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Electrochromic properties of electrochemically synthesized porphyrin/3-substituted polythiophene copolymers

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ABSTRACT

Porphyrins bearing 2-thienyl substituent were copolymerized with 3-methylthiophene and 3-hexylthiophene by using an electrochemical polymerization method in a tetrabutylammonium hexafluorophosphate/dichloromethane (TBAPF6/DCM) solution. The copolymers were examined with FT-IR, UV–vis spectrometer and cyclic voltammetry analyses. Electrochromic properties of the electrodeposited copolymers were investigated and a rapid and persistent coloration process based on redox reactions of the films was observed. The pale yellow color of thin films switched to gray when anodic potential was applied. Optical contrast at 600 nm was recorded by a spectrophotometer of the solid state devices and their durability was tested by chronoamperometric measurements during 1000 cycles.

1. Introduction

Electrochromic (EC) devices change their optical properties reversibly and persistently under applied DC voltages and have found applications, such as smart windows, optical displays and rear-view mirror [1,2]. A variety of materials such as transition metal oxides (TMOs) and polymers have been studied intensively for last decades to obtain electrically color changing EC devices [3,4]. Compared to TMOs, polymeric materials show superior EC performance because of their multicoloration effect and rapid response time to the applied voltage [5–7]. Moreover, the higher molar absorption potential of the polymers increases the coloration efficiencies of EC devices compared to inorganics [8,9]. Composite polymers [10–13] and copolymers [14–17] were studied in order to further improve EC properties.

Porphyrins have excellent electronic and optical properties because of their large π-electron conjugation system [18,19]. However, EC applications of porphyrin based materials are very limited and need further studies. For instance, electropolymerized triphenylamine substituted porphyrins showed multicolor EC characteristics in a liquid electrolyte medium [20]. In this approach, polythiophene derivatives can be used to improve the EC properties of porphyrins [21–23]. There are many methods to synthesize new conducting materials based polythiophene [24,25]. One of the most convenient methods among them is the direct copolymerization of thiophene monomer with conducting monomers by using either chemical or electrochemical process [26,27]. Electrochemical route is coming forward since it enables easy and fast film forming onto surface of various electrodes [25]. Electrochemical synthesis of thiophene copolymers with various monomers has been reported [28–30]. On the other

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hand, there are only a few studies exist on the co-polymerization of thiophene and porphyrin derivatives. Copolymerizations of bithiophene and porphyrin, bearing thiophene moiety, have been studied recently [31–35]. It was shown that electrochemically synthesized copolymer film of 5,10,15,20-tetra(3-hienyl)porphyrin (TThP) and bithiophene (BiTh) exhibited good efficiency for solar cell application [34]. As another derivate, the alkyl side chain length of alkylthiophene types also provide appropriate molecular structure as well as good electrical and optical properties for the compositions [36,37].

In the present study, four types of copolymers were synthesized by 3-alkylthiophene derivatives (3-methylthiophene and 3-hexylthiophene) and porphyrin monomers (mezo-tetrakis(2-thienyl)porphyrin and mezo-tetrakis(2-thienyl)porphyrin zinc(II)) by using the anodic electrochemical polymerization in the tetrabutylammonium hexafluorophosphate/dichloromethane (TBAPF6/DCM) electrolyte. Currently, the molecular effect of the alkyl side chain in copolymer structures and their EC properties was investigated by potentiometric and spectrophotometric measurements.

2. Experimental

2.1. Materials

3-Methylthiophene (Aldrich, 98%), 3-hexylthiophene (Aldrich, ≥99%), dichloromethane (DCM, ≥%99,5), lithium perchlorate ($LiClO_4$), propylene carbonate (PC), polymethylmetacrylate (PMMA), and acetonitrile (ACN) were purchased from Sigma-Aldrich. Tetrabutylammonium hexafluorophosphate (TBAPF6) was purchased from Alfa-Aesar. All the materials were used as received. Meso-tetrakis(2-thienyl)porphyrin (Por) and meso-tetrakis(2-thienyl)porphyrin zinc(II) were synthesized as described in the literature [38,39].

2.2. General method for preparation of porphyrin/polythiophene copolymers

The porphyrin/polythiophene copolymer films were synthesized by using the electrochemical polymerization method. The experiments were carried out in a typical three electrodes cell in which a glass sheet with deposited indium-tin-oxide (ITO) was used as the working electrode, a platinum wire was used as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. The ITO was cleaned ultrasonically in ethanol and then in DCM before use. The electrochemical experiments were performed with a Gamry PCl4/300 potentiostat/galvanostat. The chemical structures of porphyrin and thiophene monomers are shown in Fig. 1.

A DCM solution containing 2.5 mM Por, 15 mM 3-MT and 0.1 M TBAPF6 was prepared for polymerization. The potential applied to the working electrode was scanned between 0 and +2 V at scan rate of 25 mV s^{-1}. The ITO working electrode was removed from the solution, rinsed thoroughly with the DCM to remove the soluble monomer and oligomers on the film and finally dried in the air to obtain Por/3MT film. The other copolymer films of ZnPor/3MT, Por/3HT, and ZnPor/3HT were fabricated in the same way. The homopolymers of Por,

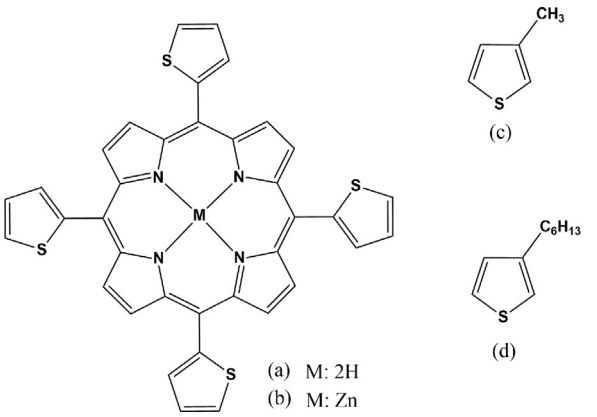

Fig. 1. The chemical structure of porphyrin (a), zinc porphyrin (b), 3-methlthiohene (c) and 3-hexythiophene (d) monomers.

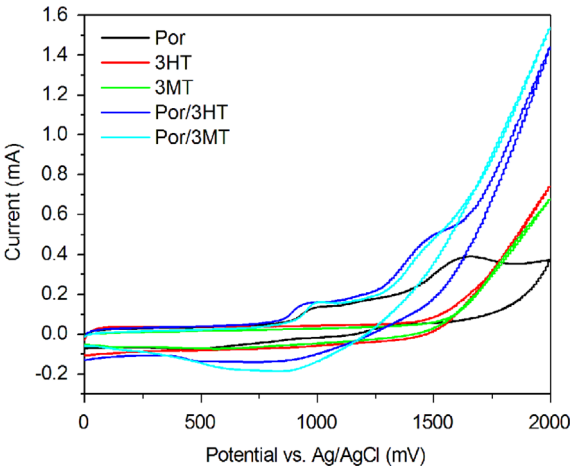

Fig. 2. The CVs of Por, 3HT, 3MT, Por/P3HT and Por/3MT in DCM solution containing 0.1 M TBAPF6. Working electrode: ITO, scan rate: 25 mV s^{-1}.

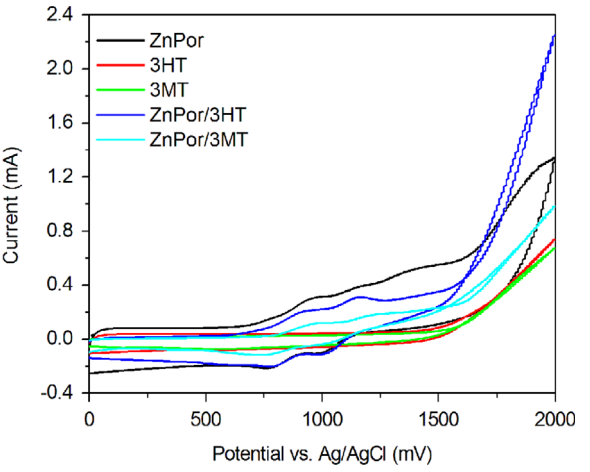

Fig. 3. The CVs of ZnPor, 3HT, 3MT, ZnPor/P3HT and ZnPor/3MT in DCM solution containing 0.1 M TBAPF6. Working electrode: ITO, scan rate: 25 mV s^{-1}.