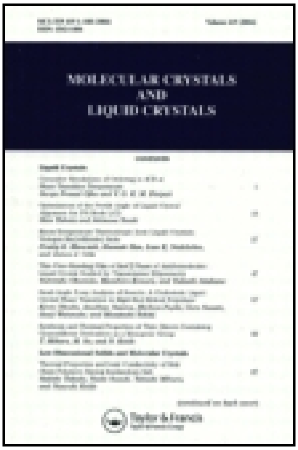

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STRUCTURAL INVESTIGATIONS OF POLYACETYLENE AND POLYPHENYLENE BY NEUTRON SCATTERING

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Wide angle neutron scattering patterns of deuterated cis- and trans-polyacetylene (PA) and deuterated polyphenylene (PPh) doped with AsF_5 have been measured. For undoped trans-PA a refined crystal structure is proposed to reproduce the neutron scattering data. Doping of PA with AsF_5 is explained on the basis of an intercalation model. Deuterated PPh has been prepared by different polymerisation procedures, variing the crystallinity of the undoped material in a wide range. Strong extra peaks are observed during doping with AsF_5, whereas the crystallinity of the samples remains essentially unchanged. An intercalation model similar to AsF_5-doped graphite is proposed.

INTRODUCTION

Polyacetylene (PA) and poly-p-phenylene (PPh) are polymers which are known already since a long time (1,2). Because of their poor solubility and processibility they have only occasionally been investigated by physical methods, which, however, changed drastically in the last few years since it has been discovered that these materials become conducting upon doping with various dopants (3,4). In an attempt to understand the conduction mechanism of these polymers the knowledge of the crystal structure is of course inevitable.

A detailed X-ray analysis of cis- and trans-PA has been performed by Baughman et al.(5,6). The structure of cis-PA can be determined from the X-ray data, whereas for trans-PA certain unit cell parameters are not obtained from the X-ray experiments. The most probable unit cell for trans-PA is monoclinic (space group $P2_1/a$) with a (sin ß) = 4.08Å and b = 7.41Å. By a comparison with oligomers the lattice parameter c and the monoclinic angle ß may be estimated to c ~ 2.48Å and ß ~ 99-100°. The setting angle Φ between the (100)-plane and the chain backbone is obtained from packing calculations to $\Phi = 47.8^\circ$ (6).

Additional information on the structure of cis- and trans-PA has been deduced from electron diffraction investigations (7,8). A different polymersation method was used and under certain conditions diffraction patterns of small single crystals could be obtained by focusing the electron beam to very small areas of the sample. The structure derived for cis-PA is very similar to the previons X-ray results, whereas, however, for trans PA a different structure has been proposed. The unit cell in this case is monoclinic with a = 3.73Å, b = 3.73Å, c = 2.44Å and $\gamma = 98^\circ$. The setting angle Φ and the space group are not obtained from the experiments. Thus in particular for trans-PA the crystal structure is still not very well known and further investigations seem to be necessary. The method of neutron scattering offers here some further possibilities.

The big advantage of neutron scattering for the use in structure determinations of polymers is that the H-positions can equally well be determined by the use of deuterated samples. Deuterium has a large scattering length for neutrons - comparable to carbon or oxygen - and shows on the other hand only a very small incoherent scattering. The large incoherent scattering of hydrogen makes the use of non-deuterated samples impracticable. In the case of deuterated trans-PA thus the neutron scattering pattern should be fairly sensitive on the setting angle Φ since already a small change in Φ causes a large change in the position of the deuterium atoms and thus a big effect in the neutron scattering pattern. One may then obtain independent additional information on the structure of trans-PA since of course also the scattering length of carbon is different to X-ray scattering.

The crystal structure of PPh on the other hand has been investigated by X-ray scattering, too (9). Here again the probable unit cell is monoclinic and the lattice parameters are a = 7.81Å, b = 5.53Å and c = 4.20Å. The space group and the monoclinic angle ß can be estimated by a comparison with oligomers (ß ~ 90-95°, space group $P2_1/a$). The structure of the phenyl rings may not be planar, since also in oligomers of PPh the rotation angle between subsequent phenyl groups may be as large as 25° (10).

On the structure of the doped polymers only very little is known. As a general feature the crystallinity of the samples decreases upon doping and sometimes an extra-peak at small angles is observed. An interpretation is given in terms of an intercalation model (6,11). In doped PA for example usually stage 1 intercalation is observed. It is assumed that the dopant forms sheets in certain crystallographic directions which are regularly stacked. In a stage 1 compound of PA there are alternating PA- and dopant sheets. A similar structure may be observed in doped graphite (12).

It is the purpose of this investigation to provide further and new information on the crystal structure of undoped and doped PA and PPh. In the experimental section the sample preparation and neutron scattering technique will brievely be described. In the discussion the crystal structures and further informations which can be obtained from the neutron spectra of the undoped and doped polymers will be discussed.

EXPERIMENTAL SECTION

Deuterated cis- and trans-PA have been prepared using the well known Shirakawa technique (13) and deuterated acetylene. The samples were repeatedly washed with HCl, water and methanol and dried under vacuum. They were then doped with AsF_5 for 24h to 9.5 mol% AsF_5 (cis -PA) and 11.4 mol% (trans-PA) and sealed in quartz tubes (diameter 0.8cm, approx. 0.8g PA).

The concentrations were determined from the weight uptake during doping.

Deuterated PPh has been prepared by three different reactions:

(i) samples of high crystallinity (PPh-1): Grignard reaction (14) with deuterated p-dibromobenzene, $CoCl_2$, Mg and THF, powder of poly-p-phenylene obtained.

(ii) samples of medium crystallinity (PPh-2): oxidative cationic polymerisation (15) with $CuCl_2$, $AlCl_3$, H_2O and deuterated benzene, probably not exclusively poly-p-phenylene obtained.

(iii) sample of low crystallinity (PPh-3): Addition of o-$C_6H_4Cl_2$ to reaction (ii) (16) yields a material of much lower crystallinity. It contains 6% Cl, is probably strongly cross-linked and may contain to a large extend meta- and ortho-connections of benzene.

All samples were annealed under vacuum at 420°C for 24h to increase the crystallinity and subsequently doped with AsF_5 for 24h. The dopant concentrations obtained from the weight uptake were 0.31, 0.52 and 0.42 mol% for sample PPh-1 to PPh-3, respectively. The samples were sealed in quartz tubes (diameter 1.0 to 1.3 cm, 0.9 to 1.3g PPh) for the scattering experiments.

Neutron scattering experiments have been performed at the Hahn-Meitner-Institut in Berlin using the multidetector neutron diffractometer with 400 cells covering an angular range of 80°. The neutron wavelength was 2.4Å. The background scattering from the container has been subtracted and typical scattering diagrams of PA and PPh are shown in Fig. 1, 2 and 3. The experiments were performed at room temperature and will be discussed in detail in the following section.

DISCUSSION

Undoped PA

A neutron scattering pattern of deuterated trans-PA is shown in Fig. 1a. In the shown angular range one observes three big crystalline peaks as compared to one peak in the X-ray diagram. This difference is

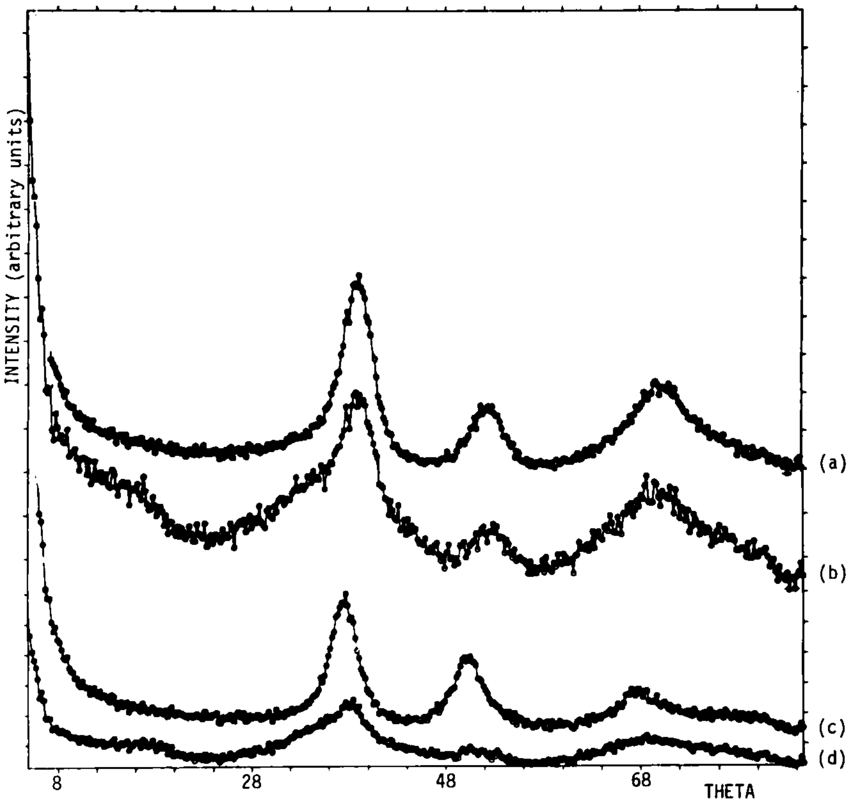

FIGURE 1 Neutron scattering spectra of (a) deuterated trans-PA, (b) deuterated trans PA doped with AsF_5 (11.4mol%), (c) deuterated cis-PA, and (d) deuterated cis-PA doped with AsF_5 (9.5mol%). The intensity scale is arbitrary and the angle theta corresponds to the scattering angle (λ = 2.4Å).

due to the different scattering lengths for neutrons and X-rays. The peaks may be assigned on the basis of the monoclinic unit cell of Baughman et al. (6) to a superposition of first the (020), (110)- and (-110), second the (120) and (-120) and third the (130), (-130), (101), (021), (111) and (-111) reflections, the (101) and (021) reflections giving the strongest contribution to the third peak.

From the halfwidth of the peaks one may obtain a coherence length of 30-40Å, which is a measure of the size of the crystalline areas which contribute to the Bragg reflections. The coherence length is fairly small indicating that the crystalline areas of PA are fairly imperfect and/or small. If one assumes on the other hand a two phase model for PA - as it is usually done for crystalline polymers - assuming well defined crystalline and amorphous regions one would obtain a fairly high crystallinity of the order of 80 to 90 per cent. The scattering from the amorphous regions usually superimposed on the crystalline Bragg reflections is hardly distinguishable from the observed spectra of PA. The strong small angle scattering finally indicates the presence of a large number of voids a fact which is already known e.g. from the low density of the material and electron microscopy investigations. Very similar conclusions hold for deuterated cis-PA, shown in Fig. 1c.

Since the crystal structure of trans-PA is only incompletely known we tried a refinement of the unknown parameters ß and Φ taking the space group $P2_1/a$, the lattice parameters a = 4.08Å, b = 7.41Å and c = 2.44Å as well as usual bond lengths and angles fixed. Assuming the proposed parameters of Baughman et al. (6) for the calculation, (ß = 100° and Φ = 48°) the first peak turns out to be smaller than the second peak which is in contradiction to the experiment. There should be also an (001)-reflection at a scattering angle of 63° which is not observed. A best agreement beween experiment and calculation is obtained for $ß \sim 95°$ and $\Phi \sim 54°$. A more detailed analysis will be published elsewhere.

Doped PA

The neutron scattering spectra for AsF_5-doped cis- and trans-PA are shown in Fig. 1d and Fig. 1b, respectively. In both spectra there appears a broad extra-peak corresponding to a d-spacing of 8.0 to 8.5Å. A similar peak is observed in the X-ray spectra (6,11) and can be explained on the basis of a stage 1 intercalation with AsF_5. The exact nature of the dopant can of course not be obtained from the neutron spectra.

One further observes a decrease of the crystalline peak intensities during doping which, however, is not connected with a shift in the peak positions. There is therefore no indication for a cis-trans isomerisation during doping, but the results may be explained by a two phase model, one phase consisting of the undoped and the second consisting of the doped material. This would be consistent with a percolation model as well as a model of inhomogenious doping. Indicative for the latter is also the change of the small angle scattering during doping which can be explained by a filling of voids by the dopant.

It is evidently very difficult, to give a detailed picture of the doping process in PA since there is only very limited information available from the spectra. The situation is better for deuterated PPh since in this case the crystallinity of the starting material can be changed in a wide range.

Undoped and doped PPh

Wide angle neutron spectra of PPh-1 are shown in Fig. 2. The undoped material, Fig. 2a, has a high crystallinity and the scattering from the amorphous regions is clearly superimposed on the Bragg scattering of the crystalline regions. The coherence length obtained from the half width of the crystalline peaks is of the order of 150Å - a value similarly observed in other polymers like polyethylene and polypropylene. Void scattering is not observed within the investigated angular range. Upon doping with AsF_5 there is a continuous decrease of the intensities of the original crystalline Bragg reflections whereas new peaks ar arising at positions which correspond to d-spacings of 10.5Å, 3.4Å and 2.1Å. There is again no shift in the peak positions of the original crystalline Bragg reflections upon doping and the amorphous halo does not change in intensity or shape during doping. One thus has again a superposition of the spectra of the original polymer and the AsF_5-doped regions indicative for percolation or inhomogenious doping. The doping then seems to affect essentially the crystalline regions whereas the amorphous regions seem to be fairly unchanged. Thus for example the crystallinities of undoped and doped PPh seem to be approximately the same.

In Fig. 3a a neutron spectrum of PPh-2 is shown. The crystallinity of this material seems to be slightly smaller and also the coherence length obtained from the half width of the Bragg peaks is only 50Å indicating smaller crystallites or less crystal

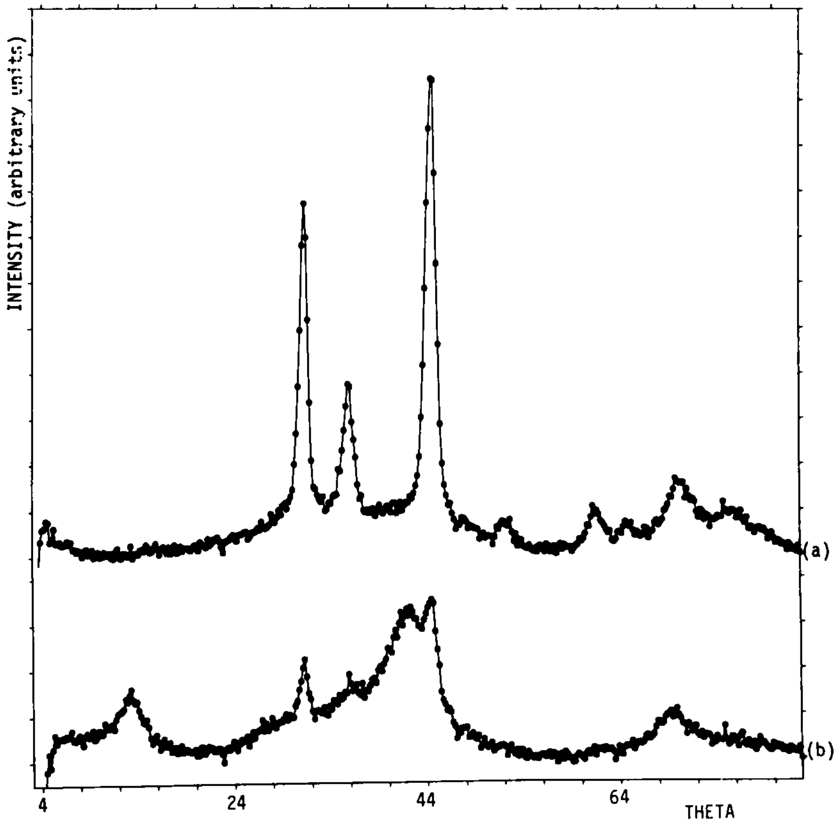

FIGURE 2 Neutron scattering spectra of (a) deuterated PPh of high crystallinity (PPh-1) and (b) deuterated PPh doped with AsF$_5$ (0.31mol%). (a) and (b) are in the same intensity scale.

perfection. This may be expected from the particular polymerisation reaction which causes also non-para-connections of the phenyl-groups. At small angles an appreciable void scattering is observed. Upon doping (Fig. 3b) again the original Bragg reflections disappear and new broad peaks at 10.5Å, 3.4Å and 2.1Å arise. No shift in the positions of the original Bragg peaks upon doping is observed and the amorphous component stays approximately constant. The void scattering on the other hand decreases in intensity. Thus the conclusions which can be drawn on PPh-2 are very similar to PPh-1, and even PPh-3 shows a similar behaviour. This material has a very low crystallinity and the Bragg peaks are not very

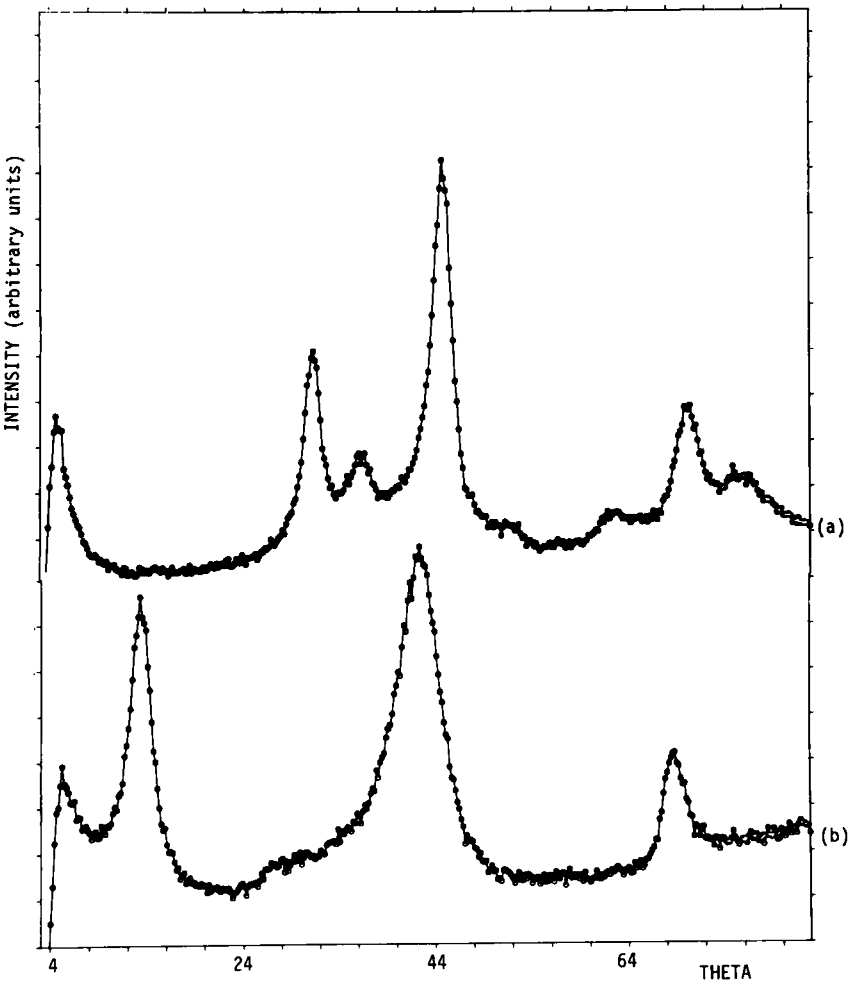

FIGURE 3 Neutron scattering spectra of (a) deuterated PPh of medium crystallinity (PPh-2) and (b) deuterated PPh doped with AsF_5 (0.52mol%). (a) and (b) are in the same intensity scale.

well resolved. Upon doping, however, they disappear and a small peak at 10.5Å arises.

There remains still the problem to explain the occurence of the peaks at 10.5Å, 3.4Å and 2.1Å. Having an eye to graphite again the spacing of 10.5Å may be caused by intercalation of AsF_5 and PPh. The peaks at 3.4Å and 2.1Å are then higher order reflections of this spacing, 3.4Å being the third order and 2.1Å being the fifth order. From the doping of PA with AsF_5 it is known (11) that the thickness of the AsF_5 layer is 4.98Å. This compares very well with a value of 4.97Å for PPh if one assumes a stage 2 com-compound with (020)-planes of PPh. One thus has a layer structure of two PPh-layers of total thickness of 5.53Å corresponding to the length of the b-axis and one layer of AsF_5 (or a related compound as e.g. AsF_6^-) of thickness 4.97Å. The difference to PA is essentially that in PPh only stage 2 intercalation is observed. The stacking sequence in PPh-1 and PPh-2 seems to be very regular since various orders of the 10.5Å spacing are observed.

It should be noted that also from a packing density analysis of PPh for the maximal possible dopant content a compound with a stage higher than stage 1 seems to be probable (17). For the stage 1 compound a maximal dopant concentration of 71mol% is expected whereas the highest observed dopant concentration lies between 4o and 5omol%.

In conclusion it has been shown by the present investigation that by the method of neutron wide angle scattering on deuterated compounds interesting additional information on the structure of the undoped as well as the doped polymers can be obtained.

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