Communications

^{15}N CPMAS NMR Study of the Structure of Polyaniline**

By *Bernd Wehrle, Hans-Heinrich Limbach,** *John Mortensen,* and *Jürgen Heinze**

Dedicated to Professor Christoph Rüchardt on the occasion of his 60th birthday

In the last few years the structure and properties of polyaniline (PANI) have attracted much interest.[1-12] Among the different techniques used in these studies, high resolution solid state ^{13}C NMR spectroscopy under the conditions of ^{1}H cross-polarization (CP), magic angle spinning (MAS), and proton decoupling[13-16] has been employed in order to elucidate the structure and the reactivity of this compound.[17-22] Using this method on chemically synthesized PANI, evidence for the emeraldine structure **I** (Fig. 1), which consists of alternating phenylenediamine and chinonimine units with y = 0.5 has been obtained. It is not known, however, whether PANI prepared by electropolymerization in media of different acidities[1,7,8,20] is characterized by the same structure or whether structures with different y values as well as structures **II** to **V** (Fig. 1) also have to be considered.

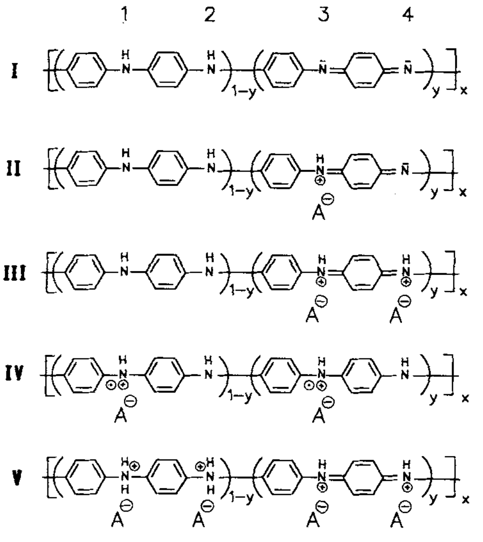

Fig. 1. Possible structures of polyaniline (PANI). Leucoemeraldine: **I**, y = 0; emeraldine: **I**, y = 0.5; pernigraniline: **I**, y = 1.

Since solid, nitrogen containing heterocycles can conveniently be studied by ^{15}N CPMAS NMR spectroscopy of ^{15}N enriched materials[23-32] it is surprising that only one preliminary ^{15}N CPMAS paper on chemically synthesized PANI has been published.[32] Therefore, we report here the results of ^{15}N CPMAS NMR experiments[33] on various PANI-samples synthesized by electropolymerization[35] in $HClO_4$/water mixtures and subsequent discharge in acetonitrile.

Figure 2 shows ^{15}N CPMAS NMR spectra of three samples. The spectrum of sample 1 (Figure 2a) contains a sharp high field signal at ~ 60 ppm and a broad band at ~ 320 ppm. Figure 2b shows the result of a dipolar dephasing experiment[37] on the same sample in which only the magnetization of non-protonated nitrogen atoms survives. When sample 1 is carefully washed[35] we observe in

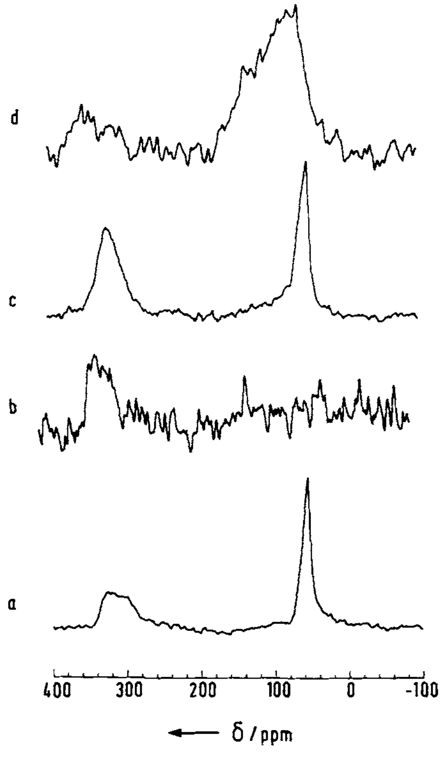

Fig. 2. ^{15}N CPMAS NMR spectra of electrochemically synthesized polyanilines (PANI): a) discharged sample 1; b) dephasing experiment performed on sample 1 with a delay of 100 µs; c) sample 2, as sample 1 but after thorough washing; d) sample 3, prepared in highly acidic conditions.

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the ^{15}N spectra of the resulting sample 2 slight changes of the signal at low field as shown in Figure 2c.

The ^{15}N spectra of samples 1 and 2 are very similar to the spectrum shown in the literature[32] which was interpreted in terms of the emaraldine structure **I** with $y \approx 0.5$. The dipolar dephasing experiment in Figure 2b supports the assignment of the high field line to the protonated nitrogen atoms 1 and 2 in **I**. Their chemical shift is consistent with what is known about the chemical shifts of model compounds such as diphenylamine (65 ppm)[38] or the NH-nitrogen atoms of azophenine (Figure 3).[31] Note that unsubstituted aniline and anilinium appear at higher field, i.e. at 33 ppm and 20 ppm.[38] The dephasing experiment strongly indicates that the low field line has to be assigned to the non-protonated nitrogen 3 and 4 in **I** although they absorb at slightly lower field than the corresponding atoms in azophenine (~ 265 ppm).[31] Thus, our results support similar structures of PANI when synthesized chemically and electrochemically.

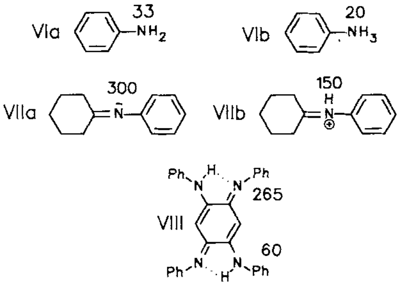

Fig. 3. ^{15}N chemical shifts of model compounds for PANI. **VI**: aniline, [38] **VII**: N-phenylcyclohexanonimine, [39] **VIII**: azophenine [31].

Dramatic changes of the spectra are, however, found when PANI is prepared electrochemically under strongly acid conditions (sample 3).[35] For such material, salt structures **III** and **IV** (Fig. 1) have been proposed.[20, 32] As shown in Figure 2d we observe for sample 3 two very broad lines at ~ 100 and ~ 350 ppm which represents a shift to lower field. The observation that the relative intensity of the high field line has increased, indicates a higher mole fraction of protonated ^{15}N atoms in sample 3.

These results are consistent with the presence of a superposition of all structures **I**, **II** and **III** in sample 3. Also, structure **V** cannot be completely excluded. We tentatively assign the low-field line in Figure 2d to the non-protonated nitrogen atoms 4 in **II**. By comparison with the protonation shift of compound **VII** in Figure 3 which is of the order of +150 ppm[39] we also tentatively assign the low field part of the high field line to atoms 3 and 4 in **III** as well as to atom 3 in **II**. The high field part stems then probably from the atoms 1 and 2 in **II** and **III**.

There are different phenomena which might contribute to the broadness of the high field line in Figure 2d. Firstly, one has to consider the effect of proton disorder arising from a superposition of **I**, **II**, and **III**. One also has to take a distribution of intermolecular interactions of the PANI subunits with the anions $A^{\ominus}$ into account. A look at structure **III** shows that the positive charge can only be localized as indicated if the $A^{\ominus}$ ions interact with particular nitrogen atoms. At longer distances between the nitrogen atoms and counter ions the differences of electronic charges and, subsequently, of nitrogen chemical shifts between the two subunits in **III** will disappear. Thus, a broad nitrogen-anion distribution function will lead to a broad distribution of chemical shifts in the region between 150 and 50 ppm, as observed in Figure 2d. Note that we can also not exclude the presence of semiquinone structures **IV**. Evidence for the existence of **IV** has been obtained by EPR[40] and magnetic susceptibility measurements.[41] Unfortunately, it is difficult to know where the ^{15}N signals of **IV** appear because they might be subject to paramagnetic or Knight shifts as well as to line broadening.

Finally, the linewidths in Figure 2d could also be influenced by electron and nuclear motions as well as spin dynamics. A fast migration of anions should lead to a breakdown of the nitrogen-anion distribution function, i.e. to line broadening and line narrowing of the lines in Figure 2d. Since the *p*-tolylsulfonate anions are bulky it is, however, not very probable that this phenomenon occurs within the NMR timescale. However, the situation could be different if smaller anions were employed.

We have shown that ^{15}N CPMAS NMR spectroscopy is a promising technique, useful for studying the structure of nitrogen containing heterocyclic polymers. Besides PANI we have also studied other materials such as polypyrrole (PPy) and related compounds. In contrast to PANI, we find for PPy only one inhomogeneously broadened ^{15}N signal at 120 ppm which is not significantly altered when the substance is oxidized. This means that even in neutral PPy, only protonated nitrogen atoms can be detected, as expected for a structure $(P^{y\oplus}X_y^{\ominus})_n$, $y \geq 0$. Further ^{15}N CPMAS results obtained for a completely different class of nitrogen containing polymers have been reported.[42]

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^{15}N CPMAS NMR Study of the Structure and Reactions of Phthalocyaninatopolysiloxane and its Precursors in the Solid State**

By *Bernd Wehrle, Hans-Heinrich Limbach**, *Tilman Zipplies*, and *Michael Hanack**

Dedicated to Professor Christoph Rüchardt on the occasion of his 60th birthday

The class of phthalocyaninatopolymetalloxanes (PcMO)$_n$ (Pc ≡ phthalocyanine, M ≡ Si, Ge, Fig. 1) has attracted considerable interest because of the high conductivity of these molecules after doping with iodine or other electron acceptors.[1-5] Since it has not yet been possible to perform crystal structure analyses on these compounds, information about the molecular structure of these materials has mainly been obtained[1-5] by solid state ^{13}C CPMAS NMR spectroscopy under the conditions of cross polarization (CP) and magic angle spinning (MAS).[6-9] Unfortunately, the ^{13}C CPMAS spectra of (PcMO)$_n$ contain a manifold of various aromatic carbon atoms sites which differ only slightly in their chemical shifts and which are difficult to assign.

In the past it has been shown that the structure and reactions of solid, nitrogen containing heterocycles can conveniently be studied using ^{15}N CPMAS NMR spectroscopy which requires, however, ^{15}N enriched samples.[10] We show here that this technique is also useful for studying the structure and the solid state reactivity of phthalocycaninatopolymetalloxanes.

The ^{15}N labeled compounds studied were prepared according to standard methods from 95% ^{15}N enriched phthalodinitrile via diimidoisoindoline.[11] This was reacted with SiCl$_4$ in quinoline to form dichlorophthalocyaninatosilicon PcSiCl$_2$ which was hydrolyzed in a mixture of pyridine and NaOH to form dihydroxyphthalocyaninatosilicon ^{15}N labeled PcSo(OH)$_2$, (**I**) whose structure is shown in Figure 1. **I** was then polymerized in a thermal balance under nitrogen at 450 °C to form ^{15}N labeled μ-oxo-phthalocyaninatosilicon [PcSiO]$_n$ (**II**); **II** was subsequently doped with iodine according to a literature method.[2] Thus, the ^{15}N labeled product [(PcSiO)I$_{1.1}$]$_n$ (**III**) was obtained. ^{15}N NMR experiments were carried out on all compounds **I**–**III** using instrumentation previously described.[11] For the low temperature experiments a self-built heat exchanger[12] was employed.

The room temperature ^{15}N CPMAS NMR spectra of the various phases of phthalocyaninatopolysiloxanes are shown

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