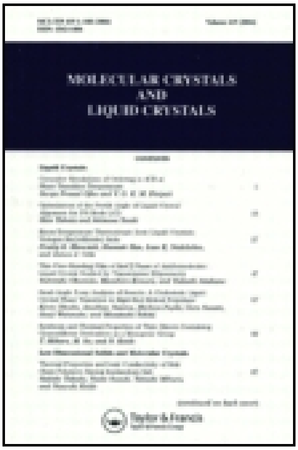

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Dynamics of SBF_5, IBR and I_2-Sorption by Polyacetylene

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DYNAMICS OF SbF_5, IBr AND I_2-SORPTION BY POLYACETYLENE

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Abstract The kinetics of polyacetylene doping by SbF_5, IBr and I_2 was studied by real time neutron diffractometry. Fickian behaviour was observed for SbF_5 and IBr. The deviation from a Fickian behaviour observed for the doping with gaseous I_2 is explained by a nucleation/growth process.

INTRODUCTION

In this note we present data on the doping kinetics of polyacetylene by gaseous SbF_5, IBr and I_2. The experiments were performed by real time diffractometry which probes the change in long range order of the fibrils.[1] Structural transformations have been verified for the dopants mentioned.[2] In view of the slow bulk doping processes, neutron diffractometry with a temporal resolution (t_s) of 300 s could be used. A methodic advantage of this technique over X-ray diffraction is that the change in transmission upon doping can be neglected in first order.[1]

EXPERIMENTAL

Foils of deuterated polyacetylene (D-PA) were grown according to the Shirakawa technique on the solution containing the catalyst.[3] Electron microscopy of the ~ 150 µm thick foils shows that ~ 90 % of a foil is made up of 200-500 Å thick fibrils and that a further fraction of up to 3000 Å thick fibrils exists. All dopants were distilled and the polymer was handled usually under inert gas. After pumping to 10^{-6} mbar, the foils were exposed at r.t. to a constant dopant pressure.[2] Diffraction patterns were recorded using the D1B position sensitive detector at the I.L.L. Grenoble. In one case (trans D-PA/I_2) the polymer foils were exposed to air prior to doping.

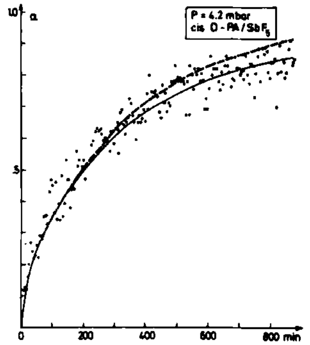

FIGURE 1a Development of the lattice degree of reaction α upon doping cis D-PA by SbF_5. (--- theory (see text); —— guide line to the eye).

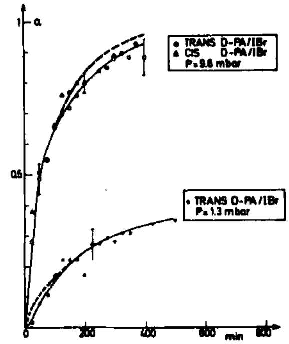

FIGURE 1b Development of α upon doping cis- and trans D-PA at two different IBr-pressures. (--- theory; —— guide line to the eye). Every 5 data points averaged.

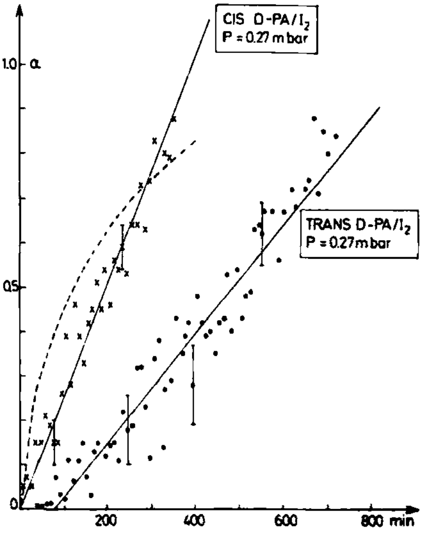

FIGURE 1c Development of α upon doping cis- and trans D-PA by I_2. (—— guide line to the eye; --- theory $D=1.5\cdot10^{-9}\,cm^2\,s^{-1}$) P = 0.27 mbar

RESULTS AND DISCUSSION

The variation of the lattice degree of reaction α derived from the 201 (cis D-PA) and 120 (trans D-PA) reflections upon doping[1,4] is shown in Figs. 1a, b, c. In all cases but the system trans $D\text{-}PA/I_2$, the reaction starts with the exposure to the gas. The different behaviour of the latter system may be due to a surface barrier of oxidized material.[5]

The sorption of SbF_5 and IBr can be analyzed in terms of a diffusion into a foil of thickness d. A macroscopic coefficient of diffusion -D- can be calculated according to:[6]

$$\alpha = 1 - \frac{8}{\pi^2} \sum_{k=0}^{\infty} \frac{1}{(2k+1)^2} e^{-(\frac{2k+1}{d}\pi)^2 D\cdot t} \tag{1}$$

where t is the time. The calculated α-values (dashed lines in Figs. 1a, b) suggest that the data on the sorption of SbF_5 at 4.2

mbar ($D=1\cdot10^{-9}cm^2s^{-1}$), IBr at 9.6 mbar pressure ($D=3\cdot10^{-9}cm^2s^{-1}$) and at 1.3 mbar ($D=0.22\cdot10^{-9}cm^2s^{-1}$) are quite well described by this theory. Note that these values are rather similar to those derived by macroscopic methods[6,7] which, for example in the case of SbF_5, were determined from the temporal variation of the dopant concentration across the foil. This suggests that the rate determining step in the breakdown of the polymer lattice is the interfibrillar diffusion.

The sorption of I_2 differs, however, from a Fickian behaviour (Fig. 1c). The rate determining step in the breakdown of the polymer lattice is therefore no longer the interfibrillar diffusion. We find that the data are well described by the Avrami equation[8] which provides an empirical description of bulk transformations involving nucleation and growth processes (Eq. 2, Fig. 2). This suggests that the kinetics is dominated by the structural conversion of the fibrils.

$$\alpha = 1 - e^{-k\cdot t^n} \qquad (2)$$

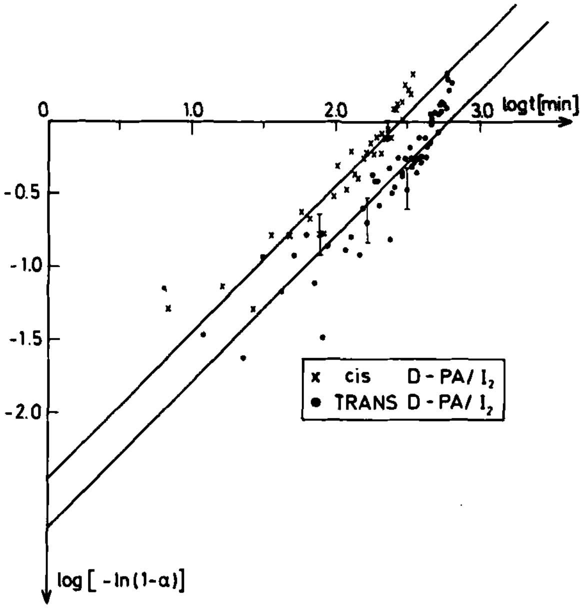

FIGURE 2 Avrami plot of the lattice degree of reaction upon doping cis- and trans D-PA by I_2. The solid lines correspond to n=1, k=0.0035 min^{-1} and k = 0.0016 min^{-1} (Eq. 2). The trans D-PA data have been corrected by 80 min. (see text).

k is a constant and n depends on the shape of the growing nuclei. An analoguous approach has also been used for intercalation reactions.[9] In the case of cis D-PA we derive $k=0.0035\ \mathrm{min}^{-1}$ and $n=1$ which is expected for the athermal nucleation and growth of rods normal to the rod axis. This agrees to the fibrillar morphology of PA which is retained upon doping.[10]

In the case of trans D-PA, we assume that the reaction starts at $t=80$ min due to the presence of a surface barrier. The data points corrected for this value agree rather well to $n=1$.Trans D-PA ($k=0.0016\ \mathrm{min}^{-1}$) appears to react slower with I_2 than cis D-PA. A surface barrier may also explain the slow onset of the reaction found by other authors.[6,11]

Systematic differences between theory and experiment exist at longer reaction times. Whether this is due to the theory or due to the inhomogeneous morphology cannot be said at present.

Note that a further, more rapid structural process has been observed by synchrotron radiation diffraction.[1] As the time scale of this process is comparable to the increase in conductivity[5,11] we tentatively assume that the more accessible surface layers are initially doped.

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