Morphology and mechanical properties of electrochemically prepared polythiophene films

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The mechanical properties of electrochemically polymerized polythiophene films were studied in relation to the structure of the films. Both tensile modulus and strength of as-polymerized and neutralized films decreased with increasing current density during polymerization. At a given current density, the tensile properties of neutral films were superior to those of as-polymerized films. The deformability of neutralized films decreased with increasing current density. These results were closely related to the microscopic heterogeneity and chain orientations of as-polymerized films.

(Keywords: conducting polymer; drawn polythiophene; mechanical properties; X-ray analysis; morphology; crystal structure)

INTRODUCTION

Polythiophene is an environmentally stable conjugated polymer for both neutral and oxidized states. The stability is important for practical applications of electroconductive polymers. It is reported[1-4] that the conditions for electrochemical polymerization of thiophene have appreciable effects on electrical conductivity, appearance, toughness, morphology and drawability. We reported[3] that wide-angle X-ray diffraction photographs from cross-sections of electrochemically polymerized polythiophene films exhibited a fibre texture. Further, the direction of fibre alignment changed with current density during polymerization. Control of the morphology of as-polymerized polythiophene films seems to be important from both fundamental aspects of the polymerization process and practical viewpoints.

In this work, we studied the relation between the morphology and mechanical properties of electrochemically polymerized polythiophene films prepared under various conditions. The mechanical properties and deformability of the films were closely related to the current density during polymerization.

EXPERIMENTAL

Polythiophene (PT) films were electrochemically generated on a platinum electrode in a beaker-type cell in an atmosphere of dry nitrogen. The distance between the two electrodes was approximately 10 mm. The electrolyte solution used was a mixture of 0.03 M tetrabutylammonium perchlorate ($TBAClO_4$) and 0.3 M thiophene monomer in dehydrated nitrobenzene. The polymerizations were carried out at 5°C with a constant current density ranging from 0.7 to 5.0 mA cm^{-2}. The anode potential on polymerization was measured *versus* a saturated calomel electrode (SCE). The polymerization process leads directly to an oxidized (doped) state. The doped films were electrochemically reduced to the neutral state. The drawn polythiophene films were prepared by uniaxial stretching with a tensile tester at room temperature.

The tensile properties of the samples were measured at room temperature and at a strain rate of $1\times10^{-3}\,s^{-1}$ using a tensile tester HTM-100 (Toyo Baldwin). Wide-angle X-ray diffraction (WAXD) photographs of the samples were obtained by a Rigaku RU-200 X-ray generator using Ni-filtered Cu Kα radiation.

RESULTS AND DISCUSSION

Mechanical properties

Mechanical properties such as tensile modulus and strength as well as deformability of PT films were greatly affected by the current density during polymerization. *Table 1* shows the tensile properties of as-polymerized PT films and their neutral samples prepared at a constant current density ranging from 0.7 to 5.0 mA cm^{-2}. The results demonstrate that both modulus and strength of as-polymerized and neutral films decrease with increasing current density. Further, at a given current density, the tensile properties of the neutral film are superior to those of as-polymerized films. The neutral films were deformable. *Figure 1* shows nominal stress–strain curves recorded at room temperature for neutral films. With

Table 1 Mechanical properties of as-polymerized and neutral polythiophene films

Samples	Current density (mA cm^{-2})	Modulus (GPa)	Strength (MPa)
As-polymerized films	0.7	2.6	74
	3.0	2.1	60
	5.0	1.8	35
Neutral films	0.7	3.3	82
	3.0	2.6	67
	5.0	2.0	30

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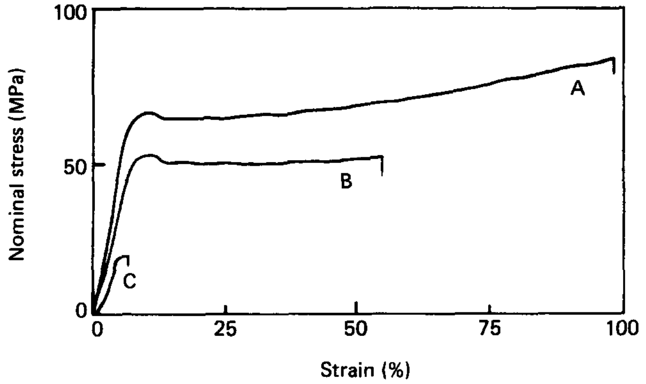

Figure 1 Nominal stress–strain curves for the neutral films prepared at (A) 0.7, (B) 3.0 and (C) 5.0 mA cm^{-2}

decreasing current density, the deformability of the films parallel to the film surface increases, and the films prepared at 0.7 mA cm^{-2} could be elongated up to 1.8 times their original length.

The morphology of as-polymerized films was also affected by the polymerization conditions. Scanning electron microscope (SEM) photographs of the as-polymerized film surfaces (solution side) are shown in *Figure 2*. It is clearly seen that the surface roughness increases with increasing current density. Tourillon and Garnier have reported[1] that the roughness depends on the film thickness and on the polymer and dopant species. In this study, the film thickness in each polymerization was adjusted to about 15 μm. Another factor must be considered to explain the difference in roughness observed in this study. *Figure 3* shows SEM photographs of the film surface and cross-section of as-polymerized film prepared at 3.0 mA cm^{-2} and its neutral film. For the as-polymerized sample, an irregular nodule structure is observed on both surface and interior. By the electrochemical reduction, most of the large nodules disappeared. During the electrochemical reduction, powdery deposits were excluded from the films. The amounts of deposits increased with increasing current density during polymerization. *Figure 4* shows the anode potential (vs. SCE) as a function of the electrolytic current density. The potential curve for an electrolytic solution without monomer is also indicated for reference. The potential was measured at the electrolytic charge of 0.5 C cm^{-2}. Below the current density of 2 mA cm^{-2}, the potential is about 1.65 V vs. SCE, which is almost independent of current density. This value corresponds to that for the oxidation potential of thiophene monomer[5]. When the current density exceeds the value of 2 mA cm^{-2}, the potential begins to shift to the noble side with increasing current density and reaches the value of 2.9 V vs. SCE at current density 5 mA cm^{-2}. In addition, the efficiency of polymerization decreased from 80% at 2 mA cm^{-2} to 50% at 5 mA cm^{-2}. When the polymerization potential exceeds the oxidation potential of monomer, the polymerization proceeds with side reactions such as oxidations of solvent and electrolyte, which may decrease the efficiency of polymerization and macroscopic homogeneity of the resultant polymer films.

Structure

As shown in *Figure 1*, the neutral sample polymerized at 0.7 mA cm^{-2} (neutral PT-0.7) could be drawn up to a draw ratio (λ) of 1.8. In *Figure 5*, the tensile modulus and strength are plotted against draw ratio of neutral PT-0.7. Both modulus and strength increase almost linearly with increasing draw ratio. The highest values recorded in this study were 8.5 GPa and 265 MPa for modulus and strength, respectively. Although the attainable maximum draw ratio is quite low compared with that for polyacetylene, the maximum tensile strength of 265 MPa is almost twice as high as that for highly drawn polyacetylene[6]. In the previous paper[3], we showed that WAXD photographs of as-polymerized PT films displayed a texture suggesting a preferential chain

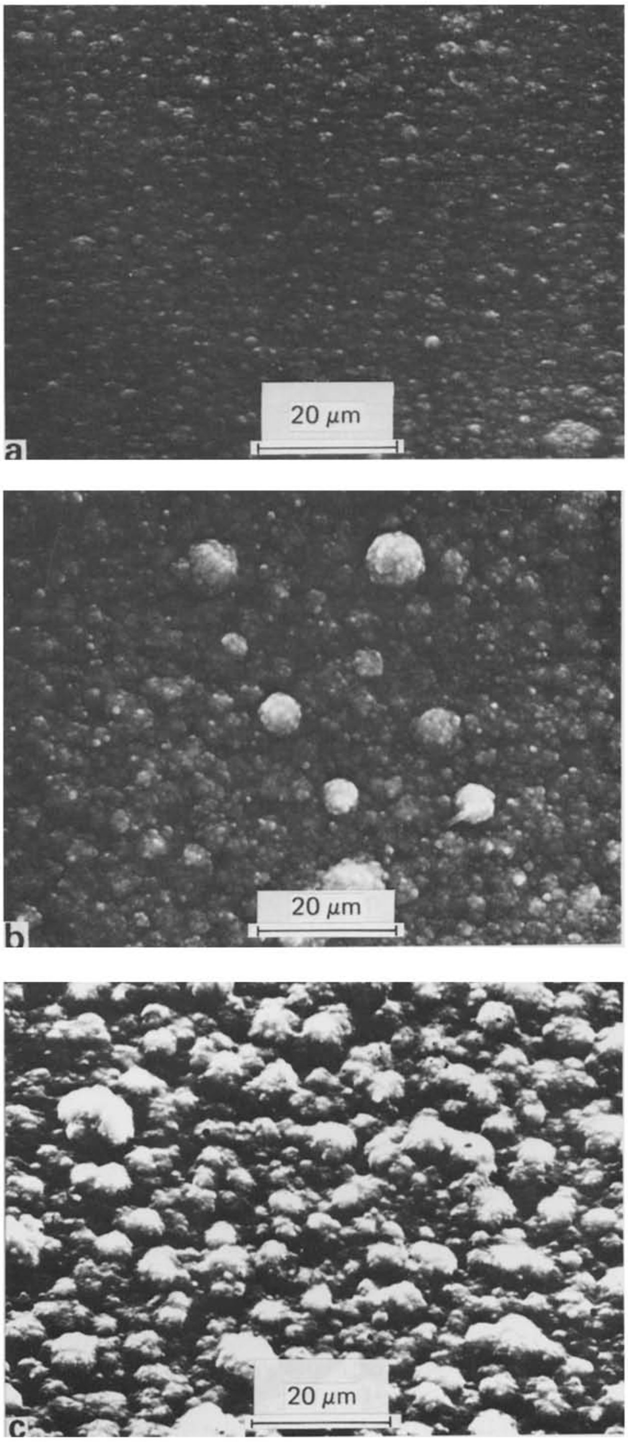

Figure 2 SEM photographs of as-polymerized film surfaces (solution side) prepared at (a) 0.7, (b) 3.0 and (c) 5.0 mA cm^{-2}

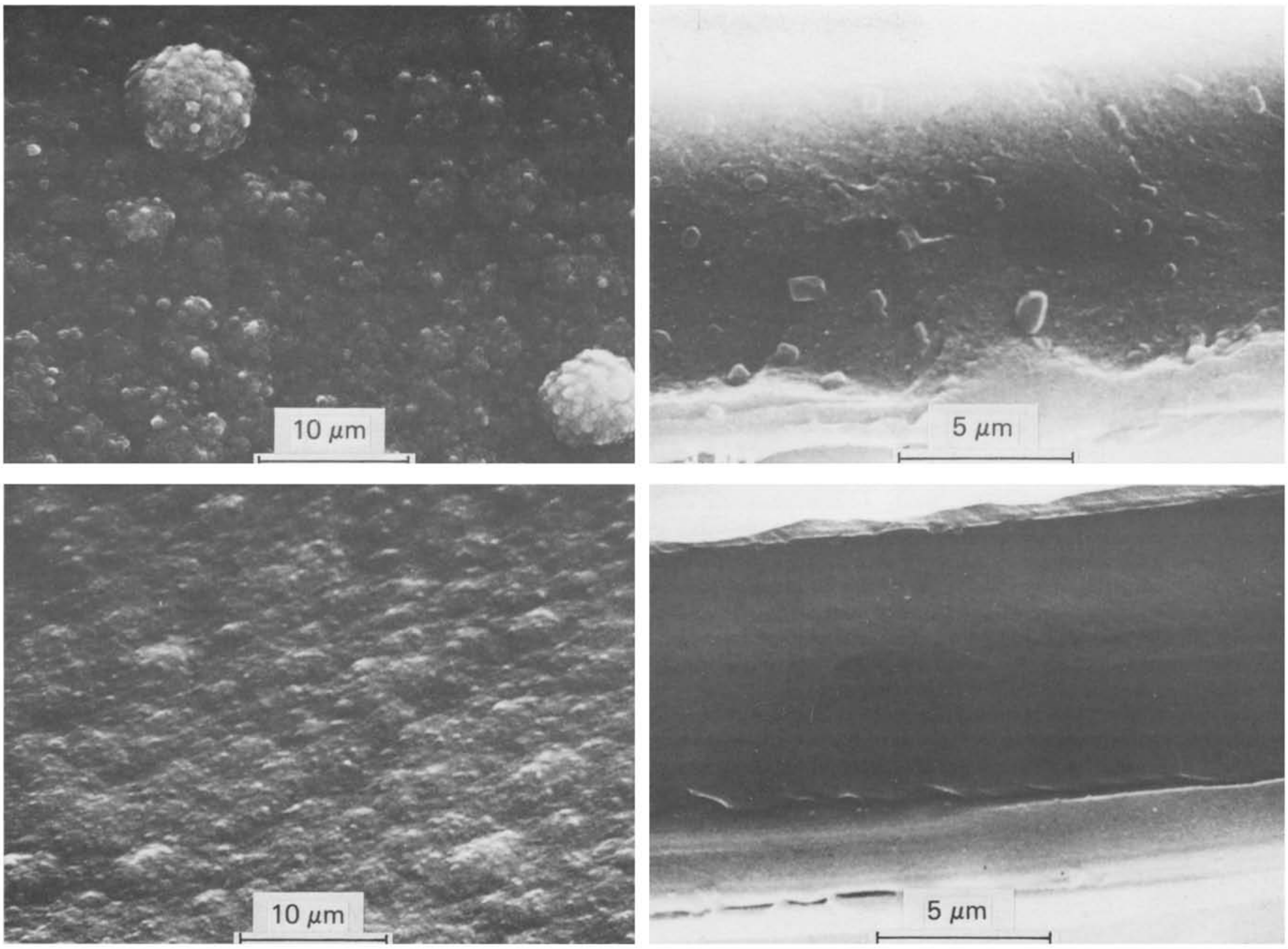

Figure 3 SEM photographs of (top) as-polymerized and (bottom) neutral films prepared at 3.0 mA cm^{-2}: (left) surface (solution side); (right) interior

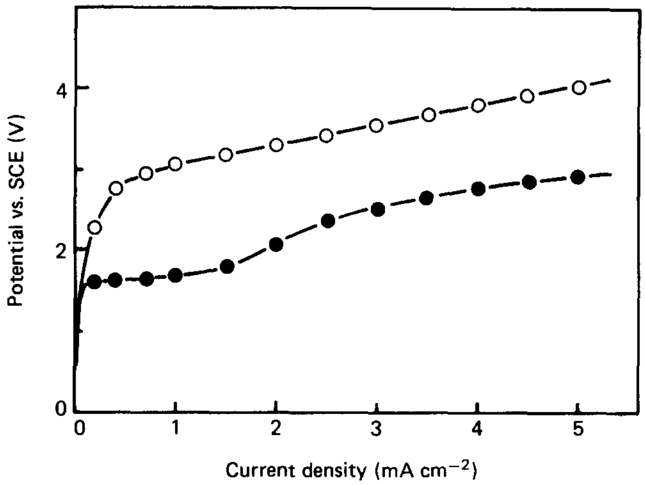

Figure 4 The anode potential vs. SCE as a function of the electrolytic current density: (●) $TBAClO_4$+monomer; (○) $TBAClO_4$

orientation in the films. The initial morphology of the samples is expected to have an effect on their deformability.

In this study, wide-angle X-ray analysis was carried out on the neutral PT-0.7 and its drawn sample. *Figure 6* shows WAXD photographs of a 50-layer stack of carefully aligned pieces cut from a single neutral PT-0.7 film. The sample geometry for the measurements is also indicated in the figure, where the *x–z* plane is parallel to the film surface and the *y* axis is parallel to the thickness direction. The photograph obtained with the incident X-ray beam parallel to the *y* axis showed two Debye–Scherrer rings. The *d* spacings evaluated from the

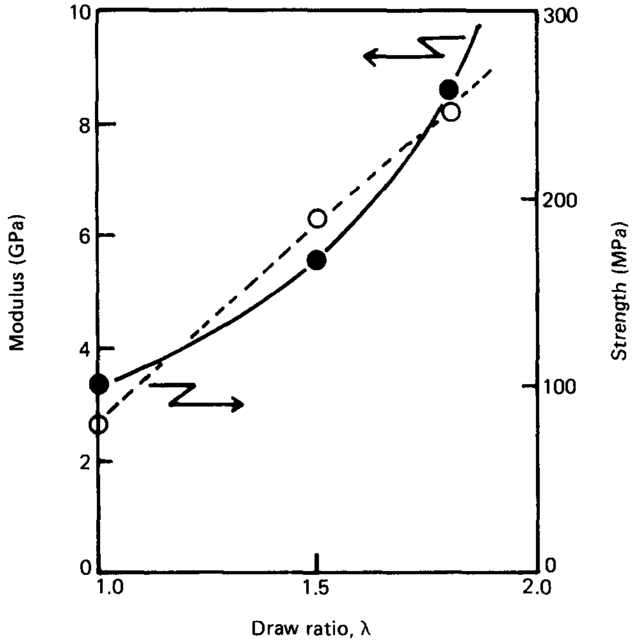

Figure 5 The tensile modulus (●) and strength (○) as a function of draw ratio for the neutral PT-0.7

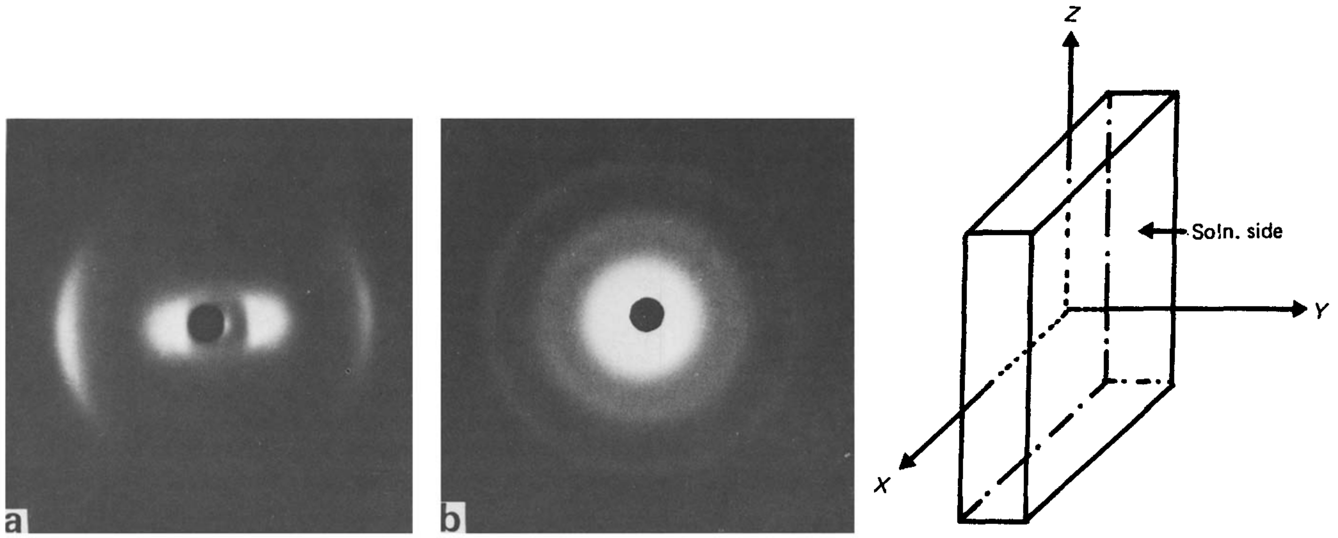

Figure 6 WAXD photographs of neutral PT-0.7: (a) X-ray beam parallel to the x axis; (b) beam parallel to the z axis

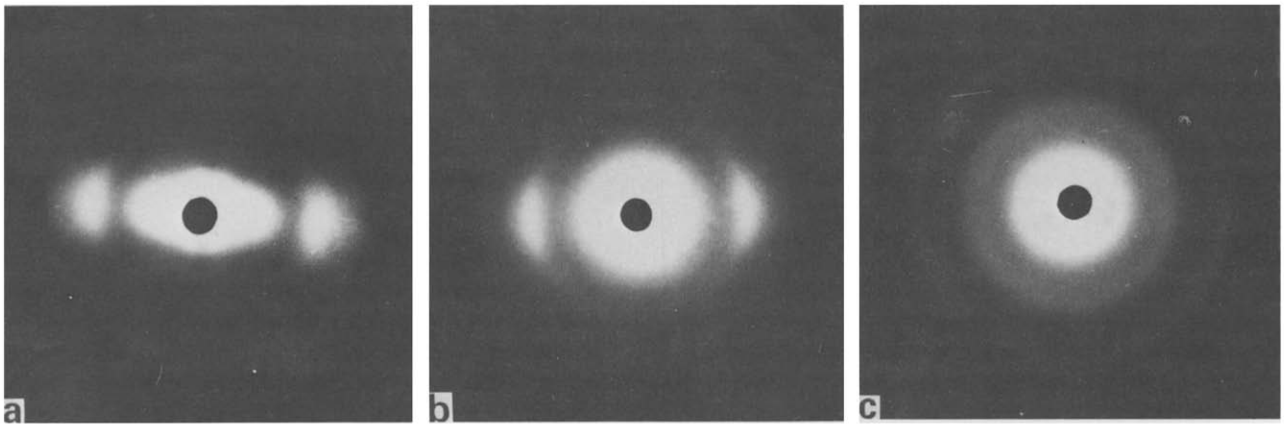

Figure 7 WAXD photographs of drawn sample ($\lambda = 1.8$) prepared from neutral PT-0.7 films: (a) X-ray beam parallel to the x axis; (b) beam parallel to the y axis; (c) beam parallel to the z axis

diffraction patterns are about 3.5 and 5.0 Å. In addition, two diffuse scatterings in the small-angle region with d spacings of 10 and 14 Å were observed. When the photograph was taken with the incident beam parallel to the x or z axis, a sharp reflection with d spacing of 3.5 Å was seen on the equator. Further, two low-angle reflections with d spacings of 10 and 14 Å appeared on the equator. In order to characterize these spacings, WAXD photographs were taken for drawn samples. *Figure 7* shows WAXD photographs of drawn film ($\lambda = 1.8$) prepared from neutral PT-0.7 films. The sample geometry for the measurements is the same as in *Figure 6*, and the draw direction is parallel to the z axis. The photographs obtained with the incident X-ray beam parallel to the x and y axis show maxima of reflection intensity on both the meridian and the equator, although the orientation is inherently broad. On the other hand, the photograph taken with the incident beam parallel to the y axis is similar to that for an undrawn sample taken with the beam parallel to the z axis. The precise determination of the crystal structure was difficult owing to the small number of reflections and their broadness. The crystal structure of polythiophene has been estimated from the analyses of electron diffraction data[7] and X-ray powder patterns[8] and from the theoretical calculations[9]. Mo *et al.*[8] reported that wide-angle X-ray data for polythiophene are consistent with an orthorhombic unit cell with lattice constants $a = 7.80$ Å, $b = 5.55$ Å and $c = 8.03$ Å or a monoclinic unit cell with $a = 7.83$ Å, $b = 6.55$ Å, $c = 8.20$ Å and $\beta = 96°$. Based on these unit-cell data, attempts have been made to index the observed reflections by assuming the orthorhombic structure. For the photograph in *Figure 7b*, the strong but rather broad reflection on the equator corresponds to a d value of 4.0–5.1 Å, which is close to the spacing related to the (110) plane[8]. A d value of 3.5–5.0 Å was calculated from the broad reflection on the photograph in *Figure 7a*. The values of 3.5 and 5.0 Å correspond to those calculated from the Debye–Scherrer rings that appear on the photograph in *Figure 7c*. The value of 3.5 Å seems to be related to the (200) plane[8]. For *Figure 7a*, it is plausible that the broad reflection on the equator arises from coupling of reflections from the (200) and (110) planes. Although the crystallographic data obtained are incomplete, the results suggest that the equatorial reflection observed for the undrawn sample (*Figure 6a*) is related to the (200) plane. If so, the results indicate a preferential a axis orientation parallel to the film thickness direction, resulting in a c axis orientation parallel to the surface of the film. This specific structure might enhance the deformability along the surface of neutral PT-0.7 films.

On every photograph, diffuse scatterings were observed in the small-angle regions similarly to our previous results[3]. In some cases, the scatterings have their intensity maxima on the equator (*Figures 6a* and *7a*). The *d* spacings evaluated from the scattering patterns are in the range 10–12 Å for neutral PT-0.7 (*Figure 6a*) and 8–10 Å for the drawn sample (*Figure 7a*). These ranges are too wide to permit quantitative analysis. However, the facts that the patterns show anisotropy and change with deformation suggest the existence of periodicity of supermolecular structure in the as-polymerized film.

CONCLUSIONS

The mechanical properties of electrochemically polymerized polythiophene films are greatly affected by the current density during polymerization and by electrochemical reduction.

As-polymerized films involve powdery deposits. The amounts of the powdery deposits decrease with decreasing current density during polymerization. Furthermore, the deposits can be removed by electrochemical reduction of the as-polymerized films. The mechanical properties of as-polymerized films can be improved by reducing the amounts of deposits in these films.

For as-polymerized films prepared at a low current density ($< 2\,\mathrm{mA\,cm^{-2}}$), a preferential chain orientation is observed. The chains are oriented parallel to the surface of the film, which might enhance the deformability along the surface of the as-polymerized films.

REFERENCES

1 Tourillon, G. and Garnier, F. *J. Polym. Sci., Polym. Phys. Edn.* 1984, **22**, 33
2 Tanaka, S., Sato, M. and Kaeriyama, K. *Makromol. Chem.* 1984, **185**, 1295
3 Ito, M., Shioda, H. and Tanaka, K. *J. Polym. Sci., Polym. Lett. Edn.* 1986, **24**, 147
4 Satoh, M., Yamasaki, H., Aoki, S. and Yoshino, K. *Polym. Commun.* 1987, **28**, 144
5 Tourillon, G. and Garnier, F. *J. Electroanal. Chem.* 1984, **161**, 51
6 Pedretti, G. and Perego, G. *J. Polym. Sci., Polym. Lett. Edn.* 1985, **23**, 129
7 Garnier, F., Tourillon, G., Barraud, J. and Dexpert, H. *J. Mater. Sci.* 1985, **20**, 2687
8 Mo, Z., Lee, K., Moon, Y., Kobayashi, M., Heeger, A. and Wudl, F. *Macromolecules* 1985, **18**, 1972
9 Orchard, B., Fredenreich, B. and Tripathy, S. *Polymer* 1986, **27**, 1533