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n- and p-Doped Poly(3,4-ethylenedioxythiophene): Two Electronically Conducting States of the Polymer

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ABSTRACT: Neutral poly(3,4-ethylenedioxythiophene) (PEDOT) thin films can be switched to an electronically conducting form either by oxidation (p-doping) or reduction (n-doping) in anhydrous organic solvents. The maximum attainable n-conductivity is ca. 1% of the maximum p-conductivity. However, based on spectroelectrochemical and in-situ conductance measurements, the p-conductivity regime can be divided into two domains, in which either positive polarons or bipolarons and free carriers are the major charge carriers. In the n-conductivity regime, voltammetric, spectral, and conductance data suggest only the generation of negative polaron-type carriers. These results imply that the conductivity due to positive or negative polarons is of the same order of magnitude and that the higher maximum p-conductivity may be attributed to the generation of other charge carriers in the highly stable oxidized PEDOT films. The reduced form is not stable even in an extremely dry oxygen-free environment, which severely hampers the use of n-doped PEDOT in practical applications. The conductivity of pristine PEDOT films can be markedly enhanced by successive p-doping and undoping. In addition, the conductance slowly increased after an anodic potential step. The origin of these effects is not known.

Introduction

Electronically conducting polymers derived from substituted thiophenes constitute an important and widely studied class of conjugated polymers.[1] The relatively facile derivatization of the parent thiophene has led to a variety of monomers and polymers with a wide spectrum of interesting properties. The properties of the neutral polymers can further be altered by chemical or electrochemical oxidation (p-doping) or reduction (n-doping). The term electrochemical p-doping (n-doping), in connection with conducting polymers, is generally understood as a process that involves both oxidation (reduction) of the polymer backbone and the concomitant changes in the electronic structure. These changes manifest themselves in spectral and mass changes and, above all, in the insulator-to-conductor transition of the material. Combining modern in-situ techniques, such as VIS−NIR spectroelectrochemistry, electrochemical quartz crystal microbalance (EQCM), and conductance measurements, provides an effective way to study the processes and the mechanisms involved. Among conducting polymers, one of the most promising materials for practical applications is poly(3,4-ethylenedioxythiophene) (PEDOT) because of the high stability and conductivity of the p-doped state.[2,3] The high stability makes it also a good material for the studies of the basic mechanisms involved in the polymer redox processes. The stability has been attributed to favorable ring geometry and the electron-donating effect of the oxygen atoms at the 3,4-positions, which stabilize the positive charge in the polymer backbone. Furthermore, the polymer is almost transparent in the oxidized state and opaque in the neutral state, which makes it suitable for various optical applications, e.g., electrochromic displays.[4] Although the properties of the p-doped and neutral PEDOT are well-known through studies by a variety of methods, the properties of the n-doped material are almost unexplored.[5−8] Only a few earlier papers mention the n-doping of PEDOT without any further characterization of this negatively charged state.[9−11] However, both reversible p- and n-doping are important for applications in rechargeable batteries,[12] light-emitting electrochemical cells,[13] and type III supercapacitors.[14] Therefore, we gave an effort to determine the properties of PEDOT in the reduced state. Furthermore, PEDOT serves as a model for the comparison of these two conducting states, and we think that the results obtained can be, at least partly, generalized to other polythiophene derivatives.

Experimental Section

The monomer 3,4-ethylenedioxythiophene (EDOT), a kind donation from Bayer AG, was used as received. Anhydrous solvents, acetonitrile (Lab Scan), nitrobenzene (Aldrich), and benzonitrile (Aldrich), were stored over molecular sieves (Riedel-de Haën, 3 Å). Tetrabutylammonium hexafluorophosphate ($TBAPF_6$, 99% Fluka) was dried in a vacuum over P_2O_5 at 120 °C for 48 h. All solvents and solutions were kept inside a glovebox (M. Braun GmbH) in nitrogen atmosphere (H_2O < 5 ppm, O_2 < 1 ppm). The water content of the solutions was checked before measurements using a Karl Fischer coulometric titrator and was typically found to be below 10 ppm after purging with nitrogen for 10 min. All the experimental work was conducted inside the glovebox unless otherwise stated.

The in-situ conductance measurements were carried out at room temperature as described previously.[15] Poly(3,4-ethylenedioxythiophene) (PEDOT) films were deposited in a one-compartment, three-electrode electrochemical cell on the double-band platinum microelectrode with the surface area of 0.005 cm^2 and a gap of 15 μm between the platinum bands. The length of the platinum bands is 0.2 cm. The counter electrode was platinum wire, and as reference an Ag/Ag^+ electrode (0.01 M $AgNO_3$ + 0.1 M $TBAPF_6$ in acetonitrile) was used. The redox potential of the ferrocene/ferrocenium couple was found to be + 230 mV against this reference electrode. The electropolymerization was carried out potentiodynamically by cycling the potential between −0.5 and +1.2 V at 100 mV/s in the solution of 0.1 M EDOT and 0.1 M $TBAPF_6$ in acetonitrile, benzonitrile, or nitrobenzene. The thickness of the polymer film was controlled by the number of polymerization cycles and deter-

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mined using the published relation of the thickness vs the polymerization charge.[16] As the film thickness is a function of polymerization conditions, the absolute conductivities may contain a systematic error. However, their precision, i.e., the reproducibility of the calculated conductivities for films of different thickness, is good (5−10%). In addition, the conductivities obtained (ca. 10 S/cm) are close to the values reported by Reynolds et al. using an in-situ technique resembling ours.[17] The possible systematic error in the accuracy does not affect the conclusions of the present work. The thickness of the films was typically in the range of 0.5−3 μm, i.e., considerably thinner than half of the gap between the platinum electrodes, which allows us to assume uniform current distribution over the whole film and conversion of the measured conductance to conductivity by eq 1.

$$G = \sigma \frac{A}{d} \tag{1}$$

where A is the cross-sectional area of the film between the band electrodes a distance d apart. The lower limit of measurable conductance was set by the noise level and the conductance of the adjacent electrolyte solutions, both of the order of a few microsiemens.

Potentiostatic polymerization and cyclic voltammetry were performed with an EG&G Princeton Applied Research potentiostat model 283. The films were equilibrated at −1.2 V for 2 min before cyclic voltammetric measurements.

The spectra during the in-situ VIS−NIR spectroelectrochemical measurements of PEDOT films deposited on ITO electrodes (Balzers) were recorded on a Varian Cary 5 spectrophotometer using the spectroelectrochemical cell similar to that described previously.[18] Due to the strong absorption coefficient of neutral PEDOT, the films polymerized on the ITO electrodes were considerably thinner (typically ca. 200 nm) than in the conductance experiments on platinum electrodes. Nevertheless, the voltammetric behavior of the films on these two different substrates and thickness was essentially the same.

Results and Discussion

Voltammetry of Poly(3,4-ethylenedioxythiophene) Films. The polymerization solvent, either acetonitrile, benzonitrile, or nitrobenzene, did not have any marked effect on the polymer properties. Figure 1A shows the cyclic voltammograms of a PEDOT film (polymerized in benzonitrile) in a monomer-free 0.2 M TBAPF$_6$ acetonitrile solution. The anodic part of the voltammogram (curve a) exhibits the features common to most polythiophenes and is similar to that reported previously. A broad oxidation peak is observed at ca. 0.0 V, followed by a current plateau and two cathodic peaks at −0.05 and −0.65 V on the reverse scan.[2,19] The cathodic branch of the voltammogram (curve b), on the other hand, exhibits increasing cathodic currents during downward sweep after a small shoulder at ca. −2.2 V and a single anodic peak at −2.05 V on the return sweep. This kind of voltammetric behavior has generally been attributed to n-doping with polythiophene derivatives.[9−11] In addition, whenever the potential sweep was extended to the opposite side of the voltammogram, sharp prepeaks on the anodic and cathodic branch could be seen at ca. −0.5 and ca. −1.8 V, respectively (curve c). Similar behavior has been observed previously with several polythiophenes and has been attributed to charge trapping, i.e., charged domains imbedded within the matrix of insulating film.[20,21] On the other hand, after oxidation of the polymer the trapped positive charge was released during n-doping. The sharp cathodic prepeak associated with the trapped charge disappeared after a few cycles in the cathodic region. Although no extensive stability experiments were carried out, the p-doping charge was highly reversible. The n-doping charge decreased gradually upon cycling and displayed a Coulombic recovery of only ca. 70% even in dry anaerobic conditions (oxygen and water levels below 5 ppm). In measurements performed outside the glovebox (using solutions dried with molecular sieves), the Coulombic efficiency dropped to ca. 50%, showing that the reduced polymer is readily attacked by residual water and/or oxygen. The instability of the reduced polymer severely hinders the use of n-doped PEDOT under atmospheric conditions. The EDOT molecule contains electron-donating oxygen groups, which lower the oxidation potential of the monomer and the polymer but do not favor reduction. Indeed, the reduction potential of the PEDOT polymer (ca. −2.1 V) seems to be only slightly modified compared to that of the parent polythiophene.[22] This indicates that the HOMO level of PEDOT has been lifted upward and the LUMO level remains at same position as in the polythiophene, resulting in a lower HOMO−LUMO separation (or band gap). This difference can be estimated from the onset potentials for oxidation and reduction in the voltammograms, which yield a value of 1.2 eV, in accordance with previous reports.[9,10] A more accurate value (1.1 eV)

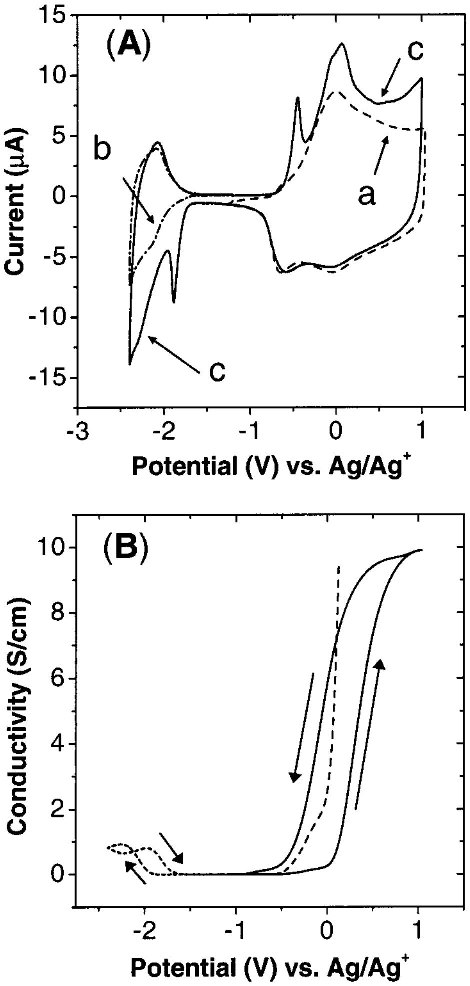

Figure 1. (A)Steady-state voltammograms of a PEDOT film on Pt electrode in 0.2 M TBAPF$_6$ + acetonitrile (H_2O < 4 ppm). Scan rate 100 mV/s. (a) The anodic region (dash), (b) fifth cycle to the cathodic region (dash−dot), and (c) the wide potential range (solid). (B) In-situ conductivity of a PEDOT film. Dashed lines multiplied by a factor of 10.

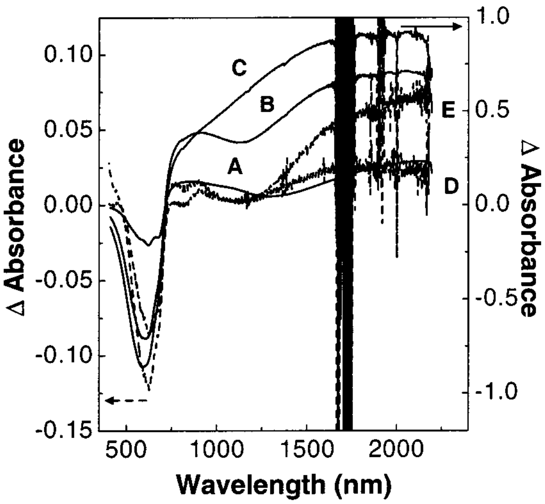

Figure 2. Steady-state difference spectra of PEDOT on an ITO electrode at different potentials. The spectrum of the neutral polymer at −1.2 V has been taken as the reference: A (−0.35 V), B (0.0 V), C (+0.55 V), D (−1.8 V), and E (−2.3 V). The strong signal at ca. 1700 nm is due to water vapor and solvent.

can be estimated from the conductance measurements (vide infra).

Spectral Characterization. Figure 2 shows the steady-state spectra recorded during the p- and n-doping of relatively thin PEDOT films on indium−tin oxide (ITO). During the steady-state oxidation (p-doping) the first spectral changes coincide with the appearance of p-conductance (vide infra). The spectral behavior is essentially the same as reported earlier by Inganäs et al.[19] Concomitant with the decrease of the $\pi-\pi^*$ transition of neutral PEDOT at 610 nm, we see three weak subgap features to appear at ca. 860, 1100, and 2050 nm (1.4, 1.1, and 0.6 eV, respectively) in the potential region between −0.55 and −0.35 V. All the transitions agree well with those previously reported for polaron-type carriers in PEDOT.[19] At higher doping levels, the two midgap transitions with higher energy merge to a single transition, and finally, only a broad band extending over the whole NIR region evolves. These further changes have been assigned to the evolution of bipolaron states and the so-called metallic state within the film.[19,23] The optical band gap edge estimated from the onset of absorption of the neutral film is 1.6−1.7 eV, close to the values reported in the literature.[7,9] The observed spectral features are too weak to allow any conclusions to be made about π-dimerization in the films.[24,25] Upon reduction of the neutral film the optical changes are weaker but again coincide with the appearance of the n-conductivity. A clear new transition can be seen at ca. 1800 nm (0.7 eV). Other peaks are much weaker, but two transitions can be identified at ca. 800 and 900 nm (1.5 and 1.3 eV, respectively; see also the Supporting Information), analogous to p-doping (Figure 2). Together with voltammetric and conductance data (vide infra), these observations suggest the formation of negative polaron-type charge carriers as the most plausible explanation. No other spectral features evolved as the potential was made successively more cathodic, which may be related to the low stability of the n-doped state observed already in the voltammetric measurements. (In the steady-state spectral measurements instrumental limitations prevented working in glovebox conditions.)

Conductance of PEDOT. Figure 1B shows the conductivity of a PEDOT film measured simultaneously with the steady-state voltammograms. The roots of the prepeaks coincide with the appearance of the conductivity, in accordance with their assignment to the charge trapping. During oxidation of the film, the sigmoidal p-conductivity curve reaches the maximum (ca. 10 S cm^{-1}) at the end of the current plateau. A large hysteresis in the conductance behavior is observed at the voltammetric time scale. Interestingly, a small shoulder in the p-conductivity curve is observed at ca. −0.2 V, just before the sharp increase of conductivity. This implies that more than one kind of charge carriers could be involved. The spectroelectrochemical studies showed that polarons were formed at the potentials corresponding to the shoulder and that the appearance of bipolarons coincides with the rapid increase of p-conductivity. This suggests that the p-conductivity mechanism in PEDOT involve polaronic, bipolaronic, and free carriers at low, medium, and high p-doping levels, respectively. As discussed earlier, the presence of polaron π-dimers cannot be deduced from the present data, but dimerized polarons should be rather localized and not contribute to conductivity.[26] Similar behavior has been observed previously with other polythiophene derivatives and has been associated with the conductivity by polaronic and bipolaronic carriers.[27] On the other hand, the conductivity in the n-doping regime displays a bell-shaped curve with a maximum (ca. 0.1 S cm^{-1}) at ca. −2.3 V. This maximum is only 1% of the maximum p-conductivity, in accordance with previous reports on several other polythiophenes.[28] The large difference between the p- and n-conductivities has usually been attributed to a hindered diffusion of the bulky cations in the film and to a larger separation between the chains incorporating large counterions. On the other hand, our results show that the maximum n-conductivity is of the same order of magnitude than the p-conductivity corresponding to a similar doping level (at potentials corresponding to the shoulder in the conductivity−potential curves; see Figure 1B). Because only polaronic features were observed in the steady-state n-doping spectra, this implies that the conductivity due to positive and negative polarons are similar in PEDOT films. The large difference in the observed maximum p- and n-conductivities can, therefore, be attributed to the formation of different charge carriers in the two doping regimes.

The n-conductivity exhibits a marked hysteresis, which depends on the scan rate and disappears at scan rates of 10 mV/s or lower. Continuous cycling in the n-doping regime leads to a marked decrease in both the n- and p-conductivity. After 15 combined p- and n-doping cycles, the p- and n-conductivities drop by ca. 90% and 40%, respectively. The large decrease in conductivity is in striking contrast to the stable electrochemical behavior of the PEDOT film under glovebox conditions. This alleviates the fact that the transport phenomena are much more sensitive probes for the polymer stability than the purely electrochemical ones.[29] Interestingly, the p-conductivity was affected more than the n-conductivity. However, the relative decrease of the p-conductivity was much less at the low doping levels corresponding to the conductivity shoulder, and the major loss of conductivity was observed at higher potentials. This indicates that the p-conductivity due to bipolarons and free carriers is more sensitive to

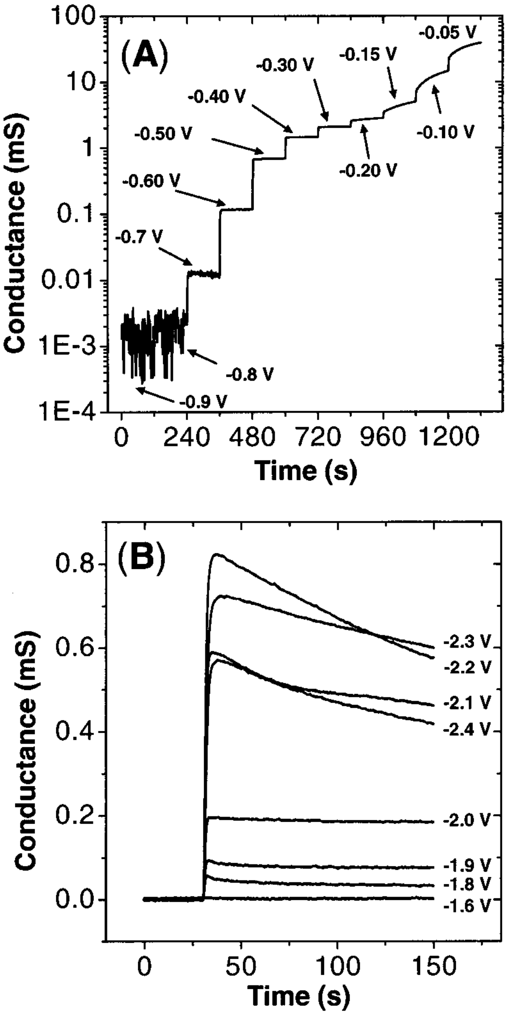

Figure 3. (A) p-Conductance transients after potential steps (Δt_{step} = 120 s). Conductance below −0.8 V due to the electrolyte solution. (B) n-Conductance transients after the steps from a nonconducting state to different negative potentials.

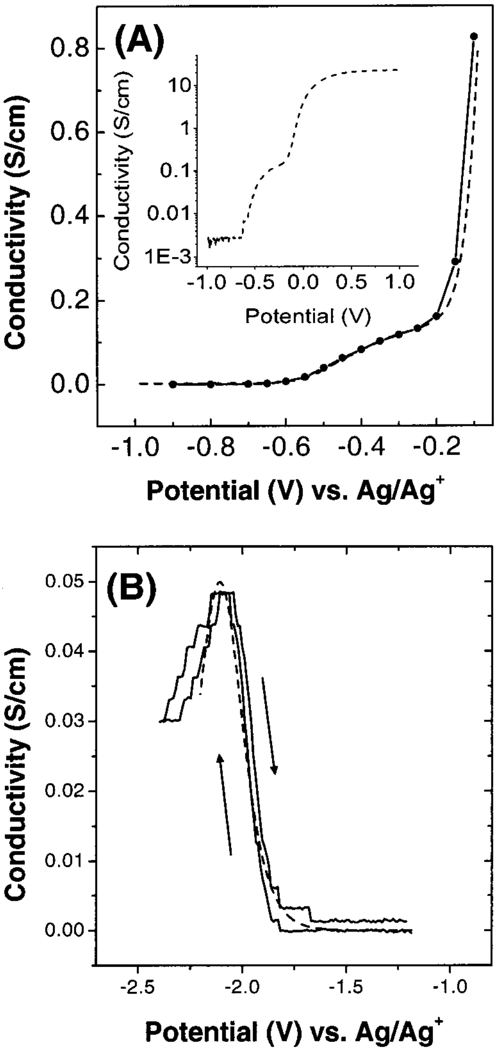

Figure 4. (A) Steady-state p-conductivity values calculated from data in Figure 3A (solid). The conductivity measured at the scan rate of 1 mV/s is also shown (dashed). Inset: data in logarithmic scale to better show the conductivity shoulder. (B) n-Conductivity measured at the scan rate of 10 mV/s (solid line) and the fit to a mixed-valence model (dashed line).

polymer degradation than the polaron conductivity. On the other hand, if a pristine PEDOT film is cycled between the neutral and oxidized states, the p-conductivity increases from cycle to cycle, resulting in an enhancement of conductivity even by a factor of 10. Depending on the sweep rate the maximum conductivity is achieved after some tens of cycles. (All measurements reported in this study refer to films preactivated in this way.) In addition, a marked hysteresis in the conductivity–potential curve is observed even at scan rates down to 1 mV/s. Studying several films with different thickness and varying the scan rate between 1 and 100 mV/s, the shape of the p- and n-conductivity curves remained unaffected. Only with very thick films (>3 μm) the small shoulder in the p-conductivity curve was absent.

The persistent hysteresis in the properties of PEDOT films, characteristic of conducting polymer films in general, emphasizes the need of steady-state measurements in order to eliminate the effect of nonequilibrium factors on the conductivity data. Figure 3 depicts typical in-situ conductance transients of a PEDOT film on a double-band platinum microelectrode after a potential step. When a nonconducting film was stepped gradually to potentials where it becomes conducting (p-doped), the oxidation current typically decreased back to the base level within few seconds. The measured conductance, on the other hand, exhibited a rapid initial rise followed by a slow increase, and a steady-state conductance was not attained even within a measurement time of 10 000 s. The origin of this slow conductance increase is not known for certainty. The reorientation of the polymer chains either in the pristine film or during potential poising may explain the large enhancement of the conductivity of newly polymerized films or the slow increase following a potential step. However, there is no direct experimental evidence in favor of this hypothesis. In the step experiments the slow conductance drift was observed only at the potentials beyond the conductance shoulder, i.e., at potentials higher than −0.25 V. At low oxidation levels, the p-conductance reached a steady state in a few seconds. If the steady-state p-conductivity values are plotted as a function of the potential, the shoulder is still observed at low doping levels before the rapid increase of conductivity (Figure 4). This ascertains that the shoulder is not an artifact due to nonequilibrium effects but a real property of the conductivity behavior of PEDOT films. In the n-doping regime, the n-conductance reached a maximum within a few seconds but decreased to a steady-state value in ca. 30 s (Figure 3B). The maximum (transient) n-conductance was observed at −2.2 V. If the step potential was made more cathodic than −2.0 V, only a constant decrease could be observed, which indicates low stability of the highly reduced polymer.

The electrical conductivity in polythiophenes has been studied mainly in the neutral state or in the metallic regime.[30] In the neutral state, mobilities of the injected charge carriers have been obtained using time-of-flight (TOF) or current−voltage measurements in transistor configurations. Hole mobilities obtained are generally in the range of ca. 10^{-4}−10^{-2} cm^2 V^{-1} s^{-1}. Studies in the metallic state have shown that conducting polymers can be described as disordered metals. On the other hand, there are relatively few studies dealing with the intermediate conductivity range where polarons and bipolarons are assumed to act as charge carriers. In these studies, using electrochemical techniques similar to ours, a large increase in the apparent mobility as a function of the doping level has been demonstrated.[31] In poly(3-methylthiophene), the apparent mobility increases from 2×10^{-5} cm^2 V^{-1} s^{-1} in the neutral state to 0.13 cm^2 V^{-1} s^{-1} at high doping levels. These observations have been explained by assigning independent mobilities of 2×10^{-5} and 10^{-3} cm^2 V^{-1} s^{-1} to polarons and bipolarons, respectively. On the other hand, a mixed-valence conduction mechanism has been suggested for conducting polymers.[32,33] In this mechanism, typical for redox polymers, the conductivity is proportional to the product of the occupied and unoccupied sites in the lattice.[34] This leads to a bell-shaped conductivity curve as a function of potential (or charge) while the conductivity of polythiophenes generally exhibits a sigmoidal dependence on the doping level. On the other hand, the conductivity of the n-doped PEDOT exhibits a reversible bell-shaped curve, which strongly suggests a mixed-valence-type mechanism (Figure 4B) because no dimerization (resulting in localized species[26]) has been observed with oligomeric thiophene anion radicals.[35] If we adopt the Brown−Anson model for interacting redox species and the mixed-valence-conductivity formalism, the rising part of the n-conductivity curve can be well described.[36,37] However, after the maximum conductivity, the observed conductivity decreases more slowly, which may be caused by the generation of other carriers in this non-steady-state measurement or the expansion of the reduced film.

The conduction mechanism in the p-doped polymers is relatively complex, with the polaron, bipolaron, and metallic conductivities overlapping. In poly(3-methylthiophene), for example, it has been suggested that the metallic conductivity contributes to the overall conductivity already at the doping level of ca. 1%.[31] The p-conductivity of PEDOT exhibits a sigmoidal dependence on the potential, as generally observed with polythiophenes.[38] The initial conductivity shoulder, although small, is reproducible and can readily be appreciated in the logarithmic representation (see inset of Figure 4A). If the shoulder is attributed to positive polarons, we can estimate the apparent mobilities of the carriers using the measured conductivities divided by doping charges. Both mobilities exhibit maxima (at −0.33 and −2.1 V; cf. Figure 1A), which yield the approximate values 0.008 and 0.010 cm^2 V^{-1} s^{-1} for positive and negative polarons, respectively. This is noteworthy because theoretical calculations on thiophene oligomers suggest that negative charge is largely localized at sulfur atoms, which should lead to lower mobility of the negative charge carriers.[35] A similar conductivity shoulder has been reported with certain poly(dialkoxybithiophene) derivatives, but it is not generally observed.[33] In solution, the first and second oxidation potentials of oligothiophenes tend toward the same value as the chain length increases.[39] In the solid state this is not expected because of strong interchain interactions, which affect the energy levels of the polymer chains. Therefore, in polymer films the polaron and bipolaron conduction regimes may be separated. Possible mechanisms leading to the observed conductivity behavior can be suggested, either (i) a mixed-valence conductivity involving polarons with the formation potential clearly different from that of bipolarons or (ii) the formation of immobile π-dimers as the polaron concentration is increased. Independent data on the concentration of some species involved would be needed to clarify the mechanism. On the other hand, we may postulate tentative elementary steps in the conductivity mechanism. In conducting polymers, before the onset of metallic conduction, the interchain charge transfer takes place via a hopping mechanism.[40] We may assume that the elementary charge transfer reaction is a one-electron process. The reactants and products are the same, the only effect being the stepwise movement of charge to the propagation direction. Therefore, our results suggest that in PEDOT films the conductance occurs by charge hopping between mainly polarons and neutral segments or bipolaron and polaron sites at low and medium doping levels, respectively. The conformational change between the neutral and polaron state is larger than between polaron and bipolaron state. This decrease in the activation energy of hopping can explain the large difference in the polaron and bipolaron conductivity.

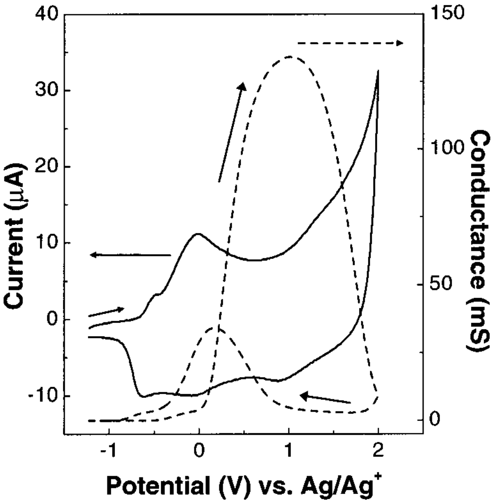

Figure 5. Cyclic voltammogram (solid) and p-conductivity (dashed) of PEDOT film at high anodic potentials (measured at 100 mV/s in order to reduce polymer degradation).

A bell-shaped curve of p-conductivity can be obtained if the potential sweep is extended to very positive potentials (Figure 5). At the same time degradation of the polymer film takes place as shown by the marked decrease in conductivity on the reverse sweep. However, the conductivity exhibits a bell-shaped potential dependence also on the return scan, which indicates that the form of the curve is not due to irreversible degradation of the film. A similar finite potential window of p-conductivity with polythiophenes and polyacetylene at low temperatures has been reported by Wrighton et al.[41,42] The highest conductance appears at the current plateau following the main oxidation peak, where the polymer film is in the metallic state. In the metallic state, there is a finite density of states immediately above and below the Fermi level; i.e., the Fermi level is situated within a partially depopulated band. Electrons can still be withdrawn from this highest occupied band (or closely spaced molecular orbitals) as evidenced by a high current density after the peak. Emptying of the band reduces the number of charge carriers in the metallic polymer and results in decreasing conductance. The disappearance of the conductance and its reappearance on the return sweep coincide with the extra peak pair in the voltammogram (at ca. 1.3 and 0.88 V for anodic and cathodic peaks, respectively). The existence of the extra peaks implies that the continuum of states is depleted, and the electrons are removed from more localized states, signifying the loss of the metallic character of the polymer.[42] The peaks are very sensitive to the presence of water and solutions with water level below ca. 20 ppm are required. However, it is noteworthy that the extreme stability of PEDOT in the oxidized state allows us to observe these phenomena at room temperature. Further oxidation results in irreversible overoxidation of the film as seen from the steeply rising current at the positive turning point of the voltammogram.

Conclusions

Poly(3,4-ethylenedioxythiophene) (PEDOT) can be polymerized from various organic solvents (acetonitrile, benzonitrile, and nitrobenzene) to yield a highly conducting polymer, which is very stable in the oxidized state. It can also be reduced to an n-conducting state, but the reduced polymer is relatively unstable even at dry conditions in inert atmosphere. This severely hinders the use of n-doped PEDOT in practical applications. In addition, the maximum attainable n-conductivity is ca. 1% of the maximum p-conductivity. Spectroelectrochemical results suggest that negative polarons are the only charge carriers in the reduced polymer. The n-conductivity exhibits a reversible bell-shaped curve, indicative of a mixed-valence-type conductivity mechanism. During the oxidation of PEDOT, the p-conductivity exhibits a shoulder at potentials where polarons are the major charge carriers. Further oxidation results in a marked increase of conductivity and the appearance of bipolarons and free carriers. The polaron, bipolaron, and free carrier conductivities overlap and hinder a closer analysis of the mechanism. However, the conductivity due to negative and positive polarons is of the same order of magnitude (ca. 0.1 and 0.2 S/cm, respectively). Therefore, the higher maximum p-conductivity generally observed with polythiophenes may not be an inherent property of the n-doped state but can be related to the instability of the reduced form of the polymer, which hinders the generation of other charge carriers. The time dependence of the p-conductance of the bipolaronic and metallic PEDOT exhibits a slow component, the origin of which could not be concluded with certainty. The high stability of PEDOT toward oxidation allowed the removal of all the delocalized electrons of the metallic polymer at room temperature. This produces a bell-shaped p-conductivity curve, previously only observed at low temperature with other conducting polymers.

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Supporting Information Available: Comparison of the original and differential spectra recorded during p- and n-doping of PEDOT films. This material is available free of charge via the Internet at http://pubs.acs.org.

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(37) In the Brown−Anson model (ref 36) the Nernst equation for the generation of negative polarons can be written as $E = E^{o\prime} + (RT/\zeta F) \ln (n_N/n_P)$, where ζ is the interaction parameter and n_N or n_P concentrations of the neutral or polaronic forms. For mixed-valence conductance (ref 34) in this case (written using mole fractions) $\sigma = 4\sigma_{max}x_Nx_P$. The fit in Figure 4B has been obtained with $\zeta = 0.35$, $E^{\circ\prime} = -2.11$ V, and $\sigma_{max} = 0.05$ S/cm.

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