

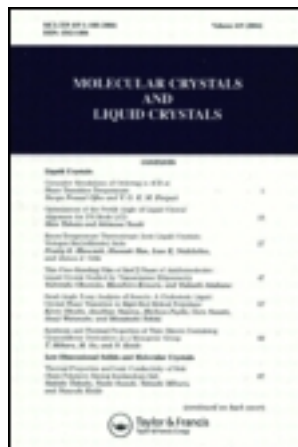
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Jean-Yves Goblots^a, Francois Maurice^a, Gerard Froyer^a & Yvan Pelous^a

^a C.N.E.T LAB-ROC/TIC, B.P. 40, 22301, Lannion, France

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DOPING KINETICS AND STRUCTURAL STUDY OF AsF₅ DOPED POLYPARAPHENYLENE

JEAN-YVES GOBLOT, FRANCOIS MAURICE, GERARD FROYER, YVAN PELOUS
C.N.E.T., LAB-ROC/TIC, B.P. 40, 22301 Lannion, France

Abstract Kinetics of AsF₅ doping on polyparaphenylene (PPP) powder synthesized by the Kovacic method (1) were carried out for different pressures and different temperatures. The results are explained in terms of physical adsorption on the high specific area of PPP and diffusion of AsF₅ into PPP fibrils. Undoped regions and doped ones are seen by X-ray analysis depending on the doping level.

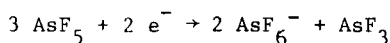
EXPERIMENTAL

A stainless steel vacuum line is used to do all the doping experiments. The vacuum upon the PPP powder is about 10⁻³ torr and the powder is in a glass cell. AsF₅ is cryogenically distilled at - 96°C (acetone "slush" bath) and then stored at 77 K. We measured the variation of the pressure ΔP in the cell volume around a given pressure P. A quantity of AsF₅ is then introduced in the cell to readjust the pressure to P. Integration of all these variations gives us the AsF₅ consumption. Samples used for X-ray analysis were Lindeman's tubes of 0.3 mm diameter filled with doped powder and sealed in argon atmosphere. Debye Scherrer patterns were obtained in a chamber of 360 mm circumference and from the monochromatic λ_{Kα₁} of copper (1.54056 Å).

RESULTS AND DISCUSSION

Dopant species

One AsF₃ molecule was produced (and trapped in a cold finger) for every three to four AsF₅ molecules consumed, in rough agreement with the reaction proposed by Clarke et al (2) :



So that we assume AsF_6^- to be the dopant anion.

Kinetics of doping

The integrated AsF_5 consumption versus square root of time curves for PPP powder doping at 100 mb AsF_5 present two roughly linear parts of different slopes corresponding to two different regimes (fig. 1) :

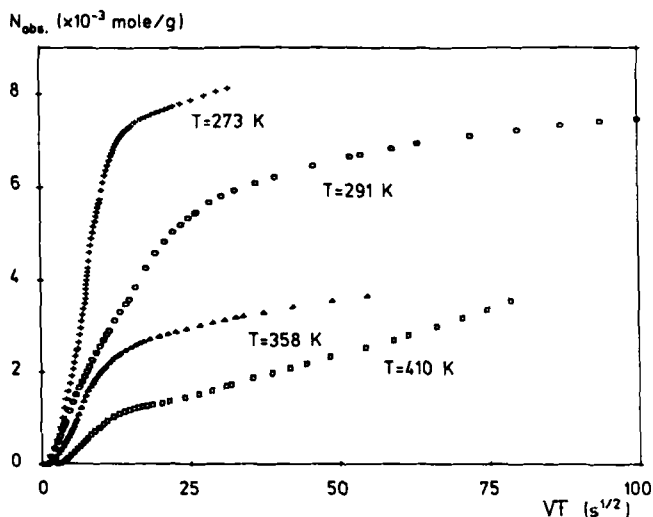


FIGURE 1 AsF_5 doping of PPP powder at 100 mb pressure :
integrated consumption versus square root of time.

1/ First a fast adsorption, characterized by a negative temperature dependence of the adsorption rate and equilibrium surface concentrations.
2/ Then a slower, temperature activated diffusion of AsF_5 through the doped outside part of the fibrils before reaching and doping the inner, undoped cores. The adsorption rate being much higher than the diffusion one, the surface concentration of liquid or solid AsF_5 stays at its equilibrium value. We have modelled this process (3) and estimated the diffusion coefficient of AsF_5 in doped PPP to be about $10^{-15} \text{ cm}^2/\text{s}$ with an activation energy of 0.25 eV.

We have run adsorption-desorption experiments on the fully doped powder (figure 2).

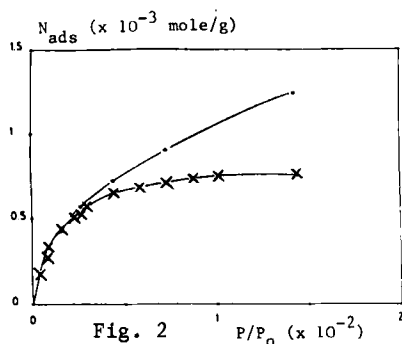


FIGURE 2 Room temperature adsorption, (\circ), and desorption (\times), of AsF_5 on doped PPP powder. P_0 is the room temperature vapour pressure of AsF_5 .

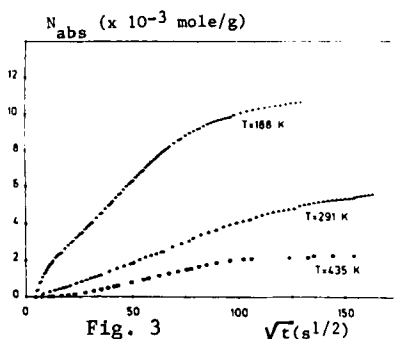


FIGURE 3 AsF_5 doping of PPP powder at 30 mb : consumption vs square root of time.

A B.E.T. (4) analysis of the data gives a specific area of $100 \text{ m}^2/\text{g}$ for the doped polymer, so that the amount of adsorbed AsF_5 is about 3 to 4 percent of the phenyl groups.

For a reduced doping pressure of 30 mb AsF_5 (figure 3) the adsorption rate is lower than the diffusion-doping process, and then limits the kinetics of doping with negative temperature dependence.

X-RAY ANALYSIS

Only three broad rings are visible on diffraction pattern of highly doped PPP (fig. 4 a) with the following d-spacings :

5,21 Å, 3,35 Å and 2,12 Å.

For lightly doped PPP, an intermediate diffraction pattern with the superposition of the pure PPP diffraction pattern and the doped PPP one is seen as in figure 4 b. The three broad rings are always peaked at the same position whatever the doping level is. The rings concerning the pure PPP structure disappear when the doping level increases.

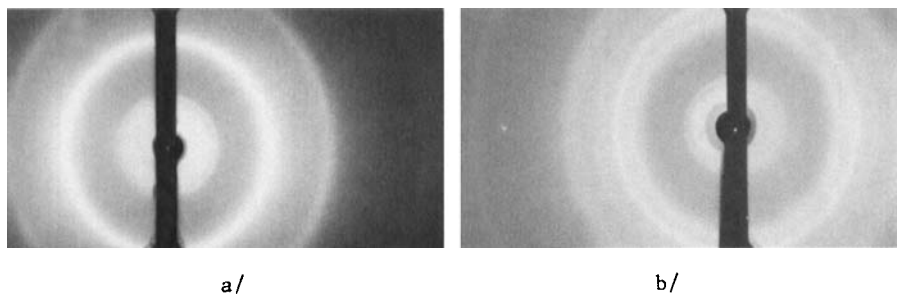


FIGURE 4 Diffraction pattern of a/ highly doped PPP and b/ lightly doped PPP

CONCLUSION

The diffusion of AsF_5 into the PPP fibrils is a very slow process. The dopant species formed during doping experiment is AsF_6^- . AsF_5 gas does not dope homogeneously PPP powder and this type of doping does not seem to be a convenient method to obtain homogeneous lightly doped samples.

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