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The synthesis and characterization of soluble poly(isothianaphthene) derivative: poly(5,6-dihexoxyisothianaphthene)

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Abstract

Poly(5,6-dihexoxyisothianaphthene) (PDHOITN) is synthesized by introducing hexoxy groups on 5 and 6 positions on the repeat unit of poly(isothianaphthene) (PITN) in order to improve its solubility and processability. The PDHOITN film has a band gap of about 0.95 eV and exhibits a high contrast and reversible color change from bluish black at the neutral state to transparent light yellow (close to colorless) at the doped state. Both the neutral and doped states of this polymer can be dissolved in common organic solvents and cast into free standing film. After doping with ferric chloride, the conductivity of the film increases 5×10^{-5} to 2×10^{-2} S/cm. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(5,6-dihexoxyisothianaphthene); Poly(isothianaphthene); Band gap

1. Introduction

Low band gap polymer is one of the important conjugated conducting polymers that possesses moderate intrinsic conductivity at neutral state and therefore is environmentally stable [1]. It can become transparent upon doping due to a shift of the absorption maximum from the UV–vis region to the near infrared region [2,3]. Among the various types of low band gap polymers that have been studied, poly(isothianaphthene) (PITN) is of particular interest because it is one of the lowest energy gap polymers known ($E_g \cong 1.0$ eV). Prepared electrochemically, its film exhibits a high contrast and reversible color change from blue at the neutral state to nearly transparent light greenish-yellow at the doped state [3]. However, practical applications of this polymer have been greatly hindered by lack of solubility in common organic solvents. Its film can only be obtained by deposition on a substrate [3–6]. Recently, stable dispersions of PITN in dichloromethane were obtained as reported in our previous works [7,8]; although a film of PITN can be prepared on an appropriate substrate by casting, its surface is rough and the film can not be peeled off. Pomerantz et al. [9] introduced a decyl group at the 5-position of the isothianaphthene ring to improve its solubility at both neutral and doped states. The poly(5-decylisothianaphthene) (PDITN) is a dark blue-black material soluble in a variety of organic solvents with band gap of 1.0–1.3 eV. Ikenoue et al. [10] introduced the electron-donating group (dioxymethylene group) at the 5- and 6-positions of the isothianaphthene (ITN) ring (i.e., poly(5,6-dioxymethyleneisothianaphthene), PDOMITN) and found that, after doping, it exhibits an improved environmental stability over the doped PITN; however, this polymer is still insoluble.

In this work we introduce the electron-donating substituent with long alkyl length, hexoxy group, on 5- and 6-positions of the isothianaphthene ring in order to obtain a low band gap polymer soluble in both neutral and doped states. It is also hoped that, after doping, the polymer might appear light in color and transparent (or close to colorless), as it actually is.

2. Experimental section

The synthetic route of poly(5,6-dihexoxyisothianaphthene) is shown in Fig. 1. A solution of 1,2-dihydroxybenzene (22.0 g) and sodium methoxide (25.0 g) in dry ethanol (350 ml) was purged with dry nitrogen gas, stirred at room temperature, and then 1-bromohexane (70.0 g) added dropwise into the solution. The mixture was heated to and maintained at 75°C with stirring to allow reaction for 24 h. The resulting mixture was further subjected to extraction with ether/deionized (DI) water (1:1 volume ratio). The organic layer was dried over Na_2SO_4 and filtered.

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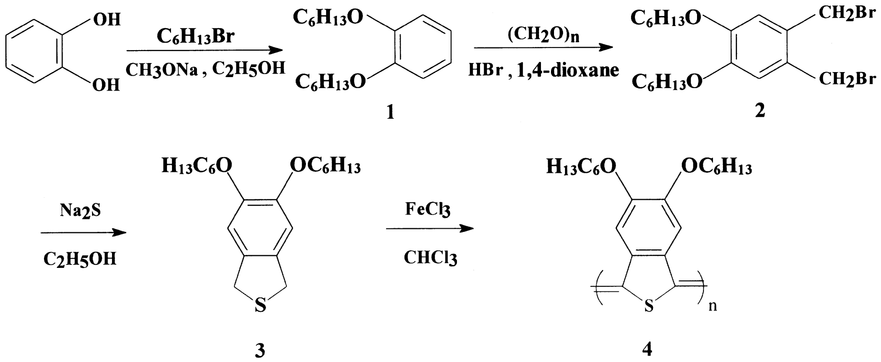

Fig. 1. Synthetic scheme for poly(5,6-dihexoxyisothianaphthene).

Recrystallization from ethanol gave pure 1,2-dihexoxybenzene (**1**) [11]. A solution of compound **1** (6.95 g) and paraformaldehyde (5.00 g) in 1,4-dioxane (90 ml) was purged with dry nitrogen gas and then HBr added (42.5 ml) to allow reaction at 75°C for 72 h, during which paraformaldehyde (3.0 g) and HBr (30 ml) were added at each 24 h interval. For all stages, gaseous HBr was introduced by bubbling through the reaction mixture. After the reaction was completed, the precipitate was collected and then recrystallized from *n*-hexane to give 1,2-bis(bromomethyl)-4,5-dihexoxybenzene (**2**) [12]. To a stirred solution of Na_2S (2.0 g) in dry ethanol (250 ml), compound **2** (2.6 g) in dry ethanol (150 ml) was added dropwise over a 2 h period at 70°C. After stirring for 3 h, the solvent was removed, double extracted with $CHCl_3$ (50 ml), washed with DI water (twice with 50 ml), dried over Na_2SO_4 and filtered. Recrystallization from *n*-hexane gave 1,3-dihydro-5,6-dihexoxyisothianaphthene (**3**) [13]. The chemical polymerization of compound **3** with an oxidizing agent, $FeCl_3$, was carried out essentially according to the procedure for the polymerization of DHITN described in the literature [14]. To a solution of compound **3** (0.5 g) in dry chloroform, a solution of anhydrous $FeCl_3$ (0.25 g) in dry chloroform was added at room temperature. The resulting solution was stirred for about 5 h at room temperature, then poly(5,6-dihexoxyisothianaphthene) (**4**) in doped state in chloroform was obtained, which can be cast into free standing film. The bluish black poly(5,6-dihexoxyisothianaphthene) powder was obtained by reprecipitation with methanol, then successive Soxhlet-extraction with methanol and acetone to remove residual oxidant and oligomers. After dedoping with hydrazine, poly(5,6-dihexoxyisothianaphthene) in neutral state was obtained, which can be dissolved in a variety of organic solvents, including $CHCl_3$, to give a bluish black solution.

Table 1
Assignment of the main peaks in the IR spectrum of neutral poly(5,6-dihexoxyisothianaphthene)

Wavenumber (cm^{-1})	Assignment
1022,1096	Alkyl C–O–benzene str.
1221	Aromatic C–O str.
1256	Aromatic C–O str.
1285	Aromatic C–O str.
1386	v6 thiophene ring deformation absorption
1601	Benzene C=C str.
2927	C–H str. of O–CH_3

3. Results and discussion

Structural characterization of poly(5,6-dihexoxyisothianaphthene) (PDHOITN) was carried out by means of infrared spectroscopy, elemental analysis and ^1H NMR. Table 1 shows the assignment of the main peaks of the IR spectrum of PDHOITN. Elemental analysis indicates an empirical formula of $(C_{20}H_{28}S_{0.97}O_2)\cdot(H_2O)_{0.41}$, which is very close to the theoretical formula of PDHOITN, $(C_{20}H_{28}S_1O_2)\cdot(H_2O)_x$. The ^1H NMR ($CDCl_3$) spectrum of PDHOITN is shown in Fig. 2, where the assignment of the different protons is also shown. These results support that the PDHOITN so prepared is in agreement with its theoretical structure.

Gel permeation chromatography (GPC) analysis on the PDHOITN with chloroform as eluent shows $\bar{M}_n = 40\,870$ and $\bar{M}_w/\bar{M}_n = 1.57$ relative to the polystyrene standards, which corresponds to a degree of polymerization (DP) of approximately 123.

The thermal stability of PDHOITN under nitrogen atmosphere as determined by thermogravimetric analysis (TGA) shows that the onset of the weight loss is at about 200°C, which is the same as that of PITN [3]. As the scanning temperature reaches 300°C, less than 10% weight loss was observed; at 600°C the weight loss is about 50%. These values are higher than those of PDOMITN (8% and 35%, respectively) [10].

Fig. 3a shows the UV–vis–near-IR spectrum of the present neutral PDHOITN film coated on quartz. As can be seen, an absorption maximum at 717 nm is observed, which can be ascribed to the π–π^* transition in the conjugated backbone, and the band gap determined from the band edge at about 1310 nm is 0.95 eV. The dark blue PDHOITN film after doping with $FeCl_3$ in methanol becomes a light yellow transparent film. It has an absorption peak at about

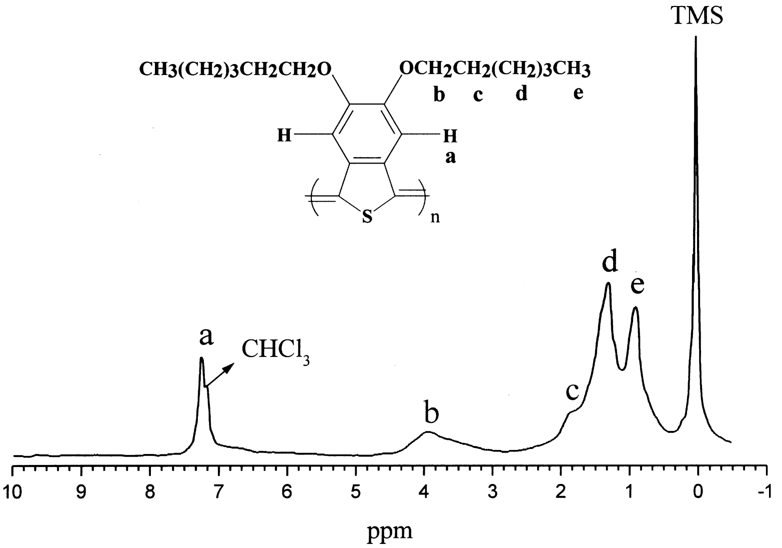

Fig. 2. ^{1}H (at 300 MHz) NMR spectrum of poly(5,6-dihexoxyisothianaphthene) in $CDCl_3$.

1380 nm (Fig. 3b) due to the formation of polaron/bipolaron in the conjugated backbone, while the peak at 717 nm of the neutral state disappears. The PDHOITN in chloroform after doping with $FeCl_3$ (at the amount of 0.2 equivalent based on the monomer unit) yields an absorption peak at 1800 nm (Fig. 3c) arising from the polaron/bipolaron in the conjugated backbone. The solution-cast films obtained from this doped solution show the expected red shift, an absorption maximum at 1995 nm (Fig. 3d).

In comparison with the soluble PITN modified with a decyl group at the 5-position of the ITN ring (PDITN) [9], the present soluble PDHOITN with the dihexoxy groups at the 5- and 6-positions of the ITN ring has a lower band gap and longer λ_{max} than the former ($E_g \cong 1.0 \sim 1.3$ eV and $\lambda_{max} = 512$ nm). After doping, the λ_{max} of PDHOITN (1995 nm) is much longer than that of PDITN (870 nm), indicating that the PDHOITN has lighter color (or is more close to colorless). Thus PDHOITN is more suitable for use as a conductive coating where colorless transparent is required.

The dc conductivity of the neutral PDHOITN film measured by the four-probe technique at room temperature is 5×10^{-5} S/cm. This polymer, after doping with $FeCl_3$ in $CHCl_3$, and then casting into free standing films, has a conductivity of 2×10^{-2} S/cm.

In conclusion, the introduction of dihexoxy groups at the 5- and 6-positions of the ITN ring in PITN provides a light color (close to colorless transparent) conductive film after doping, in addition to the improved solubility in both neutral and doped states.

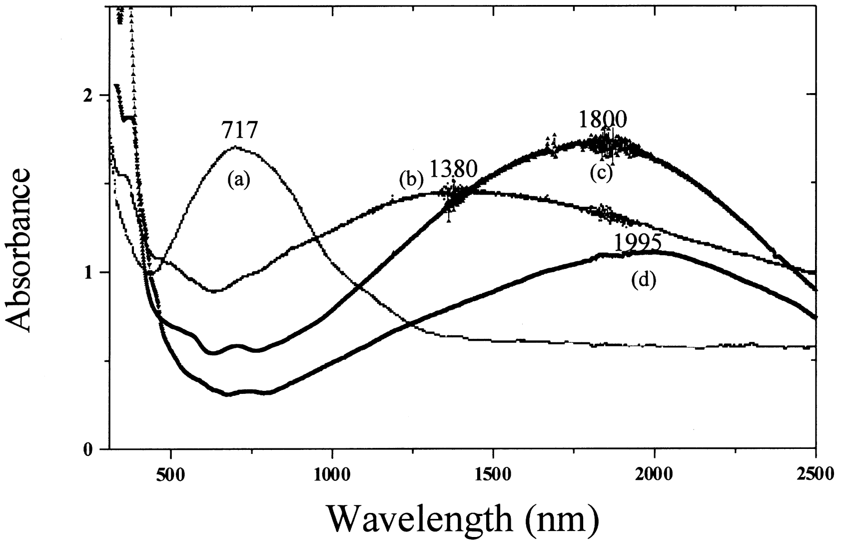

Fig. 3. UV–vis–near-IR spectrum of poly(5,6-dihexoxyisothianaphthene) at room temperature: (a) neutral film coated on quartz; (b) film doped with $FeCl_3$ in methanol; (c) $FeCl_3$-doped form in chloroform; (d) solution-cast film from the doped solution.

Acknowledgements

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