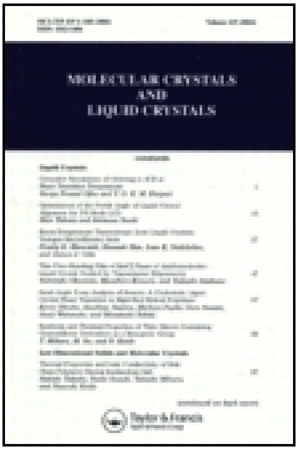

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Crystal Structure of Undoped and Lithium-Doped Polyparaphenylene

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CRYSTAL STRUCTURE OF UNDOPED AND LITHIUM-DOPED POLYPARAPHENYLENE

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Abstract The crystal structure of prisitine and Li-doped polyparaphenylene (PPP) has been investigated by electron diffraction. The chain setting angle of pristine PPP has been refined to $\Phi = 45^{\circ}$. For Li-doped PPP, a superposition of amorphous and crystalline scattering is observed. A simple intercalation model for the crystalline component is in good agreement with the experimental data.

INTRODUCTION

Polyparaphenylene (PPP) is a polymer which has a high crystallinity and is stable at air. Its crystal structure has been investigated by various methods, including XR[1] and neutron[2,3] diffraction. During doping with AsF_5, strong structural changes are observed[2-5]. At small doping levels, the crystal structure of the pristine material and the newly formed structure of the doped material are coexisting in different regions of the sample. At higher doping levels, a homogeneous phase is formed, which changes slightly with increasing AsF_5 concentration[3]. The exact crystal structure of the doped material is not fully understood because of the limited information which can be obtained from the neutron spectra. The use of oriented samples[4] or the use of partially deuterated PPP[6] improves the situation, but still additional information would be desirable. One possibility is the use of a different sort of radiation.

In this paper, we describe electron diffraction experiments on thin oriented films of undoped and doped PPP. With neutrons and electrons, it is possible to locate light elements in the presence of heavy ones. Using electrons as a probe yields independent structural information and offers the additional possibility to obtain by inelastic electron scattering information on electronic excitations and the band structure of the material [7-9]. It requires, however, a special sample preparation technique to obtain very thin films of PPP where dynamic scattering effects can be neglected. The diffraction data will be discussed on the basis of model calculations and compared with other experimental data.

EXPERIMENTAL

Thin oriented films of PPP can be prepared in a shear gradient on a glass wall[10] and are then carefully washed off with diluted HF. The Kovacic method[11] was used. The thickness of the films is estimated to be smaller than 1000Å. From transmission experiments, the films were annealed under vacuum for 24 hours at a temperature of 420°C to remove impurities. The Li-doping and the diffraction experiments were performed in an electron loss spectrometer under UHV-conditions. Li was evaporated onto the films and diffused at room temperature within several hours into the films. The relative intensities of the Li and C K-absorption edges were used as a measure of the Li-concentration. The incident electron energy was 170 KeV, and the elastic scattering intensity was recorded with a Q-resolution of 0.04 - 0.1 $Å^{-1}$. Since the orientation of the chains was not perfect, we observed in general for a certain orientation a small contribution in the diffraction pattern originating from the other orientation.

This was numerically subtracted. Similarly a smooth background was subtracted using a spline-fit.

RESULTS

The electron diffraction data of pristine PPP are shown in Fig. 1a. The material has a high crystallinity and is well oriented. No amorphous halo can be detected. The indices are based on a monoclinic unit cell proposed by Kovacic[4]. (hk0) and (001) - reflections can well be separated for Q perpendicular c and Q parallel c using the technique described in the experimental section. The unit cell of PPP has been refined already on the basis of neutron scattering experiments[3]. Similarly, we refine the setting angle Φ between chain axis and a-axis on the basis of the electron diffraction results. The formfactors for electron scattering are taken from the International Tables for X-ray Crystallography. Using bond angles and distances as well as unit cell parameters, temperature factors, etc. from ref. 3, we obtain good agreement between observed and calculated intensities for $\Phi = 45^{\circ}$ (Fig. 1b). This value is considerably smaller than the value obtained from neutron scattering ($\Phi = 57^{\circ}$), but the sample preparation in both experiments is very different, too. In polyacetylene for comparison, one observes a completely different crystal struture if the polymersation is performed in a shear gradient[12], and also for usual polymers like polyethylene the setting angle Φ is known to be sensitive on the specific preparation conditions[13]. It thus seems to be reasonable to assume that the observed difference in the setting angles Φ obtained from electron and neutron diffraction is caused by the different preparation methods.

The electron diffraction pattern of Li-doped PPP is shown in Fig. 2. The Li-concentration is approximately 50 mol%. The material is still crystalline, but the crystal struture has changed. In the direction parallel c, essentially the intensity

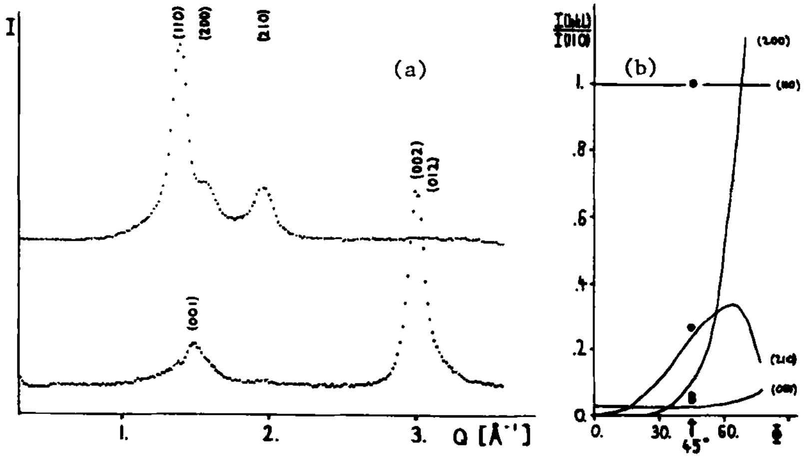

FIGURE 1 (a) Electron diffrction pattern of shear oriented pristine PPP. The intensity scale of the upper curve ($Q \perp c$) is reduced by a factor of 5.56 as compared to the lower curve ($Q \parallel c$). Miller indices correspond to a monoclinic unit cell (see text). (b) Calculated (—) and experimental (●) intensities as a function of the setting angle Φ .

of the peaks changes. The position and half-width of the reflections changes slightly. The (002)-reflection shows a shift to smaller Q if a separation of the two peaks is performed. In the direction perpendicular to c, one observes a group of peaks in the region of approximately 1-2 $Å^{-1}$. Besides the first reflection of approximately 1.0 $Å^{-1}$ those peaks are already present in the pristine spectrum but the intensities and halfwidths have changed. If one tries a separation of those peaks, it seems to be appropriate to assume that a broad "amorphous" component at roughly 1.4 $Å^{-1}$ is superimposed (see Fig. 2). Similarly, at 3.1 $Å^{-1}$ in the direction parallel c such a broad halo is observed.

In previous neutron diffraction experiments we investigated PPP doped with Li which was dissolved in liquid NH_3. In these studies, no crystalline peaks were observed but only the amorphous halos described above plus a broad reflection at 0.72

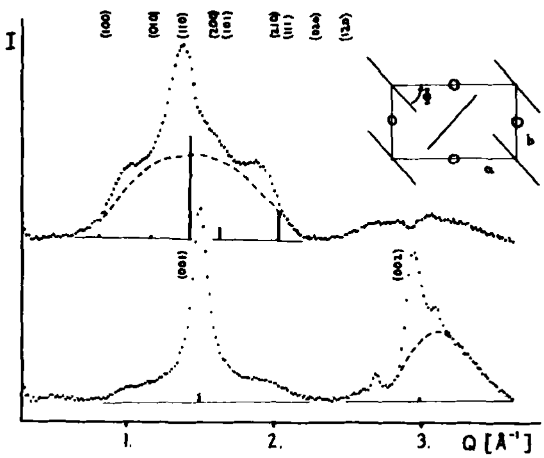

FIGURE 2 Electron diffraction pattern of Li-doped PPP (x_{Li} = 0.5) The intensity of the upper curve (Q ⊥ c) is reduced by a factor of 1.08 as compared to the lower curve (Q ∥ c).

Å^{-1}. It could be concluded from the large incoherent background that NH_3 was also incorporated into the doped material. In the present study, the doping was done with Li-vapour which obviously seems to preserve the crystal structure to a certain extent. Also in AsF_5-doped PPP with low-starting crystallinity (sample PPP-3 of ref. 2) only the "amorphous" scattering is observed. From the electron diffraction of oriented PPP we thus can conclude that the first halo comes from disorder in the ab-plane whereas the second halo results from a disorder along the c-direction, probably from some bending of the chains.

Looking on the crystalline component again, one can perform model calculations assuming different intercalation models. Since, however, most reflections do not change in position during doping, the most simple model would be to assume that Li which is a very small atom is incorporated into the PPP crystal by simply filling empty spaces between the chains (see Fig.

2). We get a reasonable agreement between observed and calculated intensitis if we assume identical parameters to the pristine PPP structure except $\beta = 90^\circ$ and $\Phi = 40^\circ$. Lithium is located at $(\frac{1}{2}\,0\,\frac{1}{2})$ and $(0\,\frac{1}{2}\frac{1}{2})$ with an occupancy of 0.5. Calculated intensities are also shown in Fig. 2. We tried a variety of other models which did not give a better agreement.

In conclusion, we can explain both the undoped and Li-doped crystal struture of PPP on the basis of a quantitative analysis of electron diffraction data. We observe an increase of the "amorphous" scattering of PPP during doping. In the crystalline component lithium is incorporated on empty sites of the pristine structure.

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