Preparation of a Polymer with Limited π-Conjugation Length: A Polymer Containing Quaterthiophene Units

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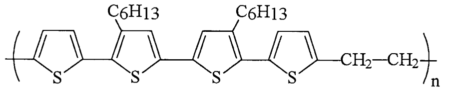
A polymer containing quaterthiophene units in the main chain was prepared by electrochemical polymerization of 1,2-bis(3'-hexyl-2,2'-bithiophene-5-yl)ethane. The obtained green film had a conductivity of 2 x 10^{-2} S cm^{-1} in oxidized states and was neutralized by immersing in methanol. The cyclic voltammograms of the neutral film showed only an oxidation process in the first cycle.

π-Conjugated polymers have attracted considerable attention because of their possible application in electronic and optical devices. Polyalkylthiophenes were prepared by chemical[1a] and electrochemical methods,[1b,c] had electric conductivities of $4x10^{-1}$ and $1x10^{0}$-$5x10^{2}$, respectively. The preparation of soluble conjugated polymers such as poly[3-(long alkyl)thiophenes] progressed the understanding of the properties on the polymers.[2] NMR measurements of the poly(alkylthiophenes) showed that the polymers contained approximately 25 mole-% head-to-head configuration, indicating that the effective conjugation length is limited by twist of the polymer chain.[3] Recently, several researchers prepared oligothiophenes that have well-defined structures and found the interesting properties.[4] The electrical and optical properties of the π-conjugated polymers depend on their electronic structures, which are influenced by the conjugation length. In this report, we show the electrochemical preparation of poly[(3',4"-dihexyl-2,2':5',2":5",2'"-quaterthiophene-5,5'"-diyl)ethylene] **1** possessing limited conjugation length in the main chain and their properties.



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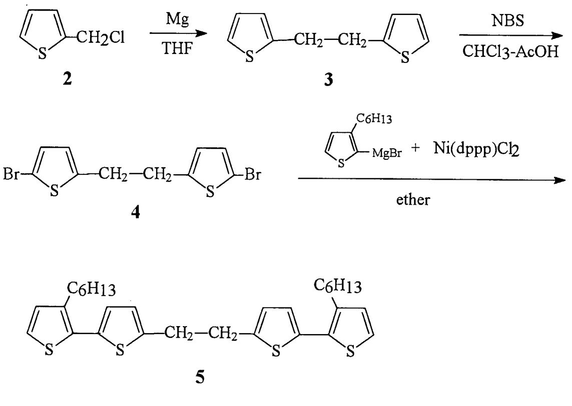

The monomer, 1,2-bis(3'-hexyl-2,2'-bithiophene-5-yl)ethane **5**, was prepared as follows. 2-Chloromethylthiophene **2**[5] was treated with magnesium in tetrahydrofuran (THF) to give 1,2-dithienylethane **3**. Compound **3** was brominated with N-bromosuccinimide (NBS) in a mixture of chloroform and acetic acid (AcOH) to give the corresponding dibromide **4**, which was coupled with 3-hexyl-2-thienyl magnesium bromide in the presence of dichloro[1,3-bis(diphenylphosphino)propane] nickel (II) ($Ni(dppp)Cl_2$) in ether to give **5** as a pale yellow viscous liquid. All structures were ascertained by ^1H NMR and IR spectroscopies and mass spectrometry.

The electrochemical vessel consisted of an one-compartment cell equipped with a platinum plate as the cathode and an indium-tin oxide conducting glass plate for spectroscopic measurements or a polished platinum disk electrode (s = 0.024 cm^2) for cyclic voltammetry as the anode. The electrochemical polymerization was performed at a constant current density of 2 mA cm^{-2} under a nitrogen atmosphere and continued until the charge reached 0.36 C cm^{-2}. Nitrobenzene was used as solvent. The concentration of the monomer **5** and electrolyte (Et_4NPF_6) were 0.1 and 0.025 mol dm^{-3}, respectively. An obtained film was green in color and had the conductivity of 2 x 10^{-2} S cm^{-1}. This value is comparable to those of all-conjugated copolymers composed of thienylene and ethylene units, 10^{-1} ~ 10^{-6} S cm^{-1},[6] and higher than those of vinyl polymers containing oligothiophenes as pendant groups, 10^{-5} ~ 10^{-8} S cm^{-1}.[7] Analysis for sulfur and phosphorous indicated that an as-grown film contained 2.1 unit of dopant per repeating quaterthienylene unit. A neutral, undoped, film obtained by immersing an as-grown film in methanol was yellow in color and showed the conductivity of less than 10^{-8} S cm^{-1}. Contrary to expectation, the neutral film was insoluble in organic solvents such as chloroform, benzene, and hexane. IR spectrum of the neutral film indicated that the polymer was identified with **1**.[8]

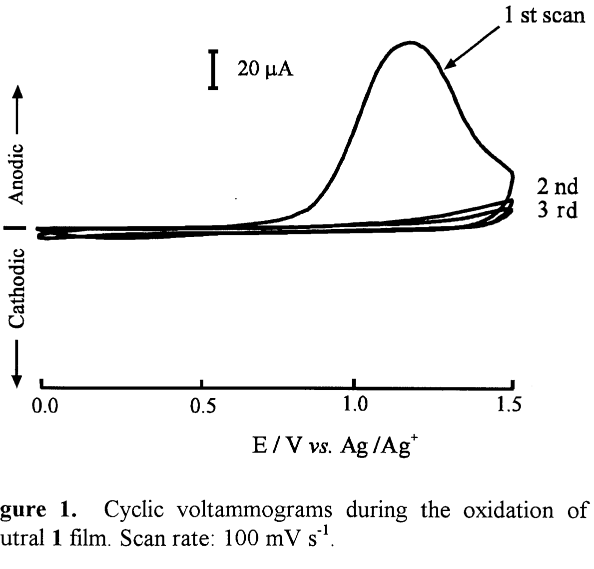

Figure 1. Cyclic voltammograms during the oxidation of a neutral **1** film. Scan rate: 100 mV s^{-1}.

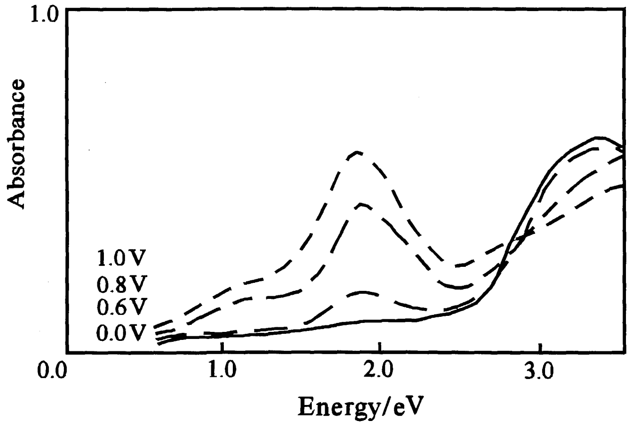

Figure 2. Spectral change of a neutral **1** film during electrochemical oxidation. Applied voltage is shown on the left.

The polymer film was synthesized in nitrobenzene with charge 0.12 C cm^{-2} and then neutralized by use of methanol for cyclic voltammetry. Figure 1 shows the cyclic voltammograms of the **1** film on a platinum disk in acetonitrile solution containing 0.1 M Et_4NPF_6. The cyclic voltammograms of the monomer **5** in acetonitrile displayed an anodic peak at 1.45 V *vs* Ag/Ag^+ with a shoulder at 0.95 V and no cathodic peak. In the first cycle of the **1** film, a distinct anodic peak at 1.2 V and no cathodic peak, an irreversible redox peak, was observed. The oxidation process was accompanied by the color change to green. Consecutive cycles of the oxidized film show that the film is hardly electroactive. Immersing of the film in methanol caused it to reactivate and show similar cyclic voltammograms in about 90 % of the original peak strength.

The change in visible-near IR spectra of the neutral film during electrochemical oxidation, doping, is shown in Figure 2. In the neutral state, only a π–π^* transition was observed at 3.2 eV. The value is higher than that of π–π^* transition observed in the monomer **5**, 314 nm (3.95 eV), and very close to that in α-quaterthiophene, 391 nm (3.17 eV),[4a] indicating that the obtained polymer has the limited conjugation length as shown in the chemical structure. When a **1** film was electrochemically oxidized, one additional peak, at 1.5 eV, appeared in the gap region and the peak height of the π–π^* transition decreased. This additional peak is similar to that of heavily oxidized α,α'-dimethylquaterthiophene.[9] Several researchers have reported that light oxidation of oligothiophene yielded cation radicals and further oxidation produced heavily oxidized species, such as dications,[10] π-dimmers of cation radicals,[11] or poly(cation radical)s.[12] Therefore, the addition peak yielded by electrochemical oxidation of **1** would be attributed to heavily oxidized species. This presumption was supported by the result of elemental analysis noted above.

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8 **1**: IR (film): 3060, 2960, 2925, 2855, 1530, 1455, 1375, 1040, 835, 795, 725 cm^{-1}; Anal: Found: C = 67.32, H = 6.65 %, Calcd for $(C_{30}H_{36}S_4)_n$: C = 68.65, H = 6.91 %. **5**: IR (KBr): 3105, 3060, 2960, 2925, 2855, 1530, 1460, 1375, 1040, 835, 800, 725, 690, 655 cm^{-1}; Anal: Found: C = 68.21, H = 7.07 %, Calcd for $C_{30}H_{38}S_4$: C = 68.39, H = 7.27 %.

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