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STRUCTURE OF SAMPLES OF CONTROLLABLY DOPED POLYANILINE, AND ITS INFLUENCE ON ELECTRICAL CONDUCTIVITY AT LOW TEMPERATURES

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ABSTRACT

We used x-ray diffraction to investigate the structure of controllably doped samples of polyaniline. The diffraction was performed with x-ray diffractometer for powder samples of the type "Philips PW 1820". This diffractometer has no film, but it uses radiation detectors and automatically stores data in a digital format. The used wave length of the x-ray radiation was 0,1542 nm, which corresponds to the characteristic radiation line of Copper K_α. *On the basis of the dependence of the x-ray diffraction intensity from the scattering angle, it can be clearly observed how the doping and the structure of samples influence the electrical conductivity of polyaniline.*

Keywords: polymers, polyaniline, doping, structure, x-ray diffraction, conductivity, crystal areas.

1. INTRODUCTION

Concerning the physical states of matter, polymers can have two states: liquid and solid. They can not have gaseous state of the matter, because the vapour pressure is insignificant and vapour is dispersed. Amorphous solid polymers change into solid state through an inter-phase which is called highly-elastic state. An increase in temperature causes an increase in internal energy which causes certain heat movements, causing weakening of attractive intermolecular forces, and resulting in changing of substance from solid into liquid state. An increase in the degree of polymerization also change the physical properties of polymers (viscosity, solidity, meltability etc.). Each molecule is represented by the length of chain, which consists of particular members which can have the same or different type of chemical composition. Depending on the degree of order and the density of mutual chain positions a polymer can be: partially crystal and completely amorphous.

2. EXPERIMENTAL RESULTS

Polyaniline samples used for experimental researches in this paper were obtained with direct oxidization of aniline [1]. Then was performed doping of samples with Hydrochloric acid (HCl) solution in various concentrations [2]. Thereafter, the structure of polyaniline samples (PANI) was investigated with x-ray diffraction. Diffraction was made with a commercial x-ray defractometer for powder samples. The given characteristic line occurs after ”bombarding” of Copper with high-energy electrons (higher than 20 keV) in the x-ray tube.

Figures 1 and 2 show the dependency of x-ray diffraction intensity from the 2Θ angle, for a non-doped Sample 1, and for poorly doped polyaniline sample (Sample 2., pH=3,04) :

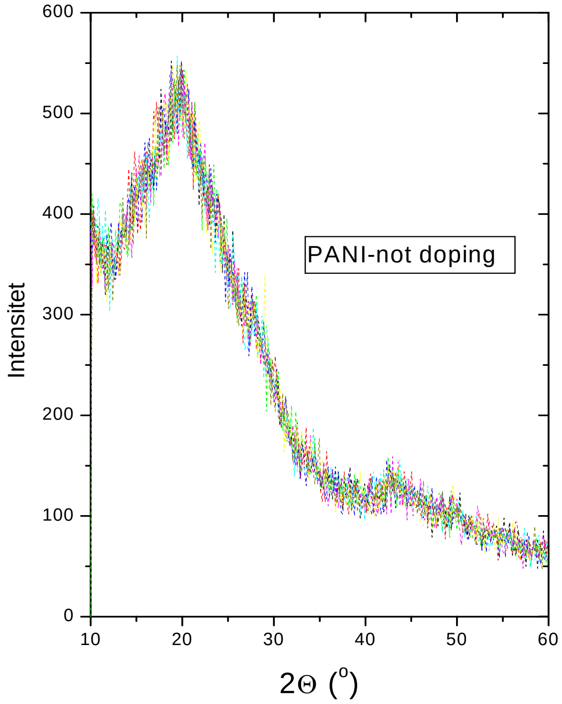

Figure 1. X-ray diffraction intensity as a function of the scattering angle 2Θ, for a non-doped sample

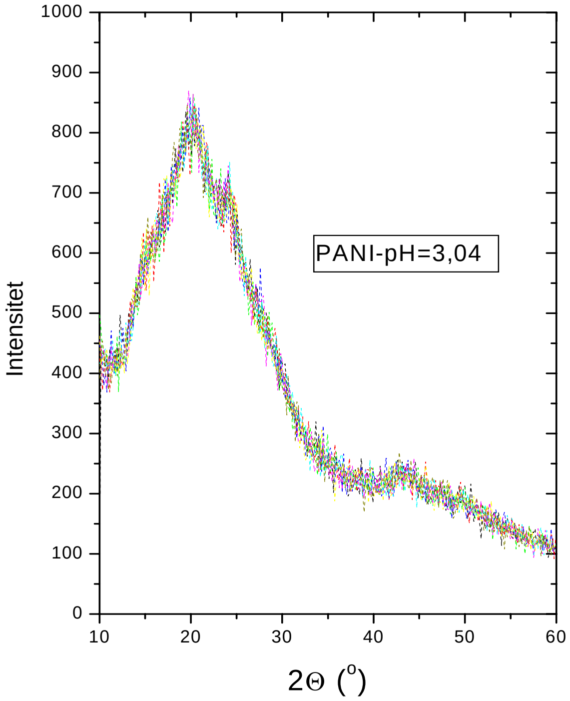

Figure 2. X-ray diffraction intensity as a function of the scattering angle 2Θ, for the Sample 2.

On the Figure 1, for the angle 2Θ= 20° there can be seen a wide maximum as a result of the amorphous structure of the sample. From the position of the maximum center, using the Bragg's Law:

$$2d\sin\Theta = n\lambda \qquad (1)$$

can be determined the mean distance between first neighbours. Whereas from the maximum width at the half-height ($\Delta\omega$), with the Scherrer's formula:

$$D = 0{,}9\ \lambda / \Delta\omega(\cos\Theta) \qquad (2)$$

can be determined the size of the crystal area.

For the Sample 1, the maximum center lies at $2\Theta= 20^o$, hence the mean distance between first neighbours is d=0,45 nm. Maximum width is $\Delta\omega$=12,6º, hence the size of the effective crystal area is D= 0,65 nm.

From the Figure 2, it is seen that for the angle value $2\Theta=25^o$ there occurs a new maximum superponed on the maximum of the amorphous matrix, which indicates that by doping a system becomes more ordered, i.e. ”crystal” areas are being created.

Figure 3 shows a difractogram of the more doped sample (Sample 3, pH=0,03).

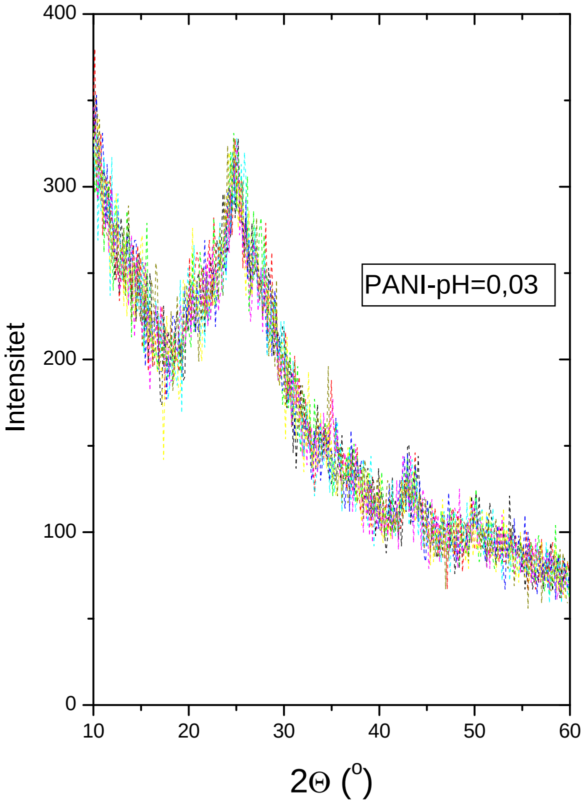

Figure 3. Intensity of X-ray difraction as a function of the scattering angle 2Θ, for the Sample 3.

From the Figure 3, it is seen that the superponed maximum at $2\Theta=25^o$, which occured as a result of doping, has exceeded the maximum of the amorphous matrix.

From the expressions (1) and (2), it is obtained that the mean distance between first neighbours within the ”crystal” area for this sample is d=0,35 nm. The mean size of the ”crystal ” area is D=3,0 nm, so that the ”crystal” area extends up to the first ten neighbours.

As a result of X-ray difraction, the doped samples consist of amorphous matrix in which are found areas with higher order, so called ”crystal” areas.

From these results it is seen that ions of Chlorine (Cl^-), in addition to their influence on the electron structure of the molecule (because they conduct current), also influence the morphologic structure of the sample because they enable partial ordering of molecule chains.

3. CONCLUSION

Diffraction of x-rays affirms the theory of conductivity in polyaniline. Namely, a common characteristic of all doped conductive polymers is having a large degree of structural disorder and complex morphology which depends on the synthesis method and postprocessing of the sample. A result of such structure is localization of wave functions of charge carriers. Charge carriers can no longer move freely but only by ”hopping” between localized states.

A doped sample of polyaniline consists of ”crystal” areas where chains are well arranged, and a surrounding amorphous area.

Wave functions of charge carriers in the arranged area are 3d delocalized (average size from 3 nm to 10 nm).

Amorphous area consists of poorly arranged and disordered chains, which causes localization of charge carriers. Since ”crystal” areas are mutually far from each other, direct tunneling between them is not possible.

A charge can move between ”crystal” areas (through amorphous area) only by hopping over localized states in a chain and between chains, hence the conductivity is described with the variable range hopping model [3]. By higher doping (smaller pH value) obtained are samples with larger dimensions of their "crystal" areas, and hence a better electrical conductivity.

4. REFERENCES

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