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STRUCTURAL CHANGES IN POLYPARAPHENYLENE BY THE DOPING WITH AsF₅ AND ALKALI METALS

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Résumé - Nous avons effectué des expériences de diffusion de neutrons sur du poly paraphénylène (PPP) dopé et non dopé préparé par différentes méthodes. La structure du PPP non dopé est améliorée et divers modèles structuraux du PPP dopé sont discutés.

Abstract - Neutron Scattering experiments have been performed on both doped and undoped poly paraphenylenene (PPP) prepared by different methods. The structure of undoped PPP is refined and different structural models for doped PPP are discussed.

Poly paraphenylenene (PPP) is a polymer which becomes a metallic conductor by doping with e.g. AsF₅ and alkali metals. Its behavior in many respects is very similar to the more popular conducting polymer polyacetylene (PA). It offers, however, the advantage that it is less air sensitive, exists only in one modification and may be produced in the form of long oriented fibers. For an understanding of its electrical properties and conduction mechanisms the knowledge of its structural features is inevitable.

In the present paper we therefore first discuss different preparation methods for PPP, present neutron scattering data on undoped and doped PPP and try to develop structural models for both the undoped and doped state on the basis of model calculations.

Experimental

PPP may be prepared by different methods. The most popular method has been proposed by Kovacic et al.(1) and proceeds by a dehydrogenation of benzene in the presence of CuCl₂ and AlCl₃.

\[
\begin{align*}
\text{H} & \text{Cl} \quad \text{Cl} \\
\text{H} & \text{H} \\
\text{Cl} & \text{Cl} \\
\text{H} & \text{H}
\end{align*}
\]

⇒

\[
\begin{align*}
\text{H} & \text{H} \\
\text{H} & \text{H} \\
\text{H} & \text{H} \\
\text{H} & \text{H}
\end{align*}
\]

In this Friedel-Crafts synthesis a material of fairly high crystallinity, but a certain degree of non-para connections and other defects(2) is produced. The degree of polymerisation n is of the order of 10-20. Addition of o dichlorobenzene decreases the crystallinity drastically probably because of the inclusion of ortho connections (3). The material of high and low crystallinity is denoted by PPP-1 and PPP-1a, respectively.

A second polymerisation method proposed by Yamamoto et al.(4) starts from p-dibromobenzene using Mg and NiCl₂(bpy) as a catalyst.

\[
\begin{align*}
\text{Br} & \text{Br} \\
\text{Br} & \text{Br}
\end{align*}
\]

⇒

\[
\begin{align*}
\text{H} & \text{H} \\
\text{H} & \text{H} \\
\text{H} & \text{H} \\
\text{H} & \text{H}
\end{align*}
\]
This material (PPP-2) has a high degree of crystallinity, preferentially para connections and a degree of polymerisation n of the order of 10. The samples for neutron scattering were prepared using deuterated benzene and p-dibromobenzene, respectively. To increase crystallinity and purity they were annealed at 420°C under vacuum for 24 h. By chemical analysis the following compositions were found: (i) PPP-1 C: 89.5% (90%), D: 10.4% (10.0%), Cl: <0.5%, (ii) PPP-1a C: 69.5%, D: 5.4%, Cl: 6.6%. Approximately 0.7 g of the powder was used in one scattering experiment.

The doping with AsF$_5$ was performed in the gas phase whereas doping with Li was done in solution using liquid NH$_3$ as a solvent. The doping level was determined from the weight uptake during doping and in some cases by chemical analysis.

The neutron scattering experiments have been performed at the instrument SV4 in Jülich and partially at the Hahn Meitner Institut in Berlin. The incident wavelength was 2.4 Å. Background scattering was negligible because a vanadium (or aluminium) container was used. Samples were never exposed to air but kept under argon or vacuum.

![Neutron scattering spectra of PPP-1 as a function of AsF$_5$-content. Theta is the scattering angle. The indices are based on the monoclinic unit cell of pristine PPP and on the model shown in fig.5c for AsF$_5$ doped PPP.](image-url)
Results and Discussion

Undoped PPP

Neutron wide angle scattering spectra of undoped PPP-1 and PPP-2 are shown in fig.1a and 2a. The crystal structure of PPP-1 is known to a certain extend from x-ray investigations of Kovacic et al. (6). Unit cell parameters are given to $a = 7.81\,\text{Å}$, $b = 5.53\,\text{Å}$, and $c = 4.20\,\text{Å}$. The monoclinic angle $\beta$ can only be estimated from a comparison with oligomers (space group $P2_1/\alpha$, $\beta \approx 90-100^\circ$). In these oligomers on the other hand adjacent phenyl rings are not planar but are turned to each other at an angle of e.g. 26° in the case of p-terphenyl (7). Because of the statistical nature of this non-planarity at room temperature and the equal orientation distribution of the two states one observes an apparent planar structure in structural investigations (8). One thus also would not expect to observe deviations from planarity in the present neutron scattering experiments on PPP.

Looking at fig.1a and 2a we may first note that the crystallinity of the samples is high (approx. 0.7-0.8). The crystal perfection is much better in the case of PPP-2 and may be estimated from the width of the Bragg peaks (coherence length approx. 60Å for PPP-1 and 150Å for PPP-2). For a calculation of neutron scattering intensities we have to know the positions of all atoms within the unit cell. For PPP no atomic coordinates are available, but by a comparison with e.g. p-terphenyl one may obtain a good estimate for bond angles and dis-
stances. We used the following values: \(d(C_{\text{arom}}) = 1.36 \text{Å}, d(C-C_4) = 1.49 \text{Å}, d(C-D) = 1.08 \text{Å}, \phi(C_4) = 118.3^\circ, \phi(C_2) = 120.9^\circ,\)

planar structure, overall temperature factor \(B = 8.0 \text{Å}^2,\) two chains per unit cell, space group \(P2_1/a, a = 7.81 \text{Å}, b = 5.53 \text{Å}, c = 4.25 \text{Å}.

Because of the limited experimental information we tried only to refine the monoclinic angle \(B\) and the setting angle \(\phi\) which is the angle between chain axis and \(a\)-axis. During the calculation it turned out that the calculated neutron intensities are fairly insensitive to variations in \(B\). We therefore took \(B = 100^\circ\). Calculated intensities for varying \(\phi\) are compared with experimental data in fig. 3. Relative intensities scaled to \(I(110)\) are shown since the experiments have not been performed in an absolute scale. Best agreement is obtained for \(\phi = 57^\circ \pm 3^\circ\) and we thus have a good description of the structure of the pristine polymer which may be used as a starting point for the understanding of the structure of the doped material.

**Fig. 5 (right)**
Intercalation models for AsF\(_5\)-doped PPP. Always one unit cell is schematically shown. Calculated intensities are scaled to largest peak. For details see text.

**Fig. 4 (above)** Concentration dependence of some Bragg peaks of AsF\(_5\)-doped PPP-1 (comp. Fig. 1)
Doped PPP

Neutron scattering spectra of AsF$_5$-doped PPP of different doping levels are shown in fig.1 and 2. One observes the development of a new crystal structure during doping and at intermediate states a superposition of the old and new spectra. A shift of peak positions during doping is not observed (exception (002)-peak, see below).

The concentration dependence of some peak intensities is shown in fig. 4. One may distinguish between two regions. At low AsF$_5$ content the old crystal peaks are dimishing and new peaks are rising. There exist two phases - an undoped and a doped phase - and doping is inhomogeneous. In a simple picture one could assume that the dopant first penetrates the surface of PPP crystals and then at higher doping levels inner parts of the crystals will be reached. Also a percolation model cannot be excluded (9). This first process is finished at a doping level of approx. 0.3. From this point the old structure has disappeared and the already existing new peaks only increase in intensity. One may assume that additional AsF$_5$ is thus still incorporated into the new structure occupying previously empty sites.

If we look on the (002)-peak during doping we do not observe a big change in intensity, but only a slight shift to smaller angles (\( \Delta d = 0.03 \AA \)). This can be explained by a change in the monoclinic angle \( \beta \) during doping from 100° to 90°, if one assumes that covalent bond lengths of the monomers stay approx. constant. Following the bipolaron model of Bredas et al. (10) there may be, however, also a change in bond length at least locally. This change corresponds to a chain shortening of up to 0.02 \AA per phenyl group and is thus just the contrary effect to the observed increase in d-spacing of 0.03 \AA.

To explain the structural changes in AsF$_5$-doped PPP one may start from the structure of the pristine material (fig.5a). There are essentially two sites per unit cell at \((0.5,0.5)\) and \((0,0.5)\) where AsF$_5$ possibly could be build in. Rotating the chains and expanding the lattice leads to the structure shown in fig.5b. A minimum of rearrangement is needed. It turns out that the actual consideration of all atoms in the unit cell is necessary for a realistic picture and that the orientation of AsF$_6$ has only a minor influence on the calculated intensities. The following parameters are taken for the calculations: bond length and angles as before, \( d(\text{As-F}) = 1.7 \AA, a = 10.5 \AA, b = 4.7 \AA, c = 4.25 \AA, \beta = 90° \). One AsF$_6$ at the position \((0.5,0.5)\).

A best fit is obtained for \( \phi = 35° \), but there remain some discrepancies to the experiment (e.g. (200) peak at 26.4° has too high intensity). Both unit cells and intensities of fig.5 are drawn very schematically and shall show general features. Structures have not been refined to small details.

One can think of course of a large variety of possible structures for PPP, and we will discuss here only two others, which may be suggested from similarities to other organic conductors. In charge transfer salts for example stacks of planar molecules are observed as shown in fig.5c. For PPP we assume \( a = 10.5 \AA, b = 6.6 \AA, \phi = 90° \), and AsF$_6$ at \((0.5,0.5,0.5)\). Although there are still discrepancies concerning the exact intensities, this model fits best to the experimental data. The exact position of AsF$_6$ may still be varied along the b-direction. Using this model also spectra of partially deuterated PPP doped with AsF$_5$ can be described.

From the peaks at 3.3 \AA and 10.5 \AA as well as the stoichiometry of C$_6$H$_4$ to AsF$_5$ (ratio 2:1) a stage 2 intercalation structure (fig.5d) similar to graphite may be proposed (11, 12, 13). Parameters for PPP would be \( a = 10.5 \AA, b = 5.8 \AA, \phi = 90° \), PPP at \((0,0,0)\) and \((0.31,0,0)\), AsF$_6$ at \((0.65,0,0)\). The agreement with the experiment is, however, worse as compared to model 5c (peaks at 23° and 54°).
As a general feature the proposed models differ not very much with respect to the calculated intensities. It is therefore difficult to favour one structure—especially also having in mind that we have discussed only some of very many possible structures. Model 5c seems to be slightly advantageous as far as the comparison of calculated and experimental neutron scattering intensities is concerned. Furtheron its formation seems easier to understand than e.g. model 5d where the stage 1 structure should be preferred. Similarly interatomic distances are much more reasonable than in model 5b and e.g. a stacking distance of 3.3Å is often observed in charge transfer salts.

For a better understanding of the structure still further experiments are desirable, and of course also doping with different dopants gives additional information. Using alkali metals the size of the dopant can be varied over a wide range. Lithium for example is a very small molecule and one could suggest that the pristine structure will be less disturbed during the doping with Li than with AsF₅. Using the doping procedure described before we obtain, however, a material with much less order than in the case of AsF₅. This may be due to an incorporation of NH₃. Further investigations are in progress. We acknowledge the help of Dr. H. Grimm, Dr. H. Poerschke and B. Walker during the experiments.

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