X-ray Diffraction Study of Poly-p-Phenylene doped with SbF_5 and SbCl_5

Abstract

X-ray diffraction experiments have been performed on SbF_5 and SbCl_5 doped PPP prepared by the Kovacic method. Results are discussed in terms of two structural models which account for the regular intercalation of dopants within the polymer crystal lattice.

Introduction

X-ray and neutron scattering experiments have been carried out on both undoped and AsF_5 -doped polyparaphenylene (PPP) and various structural models for doped PPP have been suggested (HÄSSLIN and RIEKEL, 1982; STAMM and HOCKER, 1983; PRADERE and BOUDET, 1988). The doping process leads to a strong modification of crystalline order within the polymer as revealed by the decreasing number of broad reflections left. Doping of PPP with AsF_5 resembles intercalation reactions with graphite with acceptor molecules. For polyacetylene and PPP doped with alkali metals and AsF_5 a channel structure with dopant molecules located mainly along rows parallel to the polymer chains has been proposed (BAUGHMAN et al., 1983 and 1985). The aim of the present report is to complement the above studies to the case of the structure modification of PPP doped with SbF_5 and SbCl_5 .

Experimental

Poly-p-phenylene (PPP) was synthesized following the Kovacic method (KOVACIC and OZIOMEK, 1964). The PPP powder obtained was subsequently purified by thermal treatment at 400°C for 36h under high vacuum. Sintering of the thermally-treated PPP gave rise to samples with a higher porosity (apparent density 0.8 g cm^{-3}) than the pristine sintered PPP (1.2 g cm^{-3}) (RUEDA et al., 1987). Owing to the inherent porosity of the annealed

Fig. 1. *X-ray diffraction patterns of: pristine poly-p-phenylene (top), PPP doped with SbF_5 (middle) and PPP doped with SbCl_5 (bottom) after 2 hours doping time*

material SbF_5 and SbCl_5 vapour doping occurred easily through the thickness of the samples. X-ray diffraction experiments from the doped samples stored in air were carried out using $\text{CuK}_\alpha(\text{Ni})$ radiation and a flat camera with pinhole (0.3 mm) collimation, complemented occasionally with a Debye camera and a vertical goniometer. The doped sintered samples (0.3mm thick) were examined directly and/or after grinding them to fill a glass capillary ($\phi=0.7$ mm).

Results and Discussion

Fig. 1 illustrates the X-ray diffraction patterns of undoped and doped sintered PPP for both dopants (SbF_5 and SbCl_5) used. It is immediately seen that the X-ray diffraction pattern of PPP is notably modified upon doping. The new doped structure is, in addition, very sensitive to subsequent manipulation. Indeed, for a sufficiently ground doped sample the intensity of the inner reflections (higher spacings) markedly decreases while the crystalline reflections the undoped PPP sample reappear becoming dominant. The low number of reflections of the doped structure suggests the occurrence of a large disorder in the packing of PPP chains and an additional lack of crystallographic register along the chain axis. Table I collects the measured spacings for the reflections and relative intensities observed at $2\theta < 45^\circ$. In all cases a substantial modification of the initial PPP structure takes place. In case of SbCl_5 -doped PPP the spacing at 1.56nm disappears after light grinding and it is replaced by a new reflection at 1.07 nm which finally disappears after further grinding of the sample. In case of SbF_5 -doped PPP the first reflection disappears after grinding but that at 0.60 nm still remains observable, although very weak, even after extraction of the doped sample with hydrochloric solution (1:1) for 6h.

TABLE I

Lattice spacings (nm) and relative intensities of the X-ray reflections observed for sintered Poly-p-phenylene before and after doping

undoped PPP	SbCl_5 -doped PPP	SbF_5 -doped PPP
————	1.56 s	1.04 s
————	0.62 s	0.60 s
0.452 vs	0.45-0.38 mw	0.45-0.38 w
0.390 s		
0.315 s	0.31-0.30 ms	0.305 m

An attempt to derive a crystal packing by assuming that the rigid PPP chains run perpendicularly to the *a b* plane has been made. A *c* value=0.42nm has been used (KOVACIC et al., 1968). In the case of SbF_5 -doped PPP an

hexagonal packing with $a=1.20\text{nm}$ fits quite well with the observed reflections (calculated spacing values for: $d_{100}=1.039\text{nm}$, $d_{110}=0.600\text{nm}$ and $d_{200}=0.300\text{nm}$). In contrast, the structure observed for SbCl_5 -doped PPP could be described by means of a 'rectangular' packing with $a=1.56\text{nm}$ and $b=0.62\text{\AA}$ ($d_{100}=1.560\text{nm}$, $d_{010}=0.620\text{nm}$ and $d_{120}=0.304\text{nm}$). A similar packing to the hexagonal one with $a=1.23\text{nm}$ would correspond to the doped structure observed for SbCl_5 -doped PPP after light grinding. Let us examine next the way in which the PPP chains can accommodate together with the dopant species within the unit cell proposed. By considering atomic radii values the resulting maximum distances, X-Sb-X, would be 0.668 and 0.848nm for X=F and Cl respectively. Furthermore, a mean diameter of 0.524nm is derived for the PPP chain from its crystal cross section (0.216nm^2) (KOVACIC et al., 1968). Hence the hexagonal parameter a could allow the inclusion of one PPP chain between the nots of the hexagonal lattice (Fig. 2a) occupied by the dopant molecules leading to a packing of 3 PPP chains per unit cell projection.

Fig. 2. Suggested packing in the *ab* plane for SbF_5 -doped PPP (left) and SbCl_5 -doped PPP (right).
PPP chain direction (*c*-axis): perpendicular to the *ab* plane

For the structure of SbCl_5 -doped PPP the parameter $a=1.55\text{nm}$ can accommodate two PPP chains stacked parallel to each other (stacking distance: 0.66nm) between the dopant molecules (Fig. 2b). This packing mode is one of the possible ones suggested previously (STAMM and HOCKER, 1983; HÄSSLIN and RIEKEL, 1982) for AsF_5 -doped PPP. The b parameter coincides reasonably well with the width of a planar PPP chain. Since the diameter of the dopant molecule is larger than b an interpenetration of the dopant molecules in adjacent unit cells may be expected (Fig. 2b). It is to be noted that our experimental results differ substantially from those reported for AsF_5 -doped PPP. While in the case of AsF_5 doped material the main reflections appear at 1.05, 0.339 and 0.212nm, in our study a reflection at 0.34nm was never observed. Since the reflection at 0.339nm was related to the interplanar spacing between extended chains of PPP with indices 020,

the parallel stacking of PPP chains, whenever present, is not monitoring in our case the lattice parameter b , as in the case of PPP doped with AsF_5 .

In conclusion, we have observed a change in the crystal structure of PPP after doping with SbF_5 and SbCl_5 . It suggests a penetration of the dopant molecules inside the crystals. Two intercalation models —hexagonal packing for the former and 'rectangular' packing for the latter— could account for the new diffraction pattern as an average. It is, finally, worth pointing out that the hydrolysis of the dopant species (SbF_6^- or SbCl_6^-) in the presence of ambient atmosphere provoked during grinding would result in an hydroxysalt of antimony with a volume comparable to SbF_6^- ($\text{O-Sb-O}=0.684\text{nm}$) and much lower than SbCl_6^- . This could probably account for the crystal modification observed in case of SbCl_5 -doped PPP (change from a rectangular to hexagonal packing). For a more accurate description of the structure further experiments are still desirable.

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