PM)_y]_n$, $x=y=0.5$ (Fig. 2). One could, for example, argue that the treatment with ammonia does not deprotonate all PMH^+ units because they might not be all accessible to the solvent. It is more probable to assume that in fact $x>y\simeq 0.2$ in $[(PMH)_x(PM)_y]_n$. It is clear that the PMH units cannot be deprotonated by NH_3. As mentioned above, CRR'P might be present also.

Furthermore, we investigated what happens when PPM is treated with HCl/H_2O (Sample IV). The results of the ^{15}N CPMAS measurements are shown in Fig. 4(a) and (b) where experiments were performed at 7 T at a frequency of 30.4 MHz. Figure 4(a) corresponds to Sample I of which the spectrum at 2.1 T is already shown in Fig. 3(a); after HCl treatment the shoulder at

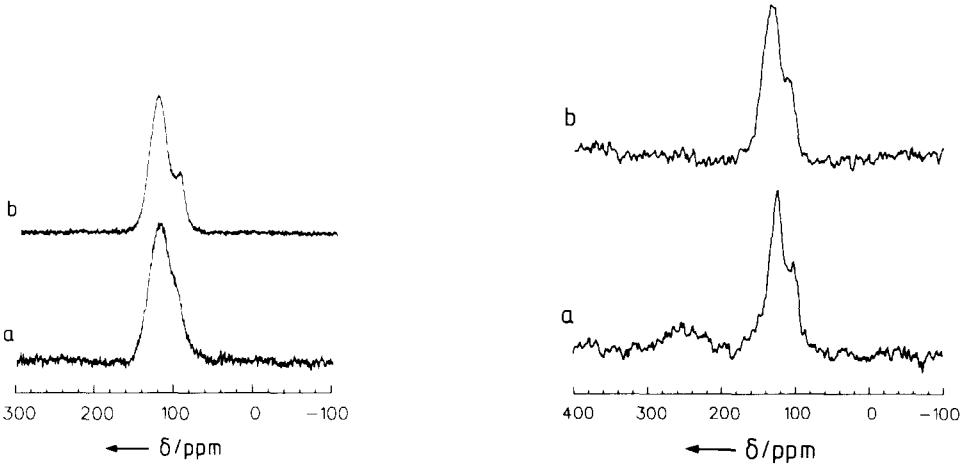

Fig. 4. 30.4 MHz ^{15}N CPMAS NMR spectra of PPM at 7 T: (a) raw material; (b) after treatment with HCl. Experimental conditions: 2000 scans, 20 kHz sweep width, 20 Hz line broadening; 3.12 s repetition rate, 10 μs 90° pulses, 5 ms cross-polarization time.

Fig. 5. 9.12 MHz ^{15}N CPMAS NMR spectra of ^{15}N-enriched polypyrrylfurylmethine (PPFM) at 2.1 T: (a) uncharged compound, 22 848 scans, 7 kHz sweep width, 6 ms cross-polarization time, 3 μs 90° pulses, 2.773 s recycle delay; 1K/4K zero-filing; 30 Hz line broadening, 3.7 kHz rotation frequency; (b) charged compound after doping with iodine, 10 000 scans, repetition time 3.11 s, rotation frequency 2.3 kHz, otherwise same conditions as (a).

about 110 ppm, present already in Figs. 3(a) and 4(a), is much more pronounced. The position of this new line is consistent with positively charged protonated nitrogen atoms. However, we are not sure whether these are the nitrogen atoms of PMH^+ units. It would be more plausible to assign this high field line to the nitrogen atoms of doubly protonated pyrrole units, i.e. PMH_2^+.

The results of the ^{15}N CPMAS NMR experiments on PFPM are shown in Fig. 5. From the synthesis one could expect a formal porphyrin analog of the type $[FMPM]_n \equiv [(FM)_x(PM)_y]_n$ with $x=y=0.5$ (Fig. 2), where the pyrrole units carrying an azomethine nitrogen atom are replaced by furan rings. As in the case of PPM, this ideal structure is not realized as can be inferred from the ^{15}N CPMAS spectrum of sample V shown in Fig. 5(a). This spectrum revealed not only the presence of nonprotonated nitrogen atoms typical for the azomethine PM units (broad peak at 250 ppm), but also two peaks characteristic of PMH, PMH_2^+ and PMH^+ units (104 ppm and 127 ppm). These results are consistent with the structure $[(FM)_r(PMH)_x(PM)_y(PMH^+)_z]_n X^-_{zn}$.

When the material is oxidized with iodine (Sample VI) the low field line disappears as shown in Fig. 5(b). Only the two high field lines survive. Peak deconvolution shows that their linewidth is increased from 180 Hz (20 ppm) to about 300 Hz (33 ppm). The centers of the two lines appear now at 114 and 135 ppm; however, in view of the linewidth increase this shift is insignificant. The intensity ratio of the two lines is about 3 to 1, i.e. the same as in the undoped sample. At present, we do not understand what happened to the azomethine line of the PM units. It could be that the oxidation process induces very large Knight shifts of the nitrogen atoms in the PM units. Such ^{15}N Knight shifts on doping with iodine have been observed recently for nitrogen-containing conducting polymers [20]. In this case it was shown that there are domains of doped and undoped material. Thus, it could be that the signals in Fig. 5(b) stem from undoped domains.

Conclusions

It has been shown that interesting structural information on two novel nitrogen-containing conducting polymers, which are formally the polymer analogs of porphyrin, can be obtained using ^{15}N CPMAS NMR spectroscopy. This technique also allowed the monitoring of structural changes when treating the polymers with bases and acids. The results show that the structure of PPM and PFPM corresponds only partially to the ideal structure. However, ^{15}N CPMAS NMR spectroscopy may present a way in the future to know whether this goal has been achieved in an improved synthesis.

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References

1 G. B. Street, S. E. Lindsey, A. I. Nazzal and K. W. Wynne, *Mol. Cryst. Liq. Cryst.*, *118* (1985) 137.
2 R. H. Geiss, G. B. Street, W. Volksen and J. Economy, *IBM J. Res. Dev.*, *27* (1983) 342.
3 H. Bräunling and R. Becker, *Ger. Offen. Patent Applic. No. 3 710 657* (Mar. 31, 1987).
4 (a) R. Jira and H. Bräunling, *Synth. Met.*, *17* (1987) 691; (b) H. Bräunling and R. Jira, *Ger. Offen. Patent Applic. No. 3 531 600* (Sept. 4, 1985).
5 J. Schaeffer and E. O. Stejskal, *J. Am. Chem. Soc.*, *98* (1976) 1031.
6 J. R. Lyerla, C. S. Yannoni and C. A. Fyfe, *Acc. Chem. Res.*, *15* (1982) 208.
7 C. A. Fyfe, *Solid State NMR for Chemists*, C. F. C. Press, Guelph, Ontario, 1983.
8 G. B. Street, T. C. Clarke, M. Krounbi, K. Kanazawa, V. Lee, P. Pfluger, J. C. Scott and G. Weiser, *Mol. Cryst. Liq. Cryst.*, *83* (1982) 253.
9 H. H. Limbach, J. Hennig, R. D. Kendrick and C. S. Yannoni, *J. Am. Chem. Soc.*, *106* (1984) 4059.
10 H. H. Limbach, B. Wehrle, M. Schlabach, R. D. Kendrick and C. S. Yannoni, *J. Magn. Reson.*, *77* (1988) 84.
11 H. H. Limbach, B. Wehrle, H. Zimmermann, R. D. Kendrick and C. S. Yannoni, *Angew. Chem.*, *99* (1987) 241; *Angew. Chem., Int. Ed. Engl.*, *26* (1987) 247.
12 R. D. Kendrick, S. Friedrich, B. Wehrle, H. H. Limbach and C. S. Yannoni, *J. Magn. Reson.*, *65* (1985) 159.
13 B. Wehrle and H. H. Limbach, *Chem. Phys.*, *136* (1989) 223.
14 H. H. Limbach, B. Wehrle, H. Zimmermann, R. D. Kendrick and C. S. Yannoni, *J. Am. Chem. Soc.*, *109* (1987) 929.
15 B. Wehrle, H. H. Limbach, M. Köcher, O. Ermer and E. Vogel, *Angew. Chem.*, *99* (1987) 914; *Angew. Chem., Int. Ed. Engl.*, *26* (1987) 934.
16 B. Wehrle, H. Zimmermann and H. H. Limbach, *Ber. Bunsenges. Phys. Chem.*, *91* (1987) 941; B. Wehrle, H. H. Limbach and H. Zimmermann, *J. Am. Chem. Soc.*, *110* (1988) 7014.
17 B. Wehrle, H. H. Limbach, J. Mortensen and J. Heinze, *Synth. Met.*, *38* (1990) 293.
18 A. F. Richter, A. Ray, K. V. Ramanathan, S. K. Mannohar, G. T. Furst, S. J. Opella and A. G. MacDiarmid, *Synth. Met.*, *29* (1989) E243–E249.
19 B. Wehrle, H. H. Limbach, J. Mortensen and J. Heinze, *Adv. Mater.*, *1* (1989) 441.
20 B. Wehrle, H. H. Limbach, T. Zipplies and M. Hanack, *Adv. Mater.*, *1* (1989) 443.
21 F. D. Doty and P. D. Ellis, *Rev. Sci. Instrum.*, *52* (1981) 1868.
22 R. M. Silverstein, E. E. Ryskiewicz and C. Willard, *Org. Synth. Coll.*, *4* (1963) 831.
23 G. J. Martin and M. L. Martin, in P. Diehl, E. Fluck and R. Kosfeld (eds.), *^{15}N NMR Spectroscopy, NMR Basic Principles and Progress*, Vol. 18, Springer, Berlin, 1981.