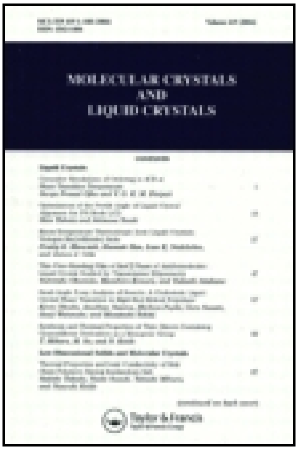

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Distribution of Iodine in Doped Polyacetylene Filme

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Version of record first published: 19 Dec 2006.

To cite this article: A. Jánossy , L. Pogány , S. Pekker & R. Swietlik (1981): Distribution of Iodine in Doped Polyacetylene Filme, Molecular Crystals and Liquid Crystals, 77:1-4, 185-195

To link to this article: http://dx.doi.org/10.1080/00268948108075240

Mol. Cryst. Liq. Cryst., 1981, Vol. 77, pp. 185–195
0026-8941/81/7701-0185$06.50/0

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

DISTRIBUTION OF IODINE IN DOPED POLYACETYLENE FILMS

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Received for publication August 17, 1981

The distribution of iodine in polyacetylene doped under conditions typical for most published work is investigated by energy dispersive X-ray analysis under an electron microscope. The 9.1 GHz dielectric constant of a series of iodine doped $(CH)_x$ is measured as a function of temperature. From the X-ray analysis we conclude that the reaction takes place in two steps: a fast reaction at the fiber surfaces and a slow reaction with the interior of $(CH)_x$ fibers. The dielectric constant of lightly doped $(CH)_x$ at the fiber surfaces and pristine $(CH)_x$ in the interior of the fibers. The temperature dependence of ε is believed to be related to the intrinsic temperature dependence of the conductivity of the highly doped fiber surface layers.

Pure polyacetylene, $(CH)_x$, is an insulator with an electronic band gap of 1.4 eV which by doping with either acceptors or donors may be transformed into a highly conducting metal. Apparently it may be doped continuously from zero concentration to several percents, about to y = 0.25 in the case of $(CHI_y)_x$. A number of physical properties have been studied as a function of dopant concentration and widely different mechanisms were proposed to explain the transition from the insulating to the metallic state. In most cases it was assumed that the doped material was homogeneous or at least quasi-homogeneous for all dopant levels. It was initially suggested [1] by the Pennsylvania group that at low concentrations localized states are formed and by increasing the concentration a Mott transition takes place. A later suggestion [14] which seems to be supported by some experiments [2] is the formation of spinless mobile carriers, solitons at low dopant concentrations. A completely different view was given by Tomkiewicz et al. [3] who suggested that even at very low dopant concentrations metallic particles are formed - it is strongly inhomogeneous.

In this paper we study the homogeneity of iodine vapour doped polyacetylene for various dopant levels. There are two scales for which an inhomogeneity is to be considered.

a.) Polyacetylene films consist of loosely packed fibers with an apparent density of 1/3 to 1/2 of that of the fibers. A typical fiber diameter is 200 Å. During the doping the iodine vapour diffuses into the sample in the space between the fibers. As part of the iodine is trapped by the fibers a relatively large scale concentration gradient appears.

b.) On the other hand the solid state reaction of $(CH)_x$ fibers with iodine vapour may lead to an inhomogeneity on the scale of a fiber diameter. This may be due to either a lack of ability for iodine ions formed at the surface to diffuse or dopants interactions leading to a segregation of doped and undoped phases.

We show by energy dispersive X-ray analysis in a scanning electron microscope that under our conditions of iodine doping, which are typical for most published work, the large scale penetration depth of iodine is about 50 μm for low doping levels.

We present also a study of the dielectric properties, measured at 9.1 GHz, indicating that the reaction within the fibers is strongly inhomogeneous: at low dopant levels the surface of the fibers becomes metallic while the interiour remains intact.

Cis-polyacetylene films were prepared by the Ziegler-Natta polymerisation at -78°C [4]. Prior to doping the films were transformed to the trans isomer by heating at 180°C for half an hour under a dynamic vacuum. Films were doped in iodine atmosphere at room temperature for various lengths of time. The average iodine concentrations of the samples were determined by measuring the weight increase. As grown films have a density of 0.4-0.6 g/cm^3.

Large Scale Iodine Distribution

Energy dispersive X-ray analysis was performed with a JEOL JSM-35 scanning electron microscope and a PGT-1000 analysing system. The freshly cut surfaces of doped samples were scanned to determine the iodine concentration distribution across the sample. The electron beam energy was 10 keV and the L_α, $L_{\beta 1}$ and $L_{\beta 2}$ characteristic iodine X-ray lines were detected. Although the electron beam diameter was only 20 nm the spatial resolution for this low density material is 10 μm [5] as it is determined by the diffusion of injected electrons. This value for the resolution was verified by the profile of doped films placed tightly between undoped films. Scanning was performed with a repetition rate of 1 Hz. A typical measuremetn consisted of 60 scans. The electron beam gave rise to a trace on the surface with a depth less than 1 μm. Corrections other than for background effects were not made thus the profils are not proportional to the true concentration distribution since the variation in density and instrumental resolution distort them somewhat.

Figure 1 displays the iodine profiles across about 150 μm thick samples with average concentrations y = 0.003 and 0.020. Figure 2a gives the distribution for a 680 μm thick sample with an average concentration y = 0.006.

These profiles are similar: the iodine concentration drops significantly within about 50 μm from the surface. Samples kept under vacuum for a week showed the same profiles. At first sight it may be surprising that in a sponge-like material

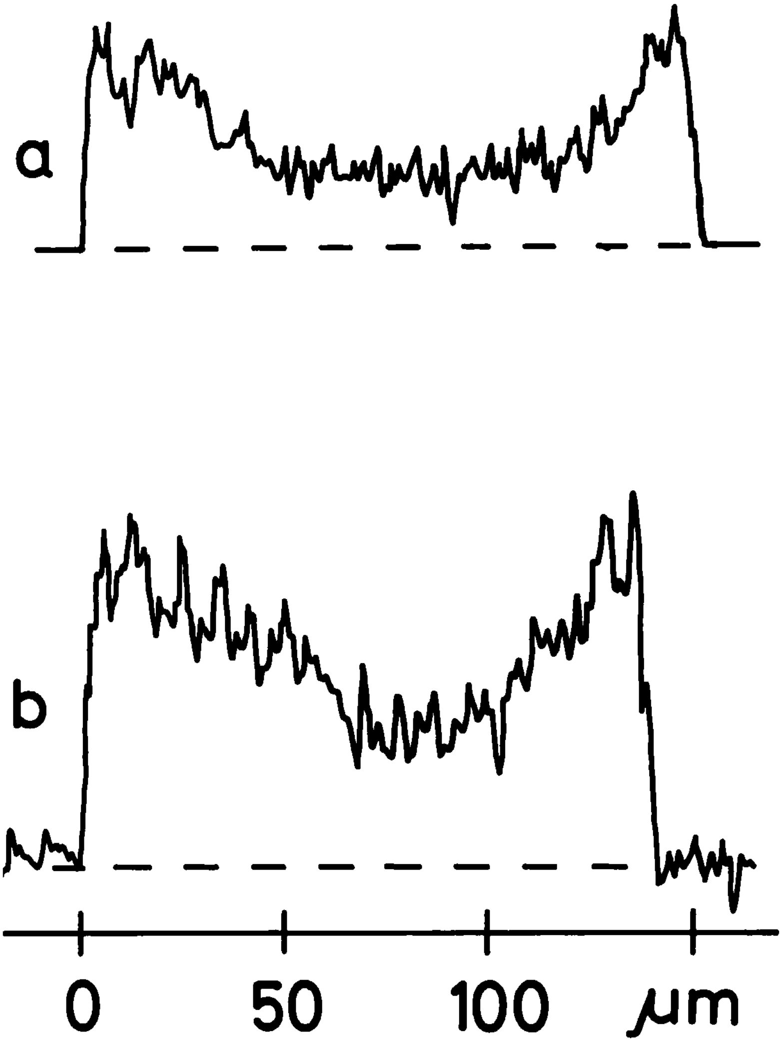

FIGURE 1 Iodine energy dispersive X-ray analysis profiles of doped polyacetylene. The ordinate is the distance from sample surface. The intensities are roughly proportional to iodine concentration across the samples. Average concentrations are a) y = 0.003 (vertical scale amplified by a factor of 2), b) y = 0.020

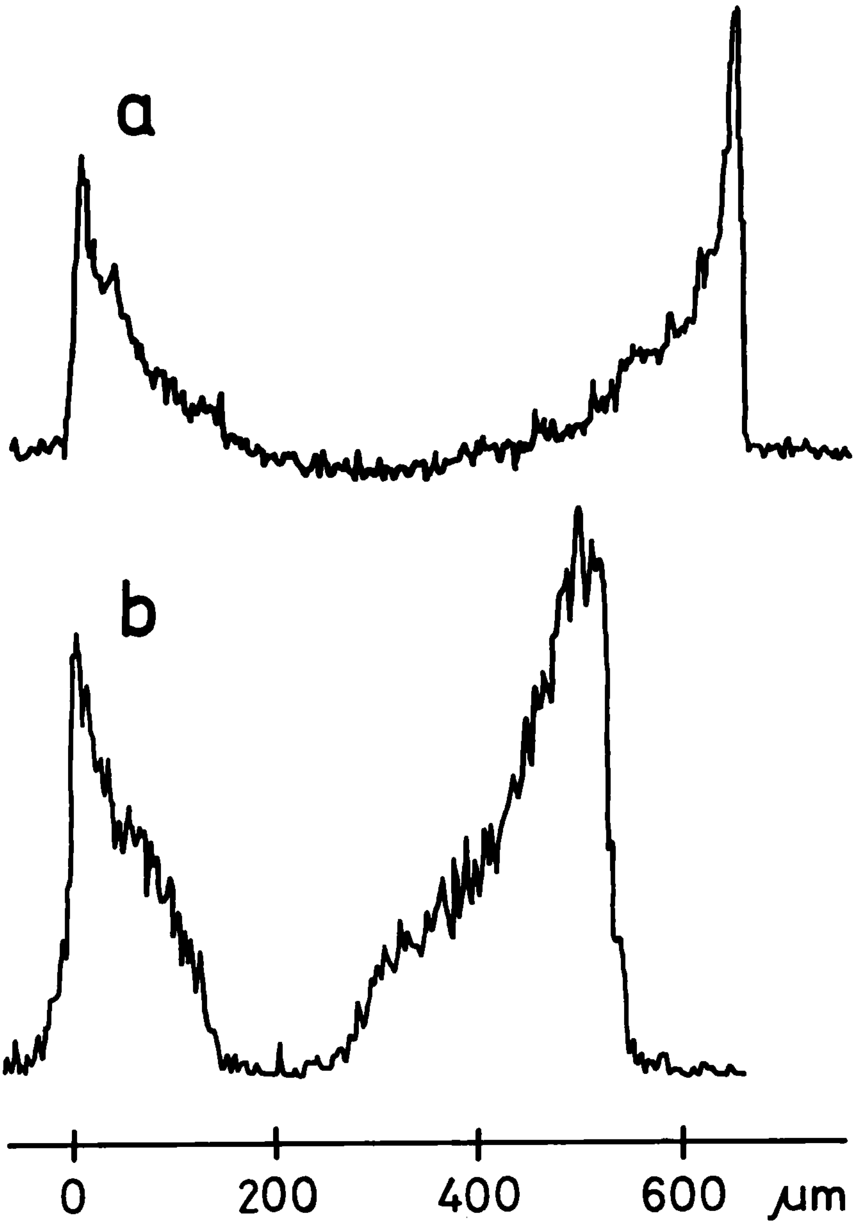

FIGURE 2 Iodine energy dispersive X-ray analysis profile for thick samples a) y = 0.006, b) y = 0.034. Note the steps at 100 and 300 μm.

like $(CH)_x$ such a large concentration gradient can take place. We believe this is due to a decrease of the vapour pressure of iodine from the surface towards the interior of the samples. Since the mean free path in iodine vapor at rooms temperature ($p \sim 0.3$ torr) is about $\lambda = 2.5$ μm in free space, its value within the sample is determined by the dimension of the pores separating the fibers. According to poer size distribution measurements [6] the mean value of these is $\lambda = 400$ Å. For a diffusion through a thickness of $l = 50$ μm of the order of $(l/\lambda)^2 \sim 10^6$ collisions of every iodine molecule with polyacetylene fibers take place. Thus at low doping leves for every collision there is a probability of 10^{-6} that a reaction takes place.

Inhomogeneity Within A Fiber

In thick samples (400-600 μm) even a nominally $y = 0.10$ sample appears to be inhomogeneous, in the middle there is only a negligible amount of iodine. For high nominal concentrations ($y=0.034$, 0.059, 0.109) a "step" was found in the iodine distribution (Fig. 2a). This shows that at low concentrations the reaction is much faster than for concentrations above about a percent.

This may indicate that the reaction is confined at the early stages of doping to the surface of fibers. For 200 Å average fiber diameter $y \sim 0.03$ iodine content can cover the surface of fibers. Thus the reduction of reaction rate may indicate a decrease of iodine free fiber surface. For concentrations above a few percent the reaction slows down since only iodine diffusing across a strongly doped layer may react.

The temperature dependence of the dielectric constant at different dopant concentrations also supports the idea of a strongly inhomogeneous material. The dielectric constant was measured at 9.1 GHz by the resonant cavity method [7]. The raw data for shift and absorption were normalized to the weight of the undoped samples i.e. the dielectric constants given are characteristic to the polarization per CH unit in the effective medium approximation. Pure trans $(CH)_x$ showed a temperature independent dielectric constant of

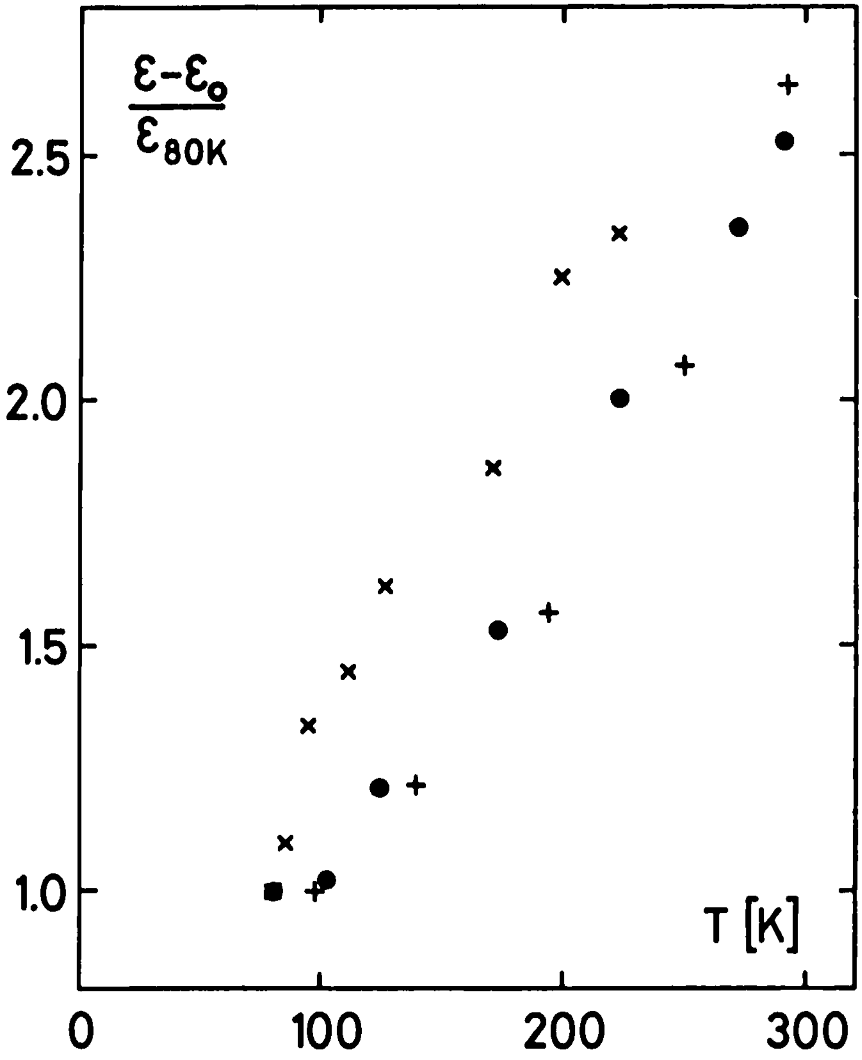

FIGURE 3 Normalized temperature dependence of the 9.1 GHz dielectric constant of iodine doped polyacetylene. Average concentrations and 80 K dielectric constants are ●: $y = 0.002$, $\varepsilon_{80K}=7.95$; x: $y = 0.009$, $\varepsilon_{80K} = 10.6$; +: $y = 0.040$, $\varepsilon_{100K} = 29.0$; $\varepsilon_o \cong 4.7$.

$\varepsilon_o = 4.7$ in agreement with previous measurements [8].

With doping increases and shows a temperature dependence. The absolute values depend somewhat on sample preparation conditions: for equal nominal concentrations thicker samples tend to show smaller dielectric constants. Since typical sample thicknesses were 150 μm this is in agreement with our findings of an inhomogeneity of doping on a 50 μm scale. The most remarkable feature of the data is the similarity of the temperature dependence of $\varepsilon(T)-\varepsilon_o$ for nominal concentrations $0.002 < y < 0.04$ (Fig. 3). The increase with temperature of $\varepsilon(T)-\varepsilon_o$ between 80 and 300 K is about a factor of 2.8 for all samples.

We have previously suggested [9] that the increase of ε by doping is due to highly polarizable bound states fomred on the polyacetylene chains. We have, however remarked that in a system of homogeneous highly polarizable centers a quasi-linear concentration dependence of the increment of ε is not to be expected. Dipole-dipole interactions give rise in a dense system of polarizable centers to a concentration dependence much faster than linear. In fact as we pointed out [9] at fairly low dopant concentrations a polarization catastrophe is expected.

The present data are easier to understand if the system is assumed to be inhomogeneous. The data indicate that a phase separation occurs at all doping levels and that only the volume of the highly doped phase is increased as the doping proceeds. This was suggested to be a possible interpretation of the proton NMR data of iodine doped $(CH)_x$ films [10].

In the light of this assumption the measured dielectric constant ε is not due to highly polarizable individual defects but rather to the capacitance of the metallic surfaces. We should like to point out, however, that isolated "small" metallic particles are not expected to give a significant contribution to ε since this would be (in the limit of very low concentration) proportional to the relative volume occupied by them. We expect in this case

$$\Delta\varepsilon \sim N \frac{\Delta V}{V} \varepsilon_o,$$

where N is an average depolarization factor $\Delta V/V$ the filling factor of isolated metallic particles. Thus we believe that already at low concentrations more or less interconnected metallic surfaces exist. Most likely a phase separation of highly doped and undoped $(CH)_x$ occurs at the surface of fibers. The main effect of doping up to a few percent nominal dose is to increase of ε is intrinsic to the doped part of the fiber surface. These highly doped surfaces, however, have not the conductivity of the fully doped material but exhibit a temperature dependent conductivity. Thus in our model the increase of ε with temperature is due to the exclusion of the electric field from the doped surfaces as the conductivity is increased with temperature.

This model is in agreement with other experimental findings. In our view there is no clear evidence in the literature for dopant concentration homogeneity on the scale of fiber dimensions. Infrared optical data [11] e.g. show the appearance of new absorption peaks in addition to that found in pure $(CH)_x$. These new peaks appear to grow in intensity as the sample becomes more doped but no shift of them is found as expected for phase segregation.

The d.c. conductivity in our view depends at low doses on the quality of interconncetions and on the intrinsic value at higher doses. For samples not much thicker than twice the penetration depth of iodine vapour (100 μm) we distinguish three concentration ranges for which the conductivity is strongly different.

a.) At very low doses a strong dispersion is found between the 9.1 GHz and d.c. conductivities [9], as expected for a conductivity determined by loose interconnections.

b.) At intermediate doses no dispersion is found at high T [9,12] and we suggest that it is no more the interconnection of doped surfaces but the intrinsic properties of very thin doped regions which determines $\sigma(T)$ and $\chi(T)$ [13].

c.) At high doses all surfaces are doped and at a slower rate, the reaction proceeds towards the interior of the fibers and the conductivity becomes truly metallic.

We conclude that polyacetylene doped with a few percent of iodine under conditions typical of most work in the field is inhomogeneous in two scales: a) there is a concentration gradient on the scale of 50 m due to trapping of iodine by the fibers and b) iodine reacts preferentially with the surface of the fibers giving rise to loosely interconnected metallic surfaces.

For higher dopant levels when all the fiber surface has reacted the reaction slows down. In this case the reaction rate is determined by the iodine diffusion through the fully doped layers.

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