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The structural properties of the PANI/CSA conducting polymer system studied by synchrotron radiation surface diffraction

1. Introduction

Polyaniline (PANI) protonated with organic acids like camphorsulphonic acid (CSA) is a particularly interesting conducting polymer because of its solubility in the conducting state (a metallic-like type of conductivity within a certain temperature range), and its high degree of crystallinity. Only a few more detailed studies of the structure of the films cast from *m*-cresol have been published so far (see [1] for a recent review), but the crystalline structure of this polymer system is still somewhat unclear. Some new speculations were published very recently by M. J. Winokur *et al.* [2]. Moreover, some unexpected anisotropy effects have been reported [3]. The main result of these studies is the conclusion that there are significant differences between the diffraction patterns of the PANI/CSA films recorded in reflection and transmission geometry. Strictly speaking, the second crystalline reflection (related to the interplanar distance of 0.94 nm) is visible only for transmission geometry, and never occurs for common Bragg-Brentano reflection geometry, even for thicker samples. Such behaviour suggests that the polymer systems investigated exhibit significant structural anisotropy. Therefore we have undertaken a more careful study of both the orientation of the crystalline reflections, as well as the influence of the choice of solvent used in film preparation for its structural properties. Because for the measurements in the two geometries discussed above, there are only two possible orientations of the scattering wave vector (where it is perpendicular or parallel to the sample surface) it is necessary to have a more powerful experimental method. We decided to make use of the grazing incident beam technique. In this case, it is possible to measure the scattered intensity for any orientation of the scattering wave vector in respect to a sample plane, and moreover, it is possible to investigate the structure of a genuinely thin film, due to the total reflection from the substrate.

Abstract

Polyaniline (PANI) protonated with camphorsulphonic acid (CSA) has received much interest, but its molecular and crystalline structure is still unclear. We undertook detailed studies of thin films cast from m-cresol and trifluoroacetic acid (TFAA) solutions. Such samples were subjected to diffraction measurements by use of the grazing incident beam technique, applying the z-axis diffractometer installed at the BW2 beamline at HASYLAB. We obtained very important information concerning the anisotropy of the crystalline reflections for all the samples investigated. These results demonstrate the significance of the solvents on the structural ordering, and the anisotropy we observed plays an important role in new attempts at modelling the crystalline structure.

Keywords: X-ray diffraction; polyaniline and derivatives; polycrystalline thin films.

The geometry of such measurement is schematically sketched in Figure 1.

2. Experimental

The samples cast from *m*-cresol and trifluoroacetic acid (TFAA) were subjected to diffraction measurements by use of the grazing incident beam technique, applying the *z*-axis diffractometer installed at the BW2 beamline of HASYLAB.

The wavelength of the synchrotron radiation was 0.137 nm, and the incident angle α was selected for each sample in the range 2 to 8 mrad. We recorded the intensity of the diffracted beam for the outgoing angles γ and δ varying in the range 0.02 to 0.45 rad, obtaining up to nine radial scans (shown in Figure 2) of a two dimensional (γ , δ) diffracted intensity map. If a sample is isotropic, the intensity along each ring (equivalent to the so-called Debye ring for powder diffraction) with its radius determined by Bragg's law should be constant. The scattering angle has to be calculated using the formula:

$$2\Theta = \arccos [\cos (\delta+\alpha) A \cos (\gamma)]. \quad (1)$$

It should be mentioned that the scan obtained for δ close to zero is equivalent to the diffraction in reflection geometry, and the scan obtained for γ close to zero is equivalent to the diffraction in transmission geometry (both for free-standing film samples). These two scans are sometimes called the 'equato-

rial scan' and 'meridional scan' respectively. The experimental intensity has been corrected by the factor $\sin \gamma$ due to the so-called 'area correction' [4].

The first example of the results obtained in this way is presented in Figure 3. These three main scans were recorded

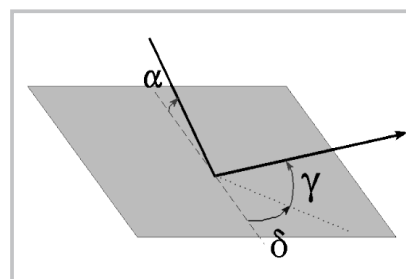


Figure 1. The geometry of the surface diffraction measurement: α - incoming angle, γ and δ - outgoing angles.

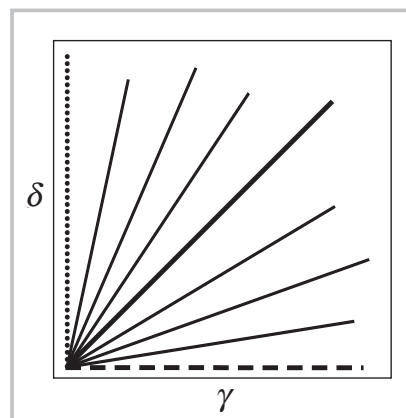


Figure 2. Radial scans, along which the scattered intensity was measured. Dashed line: transmission, dotted line: reflection.

for the PANI/CSA film cast from *m*-cresol (provided by J. Laska) with the thickness of ca. 50 μm . One can see that the anisotropy of this sample is not particularly high. Apart from the last crystalline reflection, the intensity is more or less identical for all scans. The second peak is visible only for the equatorial scan, which is in good agreement with the results discussed previously. The fifth diffraction reflection (related to the interplanar distance of 0.35 nm) exhibits stronger anisotropy: it has maximum intensity for the meridional scan and almost vanishes for the equatorial scan. Such behaviour serves as evidence that the crystal planes related to this reflection are mainly oriented in parallel to the sample plane.

The second experimental result is shown in Figure 4. These scans were

recorded for the PANI/CSA thin film cast from *m*-cresol (provided by E. Bařka) with the thickness of ca. 10 μm . One may observe the very distinct anisotropy of all the crystalline reflections. The first peak (related to the interplanar distance of 1.93 nm) is visible for all scans, but its intensity decreases along the ring as one proceeds from the equatorial scan to the meridional one. The second peak exhibits extremely high anisotropy; it is visible only for the equatorial scan. Such behaviour suggests that the crystal planes separated by the distance of - 0.94 nm are highly oriented: they can only be perpendicular to the sample plane. The third maximum shows intermediate orientation: its intensity has the maximum for the scan obtained for $\delta = \gamma$ which proves that the crystal planes separated by the distance of -

0.60 nm are mainly acute in respect to the sample plane. Finally, the fifth maximum is again very anisotropic, which proves that almost all the crystal planes related to this reflection are parallel to the sample plane.

Because this sample exhibits such strong anisotropy, we decided to calculate the full two-dimensional intensity distribution map. Such 2-D maps come from the interpolation process, and they give the intensity distribution only approximately, particularly for greater values of the scattering angles, where the density of the points for which we measured values of the intensity is low. The map obtained for the results as discussed in Figure 4 is presented in Figure 5.

One can observe that these results are to some extent in qualitative agreement

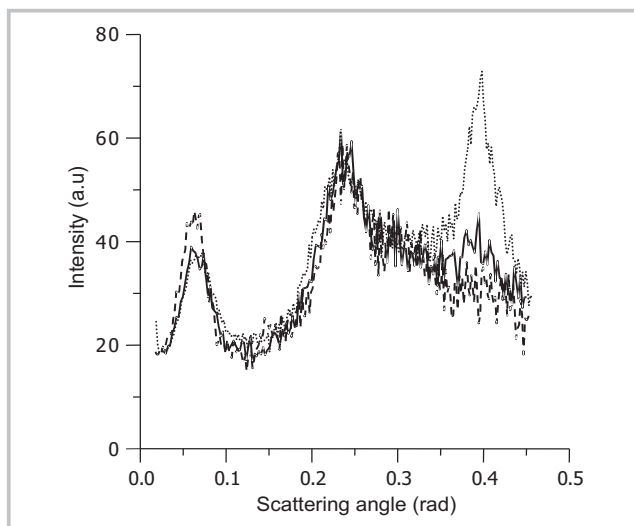


Figure 3. The surface diffraction patterns of PANI/CSA/*m*-cresol thin film (sample no.1) obtained for: $\gamma = 0.02$ rad (dotted line); $\delta = 0.02$ rad (dashed line); $\delta = \gamma$ (solid line).

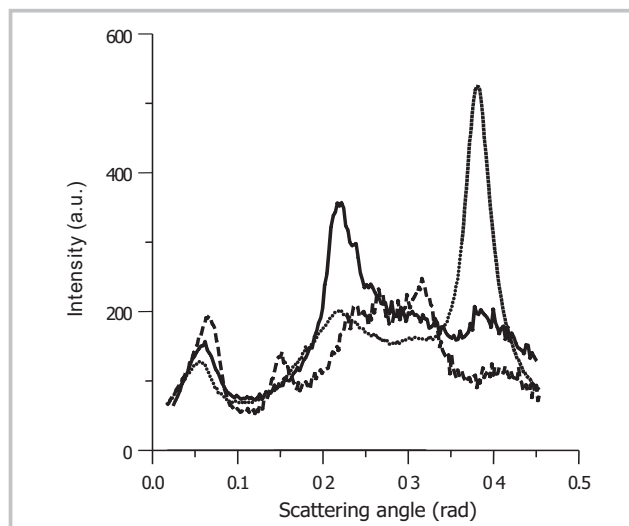


Figure 4. The surface diffraction patterns of PANI/CSA/*m*-cresol thin film (sample no.2) obtained for: $\gamma = 0.02$ rad (dotted line); $\delta = 0.02$ rad (dashed line); $\delta = \gamma$ (solid line).

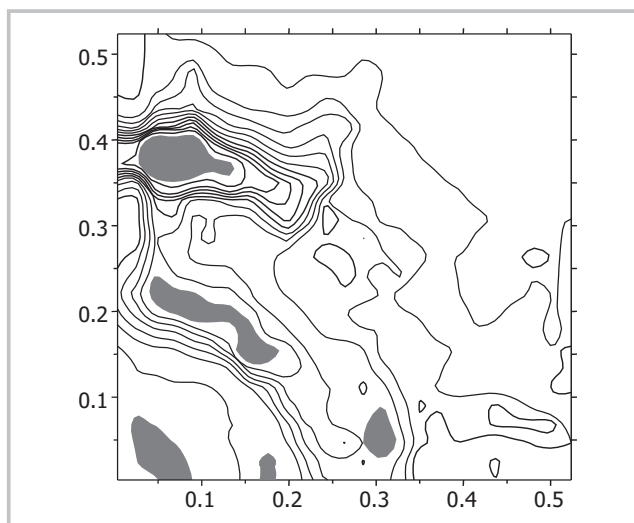


Figure 5. Two-dimensional intensity distribution map for the PANI/CSA/*m*-cresol sample no.2. The maximum of each crystalline reflection is shadowed for better clarity of the picture.

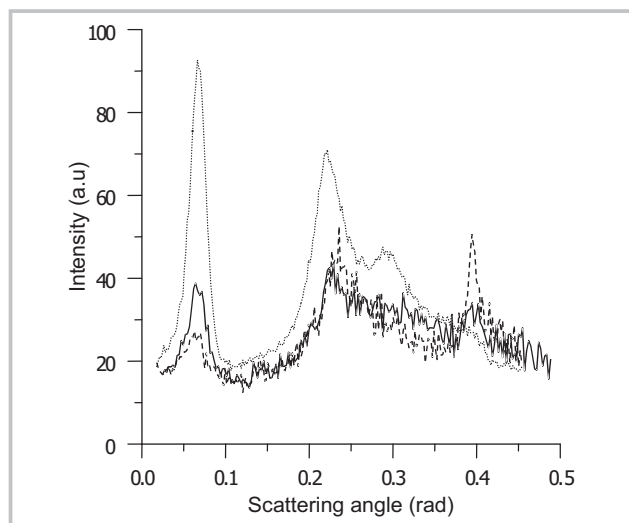


Figure 6. The surface diffraction patterns of PANI/CSA/TEAA thin film (sample no.3) obtained for: $\gamma = 0.02$ rad (dotted line); $\delta = 0.02$ rad (dashed line); $\delta = \gamma$ (solid line).

with the conclusions of the paper by Minto *et al.* [5]. However, some important differences should be underlined; for example, the anisotropy of the first diffraction maximum (related to the interplanar distance of close to 1.93 nm) is different. The second maximum shows extremely high anisotropy for all samples where it exists, and the poor correlation of its characteristics with the anisotropy of the first peak shows that they cannot be indexed as the reflections (0 0 1) and (0 0 2) respectively, as was proposed in [6]. On the other hand, these results well confirm the fact that the second peak is not observed in reflection geometry [3].

Finally, we present the third experimental result obtained for the PANI/CSA thin film cast from TFAA (provided by J. Nizioł). The three main scans recorded for this sample are shown in Figure 6, whereas the related full 2-D intensity contour map is presented in Figure 7. The striking differences between these results and those discussed above are visible. Apart from the second peak, which is very low in this case, the remaining four diffraction reflections show opposite anisotropy than for the *m*-cresol type samples. The first peak is dominant for the meridional scan, the third maximum shows the lowest intensity

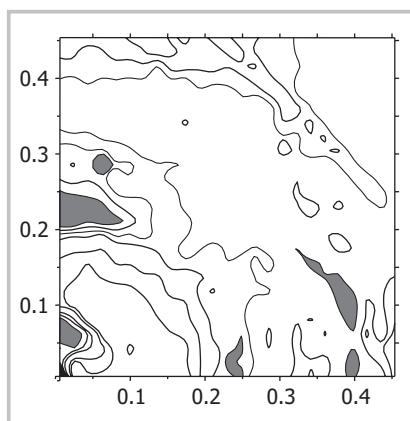


Figure 7. Two-dimensional intensity distribution map for the PANI/CSA/TFAA sample no.3. The maximum of each crystalline reflection is shadowed for better clarity of the picture.

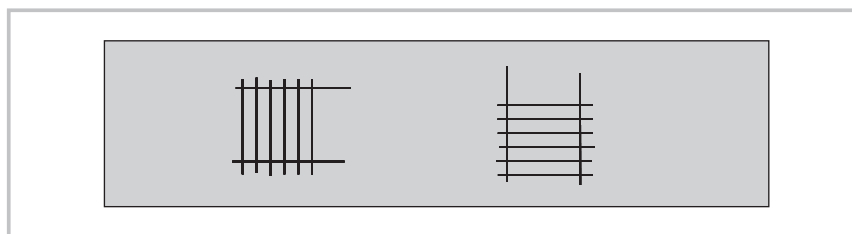


Figure 8. Schematic diagram of the possible orientations of the two series of crystalline planes separated by the distance 1.93 and 0.35 nm, in respect to the sample plane. Left: sample no.2, right: sample no.3. The polymer chains (*z*-axis) are almost perpendicular to the plane of the picture.

for the intermediate scan obtained for $\delta = \gamma$, and the fifth peak exhibits its maximum for the equatorial scan. In other words, the intensity distribution map obtained for the PANI/CSA/TFAA sample is very similar to the mirror image of the intensity distribution map obtained for the PANI/CSA/*m*-cresol sample by interchanging both axes. This suggests that the structure of both polymer systems may be described in frames of one model, but the orientations of the crystalline phase may be completely different for samples cast from various solvents.

3. Discussion and conclusions

The main conclusion that may be drawn from the experimental results discussed above is obvious: the structural anisotropy of PANI/CSA thin films is very important, and strongly depends both on the film thickness as well as on the solvent used for the film preparation. These results give strong support for an elucidation of a new model of the PANI/CSA system crystalline structure.

Concerning the orientation of the crystal planes related to the main diffraction reflections, first of all it is reasonable to notice that because the planes separated by the distance of 0.94 nm are always perpendicular to the sample plane, they should be also perpendicular to the polymer chains. This is implied from the fact that in thin films macromolecules must be oriented parallel to the film surface. The next conclusion is that the planes separated by the distance of 0.35 nm are always practically perpendicular to the planes separated by the distance of 1.93 nm; moreover, there are two possible orientations of these planes in respect to the sample plane (see Figure 8). Working with these assumptions, we obtained the well justified starting point for creating of the new model:

- The first reflection (with $d = 1.93$ nm) comes from ordering chains in a direction almost perpendicular to them (*x*-axis; the crystalline indices (1 0 0) or equivalent);

- The second reflection ($d = 0.94$ nm) comes from ordering along chains (*z*-axis; the crystalline indices (0 0 1) or equivalent);
- The fifth reflection is related to the distance $d = 0.35$ nm typical of the chain stacking. Therefore it is reasonable to state that it comes from ordering chains in the direction almost perpendicular to them and the *x*-axis (*y*-axis; the crystalline indices (0 1 0) or equivalent).

Because the period along the chains, as determined by the configuration of atoms in an aniline unit, is $c = 1.01$ nm, it is necessary to assume that the angle between the *z*-axis and chains is not a right angle, and its value may be calculated from the equation:

$$\sin \phi = d_{(001)} / c \quad (2)$$

in the case of a monoclinic unit cell. This leads to the angle $\phi = 110^\circ$, which is a value sufficiently close to the right angle, considering the experimental results discussed above. Moreover, this assumption is in good agreement with the fact that the position of the maximum of reflection (0 1 0) shown in the 2-D diffraction pattern (see Figure 5) recorded for all *m*-cresol cast samples is located not precisely on the meridional scan, but is slightly shifted along its ring. Strictly speaking, this maximum shows the highest intensity for the scan inclined by the angle of 70° to the direction of the equatorial scan.

The next important conclusion from our attempts at structure modelling (applying the assumptions discussed above) shows that the calculated intensity of the first (1 0 0) reflection is high enough only in one case. Namely, if the arrangement of two species forming the structure chains ("C") and dopant molecules ("D") along the *x*-axis is not simply alternating -C-D-C-D-C-D-C- as is usually assumed, but is 'doubled': -C-C-D-D-C-C-D-D-C-C-. This statement has been recently confirmed by the comparison of two diffraction patterns. Use of the neutron diffraction for the powder sample with fully deuterated PANI chains (and no deuterated CSA molecules) obtained the first one, by David Djurado *et al.* [7]. The main feature of this data is an enlargement of the relative intensity of the first peak by a factor of close to ten. The second diffraction curve was calculated for our tentative model constructed in accordance with the assumptions proposed above, but substituting two times greater scattering

power of all atoms within the polymer chains. As a result, we have obtained the calculated relative intensity of the first peak at least ten times higher, which gives strong support for 'doubling' the structure along the x -axis.

Unfortunately, we are not yet able to present the final version of the structure model of PANI/CSA system. The crucial problem that we encountered is related to the apparent disagreement between two important statements. The first one is the requirement that the unit cell angles should not be significantly acute, which is implied from our surface diffraction data. The second is the value of the unit cell volume as calculated for assumed lattice constants determined from the interplanar distances observed. Strictly speaking, the calculated unit cell volume is too small, which leads to the overestimation of the density of the system. It is possible that one of the main diffraction reflections discussed above is not related to the main axis of the crystal lattice, but this should be described by mixed crystal-line indices, (1 1 0) for example. This means that the interplanar distance related to this reflection should not be considered as the lattice constant. Intensive studies into these problems are being continued.

□

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References

1. D. Djurado, Y.F. Nicolau, P. Rannou, W. Luźny, E.J. Samuelsen, P. Terech, M. Bee, J.L. Sauvajol, *Synth. Met.*, 101, 764, (1999)
2. M.J. Winokur, H. Guo, R.B. Kaner, *Synth. Met.*, 119, 403, (2001)
2. E. Bańka, W. Luźny, *Synth. Met.*, 101, 715, (1999)
3. E. Vlieg, *J. Appl. Cryst.*, 30, 532, (1997)
4. C.D.G. Minto, A.S. Vaughan, *Polymer*, 38, 2683, 1997)
5. W. Luźny, E.J. Samuelsen, D. Djurado, Y.F. Nicolau, *Synth. Met.*, 90, 19, (1997)
6. D. Djurado, private communication (2001)

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The University of Bielsko-Biała the Youngest Polish University with a Textile Faculty

Rector: Professor Marek Trombski, Ph.D., D.S.C..

Dean of the Faculty of Textile Engineering and Environment Protection and Director of the Institute of Textiles and Polymer Materials: Professor Stefan Boryniec, Ph.D., D.Sc.

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