Electrochemical Deposition of Films of p-Doped Regioregular Poly(3-hexylthiophene-2,5-diyl)

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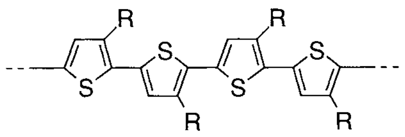
Electrochemically oxidative deposition of regioregular poly(3-hexylthiophene-2,5-diyl) gave a film in which p-doped polymer molecules took an ordered structure. According to the p-doping, the ordered structure of the neutral original polymer in the solid was changed. Conditions for the preparation of the film and electrically conducting properties of the film are described.

Electrochemical oxidation of electron-donating compounds such as tetrathiafulvalene and its derivatives has provided a strong tool for the preparation of electrically conducting salts of the electron-donating compounds.[1] The electrically conducting salts are deposited on the surface of the anode.

In contrast to the electrochemical deposition of the salts of the low molecular weight compounds, electrochemical deposition of electron-donating polymers has received much less attention. Electrochemically oxidative polymerization of electron-donating thiophene, pyrrole, and their derivatives has been actively investigated, and utilization of the polymer film to modify electrodes has also been carried out.[2] However, the electrochemically oxidative polymerization of 3-alkylthiophene usually gives a film of p-doped regio-random poly(3-alkylthiophene-2,5-diyl), P3RTh.

In view of recent success of synthesis of regioregular head-to-tail (HT)-poly(3-alkylthiophene-2,5-diyl), which shows interesting electronic and optical properties as well as a strong tendency to form an organized stacked structure,[3] we have carried out electrochemically oxidative deposition of HT-poly(3-hexylthiophene-2,5-diyl), HT-P3HexTh. By the electrochemical deposition, one can obtain smooth films of p-doped HT-P3HexTh which are not prepared by the electrochemically oxidative polymerization of 3-alkylthiophene. We here report the conditions to prepare the films, packing information of the polymer in the film, and electrically conducting properties of the film.



HT-P3HexTh
R = hexyl

The electrochemically oxidative deposition of commercially available HT-P3HexTh [3b,c] was carried out in a usual H-type cell with two compartments separated by a sintered glass filter at room temperature under N_2. Anhydrous solvents, tetrabutylammonium salts, $[NBu_4]Y$, and an Pt electrode (1 cm x 2 cm) were used. Among three kinds of solvents tested (THF, chloroform, and methylene chloride), THF gave the film most successfully. HT-P3HexTh showed too high solubility in chloroform and methylene chloride,[3c] and the solvents did not seem suited for the electrochemically oxidative deposition. HT-P3HexTh was insoluble in acetonitrile and DMSO, and carrying out the electrochemically oxidative deposition in these solvents was not possible. Selection of the salts of BF_4^-, PF_6^-, and ClO_4^- gave the smooth film in a concentration range of 0.005-0.10 M, however, use of SCN^- and I^- salts did not give the film with good quality. Galvanostatic electrolysis in an electric current range of 1-100 μA, preferably at 1-2 μA, successfully afforded the smooth film. Control of the electrolysis at a potentiostatic mode was also possible. However, prolonged electrolysis at the potentiostatic

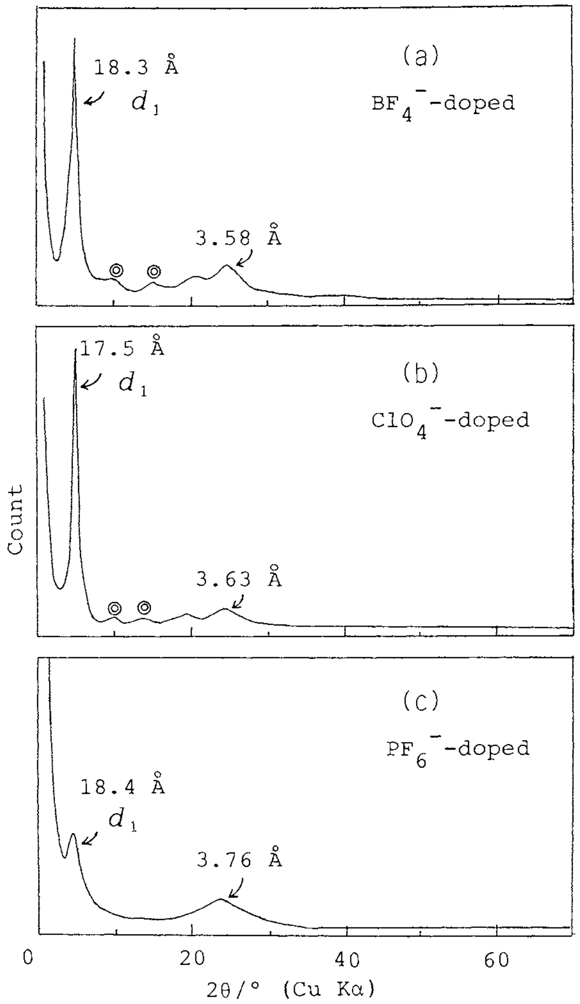


Figure 1. Powder X-ray diffraction patterns of the electrochemically deposited p-doped HT-P3HexTh films. Conditions for the electrochemical deposition: (a) at 1 μA in THF containing $[NBu_4][BF_4]$ (0.01 M); (b) at 100 μA in THF containing $[NBu_4][ClO_4]$ (0.01 M); (c) at 100 μA in THF containing $[NBu_4][PF_6]$ (0.005 M). The small peaks with the ◎ mark are assigned to the second and third peaks of the main peak (d_1). Appearance of these peaks indicates high ordering of the HT-P3HexTh molecules in the film.

mode usually led to a color change of the elecrolytic solution from brown to dark brown, suggesting formation of by-products.

The IR spectrum of the obtained film was similar to that of p-doped P3HexTh prepared by the electrochemical polymerization of 3-hexylthiophene and showed a peak due to the anion dopant, supporting that the obtained polymer film had essentially the same chemical composition as that of p-doped P3HexTh prepared by the electrochemical polymerization. Polythiophene and P3RThs are usually electrochemically oxidized at a doping level (the molar ratio between the anion and the thiophene ring) of about 0.3, and the rate of growth of the HT-P3HexTh film agreed with the structure of the p-doped HT-P3HexTh with the same doping level.[4]

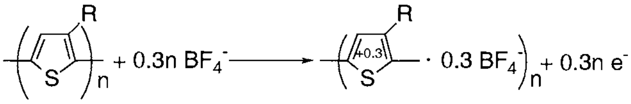
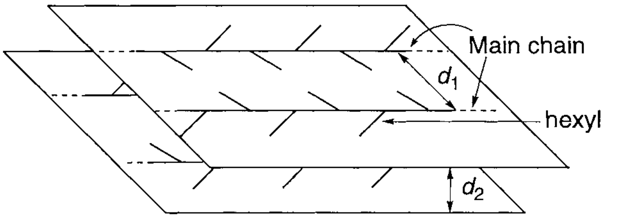


Figure 1 shows powder X-ray diffraction (XRD) patterns of the electrochemically deposited p-doped HT-P3HexTh. As seen in Figure 1, the XRD patterns of the BF_4^-- and ClO_4^--doped samples exhibit a sharp diffraction peak (half width of the peak = 1.1±0.1°) in a low angle region which can be assigned to a distance d_1 between the core main chains separated by the hexyl groups.[3c] In addition to this peak, the sample gives a peak at about d = 3.6 Å, which is assigned to a face-to-face distance d_2 between the π-stacked HT-P3HexTh molecules.[3] Appearance of these peaks indicates that the electrochemically p-doped HT-P3HexTh molecules also take a microcrystalline stacked structure in the film, similar to neutral HT-P3HexTh in the solid.[3]

However, the distance d_1 between the core main chain separated by the hexyl groups is somewhat longer (17.5-18.3 Å; cf. parts (a) and (b) in Figure 1) than that (16.7 Å) observed with neutral HT-P3HexTh.[3c]



On the other hand, the face-to-face distance d_2 became shorter (3.58-3.63 Å; Figures 1a and 1b) than 3.84 Å of neutral HT-P3HexTh,[3c] by the electrochemical p-doping. These results indicate that inclusion of the BF_4^- or ClO_4^- anion leads to elongation of the distance d_1 and suggest that the p-doping make the electronic attractive force between the HT-P3HexTh molecular planes stronger to give a shorter face-to-face distance d_2. It was reported that a monocation of an oligothiophene with butyl side chains took a similar face-to-face distance (3.47 Å) as proved by single crystal X-ray crystallography.[5] In contrast to the BF_4^-- and ClO_4^--doped HT-P3HexTh, the PF_6^--doped HT-P3HexTh showed only a broad (half width = 3.4°) diffraction peak in the low angle region (Figure 1c), suggesting that the PF_6^- anion does not fit well the packing structure of p-doped HT-P3HexTh. In relation to this, it has been found that electrochemical doping of a HT-P3HexTh film gives somewhat larger doping level (0.31) in the presence of $[NBu_4]BF_4$ than that (0.26) in the presence $[NBu_4]PF_6$. P3HexTh prepared by the electrochemically oxidative polymerization of 3-hexylthiophene in the presence of $[NBu_4]BF_4$ also showed rather broad (half width = 1.9°) peak at d = 18.2 Å, presumably due to its containing head-to-head units in addition to the HT units.[3]

The electrochemically deposited p-doped HT-P3HexTh was electrically conductive, and the BF_4^--, ClO_4^--, and PF_6^--doped samples gave electrical conductivity of 7.3×10^{-3}, 5.2×10^{-2}, and 0.4 S cm^{-1}, respectively, at room temperature. For the BF_4^--doped sample, it showed a temperature dependence of the electrical conductivity which seems to be explained by a three dimensional variable range hopping conduction model,[6] in a temperature range of 50-300 K. Below 50 K, the sample sometimes showed steep increase in the electrical conductivity. Shortening of the packing distance at the low temperature may be the origin of the increase in the electrical conductivity. Conduction mechanism and the origin of the increase in the electrical conductivity is under investigation.

As described above, electrochemical deposition of regioregular HT-P3HexTh can give a film in which the p-doped HT-P3HexTh molecules take an ordered structure. The results are expected to contribute to design of new electrodes modified with the polymer film[2b,c] and to better understanding of electrochemical doping of π-conjugated polymers.

References and Notes

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4 The p-doping equation corresponds to 650 g of the product per 1 *F*, which gives about 1 mg of the product after passing 1.5 μA electric current for 24 h (0.130 C or 1.35×10^{-6} *F*).

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