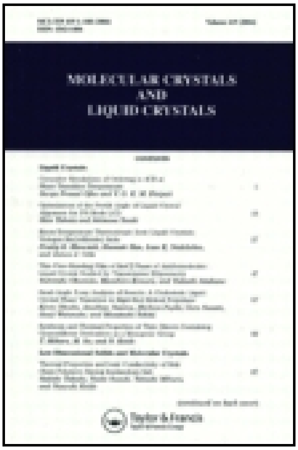

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Crystal Structure of Drawn Polythiophene Film

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Crystal Structure of Drawn Polythiophene Film

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The crystallographic structure of the drawn polythiophene film prepared electrochemically was investigated by a wide angle x-ray diffraction. The film showed the distinguishable pattern. The results obtained indicated the crystal structure of an orthorhombic unit cell with lattice constants a = 10.8 Å, b = 4.74 Å and c = 7.56 Å, which was very different from that proposed for the chemically prepared polythiophene powder.

INTRODUCTION

Polythiophene has a molecular structure consisting of aromatic thiophene rings linked at its 2,5-position and is characterized as a conducting polymer, since it becomes highly conductive on doping with electron donors or acceptors.[1,2] This polymer is an intractable material that is insoluble and infusible. A number of different procedures have been applied for the preparation of polythiophene.[3–6] The electrochemically prepared polymer has well defined chemical structure.[7] So far, the crystallographic data of orthorhombic or monoclinic structure for polythiophene powder, which was synthesized by chemical coupling of 2,5-diiodothiophene, were reported by Mo *et al.*[8] On the other hand, Tourillon *et al.*[9] found that the electrochemically prepared poly(3-methylthiophene) had a crystal structure of hexagonal lattice being consistent with a coil structure. However, the electrochemically prepared polythiophene film has been related to fully amorphous and compact morphology.[2,10] It is pointed out that the regularity and the homogeneity of the structure must be the principal factors to determine its electrical conducting behavior. Thus the control of the higher order structure of the polythiophene film is very important in this respect.

Recently, we have succeeded to prepare the polythiophene film with ability for the draw in the selected polymerization conditions of electrochemical method, and obtained the drawn films with various elongation ratios up to 60% of initial length.[11] The drawn polythiophene film exhibited the anisotropic electrical and thermal properties in the parallel and perpendicular to the draw direction. The tensile strength of the drawn film measured along the drawn direction was found to be 170 MN/m^2 and twice as large as that of the parent undrawn polythiophene film (80 MN/m^2).

This report describes the crystallographic structure of the drawn polythiophene film from a wide angle x-ray diffraction investigation. The relations between the structure and properties will be also discussed.

EXPERIMENTAL

The polythiophene film was prepared electrochemically at applied voltage of 14 V from the electrolytic solution of benzonitrile containing $LiBF_4$ (0.25 mol/l) and thiophene (0.1 mol/l). The film obtained was undoped electrochemically in the same electrolytic solution. The drawing was carried out by the uniaxial stretching with a hand-made apparatus. The more detailed preparation method of the parent polythiophene film and the drawing procedure have been described previously.[11]

The x-ray diffraction experiments were performed on a RIGAKU Geigerflex apparatus employing Ni filtered CuKα radiation. The apparent density of the films was measured by a floating method using carbontetrachloride and acetone. The electrical conductivity of the I_2 redoped drawn films was measured in the parallel to the draw direction by four-probe d.c. technique at room temperature.

RESULTS AND DISCUSSION

The apparent density of the electrochemically prepared polythiophene film (1.49 g/cm^3) was larger than that of the chemically prepared powder (1.2 g/cm^3).[8] Figure 1 shows the apparent density as a function of elongation ratio. The density decreased steeply from 1.49 g/cm^3 to 1.44 g/cm^3 with increasing the elongation ratio until ca. 20%, and became constant with further elongation ratios. This seems to be unusual and suggest an individual structural change of the polythiophene film with drawing. In the case of the conventional polymers, the density increases with increasing the elongation ratio, accompanying the increase of the crystallinity, because the density of the crystal phase is larger than that of the amorphous phase.

Figure 2 shows the wide angle x-ray diffraction photographs (through view) of undrawn (a) and 50% drawn (b) polythiophene films. As shown in this figure, the undrawn film showed only halo rings, indicating no ordered, i.e., amorphous, structure. In contrast, the drawn film showed the distinguishable pattern indicating ordered structure. In addition, the weak concentrations of x-ray diffraction rings observed in drawn film indicate the weak chain orientation of this polymer. The anisotropy of electrical and thermal conductivities observed in drawn film can be, however, explained in terms of the chain orientation.

From the observed x-ray diffractions, it could determine the unit cell constants of the crystal which generated by drawing. With the

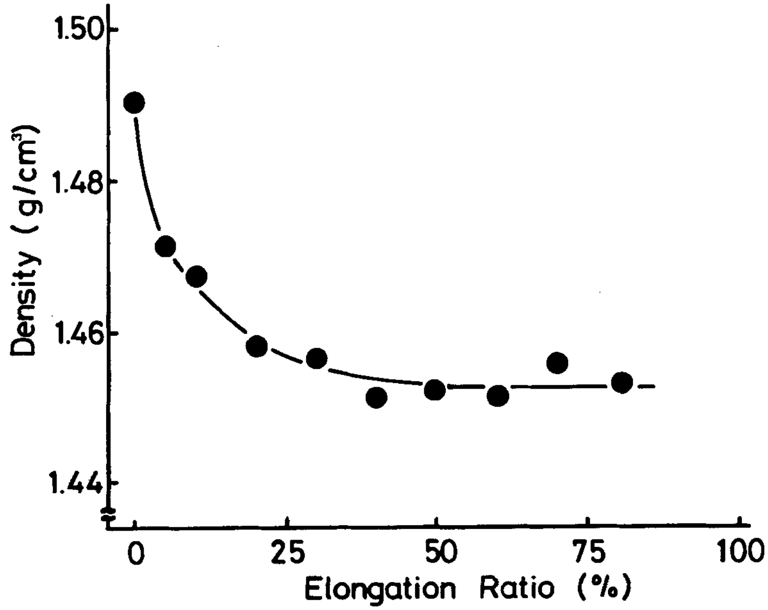

FIGURE 1 Dependence of the apparent density of the electrochemically prepared and drawn polythiophene film on elongation ratio.

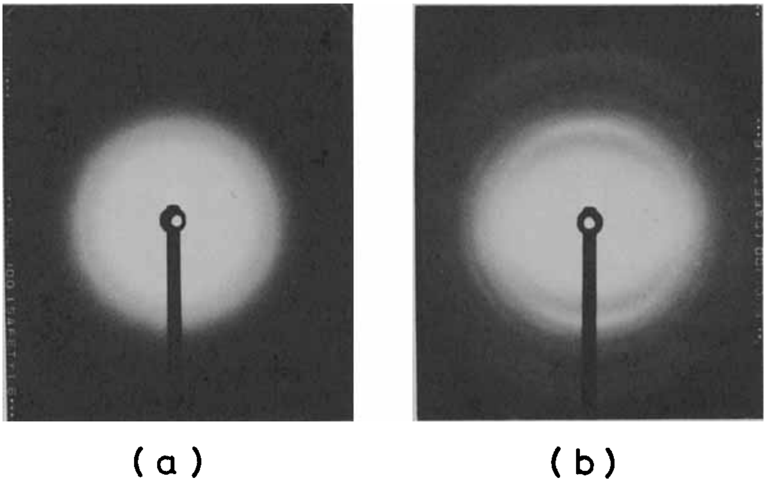

FIGURE 2 Wide angle x-ray diffraction photographs of electrochemically prepared undrawn (a) and drawn (b) polythiophene films.

use of the indices of chemically prepared polythiophene as a guide,[8] we were able to index the observed x-ray diffractions in the drawn film by assuming the crystallographic structure of an orthorhombic unit cell with lattice constants of a = 10.8 Å, b = 4.74 Å and c = 7.56 Å. Table I lists the observed and calculated d spacings and line indices. This crystal structure of the drawn film is in agreement with the chain structure of polythiophene. The repeat unit of this polymer along c axis can be estimated from the known chemical structure of thiophene monomer. The obtained value of 7.56 Å for c implies the existence of two thiophene rings per unit cell and the chain structure for the drawn polythiophene in which the thiophene units alternate similar to that of chemically prepared polythiophene.[8] The present result coincides to the calculated value (7.8 Å) from analysis of minimum-energy configuration for quaterthiophene by Bredas et al.[12] For polyheterocycles, such an alternating structure along the chain axis is generally accepted. It should be pointed out in this table to the good agreement between the obtained and calculated data. However, the unit cell constants are very different from that proposed by Mo *et al.*[8] for the chemically prepared and annealed polythiophene. The space-group of the crystal in drawn polythiophene cannot be determined from the present results.

The crystallization caused by drawing may be the reason for observed high tensile strength and electrical conductivity of the drawn film. Figure 3 shows the electrical conductivity of the I_2 redoped

TABLE I

X-ray diffraction data for drawn polythiophene film

20 (deg)	d spacings (Å) obsd.	d spacings (Å) calcd.	Millar indices (hkl)
8.8	10.8	10.8	100
11.8	7.49	7.56	001
16.5	5.37	5.40	200
18.8	4.71	4.74	010
20.1	4.39	4.39	201
		4.34	110
22.0	4.01	4.02	011
23.5	3.77	3.78	002
		3.76	111
24.9	3.57	3.60	300
		3.57	102
		3.56	210
27.9	3.19	3.25	301
		3.22	211
31.0	2.86	2.87	310
		2.85	112
33.4	2.68	2.68	311
37.3	2.40	2.37	020
39.5	2.28	2.31	120
		2.26	021
42.2	2.14	2.17	220

drawn film as a function of elongation ratio. This conductivity change is similar to that of the apparent density, *i.e.*, it increased steeply with increasing the elongation ratio until ca. 20%, and became constant with further elongation ratios. This increase of conductivity is accompanied by the crystallization and chain orientation of the film with drawing.

The loose packed structure is indicated from the crystallographic data presented here. Assuming the two chains per unit cell, the density calculated from these lattice parameters is 1.42 g/cm^3. This figure is smaller than that of the undrawn polythiophene (1.49 g/cm^3) as described above. It indicates that the compact packed and disordered structure of electrochemically prepared polythiophene film turns to the loose packed and ordered one with drawing. The calculated density of the polythiophene crystal is recognizable taking the partially crystallized structure. Further, the change of the apparent density and conductivity with drawing (Figures 1 and 3) shows that the phase transition takes place at the range of elongation ratio of 0–20%. The amorphous or disordered phase in the electrochemically prepared polythiophene has a compact morphology and may differed from that

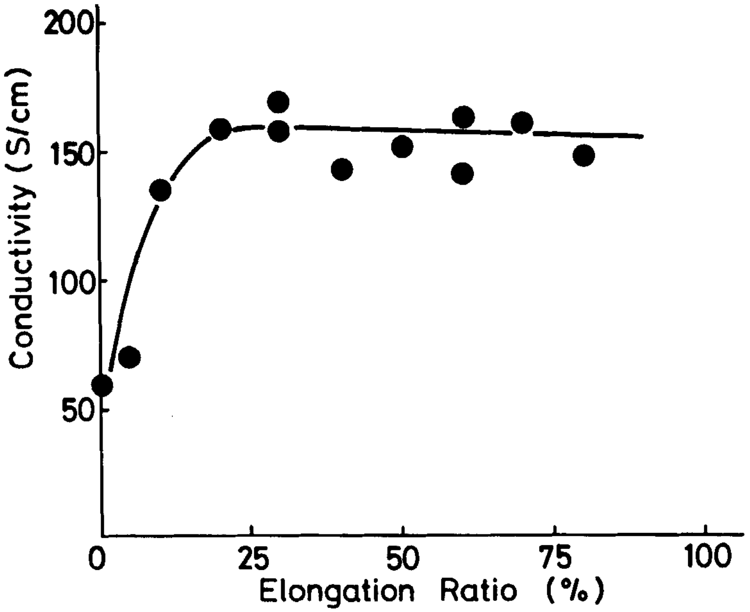

FIGURE 3 Dependence of the electrical conductivity of drawn and I_2 redoped polythiophene film on elongation ratio.

of the other crystalline polymers. These structural change with drawing seems to be a quite unique. The crystallization with drawing has not observed for polypyrrole film.[13]

CONCLUSION

The drawing of the electrochemically prepared polythiophene leads to the structure which shows the distinguishable patterns in x-ray diffraction. It suggests the phase transition of this polymer from amorphous to crystal with drawing. The results for the drawn film indicate the crystal structure of an orthorhombic unit cell with lattice constants a = 10.8 Å, b = 4.74 Å, and c = 7.56 Å. With these lattice parameters the calculated density (1.42 g/cm^3) is recognizable taking the partially crystallized structure.

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