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CONDUCTING ISLANDS CONCEPT FOR HIGHLY CONDUCTIVE POLYANI-LINE - RECENT RESULTS OF TEM-. X-RAY-DIFFRACTION-. EPR-. DC. CONDUCTIVITY- AND MAGNETIC SUSCEPTIBILITY-MEASUREMENTS

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ABSTRACT

Polyaniline (PANI) is a prominent intrinsically conductive polymer, because of the unique combination of high conductivities and ease of preparing the polymer itself and technological useable products like films and fibres. Despite the commercial interest in PANI, it has also gained considerable interest by scientists. Central to their work are the charge carriers and the way in which they move in the anisotropic polymer structure. Recently, we succeeded in the preparation of TEM-pictures of highly conducting PANI, which strongly support the conducting island concept for polyaniline, proposed by Epstein et al. The current work presents the results of detailed X-ray-diffraction, EPR-, temperature-dependent d.c. conductivity- and magnetic susceptibility-measurements, performed to obtain a full understanding of the structure of our PANI powder as it results from the TEM investigations.

INTRODUCTION

In addition to the industrial interest in PANI, there is also a large amount of scientific work concerned with it. This work deals mainly with the kind of charge carriers and the way in which they move in the anisotropic polymer structure. As it results from X-ray diffraction experiments, EPR-investigations and related studies, [1 - 5] the micro-level structure of PANI should consist of highly conducting crystalline islands embedded in a non-conductive amour-

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phous sea. The size of the conductive domains seem to depend on the specifics of the synthesis route of the polymer. Epstein and MacDiarmid [1, 2, 4] found the size of the conducting islands in the range of 5 nm^3 whereas Ginder [5] quoted a value of 30 nm for the (one-dimensional) extension of the islands. On the basis of their experimental and theoretical results, Epstein and MacDiarmid [2] claimed that the charge carriers are polarons and move along the individual polymer chains.

Aside from the indirect arguments for conductive islands within doped PANI, Epstein et al. have not published REM and/or TEM pictures of such structures until now.

Recently, we succeeded in the polymerization of highly conductive PANI via a modification of the general oxidation route with $(NH_4)_2S_2O_8$ in 1.0 M hypochloric acid [6]. It will be shown in this paper that the results of TEM-, X-ray diffraction, temperature dependent d.c. conductivity and magnetic susceptibilty measurements give supports for the conductive islands concept. However, the results of the EPR- and magnetic susceptibility studies also suggest that pristine and doped polyaniline contain at least two types of spin (charge) carriers.

RESULTS

Figs. 2a - d are examples of our TEM-investigations. The photographs show that a serious rearrangement of the individual macromolecules takes place during the doping procedure. Whereas the undoped polymer got a foamy structure, the structure of the doped samples becomes more scaly, finally leading to the appearance of small black islands (diameter: 1 -30 nm) in a less dense matrix. The structure of the most conductive samples corresponds very well to the "conductive islands"-structure of Epstein et al. However, at times the distance between the individual islands seems to be too large to allow for the charge carrier motion.

Fig. l gives the results of our wide-angle X-ray-diffraction measurements. They were carried out in order to check the existence of the emeraldine salt (ES-1) structure of the polyaniline powder. It is apparent from Fig.l, that our PANI powder has the ES-1 structure, although the positions and intensities of the individual reflections do not fit exactly the picture, given by Epstein et al. [1].

The results of the temperature-dependent d.c. conductivity measurements are given in Figs. 3 and 4. The purpose of these measurements was to confirm the dependence of the characteristic temperature T_0 on the doping level (pH value of the doping solution), as it was found by Ginder [5]. The data show that the d.c. conductivity varies according to Mott's model of variable range hopping of charge carriers (although the explanation according to the model of Sheng might also be possible) and that T_o varies nearly exponentially with the pH value of the doping solution. These observations are in accordance with the model of Epstein et al. However, the absolute value of T_o for the highest doping level (T_o = 870 K) is about one order of magnitude lower than the value given by Ginder (T_o = 5000 K).

The analysis of our magnetic susceptibility and EPR measurements have not been conclusive until now. On the one hand, the results of the susceptibility measurements can be manipulated to obtain a χ^{Pauli}/Doping level plot, as given by Ginder [5], Fig. 6. Furthermore, the considerable narrowing of the EPR signals (Figs. 5 and 7) and an accompanying increase in the spin concentration suggest an increase in the amount and mobility of the spin (charge) carriers. On the other hand, the nature of the spin carriers is not well understood. Fig. 7 shows that the EPR spectra of undoped PANI at room temperature consist of two lines. Moreover, irregularities appear in the measured magnetic suceptibilities and the linewith of the EPR signals, if the temperature is

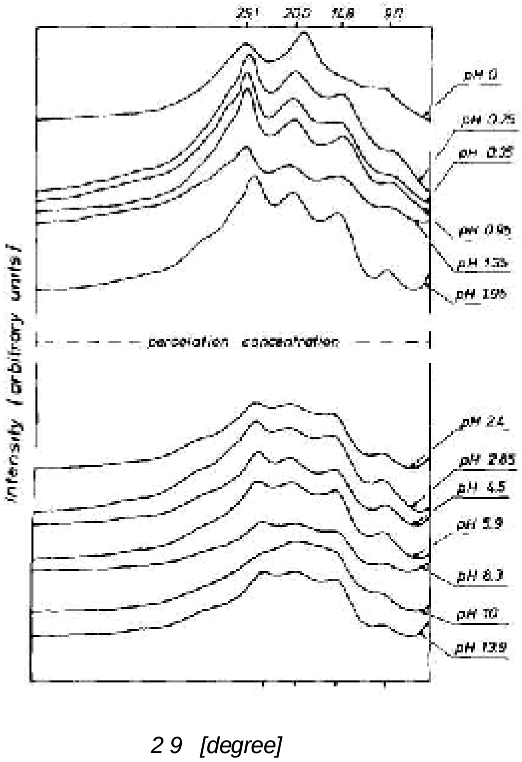
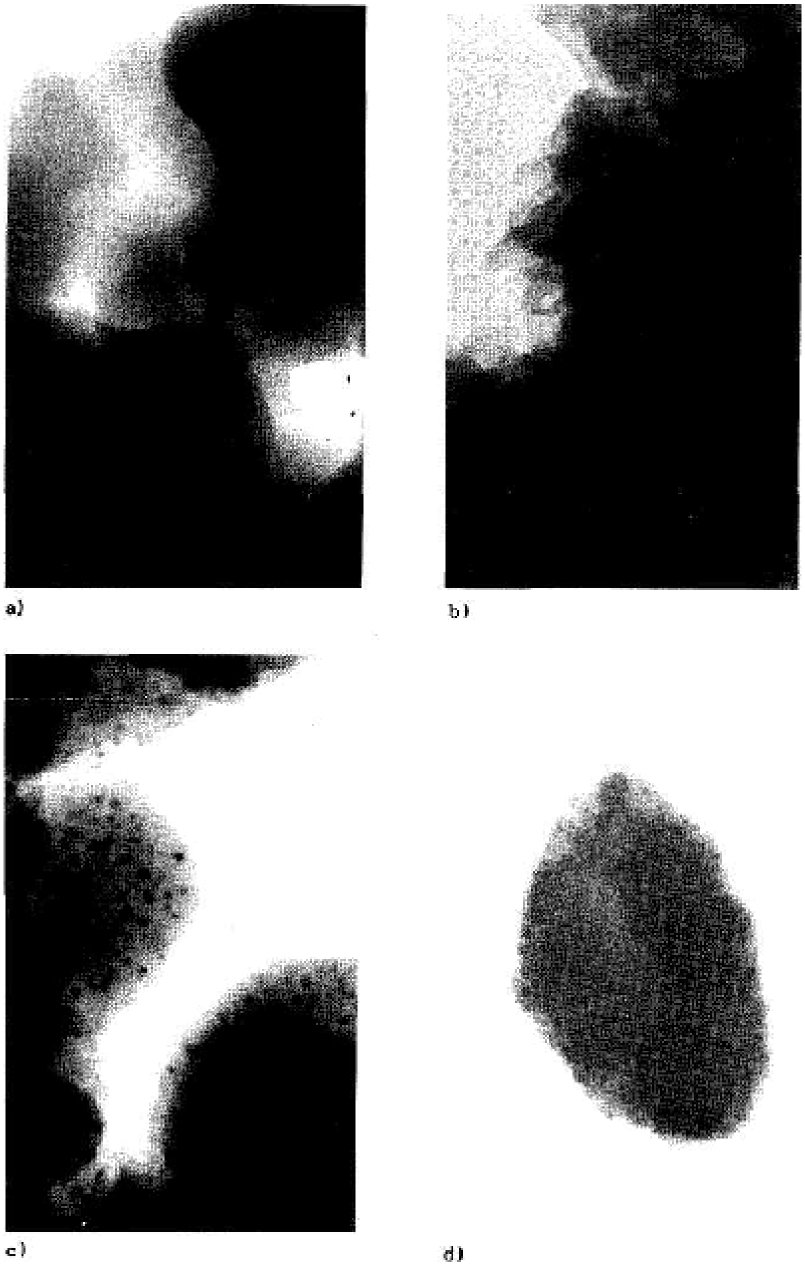


Fig.1. Set of microdensiometer readings of our wide-angle X-ray investigations showing the continuous evolution from the undoped PANI base to the fully doped ES-1 structure as a function of the pH value of the powder; the various tracings are not scaled to each other



a)

b)

c)

d)

Fig.2a-d. TEM pictures of our PANI powder equilibrated with acidic solutions of different pH value; a) pH10, magnification 88.200; b) pH1.35, magn. 98.800; c)pH 0.25, magn. 105.000; d) pH 0, magn. 147.500

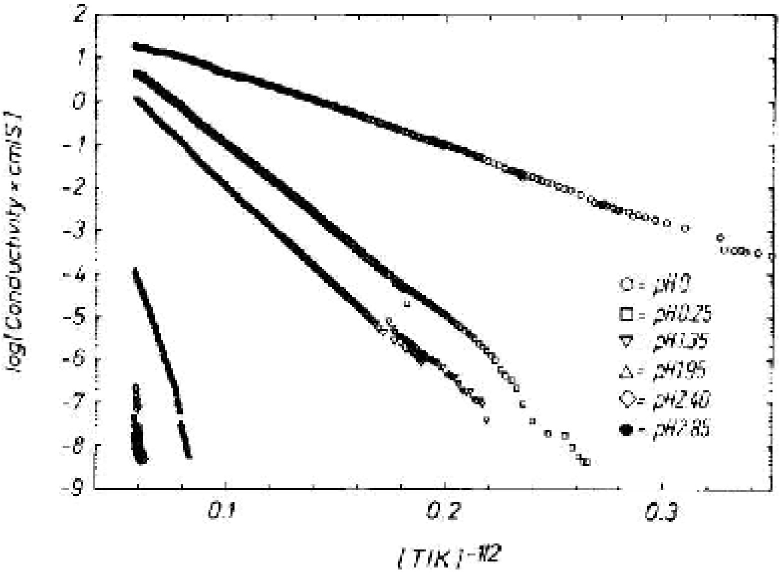
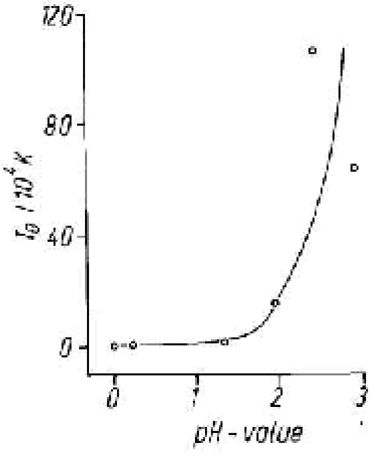


Fig.3. Conductivity of protonated PANI samples as function of $T^{-1/2}$ on a semi-logarithmic scale



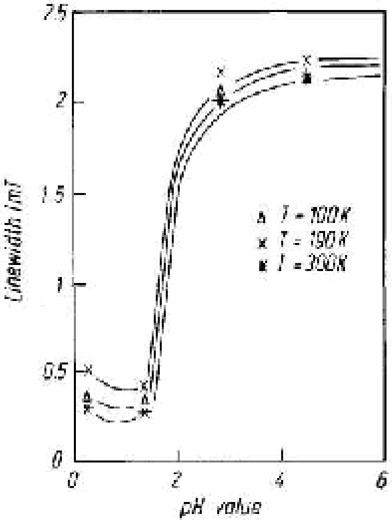


Fig.4. Variation of the characteristic temperature T_0 with the pH value of PANI

Fig.5. Variationof the EPR linewidth with the pH value of PANI at different temperatures

lowered to 4 K. These findings might be indicative of some sort of equilibrium between different spin (charge) carriers, i.e. different kinds of polarons and bipolarons.

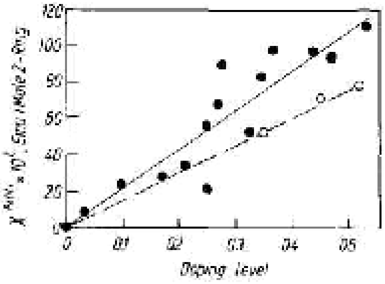


Fig.6. Increase in the Pauli paramagnetic susceptibility with protonation; (■) results of Ginder [5]. $T \to \infty$ (O) our results, T = 300 K

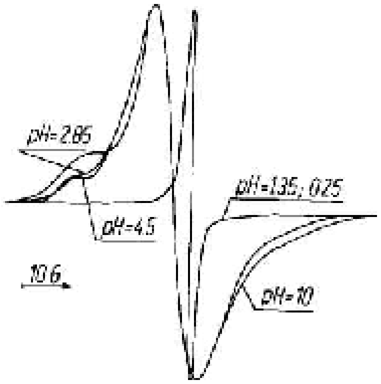


Fig.7 Variation of the EPR signals with the pH value of PANI at room temperature

CONCLUSIONS

Concluding, we have prepared for the first time TEM pictures of the conducting islands within PANI. Nevertheless, the nature of the spin (charge) carriers is not clear until now and needs further investigations.

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