Conducting Ladder Polymers: Insulator-to-Metal Transition and Evolution of Electronic Structure upon Protonation by Poly(styrenesulfonic Acid)

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The electrical, electrochemical, and optical properties of new ambient air stable conducting polymers, prepared by complexation of ladder poly(benzobisimidazobenzophenanthroline) (BBL) and its semiladder analogue BBB with poly(styrenesulfonic acid), are reported. The transition from insulator ($<10^{-12}$ S/cm) to electronic conductor (2 S/cm) occurs when neutral BBL or BBB is about 70−100 mol % singly protonated. This transition is accompanied by a large shift of the formal reduction potential from −0.85 and −0.69 V for neutral BBL and BBB to 0.35 and 0.33 V versus SCE, respectively, for the protonated conducting forms. Although the HOMO−LUMO optical band gap remains unchanged at 1.8 eV, the electron affinity (LUMO level) estimated from cyclic voltammetry was found to shift from 4.2 and 4.5 eV in the neutral BBL and BBB to 5.3 and 5.4 eV, respectively, in the protonated conducting polymers. Thus, contrary to previous thought the electronic structures of this conjugated ladder polymer and its semi-ladder analogue undergo a large change upon protonic acid doping. The stability and unusually large electron affinity of the conducting BBL/PSSA and BBB/PSSA complexes make them attractive as electron injection/collection layers in polymer-based optoelectronic devices.

Introduction

Much progress has been made in the experimental and theoretical understanding of the excitations and charge transport in *single-stranded*, linear chain, conducting polymers such as polyacetylene, polyaniline, polypyrroles, and polythiophenes.[1−4] The central roles of solitons, polarons, bipolarons, and polaron pairs in the electronic and optoelectronic properties of these conducting polymers are now well established.[1−4] In contrast, very little is currently known about the electronic excitations and charge transport properties of *double-stranded* or *ladder* conjugated polymers, with the possible exception of the side-chain derivatized ladder polyphenylenes.[5] Conjugated ladder polymers have many novel features of broad fundamental interest as amply demonstrated in early, largely theoretical, studies.[6−8] Intrinsic metallic properties[6−8] and even high-temperature superconductivity[8] have been predicted for some ladder polymer structures but have never been observed experimentally. There is thus a current need for experimental studies of conjugated ladder polymers to try to bridge this gap.

One interesting conjugated ladder polymer whose electronic and optical properties have been studied by our group and others is BBL.[9−17] Pristine BBL has an optically determined semiconductor band gap of 1.8 eV but an insulating dc conductivity (10^{-14} to 10^{-12} S/cm).[11,17] It has large nonlinear optical properties,[15] good photoconductivity,[17] and in bilayer thin films with donor molecules was demonstrated in xerographic imaging devices.[12] Efficient photovoltaic cells and photodetectors have recently been fabricated from pristine BBL thin films.[17b] Multicolor electrochromic properties and scanning electrochemical microscopy of BBL and its semi-ladder analogue (BBB) have been reported.[14d] Of particular significance to the promise of this conjugated ladder polymer as an electronic material is the recent demonstration of *n-channel* thin film transistors based on BBL.[18,19] Field-effect mobility of *electrons* was found to be as high as 5×10^{-4} cm²/Vs in spin coated BBL thin films.[19]

Earlier chemical and electrochemical redox doping studies on BBL showed electronic conductivities as high as 1−20 S/cm.[9,11,13] Protonic acid (H_2SO_4) doped BBL and BBB films were found to be highly conducting (2 S/cm) but very unstable.[9] However, unlike other known conducting polymers that usually exhibit doping induced new absorption features in the band gap,[1−4] protonic acid doped BBL does not show any such intragap absorption features.[9] The origin of this fundamental difference of BBL from other conjugated polymers has been theoretically suggested to be due to the lack of protonation induced changes in the geometrical and electronic structures of the ladder polymer.[9c]
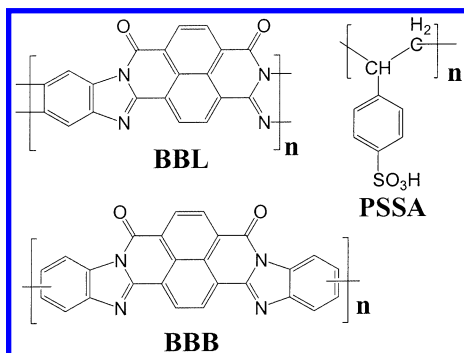
In this paper, we report the preparation and the electrical, optical, and electrochemical properties of new highly conducting and stable complexes of BBL and BBB with poly(styrene-sulfonic acid) (PSSA). The molecular structures of these polymers are shown in Chart 1. We also show that contrary to previous thought the protonation induced insulator-to-conductor transition in BBL or BBB is accompanied by a large change in the electronic structure of the ladder or semiladder polymers. The new conducting polymer/polymer complexes represent good model systems for studies of charge transport and electronic properties of conducting ladder polymers as well as promising materials for optoelectronic applications such as solar cells[17b] and photodetectors.[17a]

Experimental Section

Poly(styrenesulfonic acid) (PSSA) (Polysciences, Inc., Warrington, PA) was received as a 30 wt % solution in water. Solid PSSA samples for preparing solutions in formic acid were obtained from the aqueous solution by evaporating the water. Samples of the polymers, with an intrinsic viscosity of 32 dL/g

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CHART 1

Figure 1. Room-temperature dc conductivities of BBL/PSSA and BBB/PSSA complexes as a function of composition.

for BBL and 5.24 dL/g for BBB in methanesulfonic acid (MSA) at 30 °C, were synthesized in our laboratory as previously described.[11,20–22] The BBL/PSSA complexes were prepared by two methods. Complexes of up to 50 mol % PSSA (repeat unit basis) were prepared by mixing a solution of BBL in MSA with a solution of PSSA in formic acid. The resulting blend solutions where homogeneous and subsequently spin coated onto glass substrates. The thin films of BBL/PSSA complexes were washed with methanol several times and then soaked in methanol overnight to remove any remaining MSA, and then dried in a vacuum oven at 100 °C for 8 h.

A second method of preparing the BBL/PSSA complexes was necessitated by the observation that when blend solutions of BBL in MSA and PSSA in formic acid were mixed, the complexes with greater than 50 mol % PSSA precipitated out of the solution. Thin films of complexes with greater that 50 mol % PSSA were prepared by soaking pristine BBL thin films (spin coated from a solution of BBL in MSA) in aqueous PSSA solutions of different concentrations overnight. Complexation reaction between the blue pristine BBL thin films and colorless PSSA could be inferred from the red colors of the resulting BBL/PSSA complexes. These later complexes were also dried in a vacuum oven at 100 °C for 8 h. The composition (mol % PSSA) of the BBL/PSSA complexes, prepared by this second method, was determined by an optical absorption technique. A linear relationship of the absorption intensity at 2930 nm with composition was observed for the BBL/PSSA complexes prepared by mixing known amounts. Extrapolation of the linear absorption intensity versus mol % PSSA provided a means to determine the composition of the complexes prepared by soaking BBL films in aqueous PSSA solutions. BBB/PSSA complexes were similarly prepared as described above for BBL/PSSA complexes. The film thickness was measured using a model 500 Alpha Step profilometer (Tencor Instrument, San Jose, CA) which has a resolution of ±1 nm.

The room-temperature dc conductivity of thin films (30–35) ±1.5 nm of the complexes was measured by the four-point probe technique (Alessi Model CPS-06) using a Keithley electrometer (Model 617) and a Keithley current source (Model 220). Fourier transform infrared (FTIR) spectroscopy of BBL, BBB, and their PSSA complexes was done on pressed KBr pellets by using a Perkin-Elmer 1720 FTIR spectrometer. Optical absorption spectra of BBL, BBB, and their PSSA complexes were obtained by using a Perkin-Elmer Lambda 900 spectrophotometer.

Cyclic voltammetry experiments were done on an EG&G Princeton Applied Research potentiostat/galvanostat model 273A. Data were collected and analyzed by the Model 270 Electrochemical Analysis System Software on a PC computer as previously described.[23] A three-electrode cell was used in all experiments. Platinum wire electrodes were used as both
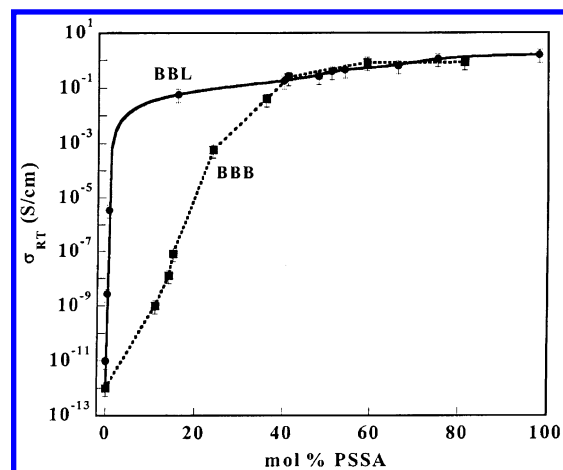
counter and working electrodes and silver/silver ion (Ag in 0.1 M $AgNO_3$ solution, Bioanalytical System, Inc.) was used as a reference electrode. The Ag/Ag^+ ($AgNO_3$) reference electrode was calibrated at the beginning of the experiments by running cyclic voltammetry on ferrocene as the internal standard in an identical cell without any polymer on the working electrode. By means of the internal ferrocenium/ferrocene (Fc^+/Fc) standard, the potential values obtained in reference to Ag/Ag^+ electrode were converted to the saturated calomel electrode (SCE) scale. The polymer or polymer/PSSA complex was coated onto the Pt working electrode by dipping the Pt wire into the viscous polymer solution. The BBL, BBB, or their PSSA complex coatings on the Pt wire electrode were treated in methanol for 24 h to remove the MSA and then dried in a vacuum oven at 100 °C for 8 h. Acetonitrile (ultrapure, 99.93+%, <0.005% water) and tetrabutylammonium hexafluorophosphate ($TBAPF_6$) were obtained from Aldrich and used as received. Electrolyte solutions of 0.1 M $TBAPF_6$ in acetonitrile were used in all experiments. All solutions in the three-electrode cell were purged with ultrahigh-purity N_2 for 10–15 min before each experiment and a blanket of N_2 was used during the experiment.

Results and Discussion

Figure 1 shows the room-temperature dc conductivity of thin films of BBL/PSSA and BBB/PSSA complexes as a function of composition. An insulator-conductor transition is observed at about 20 mol % PSSA in the BBL complex. The conductivity saturates at about 70–100 mol % PSSA with a maximum value of 2 S/cm. This represents over 12–14 orders of magnitude increase in the electrical conductivity of BBL in the protonated state compared to the neutral intrinsic polymer.[9,11,17] A similar insulator to conductor transition was observed for BBB/PSSA complexes with a maximum conductivity of 1 S/cm at about 80 mol % PSSA (Figure 1). This is very similar to well-known protonation induced insulator−metal transition in polyaniline.[3] We point out that although a similar enhancement of the conductivity of BBL has previously been reported for H_2SO_4 protonation, such sulfuric acid-doped BBL films were reported to be very unstable in air.[9] In contrast, the present PSSA-doped BBL films are conducting *polymer/polymer complexes* with good ambient air stability (Figure 2) as well as after heating them to temperatures as high as 100 °C. The dc conductivity of the complexes was measured as a function of time over the course of 7 months of storage in air (Figure 2). Only a slight decrease in conductivity with time was observed for BBL/PSSA
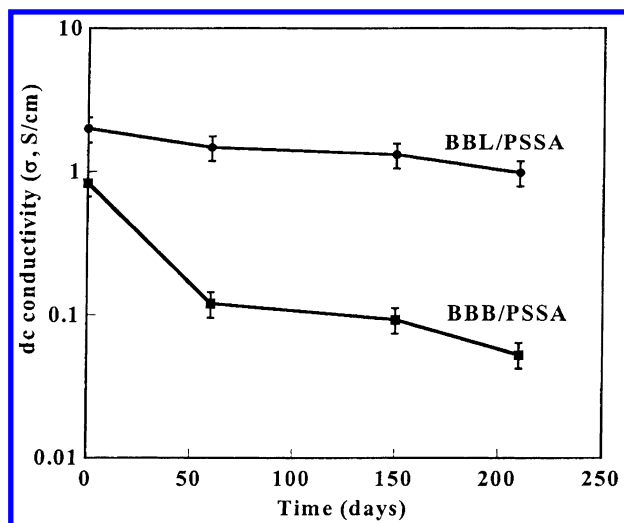
Figure 2. The dc conductivities of BBL/PSSA and BBB/PSSA complexes as a function of time stored in air.
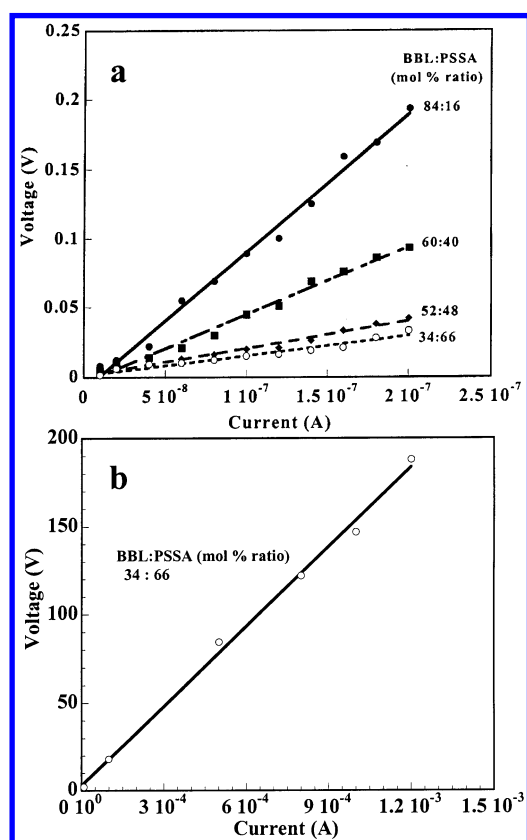
Figure 3. Current-voltage curves during the dc conductivity measurements of BBL/PSSA complexes.

complexes whereas an order of magnitude decrease was seen in the BBB complexes. This stability in the doped state is by virtue of the nonvolatile nature of the poly(styrenesulfonate) (PSS$^-$) counterion and the inherent stability of both protonated BBL (HBBL$^+$ or H$_2$BBL^{2+}) and PSS$^-$ under ambient humid air. Our observed stability of conducting PSSA-doped BBL is also in accord with earlier observations that BBL was highly stable (>10^4 cycles) in electrochemical redox/protonation experiments in aqueous acidic media.[13]

Figure 3 shows the current−voltage curves obtained during the dc conductivity measurement of BBL/PSSA complexes with different compositions. Linear current−voltage characteristics were observed in all compositions of the BBL and BBB
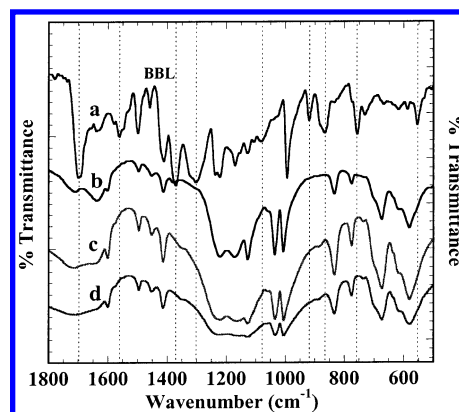

Figure 4. FT-IR spectra of BBL (a) and BBL/PSSA complexes (b, 40; c, 75; d, 98 mol % PSSA).

complexes, confirming the electronic (Ohmic) nature of the measured conductivity. Even higher amount of current of up to 1.2 mA (Figure 3b) was applied for 5−6 min resulting in 0.36 coulombs of charge passing through the sample to provide a polarization of any ionic carriers. We found that the resistance and dc conductivity of the samples remained constant even at such high currents and correspondingly high voltage (~180 V). The electronic nature of the charge transport in these PSSA-doped conjugated polymers is facilitated by the highly delocalized electronic structures of both BBL and BBB. We point out that there is precedence for high electronic conductivity in a conjugated polymer doped by PSSA. Commercial poly-(ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT/PSS) complexes have been studied extensively.[24]

The site of protonation on the BBL molecule was investigated by FTIR spectroscopy of the conducting BBL/PSSA complexes (Figure 4). The imine stretching band ν(C=N) at 1580 cm^{-1} in pristine BBL has completely disappeared in the complexes with PSSA. The relatively sharp carbonyl stretching band ν(C=O) at 1700 cm^{-1} in pristine BBL was broadened and slightly shifted to higher frequency in the complexes. These and other FTIR spectral changes are evidence of protonation occurring at the imine nitrogen sites of BBL with consequent significant charge density redistribution in the BBL repeat unit. Essentially similar spectral changes and their interpretation have been reported for sulfuric acid-doped BBL.[9] That protonation of the imine nitrogens of BBL are favored over the amide carbonyl oxygens was also previously established in electrochemical studies in acidic media.[13] Along with the characteristic vibrational spectral changes, the percent transmittance of the FTIR specta of the BBL/PSSA complexes decreased with increasing mol % of PSSA compared to that of the pristine BBL. This progressive decrease of infrared transmission may be due to electronic absorption in the conducting complexes. Similar vibrational spectral changes were also observed in the BBB/PSSA complexes, providing similar evidence of protonation at the imine nitrogen sites of BBB.
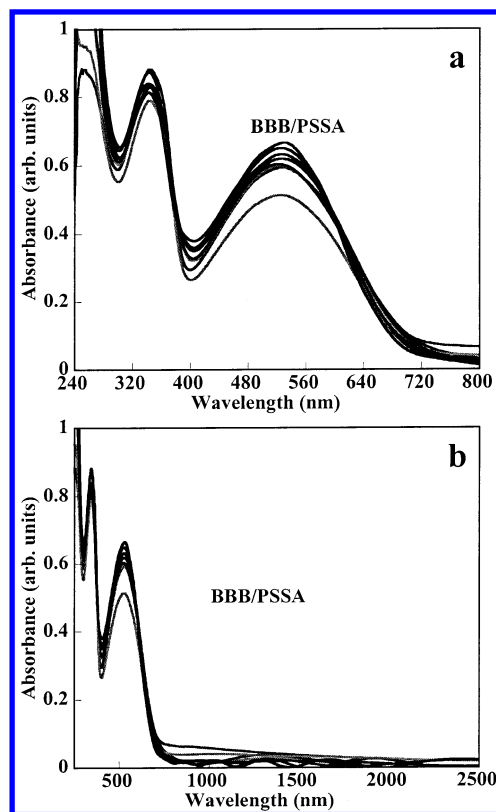
The electronic absorption spectra of thin films of pristine BBL and its PSSA complexes are shown in Figure 5. An absorption maximum at 570 nm (2.2 eV) and an optical absorption edge (band gap) of 700 nm (E$_g$ = 1.77 eV) were observed in the pristine polymer. A very small blue shift in the absorption maximum (λ_{max} = 550 nm), but unchanged absorption edge (E$_g$ = 1.79 eV), was observed in the BBL/PSSA complexes. No new absorption features were observed in the electronic absorption spectra of the conducting complexes in the 700−2600 nm range. These observations are in agreement with prior reports for both the sulfuric acid-protonated and redox-doped BBL.[9,11]

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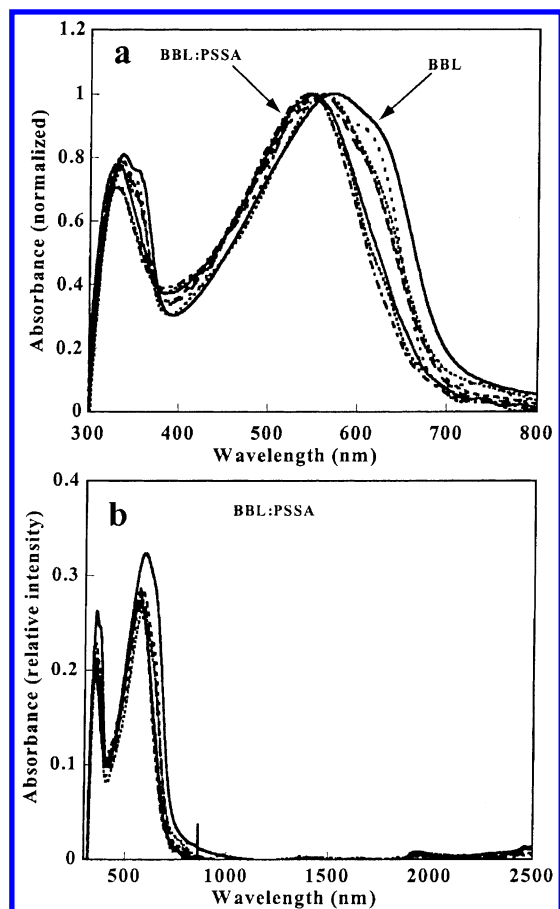
Figure 5. Optical absorption spectra of thin films of BBL/PSSA complexes as a function of composition at two wavelength scales (a, b).


Figure 6. Optical absorption spectra of thin films of BBB/PSSA complexes as a function of composition at two wavelength scales (a, b).

On the basis of computational modeling, such results have been interpreted as a consequence of the lack of geometric (Peierls) distortions in protonated or redox-doped BBL and the similarity of the electronic structures of the neutral and charge-bearing BBL chains.[9c] Figure 6 shows the electronic absorption spectra of thin films of BBB and its PSSA complexes. Similar to BBL/PSSA complexes, no new absorption features were observed in the electronic spectra of the conducting complexes. For example, the absorption maximum (λ_{max} = 530 nm) and absorption edge of 700 nm (E_g = 1.77 eV) in the pristine BBB were unchanged after varying degree of PSSA complexation.

We have also probed the effects of protonation on the electronic structure of BBL by performing electrochemical experiments on thin films of the pristine polymer and its PSSA complexes at neutral pH in acetonitrile. The cyclic voltammetry (CV) results for the neutral BBL are shown in Figure 7a. They are nearly identical to previous CV data for the pristine ladder polymer.[11b,13,14b] The formal potential $E^{o'}$ of the first wave is -0.85 V and the onset reduction potential (E_{red}^{onset}) is -0.56 V (vs SCE). An approximate electron affinity (or LUMO level) of the pristine BBL, estimated from the onset reduction potential by using a value of -4.8 eV as the SCE energy level relative to the vacuum level, is thus 4.2 eV. The cyclic voltammograms of all BBL/PSSA complexes showed only a single reduction wave in the potential range of -2 to 2 V (vs SCE). A representative CV is also shown in Figure 7a for the 98 mol % PSSA complex. The scan rate v dependence of this reduction wave of the complex is shown in Figure 7b; linearity of the peak currents (i_{pa}, i_{pc}) versus $v^{1/2}$ was found. The main effect of the composition on this reduction wave (E_{pc} = 0.45 V; E_{pa}
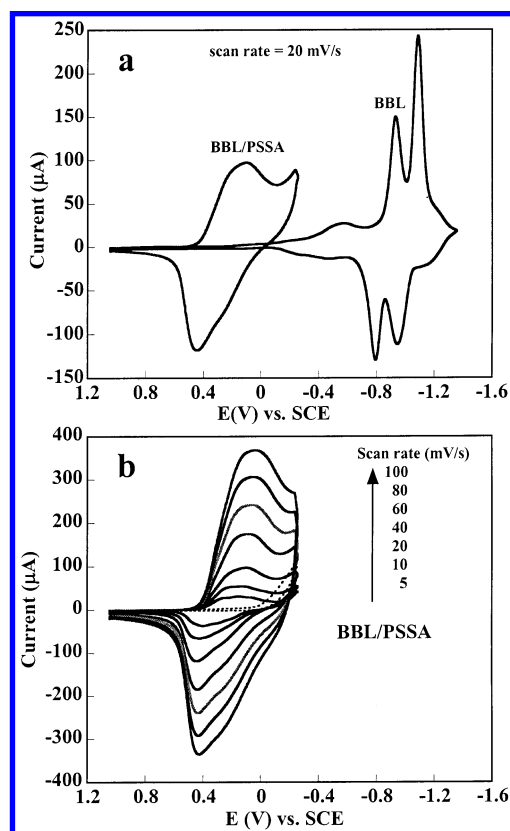
Figure 7. Cyclic voltammograms of (a) BBL and BBL/PSSA complex (98 mol % PSSA) and (b) the same BBL/PSSA complex at different scan rates. The dotted line in (b) is the CV of pure PSSA at 20 mV/s.

= 0.25 V) was the increase of the peak current with increasing amount of PSSA incorporated into the complex at a fixed CV
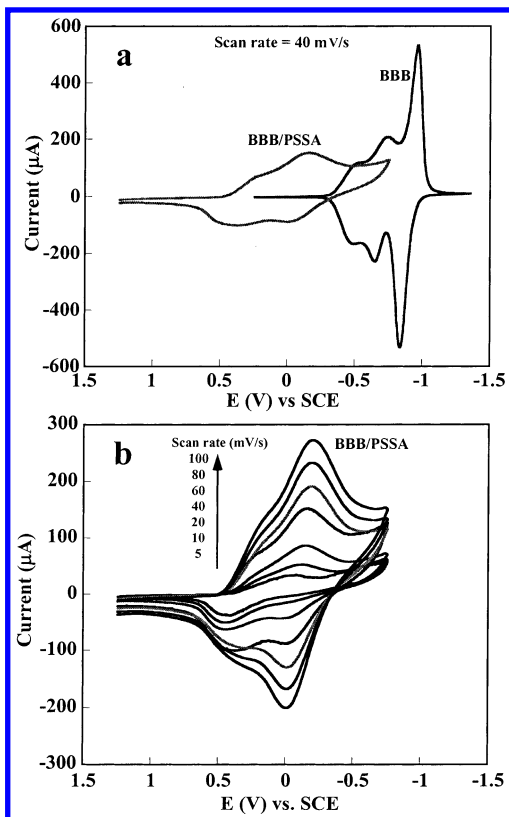
Figure 8. Cyclic voltammograms of (a) BBB and BBB/PSSA complex (80 mol % PSSA) and (b) the same BBB/PSSA complex at different scan rates.

Figure 9. Schematic of the evolution of electronic structures from (a) BBL to the protonated BBL/PSSA complex and (b) BBB to the protonated BBB/PSSA complex as estimated from optical absorption spectra and cyclic voltammetry.

scan rate. The formal reduction potential of this wave is 0.35 V and the onset potential is 0.5 V. A similar estimate of the electron affinity (or LUMO level) of the BBL/PSSA complexes gives 5.3 eV.

The cyclic voltammograms of pristine BBB and BBB/PSSA complex at neutral pH are shown in Figure 8. The estimated electron affinity or LUMO level of BBB is 4.5 eV from the onset reduction potential of −0.33 V (vs SCE). A representative CV scan of the BBB/PSSA complex and its scan rate dependence are shown in parts a and b of Figure 8, respectively. Linearity of the peak currents (i_{pa}, i_{pc}) versus $v^{1/2}$ was found. The onset reduction potential in the CV of the BBB/PSSA complex is 0.58 V. A similar estimate of the electron affinity or LUMO level of the BBB/PSSA complexes is 5.4 eV. The LUMO levels of BBB and its PSSA complexes are thus slightly lower lying compared to the corresponding BBL.

The above spectroscopic and electrochemical results can be combined to provide a picture of the effects of PSSA protonation on the electronic structures of BBL and its semi-ladder analogue BBB. A schematic of the evolution of electronic structures in going from the neutral polymers to the protonated conducting BBL/PSSA and BBB/PSSA complexes is shown in Figure 9. Compared to pristine BBL, the HOMO/LUMO energy levels of the BBL/PSSA complex are both lowered by 1.1 eV. This change in electronic structure preserves the HOMO−LUMO optical band gap at 1.8 eV, which explains the lack of new intragap absorptions in protonic acid-doped BBL.

In the case of BBB/PSSA complexes, the maximum conductivity was 1 S/cm and the HOMO/LUMO energy levels of the complexes, estimated from cyclic voltammetry, were lowered by about 0.9 eV compared to the pristine BBB. Since the main difference between BBL and BBB is in chain structure (rodlike
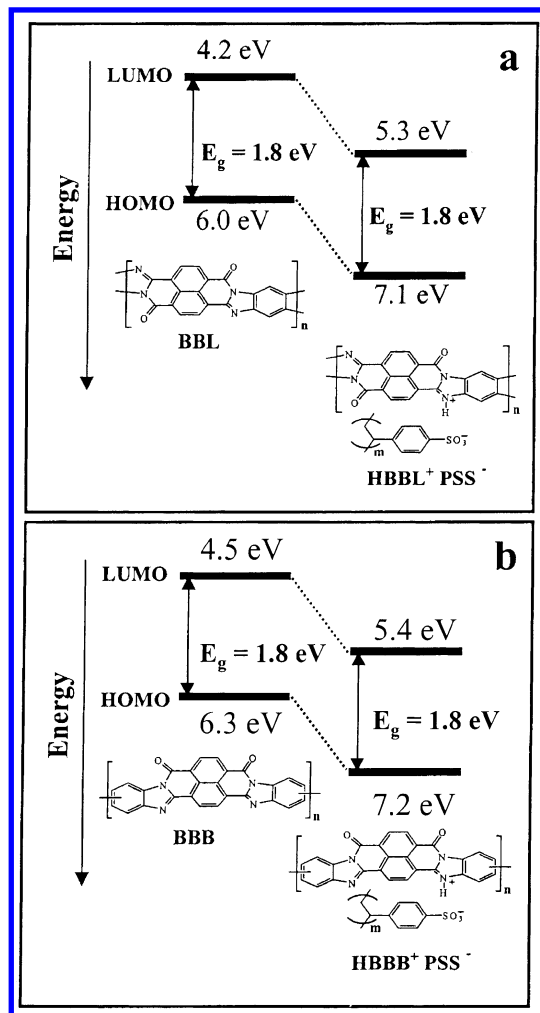
ladder versus semirigid semiladder) rather than molecular structure,[20−22] the similarity of the insulator−metal transition and electronic structure evolution of BBB/PSSA complexes to the BBL/PSSA complexes highlight the specific molecular structures of BBL and BBB as one of the main sources of the difference from other conducting polymers.

The absence of the usual intragap absorptions, and thus signatures of the current carrying quasi-particles,[1−4] and associated geometric distortions in conducting BBL greatly challenges our understanding of the charge transport mechanism in this ladder polymer. The increase in conductivity upon protonation has been suggested to result from a Lewis acid-type charge-transfer complexation of the imino nitrogens and imide regions of BBL that somehow leads to the formation of mobile positive charge carriers.[9] However, prior extensive studies of Lewis acid (AlCl$_3$, GaCl$_3$, FeCl$_3$) complexes of BBL, BBB, and other conjugated polymers showed them to be insulators.[21,22] In the case of redox-doped BBL, the current carrying species were shown[14a] to have spin $^1/_2$ and the conduction was suggested to be a redox hopping process.[13,14a] In the absence of similar electron spin resonance spectroscopy studies on BBL/PSSA complexes it is unclear if such a mechanism is applicable.

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Conclusions

In summary, we have prepared poly(styrenesulfonic acid) complexes of the conjugated ladder polymer BBL and observed that they undergo an insulator−metal transition which is accompanied by a large change in the HOMO/LUMO levels. A similar observation was made on the semiladder polymer BBB. The ambient air stability of these conducting polymer/polymer complexes and their unusual optical and charge transport features make them good model systems for understanding the electronic properties of conjugated ladder polymers. Similar to other PSSA-doped conducting polymers, such as poly-(ethylenedioxythiophene),[24] the conducting BBL/PSSA and BBB/PSSA complexes may be useful for the fabrication of photovoltaic cells and light-emitting diodes.

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