Poly[3-(4-octylphenyl)thiophene], a New Processible Conducting Polymer

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ABSTRACT: A new, processible conducting polymer, poly[3-(4-octylphenyl)thiophene] has been chemically synthesized in chloroform using $FeCl_3$ as the oxidant/reagent. The polymer, which is soluble in organic solvents such as chloroform, has been characterized using optical, electrical, and electrochemical methods. We observed a suppressed thermochromism and thermal undoping in this polymer compared to the case of poly(3-alkylthiophene) due to the separation effect of the benzene rings between the poly(thiophene) main chain and the flexible alkyl side chains. At low doping levels, polarons are found to be the charge carriers.

Introduction

Electrically conducting polymers have received much attention from when they were first discovered, as they promise to combine the optoelectronic properties of metals and semiconductors and the processibility of polymers. Unfortunately, almost all of these polymers are nonprocessible and/or stable, preventing many of their potential applications. Many efforts have been made in the search of processible conducting polymers.[1] A major advance in recent years is the solubilization of conducting polymers by attaching long flexible side chains onto the conjugated main chains. Poly(3-alkylthiophene)s (P3AT's) with the alkyl side chains being *n*-butyl or longer are a notable example.[2,3] It has been found that the addition of long alkyl chains not only renders the conjugated polymer chains soluble in common organic solvents and fusible in some cases but also results in such associated phenomena as thermochromism and solvatochromism occurring in the undoped polymers.[4,5] The driving force is believed to be the distortion along the conjugated main chains, caused by steric interaction between the bulky side chains after thermal excitation or in good solvents.[4-6] In addition, P3AT's in the doped state are not stable, especially at elevated temperatures.[7,8] The mechanism behind this so-called "thermal undoping" was suggested to be due to the side chain interaction as well.[9]

One successful way to suppress thermal undoping is obtained by separating thiophene mers bearing long side chains with mers without long side chains.[10] Another remedy, we think, may be to separate the long flexible side chain from the conjugated main chain through a rigid benzene ring. In such a polymer, the benzene rings are likely conjugated with the poly(thiophene) chain,[11,12] and the influence of the interaction between flexible side chains on the poly(thiophene) chain is thus alleviated by the benzene bridge. Thus poly[3-(4-octylphenyl)thiophene] has been prepared. The effects of the benzene ring bridge on the integral properties of the polymer have been studied and compared with P3AT's.

Experimental Section

Poly[3-(4-octylphenyl)thiophene] (POPT) was prepared as follows. 1-Phenyloctane (Aldrich) was brominated with Br_2 in the presence of finely divided Fe powder. The obtained 1-(bromophenyl)octane (boiling point 108–111 °C/0.8 Torr) was Grignard coupled to 3-bromothiophene using nickel(II) bis(1,3-diphenylphosphino) chloride as the catalyst. After washing with water and a saturated aqueous solution of $NaHCO_3$ and drying with Na_2SO_4, the excess 3-bromothiophene was removed by distillation. The crude, solid 3-(4-octylphenyl)thiophene was recrystallized and distilled at 148–160 °C/0.3 mbar. Polymerization was carried out by stirring a chloroform solution containing 0.13 M of the pure monomer and 0.52 M of $FeCl_3$, as both the oxidant and reagent, at room temperature for 30 min. The mixture solution was precipitated with ethanol containing 3.6 vol % of concentrated HCl and filtrated. The crude polymer was then dissolved again in chloroform and washed twice with water. It was dedoped with 2.3% ammonium hydroxide solution in water and washed twice with water, leading to neutral POPT. This POPT was further dissolved in chloroform, precipitated with ethanol, filtrated, and then washed with water in the same way. At last it was washed with ethanol and dried in vacuum at room temperature.

The structure of the obtained POPT was confirmed by FTIR and NMR spectroscopy, and the polymer had a degree of polymerization of 50–70, as determined by gel permeation chromatography. As-synthesized, neutral POPT can be readily dissolved in hot chloroform. After cooling down, it still remains soluble in the solvent. A solution of 10 mg of POPT in 2 mL of $CHCl_3$ was prepared from which POPT films (1–10 μm thick) were cast onto glass or indium–tin–oxide (ITO) coated glass substrates for the following studies.

Optical characterization of thermochromism and thermal undoping was carried out using a Perkin-Elmer Lambda 9 UV/vis/near-IR spectrophotometer. The sample films on either glass or ITO glass substrate were inserted into a copper block, the temperature of which was controllable. The block was then put in a small vacuum jar. This jar was connected to a dynamic pump and placed across the beam passway of the spectrometer. An Olympus BH-2 polarizing microscope was used to observe the color change and fusibility of POPT films during heating. On the objective stage of the microscope was mounted a Mettler FP82 HT hot stage for regular heating. The sample was inserted into the hot stage (exposed to lab air) and heated at a rate of 10 °C/min. To get the stability data of conductivity, POPT films were cast onto a glass substrate with an evaporated four-probe gold pattern. The samples were doped and then mounted onto a sample holder, the temperature of which could be controlled. The conductivity decay at 110 °C in lab air was taken through measuring the change of the four-probe conductivity. A BAS-1000 electroanalytical system equipped with a standard one-compartment three-electrode cell with a POPT film-coated ITO working electrode (ca. 1 cm × 1 cm), a Pt-wire counter electrode, and an Ag/AgCl reference electrode was used for controlled electrochemical doping and cyclic voltammetry.

Results and Discussion

1. Solvatochromism. The optical absorption spectrum (Figure 1) of POPT in chloroform (0.5 mg/mL) shows a sharp peak at 2.7 eV (band gap absorption). As a

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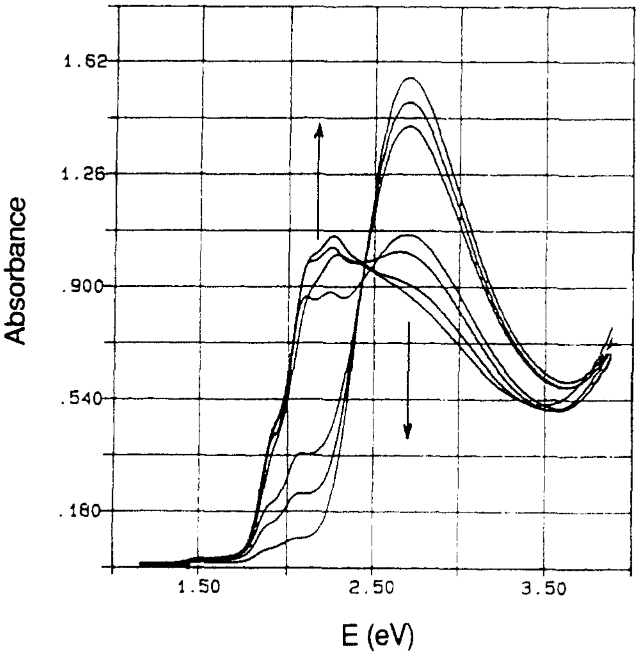

Figure 1. Optical absorption spectra of POPT in solutions (0.5 mg/mL) in $CHCl_3$, 90% $CHCl_3$/10% CH_3OH (volume ratio), 80% $CHCl_3$/20% CH_3OH, 66% $CHCl_3$/34% CH_3OH, 60% $CHCl_3$/40% CH_3OH, 50% $CHCl_3$/50% CH_3OH, and 10% $CHCl_3$/90% CH_3OH, in the sequence shown by the arrows.

comparison, the corresponding peaks of poly(3-octylthiophene) (P3OT)[13] in chloroform, poly(3-phenylthiophene)[12] (PPT) in *N*-methyl-2-pyrrolidone, and thiophene oligomer (11 thiophene units with dodecyl groups at the 2nd, 6th, and 10th units)[14] in chloroform are at 2.8, 2.8, and 2.7 eV. The pendant phenyl and alkyl groups influence the coplanarity of the polymer backbone due to steric hindrance of the pendant groups. In addition, the phenyl groups may be conjugated with the poly(thiophene) backbone. These two effects have opposite effects on the width of the band gap. Thus the band gap in POPT is close to that in the oligothiophene where the dodecyl side groups are distantly separated. The difference between POPT and PPT is, however, not fully understood by the above argument.

The absorption spectrum of POPT in chloroform also shows two very weak peaks at around 1.8 and 2.1 eV. When methanol, a poor solvent, was added to the solution (POPT concentration in the solution was roughly fixed at 0.5 mg/mL solution), the absorption intensity in this region increased in accordance with the decrease of the band gap absorption peak at 2.7 eV. As more methanol was added, the absorption in the range 2–2.5 eV became very strong with two minor peaks at 2.1 and 2.23 eV and a shoulder at 1.9 eV. The absorption peak at 2.7 eV continued to decrease and vanished when the solvent is composed of 1:9 $CHCl_3$:CH_3OH (v/v). The minor peaks, as previously observed and discussed in P3AT films at low temperatures or in solutions in poor solvents, are presumably due to vibronic structure.[15] It is interesting to compare the solvatochromism of POPT and poly(3-hexylthiophene) (P3HT).[5] In the case of P3HT, the band gap absorption peak shifts continuously to lower energy with increasing amount of methanol in the solvent. Such a solvatochromism has been interpreted as the gradual recovery (in poorer solvent) of the planarity on the conjugated backbone, twisted due to solvent-disordered side groups in the good solvent. In the case of POPT, however, the position of the peaks, especially the band gap absorption peak at 2.7 eV, remains fixed, and only the relative intensity of the peak changes. The solvatochromism of POPT probably indicates that at least two distinct phases of POPT exist in the solutions; one refers to the twisted POPT chains due to solvatochromism (E_g = 2.7 eV). The other is the untwisted π-electron-extended POPT chains (E_g in the range 2–2.3 eV). The enhanced chain stiffness due to pendant phenyl groups may cause the presence of untwisted POPT chains in solution. As the quality of the solvent changes, interphase transition occurs. An additional result supports this interpretation. The absorption spectrum of POPT in the solution in poor solvent is close to that in solid films, in which the absorption maximum is just at around 2.3 eV (see below).

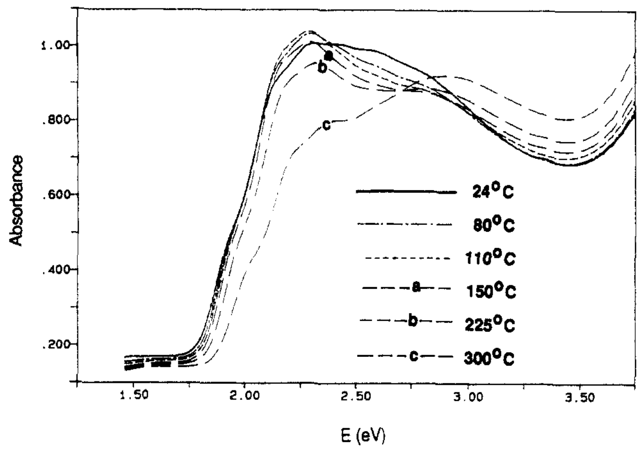

Figure 2. Optical absorption spectra of POPT films in dynamic vacuum at various temperatures.

2. POPT Films at Elevated Temperatures. Optical absorption spectra of POPT films at various temperatures in dynamic vacuum are shown in Figure 2. The spectrum at room temperature has a very broad peak in the range 2.2–2.7 eV with a maximum at 2.3 eV. The band edge (the onset of the band gap absorption peak) occurs at 1.8 eV. Both values are lower than those in P3OT (2.4–2.5, 2.0 eV)[5] but are higher than those in PPT (2.2, 1.7 eV),[11] possibly resulting from the competing effects of enhanced π-electron extension of POPT and PPT due to the phenyl groups and of steric hindrance in POPT due to the long octyl groups. As the sample was heated, the absorption in the range 2.4–3.0 eV decreased, yet the absorption maximum remained fixed until up to about 200 °C. The thermochromism generally observed in conjugated polymers with long flexible alkyl chains such as P3AT and poly(alkyldiacetylene) is suppressed by the phenyl groups in POPT. The benzene rings are conjugated to the poly(thiophene) backbone and enhance rather than disturb the backbone coplanarity at moderate temperatures. They act both as a bridge and a separator between the backbone and the flexible alkyl chains. Thus steric interference of the thermally disordered alkyl chains on the backbone coplanarity is effectively suppressed. At very high temperatures, e.g., 300 °C, a considerably larger change occurs, the absorption maximum moves from 2.3 to 2.9 eV, indicating that the benzene rings may lose their conjugation with the backbone and that the backbone may be considerably distorted by the side groups. Upon cooling down, the spectrum develops gradually toward that for pristine POPT at room temperature, but never reaches that. Some irreversible change must have taken place.

POPT films were also heated in lab air at a heating rate of 5.0 °C/min and observed under a polarizing microscope. Their color was red at room temperature and remained this color up until about 280 °C, but changed as the temperature rose further, and turned to yellow at around 300 °C. After cooling down, the color did not change back.

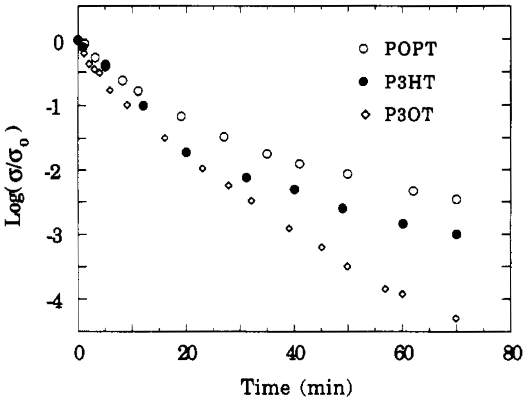

Figure 3. Conductivity decay of $FeCl_3$-doped POPT, P3HT, and P3OT films heated at 110 °C in lab air. σ and σ_0 are the conductivities of the sample at 110 °C at a given time and at time zero.

Thus the previous color change was an irreversible one, due to some kind of degradation. Repeated observations indicated that POPT is infusible. During heating, the solid POPT film softened in the temperature range 160–200 °C. At this stage, it was a sticky solid and could be sheared and spread on the glass substrate. No optically active, liquid crystalline phase was observed under crossed polarizers. With temperatures higher than 250 °C, the softened sample gradually solidified. Some chemical cross-linking may have occurred. The POPT sample was no longer soluble in hot chloroform after this treatment.

3. POPT Films Doped with $FeCl_3$. POPT films were chemically doped in 0.1 M $FeCl_3$ anhydrous solution in acetonitrile, washed with acetonitrile, and dried in ambient conditions. The four-point conductivity of the as-doped films (noted below as POPT($FeCl_3$)) was in the range 0.1–1 Ω/cm, 1 order of magnitude lower than that of P3AT. The thermal stability of the conductivity was measured by heating the sample in lab air on a hot stage, the temperature of which was controlled at 110 ± 5 °C. The result is shown in Figure 3 and compared to those for P3HT[7] and P3OT obtained by the same procedure. Neutral P3OT and P3HT were obtained from Neste Oy as neutral powders. The conductivity of POPT, P3HT, and P3OT degrades 2.5, 3, and 4 orders of magnitude respectively in 1 h. The thermal stability of POPT($FeCl_3$)) was thus improved to some extent by the introduction of bridging phenyl groups.

The thermal stability of POPT($FeCl_3$) was further studied by observing its optical absorption spectrum during heating. Figure 4 shows the UV/vis/near-IR absorption spectrum of POPT($FeCl_3$) sustained at a specific temperature for 20 min in a dynamic vacuum chamber. At room temperature it shows two peaks in the near-IR region, a strong one at around 0.6 eV, and a weaker one at around 1.5 eV, typical of bipolaron-conducting polymers. As the temperature is elevated, the 0.6-eV peak moves to lower energy and its intensity decreases, while the 1.5-eV peak first intensifies and then turns to decrease. The absorption around 2.5 eV, due to the band gap transition, increases according to a gradual undoping process. This process is an irreversible one, as the spectrum does not change back at all as temperature drops down to room temperature. The spectrum at 130 °C indicates that at this temperature the sample is still conductive, though less so than the pristine POPT($FeCl_3$). But after continuing for 2 h, the spectrum changes a lot and now appears like the spectrum of the polymer at very low doping levels. The two peaks at 1.2 and 1.5 eV and the peak at <0.5 eV probably imply a polaron-dominating state (vide infra). Figure 5 shows the spectrum change at 110 °C through a period of more than 20 h. The spectrum still retains the characteristics of a doped conjugated polymer even after 20 h, indicative of a thermally stable conducting polymer. The optical spectrum of $FeCl_3$-doped P3AT, on the other hand, develops much more rapidly toward that for undoped P3AT.

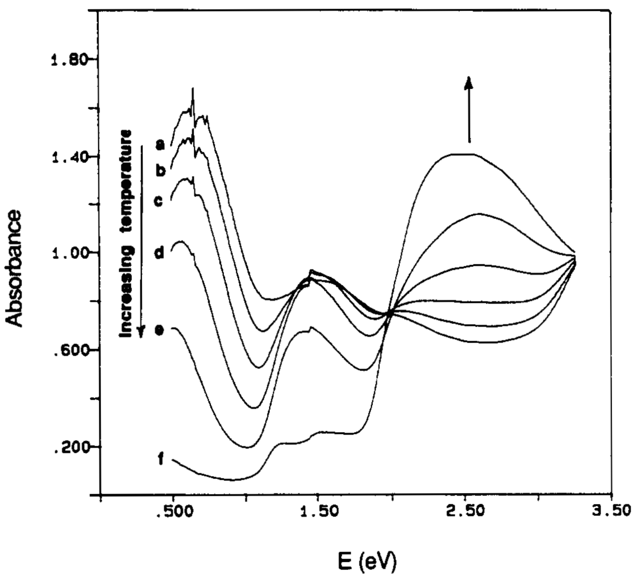

Figure 4. Optical absorption spectra of POPT($FeCl_3$) films before heating (a) and heated at 70 °C (b), 90 °C (c), 110 °C (d), and 130 °C (e) for 20 min, and at 130 °C for 2 h (f) in dynamic vacuum.

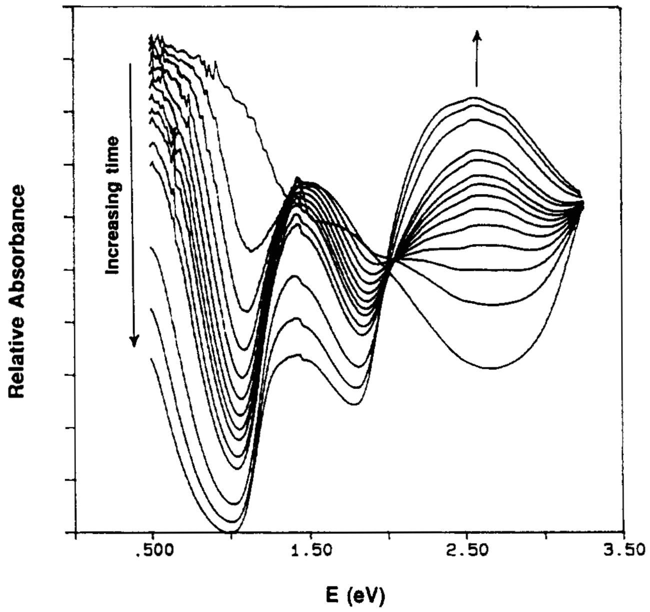

Figure 5. Evolution of the optical absorption spectrum of a POPT($FeCl_3$) film being heated at 110 °C in dynamic vacuum for 0, 30, 60, 90, 120, 150, 180, 210, 240, 300, 360, 600, 900, and 1200 min.

It is not clear why the conductivity of POPT($FeCl_3$) decays rather rapidly at 110 °C in lab air (Figure 3). One possibility is that some groups, maybe the phenyl groups, react with O_2 in air at elevated temperature. The absorption of the optical spectrum in the near-IR region is due to bipolaron transitions in the polymer, and the absorbance represents the bipolaron concentration. Thus the absorbance at 0.6 eV during heating at 110 °C (Figure 5) is plotted versus time to show the rate of the thermal undoping (Figure 6a (top)). From these data the best fit

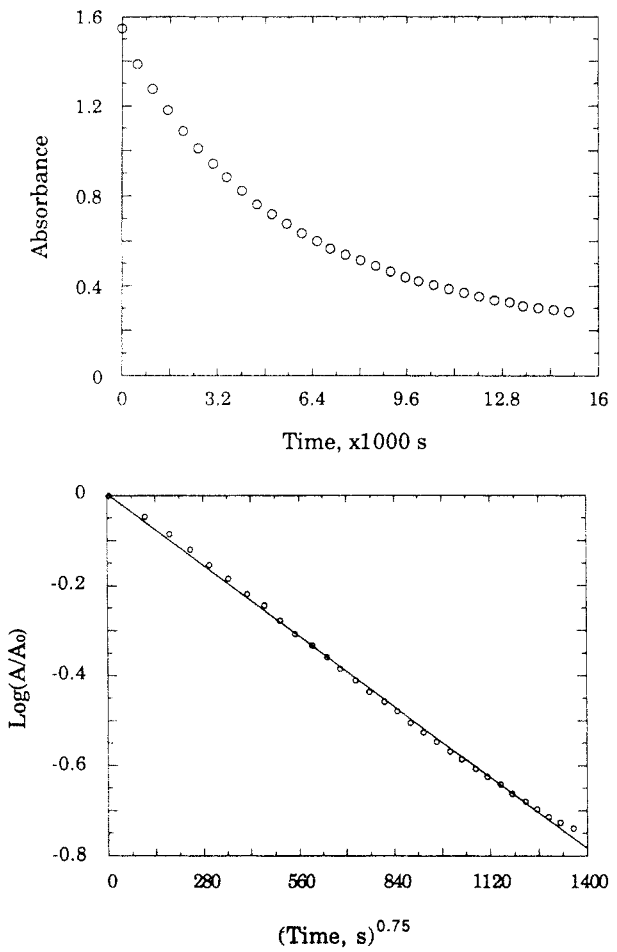

Figure 6. Intensity decay of the near-IR peak at 0.6 eV in the optical absorption spectrum of a POPT($FeCl_3$) film being heated at 110 °C in dynamic vacuum.

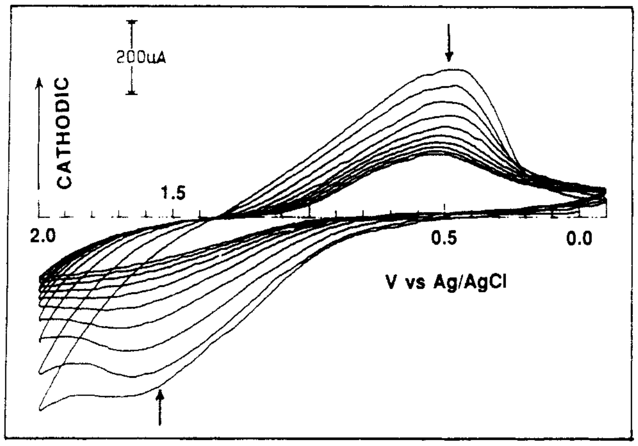

Figure 7. Cyclic voltammograms of a POPT film on an ITO electrode in 0.1 M $LiClO_4$ solution in acetonitrile. Scan rate: 100 mV s^{-1}.

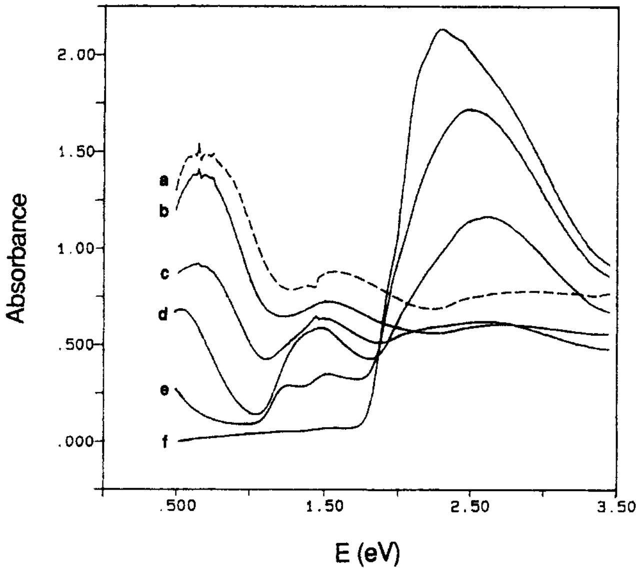

Figure 8. Optical absorption spectra of POPT films at various potentials in 0.1 M $LiClO_4$ solution in acetonitrile: (a) 2.0, (b) 1.6, (c) 1.2, (d) 1.0, (e) 0.8, and (f) 0.0 V vs Ag/AgCl.

relation between the absorbance (A) and time (t) is

$$\log (A/A_0) = 0.000557t^{0.75}$$

as shown in Figure 6b (bottom). This stretched exponential form of the kinetics of undoping is different from that observed in P3AT's, where two stages are observed.[9]

Under a microscope, POPT($FeCl_3$) is blue-green. Upon heating at 5.0 °C/min in lab air, it turns gradually to blue-yellow at ≥120 °C, and to red-yellow in the temperature range 170–200 °C. Both are irreversible processes.

4. Electrochemical Redox Properties; Polaron Formation at Low Doping Level? Cyclic voltammograms of a POPT-coated ITO electrode (0.12 mg of POPT, 1-cm^2 area) were recorded in a one-compartment three-electrode cell with a Pt-wire counter electrode and an Ag/AgCl reference. The electrolyte solution was 0.1 M $LiClO_4$ in acetonitrile. The cathodic and anodic peaks, at 0.5 and 1.6 V vs Ag/AgCl, during the first cycle are separated by 1.1 V (Figure 7). This polymer should be stable in its neutral state, but not at the oxidatively doped state. The redox stability of POPT is poor, and its capacity decreases by 1–2 fold after 10 cycles.

Figure 8 shows the optical absorption spectra of POPT at various oxidation levels or doping states. At 0.0 V vs Ag/AgCl, where the polymer is completely undoped, only a strong band gap absorption peak appears, indicative of a neutral and highly-conjugated polymer (E_g = 2.3 eV). At 0.8 V, where it is just slightly doped, three peaks appear in the spectrum, at 1.2, 1.5, and 2.5 eV. The spectrum also indicates an additional peak at <0.5 eV. This spectrum is typical for a polaron domain with two polaron states in a gap of 2.5-eV (or 2.7-eV) width.[16] Polarons and/or bipolarons, depending on the doping level, have been suggested to be the charge carriers in conjugated polymers with a nondegenerate ground state.[16] However, in only a few cases have people observed the presence of polarons in these polymers from their optical spectra.[17,18] Here we provide another evidence for the presence of polarons at low doping levels. The widening gap during doping could be understood as the consequence of extraction of electronic states close to the band edges in the formation of polaron states in the gap.

The present result provides evidence that polarons are the main charge carriers at low doping levels in POPT. With increasing doping level, the absorption in the near-IR region increases while the band gap absorption decreases and the gap enlarges. At 2.0 V where POPT is fully doped, the spectrum shows two broad peaks in the near-IR region, a strong one at 0.6–0.7 eV and a weaker one at 1.6 eV, probably due to a bipolaron domain. The band gap absorption peak is now hardly noticeable. These processes are all reversible.

A comparison of Figures 4 and 8 indicates that the thermal undoping of POPT($FeCl_3$) resembles its electrochemical undoping. Bipolarons in the doped polymers transform to polarons upon heating. The polarons are then quenched upon further heating, and a nonconducting or poorly conducting polymer results.

Conclusion

In conclusion, a new soluble conducting polymer, POPT, has been chemically synthesized. In its solutions there are at least two POPT phases present. One is planar, π-electron-extended chains, and the other is the distorted POPT main chains. A phase transition (solvatochromism) occurs as the quality of the solvent changes. Thermochromism and thermal undoping, which are observed by optical spectroscopy, have been effectively suppressed in POPT compared to the case of P3AT's due to the separation effect of the benzene rings between the poly(thiophene) main chain and the flexible alkyl side chains. The conductivity stability of $FeCl_3$-doped POPT has also been improved to some extent, but not as much as we expected. Charging–discharging stability is poor.

An interesting aspect is that the main charge carriers at low doping levels in POPT are probably polarons with four transitions in the optical spectra at 2.5, 1.5, 1.2, and <0.5 eV. Bipolarons are the main carriers at high doping levels. Thermal undoping appears similar to electrochemical undoping, as evidenced in optical spectra. Polarons are first generated, which are then quenched upon further heating.

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Registry No. POPT (homopolymer), 141807-85-4; $FeCl_3$, 7705-08-0; 1-phenyloctane, 2189-60-8; 1-(bromophenyl)octane, 51554-93-9; 3-bromothiophene, 872-31-1; 3-(4-octylphenyl)thiophene, 141807-84-3.