Solvato-Controlled Doping of Conducting Polymers

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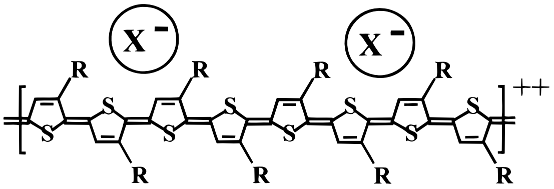
Silver(I) is employed to dope poly(3-alkylthiophenes) (P3ATs) and other conjugated polymers. Solutions containing silver(I) salts and P3ATs, which usually undergo spontaneous reaction, doping, and precipitation, were stabilized using coordinating ligands that modify the reduction potential of the Ag(I) species. Upon removal of the coordinating ligand, spontaneous oxidative doping of the polymer occurred. Uniform electronically conducting films were thus obtained by simultaneous evaporation of both solvent and Ag(I)-coordinating ligand—a process termed "solvato-controlled doping". Doping was observed with a variety of silver(I) salts consisting of relatively electronegative counterions, whereas a series of poly(3-alkylthiophenes) possessing increasing head-to-head dyad content showed a decreasing tendency to undergo Ag(I)-doping due to the increasingly positive oxidation potential of the polymer. Solvato-controlled doping of polyaniline and poly(3-methoxythiophene) with Ag(I) is also described, thus demonstrating the applicability of this approach to other conducting polymer systems.

Introduction

There have been significant advances in rendering polythiophenes processable by the attachment of long alkyl chains to the α- and β-position of the thienyl ring.[1] However, the *oxidized*, electronically conducting forms of these materials are generally insoluble and unprocessable as a result of the increased interannular double-bond character and resultant rigidity (Scheme 1).

Scheme 1. Oxidized, Conducting Form of Poly(3-alkylthiophenes) (X− Represents the Counterion)



Invariably, the oxidizing agent chosen to "dope" a particular conjugated polymer possesses a reduction potential that is electrochemically more positive than the oxidation potential of the polymer. Upon the addition of the oxidizing agent to a solution of the polymer, the solution immediately discolors indicating doping, and the doped polymer precipitates from solution. Since the majority of potential applications of conducting polymers requires the formation of thin films, the neutral, soluble polymer is first cast as a thin film and then subsequently doped with a solution of the oxidizing agent to impart conductivity. This method can lead to considerable strain in the film, resulting in poor film morphology and cracking since the charge-balancing counterions are required to imbibe into a dense partially crystalline, film. Furthermore, this method requires additional processing and rinsing steps that may interfere with processing of technological devices. There is a need, therefore, to develop new chemistry in which conducting polymers can be made soluble, and the conducting polymer spin-cast and formed in a single step. In this regard, the work of Cao et al., in which polyanilines are solubilized with large counterions remains a major advancement in processing conducting polymer solutions.[2] However, their technique appears restricted to polyanilines and has not been successfully implemented for other classes of conducting polymer.

We have taken a different approach to the problem of solution processability. It involves the predication that the reduction potential of the oxidizing agent, and thus its ability to dope polymers, can be decreased through coordination chemistry. That is, the doping agent can be switched between non-oxidizing and oxidizing by the presence or absence of a coordinating ligand. Removal of the coordinating ligand during thin-film processing should enable the oxidizing agent to dope the polymer. As proof of this concept, we first describe oxidative doping of poly(3-alkylthiophenes) (P3AT) using silver(I) salts and, in particular, silver triflate (AgOTf). The mechanism of Ag(I) doping, the properties of the resulting materials, and the limitations of the doping process in terms of the range of applicable Ag(I) salts and conjugated polymers are described. This paper then describes stabilization of conducting polymer

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(1) (a) Elsenbaumer, R. L.; Jen, K. Y.; Oobodi, R. *Synth. Met.* **1986**, *15*, 169. (b) Sato, M.; Tanaka, S.; Kaeriyama, K. *J. Chem. Soc., Chem. Comm.* **1986**, 873. (c) Roncali, J. *Chem. Rev.* **1992**, *92*, 711.

(2) Cao, Y.; Smith, P.; Heeger, A. J. *Synth. Met.* **1989**, *55−57*, 3514.

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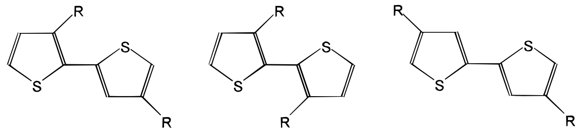
Scheme 2. Configuration of Dyads in P3ATs



(a) HT dyad (b) HH dyad (c) TT dyad

solutions by the addition of complexing agents to solutions containing both P3ATs and silver triflate. The complexing agent prevents the doping action of Ag(I). Upon removal of the complexation agent doping proceeds. As will become evident, the simplest method of removing the stabilizing coordination compound is through evaporation. This strategy allows preparation of conducting polymer films from stable polymer solutions.

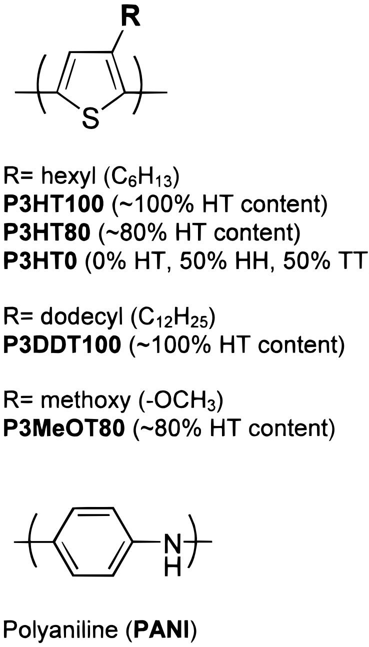
Experimental Section

Chemicals. Silver(I) triflate, magnesium, 1-bromododecane, 1-bromohexane, 3-bromothiophene, Ni(dppp)Cl$_2$, MgBr$_2$·Et$_2$O (Aldrich Chemical Co.) were used as received. Acetonitrile, nitromethane, and chloroform (spectroscopic grades) and anhydrous FeCl$_3$ were purchased from BDH Chemicals. Pyridine (Caledone Laboratories Ltd.) was distilled over potassium hydroxide, and xylene (Caledone) was used without further purification. Methanol was dried over CaH$_2$ and freshly distilled.

Polymer Synthesis. 2,5-Coupling of the 3-alkylthiophenes results in three different regiochemical dyads: the "head-to-tail" dyad (HT), i.e., 2,5′-coupling; the "head-to-head" dyad (HH), 2,2′-coupling; and "tail-to-tail" dyad (TT), 5,5′-coupling (Scheme 2).

Poly(3-hexylthiophene) and poly(3-dodecylthiophene) of high head-to-tail ratio (>98%) were synthesized according to the procedure described by McCullough et al.[3] The number average molecular weight of the chloroform soluble fraction was 7600, and the molecular weight distribution was 1.22. Poly(3-hexylthiophene) possessing 80% head-to-tail ratio was prepared by oxidative coupling of 3-hexylthiophene using ferric chloride.[4] The number average molecular weight was found to be 80 000, and the molecular weight distribution was 2.5. Poly(3,3′-dihexyl-2,2′-bithiophene), which is absent of HT linkages, and consisting solely of HH and TT linkages was prepared in the following manner. 2-Bromo-3-hexylthiophene was first prepared by reacting 3-hexylthiophene (0.37 mol), dissolved in 550 mL of a 1:1 mixture of chloroform and acetic acid, with *N*-bromosuccinimide (0.37 mol) at 4 °C. The white suspension was allowed to warm to room temperature over a period of 1 h to form a pale yellow solution. The reaction mixture was diluted with diethyl ether and subsequently extracted with an aqueous potassium hydroxide solution. The solvent was removed to give yellow liquid, bromo-3-hexylthiophene, with 79.4%. This product was used to prepare 3,3′-dihexyl-2,2′-bithiophene via oxidative coupling of 2-lithium thiophene: 2-bromo-3-hexylthiophene (0.15 mol) was dissolved in 70 mL of freshly distilled dry diethyl ether. The solution was cooled to −68 °C using a dry ice/acetone bath. *n*-Butyllithium in ether (400 mL, 0.156 mol) was added to the above solution over a period of 45 min. The temperature of the reaction mixture was kept between −60 °C and −70 °C during the addition. After stirring the solution for 25 min at −70 °C, anhydrous cupric chloride (0.30 mol) was added, and the resultant green suspension was stirred for 30 min. The suspension turned brown and then black as the reaction mixture was allowed to warm over a period of 12 h. A brown solid and a red solution was obtained. The reaction mixture was refluxed for 3 h before quenching with an aqueous solution of ammonium chloride and potassium cyanide. The crude product was extracted with diethyl ether, the solution was dried over anhydrous magnesium sulfate, and the solvent was removed. The product was purified by fractional distillation to give a 25% yield. 3,3′-Dihexyl-2,2′-bithiophene (3.20 mmoles) was polymerized using ferric chloride (14.44 mmol) dissolved in 12 mL of chloroform. A green solid was obtained which turned yellow with treatment with a 29% NH$_3$ aqueous solution. The polymer was extracted and purified to yield 87% of poly(3,3′-dihexyl-2,2′-bithiophene). This polymer is abbreviated **P3HT0**, the zero indicating the absence of HT dyad linkages.

Scheme 3. Structures and Abbreviations of Polymers Used in This Work



R= hexyl (C$_6$H$_{13}$)
P3HT100 (~100% HT content)
P3HT80 (~80% HT content)
P3HT0 (0% HT, 50% HH, 50% TT)

R= dodecyl (C$_{12}$H$_{25}$)
P3DDT100 (~100% HT content)

R= methoxy (-OCH$_3$)
P3MeOT80 (~80% HT content)

Polyaniline (**PANI**)

3-Methoxythiophene was prepared by the procedure outlined by Gronowitz.[5] A flask containing sodium (0.44 mol) was washed with hexane, pumped dry, and purged with N$_2$. The flask was cooled and freshly distilled methanol was slowly added. The mixture was stirred for an hour and 3-bromothiophene (0.18 mol) was added dropwise. Dry CuO (9.0×10^{-2} mol) and KI (1×10^{-3} mol) were added to the flask, and the mixture refluxed for 2 days. The reaction was quenched, and the 3-methoxythiophene extracted using anhydrous ether and dried over anhydrous MgSO$_4$ to yield a colorless monomer (3MeOT, 70% yield). Polymerization of P3MeOT was achieved using a procedure adapted from Sugimoto.[4] Anhydrous FeCl$_3$ in CHCl$_3$ (4 equiv, distilled, 125 mL) was reacted with 1 equiv of 3-methoxythiophene for 2 h. The polymer was precipitated with methanol, washed with aqueous ammonia, and dried to yield 20−30% of poly(3-methoxythiophene). Polyaniline was synthesized and doped by camphorsulfonic acid according to a reported procedure.[6] The polymers used in this study and their abbreviations are shown in (Scheme 3).

Instrumentation and Procedures. Elemental analyses were performed by Canadian Microanalytical Service, Ltd., Delta, B.C. Head-to-tail ratios of polymers were determined by NMR spectroscopy using a Bruker-AMX 400 spectrometer.[7] Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC, Waters) using polystyrene as a standard and corrected for the differ-

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(3) McCullough, R. D.; Lowe, R. D. *J. Chem. Soc., Chem. Commun.* **1992**, 70.

(4) Sugimoto, R.; Takeda, S.; Gu, H. B.; Yoshino, K. *Chem. Express* **1986**, *1*, 635.

(5) Gronowitz, S. *Ark. Kemi* **1987**, *12*, 239.

(6) Mattoso, L. H. C.; MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1994**, *68*, 1.

ence in hydrodynamic volumes.[8] UV–visible spectra of polymer solutions and polymer films on glass slides were recorded on a Cary 3E spectrophotometer. Conductivities of doped polymer films were measured with a collinear four-point probe. Thin, free-standing polymer films for transmission electron microscopy (TEM) were obtained by dropping a 10 mg/mL chloroform solution onto a surface of distilled water. Evaporation of the chloroform resulted in a thin film that was collected on a copper grid. An Hitachi H-8000 transmission electron microscope equipped with a LINK QX2000 thin-window energy-dispersive X-ray analyzer was operated at 200 kV to obtain electron micrographs and to collect X-ray emission spectra. Doped samples were obtained using the above method followed by immersion into a 0.1 M diethyl ether solution of AgOTf for 5 min followed by two rinses with dry diethyl ether. Polymer films which were doped using solvato-controlled doping techniques were also examined using TEM; however, these could not be formed on aqueous media because the dopant dissolved into the aqueous layer. Thus, solutions containing ~5 mg/mL polymer and AgOTf (~6:1 monomer to dopant ion ratio) were dissolved in a 1:1:0.1 $CHCl_3$/toluene/pyridine mixture and filtered through a 0.22 μm Millipore Millex GV disposable filter. Thin films were spin cast onto a glass substrate and covered by a layer of evaporated NaCl and subsequently a layer of carbon. The carbon impression of the surface was released by slow immersion of the sample edge into distilled water. The TEM sample grid was then lifted through the carbon extraction film.

Electron paramagnetic resonance (EPR) measurements were performed on polymer samples using an X-band (9.5 GHz) Bruker ECS106 spectrometer at room temperature. Freshly recrystallized DPPH (α,α'-diphenyl-β-picrylhydrazyl) was used as the reference for g-value and intensity calibration. The EPR line width for DPPH was ca. 1.5 G. The microwave power was set to well below the sample saturation level and the modulation amplitude was kept at ca. 25% of the peak-to-peak line width. Spectra were obtained at 25 °C and ambient pressure.

A conventional three-electrode cell employing a glassy carbon working electrode (0.07 cm^2), a Pt gauze counter-electrode, and a saturated calomel reference electrode (SCE) were used for electrochemical measurements. The working electrode was polished with diamond paste, rinsed thoroughly in deionized water, and dried. The electrochemical measurements were conducted in 0.1 M solutions of $Bu_4N^+ClO_4^-$ in nitromethane or acetonitrile by sweeping the potential at 100–250 mV s^{-1}. Prior to measurements, electrolytes were deaerated by purging with nitrogen. Poly(3-alkylthiophenes) were deposited on a glassy carbon electrode from a toluene solution and dried for 1 h at room temperature. Where required, cyclic voltammetry was performed on polymer solutions using in 0.1 M solutions of $Bu_4N^+ClO_4^-$ in dichloromethane. Electrochemical measurements on dopants were performed on 1 mM solutions at room temperature.

Two methods of Ag(I) doping were employed: (a) Polymer films(~40–200 nm) were spin-cast onto glass slides from solutions of polymer in chloroform or xylenes/chloroform (1:1 mixtures) and doped by immersion into solutions of the dopant in nitromethane or ether; (b) spin-casting of polymer films from solutions of the polymer and silver(I) triflate in xylenes/chloroform/pyridine (1:1:0.1 vol %), followed by drying at 65 °C for 20 min led to films of doped polymer.

Results and Discussion

Figure 1 shows the change in UV/vis absorption spectra of regioregular poly(3-dodecylthiophene) (P3DDT100) possessing ~100% HT dyads, in a solution of toluene/heptane (volume ratio 1:1),[9] upon addition of 3.5 mM AgOTf. The broad absorption band at 440 nm, indicating extensive π-delocalization, gradually diminishes over a period of 6 h. A broad absorption band emerges at 844 nm indicating the formation of bipolarons. As oxidization nears completion the polymer precipitates from solution. Similar results were obtained with regioregular poly(3-hexylthiophene) (P3HT100). Films of P3DDT100 and P3HT100 exhibited similar changes in the absorbance spectra when immersed into toluene/heptane solutions of AgOTf. Doping of thin polymer films was complete after less than 1 min and they exhibited a new absorption band in the NIR region at 2111 nm. The doping level of a P3HT100 film following immersion into a solution of AgOTf was determined to be 20% by chemical analysis, i.e., one Ag per five thienyl rings. Doped films of P3DDT100 and P3HT100 possessed conductivities in the range 1–20 S/cm.

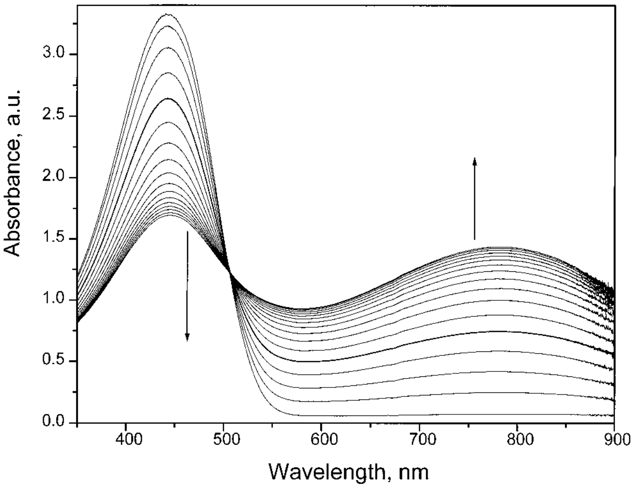

Figure 1. Evolution of UV–vis spectra of poly(3-dodecylthiophene)–100% HT (P3DDT100) (1 mg/mL) in the presence of silver triflate (3.5 mM) over a period of 6 h in toluene/heptane solutions (volume ratio 1:1). Spectra were recorded 20 min apart.

TEM. Micrographs collected from pristine P3HT100 films, and carbon films extracted from the surface of these films were relatively featureless, while those films that had been oxidatively doped with AgOTf showed the presence of small particles ranging from 60 to 250 nm in size (Figure 2). The particles and the surrounding film were differentiated using the energy-dispersive X-ray analysis. Analysis of the particles indicated they were crystallites of metallic silver, whereas the surrounding polymer matrix showed no evidence for the presence of silver.

Since it is possible that 200 kV electrons could generate the silver particles from silver(I), an indirect method was used to determine whether silver was initially present as silver(I) or as metallic silver particles prior to exposure to the electron beam. Carbon extraction films lifted from the surface of P3HT100 films, which had been doped using both immersion as well as solvato-controlled techniques, were found to contain particles that were of similar size to, and contained the same elements as, those found in films which had been observed directly by TEM. Thus, the silver particles must have been formed during the oxidative doping process.

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(7) Sato, M.; Morii, H. *Macromolecules* **1991**, *24*, 1196.

(8) Holdcroft, S. *J. Polym. Sci., Polym. Phys.* **1991**, *29*, 1585.

(9) This solvent mixture was chosen because (a) it dissolved both the polymer and Ag(I) salt and (b) it did not strongly coordinate with Ag(I).

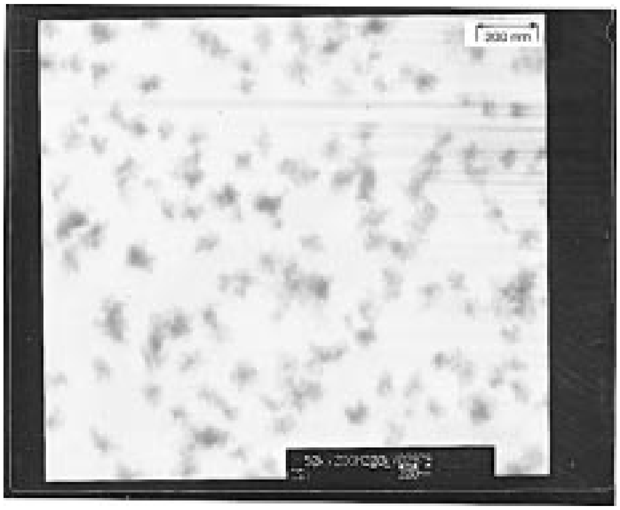

Figure 2. Transmission electron micrograph of a P3HT100 film doped with silver triflate.

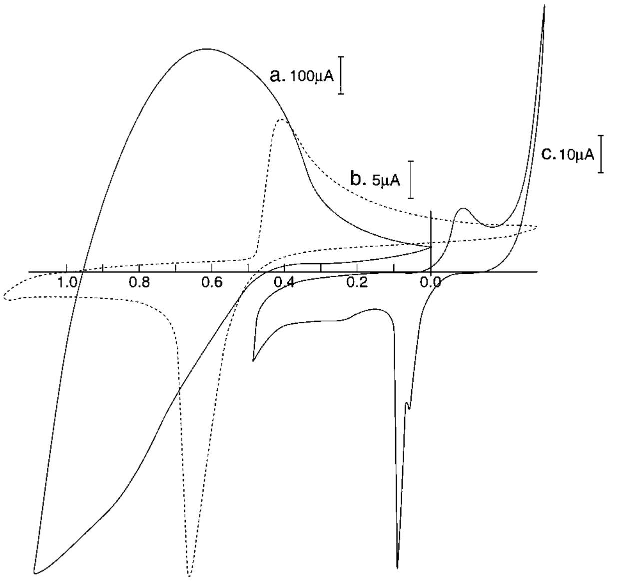

Figure 3. Cyclic voltammetry of (a) a P3HT100 film, (b) 1 mM AgOTf, and (c) 1 mM AgOTf in the presence of pyridine (5 vol %). Electrolyte: 0.1 M tetrabutylammonium perchlorate in nitromethane.

Electrochemistry. The extent of oxidative doping of conducting polymers is usually dependent on the reduction potential of the oxidant in relation to the oxidation potential of the polymer. Thus it was useful to determine the redox potentials associated with oxidation of the polymer and reduction of the Ag(I) salt. Figure 3a shows a voltammogram of a P3HT100 film in 0.1 M tetraethylammonium perchlorate in nitromethane. The onset of oxidation occurs at $\sim$+0.5 V versus SCE, but the potential required to fully rereduce the films on the reverse scan is several tenths of a volt less positive than this ($<+0.3$ V) because oxidation of the polymer is followed by relaxation of the backbone to a more coplanar and energetically more stable quinoidal form. The cyclic voltammetry of AgOTf in the same electrolyte (Figure 3b) indicates a reduction peak potential of $\sim$+0.4 V for $Ag^+ + e^- \rightarrow Ag^0$. The overlap of the two voltammograms is such that electron transfer between Ag^+ and the polymer can occur. This is indeed supported by the observation of oxidative doping of the polymer and the formation of metallic silver. The oxidative doping reaction is given below. These results are consistent with previous studies which show that electroless deposition of silver occurs on polyacetylenes.[10]

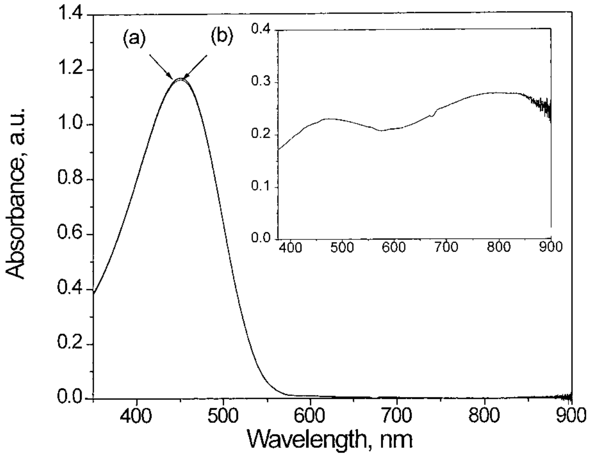

Figure 4. UV–vis spectra of P3DDT100 (1 mg/mL) in toluene/heptane/pyridine solution (volume ratio 1:1:0.1): (a) in the absence of silver triflate, (b) 6 h after the addition of silver triflate (3.5 mM). Inset: Spectrum of the polymer film cast from solution (b).

$$\mathrm{P3AT} + 2[\mathrm{Ag^+OTf^-}] \rightarrow \{[\mathrm{P3AT}]^{2+}2\mathrm{OTf^-}\} + 2\mathrm{Ag}^0 \quad (1)$$

Solvato-Controlled Doping. It is well-known that Ag(I) forms coordination complexes with a wide variety of ligands.[11] Coordination changes the redox potential of the $Ag^{+/0}$ couple because of the additional electron density provided by the ligand. We postulated, therefore, that if a Ag-coordinating ligand shifts the reduction potential of Ag(I) to values more negative than the oxidation potential of the polymer, it will prevent the doping process. Indeed pyridine, a strong coordinating ligand for Ag(I), was found to shift the electrochemical reduction of Ag(I) to −0.1 V vs SCE (Figure 3c). The addition of pyridine to a toluene/heptane solution of 4:1 mol ratio of AgOTf/P3HT100 (or P3DDT100) completely suppressed doping of the polymer as shown in Figure 4. The solutions remain unchanged on standing indefinitely. We also note that other Ag(I)-coordinating ligands, e.g., acetonitrile, benzonitrile, and triethylamine, stabilize P3HT100/AgOTf solutions to varying extents. This supports the following generalized equilibrium reaction describing the competition for the Ag(I) species.

$$[\mathrm{P3AT}]^{2+} + 2\mathrm{Ag} + 2nL \leftrightarrow P3AT + 2[\mathrm{AgL}_n]^+ \quad (2)$$

Upon evaporation of the orange colored solution of P3HT100/AgOTf stabilized with pyridine the resultant polymer film turns blue in color indicating that it becomes doped by Ag(I). Transmission electron micrographs of these films were similar to those obtained by immersion of the neutral film into a solution of silver

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(10) Clarke, T. C.; Geiss, R. H.; Kwak, J. F.; Street, G. B. *J. Chem. Soc., Chem. Commun.* **1978**, 489.

(11) For example, in aqueous solution the coordination constants for stepwise complexation of Ag^+ with NH_3, to form AgL_2^+, are 2.1 × 10^3 and 2.1 × 10^3, respectively.

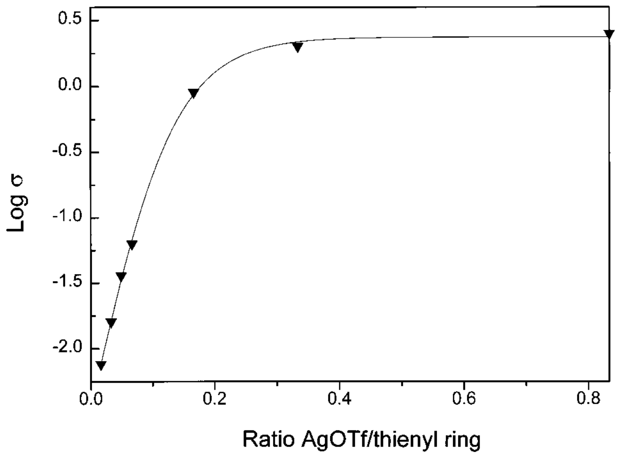

Figure 5. Plot of conductivity of P3DDT100 films vs molar ratio of AgOTf:thienyl group present in the films.

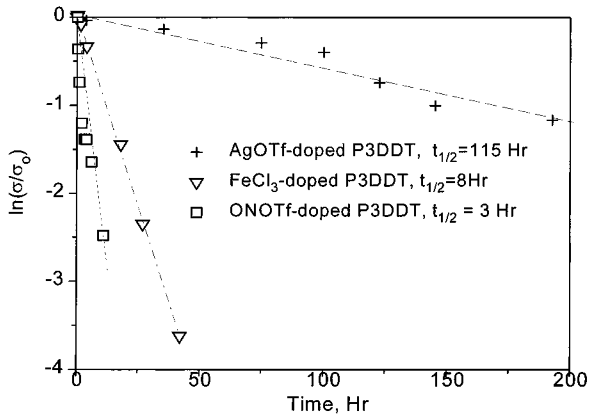

Figure 6. Plots of normalized conductivity vs time for various doped films of poly(3-dodecylthiophene)—100% HT (P3DDT100). Films (100 nm thick) were kept in the dark and exposed to an ambient laboratory atmosphere.

triflate (Figure 2). Thus doped poly(3-alkylthiophene) films can be prepared from a single solution by solution- or spin-casting. We term this process *solvato-controlled doping*. Figure 4 (inset) shows the UV/vis absorption spectra of a doped P3HT100 film prepared by spin-casting a toluene/heptane/pyridine solution of P3HT100/AgOTf, followed by heating to 80 °C to remove the solvent and the volatile pyridine ligand. The spectrum shows a substantial decrease in the $\pi-\pi^*$ transition, compared to the neutral polymer, and the emergence of a new peak at 800 nm indicating that doping of the polymer had occurred. FT-NIR measurements indicates the emergence of an absorption band at 2111 nm supporting the formation of bipolarons. XPS analysis indicated the absence of pyridine in the films.

The ratio of AgOTf to P3AT100 required to produce doped polymer films using the solvato-controlled doping procedure was determined by varying the molar ratio of polymer to AgOTf in the pyridine-stabilized solutions prior to solution casting. Upon casting the polymer/AgOTf ratio was retained in the film. The conductivity of the polymer films was found to be dependent on this molar ratio. Figure 5 shows a plot of log σ versus molar ratio of Ag to thienyl rings for P3DDT100. Low ratios of AgOTf/P3DDT100 in the original solution resulted in cast films that exhibited low conductivity. A maximum conductivity (1–20 S/cm) was achieved for a AgOTf/thiophene ratio of 0.25. This corresponds to a doping level of one Ag(I) dopant every four rings. This is consistent with the degree of doping found by immersion of neutral P3DDT100 films into solutions of AgOTf.

AgOTf-doped P3ATs were compared to the same polymers oxidized by immersing the neutral films into solutions of a different oxidizing agent, namely, nitrosonium triflate. In the latter, nitrogen monoxide gas is eliminated during oxidative doping, and $^-$OTf counterions balance the positive charge associated with bipolarons. Thus NOOTf-doped polymers serve as models for comparison with AgOTf-doped P3ATs because any differences between the two are the result of the presence of Ag(0) in the polymer. Poly(3-alkylthiophenes) underwent complete doping with NOOTf as indicated by the loss of the $\pi-\pi^*$ transition and the emergence of absorption peaks in the NIR region of the spectrum associated with bipolaronic transitions. Both AgOTf- and NOOTf-doped polymers exhibit conductivities between 1 and 20 S/cm but the lifetimes of doped films (<100 nm thick) under ambient conditions were considerably different (Figure 6). NOOTf-doped polymers showed a rapid decrease in conductivity ($t_{1/2} \sim 3.5$ h) whereas AgOTf-doped polymers of similar thickness exhibited lifetimes in the range 115–150 h.[12] These values are much better, even, than ferric chloride-doped polymers (~8 h, for <100 nm thick films), which are generally regarded as being among the better dopants, but they are lower than AuCl$_4^-$ -containing conducting polymers.[13] These differences raise important questions about the role of the counterion, and in the present case, the role of metallic silver, on the stability of conducting polymers. The origin of these differences is under current investigation.

X-ray Diffraction. X-ray diffraction analysis was used to investigate the morphology of AgOTf-doped conducting polymer films prepared by solvato-controlled doping. Figure 7 shows the X-ray diffraction peaks corresponding to the 100 plane for P3HT100 films doped by immersion into AgOTf and NOOTf, respectively. The angular positions of the peaks were used to determine the interlamellar separations according to the standard diffraction condition. The lattice spacings were 16.9 Å for the pristine polymer, 17.66 Å for the AgOTf-doped polymer and 17.44 Å for the NOOTf-doped polymer. The angular dispersions (fwhm) of the diffraction peaks yield information about the dimensions of the crystalline region responsible for scattering X-rays. The crystallite size, as it corresponds to the *c*-axis, can be calculated using the Scherrer formula:

$$t = K\lambda/B\cos\theta \qquad (3)$$

where t is the crystallite size in nanometers, K is a constant (0.9), $\lambda = 1.5418$ Å, B is the angular dispersion of the peak in radians, and θ is the peak's position in degrees. While data on the crystallite size only represents dimensions corresponding to changes in the interlamellar spacing and thus are not absolute values,

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(12) The following authors have shown FeCl$_4^-$-doped polymers exhibiting a longer lifetime than our results: Wang, Y., Rubner, M. F. *Synth. Met.* **1991**, *41–43*, 567; **1990**, *39*, 153. Loponen, M. T.; Taka, T.; Laasko, J.; Vakiparta, K.; Suuronon, K.; Osterholm, J. E. *Synth. Met.* **1991**, *41–43*, 479. However, those studies use substantially thicker films, which accounts for the apparent anomaly.

(13) Abdou, M. S. A.; Holdcroft, S. *Synth. Met.* **1993**, *60*, 93.

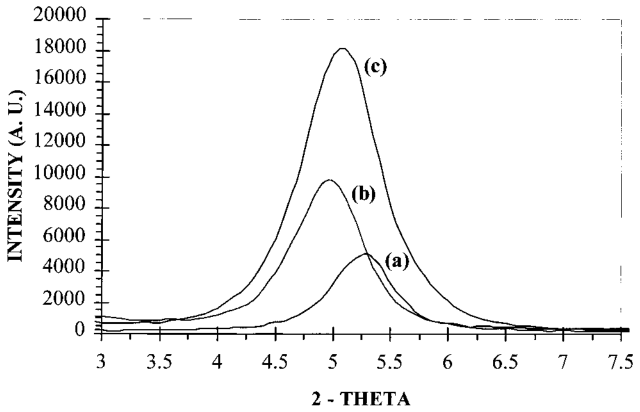

Figure 7. X-ray diffraction (XRD) of (a) a pristine P3HT100 film, (b) a P3HT100 film oxidized with AgOTf, and (c) a P3HT100 film oxidized with NOOTF.

Table 1. EPR Data of Pristine and Doped P3HT100[a]

	ΔH (G)	spins/g	A/B	λ (cm^{1})
pristine sample	5.862	1.5×10^{15}	1.138	25.4
AgOTf doped	6.298	3.51×10^{19}	0.942	18.1
$FeCl_3$ doped	NA	$<10^{14}$	NA	NA

[a] NA: not applicable, spins could not be detected.

changes in the values reflect changes in the crystal structure of the polymer. The crystallite sizes were 13.3 nm for the pristine polymer, 12.8 nm for the AgOTf-doped polymer, and 12.7 nm for the NOOTf-doped polymer. Thus while it appears that there is a significant increase in the lattice spacing in order to accommodate the counterion upon doping, there appears to be only a minor difference in the lattice expansion between polymers doped with AgOTf or NOOTf. The small difference can be interpreted to be due to the accommodation of Ag in the former.

The interlamellar separations of the polymer doped by solvato-controlled doping with AgOTf was found to be 17.32 Å (not shown). This is slightly smaller than films doped by immersion into an AgOTf solution (17.44 Å). This may reflect a greater degree of intercalation of the alkyl side chains and a denser crystalline morphology as a result of the unique casting process.

EPR. EPR spectra were obtained and analyzed for samples of pristine P3HT100, AgOTf-doped polymer, and $FeCl_3$-doped polymer (Table 1). The spin density for the pristine 100%HT sample is relatively low and is indicative of polaronic residues arising from impurities and/or chemical defects. The spin–orbit coupling constant (λ), was calculated from $\lambda = (g - g_e)E_g$, where the bandgap, E_g, was taken as 2.1 eV (1.69×10^4 cm^{-1}). This value was 25.4 cm^{-1} for the pristine polymer and is similar to the spin–orbit coupling constant of carbon ($\lambda_{C2p} = 28$ cm^{-1}) and much smaller than that of sulfur ($\lambda_{S3p} = 382$ cm^{-1}) indicating that the paramagnetic species is delocalized along the carbon backbone and not localized on the sulfur atoms. The A/B ratios, i.e., the relative amplitudes of the positive and negative lobes of the EPR spectra, are close to unity indicating a Lorentizian line shape and a delocalized spin.

Upon doping the polymer with AgOTf, a substantial increase in the spin density is observed. This is significantly different to what is commonly observed upon oxidation with conventional dopants. For instance, upon doping with $FeCl_3$, the spin density decreases to negligible values due to the coalescence of paramagnetic polarons to form spinless bipolarons. The observation that the silver triflate-doped sample possesses $>10^5$ times a greater spin density than the $FeCl_3$ analogue indicates that these polymers are able to support a greater fraction of charge carriers in the form of polarons. However, it should be noted that even though the polaron density is substantially larger in AgOTf-doped polymers, the polaron concentration is apparently still much lower than the bipolaron concentration. This was determined by estimating the carrier concentration to be $\sim 3 \times 10^{21}$/g assuming that the doping level is 20 mol %. Thus the polaron concentration represents only 1% of the total charge carriers. The spin–orbit coupling constant of the AgOTf-doped polymers was 18.1 cm^{-1}, which is much closer to that of carbon than it is to sulfur which again indicates the paramagnetic species is delocalized along the carbon backbone and not localized on the sulfur atom.

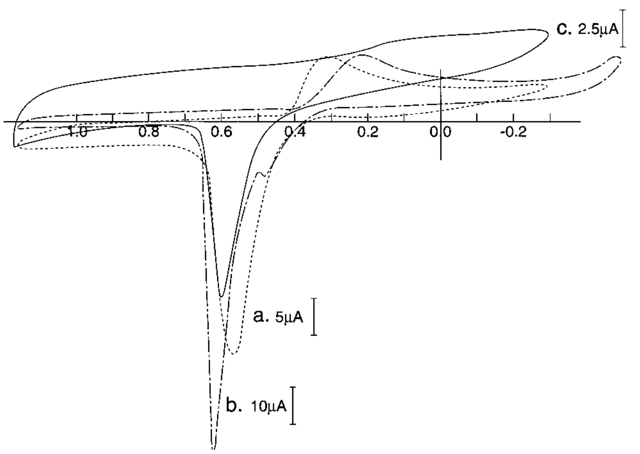

Figure 8. Cyclic voltammograms of (a) silver perchlorate (AgClO4), (b) silver trifluoroacetate (CF_3CO_2Ag), (c) silver camphorsulfonate (camphor–SO_3 Ag). Concentrations were 1 mM in 0.1 M TBAP/CH_3NO_2.

Doping Studies with Other Ag(I) Salts. The effect of the nature of the counterion of the Ag(I) salt on the doping process was investigated by first determining the electrochemistry of various Ag(I) salts, followed by spectroscopic and conductivity measurements on doped polymer films. Silver salts examined included silver perchlorate ($AgClO_4$), silver trifluoroacetate (CF_3CO_2-Ag), silver camphorsulfonate (camphor–SO_3Ag), silver dodecylsulfonate ($C_{12}H_{25}SO_3Ag$), and silver acetate (CH_3CO_2Ag). Figure 8 shows the electrochemical reduction of a few of these salts in 0.1 M TBAP/nitromethane. A large contrast was observed between the reduction peak potential, which varies with the counterion, and the oxidation potential for Ag → $Ag^+ + e^-$, which was relatively constant. This is interpreted to indicate that the Ag(I) salts exist as ion pairs in solution since the reduction potentials for the various salts would have been similar if the Ag(I) salts were fully dissociated because the supporting electrolyte, ClO_4^-, is in excess. Reoxidation of Ag^0 to Ag(I) occurs in the presence of a large excess of ClO_4^-, and thus the oxidation potential remains relatively constant for the various salts. Further evidence of ion pairing arises from the fact that dissolution of AgOTf (0.1 M), the most likely of the silver salts to ionize in solution, did not produce ionically conductive solutions in the absence of supporting electrolyte.

The reduction peak potentials were determined to be AgOTf (∼+0.4 V vs SCE), $AgClO_4$ (+0.32 V); CF_3CO_2-Ag (+0.22 V), and camphor−SO_3Ag (∼+0.1 V).[14] The reduction potential of Ag(I) can be observed to shift negatively as we transverse the series AgOTf → $AgClO_4$ → CF_3CO_2Ag → camphor−SO_3Ag. This also represents the trend indicating the strength of the interaction between the counterion and Ag(I). Thus AgOTf exhibits a greater ionic character than camphor−SO_3Ag by virtue of the greater electronegative character of OTf^-. For $C_{12}H_{25}SO_3Ag$ and CH_3CO_2Ag, the interactions between Ag(I) and the counterion are stronger, and even though no reduction of Ag(I) could be observed for these salts, we can preclude that their reduction potentials would have occurred at even more positive potentials than AgOTf, $AgClO_4$, or CF_3CO_2Ag.

Since Ag(I) can be prevented from doping P3AT100s upon shifting the reduction potential of Ag(I) positively by the addition of a coordinating pyridine ligand, similarly, we predicted that the ability of a Ag(I) salt to dope the same polymers would also decrease as the reduction potential of that salt shifted in a positive direction by virtue of the nature of the counterion. In agreement with this, of the Ag(I) salts examined, only AgOTf, $AgClO_4$, and CF_3CO_2Ag were found to dope P3AT100s.

Effect of Regioregularity of P3ATs. Coupling of 3-substituted thiophenes via the 2- and 5-position leads to polymers with various degrees of regioregularity due to the formation of head-to-head (H−H), head-to-tail (H−T), and tail-to-tail (T−T) configurational isomers (see Experimental Section). The relative predominance of one coupling reaction over another to form a particular regiochemical polymer has a pronounced effect on the electronic and optical properties of the polymer.[3,15] A property of P3ATs directly related to regioregularity is the oxidation potential. Since it has been demonstrated that the reduction potential of the Ag(I) salt influences the doping process, it is expected that the oxidation potential of the polymer so too influences the doping process. Figure 9 shows the change in the UV−vis spectra upon immersion of P3HT80 and P3HT0 films into a 0.1 M ether solution of AgOTF. These polymers contain ∼80% and 0% HT dyad content, respectively. In contrast to P3HT100 films, in which complete doping is evidenced by the presence of a large decrease in $\pi-\pi^*$ absorption, films of P3HT80 are doped to a much lesser degree as indicated by the persistence of a substantial absorption band associated with the $\pi-\pi^*$ transition (Figure 9b). The maximum conductivity observed for doped P3HT80 films was 2 S/cm, which is an order of magnitude smaller than the maximum value observed for doped films of P3HT100.

Films of P3HT0 were found to be even less affected in the presence of AgOTf as indicated by the relatively small change in the absorption spectrum upon addition of AgOTf (Figure 9c,d). Conductivities of these films remained low $<10^{-6}$ S/cm. Figure 10 shows the cyclic voltammetry of P3HT80 and P3HT0. The oxidation potential of the polymer shifts positively as the series P3HT100 (Figure 3a)→ P3HT80 (Figure 10a) → P3HT0 (Figure 10b) is progressed. This is a consequence of the decreasing head-to-tail dyad content and increasing head-to-head content. The latter are sterically encumbering linkages that force adjacent thienyl rings to twist with respect to each other. The degree of conjugation is thereby reduced, the highest occupied molecular orbital decreases in energy, and the oxidation potential shifts in a positive direction. Since there is a direct relation between the oxidation potential of the polymer and its ability to be oxidized by AgOTf, there is also a direct link between the regioregularity of P3ATs and its ability to be doped by Ag(I).

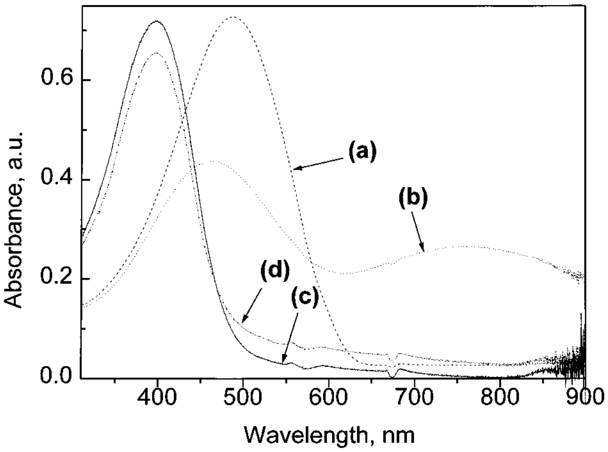

Figure 9. UV−vis spectra of (a) a neutral P3HT80 film, (b) a P3HT80 film treated with AgOTf, (c) a neutral P3HT0 film, and (d) a P3HT0 film treated with AgOTf.

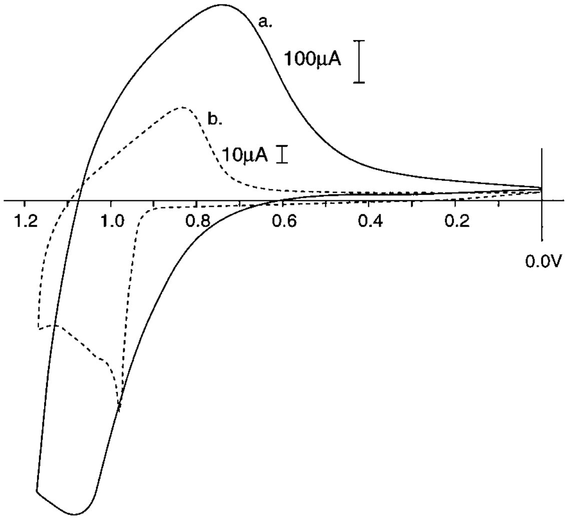

Figure 10. Cyclic voltammograms of (a) a P3HT80 film and (b) a P3HT0 film both in 0.1 M TBAP/CH_3NO_2.

Solvato-Controlled Doping of Other Conjugated Polymers. Poly(3-methoxythiophene) (P3MeOT) has been shown to possess a relatively positive oxidation potential compared to poly(3-alkylthiophenes) because of the electron-donating affect of the alkoxy group. The onset of oxidation of this polymer was ∼0.0 V (SCE) which is several tenths of a volt more negative than the reduction potential of AgOTf but still more positive than the reduction potential of Ag(I) coordinated with pyri-

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[14] Reduction peaks could not be detected for $C_{12}H_{25}SO_3Ag$ and $AgCO_2CH_3$ due to their low solubility.

[15] Mao, H., Xu, B., Holdcroft, S. *Macromolecules* **1993**, *26*, 1163.

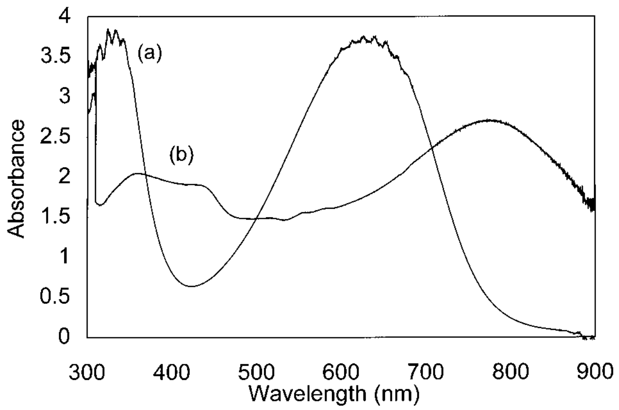

Figure 11. UV–vis spectra of (a) PANI (1.6 mg/mL) and AgOTf in *N*-methylpyrrolidinone/pyridine (1:0.1 vol %) solution and (b) after evaporation of solvent. (AgOTf /aniline molar ratio = 1:2.2).

dine. As anticipated, solutions of P3MeOT and AgOTf were stabilized by the presence of 5 vol % pyridine and blue conducting polymer films could be prepared by simple casting of this solution. Similarly, solutions of polyaniline and AgOTf in *N*-methylpyrrolidinone (NMP) were prevented from both doping by employing small amounts of the Ag(I)-coordinating ligand. Figure 11 shows UV–vis absorption spectra of PANI–AgOTf solutions in NMP/pyridine, indicating PANI's undoped nature, and the change in the spectra due to doping upon evaporation of the solvent and coordinating ligand. The presence of particulate silver was clearly observed on the doped polyaniline films, which confirms that oxidative doping is also occurring in these conjugated polymer systems.

Conclusion

Solutions of P3ATs containing Ag(I) were stabilized by the addition of species which coordinate with the doping agent. When the complexing agent was removed, for example by evaporation during solution casting, then conducting polymer films of poly(3-alkylthiophenes) were obtained. This may open up new avenues in the search for processable and stable conducting materials since a wide range of dopants/coordinating systems can be envisaged. Second, Ag(I)-doped polymers prepared in this manner appear to be more stable than many other doped systems based on poly(3-alkylthiophenes). This raises the question as to the role of Ag particles in stabilizing the oxidized conducting state of the polymer. Increases in the conductivity and stability are also observed when doping and film formation are simultaneous, i.e., solvato-controlled, rather than stepwise. This reemphasizes the fact that the morphology of conducting polymer films is important in determining their electrical properties and efforts should be made to control film morphology upon, and during, oxidative doping of conjugated polymers.

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