Electrochemical Synthesis and Properties of Poly[1,4-bis(*N*-pyrrolylalkoxy)benzene]s with a Three-dimensional Crosslinked Structure

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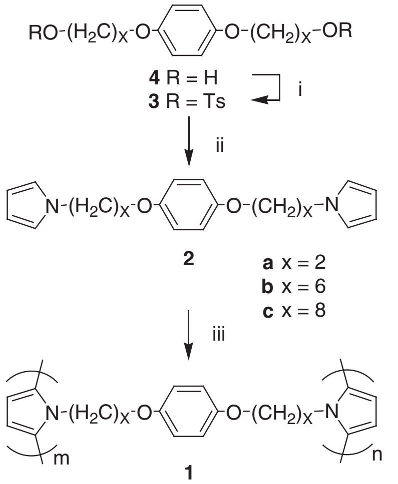
The title polymers, which were composed of π-conjugated pyrroles and dialkoxybenzene crosslinkers, were prepared by electrochemical polymerization to afford uniform thin films. These films were characterized by cyclic voltammetry (CV), scanning electron microscope (SEM), and redox stability.

Much research attention has been focused on development of carrier-transporting materials since they are important for fabrication of organic electroluminescent (EL) devices, whose efficiencies and lifetimes are largely governed by facility of carrier-injection and transportation.[1] Electrical conducting polymers are powerful candidates for these materials, some of which have been already examined, e.g., poly(*p*-phenylenevinylene) (PPV),[2] poly(3,4-ethylenedioxythiophene) (PEDOT),[3] polyaniline,[4] and polypyrrole.[5] However, applications of π-conjugated polymers are very limited because these polymers are insoluble in organic solvents without modification by large alkyl groups[6] and are difficult to prepare uniform thin films due to their highly crystalline properties. In recent papers, polythiophene[7] and tris[4-(2-thienyl)phenyl]amine[8] films accumulated on ITO (indium-tin-oxide) electrodes in electrolysis were applied for hole-transporting layers, which exhibited usefulness of electrochemical synthesis in fabrication of the devices. We have now prepared poly[1,4-bis(*N*-pyrrolylalkoxy)benzene]s (**1**), which are composed of π-conjugated pyrroles and dialkoxybenzene crosslinkers, by electrochemical polymerization of monomers (**2**) to afford thin films on ITO electrodes. We report here the electrochemical synthesis of **1** and properties of the obtained films.

Monomers **2a-c** were prepared in 39-60% yields by reactions of pyrrole anions with ditosylates (**3a-c**), which were derived from alkanediols (**4a-c**) (Scheme 1). Compounds **2** were obtained as colorless crystals after recrystallization (**2a**: mp 98-101 °C, **2b**: mp 48–49 °C, **2c**: mp 62–63 °C) and are stable for air. Cyclic voltammograms of **2a-c** showed irreversible oxidation waves. The oxidation peak potentials in acetonitrile are shown in Table 1. These values are similar to that of *N*-ethylpyrrole (**5**). Introduction of the hydroquinone moiety into 1,2-bis(*N*-pyrrolyl)ethane (**6**)[9] resulted in the higher oxidation potential of **2a**.



Scheme 1. Reagents and conditions: (i) TsCl, Et_3N, Et_3NHCl, CH_2Cl_2; (ii) pyrrole, KOH, DMSO, 65 °C, 5 h; (iii) electrochemical polymerization.

Table 1. Oxidation potentials[a] of monomers **2** and polymers **1** and onset potentials[a] for polymerization

Monomer	E_{pa}	E_{onset}	Polymer	E_{pa}
2a (x = 2)	0.88	0.66	**1a**	0.19
2b (x = 6)	0.80	0.61	**1b**	0.19
2c (x = 8)	0.81	0.61	**1c**	0.23
5	0.83	0.66	**7**	0.24
6	0.70	0.47	**8**	−0.17

[a] 0.1 M *n*-Bu_4NClO_4 in MeCN, Pt electrode, scan rate 100 mV s^{-1}, V vs Fc/Fc$^+$.

Polymers **1a-c** were prepared by electrochemical synthesis using a Pt disk (ϕ 1.6 mm) or ITO ($10\,\Omega/\square$, 12 × 8 mm^2) as a working electrode in acetonitrile containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. Minimum potentials (E_{onset}) for the polymerization were surveyed (Table 1) and the shifts from the peak potentials of monomers (E_{pa}) were almost −0.2 V. These conditions were employed for the CV method and the potentiostatic electrolysis. The oxidation potentials of polymers **1** are not dependent on the used electrodes (Pt, ITO) and are summarized in Table 1. The values are comparable to that of poly(*N*-ethylpyrrole) (**7**)[10] and are higher than that of poly[1,2-bis(*N*-pyrrolyl)ethane] (**8**).[9] Dependence of the oxidation potentials with chain length (x) was not observed in contrast to those of bis(*N*-pyrrolyl)alkane homopolymers. The cyclic voltammograms of polymer **1b** measured at various scan rates are displayed in Figure 1. 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.[11] The linear relationship was also observed in the CVs of **1a** and **1c**.

The potentiostatic electrolysis in 1.0 mM solutions of monomers **2** afforded thin films of **1a-c** with fine smooth surfaces on the ITO electrodes although the surface of poly(*N*-

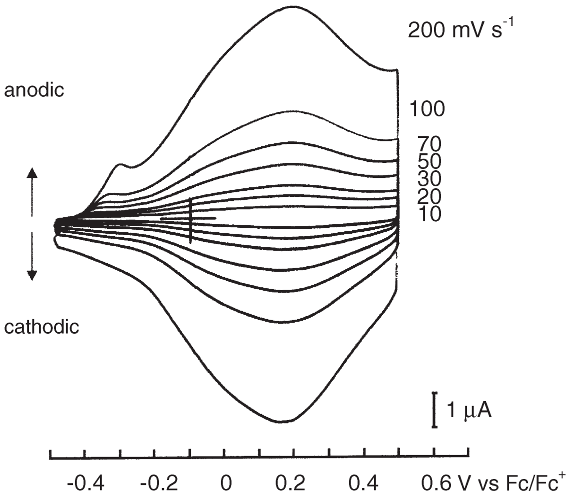


Figure 1. Cyclic voltammograms of polymer **1b** measured in a monomer-free MeCN/0.1 M n-Bu_4NClO_4 electrolyte at various scan rates under a nitrogen atmosphere. Pt electrode, Pt wire, Ag/Ag$^+$ were used as the working, counter, and reference electrodes, respectively.

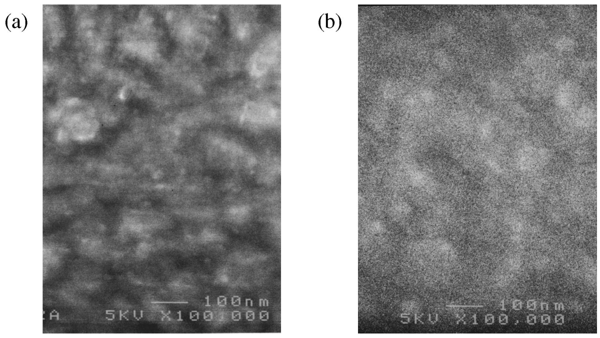


Figure 2. Scanning electron micrographs of doped thin films of polymers **1a** (x = 2) (a) and **1b** (x = 6) (b).

ethylpyrrole) **7** was rough, indicating that network structures of polymers **1** were effective for forming uniform layers. Scanning electron micrographs of polymers **1a** and **1b** were observed (Figure 2). The surface of **1b** is almost flat in the range of $800 \times 600\,nm^2$ in comparison with that of **1a**. This fact revealed that the flexible network prepared by the longer alkyl crosslinkers was superior to formation of the fine films. Thickness of the thin films was able to be controlled by electrolysis time. According to a SEM analysis of polymer **1b**, the thickness of the doped films was evaluated as *ca.* 50 nm in electrolysis for 1 min, 200 nm for 5 min, and 350 nm for 10 min.

Polymers **1** were easily dedoped by electrolysis at −0.5 V vs Fc/Fc$^+$ to afford colorless or pale yellow films, which were stable for air. The dedoping time changed depending on thickness of the films. For example, dedoping the film of **1b** with thickness of 200 nm was completed in 60 min. The redox stability of dedoped polymers **1** was also investigated by CV cycles at scan rate of 100 mV s^{-1}. Figure 3 shows current densities at oxidation peak potentials as the cycle number increases. The peak current densities of **7** and **8** significantly decreased with increasing CV cycles. On the other hand, oxidation deteriorating was not appreciably observed in **1b**, indicating that modification of crosslinker in the network structure was highly effective for stabilization of the redox cycles in the application as electronic materials.[12]

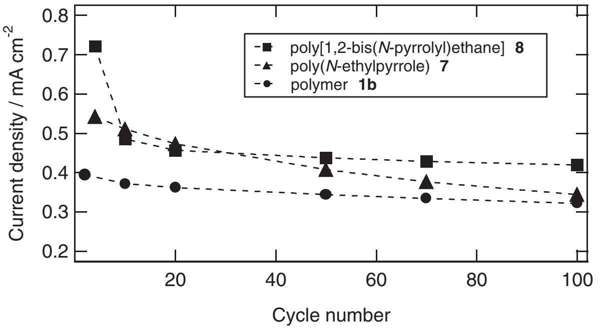


Figure 3. Peak current densities at oxidation peak potentials of dedoped polymers with increasing number of CV cycle at scan rate of 100 mV s^{-1}.

Conductivities of doped polymers **1a-c** measured by a two-probe method as a compressed pellet were 8.4×10^{-8}, 3.0×10^{-7}, and $1.7 \times 10^{-7}\,S\,cm^{-1}$, respectively. These values were lower than that of poly[1,2-bis(*N*-pyrrolyl)ethane] (**8**) ($4.7 \times 10^{-4}\,S\,cm^{-1}$).[9] This was due to increase of an insulating moiety by introduction of the hydroquinone unit as well as morphological change. Improvement for highly conducting materials is under study.

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