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Synthesis and Electrochemical Polymerization of 4,7-Di(2-thienyl)indene

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Abstract—4,7-Di(2-thienyl)indene was prepared, and its electrochemical behavior was studied.

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A novel field of molecular electronics involving the use of various organic materials, in particular, conjugated polymers and oligomers, is vigorously developing now. The diversity of such materials and the possibility of varying within wide limits their electrophysical, magnetic, optical, and electrochemical properties by modifying the structure of the monomers make these materials in many cases indispensable and



Scheme.

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Fig. 1. Cyclovoltammograms of DTI in various solvents. $c_{VI} = 10^{-3}$ M, glassy carbon, supporting electrolyte Et₄NClO₄ (0.1 M). (*I*) Current and (*E*) potential; the same for Fig. 2. (a) CH₃CN, $V_{scan} = 50$ mV s⁻¹; (b) CH₂Cl₂ : CH₃CN = 10 : 1, $V_{scan} = 50$ mV s⁻¹; (c) BF₃ · Et₂O : CH₂Cl₂ = 3 : 2, $V_{scan} = 100$ mV s⁻¹.

preferable over inorganic materials.

4,7-Di(2-thienyl)indene synthesized in [1, 2] contained unsubstituted α -positions of thiophene rings, which allowed preparation of the conjugated polymer by both chemical and electrochemical oxidation. Indene–coumarone resins prepared by polymerization of a mixture of the corresponding monomers under the action of AlCl₃ and other Lewis acids are well known in industry. Numerous studies concern electrochemical polymerization of unsubstituted indene [3–12], including its copolymerization with styrene [6], methylstyrene [7], isoprene [8], and methoxystyrene [9]. Preparation and properties of conducting polymeric composites of polyindene and polypyrrole have been reported [11, 12].

In this study we examined the electrochemical behavior of 4,7-disubstituted indene VI, which was



Fig. 2. Cyclovoltammograms of DTI, recorded on different electrodes. Solvent CH₃CN, $c_{VI} = 10^{-3}$ M, supporting electrolyte Et₄NClO₄ (0.1 M), $V_{scan} = 50$ mV s⁻¹. (1) glassy carbon, (2) platinum, and (3) ITO.

prepared as shown below. 1,4-Di(2-thienyl)butane-1,4-dione V was synthesized either by acylation of thiophene in the presence of $AlCl_3$ [13] or by Stetter's method [14]:

The possibility of preparing a polymer from 4,7-di(2thienyl)indene (DTI) **VI** was examined by cyclic voltammetry. The choice of the solvent was governed by the solubility of the components and by the quality of the film obtained. Cyclovoltammograms recorded in the examined solvents in the course of potential variation are shown in Fig. 1. The shape of the cyclovoltammograms depends on the kind of the anode, especially in going to the ITO (indium–tin oxide) electrode (Fig. 2).

The potentials corresponding to the onset of the first oxidation step E_1^{ox} , first peak E_{pa}^1 , onset of the second oxidation step E_2^{ox} , and second peak $E_{\text{p}}^2_{\text{a}}$ are given in the table.

As can be seen, an increase in the fraction of dichloromethane in the solvent (from 0 to 90%) leads to noticeable growth of the potentials of the oxidation onset and peaks. With a mixture of boron trifluoride etherate and dichloromethane (BF₃ · Et₂O : CH₂Cl₂ = 3 : 2) as solvent, the potentials are considerably lower. This fact allows E_1^{ox} to be varied in a fairly wide range

Results of cyclovoltammetric analysis of DTI

Solvent	E_1^{ox}	$E_{\rm pa}{}^1$	E_2^{ox}	$E_{\rm pa}^{2}$
	mV			
CH ₃ CN	950	1100	1150	1260
$CH_2Cl_2: CH_3CN = 10:1$	1009	1192	1202	1351
$BF_3 \cdot Et_2O : CH_2Cl_2 = 3 : 2$	700	911	1047	1181

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Fig. 3. Current efficiency β and thickness *H* of poly-DTI layer as a function of the electric charge *Q* passed through the electrolyte. Pt, CH₂Cl₂ : CH4₃CN = 10 : 1, Et₄NClO₄ (0.1 M), current density *j* = 0.55 mA cm⁻². $c_{VI} \times 10^3$, M: (*1*, *2*) 5 and (*3*) 25.

depending on the medium in which the electrochemical polymerization is performed.

The electrochemical polymerization of DTI in the examined solvents yielded in all the cases a film of a polymer insoluble in common solvents.

We studied the redox stability of the poly-DTI film at cyclic variation of the potential from -1400 to 1400 mV in a pure solvent. The polymer remains stable under these conditions and is doped in the anodic region with the counterion [ClO₄]⁻ ($E_A = 1150$ mV), and in the cathodic region, with tetraethylammonium cation ($E_K = -720$ mV).

In electrochemical polymerization of DTI in the galvanostatic mode, because of low solubility of DTI in acetonitrile and of Et_4NClO_4 in dichloromethane and nonpolar solvents, as the best medium for preparing polymer films we used the mixture CH_2Cl_2 : $CH_3CN = 10$: 1. Figure 3 shows how the thickness *H* of the deposited polymer film and the current efficiency β depend on the amount of the electricity consumed *Q*. As can be seen, with an increase in the charge passed through the electrolyte and in the film thickness, the polymer yield is a function of current decreases, showing the logarithmic dependence. An increase in the monomer concentration does not alter the result.

Figure 3 shows that the thickness of films synthesized in the course of DTI electropolymerization is limited. For the layer with H = 0.04 mm, we determined the resistance in the direction parallel to the film surface, $\rho(||) = 1.8 \times 10^7 \Omega$ cm, and also the resistance in the direction perpendicular to the film surface, $\rho(\perp) = 2 \times 10^3 \Omega$ cm.

The pronounced anisotropy of the electrical properties is due to specific features of the polymer growth in the direction perpendicular to the electrode plane. At a layer thickness of 0.010 mm, the structure becomes loose, which can be seen with an electron micrograph of the surface of a poly-DTI film.

EXPERIMENTAL

The ¹H NMR spectra were recorded with a Varian Mercury plus300 spectrometer, internal reference HMDS. The reaction progress and the product purity were monitored by TLC (Silufol, Kavalier). The reaction mixtures were separated, and the target products purified, on a column packed with silica gel (Lancaster, Silica gel 60, 0.060–0.2 mm). Cyclic voltammograms were taken on an IPC-compact potentiostat–galvanostat (Vol'taProm Limited Liability Company) with an EM-04 electrochemical sensor in a standard three-electrode cell with glassy carbon (or ITO) working electrode, platinum auxiliary electrode (ERL-02), and silver chloride reference electrode (EVL-1M4) at room temperature. The surface of the films was examined with an S-3400N electron microscope (Hitachi).

2-Acetylthiophene was synthesized by acylation of thiophene with acetic anhydride in the presence of H_3PO_4 [15]; 3-dimethylamino-1-(2-thienyl)propanone hydrochloride, by the Mannich reaction [14]; and succinyl chloride, from succinic anhydride [16]. Dimethyl sulfoxide was dried over BaO for 3 days and then distilled in an inert atmosphere from BaO. Cyclopentadiene was prepared immediately before the reaction by cleavage of commercial dicyclopentadiene [17].

4,7-Di(2-thiophen-2-yl)indene VI. To 17 ml of a 30% solution of sodium methylate preliminarily cooled to 0°C, we added over a period of 1 h a solution of a mixture of 8.15 g (32.6 mmol) of 1,4-di(2-thienyl)-1,4-butanedione and 2.9 ml (35.4 mmol) of freshly prepared cyclopentadiene in DMSO. In the process, the temperature was kept in the range from -25 to -10°C. After adding the whole amount of the reactants, the mixture was stirred for 2 h, poured into ice-cold water (300 ml), and extracted with diethyl ether (or CH₂Cl₂). The combined organic extracts were dried over calcined MgSO₄, the solvent was evaporated, and the residue was chromatographed on a column (eluent : hexane : CH₂Cl₂ = 2 : 1). White crystalline substance, yield 30%, mp. 75–76°C. ¹H NMR spectrum (CDCl₃, δ , ppm, *J*, Hz): 3.68 d (2H, <u>CH</u>₂CH=, *J* 1.8), 6.69 and 6.72 dt (1H, =<u>CH</u>CH₂, *J* 2.1), 7.12 and 7.16 two t (2H, 2 thiophene, *J* 3.6), 7.26 and 7.27 dd (1H, thiophene, *J* 3.6), 7.34 and 7.37 m (3H, thiophene + 2 phenyl), 7.40–7.42 dd (1H, thiophene, *J* 3.6), 7.48 and 7.49 (1H, thiophene, *J* 3.3); published data: 3.70 t (CH₂), 6.65 dt (CH=), 7.0–7.5 m (phenyl + thiophene) [1].

CONCLUSION

Films of a conjugated polymer derived from 4,7-di(2thienyl)indene were prepared by electrochemical polymerization on the surface of a working glassy carbon or indium–tin oxide electrode under various conditions. The redox stability of the films was evaluated, the electrical resistivity was measured, and the morphology was determined.

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REFERENCES

- 1. US Patent 5194619.
- Abashev, G.G., Romanova, V.A., and Shklyaeva, E.V., Abstracts of Papers, XVIII Mendeleevskii s"ezd po obshchei i prikladnoi khimii (XVIII Mendeleev Congr. on General and Applied Chemistry), Moscow, January 23–28, 2007, p. 72.

- 3. Bhadani, S.N. and Baranwal, P.P., *Makromol. Chem.*, 1977, vol. 178, no. 4, pp. 1049–1060.
- Bhadani, S.N. and Baranwal, P.P., *Makromol. Chem.*, 1977, vol. 178, no. 9, pp. 2637–2647.
- Akbulut, U., Eren, S., and Toppare, L., J. Macromol. Sci. Chem. A, 1984, vol. 21, no. 3, pp. 335–342.
- Toppare, L., Eren, S., and Akbulut, U., *British Polym. J.*, 1985, vol. 17, pp. 257–259.
- Toppare, L., Eren, S., and Akbulut, U., J. Polym. Sci., Polym. Chem., 1984, vol. 22, no. 11, pp. 2941–2944.
- 8. Khursid, A., Toppare, L., and Akbulut, U., *Polym. Commun.*, 1987, vol. 28, no. 11, pp. 269–271.
- Akbulut, U., Khursid, A., Hacıoğlu, B., and Toppare, L., *Polymer*, 1990, vol. 31, no. 7, pp. 1343–1346.
- Toppare, L., Handbook of Polymer Science and Technology, vol. 1: Synthesis and Properties, Cheremisinoff, N.P., New York: Dekker, 1989, pp. 271– 306.
- 11. Bozkurt, A., Akbulut, U., and Toppare, L., *Synth. Met.*, 1996, vol. 82, no. 1, pp. 41–46.
- 12. Bozkurt, A., Erçelebi, Ç., and Toppare, L., *Synth. Met.*, 1997, vol. 87, no. 3, pp. 219–223.
- 13. Nakazaki, J., Chung, I., Matsushita, M.M., et al., *J. Mater. Chem.*, 2003, vol. 13, no. 5, pp. 1011–1022.
- 14. Wynberg, J.H. and Metsebaar, J., *Synth. Commun.*, 1984, vol. 14, no. 1, pp. 1–9.
- 15. Hartought, H.D., Hochgessang, F.P., and Blick, F.F., *Thiophene and Its Derivatives. Appendix: Laboratory Preparation of Thiophene Compounds*, New York: Interscience, 1952.
- Laosooksathit, S., Chamsuksai, P., Ternai, B., and Dechaboonya, J., *J. KMITNB*, 2003, vol. 13, no. 3, pp. 29–36.
- Wilkinson, G., Organic Syntheses, Blatt, A.H., Ed., New York: Wiley, 1944. Translated under the title Sintezy organicheskikh preparatov, Moscow: Inostrannaya Literatura, 1958, vol. 8, p. 64.