

HETEROCYCLES, Vol. 64, 2004, pp. 223 - 228

Received, 10th June, 2004, Accepted, 28th July, 2004, Published online, 30th July, 2004

## ELECTROCHEMICAL POLYMERIZATION OF TETRA-METHYLENE-CROSSLINKED BIS(2,5-DI-2-THIENYL-1H-PYRROLE)

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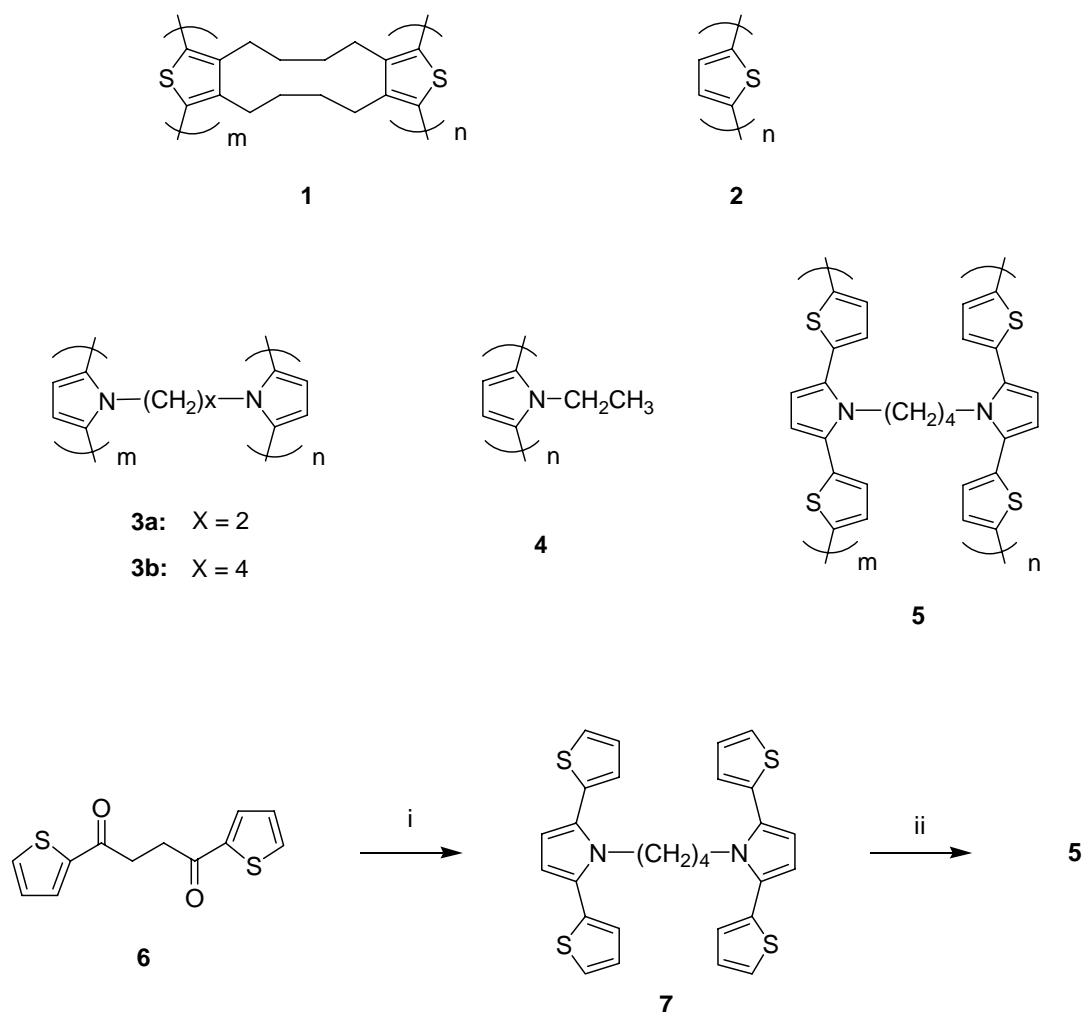
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**Abstract**—Electrochemical polymerization of 1,1'-(1,4-butanediyl)bis(2,5-di-2-thienyl-1H-pyrrole) (**7**) afforded a thin film with a smooth surface on an ITO (indium-tin-oxide) electrode due to the network structure. The potentiostatic electrolysis was finished within 15 min, indicating an effective film formation technology for organic devices.

There has been considerable interest in the development of new carrier-transporting materials together with film formation technology since they are important for fabrication of organic devices, e.g., electrochromic displays<sup>1</sup> and electroluminescent (EL) devices.<sup>2,3</sup> Electrical conducting polymers are significant candidates for these materials, some of which have been already examined.<sup>1,2</sup> Electrochemical polymerization is a promising method for organic devices as one of fabrication processes since  $\pi$ -conjugated polymers and oligomers are accumulated on ITO electrodes in the electrolysis. Recently,  $\pi$ -conjugated polymers with two- or three-dimensional crosslinked structures have been electrochemically synthesized and investigated.<sup>4-7</sup> It was found that their films had smooth surfaces and high physical strength. Furthermore, they showed high electrical conductivity and redox stability. For example, tetramethylene-crosslinked polythiophene (**1**) afforded higher electrical conductivity and tensile strength than polythiophene (**2**) (electrical conductivity/S cm<sup>-1</sup>: **1**, 300; **2**, 35, tensile strength/N mm<sup>-2</sup>: **1**, 80; **2**, 35).<sup>6</sup> Ethylene-crosslinked polypyrrole (**3a**) also has stronger electron-donating ability and higher electrical conductivity compared to poly(*N*-ethylpyrrole) (**4**) (electrical conductivity/S cm<sup>-1</sup>: **3a**, 5.9 x 10<sup>-4</sup>; **4**, 5.2 x 10<sup>-6</sup>).<sup>7</sup> However, introduction of large crosslinked moieties into the  $\pi$ -conjugated systems lowered the electrical and electronic properties because of their insulation properties. Conductivity of

**3b** was measured to be  $3.3 \times 10^{-6} \text{ S cm}^{-1}$ .<sup>7</sup> In order to extend the  $\pi$ -conjugated system of **3b**, we have now prepared crosslinked copolymer with pyrrole and bithiophene (**5**) by electrochemical polymerization of the corresponding monomer (**7**) to afford fine thin films on ITO electrodes. We report here the electrochemical synthesis of **5** and properties of the obtained films.



Scheme 1. Reagents and conditions: (i) 1,4-diaminobutane, propionic acid, toluene, reflux, 3 days; (ii) electrochemical polymerization.

Monomer (**7**) was prepared in 41% yield by the Knorr-Paal condensation of 1,4-di-2-thienyl-1,4-butanedione (**6**) with 1,4-diaminobutane in toluene containing propionic acid.<sup>8</sup> Compound (**7**) (mp 204-205 °C) was obtained as orange needles after recrystallization from toluene. The monomer is soluble in dichloromethane and benzonitrile, but not in acetonitrile. Therefore, dichloromethane and benzonitrile were selected for the solvent of electrochemical polymerization. The cyclic voltammogram of monomer (**7**) showed an irreversible oxidation wave at  $E_{\text{pa}} = +0.39 \text{ V}$  vs  $\text{Fc}/\text{Fc}^+$  in dichloromethane. Polymer (**5**) was prepared by electrochemical polymerization using a Pt disk ( $\phi$  1.6 mm) or ITO ( $10 \Omega$ ,  $12 \times 8 \text{ mm}^2$ ) as a working electrode in dichloromethane containing 0.1 M

tetrabutylammonium perchlorate ( $n\text{-Bu}_4\text{NClO}_4$ ) as supporting electrolyte. A minimum potential for electrochemical polymerization was surveyed to afford  $E_{\text{onset}} = +0.30$  V vs  $\text{Fc}/\text{Fc}^+$  in order to prevent overoxidation. The shift from the peak potential of monomer ( $E_{\text{pa}}$ ) was almost  $-0.09$  V. These conditions were employed for the cyclic voltammetry method and the electrochemical polymerization process is displayed in Figure 1a. The cyclic voltammogram of polymer (**5**) indicated symmetrical anode and cathode waves at  $E_{\text{pa}} = +0.26$  V and  $E_{\text{pc}} = +0.23$  V vs  $\text{Fc}/\text{Fc}^+$ , respectively (Figure 1b). These values are higher than those of polymer (**3b**) ( $E_{\text{pa}} = +0.09$  V,  $E_{\text{pc}} = +0.05$  V).<sup>7,9</sup> The electron-donating ability slightly decreased by introduction of bithiophene units into the polypyrrole moiety of **3b**. The peak current increased depending on the scan rates with a linear relationship, indicating that the electrode reactions were attributed to a surface-attached redox species.<sup>10</sup> The electrochemical polymerization process was strongly influenced by the conditions. The electrolysis in dichloromethane with  $n\text{-Bu}_4\text{NClO}_4$  and  $n\text{-Bu}_4\text{NPF}_6$  as supporting electrolyte gave the polymers, respectively. However, a polymer was not obtained when the electrolysis was carried out using  $n\text{-Bu}_4\text{NBF}_4$ . In addition, the polymer was not accumulated on an electrode in benzonitrile containing  $n\text{-Bu}_4\text{NClO}_4$ .

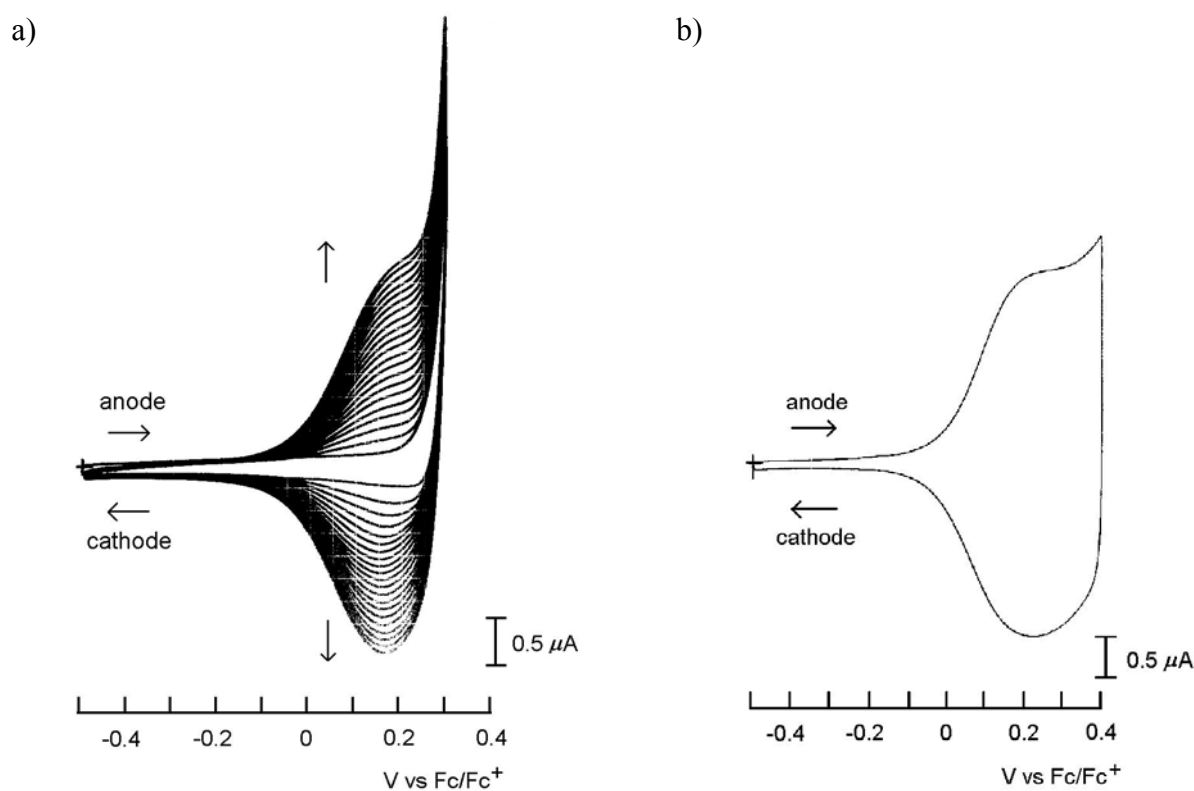


Figure 1. Cyclic voltammograms of an electrochemical polymerization process of monomer (**7**) scanning 100 times (a) and polymer (**5**) (b) measured in a  $\text{CH}_2\text{Cl}_2/0.1$  M  $n\text{-Bu}_4\text{NClO}_4$  electrolyte at  $100$   $\text{mV s}^{-1}$  under a nitrogen atmosphere. Pt electrode, Pt wire, SCE (saturated calomel electrode) were used as working, counter, and reference electrodes, respectively. The values are given in V vs  $\text{Fc}/\text{Fc}^+$ .

The potentiostatic electrolysis of 1.0 mM solution of monomer (**7**) in dichloromethane with  $n\text{-Bu}_4\text{NClO}_4$  afforded a thin film of polymer (**5**) with a smooth surface on the ITO electrode due to a network structure. As the electrochemical polymerization reaction proceeded, the current density increased until 3 min in the electrolysis at +0.32 V vs  $\text{Fc}/\text{Fc}^+$  (Figure 2). A whole surface of the electrode may be covered with the polymer at this stage. After that the current density decreased with continuous formation of the polymer film. In the electrolysis at the applied voltages of +0.28 and +0.30 V, the electrochemical polymerization reactions slowly proceeded. The decrease of the current density was small, especially the current density at the applied voltage of +0.28 V was remained to be constant.

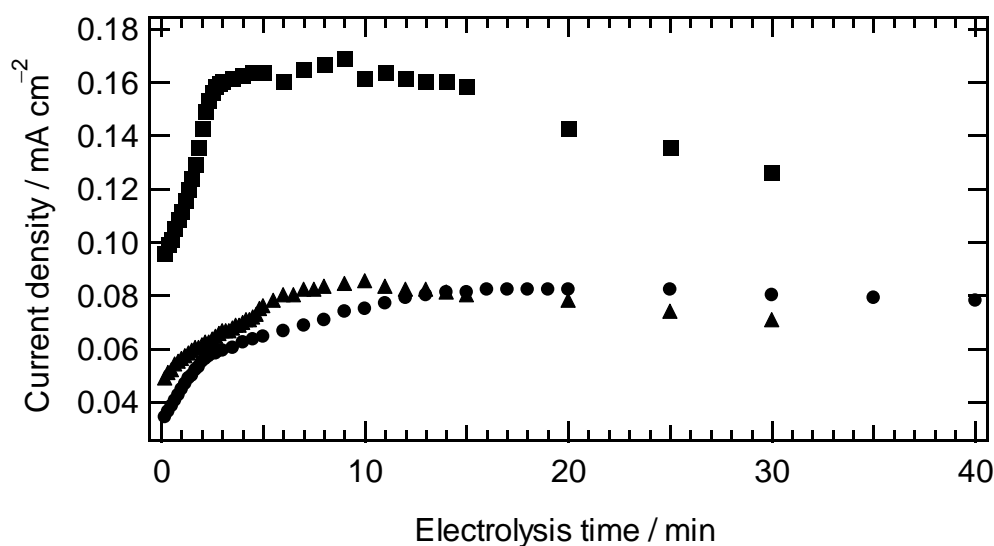


Figure 2. Current density-electrolysis time curves in potentiostatic electrolysis at +0.32 V (■), +0.30 V (▲), and +0.28 V vs  $\text{Fc}/\text{Fc}^+$  (●).

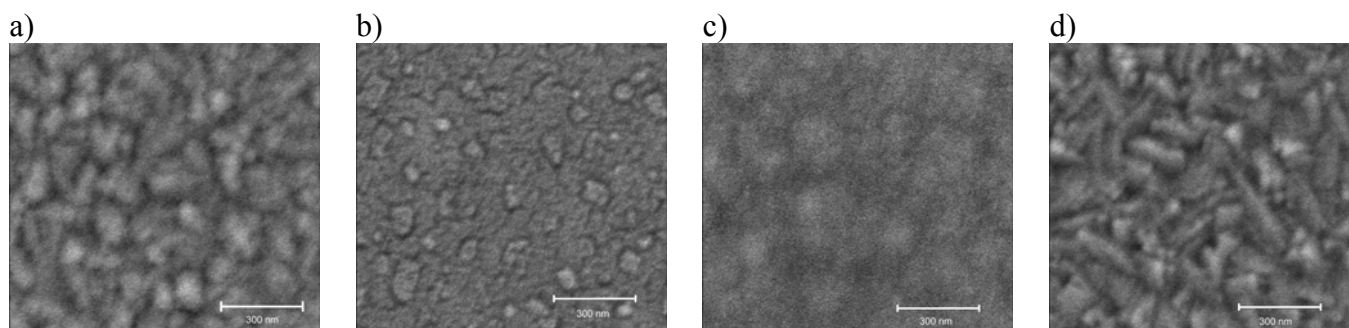


Figure 3. Scanning electron micrographs of doped thin films of polymer (**5**) prepared by potentiostatic electrolysis at +0.30 V vs  $\text{Fc}/\text{Fc}^+$  for 5 min (a), 10 min (b), and 15 min (c), and an ITO surface (d).

Scanning electron micrographs of the electrode surface ( $1.1 \times 1.2 \mu\text{m}^2$ ) in the electrolysis at +0.30 V are displayed in Figure 3. Roughness, which is attributed to the ITO surface as shown in Figure 3d, was

observed in the electrolysis for 5 min (Figure 3a). After treatment for 10 min the dim outline of roughness is seen as shown in Figure 3b. The polymer film was completely formed on the ITO electrode with a flat surface in the electrolysis for 15 min (Figure 3c). These results indicate that the electrochemical synthesis is of great advantage to film formation technology.

Conductivity of doped polymer (**5**) measured by the two-probe method as a compressed pellet was fairly low ( $4.0 \times 10^{-8} \text{ S cm}^{-1}$ ). This result was ascribable to the  $\pi$ -conjugated system of pyrrole and bithiophene without the crosslinked structure [poly(1-methyl-2,5-di-2-thienyl-1*H*-pyrrole):  $\sigma < 10^{-5} \text{ S cm}^{-1}$ ].<sup>11</sup> Investigation for organic devices is under study in addition to selection of  $\pi$ -conjugated systems for network polymers.

## EXPERIMENTAL

**Preparation of Monomer 7.**<sup>8</sup> A solution of 1,4-di-2-thienyl-1,4-butanedione (**6**) (4.00 g, 16.0 mmol), 1,4-diaminobutane (1.06 g, 12.0 mmol), and propionic acid (2 mL) in toluene (100 mL) was refluxed with a Dean-Stark apparatus for 3 days under a nitrogen atmosphere. After cooling, the precipitate was filtered to afford a crude solid (1.82 g). The filtrate was washed with a saturated  $\text{NaHCO}_3$  solution, brine, and water. The organic solution was dried over  $\text{Na}_2\text{SO}_4$  and concentrated. The residue was filtered and washed with methanol to give a solid (0.38 g). The combined solid was purified by column chromatography (silica gel,  $\text{CH}_2\text{Cl}_2 : n\text{-hexane} = 3 : 7$ ) and was twice recrystallized from toluene to afford monomer (**7**) (1.70 g, 41%) as orange needles (lit.,<sup>8</sup> 59% yield). mp 204-205 °C (lit.,<sup>8</sup> mp 198-199 °C).

**Electrochemical Measurements.** Cyclic voltammetry was performed on HOKUTO DENKO Potentiostat/Galvanostat HA-501. The electrochemical measurements were carried out in dry dichloromethane containing 0.1 M *n*- $\text{Bu}_4\text{NClO}_4$  using Pt working and counter electrodes and saturated calomel electrode (SCE) as a reference. The concentration of the sample was 1.0 mM. The solution was degassed by nitrogen bubbling. The scan rate was  $100 \text{ mV s}^{-1}$ . All values are given in V vs  $\text{Fc}/\text{Fc}^+$  (+0.49 V vs SCE).

**Electrochemical Polymerization.** The polymers were prepared by the cyclic voltammetry method and the potentiostatic electrolysis of monomer (**7**) using the above conditions. The resulting polymers on the electrode were washed with dichloromethane. The cyclic voltammograms of the polymers were measured in a monomer-free electrolyte under the same conditions. The potentiostatic electrolysis was performed at applied voltages of +0.28, +0.30, and +0.32 V vs  $\text{Fc}/\text{Fc}^+$ , respectively.

**Scanning Electron Microscope Measurements.** The measurements were performed on HITACHI Field Emission Scanning Electron Microscope Model S-4500 operating at 5 kV of the accelerated voltage. Doped polymer films formed on ITO electrodes were selected and the samples were treated by gold sputter deposition. The micrographs were taken under 100,000 magnifications.

## ACKNOWLEDGEMENTS

This work was supported by a grant from the Yazaki Memorial Foundation for Science and Technology.

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