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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 $\equiv$ phthalocyanine, M $\equiv$ 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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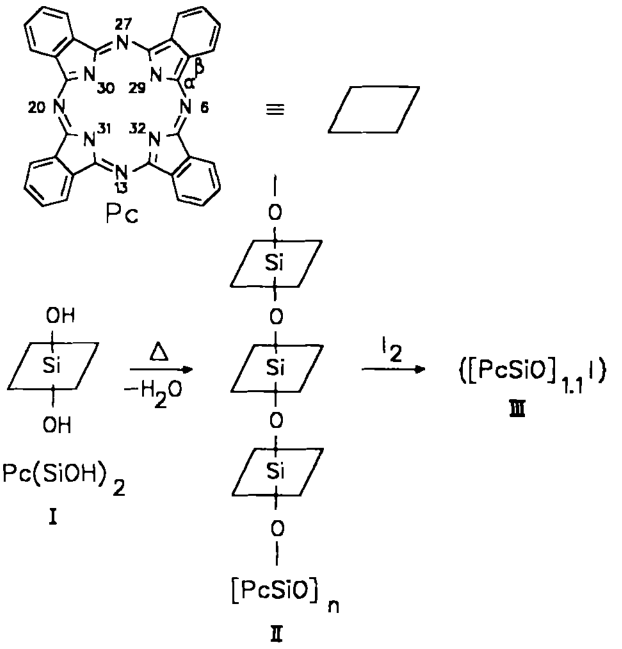

Fig. 1. Solid state polymerization of $PcSi(OH)_2$ to $(PcSiO)_n$ and subsequent oxidation to $[(PcSiO)I_{1.1}]_n$ with iodine; Pc ≡ phthalocyanine.

in Figure 2. For the monomeric precursor $PcSi(OH)_2$ three resonances are observed at 211, 199 and 170 ppm respectively. The assignment of the individual resonances are based on former ^{15}N CPMAS NMR studies of free base phthalocyanine.[11,12] The two low field lines stem from the outer nitrogen atoms N-6, N-13, N-20, and N-27. The inner core nitrogens give rise to the resonance at ~ 170 ppm. The inequivalence of the outer nitrogen atoms has been observed previously in the case of free base phthalocyanine.[11] The differences in the chemical shifts may either result (i) from a small deviation of the Pc macrocycle from a D_{4h} symmetry or (ii) from $O-H \cdots N$ hydrogen bonds between adjacent molecules as a consequence of intermolecular stacking.[13] In contrast to the monomeric form, the spectrum of the dehydrated polymeric form reveals only two resonances as shown in Figure 2b. The low field line which stems from the outer nitrogen atoms appears exactly in the middle of the monomer at 200 ppm, indicating a D_{4h} symmetry of the Pc macrocycle on the ^{15}N NMR timescale. This symmetry could be real or arise from rapid 90° jumps of the Pc macrocycle in **II**. The high field line has been shifted slightly upfield to 167 ppm as a result of small change of the electronic environment. The different signal intensities arise from different cross polarization dynamics and indicate the loss of the nearby OH protons in the polymer which facilitate cross polarization to the inner nitrogen atoms in $PcSi(OH)_2$, (**I**). Attempts to detect spin diffusion[14,15] between the outer and inner nitrogens in $[PcSiO]_n$, (**II**) were unsuccessful.

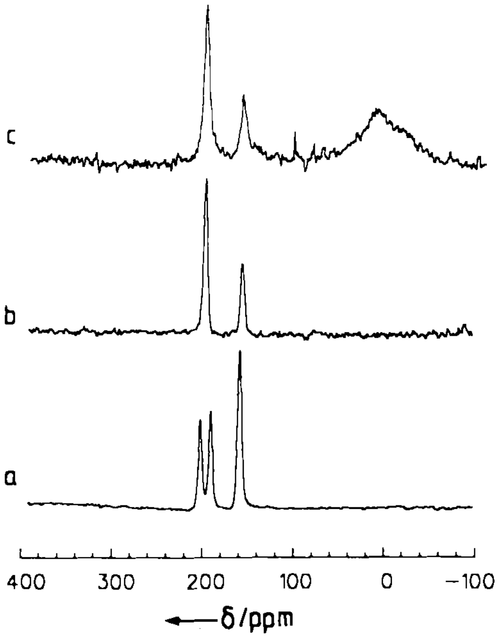

Fig. 2. ^{15}N CPMAS NMR spectra of 95% ^{15}N enriched phthalocyaninatosiloxanes at 9.12 MHz. (a) monomeric $PcSi(OH)_2$; (b) polymeric $(PcSiO)_n$; (c) partly oxidized polymeric $[(PcSiO)I_{1.1}]_n$. Experimental conditions: room temperature spectra, 5 mm o.d. rotors, spinning speed between 2.5 and 3.5 kHz, external reference $^{15}NH_4Cl$, 3 µs 90° pulses, 2.773 s repetition time, 7 kHz spectral width, 73 ms acquisition time; (a) 15 ms cross polarization time, 1480 scans; (b) and (c) 25 ms cross polarization time, 1390 scans.

On doping $[PcSiO]_n$ with iodine the spectra change dramatically as shown in Figure 2c. In addition to the familiar lines, a broad high field shifted resonance is observed. Careful line shape analysis shows that the signal consists of two lines, the stronger component appearing at 25 and the smaller component at 8 ppm; thus, in the doped compound the nitrogen signals are shifted between − 160 and − 180 ppm to high field. Note that not all material could be oxidized by doping with iodine; the observation of the presence of both shifted and unshifted signals in Figure 2c indicates the presence of coexisting clusters of conducting and isolating regions.

In order to obtain more information about **III** we have performed variable temperature measurements on this compound. The results are shown in Figure 3. Although the center of the broad high-field line seems to shift slightly to lower field as the temperature is raised, there is almost no temperature dependence on the line positions within the margin of error. This result is expected for Knight shifts resulting from interactions with conducting electrons; paramagnetic shifts arising from interactions with localized electrons should experience a much stronger temperature dependence.[16] Knight shifts are independent of the gyromagnetic ratio of the nucleus studied but proportional to the electron spin density at the latter;[16] the sign of spin densities is known to vary between adjacent atoms in π-electron systems. Thus, we can directly compare our results with the ^{13}C-Knight shifts reported previously for **III**.[6] These are + 280 ppm for the α-^{13}C atoms and −78 ppm for the β-^{13}C atoms. Thus, all carbon and nitrogen atoms adjacent to the α-^{13}C atom experience a positive Knight shift as expected. Whereas the small shift of the β-^{13}C atom signal is plausible, the much larger

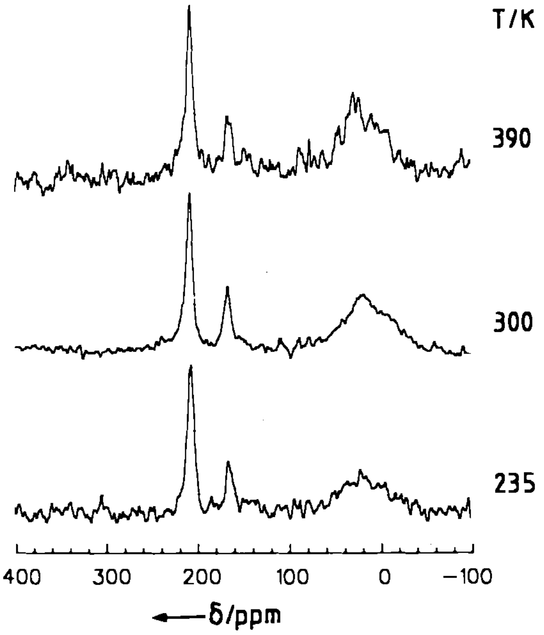

Fig. 3. ^{15}N CPMAS NMR spectra of partly oxidized $[(PcSiO)I_{1.1}]_n$ as a function of temperature. The spectra indicate slightly temperature dependent Knight-shifts of the oxidized material. Experimental conditions: 10 ms cross polarization time, 10 kHz spectral width, 52 ms acquisition time, otherwise same as Figure 2; (a) 2902 scans, (b) 15000 scans, (c) 7082 scans.

shift of the α-^{13}C spins as compared to the ^{15}N shifts needs further study.

In summary, it has been shown that structural changes of the solid state polymerization and the subsequent oxidation of ^{15}N labeled phthalocyaninatometalloxanes can be monitored by ^{15}N CPMAS NMR spectroscopy. In the oxidized state these materials are highly conductive, a fact confirmed by the observation of a ^{15}N Knight shift similar to the one observed by ^{13}C CPMAS spectroscopy. Conductive and non-conductive regions coexist and their relation can be estimated. Thus, ^{15}N CPMAS NMR spectroscopy provides interesting information on the structure and the reactions of this class of compounds.

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A New Route to Highly Conducting Polyenes

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Dedicated to Professor Wolfgang Lüttke on the occasion of his 70th birthday

Since doped polyacetylene was shown to possess metallic conductivity in 1977 this class of organic polymers has been studied intensively.[1] The polyacetylenes used for these experiments may be prepared by various routes,[2] the polymerization of acetylene with Ziegler catalysts according to Shirakawa being a widely employed method.[3] Under certain conditions this approach provides mechanically stable polymer films which are of particular importance for the preparation of conducting material.

Regardless of the catalyst system used, it is an inherent disadvantage of this type of polymerization that ultimately a washing process will be required to remove the catalyst or its residues from the desired polymer preparation. In this communication we describe a method which avoids this pitfall and provides polyene films which form a solid layer on glass surfaces, ceramic plates, tubes etc.

Allene (propadiene) is condensed under high-vacuum into a 2 l-round bottomed flask, and after several freeze-and-pump cycles to remove residual oxygen and volatile impurities the reaction vessel is sealed (internal pressure at room temperature ca. 1000 mb). After 20 h at 460 °C (high-temperature drying oven) the inner surface of the flask is covered completely by a deep-black, shiny-film which can be removed in patches and whose electric conductivity is 10^{-8} S/cm. When this film is doped by treating it for 30 min with a saturated solution of iodine in carbon tetrachloride[4] its appearance changes to a shiny gold. After solvent removal the conductivity has increased by a factor of 10^9.

Since allene is known to isomerize to propyne at elevated temperatures[5] we also investigated the polymerization of this hydrocarbon and several other alkynes under the above conditions. The results of these experiments are summarized in Table 1.

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