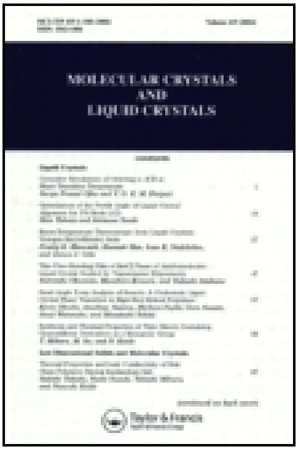

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X-Ray Studies of Doped Polyaniline Films

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X-RAY STUDIES OF DOPED POLYANILINE FILMS

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Abstract Doping and complexation of polyaniline (PANI) and dodecyl benzenesulfonic acid (DBSA) in xylene was conducted at various temperatures. As cast and isothermally treated films were examined by the wide angle X-ray scattering. Results of transmission and reflection techniques revealed that the complexation led to form a layered structure. The layered structure was also found oriented that the PANI and DBSA are stacked one another across the film thickness. The anisotropic feature of the layered structure was independent of the mixing temperatures but changed by the successive isothermal treatments. A model structure similar to smectic A was proposed to account for the very large layer spacing of 3.3 nm and the close packing of 0.35 nm between the PANI units within the layer.

INTRODUCTION

Among electrically conductive polymers, polyaniline (PANI) has drawn much attention in recent years because chemically doped PANI-ES (emeraldine salt) shows high conductivity and good environmental stability, which offers a strong potential for the technical device applications. The conductive PANI-ES can be prepared in organic solvents with functionalized acid[1,2] such as camphorsulfonic acid (CSA) or dodecyl benzenesulfonic acid (DBSA). These acids function as dopants and plasticizers enhancing processibility, solubility and mechanical strength of the film. The functionalized acids form a complex with the PANI, resulting in conductive PANI-ES. Complexation between the PANI with the functionalized acid is very similar to the hairy-rod system of stiff polymer with flexible side chains, leading to the layered structure formation[3] often observed in the hairy-rod systems. The structural order in the PANI/DBSA complex is undoubtedly a key factor to control the conductivity.

In our study, doping and complexation of PANI and DBSA was conducted in xylene. The PANI-ES films cast from the solution were then examined by the wide angle X-ray scattering. Our main research goal was to elucidate the packing geometry of the complexation between PANI and DBSA and the variations associated with the preparation conditions of the solution and the film. The variation of preparation conditions include doping temperatures and amount of dopants. The films were also annealed at the several elevated temperatures.

EXPERIMENTAL

PANI in base form was prepared by the method described in the literature but with some modification.[4] Solutions of PANI and DBSA (1: 1.3) in xylene were prepared at the several different mixing temperatures of 50, 90, 105, 120, 140 °C and the PANI-ES films were then cast on a glass slide from each solution. Some of the films were treated isothermally at 80, 120, 180 °C for 1 hour. X-ray scattered intensities from the films were collected by a conventional powder diffractometer coupled to a sealed tube Rigaku X-ray generator (Cu Kα). The generator was operated at 40 kV and 30 mA and the X-ray was monochromated by a Nickel filter.

RESULTS AND DISCUSSION

Both symmetrical transmission and reflection techniques were used to collect the scattered intensities. Combination of the two methods have proven to be very effective to study not only the structures but also their orientation relative to the film surface.[5] The scattered intensities collected from the transmission geometry reveal structures ordered in the film plane while the reflection provides the out-of-plane structural order across the film thickness. Intensity curves of transmission and reflection from the films of the PANI/DBSA are plotted in Figure1-A. The transmission pattern (Figure 1-A) shows very intense peak at the low angle corresponding to the d-spacing of 3.30 nm and a broad peak at 0.48 nm. Other weak peaks are also discernible at 0.95 nm and 0.6 nm with an amorphous halo at 0.48 nm. The pattern of high intensity peak at the low angle, often observed in the stiff polymers with flexible side chains, confirms that the polymer forms a typical layered structure. The acid apparently attached to the PANI backbone to form complexes and functioned as a spacer between the PANI backbone, resulting in a layered structure. The very broad peak at 0.48 nm can be attributed to the amorphous DBSA units within the layers. Another peak at 0.95 nm corresponds to the periodicity of the zigzag PANI backbone[6] with the zigzag angle of 120°.

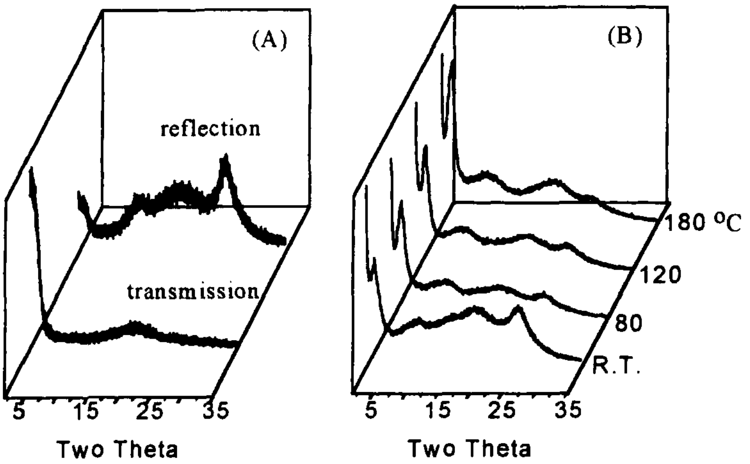

FIGURE 1 (A) transmission and reflection X-ray patterns of PANI/DBSA film; (B) reflection patterns of isothermally treated films.

The X-ray scattered intensities of the reflection method differ substantially from those of transmission. We note that much of the low angle peak intensity has been reduced in the reflection pattern but new peaks appear at 0.35 nm and near 0.9 nm. We also note that the peak at 0.35 nm is more intense as the low angle peak diminishes (Figure 1-B). The peak at 0.35 nm can be assigned to the packing order between the neighboring PANI chains in the direction normal to the benzene planes. Comparison of the reflection results with those of transmission suggests that the layered structure is anisotropically organized such that the PANI backbone and the DBSA are lying on the film surface and the complexes are stacked one another across the film thickness. The layered structure and the orientation feature appear to be common to all the films prepared from solutions of various mixing temperatures. The degree of orientation, however, changes by the isothermal treatment, as can be noted from the Figure 1-B.

The d-spacing 0.35 nm is, however, rather small considering that the amine has to be accommodated within the distance. On the other hand, the layer spacing 3.3 nm is too large, knowing that the extended length of spacer BDSA is 2.1 nm. A tilted stacking can be suggested to avoid the close packing between the PANI units. We also propose that the tilting is allowed in either direction as the model is depicted in Figure 2. The model structure resembling the smectic A type mesophase could explain the very large layer spacing (3.3 nm) with the spacer length (DBSA) of only 2.1nm.

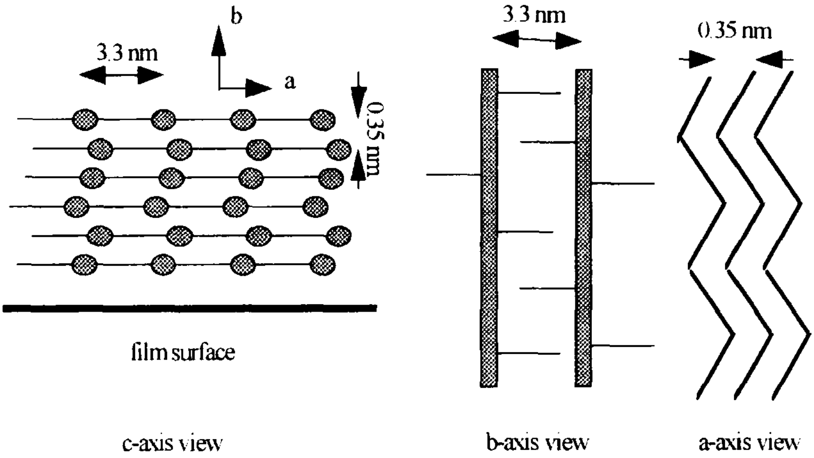

FIGURE 2 Layered structure of PANI/DBSA complex and the orientation relative to the film axes.

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