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Anodic Oxidation of N-Substituted Dipyrrolyl Linked by Polyether Bridge

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Electroactive polymer containing polyether pseudo-cages has been synthesized by anodic oxidation of 1,11-bis(1,1-pyrrole)-3,6,9-trioxaundecane (I) using acetonitrile (ACN) as solvent and tetrabutylammonium perchlorate (TBAClO₄) as supporting electrolyte. Electrochemical behavior of monomer I and its polymer, poly-I, were studied using cyclic voltammetry (CV) and UV-VIS spectroscopic techniques. Also, a doping/dedoping study was carried out using electron spin resonance (ESR) and UV-VIS spectroscopic techniques. Thermal behavior of the product was studied using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA).

Keywords electrochemical polymerization, N-substituted dipyrrolyl

Introduction

Conducting polymers functionalized with crown ethers and polyether pseudo-cages have attracted great interest due to their complexing properties towards alkaline and alkaline-earth metal cations; therefore, such molecules and their polymers are good candidates for the extraction of metallic cations (1–12). However, polypyrroles functionalized with crown ethers and polyether chains have been studied less. There are some studies on N-substituted dipyrrolyl linked with flexible or rigid spacers (13, 14). Leclerc, Simonet, and their co-workers have synthesized monomers consisting of N-substituted pyrrolyl units linked by flexible polyether spacers (15, 16). They were able to obtain a black conducting polymer film either via constant potential electrolysis (CPE) or galvanostatic electrolysis. It was reported that electroactive poly-I has complexing properties towards Ag⁺ and Co²⁺, especially in its reduced (neutral) form (15, 16). Some properties of the poly-I; CV, electronic conductivity and complexing properties with metallic cations were also reported (13, 15, 16). However, information about its spectroelectrochemical (SPEL), paramagnetism and thermal properties are still lacking.

In this work, the anodic polymerization of monomer I was monitored by using CV and *in-situ* UV-VIS spectroscopic techniques. Furthermore, SPEL, paramagnetic and thermal properties of the resulting polymer films were also studied by conventional methods.

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Experimental

Materials

Monomer I was synthesized according to a procedure already described (15). Condensation of the pyrrole salt with bis [2-(2-chloroethoxy)ethyl]ether is carried out to synthesize the monomer I (Scheme 1).

5 mL of dry DMSO, 3.15 g potassium pyrrole salt and 10 mL of freshly distilled THF are placed in a flask. Bis [2-(2-chloroethoxy)ethyl]ether (2.31 g, 10 mmol) into 8 mL THF is added dropwise under argon. The mixture is left stirring at ordinary temperature overnight. Then, THF was evaporated, water was added and the mixture was treated with ether. The organic phase was washed with water several times, dried over MgSO_4 , and the solvent was evaporated. Finally, a yellowish oily liquid was obtained via column chromatography on silica gel with hexane:ethyl acetate (3:1) as eluent.

1,11-bis(1,1-pyrrole)-3,6,9-trioxaundecane (I): Clear yellowish oil; Yield $\sim 76\%$. $^1\text{H-NMR}$ (400 MHz in CDCl_3) δ/ppm : 3.45–3.47 (m, 8 H), 3.63 (t, $J = 5.6$ Hz, 4 H), 3.94 (t, $J = 5.6$ Hz, 4 H), 5.99 (d, $J = 1.7$ Hz, 4 H), 6.56 (d, $J = 1.7$, 4 H). $^{13}\text{C-NMR}$ (100 MHz in CDCl_3) δ/ppm : 122.22, 109.71, 97.62, 72.81, 72.15, 72.08, 50.95.

Supporting electrolyte, TBAClO_4 , (Aldrich) and solvent, ACN, (Merck) were used without any further purification. Polished platinum electrodes (1.5 cm^2) were used as working and counter electrodes. For SPEL studies, indium tin oxide coated quartz glass (ITO, Delta Tech. 8–12 Ω) was used as working electrodes. Ag-wire was preferred as a reference electrode for CV and electrochemical polymerization.

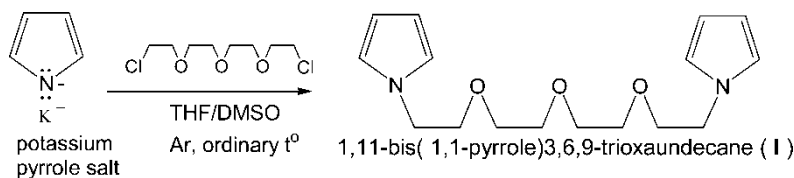
Electrochemical polymerization was achieved by CPE in a three-electrode compartment cell and the resulting polymer films were washed with solvent, peeled off from the electrode surface, and dried under vacuum.

CV and electrochemical syntheses were performed using a IEEE 488 HEKA potentiostat/galvanostat. ESR spectra were recorded on a Varian E12 ESR Spectrometer. FTIR spectra of monomer I and poly-I were taken with a Nicolet 510 FT-IR Spectrometer using KBr. To perform thermal analysis of the polymer films, a DSC 910S/TA 2000 and a Perkin-Elmer Pyres 1TGA system were used. Hewlett Packard 8453A diode array UV-VIS Spectrophotometer was used to record the electronic absorption spectra.

Results and Discussion

Electrochemical Polymerization

Electrochemical behavior of monomer I was investigated using CV in 0.1 M TBAClO_4 dissolved in ACN prior to CPE. During the first anodic scan, between 0.0 and 1.8 V, two oxidation peaks appeared at 1.15 V and 1.40 V vs Ag-wire (Figure 1(a)). However,



Scheme 1. Synthesis of monomer I.

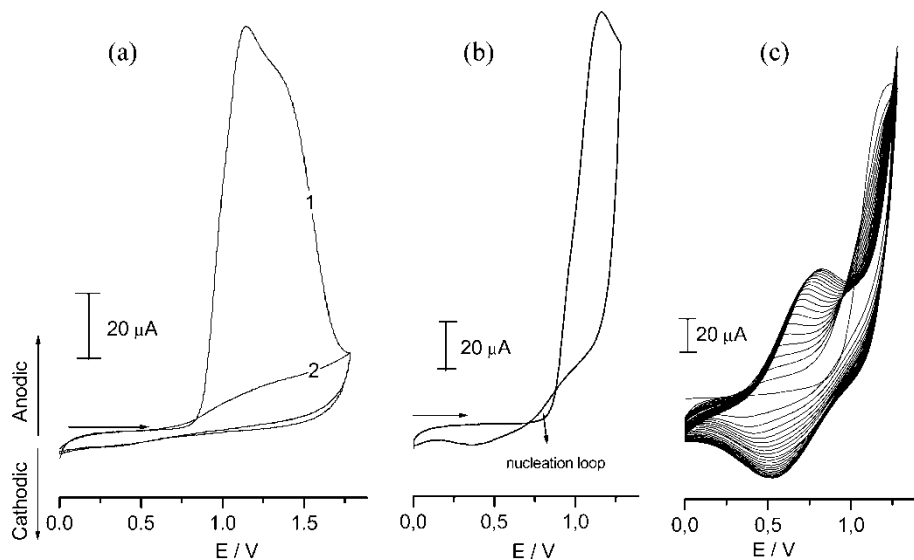


Figure 1. CVs of 3.4×10^{-3} M monomer I recorded in 0.1 M TBAClO₄ dissolved in ACN mixture at rt (a) anodic scan between 0.0 V and 1.8 V (vsr = 100 mV/s), (b) anodic scan between 0.0 V and 1.3 V (vsr = 100 mV/s) and (c) repetitive cycling between 0.0 V and 1.3 V (vsr = 500 mV/s).

during the second scan they disappeared due to passivation of the working electrode. This result clearly demonstrates that the first peak can be assigned to the oxidation of the monomer, leading to formation of oligomer species, and overoxidized oligomeric species at higher potentials (+1.40 V) passivate the electrode surface (17, 18).

Therefore, under the light of this information, the electrode is cycled between 0.0 V and 1.3 V. During the first anodic scan, as shown in Figure 1(b), an oxidation peak appears at 1.15 V. The return scan after monomer oxidation crosses the anodic wave, called the nucleation loop, is evidence for conjugated polymers deposition (19). During the second cycle, a new reversible peak appeared at 0.52 V. It is observed that the intensity of the reversible peak increases during successive anodic scans, which confirms the formation of a conducting polymer film on the electrode surface. Figure 1(c) shows the first 20 anodic scans recorded during the polymerization of monomer I. The polymer coated electrode was rinsed with electrolyte solution and the scan rate dependence of anodic and cathodic peak currents was investigated in a monomer free electrolytic solution. It should be noted that, prior to electrochemical study, all films are switched between oxidized and reduced states several times to stabilize the polymer and to get more reproducible experimental observations.

In the scan rate dependence experiments, the polymer film coated working electrode is cycled between oxidized and reduced states at various scan rates. The anodic and cathodic peak current responses are monitored as shown in Figure 2(a). If the electroactive species is electrode-confined, both the anodic and cathodic current responses will increase linearly with the scan rate. As seen from Figure 2(b), both anodic and cathodic peak current values increase linearly with an increasing scan rate, which indicates that the redox process is non-diffusional and the electroactive polymer is well adhered to the working electrode surface. The separation between oxidation and reduction peaks increases with the scan rate, probably due to the relatively slow formation of polaron or bipolarons.

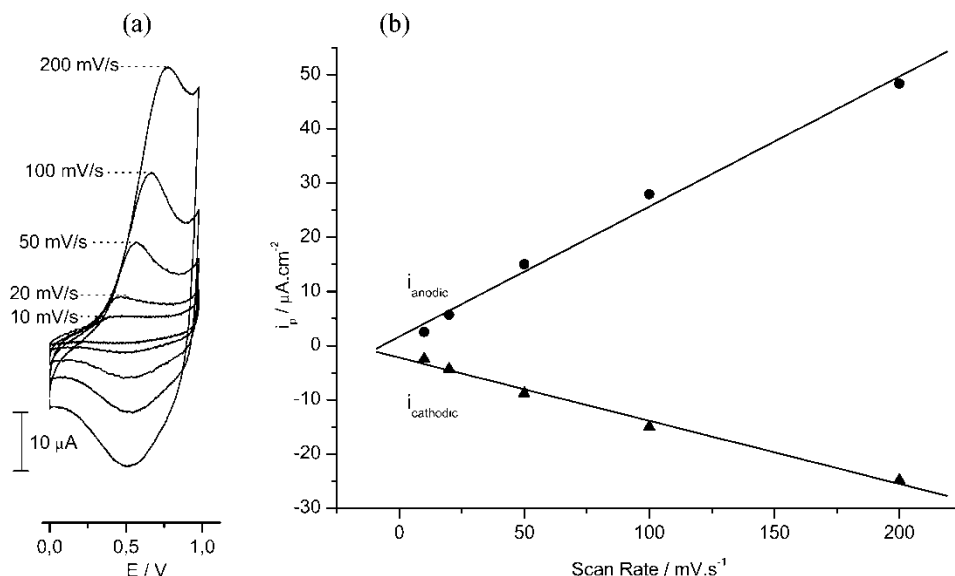


Figure 2. (a) Scan rate dependence for poly-I film in 0.1 M TBAClO₄ dissolved in ACN and (b) Relationship of anodic and cathodic peak currents as a function of the scan rate for poly-I.

Furthermore, monomer I was also polymerized by CPE at 1.1 V/Ag-wire in 0.1 M TBAClO₄/ACN. The bright black film formed at the end of CPE was peeled off from the working electrode surface and dried under vacuum after washing with ACN. The average thickness of the polymer films was measured using a micrometer and found to be 10 μm. The film was characterized using FTIR, UV and ESR spectroscopic techniques.

Polymer Characterization

Characterization of the resulting polymer was carried out using FTIR spectroscopy. Comparison of FTIR spectrum of monomer I (Figure 3(a)) revealed that the absorption bands present in the FTIR spectra of poly I (Figure 3(b) and 3(c)) correspond to the polymer.

The absorption bands attributed to dopant counter ion, ClO₄⁻, are hidden by the polymer etheric bands. In contrast, to check the presence of etheric bridges in the polymer chain, tetrabutylammonium hexafluorophosphate (TBAPF₆) was used as an electrolyte instead of TBAClO₄ due to a specific absorption band of dopant counter ion, PF₆⁻, at about 840 cm⁻¹. Therefore, the absorption bands at 839 cm⁻¹ and 1097 cm⁻¹ confirms the presence of dopant counter ion, PF₆⁻, and etheric bridges in the polymer chain, respectively (Figure 3(c)). The absence of 3099 cm⁻¹ (in monomer I) indicates a 2,5-coupling (Table 1) (14).

Resistance measurement performed on a dry polymer film doped by ClO₄⁻, affords 1.2 MΩ using a two-probe technique. The resistance value did not change in time when the polymer films are left in contact with air.

ESR and SPEL Studies on Poly-I Films

The electronic band gap (E_g) and the intergap states can be revealed using SPEL studies. Electronic absorption spectrum of the polymer film deposited on ITO by CPE at 1.10 V

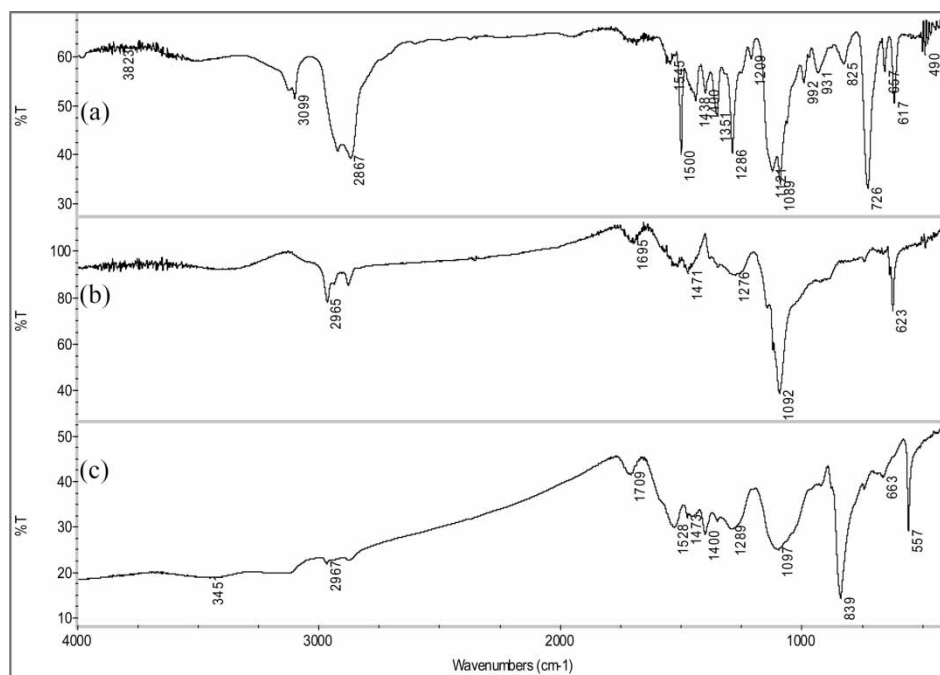


Figure 3. FTIR spectra of (a) monomer I, (b) poly-I/ ClO_4^- and (c) poly-I/ PF_6^- .

(110 mC/cm^2) was monitored with *in-situ* CV (Figure 4(b)). Poly-I forms smooth films on ITO that can be switched between a yellow/green neutral state and a dark green oxidized state. As seen from Figure 4(a), Poly-I exhibits one ill-defined absorption band at 302 nm ($\pi \rightarrow \pi^*$ transition) which loses intensity during the anodic scan from 0.0 V to 1.0 V vs Ag-wire. On the other hand, two new absorption bands at 500 nm (radical cation) and 940 nm (radical cation) intensify during the anodic scan. These bands lose intensity during the reverse scan (1.0 V to 0.0 V).

Table 1

Frequencies (cm^{-1}) and assignments of the principal bands observed for monomer I and poly-I/ ClO_4^- and poly-I/ PF_6^-

| Frequencies (cm^{-1}) | | | |
|----------------------------------|--------------------------|-------------------------|---|
| Monomer I | Poly-I/ ClO_4^- | Poly-I/ PF_6^- | Assignments |
| 3099 | — | — | -CH- (C2,C5 in pyrrole ring) |
| 2923, 2867 | 2965, 2866 | 2967, 2870 | -CH ₂ - |
| 1545 | 1545 | 1546 | -C=C- |
| 1286 | 1276 | 1289 | -N-CH ₂ - |
| 1121, 1089 | 1092 | 1097 | (-CH ₂ -O-CH ₂ -) |
| 839 | — | 839 | PF_6^- |
| — | 623 | — | ClO_4^- |

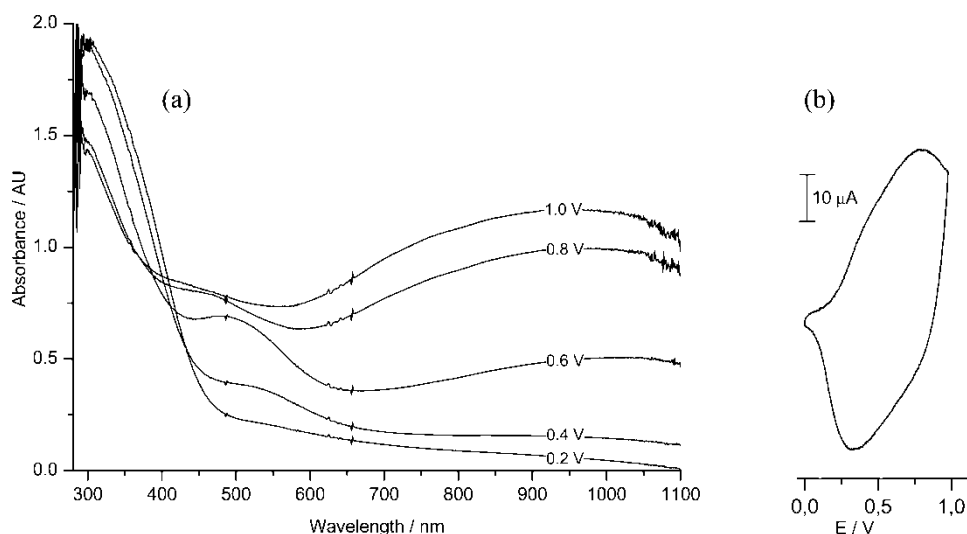


Figure 4. (a) The changes in the electronic absorption spectrum of poly-I film on ITO electrode recorded during the anodic scan from 0.0 V to 1.0 V. (0.1 M TBAClO₄ dissolved in ACN), (b) CV of poly-I coated on ITO electrode recorded in 0.1 M TBAClO₄ dissolved in ACN (vsr = 100 mV/s).

The electronic band gap of the polymer can be estimated from the onset of $\pi \rightarrow \pi^*$ transition in the neutral form. The electronic absorption spectrum of the neutral form of the polymer film exhibits only the 302 nm band and from its commencement on the low energy end, the band gap was found to be 2.8 eV. This value is slightly higher than that of polypyrrole/ClO₄⁻ films (2.6–2.7 eV); and it is consistent with the low conductivity of the polymer film.

Poly-I film exhibits an ESR singlet signal with a Dynosian and asymmetric ($A/B = 1.36$) line. We have monitored the changes in the ESR spectrum of the film during its oxidation (doping) and reduction (dedoping). Poly-I film was coated on a Pt wire (0.5 mm × 2 mm) that was used as the working electrode of the ESR cell. The oxidation and reduction of polymer film was followed in the monomer free solution containing TBAClO₄ as the supporting electrolyte. The film exhibits a singlet signal which intensifies during oxidation with a constant current of 50 μA. Similarly, the ESR signal decreases during the reduction using the same current density (Figure 5), and the same signal starts to intensify immediately upon reversal of polarity (i.e., during oxidation), indicating the reversibility of doping/dedoping processes.

Thermal Stability Measurements

Thermal stability of poly-I was investigated using DSC and TGA. In the DSC thermogram, the polymer film shows two exothermic transitions at 239°C and 372°C. The first exotherm could be due to an organizational process which is accompanied by dopant loss, and during this process, the polymer film starts to decompose slightly, especially in the structure of the polyoxochains. This decomposition mainly appears about at 372°C. On the other hand, TGA was also used to confirm DSC measurement. The TGA

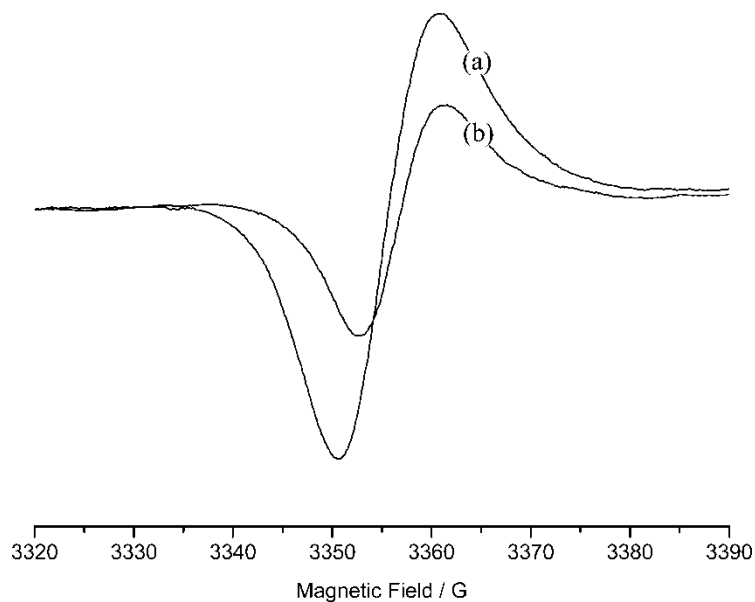


Figure 5. ESR spectra of oxidized poly-I using constant current of $50\ \mu\text{A}$ in $0.1\ \text{M TBAClO}_4$ dissolved in ACN at rt: (a) oxidized form and (b) reduced form.

thermogram (Figure 6) for the polymer shows two maximum weight losses at 235°C and 371°C , which are related to dopant loss and decomposition of polyoxochains, respectively. The polymer losses are about 10% and 42% of its weight at 235°C and 371°C , respectively, and the rest consists mainly of polypyrrole moiety. After 660°C , the polymer completely decomposed.

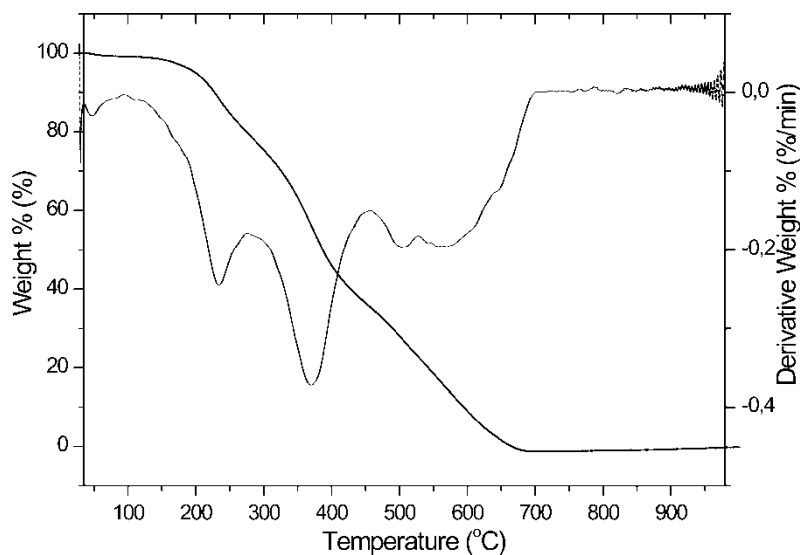


Figure 6. TGA thermogram of poly-I.

Conclusions

In this work, semiconducting polymer films were prepared by electrochemical oxidation of monomer I in a 0.1 M TBAClO₄/ACN mixture at rt. Both ESR and UV-VIS spectroscopic measurements revealed the formation of radical cation during the electrochemical polymerization. UV-VIS and CV measurements confirmed that polymer film on ITO can be reversibly cycled between 0.0 V and 1.0 V. The band gap E_g of the polymer was found to be 2.8eV from electronic absorption spectrum of the neutral form of the film.

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