Convenient Synthesis and Polymerization of 5,6-Disubstituted Dithiophthalides Toward Soluble Poly(Isothianaphthene): An Initial Spectroscopic Characterization of the Resulting Low-Band-Gap Polymers

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ABSTRACT: A new synthetic procedure toward substituted dithiophthalides, 5,6-dialkyloxydithiophthalide and 5,6-dithioalkyldithiophthalide, is presented. 5,6-Dithiooctyldithiophthalide was obtained from 4,5-dichlorophthalic acid in an eight-step reaction with an overall yield of 26%. 5,6-Dioctyloxydithiophthalide was obtained from 4,5-dihydroxyphthalic acid dimethyl ester in a seven-step reaction (overall yield = 15%). Both monomers were polymerized by a thermal and nonoxidative polymerization that resulted in soluble poly(isothianaphthene) derivatives with a band gap of about 1.2 eV. Photoinduced absorption measurements revealed the existence of charged excitations upon illumination. The photoinduced charge generation, combined with the extensive light-harvesting properties and the easy processability, makes these materials quite promising for photovoltaic applications. © 2003 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 41: 1034–1045, 2003

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INTRODUCTION

Because of their intrinsic conductivity and ability to become transparent upon doping, low-band-gap polymers have been considered for numerous applications. The optical absorption of this class of conjugated materials, which covers most of the solar spectrum, makes them excellent candidates for photovoltaic applications. An example of such a conjugated polymer with a narrow band gap (~1 eV) is poly(isothianaphthene) (PITN), which has attracted growing attention since Wudl et al. in 1984[1] established the possibility of using isothianaphthene as a precursor for a new type of polythiophene. Several pathways toward PITN, based on the electrochemical polymerization of isothianaphthene, have been described.[1-6] In the last decade, there has also been extensive work on the development of a straightforward chemical polymerization route toward PITN, in which various isothianaphthene derivatives are utilized.[7-11] Al-
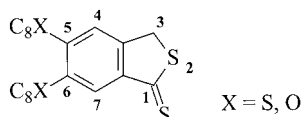
Figure 1. 5,6-Disubstituted dithiophthalide.

though important progress has been achieved in the methods of PITN preparation and in the exploration of the mechanistic aspects of its structure and formation,[12,13] the practical applications of this polymer are still limited. This is due to the poor processability, insolubility, and infusibility of PITN. A possible answer to this problem is the synthesis of substituted analogues of isothianaphthene as new monomer precursors to soluble PITN.[14–20] Another possibility, which consists of the formation of processable precursor polymers, converts to PITN in an easy and convenient way. Recently, such a stable and soluble precursor was obtained by the cationic, low-temperature polymerization of 2-thioalkylisothianaphthene.[21]

As it has previously been shown that nonsubstituted dithiophthalide is an excellent precursor monomer to PITN,[10] a convenient and new procedure toward the synthesis of dithiophthalides substituted by alkyloxy and thioalkyl groups is presented in this article. We focus our effort on the synthesis of the monomers (Fig. 1). The thermal and nonoxidative polymerization of these monomers toward poly(5,6-dioctyloxyisothianaphthene) (**16**) and poly(5,6-dithiooctylisothianaphthene) (**15**) is discussed. A lower band gap has been found for **15**, making it a better candidate for use in flexible solar cells.

RESULTS AND DISCUSSION

Monomer Synthesis

Starting with 4,5-dichlorophthalic acid (**1**), we protected the carboxylic groups by esterification with ethanol (Scheme 1).[22] A nucleophilic substitution with thiooctyl anions generated from sodium thiooctalate was performed. Although for this type of reaction, dimethylformamide (DMF) or dioxane is usually used as a solvent, we found that a toluene/N-methylpyrrolidone (NMP) solution in a 20:1 ratio ensured an effective reaction course.[23] As the preparation of the thiol salt, either with sodium metal or a sodium hydride suspension, always generates noticeable quantities of disulfides, a twofold stoichiometric excess of

thiol was used to support a sufficient concentration of the octylthiolate. After heating at 120 °C, the desired diethyl 4,5-dithiooctylphthalate (**3**) was purified by column chromatography. To obtain the respective 4,5-dialkyloxylated diester [4,5-dioctyloxyphthalic acid dimethyl ester (**8**)], we adapted a synthetic method for phthalocyanines that was published by Drager and O'Brien.[24] The commercially available 2,3-butadione (**4**) was first converted into 2,3-bis(trimethylsilyloxy)butadiene (**5**),[25] which then underwent a Diels–Alder condensation with acetylenedicarboxylic acid dimethyl ester to give the adequate cyclohexanedione (**6**). The latter was then aromatized by the reaction with bromine; next, the obtained catechol [4,5-dihydroxyphthalic acid dimethyl ester (**7**)] gave **8** in a Williamson ether synthesis with the octyl bromide.

Both the intermediate 4,5-dithioalkyldiester (**3**) and 4,5-dialkyloxydiester (**8**) were then hydrolyzed in a 20% methanolic solution of KOH, and this was followed by the acidification of the resultant salts with diluted HCl.[26] After extraction, diacids 4,5-dithiooctylphthalic acid (**9a**) and 4,5-dioctyloxyphthalic acid (**9b**) were obtained in almost quantitative yields. These last two compounds were dehydrated via heating with Ac₂O to form the respective anhydrides 5,6-dithiooctylphthalic anhydride (**10a**) and 5,6-dioctyloxyphthalic anhydride (**10b**).[22] The next step was the conversion of the anhydrides to their corresponding thio analogues, 5,6-dithiooctylphtalic thioanhydride (**11a**) and 5,6-dioctyloxyphthalic thioanhydride (**11b**), by a reaction with sodium disulfide. After the use of commercially available sodium sulfide nonahydrate, which only yielded about 20% of the desired thioanhydride, the efficiency could be substantially improved by the drying of the nonahydrate by means of an azeotropic distillation with toluene. The obtained orange sodium disulfide tetrahydrate seemed to be a better reagent, and **11a** was obtained in a yield of 75%; **11b** was obtained in a moderate yield of 43%.

Recently, our group reported the procedure for a two-step reduction reaction, from thioanhydrides to 2-thiophthalides.[27] Regarding the generality of this process, we applied it here also. After a low-temperature reduction of thioanhydrides with sodium borohydride, the respective 5,6-disubstituted 3-hydroxylated intermediates 5,6-dithiooctyl-3-hydroxy-2-thiophthalide (**12a**) and 5,6-dioctyloxy-3-hydroxy-2-thiophthalide (**12b**) were synthesized with a yield of 90%. The reduction with AcOH/HI led to the corresponding 2-thioph-
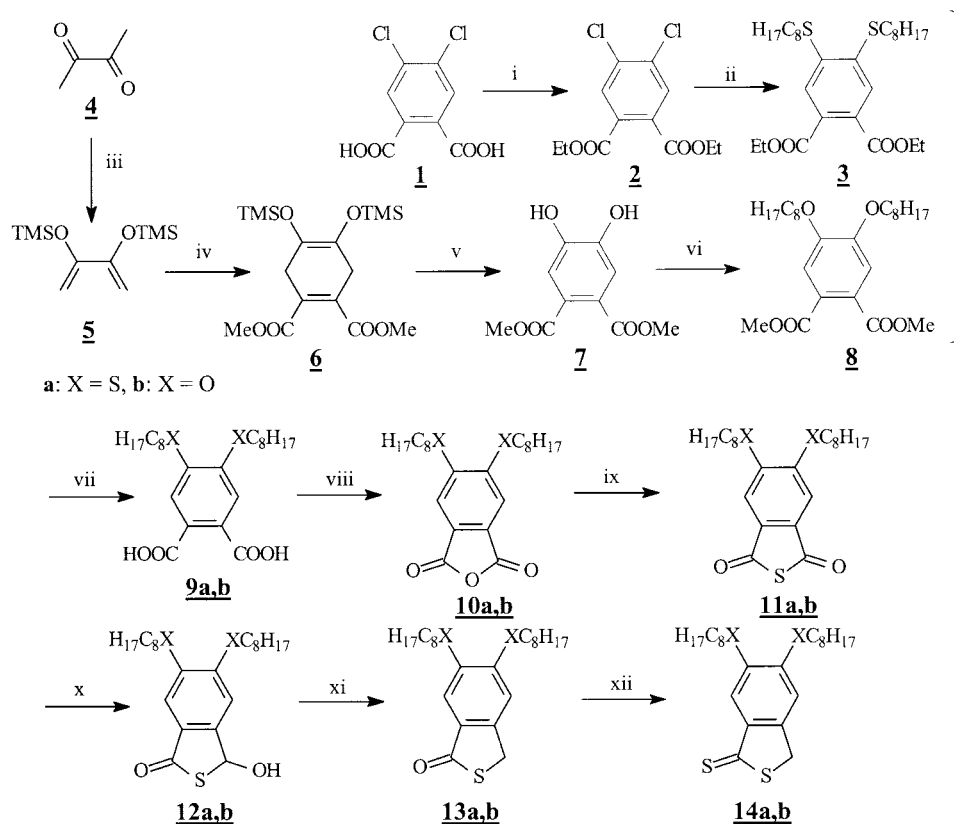
Scheme 1. Synthesis of **14a** and **14b**: (i) EtOH, toluene, H_2SO_4 catalyst, reflux; (ii) $C_8H_{17}SNa$, toluene/NMP (20/1), 120 °C, 20 h; (iii) TMSCl, LiBr/Et$_3$N; (iv) dimethyl acxetylene dicarboxylate, DA; (v) Br$_2$/CCl$_4$; (vi) $C_8H_{17}Br$, K$_2$CO$_3$, acetone, reflux, 48 h; (vii) KOH, MeOH, 40 °C, 12 h; (viii) Ac$_2$O, 120 °C, 2 h; (ix) Na$_2$S · 4H$_2$O, CH$_2$Cl$_2$, 40 °C; (x) NaBH$_4$, THF, −5 °C; (xi) 57% AcOH/HI aqueous solution, 120 °C, 2 h; and (xii) P$_4$S$_{10}$, NaHCO$_3$, CH$_2$Cl$_2$, 40 °C, 40 h.

thalides, 5,6-dithiooctyl-2-thiophthalide (**13a**) and 5,6-dioctyloxy-2-thiophthalide (**13b**). The effectiveness and high selectivity of this transformation were in good agreement with our previous experiences. The expected dithiophthalides 5,6-dithiooctyldithiophthalide (**14a**) and 5,6-dioctyloxydithiophthalide (**14b**) were finally obtained in the thionation reaction performed in the presence of P$_4$S$_{10}$ (Scheme 1).

Polymerization and NMR Characterization

Poly(5,6-dithiooctylisothianaphthene) (15)

The thermal polymerization of **14a** was performed at 155–160 °C in a 0.4 M o-xylene solution and in the presence of a catalytic amount of para-toluenesulfonic acid (p-TsOH). After the treatment with methanol (MeOH) and the removal of the solvent, a Soxhlet extraction of **15** with ace-

tone gave an oligomer fraction [15%, weight-average molecular weight (M_w) = 1167, polydispersity (PD) = 1.05] and a polymer fraction (73%, M_w = 6667, PD = 2.26). The polymer had very good solubility in chloroform, chlorobenzene, and most commonly used organic solvents.

The ^{1}H NMR spectra of monomer **14a** and polymer **15** are presented in Figure 2. For **14a**, the aromatic protons 4 and 7 are assigned to the resonances around 7.9 and 7.3 ppm (overlapping with residual CHCl$_3$ line), respectively. The benzylic protons in the 3-position, which are coupled with the aromatic protons, appear at 4.4 ppm. The methylene groups directly connected to the sulfur in the thiooctyl chain appear at 3.1 ppm. The other methylene and methyl resonances of the side chain are situated between 0.7 and 1.9 ppm. In the polymer fraction, one can notice the absence of the signal at 4.4 ppm. Because we are dealing with a rather rigid
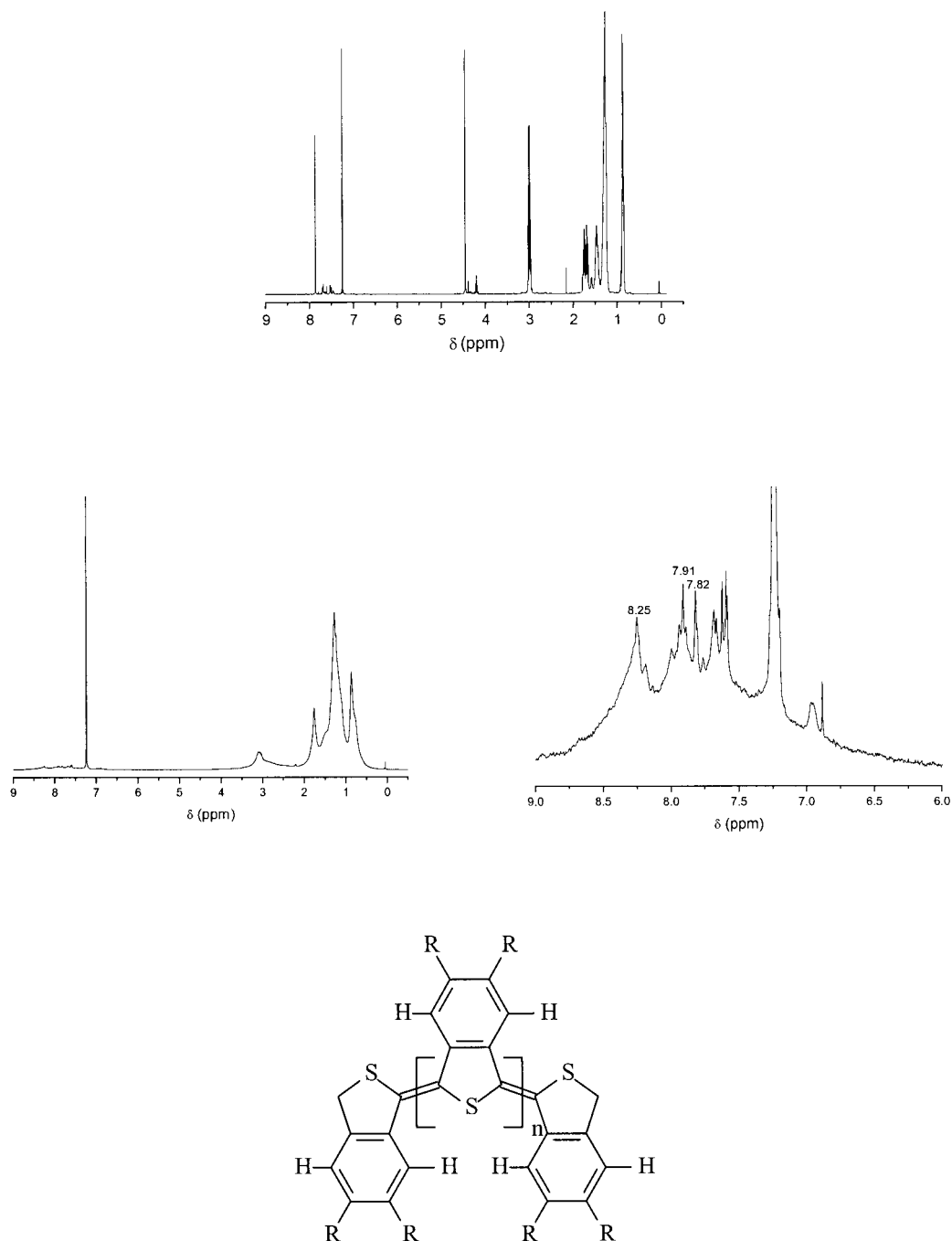
Figure 2. ^{1}H NMR spectra of **14a** (top) and **15** (middle; the spectrum at the right shows the aromatic region blown up by a factor of approximately 35) and the structure of poly(5,6-disubstituded isothianaphthene) with its aromatic protons (bottom).

polymer system and the molecular mobility is correlated with the spin–spin relaxation time (T_2), a short T_2 value will lead to broad NMR signals. The protons of the rigid aromatic rings are so broad that they even become difficult to detect: a broad band with superimposed sharp peaks is observed. The latter can be assigned to the aromatic protons of oligomers, whereas the broad line arises from higher molecular weight chains. The methylene groups directly connected to the sulfur in the thiooctyl chain appear in the area of 3.4–2.8 ppm.
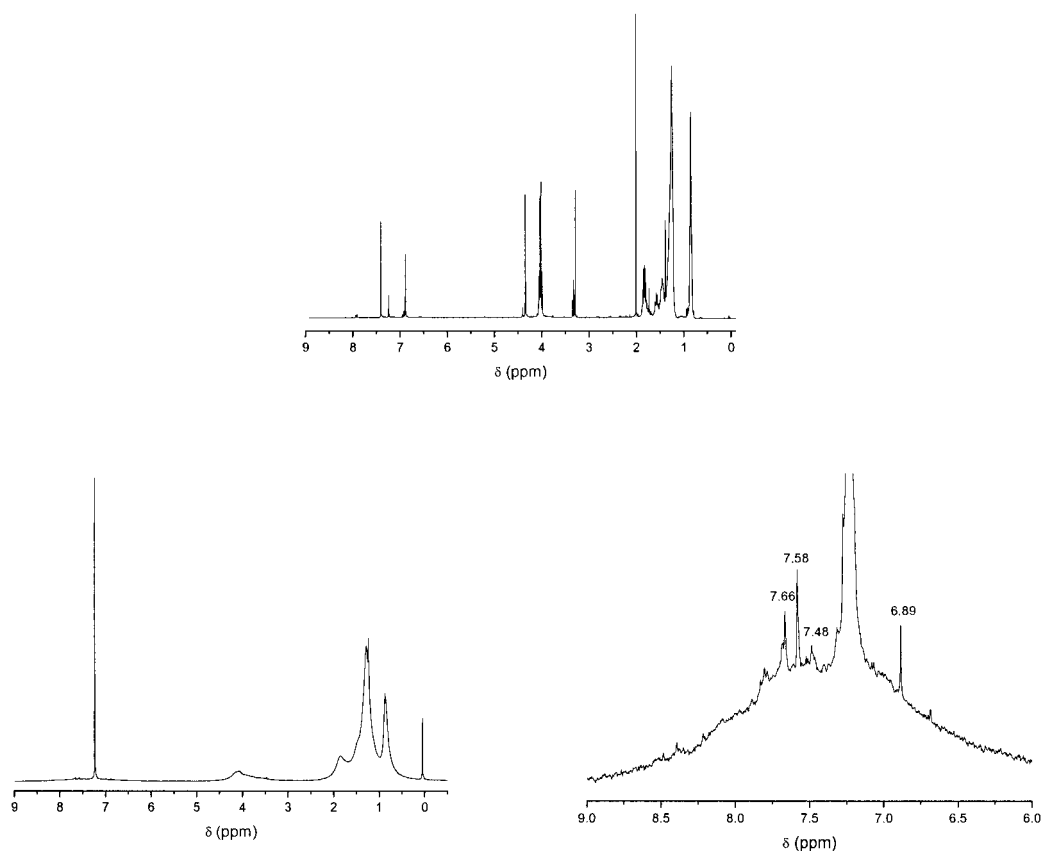
Figure 3. ^{1}H NMR spectra of **14b** (top) and **16** (bottom; the spectrum at the right shows the aromatic region blown up by a factor of approximately 35).

Poly(5,6-dioctyloxyisothianaphthene) (16)

14b in a 0.4 M *o*-xylene solution was polymerized at 155–160 °C, with a trace of *p*-TsOH as a catalyst (15 mol %). Polymer **16** with a molecular weight of 5918 (PD = 2.35) was obtained as a black, shiny material when treated with MeOH. The degree of polymerization (14) was very similar to that obtained for **14a**.

In the ^{1}H NMR spectrum (Fig. 3) of monomer **14b**, some shifts can be observed if we compare it with the spectrum of monomer **14a**: the aromatic protons 4 and 7 are assigned to the resonances around 7.4 and 6.9 ppm, respectively; the benzylic protons in the 3-position also appear at 4.4 ppm. The α-methylene protons (directly connected to the oxygen) in the octyloxy chain appear at 4.0 ppm, and the β-methylene protons appear at 3.3 ppm. The other methylene and methyl resonances of the side chain are situated between 0.7 and 2.1 ppm. Also, in the ^{1}H NMR spectrum of **16**, it becomes difficult to detect the signals of the aromatic protons, and we observe a broad band with superimposed sharp peaks. The broad peak in the area of 4.2–3.9 ppm is consistent with the protons of the methylene group next to oxygen.

Further Spectroscopic Characterization and Cyclic Voltammetry (CV)

An initial spectroscopic study was performed on one of these soluble PITN derivatives (**15**). This polymer, having the lowest band gap, is the most promising candidate for solar cell applications and is a nondegenerate ground-state conjugated polymer. It was investigated by means of ultraviolet–visible (UV–vis) spectroscopy, CV, and photoinduced absorption (PIA) spectroscopy to determine the optical gap of the material and to obtain more insight into the nature of the species generated upon illumination.

In conjugated materials, strong electron–phonon coupling can lead to nonlinear electronic excitations.[28] Charges created in the conjugated chain, by doping (chemical and electrochemical)
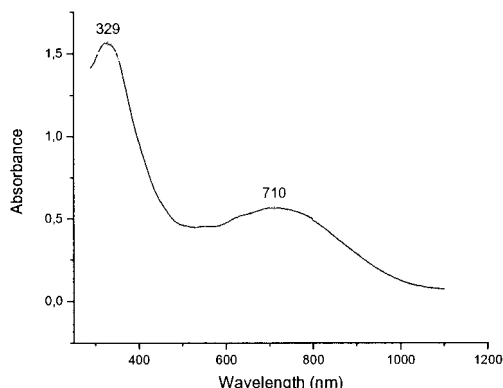
Figure 4. UV–vis spectrum of **15**.

or by photoexcitation, can generate self-localized distortions of chain segments. PIA in the visible and near-infrared regions is an appropriate technique for detecting energy levels in the gap correlated with photogenerated nonlinear electronic states.

UV–vis Absorption Spectroscopy

Films of polymer **15** were prepared via spin coating from a chloroform solution (1.5 wt %) on quartz. The polymer absorption shows two broad features peaking around 3.75 eV or 329 nm and 1.74 eV or 710 nm, the latter values corresponding to the $\pi \rightarrow \pi^*$ transition (Fig. 4). From the low-frequency onset of this absorption, a band gap of approximately 1.16 eV could be estimated.

CV

CV was applied to investigate the redox behavior of the polymers and to estimate the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels. Figure 5 shows the traces of the n-doping and p-doping processes for each polymer. Both presented stable p-doping upon cycling, whereas n-doping proved to be less stable. The anodic peak was exhibited at about 0.80 V for **15** with a corresponding cathodic peak at 0.65 V. The anodic peak was not clearly observed for **16**, and the re-reduction (p-dedoping) was located at 0.74 V. In the reduction curve, no peak was clearly defined, but two reoxidative peaks were revealed at −0.96 and −0.83 V for **15** and at −0.99 and −0.80 V for **16**.

The energy values of LUMO and HOMO were determined from the onset potentials of both n-doping and p-doping and were calculated with the ferrocene value of −4.8 eV below the vacuum level.[29,30] The onset potentials were determined

from the intersection of the two tangents drawn at the rising current and baseline charging current of the CV traces. The correlation can be expressed as follows: $E_{\mathrm{LUMO}} = -(4.8 + E_{\mathrm{onset}}^{\mathrm{red}})$ eV and $E_{\mathrm{HOMO}} = -(4.8 + E_{\mathrm{onset}}^{\mathrm{ox}})$ eV. The onset potentials in reduction and oxidation were determined, respectively, at −0.64 and 0.52 V for **15** and at −0.72 and 0.50 V for **16** versus Ag/AgCl, corresponding to −1.07 and 0.09 V for **15** and −1.15 and 0.07 V for **16** versus F_c/F_c^+ ($E^{o'}F_c/F_c^+$ = 0.43 V vs Ag/AgCl). Therefore, the LUMO and HOMO levels as well as the electrochemical band gap (E_g^{el}) can be estimated. The redox data and energy levels are listed in Table 1.

The band gaps obtained here are in good agreement with the ones derived from UV–vis measurements.

PIA

PIA measurements on **15** were excited with the 488-nm line of an Ar^+ laser. The laser beam was chopped mechanically with a frequency of about 70 Hz, providing a reference for a lock-in amplifier (SR 830, Stanford Research Systems). Samples were mounted on a cold finger of an optically accessible cryostat under dynamic vacuum at a constant temperature of 90 K. A 120-W tungsten halogen lamp provided the light for the transmis-
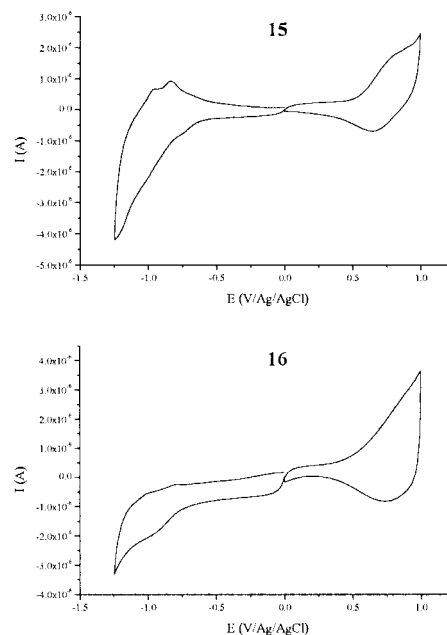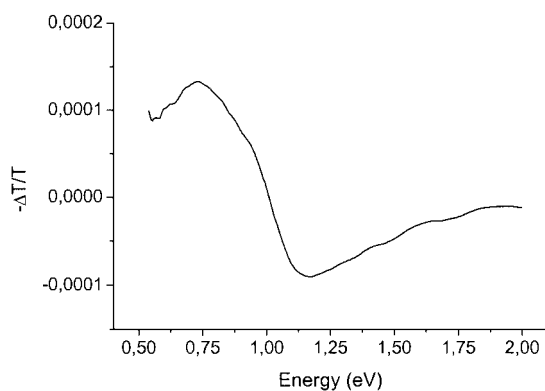

Figure 5. Cyclic voltammograms of polymer films of **15** and **16** drop-cast on Pt in an electrolytic solution of Bu_4NClO_4 (0.1 M) in CH_3CN at a scan rate of 50 mV s^{-1}.

Table 1. Electrochemical Characteristics of Polymers **15** and **16**

| Polymer	$E_{\mathrm{onset}}^{\mathrm{ox}}$ (V)	$E_{\mathrm{onset}}^{\mathrm{red}}$ (V)	E_{HOMO} (eV)	E_{LUMO} (eV)	$E_{\mathrm{g}}^{\mathrm{el}}$ (eV)
15	0.52	−0.64	4.89	3.73	1.16
16	0.50	−0.72	4.87	3.65	1.22

sion measurements. The transmission signal (with and without laser light on the samples) was detected with a SiInGaAsSb photodiode after passing through a monochromator. The spectral dependence of the negative ratio of the photoinduced changes in the sample transmission ($-\Delta T$), corrected for the weak photoluminescence, was plotted after normalization to the transmission (T). The lifetime of the photoinduced features was characterized by the measurement of the frequency dependence of the signal. Samples were prepared by the drop-casting of the material from a chlorobenzene solution [1.5% (w/v)] onto a microscopic glass substrates.

In addition, PIA spectroscopy was also performed in the IR region. For this purpose, the material was drop-cast from a chlorobenzene solution [1.5% (w/v)] onto a ZnSe substrate. In the same way described previously, the dried polymer film was mounted in an optically accessible cryostat and cooled down to the temperature of liquid nitrogen. PIA was determined by the measurement of a sequence of 300 repetitions of recording 10 coadded single-beam spectra under illumination and 10 coadded single-beam spectra in the dark. Combining the resulting spectra, we calculated the negative differential transmission, $-\Delta T/T$. For these experiments, a Bruker IFS 66S spectrometer with a nitrogen-cooled mercury–cadmium–telluride detector was used. The material was excited with the 488-nm line of an Ar$^+$ laser.

The photoexcitation of **15** resulted in the spectrum displayed in Figure 6. Two broad spectral features can be distinguished: (1) the bleaching of the ground-state absorption around 1.15 eV, which was in good agreement with the band gap determined by UV–vis spectroscopy, and (2) a broad absorption peaking around 0.75 eV that was related to photogenerated energy states, probably charged excitations. To investigate the origin of this absorption feature, we checked its dependence on the intensity of the laser modulation. This revealed a power-law dependence ($\sim I^{0.6}$) of the PIA signal, indicating a bimolecular recombination mechanism and the presence of charged excitations in the material upon photoinduction.

PIA performed in the IR region is displayed in Figure 7. Spectral features appear that are qualitatively similar to those in the spectrum previously discussed, with quantitative differences at the $\geq$1.1-eV region. The negative values of $\Delta\alpha$ at 1.2 eV (bleaching in Fig. 6) were not observed in these steady-state Fourier transform infrared PIA studies (Fig. 7), and this might be due to the different timescales of the two experiments and/or different scaling procedures of ΔT. An additional broad absorption band, peaking around 0.44 eV, appears, which is also ascribed to the characteristic absorption of the formed charged excitations. A very clear absorption due to photo-

Figure 6. PIA spectrum of **15**.
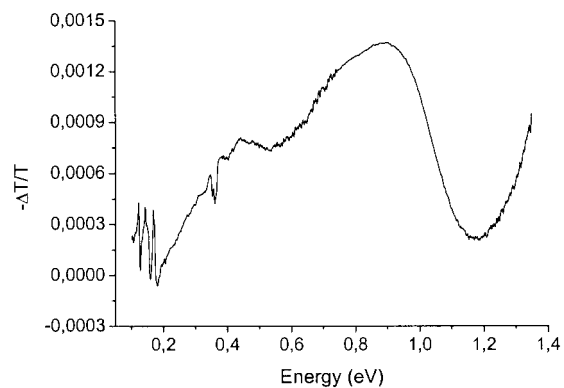
Figure 7. PIA spectrum of **15**: near-infrared and midinfrared.

induced IR active vibrations can be observed, and it confirms the creation of charged species upon illumination.

EXPERIMENTAL

All solvents used in the synthesis were distilled before use. Tetrahydrofuran (THF) was refluxed under nitrogen with sodium metal and benzophenone until a blue color persisted and was then distilled. **1** was purchased from Fluka, and the other commercially available products were purchased from Acros or Aldrich.

^{1}H NMR spectra were taken on a Varian Inova 300 spectrometer. For all synthesized compounds, ^{1}H NMR spectra were recorded in deuterated chloroform; the chemical shift at 7.24 ppm was used as a reference (relative to tetramethylsilane).

CV was performed with an Autolab PGSTAT 20 potentiostat from Eco Chemie B.V., which was equipped with General Purpose Electrochemical System software (version 4.9 for Windows), in an electrolytic solution of tetrabutylammonium perchlorate (0.1 M) in acetonitrile, at a scan rate of 50 mV s^{-1}, at room temperature, under pressure of dry nitrogen. A platinum disk (area = 1.6 mm^2) with a thin drop-cast film was used as the working electrode, and a platinum wire was used as the counter electrode. All potentials were relative to the Ag/AgCl reference electrode.

The molecular weights and molecular weight distributions were determined relative to polystyrene standards (Polymer Labs) by size exclusion chromatography. Chromatograms were recorded on a Spectra series P100 (Spectra Physics) equipped with two Mixed-B columns (10 μm, 2 × 30 cm, Polymer Labs) and a relative-index detector (Shodex) at 70 °C. A DMF solution of oxalic acid (1.1 × 10^{-3} M) was used as the eluent at a flow rate of 1.0 mL/min. Toluene was used as a flow-rate marker.

Gas chromatography/mass spectrometry (GC/MS) analyses were carried out with TSQ-70 and Voyager mass spectrometers (Thermoquest); the capillary column was a Chrompack Cpsil5CB or Cpsil8CB. Melting points (uncorrected) were measured with a digital melting-point apparatus (Electrothermal IA 9000 series). Thin-layer chromatography analyses were made on Merck aluminum sheets (20 cm × 20 cm) covered with silica gel (60 F$_{254}$).

Diethyl 4,5-Dichlorophthalate (2)

To a suspension of 23.5 g (100 mmol) of **1**, stirred in 150 mL of toluene, 50 mL of ethanol (1 mol, 46 g) and approximately 2 mL of concentrated H$_2$SO$_4$ were added. The mixture was kept under reflux, and an azeotrope of toluene/H$_2$O was collected in a Dean–Stark apparatus. After 6 h, the reaction was completed. The obtained solution was washed with 100 mL of water, 100 mL of NaHCO$_3$ (5%), and 100 mL of water, dried over MgSO$_4$, and filtered. The filtrate was concentrated in the rotavapor, and the obtained diester was crystallized from hexane. The product (27.6 g) was obtained as white crystals (95% yield).

mp: 62–63 °C. R_f: 0.41 (hexane/ethyl acetate, 9/1 v/v). ^{1}H NMR (CDCl$_3$): 7.77 (s, 2H, aromatic), 4.3 (2q, J = 7.2 Hz, 4H, aliphatic), 1.31 (2t, J = 7.2 Hz, 6H, aliphatic).

Diethyl 4,5-Dithiooctylphthalate (3)

NaH (4.8 g, 120 mmol; 60% dispersion in mineral oil) was suspended in 200 mL of dry toluene. Then, 23.2 g (160 mmol) of octanethiol, dissolved in 100 mL of dry toluene, was carefully dropped into a stirred suspension of NaH. The liberation of H$_2$ was observed. During the addition, the mixture was not allowed to reach a temperature higher than 35–40 °C. When the addition of the thiol was finished, the mixture was heated to 50 °C, and this was followed by a one-portion addition of 14.5 g (50 mmol) of **2**. The temperature was increased to 80 °C, and 10 mL of NMP was added. The temperature was again increased to 120 °C, and the reaction mixture was stirred for 20 h. Then, at room temperature, it was transferred to a separating funnel, 200 mL of EtOAc and 200 mL of H$_2$O were added, and an extraction was made. The organic layer was dried over MgSO$_4$ and filtered, and the solvents were evaporated. After column chromatography was performed on silica gel (eluent: hexane/EtOAc, in gradient, v/v) 20.95 g of the product was obtained as a yellow oil (82% yield).

R_f: 0.43 (hexane/EtOAc, 9/1 v/v). GC/MS: 510 (M$^+$), 398 (100), 286, 240, 213, 57, 43. ^{1}H NMR (CDCl$_3$): 7.46 (s, 2H, aromatic), 4.28 (2q, J = 7.2 Hz, 4H), 2.91 (2t, J = 7.2 Hz, 4H), 1.62 (2 qt, J = 7.2 Hz, 4H), 1.37–1.45 (m, 4H), 1.30 (2t, J = 7.2 Hz, 6H), 1.22–1.28 (m, 16H), 0.81 (2t, J = 7.2 Hz, 6H).

4,5-Dithiooctylphthalic Acid (9a)

3 (25.95 g, 50.9 mmol) was stirred at a temperature of 40–45 °C in a KOH/MeOH solution [KOH (16.8 g, 300 mmol) dissolved in 250 mL of MeOH]. After 2 h, the reaction was completed, MeOH was evaporated, and the residue was dissolved in 300 mL of H_2O; this was followed by acidification with 3 N HCl to pH ~ 1–2. The acidified mixture was extracted with Et_2O (3 × 200 mL). The organic layers were dried over $MgSO_4$ and filtered, the solvent was evaporated, and the residue was precipitated from hexane. The pure acid (22.0 g) was obtained as white crystals (95% yield).

mp: 79.8–81.2 °C. R_f: 0.67 (EtOAc/MeOH, 85/15 v/v). ^{1}H NMR (deuterated acetone): 7.97 (s, 2H, aromatic), 3.41 (2t, J = 7.2 Hz, 4H), 2.38–2.40 (m, 2H, 2 —O**H**), 2.01 (qt, J = 7.2 Hz, 4H), 1.62–1.88 (m, 20H), 1.18–1.22 (2t, J = 6.8 Hz, 6H). Direct insert probe mass spectrometry: 455 ($M^+ + 1$), 345 (100), 329, 261, 217, 114, 95.

5,6-Dithiooctylphthalic Anhydride (10a)

9a (22.0 g, 48.5 mmol) was refluxed for 1 h in 20 mL of acetic anhydride. The reaction mixture was then cooled to room temperature, and 50 mL of hexane was added; this was followed by cooling to 0 °C. The liquid layer was filtered off, and the solid residue was dried in air. The anhydride (19.95 g) was obtained as white crystals (94% yield).

mp: 73.8–74.2 °C. R_f: 0.45 (hexane/EtOAc, 95/5 v/v). ^{1}H NMR (CDCl$_3$): 7.61 (s, 2H, aromatic), 3.03 (2t, J = 7.6 Hz, 4H), 1.71 (2qt, J = 7.6 Hz, 4H), 1.52–1.25 (m, 20 H), 0.84 (2t, J = 7.6 Hz, 6H). GC/MS: 436 (M^+), 324, 212 (100), 71, 57, 43.

5,6-Dithiooctylphtalic Thioanhydride (11a)

10a (19.95 g, 45.6 mmol) was dissolved in a mixture of 100 mL of hexane and 100 mL of methylene chloride and was added to 16.0 g of $Na_2S \cdot$ ~$4H_2O$ obtained from the azeotropic removal of water from 25.6 g (110 mmol) of $Na_2S \cdot 9H_2O$. This two-phase reaction mixture was stirred at room temperature for 60 h (pH ~ 7–8). Then, it was acidified with a 10% HCl aqueous solution to pH ~ 1–2. Methylene chloride was distilled off. To the rest, 100 mL of H_2O was added, and the mixture was extracted with EtOAc (3 × 150 mL). Organic layers were separated, dried over $MgSO_4$, and filtered, and the solvents were evaporated. After flash column chromatography on sil-

ica gel (eluent: hexane/EtOAc, in gradient, v/v), 15.4 g (75% yield) of pure thioanhydride was obtained as a yellow solid.

mp: 47.4–48.3 °C. R_f: 0.60 (hexane/EtOAc, 95/5 v/v). ^{1}H NMR (CDCl$_3$): 7.55 (s, 2H, aromatic), 3.02 (2t, J = 7.5 Hz, 4H), 1.20–1.79 (m, 24H), 0.83–0.88 (m, 6H). GC/MS: 452 (M^+), 340, 228 (100), 168, 71, 57, 43.

5,6-Dithiooctyl-3-hydroxy-2-thiophthalide (12a)

NaBH$_4$ powder (98%; 1.42 g, 37.6 mmol) was suspended (under an atmosphere of N_2) in 100 mL of dry THF and cooled to −20 °C (NaCl–ice bath). Then, 17.0 g (37.6 mmol) of **11a** in 100 mL of THF was added dropwise to this suspension. The reaction mixture was then stirred at −5 °C, and this was followed by careful acidification with an approximately 5% HCl aqueous solution. The mixture was transferred to a separatory funnel, 100 mL of the saturated NaCl solution was added, and an extraction with 100 mL of Et_2O was made. The water layer was additionally extracted with 150 mL of Et_2O. Organic layers were combined, dried over $MgSO_4$, and filtered, and the solvents were distilled. The crude product (16.45 g) was obtained, and crystallization from hexane/EtOAc (8/2 v/v) gave 15.1 g (88%) of the pure product as a yellow solid.

mp: 47.5–49.3 °C. R_f: 0.28 (hexane/EtOAc, 9/1 v/v). ^{1}H NMR: (CDCl$_3$): 7.36 (s, 1H, aromatic), 7.34 (s, 1H, aromatic), 6.59 (s, 1H, C**H**OH), 2.86–3.02 (m, 4H), 1.25–1.78 (m, 24H), 0.82–0.87 (m, 6H). DIP MS: 454 (M^+), 340, 228 (100), 168, 97, 84, 57.

5,6-Dithiooctyl-2-thiophthalide (13a)

12a (15.1 g, 33.2 mmol) was added to a solution of 15 mL of AcOH and 5 mL of a 57% HI aqueous solution. The reaction mixture was kept at 120 °C for 2 h. Then, it was cooled to room temperature and poured carefully into 100 mL of 1 N NaOH containing 5 g of NaHSO$_3$. The mixture was extracted with 250 mL of Et_2O. The organic layer was additionally washed with a saturated aqueous solution of NaHCO$_3$ for the removal of the rest of the acetic acid, and it was then dried over $MgSO_4$ and filtered; the solvent was evaporated. The product (12.4 g, 85% yield) was obtained as a slightly brown solid.

mp: 38.6–39.8 °C. R_f: 0.34 (hexane/EtOAc, 9/1 v/v), 0.33 (hexane/chloroform, 7/3 v/v). ^{1}H NMR: (CDCl$_3$): 7.57 (s, 1H, aromatic), 7.22 (s, 1H, aro-

matic), 4.36 (s, 2H, CH_2 from thiolactone ring), 2.91–2.98 (m, 4H), 1.24–1.77 (m, 24H), 0.82–0.86 (m, 6H). GC/MS: 438 (M^+), 326, 214 (100), 181, 153, 109, 69, 57. High-resolution mass spectrometry (HRMS): calculated, 438.20848; found, 438.20839.

5,6-Dithiooctyldithiophthalide (14a)

13a (10.95 g, 25 mmol) was dissolved in 300 mL of dichloromethane. To this stirred solution, 19.05 g (85.8 mmol) of P_4S_{10} and 3.6 g (42.9 mmol) of NaHCO$_3$ were added. The resultant mixture was kept at 40 °C for 40 h, and this was followed by the addition of a saturated aqueous solution of NaHCO$_3$ to reach pH $\sim$ 6–7. After conventional layer separation, the aqueous layer was additionally extracted with 200 mL of dichloromethane; the organic layers were combined, dried over MgSO$_4$, and filtered; and the solvent was evaporated. The result was 10.4 g of a crude postreaction mixture. The crude product underwent column chromatography on silica gel (eluent: hexane/chloroform, gradient of eluents), and after purification, 4.80 g (42% yield) of the product was obtained as a brown solid.

mp: 47.5–48.5 °C. R_f: 0.36 (hexane/EtOAc, 9/1 v/v), 0.44 (hexane/chloroform, 7/3 v/v). ^{1}H NMR (CDCl$_3$): 7.85 (s, 1H, aromatic), 7.24 (s, 1H, aromatic), 4.45 (s, 2H, thiolactone), 2.96–3.02 (m, 4H), 1.26–1.76 (m, 24H), 0.84–0.90 (m, 6H). GC/MS: 454 (M^+), 421, 341 (100), 309 (100), 230, 198, 167, 121, 69, 55. HRMS: calculated, 454.18564; found, 454.18557.

4,5-Dioctyloxyphthalic Acid Dimethyl Ester (8)

7 (14.4 g, 64.3 mmol), 43.4 g (225 mmol, 38.9 mL) of octyl bromide, and 42.0 g (300 mmol) of K$_2$CO$_3$ were refluxed for 48 h. Then, acetone was evaporated, 500 mL of water was added to the reaction mixture, and this was followed by its extraction with Et$_2$O (3 × 200 mL). The organic layer was next dried over MgSO$_4$ and filtered, the solvent was evaporated, and column chromatography was performed (eluent: hexane/EtOAc, in gradient, v/v). This resulted in 23.6 g (82% yield) of the product as a white solid.

mp: 39.3–40.9 °C. R_f: 0.44 (hexane/EtOAc, 8/2 v/v). ^{1}H NMR (CDCl$_3$): 7.15 (s, 2H, aromatic), 3.99 (t, 4H, J = 6.9 Hz), 3.85 (s, 6H), 1.76–1.85 (m, 4H), 1.25–1.48 (m, 20 H), 0.83 (m, 6H). GC/MS: 450 (M^+), 419, 338, 307, 226 (100), 195, 71, 57.

4,5-Dioctyloxyphthalic Acid (9b)

8 (30.5 g, 67.8 mmol) was treated with 15.1 g (270 mmol) of KOH dissolved in 300 mL of MeOH. The mixture was stirred at 40 °C for 12 h, the solvent was evaporated, and 200 mL of water was added to the reaction mixture; this was followed by careful acidification with aqueous HCl. Next, an extraction with Et$_2$O was performed (3 × 200 mL), and after drying over MgSO$_4$, filtration, solvent evaporation, and precipitation from hexane, 27.5 g of the product was obtained as a white solid (96% yield).

mp: 137.1–139.5 °C. R_f: 0.44 (EtOAc/MeOH, 85/15 v/v). ^{1}H NMR (acetone deuterated): 7.32 (s, 2H, aromatic), 4.09 (2t, 6H, J = 6.6 Hz), 1.77–1.88 (m, 4H), 1.31–1.58 (m, 20H), 0.86–0.92 (m, 6H). DIP MS: 423 (M^+ +1) (100), 309.

5,6-Dioctyloxyphthalic Anhydride (10b)

9b (25.0 g, 59.2 mmol) was refluxed with 65 mL of acetic anhydride for 1 h. After a workup procedure analogous to that described for the **10a** synthesis, 22.1 g (92% yield) of the product was obtained as a white solid.

mp: 118.6–119.5 °C. R_f: 0.64 (hexane/EtOAc, 8/2 v/v). ^{1}H NMR (CDCl$_3$): 7.28 (s, 2H, aromatic), 4.07 (t, 4H, J = 6.6 Hz), 1.81–1.90 (m, 4H), 1.26–1.51 (m, 20H), 0.84–0.88 (m, 6H). GC/MS: 404 (M^+), 293 (100), 193, 180, 112, 71, 57.

5,6-Dioctyloxyphthalic Thioanhydride (11b)

10b (20.2 g, 50.0 mmol) was dissolved in 300 mL of dichloromethane with 12.6 g of Na$_2$S · 4H$_2$O and kept for 40 h at 45–50 °C. After a workup procedure analogous to that described for the **11a** synthesis, 9.0 g of the product was obtained as a yellow solid (43% yield).

mp: 96.3–98.5 °C. R_f: 0.69 (hexane/EtOAc, 9/1 v/v). ^{1}H NMR (CDCl$_3$): 7.27 (s, 2H, aromatic), 4.06 (2t, 4H, J = 6.6 Hz), 1.80–1.90 (m, 4H), 1.23–1.51 (m, 20H), 0.84–0.89 (m, 6H). GC/MS: 420 (M^+), 309, 209, 196 (100), 180, 112, 71, 57. HRMS: calculated, 420.23343; found, 420.23408.

5,6-Dioctyloxy-3-hydroxy-2-thiophthalide (12b)

11b (8.4 g, 20 mmol) was treated with 0.74 g (20 mmol) of NaBH$_4$. The reaction conditions were analogous to those applied for the **12a** reduction. After crystallization from hexane/EtOAc, 7.8 g of

the product was obtained as a slightly yellow solid (92% yield).

mp: 68.5–71.0 °C. R_f: 0.37 (hexane/EtOAc, 8/2 v/v). ^{1}H NMR (CDCl$_3$): 6.99 (s, 1H, aromatic), 6.93 (s, 1H, aromatic), 6.49 (s, 1H, C**H**OH, hydroxy-thiolactone), 3.97–4.04 (m, 2H), 3.88–3.94 (m, 2H), 1.75–1.88 (m, 4H), 1.23–1.45 (m, 20H), 0.84–0.88 (m, 6H). DIP MS: 423 (M$^+$ + 1), 422, 389, 310, 277, 198 (100), 165, 137, 71, 57, 43. HRMS: calculated, 422.24908; found, 422.24915.

5,6-Dioctyloxy-2-thiophthalide (13b)

12b (7.3 g, 17.3 mmol) was treated with a mixture of 9 mL of AcOH and 3.7 mL of a 57% aqueous solution of HI and kept at 120 °C for 1 h. After a workup analogous to that applied for the **13a** synthesis, which was followed by column chromatography on silica gel (eluent: hexane/EtOAc, 1/0, 9/1, and 8/2 v/v), 5.95 g of the product was obtained as a slightly yellow solid (84% yield).

mp: 50.5–51.9 °C. R_f: 0.67 (hexane/EtOAc, 8/2 v/v), 0.47 (hexane/CHCl$_3$, 6/4 v/v). ^{1}H NMR (CDCl$_3$): 7.18 (s, 1H, aromatic), 6.89 (s, 1H, aromatic), 4.32 (s, 2H, thiolactone ring), 3.98–4.06 (m, 4H), 1.77–1.90 (m, 4H), 1.26–1.49 (m, 20H), 0.84–0.88 (m, 6H). GC/MS: 406 (M$^+$), 294, 195, 182 (100), 154, 71, 57. HRMS: calculated, 406.25417; found, 406.25422.

5,6-Dioctyloxydithiophthalide (14b)

13b (5.6 g, 13.8 mmol) was dissolved in 75 mL of dichloromethane; 2.3 g (27 mmol) of NaHCO$_3$ and 10.4 g (47 mmol) of P$_4$S$_{10}$ were then added. The mixture was kept at 40–45 °C for 40 h, and this was followed by the addition of a saturated aqueous solution of NaHCO$_3$ to reach pH ~ 6–7. After a workup analogous to that applied for **14a**, followed by the purification of the crude product by column chromatography on silica gel (eluent: hexane/CHCl$_3$, in gradient, v/v), 3.1 g of the pure product was obtained as a brown solid (53% yield).

mp: 47.9–49.9 °C. R_f: 0.60 (hexane/CHCl$_3$, 6/4 v/v). ^{1}H NMR (CDCl$_3$): 7.41 (s, 1H, aromatic), 6.89 (s, 1H, aromatic), 4.35 (s, 2H, thiolactone), 3.98–4.07 (m, 4H), 1.78–1.90 (m, 4H), 1.22–1.51 (m, 20 H), 0.83–0.87 (m, 6H). GC/MS: 422 (M$^+$), 389, 359, 323, 309, 293, 211, 198 (100), 71, 57. HRMS: calculated, 422.23133; found, 422.23120.

Polymerization of 14a (15)

14a (908 mg, 2 mmol) was dissolved in 5 mL of *o*-xylene, and 57 mg (0.3 mmol) of *p*-TsOH · H$_2$O

was added. The mixture was stirred for 30 h at a temperature of 155–160 °C under an atmosphere of N$_2$. Then, the mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The black, sticky residue was treated with an MeOH/H$_2$O solution (200 mL), which was removed; this led to a decanted, sticky solid. As it was still not in the precipitate form, more MeOH (150 mL) was added, and the mixture was refluxed for 1 h. During this refluxing, the mass agglomerated in one piece. The MeOH solution was removed, and the solid was transferred to a Soxhlet tube. First, an extraction with acetone (24 h) was performed to collect the lower oligomer fraction (M_w = 1167). After solvent evaporation and drying of the residue *in vacuo*, 122.6 mg (15%) of this fraction was obtained in the form of a black solid. Then, an extraction with chloroform was performed for the residue left in the Soxhlet tube. This resulted in 611.9 mg (73%) of the polymer fraction after solvent evaporation and precipitation of the residue with MeOH (M_w = 6667).

^{1}H NMR (CDCl$_3$): 8.25 (br), 7.92 (br), 7.59 (br), 3.11 (br, 4H), 1.74 (br, 4H), 1.23 (br, 20H), 0.86 (br, 6H).

Polymerization of 14b (16)

14b (844 mg, 2 mmol) was dissolved in 5 mL of *o*-xylene, and 57 mg (0.3 mmol) of *p*-TsOH · H$_2$O was added. The mixture was stirred for 30 h at a temperature of 155–160 °C under an atmosphere of N$_2$. Then, the mixture was cooled to room temperature, and the *o*-xylene was removed under reduced pressure. The residue was treated with an MeOH–H$_2$O solution (200 mL). The black precipitate that formed was filtered and transferred into a Soxhlet extraction tube. An extraction for 24 h with MeOH was performed, followed by a 24-h extraction with acetone for the removal of lower oligomeric fractions. Both fractions were evaporated and after a period of drying *in vacuo*, 109.4 mg (14%, M_w = 809) of an MeOH-soluble fraction and 134.4 mg (17%, M_w = 6138) of an acetone-soluble fraction were obtained. Finally, the polymer was extracted with chloroform. No precipitation occurred with the addition of MeOH to the chloroform solution, so all solvents were evaporated, and the residue was treated only with MeOH. The black precipitate then formed easily. After a period of drying *in vacuo*, 358.4 mg of this polymer fraction was obtained (46%, M_w = 5918). As the M_w values for the two last fractions were

practically the same, they were combined, and the yield of the polymerization was estimated as the combined yield of these two (64%).

^{1}H NMR (CDCl$_3$): 7.67 (br), 7.59 (br), 7.53 (br), 4.21 (br, 4H), 1.87 (br, 4H), 1.27 (br, 20H), 0.92 (br, 6H).

CONCLUSIONS

Efficient synthetic pathways leading to **14a** and **14b** were elaborated, passing through the respective stable 3-hydroxy-2-thiophthalide structures. The thermal polymerization of the resultant monomers led to soluble PITN derivatives. The band gap of the obtained polymers was comparable to the band gap of PITN itself (~1 eV). PIA spectroscopy in the visible and IR regions was performed, and evidence for the existence of charged excitation upon photoinduction was found. The good processability of these polymers make them promising materials for future applications in electronic devices.

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