

# A Robust Low Band Gap Processable n-Type Conducting Polymer Based on Poly(isothianaphthene)

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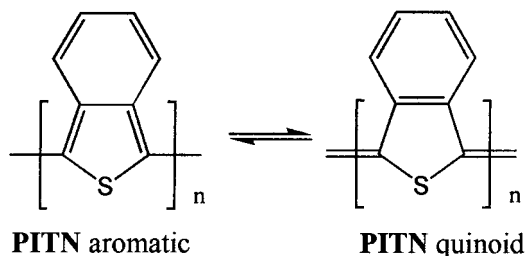
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**ABSTRACT:** The novel macromolecule, poly(benzo[*c*]thiophene-*N*-2-ethylhexy-4,5-dicarboxylic imide) (EHI–PITN), has been designed and synthesized. The polymer has a well-defined structure which was characterized by FTIR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopies, and elemental analysis. TGA analysis indicates that the polymer has good thermal stability with an onset decomposition temperature of about 328 °C ( $\text{N}_2$  atmosphere). The  $T_g$  of the polymer is about 256 °C. The optical properties of the conjugated polymer led to the conclusion that the band gap of EHI–PITN is ca. 1.24 eV, which is comparable with the parent PITN and its derivatives. The data are also supported by the value obtained from cyclic voltammetry. The electrochemically determined HOMO energy is 4.88 eV, and the LUMO energy is 3.59 eV. These values are comparable with those of the work functions of ITO and Mg/Ag, suggesting that EHI–PITN should find many organic electronic device applications.

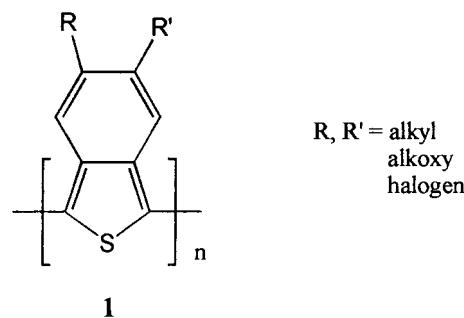
## Introduction

Low band gap conducting polymers have received increased attention due to their intrinsic physical properties.<sup>1–3</sup> These polymers are expected to be promising candidates for industrial applications.<sup>4</sup> In fact, a low band gap conducting polymer (PEDOT, Baytron) is now being commercialized. Among all the efforts toward the design of low band gap conducting polymers, poly(isothianaphthene) (PITN), which was initially developed by our group and whose band gap ( $E_g = 1.1$  eV) is about 1 eV lower than that of polythiophene (PT), was the first approach to the prototype of low band gap polymers.<sup>1</sup> Both theoretical and experimental research showed that the reduced band gap of PITN is caused by the intrinsic structure of the polymer backbone which tends to stabilize the electronic quinoid state:<sup>5–8</sup>



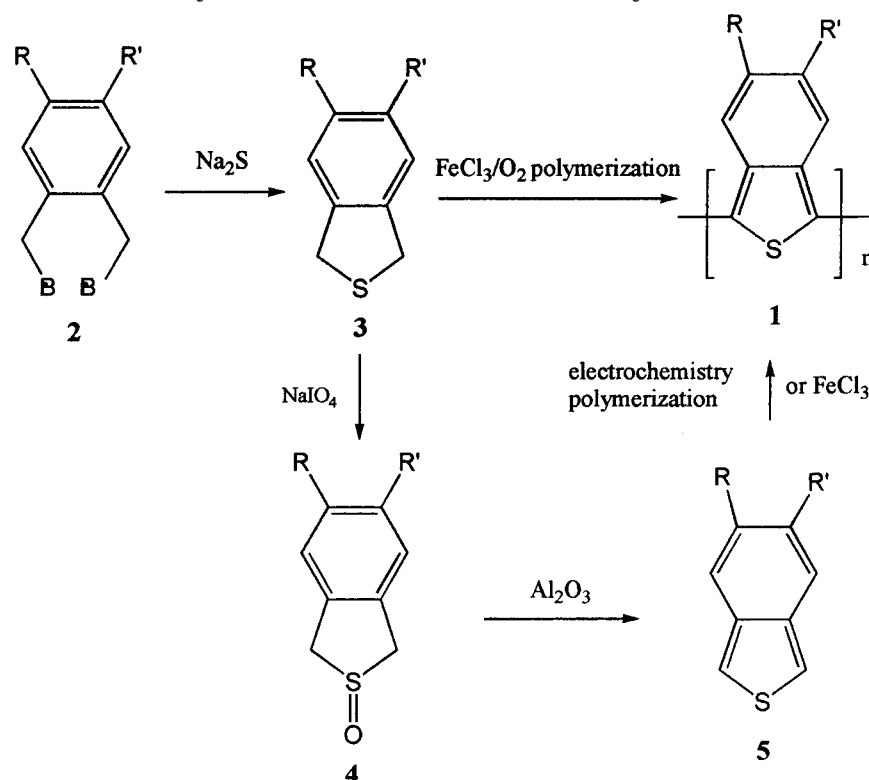
Since the first report of the small band gap conducting polymer, PITN, many publications related to the modification of its chemical structure, as well as on other polymers representing structural variations on the isothianaphthene theme, have appeared.<sup>9–11a</sup> These efforts were motivated by the desire to achieve further reduction of  $E_g$  and the development of soluble polymers.

The band gaps achieved by these soluble polymers are in the range comparable with PITN (1.0–1.4 eV). Not surprisingly, the electrochemical properties of the polymers depend on the substituents. For example, in polymer **1**, the oxidation potential was lowered compared with the parent polymer by introduction of an electron-donating group. Concomitantly, the reduction potential was shifted to more negative potentials. Since



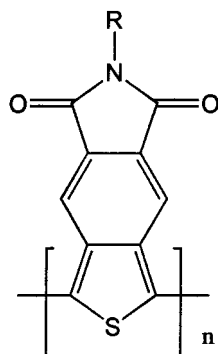
the monomer/polymer is easily oxidized (i.e., typical p-type conducting polymer), the stability of the monomers and polymers is rather poor.<sup>12</sup> Introduction of an electron-withdrawing group, such as halogen, indeed produced the reverse effect: an increase in the oxidation potential and decrease in the reduction potential. However, the expected reduction of the band gap was not confirmed by the electronic absorption, giving an optical band gap of 2.1 eV. Clearly, chemical modification of the PITN structure toward the design of n-type conductive polymers with improved stability, while keeping a low band gap, is still a challenge to chemists. As mentioned above, various modified PITN structures have been achieved, but few explorations have been devoted to synthetic methodology. To this day, the synthesis of PITN-derived polymers (**1**) is based on the synthetic route to PITN depicted in Scheme 1.

In addition, as indicated in Scheme 1, monomer polymerization to **1** can be achieved either by direct chemical polymerization of dihydroisothianaphthene (route a: from **3** to **1**) or by electrochemical/chemical polymerization of isothianaphthene monomers (route b: **5** to **1**). Results from our laboratory in the recent past showed that, compared with route a, route b produces higher molecular weight polymer with a lower band gap. So far, the reported processable PITN polymers were synthesized via route a, probably because the required monomers (**5**) are difficult to obtain or are rather unstable. Consequently, new methods toward the design and synthesis of stable monomers needed to be consid-

Scheme 1. Synthetic Routes to Monomer and Polymer EHI-PITN<sup>a</sup>

<sup>a</sup> Reagents and conditions: (i) ether, reflux 99%; (ii) 2-ethylhexylamine, DMF, Ac<sub>2</sub>O, Et<sub>3</sub>N, reflux, 98%; (iii) S<sub>8</sub>, 200–210 °C, 80%; (iv) NBS, CCl<sub>4</sub>, *hν*, 70%; (v) Na<sub>2</sub>S·9H<sub>2</sub>O, EtOH, 25 °C then reflux for 2 h, 61%; (vi) *m*CPBA, CHCl<sub>3</sub>, –20 °C, 88%; (vii) TMSCl, *i*-Pr<sub>2</sub>NEt, 25 °C then reflux for 3 h, 90%; (viii) FeCl<sub>3</sub>/CHCl<sub>3</sub>, 50 °C for 48 h, 70–80%. R = 2-ethylhexyl.

ered. Here we describe the design and synthesis of the novel PITN derivative EHI-PITN as shown:



EHI-PITN (R = 2-ethylhexyl)

We introduced the electron-withdrawing imide group to change the HOMO and LUMO energy of the molecule and consequently stabilize the n-doped form of PITN. The attached long chain on the imide N atom was expected to improve the solubility of the polymers. Because the imide moiety is planar and relatively remote from the backbone, it was expected to afford only a very minor perturbation to the PITN backbone geometry. Thus, we anticipated that EHI-PITN should have more favorable physical properties than PITN itself.

### Synthetic Strategy

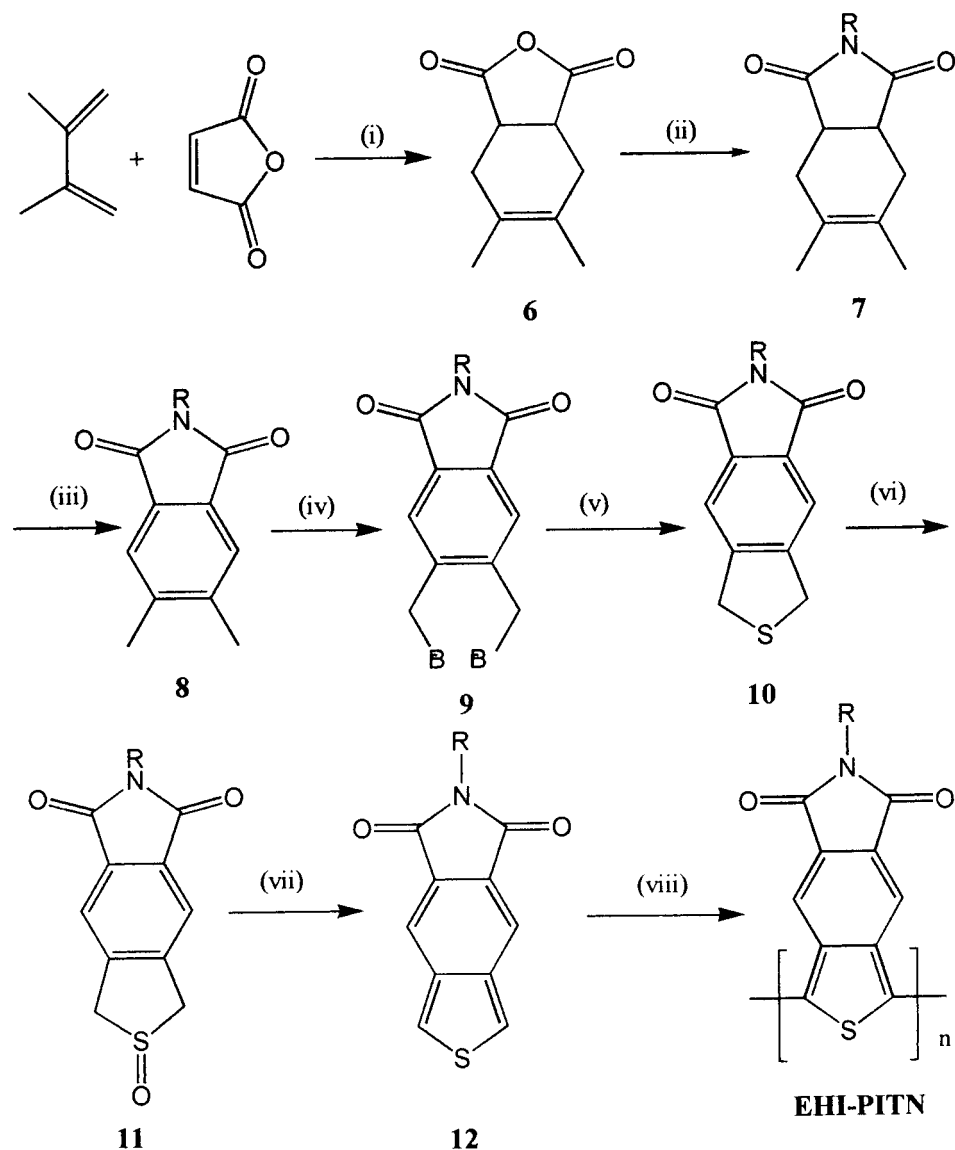
The synthetic routes for the monomers and polymers are depicted in Scheme 2. Starting from 3,4-dimethylbutadiene and maleic anhydride, through Diels–Alder

and amination reactions, **7** was obtained in nearly quantitative yield. Sulfur-mediated oxidation at 200–210 °C produced *N*-(2-ethylhexyl)-4,5-dimethylphthalimide (compound **8**) in 80% yield. NBS bromination of compound **8** in CCl<sub>4</sub> with a catalytic amount of benzoyl peroxide (BOP) produced *N*-(2-ethylhexyl)-4,5-bis(bromomethyl) phthalimide (compound **9**) in 70% yield. Compound **9** was subjected to ring closure with sodium sulfide nonahydrate to give benzo[*c*]thiophene-*N*-(2-ethylhexyl)-1,3-dihydro-5,6-dicarboxylic imide. Oxidation of compound **9** with *m*-CPBA in chloroform at –20 °C afforded sulfoxide **10** in high yield. Pummerer rearrangement of the latter with TMSCl afforded monomer **11**.

### Experimental Section

**General.** Reagent chemicals were purchased from either Aldrich or Fisher Chemical Co., unless otherwise stated. All new compounds were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, MS, and elemental analysis. Nuclear magnetic resonance (NMR) spectra were taken on a Bruker AMX 400 spectrometer. All chemical shifts were reported relative to tetramethylsilane (TMS) at 0.0 ppm and CDCl<sub>3</sub> as solvent. FTIR spectra were recorded on an ATI Mattson Infinity series spectrometer by dispersing samples in KBr disks. UV–vis spectra were obtained on a Hewlett-Packard 8453 spectrophotometer. Melting points were measured using a capillary melting point apparatus (MelTemp from Laboratory Devices) and were uncorrected. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TAC 7/DX thermal analyst system at a heating rate of 10 °C/min and at a nitrogen flow rate of 75 cm<sup>3</sup>/min. Differential scanning calorimetry (DSC) was run on a Perkin-Elmer DSC pyris instrument. Cyclic voltammetry (CV) was performed on a BAS 100B electrochemical analyzer with a three-electrode cell in a solution of Bu<sub>4</sub>NBF<sub>4</sub> (0.1 M) in acetonitrile at a scan rate of 50 mV/s. The polymer films were coated on a glassy carbon disk electrode (0.5 cm<sup>2</sup>) by dropping

Scheme 2. Synthetic Routes to PITN Polymers



the polymer solutions onto the electrode and then drying in a vacuum. A Pt wire was used as the counter electrode, and an Ag/AgNO<sub>3</sub> (0.1 M) electrode was used as the reference electrode. Its potential was corrected to the saturated calomel electrode (SCE) by measuring the ferrocene/ferrocenium couple in this system (0.31 V vs SCE). The band gap was derived from either the difference between onset potentials ( $E_{\text{onset}}^{\text{an}} = E_{\text{pc}}^{\text{onset}} - E_{\text{na}}^{\text{onset}}$ ) or half-wave potentials ( $E_g^{1/2} = E_p^{1/2} - E_n^{1/2}$ ). Elemental analysis results were obtained from Desert Analytics Co. Light scattering measurements were performed at a concentration of 8 mg/mL with a Microtrac ultrafine particle analyzer (Leeds & Northrup).

**Monomer Synthesis.** **4,5-Dimethyl-*cis*-4-enetetrahydrophthalic Anhydride (6)** was prepared according to literature methods. Yield: 99%. Mp: 77–78 °C (lit.<sup>11b</sup> 78 °C).

***N*-(2-Ethylhexyl)-4,5-dimethyl-*cis*-4-tetrahydrophthalimide (7).** Compound **6** (59.0 g, 0.328 mol) was dissolved in DMF (200 mL), and 2-ethylhexylamine (43.2 g, 0.335 mol) was added dropwise, with stirring in 0.5 h. After 20 min further stirring, acetic anhydride (80 mL), triethylamine (10 mL), and nickel acetate tetrahydrate (2 g, 1.1 mmol) were added. The mixture was stirred at 130 °C for 6 h. Upon solvent removal, the residue was further distilled under vacuum (140–142 °C/2 mmHg) to obtain a colorless liquid (93.5 g, yield 98%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 3.34 ppm (d, 2 H, –N–CH<sub>2</sub>–), 2.99 ppm (m, 1 H, –CH–), 2.22–2.44 ppm (m, 4 H, –CH<sub>2</sub>–), 1.65 ppm (s, 6 H, =C(CH<sub>3</sub>)–), 1.15–1.28 ppm (m, 9 H, –CH–, –CH<sub>2</sub>–),

0.82–0.90 ppm (m, 6 H, –CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 180.6, 126.9, 42.7, 39.8, 37.3, 30.8, 30.2, 28.5, 23.3, 23.0, 19.3, 14.1, 10.4 ppm. EI, MS *m/z* (%): 291 (85, M<sup>+</sup>), 180 (100). HR MS Calcd for C<sub>18</sub>H<sub>29</sub>O<sub>2</sub>N: 291.2198. Found: 291.2194. Single spot by TLC.

***N*-(2-Ethylhexyl)-4,5-dimethylphthalic Imide (8).** *N*-(2-Ethylhexyl)-4,5-dimethyl-*cis*-4-tetrahydrophthalimide (93.5 g, 0.32 mol) was mixed with sulfur (30.8 g, 0.96 mol), and the mixture was heated in an oil bath at 200–210 °C under Ar atmosphere for 6 h. After cooling to room temperature, the mixture was taken up in hot hexane (300 mL) and filtered to remove unreacted sulfur. The filtrate was evaporated, and the residue was further purified by silica gel flash chromatography. Sulfur was first eluted using hexane, followed by the product, which was eluted with chloroform to give 73.5 g of white crystals: yield 80%; mp 72–73 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.58 ppm (s, 2 H, ArH), 3.53 ppm (d, 2 H, –NCH<sub>2</sub>–), 2.39 ppm (s, 6 H, ArCH<sub>3</sub>), 1.82 ppm (m, 1 H, –NCH<sub>2</sub>CH–), 1.27–1.34 ppm (m, 8 H, –CH<sub>2</sub>–), 0.87–0.92 ppm (m, 6 H, –CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 169.1, 143.4, 130.1, 124.2, 41.8, 38.3, 30.5, 28.5, 23.9, 23.0, 20.6, 14.1, 10.4 ppm. EI, MS *m/z* (%): 287 (73, M<sup>+</sup>), 188 (100). Anal. Calcd for C<sub>18</sub>H<sub>25</sub>O<sub>2</sub>N: C, 74.22; H, 8.77; N, 4.87. Found: C, 74.32; H, 8.51; N, 4.83.

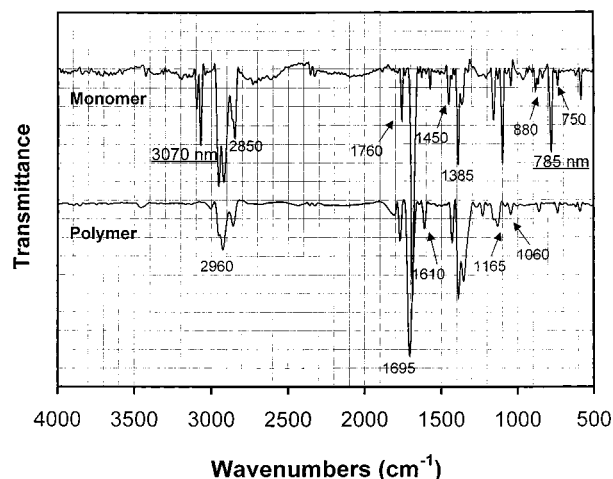
***N*-(2-Ethylhexyl)-4,5-bis(bromomethyl)phthalimide (9).** To a solution of *N*-(2-ethylhexyl)-4,5-dimethylphthalimide (**8**) (28.7 g, 0.10 mol) in freshly distilled CCl<sub>4</sub> (200 mL), purged with Ar gas to displace air, was added a mixture of NBS (37.4

g, 0.21 mol) and benzoyl peroxide (30 mg) in three portions during 2 h under UV irradiation. After the reaction mixture was refluxed (UV lamp heat) for another 6 h, it was cooled and filtered. The filtrate was washed three times with water, dried, and then evaporated. The residue was applied onto a silica gel column, and the product was eluted with hexane:ethyl acetate (8:1) to produce a white solid which was further purified by recrystallization from cyclohexane to afford 31.1 g (70% yield) of white powder; mp 78–80 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.85 ppm (s, 2 H, ArH), 4.71 ppm (s, 4 H,  $\text{BrCH}_2-$ ), 3.58 ppm (d, 2 H,  $-\text{NCH}_2-$ ), 1.82 ppm (m, 1 H,  $-\text{NCH}_2\text{CH}-$ ), 1.28–1.35 ppm (m, 8 H,  $-\text{CH}_2-$ ), 0.87–0.93 ppm (m, 6 H,  $-\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  167.5, 142.9, 132.6, 125.6, 42.1, 38.2, 30.5, 28.5, 28.2, 23.8, 23.0, 14.1, 10.4 ppm. EI, MS  $m/z$  (%): 447 (46,  $[\text{M} + 2]^+$ ), 445 (95,  $\text{M}^+$ ), 443 (48,  $[\text{M} - 2]^+$ ), 186 (100). Anal. Calcd for  $\text{C}_{18}\text{H}_{23}\text{O}_2\text{Br}_2\text{N}$ : C, 48.56; H, 5.21; N, 3.15; Br, 35.90. Found: C, 48.23; H, 5.27; N, 3.38; Br, 35.81.

**Benzo[*c*]thiophene-*N*-2-ethylhexyl-2,7-dihydro-4,5-dicarboxylic Imide (10).** To a solution of sodium sulfide nonahydrate (12.8 g, 0.053 mol) dissolved in 150 mL of absolute ethanol was added slowly with stirring a solution of 18.0 g (0.04 mol) of **9** dissolved in 200 mL of absolute ethanol in 1 h at room temperature. The reaction mixture was further refluxed for 1 h and then worked up. Upon evaporation of 300 mL of ethanol, 200 mL of water was added. The mixture was extracted with chloroform, dried with magnesium sulfate, and evaporated. Further purification via chromatography on silica gel with hexane:ethyl acetate (8:1) as eluent afforded a light-yellow powder (yield 61%); mp 113–115 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.68 ppm (s, 2 H, ArH), 4.33 ppm (s, 4 H,  $-\text{SCH}_2-$ ), 3.57 ppm (d, 2 H,  $-\text{NCH}_2-$ ), 1.82 ppm (m, 1 H,  $-\text{NCH}_2\text{CH}-$ ), 1.26–1.33 ppm (m, 8 H,  $-\text{CH}_2-$ ), 0.86–0.92 ppm (m, 6 H,  $-\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  168.2, 147.1, 131.5, 119.6, 42.0, 38.3, 37.5, 30.5, 28.5, 23.9, 23.0, 14.1, 10.4 ppm. EI, MS  $m/z$  (%): 317 (98,  $\text{M}^+$ ), 134 (100). Anal. Calcd for  $\text{C}_{18}\text{H}_{23}\text{NO}_2\text{S}$ : C, 68.11; H, 7.30; N, 4.41; S, 10.10. Found: C, 68.02; H, 7.29; N, 4.45; S, 9.86.

**Benzo[*c*]thiophene-1-oxide-*N*-2-ethylhexyl-2,7-dihydro-4,5-dicarboxylic Imide (11).** A solution of benzo[*c*]thiophene-*N*-2-ethylhexyl-2,7-dihydro-4,5-dicarboxylic imide (**10**) (7.5 g, 0.024 mol) was dissolved in chloroform (100 mL) and cooled to –20 °C in a dry ice–acetone bath. A solution of *m*-CPBA (4.12 g, 0.024 mol) in 80 mL of chloroform, cooled at –20 °C, was added dropwise to the above solution with stirring for about 20 min. The mixture was then stirred at room temperature for 5 h, the solvents were evaporated, and the residue was taken up with chloroform. The chloroform extract was washed with water, dried, and evaporated to yield the product which was further purified by chromatography on silica gel with methylene chloride:hexane (1:3) to give 7.6 g of white crystals (yield 88%); mp 184–185 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.85 ppm (s, 2 H, ArH), 4.37–4.25 ppm (dd, 4 H,  $-\text{S}(\text{O})\text{CH}_2-$ ), 3.58 ppm (d, 2 H,  $-\text{NCH}_2-$ ), 1.82 ppm (m, 1 H,  $-\text{NCH}_2\text{CH}-$ ), 1.27–1.34 ppm (m, 8 H,  $-\text{CH}_2-$ ), 0.86–0.92 ppm (m, 6 H,  $-\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  167.8, 142.2, 132.8, 121.8, 59.2, 42.1, 38.2, 30.5, 28.5, 23.9, 23.0, 14.1, 10.4 ppm. EI, MS  $m/z$  (%): 333 (100,  $\text{M}^+$ ), 187 (70). Anal. Calcd for  $\text{C}_{18}\text{H}_{23}\text{NO}_3\text{S}$ : C, 64.84; H, 6.95; N, 4.20; S, 9.61. Found: C, 64.85; H, 7.10; N, 4.31; S, 9.31.

**Monomer Benzo[*c*]thiophene-*N*-2-ethylhexyl-4,5-dicarboxylic Imide (12).** To a stirred solution of benzo[*c*]thiophene-1-oxide-*N*-2-ethylhexyl-2,7-dihydro-4,5-dicarboxylic imide (5.86 g, 0.0175 mol), in dried methylene chloride (150 mL), was added slowly *N,N*-diisopropylethylamine (20 mL, 0.12 mol) and  $\text{TMSCl}$  (15 mL, 0.12 mol) at 0–5 °C under Ar atmosphere. After stirring for 2 h, the ice–water bath was removed, and the reaction mixture was refluxed for an additional 2 h. The solvent was evaporated, and the residue was separated by chromatography on silica gel with hexane:ethyl acetate (8:1) as eluent to produce 5.0 g of a light-yellow powder in 90% yield; mp 130–132 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.13 ppm (s, 2 H, ArH), 8.02 ppm (s, 2 H, ThH), 3.63 ppm (d, 2 H,  $-\text{NCH}_2-$ ), 1.88 ppm (m, 1 H,  $-\text{NCH}_2\text{CH}-$ ), 1.29–1.36 ppm (m, 8 H,  $-\text{CH}_2-$ ), 0.86–0.94 ppm (m, 6 H,  $-\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  168.2, 138.4, 126.0, 122.8, 119.5, 42.3, 38.2, 30.6, 28.5, 23.9,



**Figure 1.** FTIR spectra of the monomer and the polymer.

23.0, 14.1, 10.5 ppm. EI, MS  $m/z$  (%): 315 (100,  $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{18}\text{H}_{21}\text{NO}_2\text{S}$ : C, 68.54; H, 6.71; N, 4.44; S, 10.16. Found: C, 68.37; H, 6.87; N, 4.54; S, 9.76.

**Polymerization. Poly(benzo[*c*]thiophene-*N*-2'-ethylhexyl-4,5-dicarboxylic Imide) (EHI-PITN).** A solution of benzo[*c*]thiophene-*N*-2'-ethylhexyl-4,5-dicarboxylic imide (3.15 g, 0.01 mol) dissolved in dry chloroform (50 mL) was added (via syringe) under an argon atmosphere to a suspension of  $\text{FeCl}_3$  (6.48 g, 0.04 mol) in 100 mL of chloroform at room temperature. The polymerization started immediately with the appearance of a brown-black color. The reaction mixture was stirred at room temperature for 24 h and then heated to 50 °C for a further 24 h. After cooling to room temperature, the mixture was poured into 400 mL of methanol. The precipitated black polymer was isolated by centrifugation.

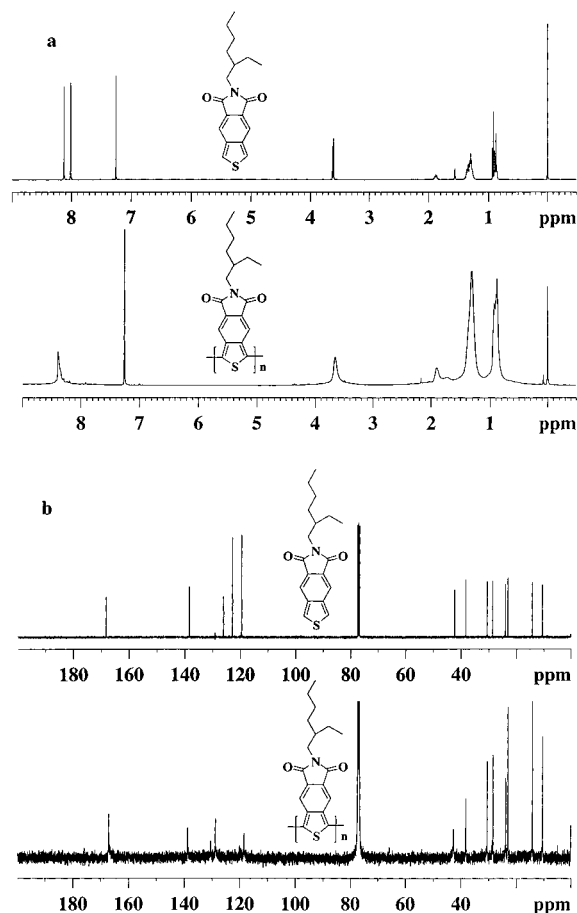
**Purification of the Polymer.** The solid product was washed several times with methanol and redissolved in chloroform and repeatedly precipitated in methanol to afford a black solid powder. After dedoping the polymer with 50% ammonium hydroxide (commercial concentrated ammonium hydroxide diluted 50% with distilled water, final concentration ca. 15%), the polymer was Soxhlet-extracted with methanol for 40 h, followed by acetone (to remove oligomers (0.25 g of brown-black oligomers, 8% yield), then with THF (to remove low molecular weight polymer (blue-black polymer, 0.43 g, 14% yield), and finally using chloroform to extract the higher molecular weight polymer (1.88 g, 60% yield). Further purification was achieved by dissolving the polymer in chloroform and precipitating in methanol, followed by centrifugation. After drying in a vacuum overnight at 40 °C, the polymer was characterized:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.34 ppm (br, 2 H, ArH), 3.64 ppm (br, 2 H,  $-\text{NCH}_2-$ ), 1.88 ppm (br, 1 H,  $-\text{NCH}_2\text{CH}-$ ), 1.29–0.87 ppm (br, 15 H,  $-\text{CH}_2$ ,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  167.2, 138.8, 130.4, 128.8, 118.4, 42.5, 38.1, 30.5, 28.4, 23.8, 22.9, 14.0, 10.3 ppm. Anal. Calcd for  $\text{C}_{18}\text{H}_{19}\text{NO}_2\text{S}$ : C, 68.98; H, 6.11; N, 4.47; S, 10.23. Found: C, 67.27; H, 6.06; N, 4.41; S, 9.79. The molecular weight ( $M_w$ ) of the polymer was determined to be 88 000 g/mol by light scattering.

## Results and Discussion

**Monomer and Polymer Synthesis.** A previous method for the dehydration of a sulfoxide by heating with activated alumina under reduced pressure in a sublimator<sup>16</sup> was not applicable for the synthesis of the monomers with long-chain substituents since the products have too low a vapor pressure. Here, the final, high yield, synthetic step of the monomer uses the homogeneous solution, Pummerer rearrangement method, under mild conditions.<sup>15</sup>

**FTIR and NMR Spectra.** FTIR spectra of the monomer and the polymer are depicted in Figure 1. The spectrum of the polymer is essentially the same as that



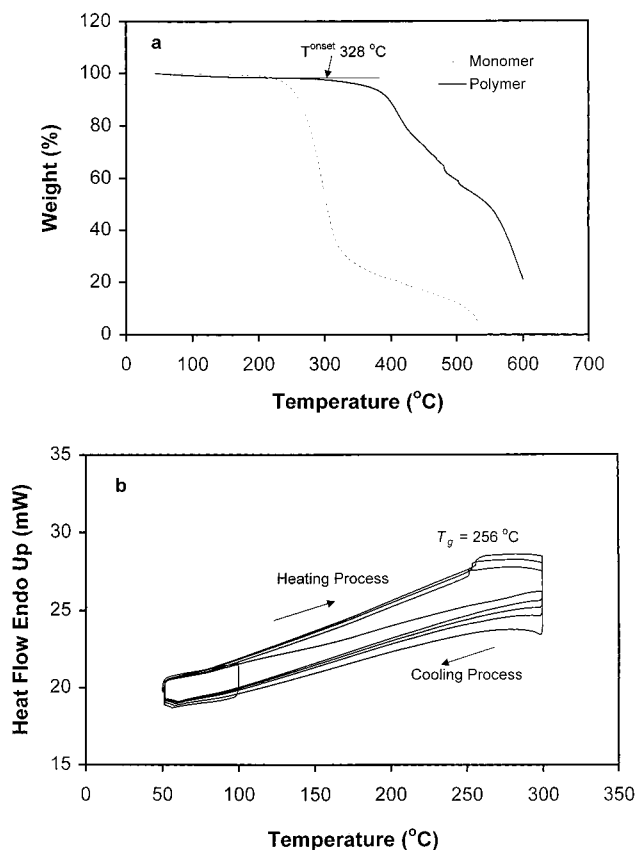


**Figure 2.** (a)  $^1\text{H}$  NMR spectra of the monomer and the polymer. (b)  $^{13}\text{C}$  NMR spectra of the monomer and the polymer.

of the monomer except for the disappearance of the  $\alpha$ -CH bands of the latter. The two main strong sharp absorption bands at 785 and 3070  $\text{cm}^{-1}$  in the monomer, which correspond to the thiophene ring  $\alpha$ -CH out-of-plane bend and the stretching mode, respectively, are absent in the polymer. This means the polymerization occurred through the thiophene ring. Similar features have been reported for polythiophenes and their derivatives.<sup>17,18</sup>

Figure 2 shows  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of the polymer, and for comparison, the monomer's NMR spectra are also shown. As expected, at low field, one single peak at 8.19 ppm, assigned to the aromatic thiophene  $\alpha$ -CH proton in the monomer, disappeared. Instead, a broad single peak, centered at 8.34 ppm and attributed to the aromatic phenyl protons, appeared in the polymer. The not unusual broadness of the signals may be explained by the polydispersity of the materials or by the large degree of the quinoidal character in the ground state of the polymer since a large contribution of quinoidal structure serves to "rigidize" the polymer backbone, decreasing the freedom of rotation about the bonds connecting the repeat units.<sup>10,19</sup> Other peaks at high field are identical for monomer and polymer due to the long side chain. Another reason for the very broad  $^1\text{H}$  NMR spectrum may also be due to paramagnetic impurities associated with residual iron salts.<sup>20</sup> The  $^{13}\text{C}$  NMR spectrum of the polymer showed the same number of carbons as in the monomer, further confirming the expected polymer structure.

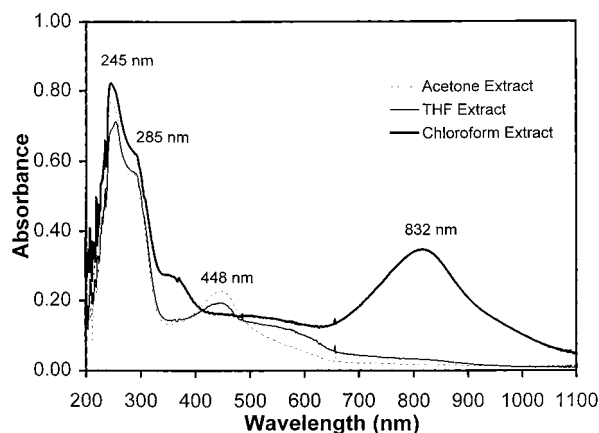
**Stability of the Monomer and Polymer.** The key issue which concerned us was the stability of the



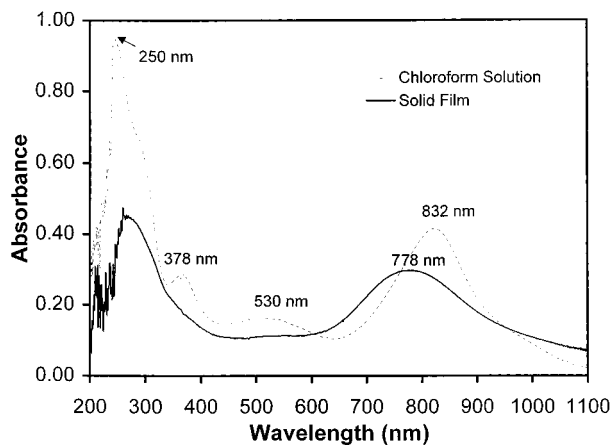
**Figure 3.** (a) Thermogram of the monomer and the polymer under nitrogen. (b) DSC scans of the polymer under nitrogen.

monomer and the polymer. The monomer is quite stable both thermally and chemically. There was no noticeable physical and chemical change of the monomer and the polymer even when the monomer powder and the polymer film were exposed to normal laboratory environmental conditions for several months. As for thermal stability, the monomer and polymer were investigated by TGA analysis under nitrogen atmosphere, and the results are shown in Figure 3. The monomer is quite stable (see Figure 3a); there is no degradation of the monomer below 220  $^{\circ}\text{C}$ . The polymer showed higher thermal stability than its monomer with an onset of weight loss at about 328  $^{\circ}\text{C}$ . Compared with other PITN derivatives, which showed a decomposition onset temperature of about 200  $^{\circ}\text{C}$  and more than 10% weight loss at 300  $^{\circ}\text{C}$ ,<sup>9–11</sup> EHI–PITN showed only a 4.5% weight loss when the temperature had reached 400  $^{\circ}\text{C}$ . We attribute this higher thermal stability to the introduction of the imide group.<sup>21</sup> Finally, DSC analysis of the polymer, as shown in Figure 3b, revealed a possible glass transition temperature ( $T_g$ ) of the polymer at about 256  $^{\circ}\text{C}$ . The value remained the same when the polymer was subjected to several heat–cool cycles. This high value is consistent with the polymer's relatively high thermal stability.

**Electronic Spectroscopy.** To study the degree of polymerization and to obtain the highest molecular weight fraction of the polymer, the polymer was subjected to extraction by several solvents. Methanol was employed to extract the  $\text{FeCl}_3$  and unreacted monomer as well as some oligomers. Acetone was used to extract the oligomers and THF to extract the low-molecular-weight polymer fraction. Finally, chloroform was used to obtain the high-molecular-weight, yet soluble, com-



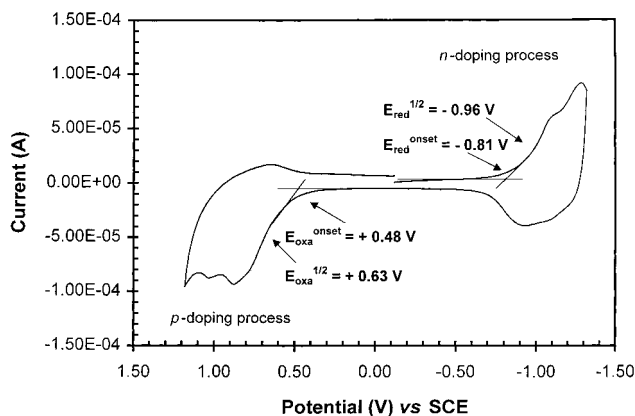
**Figure 4.** UV-vis-NIR spectra of the extraction fractions of the polymer (for chloroform extracted polymer,  $\lambda_{\text{max}}$  832 nm,  $\epsilon'_{\text{max}} = 180 \text{ g mol}^{-1} \text{ cm}^{-1}$ ).



**Figure 5.** UV-vis-NIR spectrum of an EHI-PITN film coated on a glass slide (—) and a chloroform solution of the same polymer (···).

ponent. The different extraction products were subjected to UV-vis-NIR spectrophotometry. Figure 4 shows the UV-vis-NIR spectra of the polymer obtained in different solvents. The solvent used in UV-vis-NIR measurements was chloroform for all the "polymers". As can be seen in the Figure 4, both UV-vis-NIR spectra of the acetone and THF extracts show only a short wavelength absorption with a maximum peak appearing at 245 nm and a shoulder at 285 nm. A small peak also appears at 448 nm for both materials due to the  $\pi$ - $\pi^*$  absorption of the oligomer/polymer backbone. The THF extracts also showed a shoulder around 580 nm, which extended to longer wavelength with very weak intensity. However, the UV-vis-NIR spectrum of the chloroform extract is quite different, exhibiting a low-energy absorption band centered at 832 nm, the longest wavelength absorption peak in all the PITN series.<sup>9-11</sup> The longer wavelength absorption is attributed to the  $\pi$ - $\pi^*$  absorption of the polymer backbone.<sup>22</sup> The peak at 245 nm, due to the  $\pi$ - $\pi^*$  of the isothianaphthene in all three systems, was also observed in the chloroform extraction. The 832 nm band of the chloroform extract indicates that a clean high-molecular-weight polymer was obtained.

The UV-vis spectrum of the solid film spin-coated from chloroform on a glass slide is shown in Figure 5. The film exhibits an absorption maximum at 778 nm. Surprisingly, this peak is at higher energy than the one



**Figure 6.** Cyclic voltammogram of EHI-PITN films on glass carbon electrode in 0.10 M *n*-Bu<sub>4</sub>NBF<sub>4</sub> in acetonitrile at a scan rate of 50 mV/s.

obtained in chloroform solution. This rare phenomenon has also been observed in other conjugated polythiophene systems, where a blue shift of the polymers containing mainly head-to-head dyads in solid films compared with the solution states was observed.<sup>22b,c</sup> Normally, the electronic absorption of the solid state of conjugated polymers are red-shifted compared with the solution state attributed to the more ordered conformation and an increase in  $\pi$ -conjugation length in condensed state.<sup>22d</sup> Herein, we explain this blue shift in our low band gap conjugated polymer is due to the more coplanar and robust configuration of the quinoid structure of the polymer which lead to less freedom of the interannular rings. More detailed study of this phenomenon will be reported elsewhere.<sup>22e</sup> The 1.24 eV band gap of the polymer is derived from the energy absorption edge of the spectrum, comparable with the parent PITN polymer and its derivatives.<sup>1,9-11</sup> The data are also in agreement with the value obtained from CV measurements shown below.

#### Electrochemical Study of the Polymer Films.

Depicted in Figure 6 are both p-doping and n-doping processes investigated by cyclic voltammetry (CV) of the polymer. During the p-doping process, the polymer exhibits reversible doping-dedoping properties with oxidation potential ( $E_{\text{pa}}$ ) and reduction potential ( $E_{\text{pc}}$ ) peaks at 0.88 and 0.65 V vs SCE, respectively (scan rate, 50 mV/s). The relative higher oxidation potential, compared with that of PITN, is due to the imide electron-withdrawing group and contributes to the stability of the polymer. The n-doping and dedoping process is also reversible with the reduction potential ( $E_{\text{pc}}$ ) and oxidation potential ( $E_{\text{pa}}$ ) peaks appearing at -1.10 and -0.90 V vs SCE, respectively. The reversible and facile reduction of the polymer shows the polymer can be employed as a typical n-dopable polymer.<sup>23</sup> The oxidation and reduction onset potentials, as measured for both processes, are +0.48 and -0.81 V vs SCE, respectively, which corresponds to a band gap ( $E_{\text{g}}^{\text{onset}}$ ) of 1.29 eV, somewhat higher than derived from the electronic absorption spectrum (1.24 eV). The half-wave derived band gap ( $E_{\text{g}}^{1/2}$ ) is 1.59 eV, which is much lower than that of the low band gap poly(3,4-ethylenedioxythiophene) (PEDOT) material ( $E_{\text{g}}^{1/2} = 2.08 \text{ eV}$ ).<sup>23</sup> The electrochemical oxidation/reduction reversibility of the polymer also indicates that the polymer has good charge transport properties.<sup>24,25</sup>

## Conclusion

A new synthesis route to soluble poly(isothianaphthene) derivatives has been developed. This approach should be applicable to the synthesis of a variety of PITNs. The monomer and the well-characterized polymer are quite stable and soluble in a number of organic solvents. A chloroform-soluble fraction was representative of a high-molecular-weight component whose UV-vis-NIR spectroscopic examination revealed that the  $\pi$ - $\pi^*$  transition appears at higher energy in the solid state than in solution. Elemental analysis, NMR, and FT-IR spectra confirmed a clean structure for the polymer. This new low band gap and high stability polymer indicates the PITN polymer system has substantial potential materials value in the field of conducting polymers. The unique properties of these polymers will make them useful in electronic device applications where n-doping and low band gap properties are essential. Further investigations toward the materials applications as well as design and synthesis of new functional low band gap conducting polymers and elucidation of their properties are in progress.

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