

# Poly(*N*-3-thenylphthalimide): Conductivity and Spectral Properties

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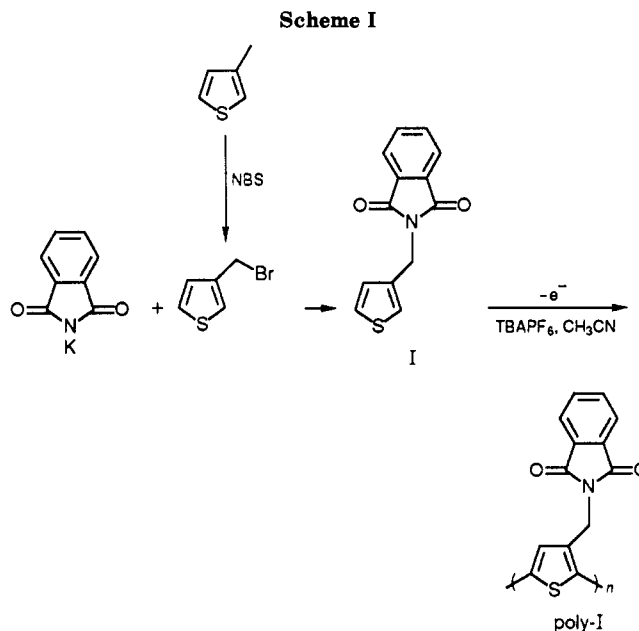
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*N*-3-Thenylphthalimide, I, was electrochemically polymerized on Pt in acetonitrile and the resulting material, poly-I, was characterized by cyclic voltammetry, UV-visible spectroelectrochemistry, and in situ electrochemical-ESR techniques. The polymer was electrochemically active at a more anodic potential than polythiophene itself and exhibited a conductivity of  $2 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$  in the oxidized state.

## Introduction

The electrochemical synthesis of electrically conducting polymers from aromatic monomers has attracted considerable attention because of the potential technological applications of these polymers.<sup>1</sup> Polythiophene and poly(3-substituted thiophenes) are among the most actively studied conducting polymers because they exhibit both high stability and conductivity.

It is known that the presence of  $\beta$ -substituents on the thiophene ring leads to drastic changes in the electronic and mechanical properties of the resulting polymeric materials.<sup>2-4</sup> The relative stability of a particular substituent toward oxidation, as well as electronic and steric factors, determines the ability of a given monomer to undergo anodic polymerization.<sup>3-5</sup> Electron-donating substituents stabilize the radical-cation intermediate in the electrosynthesis, facilitating the polymerization, while electron-withdrawing substituents produce the opposite effect, making it extremely difficult to effect controlled polymerization.<sup>3</sup> In addition, studies on the effect of sterically demanding substituents on the polymerization of branched alkylthiophenes have suggested that bulky substituents held close to the ring at the 3-position of thiophene seriously limit the degree of attainable electrochemical polymerization and cause the resulting oligomer to deviate substantially from planarity, yielding poor polymer main-chain conjugation. As a consequence, a spacer of at least two carbons between the thiophene and the side-group functionality has been claimed to be necessary to obtain polymerization.<sup>4,5</sup> Recently, conducting poly(3-substituted thiophenes) with electron-donating bulky groups directly attached to the thiophene ring (poly(3-phenylthiophene))<sup>6</sup> or one carbon away from the ring (poly(3-benzylthiophene))<sup>9</sup> have been reported. We report here the electrochemical synthesis of a conducting polymer from *N*-3-thenylphthalimide, I, a thiophene with a side group that is both electron withdrawing and bulky, and describe the characterization of this polymer, poly-I, by electrochemical and spectroscopic techniques. This is part of a larger study on the influence of substituents (with oxygen- and nitrogen-containing groups) on the electroactive properties of conducting polythiophenes currently



under investigation in our laboratory.

## Experimental Section

***N*-3-Thenylphthalimide.** The synthesis of I<sup>7</sup> (Scheme I) was accomplished by nucleophilic substitution of 3-(bromomethyl)thiophene<sup>8</sup> by potassium phthalimide (Aldrich).

**Electropolymerization and Polymer Characterization.** The electrochemical experiments were conducted in either a one-compartment or a two-compartment cell containing 0.4 M tetrabutylammonium hexafluorophosphate, TBAPF<sub>6</sub>, in acetonitrile (freshly doubly distilled from CaH<sub>2</sub>). TBAPF<sub>6</sub>, purchased from Aldrich, was recrystallized three times from ethyl acetate/hexanes and dried under vacuum for 24 h before use. The electrochemistry of I was determined by cyclic voltammetry. The initial concentration of I was 0.01 M, and the scan rate was 200 mV/s. For electrochemical polymerization, the initial concentration of the monomer was 0.1 M. Poly-I films were deposited by scanning the potential between 0.0 and +1.5 V at 20 mV/s. Platinum disks (1.7 and 0.1 mm<sup>2</sup>) and a Pt wire were used as working and auxiliary electrodes, respectively. The electrochemical potentials were recorded relative to a silver/0.1 M silver nitrate electrode, Ag/AgNO<sub>3</sub> (+0.31 V against a saturated calomel electrode, SCE). For cyclic voltammetric characterization of the polymer, Pt/poly-I electrodes were washed with acetonitrile, dried, and transferred to a one-compartment cell containing a monomer-free 0.4 M TBAPF<sub>6</sub>/CH<sub>3</sub>CN solution.

Measurements were controlled with a PAR 175 potentiostat/galvanostat equipped with a PAR 173 universal programmer,

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a PAR 179 plug-in digital coulometer, and a Houston 2000 *x-y* recorder. The Pt disk electrodes were polished with 0.3- and 0.05- $\mu\text{m}$  alumina before each experiment. All solutions were bubbled with nitrogen for 15 min prior to the experiments, which were conducted under nitrogen.

UV-visible spectra of the resulting polymers were recorded *in situ* throughout the electrochemical doping/undoping process. For this study, poly-I was electrodeposited on a 6-cm<sup>2</sup> indium tin oxide (ITO) coated glass square plate (Delta Technologies) that had been previously treated in a 1:3 ethanolamine-ethanol bath at 60 °C for 30 min, rinsed with ethanol, and dried at 150 °C overnight. After having been washed with acetonitrile, the ITO/polymer electrodes were used as working electrodes in "sandwich"-type cells suitable for absorbance measurements. The walls of the cell were an ITO/poly-I working electrode and a 6-cm<sup>2</sup> square ITO counterelectrode separated by a 2-cm-i.d., 3-mm-thick mechanically clamped Teflon O-ring. The electrode edges were covered with silver paint contacts coated by epoxy. A hole was punched through the O-ring to introduce the silver wire (0.025-mm diameter) quasi-reference electrode. Two stainless steel hypodermic needles served to fill the cell with monomer and to degas and maintain an inert atmosphere within the cell. The cell was mounted in the spectrophotometer sample cavity perpendicular to the light beam.

Absorbance spectra in the UV-visible region were measured with a Hewlett-Packard 8451-A diode array single-beam spectrophotometer equipped with an HP 9121 D/S disk drive and HP 7470-A plotter components. In a typical spectroelectrochemical experiment, absorbance spectra were recorded at various electrode potentials vs an Ag wire (+0.08 V vs SCE). Each absorbance spectrum was taken after the film was equilibrated for 2 min at a given potential. Stable spectra of poly-I were consistently obtained after this equilibration. For all absorption measurements, an ITO-electrolyte solution-ITO cell was used as a blank. Experiments were conducted under an argon blanket after the solution was purged with argon for 5 min.

For simultaneous electrochemical-electron spin resonance (*in situ* ESR) measurements, polymeric films were grown on a thin Pt mesh from 0.1 M I in a 0.4 M LiClO<sub>4</sub>/CH<sub>3</sub>CN solution. After having been rinsed with hexanes and dried, the Pt mesh/polymer film electrodes were transferred to an ESR cell.<sup>9</sup> The flat portion of this quartz cell (5 cm × 1 cm × 1 mm internal thickness) was fitted into the resonance cavity of the spectrometer. The cell was filled with 0.2 M LiClO<sub>4</sub> in CH<sub>3</sub>CN. ESR spectra (X-band) were recorded by using an IBM-3200 spectrometer operated at 100-kHz field modulation and 5-G amplitude modulation.

Resistivity measurements were carried out by a standard square four-probe method.<sup>10</sup> Film samples were obtained on a 1-cm<sup>2</sup> Pt sheet after passing 0.4 C cm<sup>-2</sup>.

Scanning electron microscopy (SEM) on a JEOL-JEM 35 CX instrument run at 25 kV was used to image oxidized poly-I, poly(3-methylthiophene), and (poly-I + poly(3-methylthiophene)) copolymer samples. To prepare poly-I samples in the oxidized state, films were deposited on ITO at +1.5 V vs Ag/AgNO<sub>3</sub> from 0.1 M I in a 0.4 M TBAPF<sub>6</sub>/CH<sub>3</sub>CN solution (deposition charge 28 mC/cm<sup>2</sup>). The resulting poly-I-coated electrode was disconnected before turning off the potentiostat. The ITO/poly-I electrodes were then washed with acetonitrile, dried at 150 °C for 2 h, and precoated with a ~100-Å gold film to minimize surface charging. Samples of poly(3-methylthiophene) were prepared from 0.1 M 3-methylthiophene in a 0.4 M TBAPF<sub>6</sub>/CH<sub>3</sub>CN solution at +1.5 V (deposition charge 80 mC/cm<sup>2</sup>). The (poly-I + poly(3-methylthiophene)) copolymer was prepared from 0.05 M I + 0.05 M 3-methylthiophene in a 0.4 M TBAPF<sub>6</sub>/CH<sub>3</sub>CN solution at +1.5 V (deposition charge 28 mC/cm<sup>2</sup>). SEM was also used to determine the thickness of the samples by rotating the target by 90°.

## Results and Discussion

The cyclic voltammogram at 200 mV/s of I (0.01 M) in the anodic region exhibits an irreversible peak at +1.92



**Figure 1.** Continuous cyclic voltammograms recorded during the room-temperature polymerization of I on a 0.1-mm<sup>2</sup> Pt disk electrode in acetonitrile containing 0.4 M TBAPF<sub>6</sub> at 20 mV/s. Consecutive scans are shown by the increasing scan numbers.

V vs Ag/AgNO<sub>3</sub> corresponding to the oxidation of the thiophene ring. Oxidation of thiophene itself under similar experimental conditions occurs at +1.54 V. This difference in oxidative peak potential reflects electron withdrawal by the phthalimide group in I. The *n* value for the electrooxidation reaction of I was 1.8, as estimated for a totally irreversible electron-transfer process, where *D* and  $\alpha$  were assumed to be equal to  $1 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup> and 0.5, respectively.<sup>11</sup> The phthalimide substituent is quasi-reversibly reduced to an anion radical at -1.89 V, as is consistent with reported values for the reduction of several *N*-substituted phthalimides in nonaqueous solvents.<sup>12</sup>

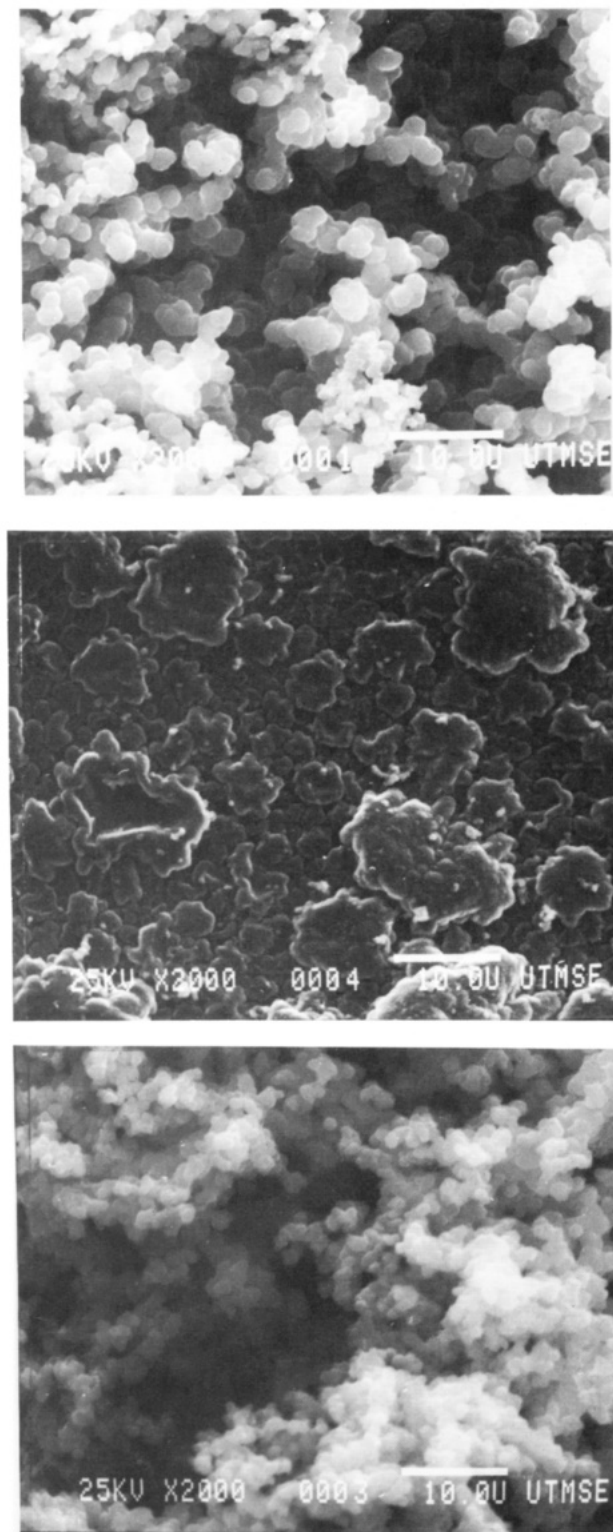
The oxidative polymerization of I (0.1 M) was accomplished by cycling the potential between 0.0 and +1.5 V, producing a solid blue film, poly-I, that had completely peeled away from the Pt surface after completing 10 potential scans. When the reaction was conducted in a one-compartment cell, the phthalimide reduction yielded a soluble green product at the Pt cathode. Continuous cyclic voltammetric curves recorded during the polymerization of I on Pt are illustrated in Figure 1. In the first scan, I is oxidized at about +1.5 V. The oxidation current increases sharply: thus, the electrooxidation reaction is fast and rotation of the phthalimide ring from the plane of the thiophene ring must be sufficiently fast to allow for effective coupling between monomer units, in contrast to previous expectation.<sup>4</sup> The current loop observed at ca. +1.4 V, upon scanning reversal, is attributed to nucleation at early stages of the polymerization. Similar "nucleation loops" have been observed for the electrosynthesis of polypyrrole<sup>13</sup> and polythiophene.<sup>14</sup> The oxidation of the

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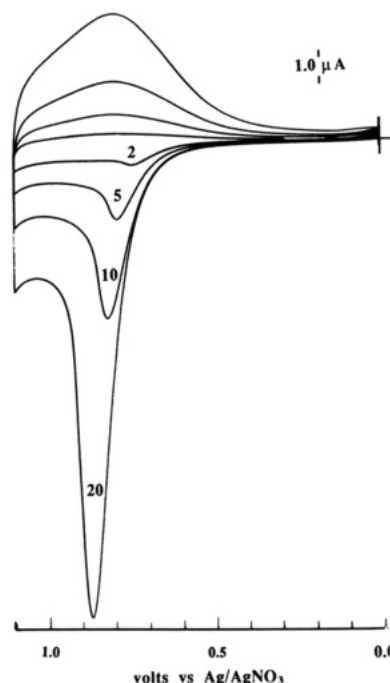
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**Figure 2.** Scanning electron micrographs ( $\times 2000$ ) magnification) of oxidized polymer films on indium tin oxide glass: (top) poly-I ( $2\ \mu\text{m}$  thick); (middle) poly(3-methylthiophene) ( $5\ \mu\text{m}$  thick); (bottom) (I + 3-methylthiophene) copolymer ( $2\ \mu\text{m}$  thick).

monomer is easier on the polymer-modified surface than on a bare Pt electrode, as shown by the shifting of the monomer oxidation peak to less positive potentials upon continuous scanning. The oxidation of the monomer on the modified surface is a complex process as shown by the



**Figure 3.** Cyclic voltammetry of a Pt/poly-I electrode in monomer-free acetonitrile containing  $0.4\ \text{M}\ \text{TBAPF}_6$  at different scan rates at room temperature. The numbers in the figure indicate scan rate in  $\text{mV/s}$ . The Pt disk area is  $0.1\ \text{mm}^2$ .

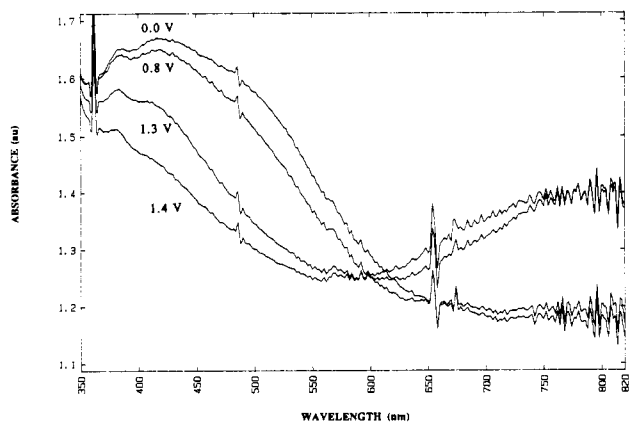
asymmetry of the oxidation peak ( $+1.46$  and  $+1.43\ \text{V}$  on the second and third forward scans, respectively). The reduction wave at around  $+0.75\ \text{V}$  in the first back scan and the oxidation wave at  $+0.86\ \text{V}$  in the second scan are assigned to the reduction and oxidation of the growing polymer. With consecutive scans, the wave attributed to oxidation of the polymer shifts to more positive potentials, indicating increasing resistance as the film grows thicker. The color of the growing film changed reversibly from red to blue as the potential was scanned from  $0$  to  $+1.0\ \text{V}$ .

The presence of the bulky phthalimide group influences the morphology of the resulting polymer. Scanning electron micrographs (SEM) of oxidized poly-I, poly(3-methylthiophene), and a copolymer of poly-I and poly(3-methylthiophene), all produced at the same potential under the same conditions (solvent, electrolyte, and electrode material), are shown in Figure 2. The thickness of the poly-I film (Figure 2, top) was  $2\ \mu\text{m}$  as estimated by SEM. The granular structure of this film fills about 70% of the total volume. The morphologies of poly(3-methylthiophene) ( $5\ \mu\text{m}$  thick)<sup>15</sup> and the copolymer ( $2\ \mu\text{m}$  thick) are shown in Figure 2, middle and bottom, respectively. The composition of the copolymer is as yet unknown but is expected to be more concentrated in 3-methylthiophene than in I since the former polymerizes at lower potentials than the latter. However, the morphology of the copolymer resembles that in Figure 2, top. Thus, the high porosity observed for poly-I and the copolymer can be attributed to the presence of the phthalimide group during nucleation and polymerization. The high porosity of poly-I might be an advantage in catalytic applications. Room-temperature electronic conductivity of a sample of poly-I in the oxidized state was  $2 \times 10^{-4}\ \Omega^{-1}\ \text{cm}^{-1}$ .

(15) Although morphology strongly depends on the thickness of the sample,  $0.5\text{-}\mu\text{m}$ -thick samples of poly(3-methylthiophene) electrosynthesized in  $\text{TBAPF}_6/\text{acetonitrile}$  already show compact morphologies, so that a  $5\text{-}\mu\text{m}$  film is expected to exhibit morphological properties nearly identical with a  $2\text{-}\mu\text{m}$  film; see: Tourillon, G.; Garnier, F. *J. Polym. Sci.* 1984, 22, 33.

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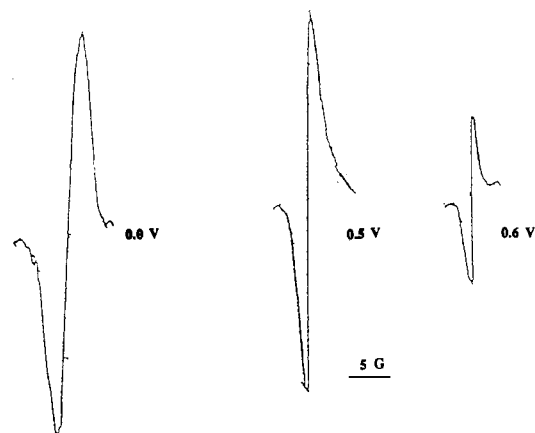
**Figure 4.** In situ absorption spectra of an ITO/poly-I electrode at several potentials. The solution is 0.4 M TBAPF<sub>6</sub> in acetonitrile. The numbers in the figure indicate potential vs Ag.

The redox properties of poly-I films were examined by cyclic voltammetry in monomer-free TBAPF<sub>6</sub>/acetonitrile solutions. Figure 3 shows a family of cyclic voltammograms at several scan rates for a poly-I film, deposited after passing 1.4 mC/cm<sup>2</sup>. The integrated charge under the oxidation wave of this film (0.11 mC/cm<sup>2</sup>) was scan-rate independent in the range 2–20 mV/s. By using the integrated charge method of Diaz and co-workers,<sup>16</sup> we estimate the percentage of the monomeric units in the oxidized form to be 16% of the polymer. The small shift of the oxidative peak toward more positive potentials as the scan rate increases implies that kinetic limitations may be associated with electrolyte and solvent motion in the polymer.<sup>1,17</sup> The cyclic voltammograms are reproducible if the potential range is held between +1.3 and –1.5 V. At more positive potentials, a second irreversible oxidation occurs, destroying the electroactivity of the film. If the cathodic sweep is extended to –2.0 V, the quasi-reversible reduction of the group at –1.90 V rapidly passivates the film.

UV-visible absorption spectra of a 6- $\mu$ m poly-I film on ITO recorded at different potentials vs Ag are shown in Figure 4. At 0.0 V vs Ag, the poly-I spectrum consists of a broad band with an absorption maximum at around 430 nm. As the potential increases, the absorption of this band continuously decreases and a new band evolves at 780 nm. These spectral changes are reversible upon scan reversal if the potential range swept is kept between 0.0 and +1.4 V vs Ag. Parallel spectral results have been reported for polythiophene and derivatives.<sup>18</sup>

The absorption spectrum allows us to estimate the bandgap of neutral poly-I as about 2.6 eV, somewhat larger than the 2.0-eV value for the bandgap of polythiophene.<sup>18</sup> The larger gap indicates partial disruption of conjugation and coplanarity of this polymer by the bulky substituent. The evolution of a band at longer wavelengths (as the potential increases) is consistent with formation of electron carrier bands within the bandgap of the polymer as the electrolyte counteranion is incorporated into the polymeric structure.<sup>18</sup>

The first derivative electron spin resonance (ESR) spectra of poly-I samples were recorded at potentials ranging from 0.0 to +1.3 V vs Ag at 100-mV intervals. At



**Figure 5.** Electron spin resonance spectra of a Pt mesh/poly-I electrode recorded in situ at different electrode potentials vs Ag. The signal gradually decreases with increasing potential and is not detected when the potential is recycled to +0.8 V. The signal does not return when the electrode potential is recycled to more positive values. The experiment was conducted at room temperature.

0.0 V, thin polymer films were characterized by a Gaussian singlet with a line width of 5.2 G,  $g = 1.9996$ . The line width of poly-I is close to the 8.0-G value found for neutral polythiophene.<sup>19,20</sup> Such narrow widths are interpreted in terms of extended conjugation and significant mobility of unpaired electrons. The absence of multiplicity in the observed ESR signal is a common feature of conjugated polymers and indicates high-spin mobility and/or high-spin density.<sup>20</sup> On the other hand, the  $g$  value and the Gaussian shape indicate that the poly-I signal can be mostly attributed to localized paramagnetic defects, as has been reported for poly(*p*-phenylene sulfide),<sup>21</sup> or crosslinks.<sup>20</sup> Although it is not clear whether the low  $g$  value found for poly-I is associated with the presence of the side phthalimide group, the  $g$  value contrasts with typical isotropic  $g$  values observed for the unpaired spins from other polythiophenes, which are not very different from the free electron value, 2.0023.<sup>20</sup>

Figure 5 shows the ESR signal from poly-I at several applied potentials. Raising the applied potential from 0.0 to +0.7 V produced a decrease in the signal line width from 5.2 to 2.5 G, and the signal intensity gradually decreased to 5% of its original value. When the potential was increased to +0.8 V, no signal could be detected. The signal did not return when the electrode potential was recycled to the lower values.

The narrowing of the line at more positive potentials could be evidence for an increase in spin mobility, but the origin of the total irreversible extinction of the signal is unknown. Other previously published studies on polypyrrole have also claimed extinction of the ESR signal.<sup>20</sup> However, the intensity of the observed ESR signal depends on polymerization conditions, since analysis of different samples has produced contradictory results. Even the total absence of an ESR signal for polypyrrole samples has been reported.<sup>22</sup> In situ ESR electrochemical experiments

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performed on other conjugated polymers have shown complex dependence of the signal intensity on electrode potential sweep rates. Future work will describe the magnetic properties of poly-I and the dependence of its ESR signal on temperature.

### Conclusions

Poly(*N*-3-thenylphthalimide), poly-I, was electrochemically synthesized, and the resulting polymeric films exhibited electrochemical and electrochromic reversibility and enhanced porosity. The bulky electron-withdrawing substituent at the 3-position widens the bandgap and favors the presence of localized charges, which, in turn,

negatively affects the conductivity of the resulting polymer.

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**Registry No.** Poly I (homopolymer), 124605-41-0; I(3-methylthiophene) (copolymer), 124605-40-9.

## Second Harmonic Generation by Merocyanine in Mesomorphic Films. An Anomalous Electrostatic Field Effect

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Poled thin films of merocyanine obtained by photo- or thermochromic conversion of spiropyran incorporated in various mesogenic molecules, including liquid-crystal polymers, quasi-liquid crystals, and blends, exhibit strong second harmonic generation (SHG). As well as the "conventional" SHG deriving from the  $\chi^{(2)}_{xxx}$  component, where  $x$  is the poling direction (in the plane of the film), the films exhibit an even stronger anomalous "perpendicular" SHG via  $\chi^{(2)}_{zzz}$  hyperpolarizability when an electric field in the  $x$  direction is reapplied to the samples at room temperature. It is believed that this anomalous SHG arises from merocyanine aggregates stacked in the  $z$  direction being rotated by the field.

Poling a polymeric film containing dopant chromophore molecules or side-chain groups with high molecular hyperpolarizabilities ( $\beta$ ) has become a widely used strategy for preparation of films with large second-order optical nonlinearity exhibiting properties such as second harmonic generation (SHG) and electrooptic modulation (see refs 1-10 and references therein). The usual method of film preparation involves applying a strong external electrostatic field (up to  $10^6$  V/cm) to a doped film heated to above its glass transition temperature ( $T_g$ ), leading to a preferential alignment of dipolar chromophore groups along the field direction. Cooling to room temperature (below  $T_g$ ) prior to removal of the field enables a "freezing in" of the net polar alignment. In practice, some residual molecular mobility is often retained, leading to a loss of the polar alignment over a period of time (ranging from minutes to months) that depends on both polymer matrix

and chromophore properties.

Second-order nonlinear optical processes such as SHG are described quantitatively by the second-order susceptibility tensor,  $\tilde{\chi}^{(2)}$ . Under the electric dipole approximation, a second-order polarization,  $P^{2\omega}$ , is induced by the incident (optical) electric field  $E^\omega$  according to

$$P^{2\omega}_i = \chi^{(2)}_{ijk} E^\omega_j E^\omega_k \quad (1)$$

The observed second harmonic generation efficiency is proportional to the square of  $P^{2\omega}$ . From symmetry considerations, it is readily apparent from eq 1 that in a centrosymmetric medium all components  $\chi^{(2)}_{ijk} = 0$ . Furthermore, in media symmetric about a plane  $i = 0$  all  $\chi^{(2)}$  components containing the index  $i$  either one or three times must similarly be zero. Thus for the case of a polymer poled in the  $x$  direction as discussed above, the only nonzero components are  $\chi^{(2)}_{xxx}$ ,  $\chi^{(2)}_{xyy} = \chi^{(2)}_{zzz}$ , and  $\chi^{(2)}_{yxy} = \chi^{(2)}_{zzz}$ .

A further property of the  $\tilde{\chi}^{(2)}$  tensor of poled films relates to the dependence of the magnitude of components to the strength of the poling field. In the limit of independent interactions of each molecular species with the poling field, a dipolar chromophore is stabilized by an interaction energy of  $\mu \cdot E = \mu E \cos \theta$ , where  $\theta$  is the angle between the molecular dipole direction and the external field. The equilibrium distribution of  $\theta$  values in the sample is determined by the appropriate Boltzmann factors, noting that usually  $\mu E \ll kT$ . In the most commonly studied case of an optically nonlinear chromophore dominated by a single molecular hyperpolarizability component along the same axis as the dipole moment, it is readily shown that the above nonzero  $\tilde{\chi}^{(2)}$  components of a poled film scale

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