Bipolar Conducting Polymers: Blends of p-Type Polypyrrole and an n-Type Ladder Polymer

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Received July 26, 1996⊗

ABSTRACT: Bipolar conducting polymers, in which both hole transport and electron transport contribute to electronic conductivity, have been explored by chemical template synthesis of p-type polypyrrole (PPy) in the matrix of an n-type conjugated ladder polymer, poly(benzimidazole−benzophenanthroline) (BBL). Transmission electron microscopy images of the conducting polymer blends show that 5−20 nm diameter × 100−180 nm long rodlike PPy particles are randomly and homogeneously distributed in the BBL matrix, with connectivity of the PPy phase occurring at a volume fraction of about 0.17. The volume fraction dependence of conductivity of the BBL/PPy blends did not exhibit a percolation threshold at volume fractions as low as 0.007 nor can it be described by percolation-type effective medium theory. Room temperature conductivities as high as 60−70 S/cm were observed in the blends compared to 2 S/cm in pure PPy. The enhanced conductivity and the nonpercolation nature of these blends originate from bipolar charge transport involving both conjugated polymer components of the blends. Existence of the oxidized (p-type) polypyrrole and reduced (n-type) BBL that facilitate bipolar charge transport in these blends was established by cyclic voltammetry.

Introduction

Polymer blends have been a source of important scientific and technological innovations in polymer science.[1] Although conducting polymers[2−7] and blends of conducting polymers with insulating polymers[8−11] have been studied for a long time, it was only very recently that research advances on conjugated polymer blends have revealed the great potential of mixtures in the field of electroactive and photoactive polymers. Photoinduced electron transfer between two conjugated polymer components of a blend,[12] enhanced third-order optical nonlinearity,[13] efficient nonradiative energy transfer,[14] enhanced efficiency of photodiodes,[15] photovoltaic cells[16a] and light-emitting diodes[16b,17] made from polymer blends, and multicolor electroluminescence[18] from blends of conjugated polymers have all been demonstrated only in the past few years. Here, we wish to explore *bipolar conducting polymers*, a novel class of electronically conducting polymers based on binary polymer blends.

All currently known doped conducting polymers or conducting polymer blends are *unipolar electronic conductors*, being either p-type (hole transporting) or n-type (electron transporting) but not both at the same time as illustrated in Figure 1a,b.[2−11] The counterions in either of these unipolar conducting polymers are spatially localized. Although polymeric counterions have previously been incorporated into conducting polymers, these were nonconjugated polyelectrolytes[4,19] with localized, discrete, counterion sites similar to those shown in Figure 1a,b (A^-, D^+). An important consequence of the spatially localized counterions of conducting polymers is that electrostatic pinning of the charge carriers in the conducting polymers significantly limits carrier mobility and hence the conductivity.[19] Our concept of a *bipolar conducting polymer system* envisions a binary blend of conjugated polymers (Figure 1c) in which one component is p-type and the other is n-type, each functioning as the other's *delocalized counterion*. In such a bipolar conducting material, both hole and electron transport will contribute to the electrical conductivity; the usual expression of conductivity (σ) in terms of concentration (n) and mobility (μ) of carriers will thus have two terms ($\sigma = n_1\mu_1q_1 + n_2\mu_2q_2$). Especially intriguing is the possibility of superconductivity in bipolar conducting polymers arising from the correlated transport of *polaron or bipolaron pairs* on adjacent chains (Figure 1c). Superconductivity has been postulated in conductive materials in which bipolarons are the key excitations.[20]

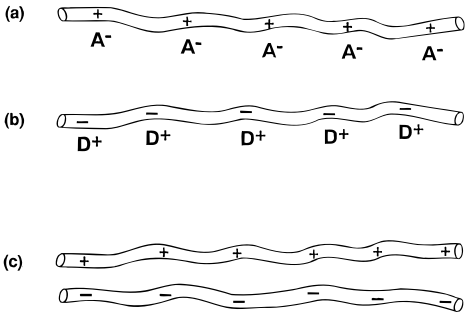

Figure 1. Schematic illustration of currently known unipolar p-type (a) and n-type (b) conducting polymers and proposed bipolar conducting polymers (c).

Ideally, one of the two conjugated polymer components of a bipolar conducting polymer blend has an ionization potential (IP) that is smaller than the electron affinity (EA) of the other. In this way the highest occupied molecular orbital (HOMO or π) band of one polymer is higher lying compared to the lowest unoccupied molecular orbital (LUMO or π^*) band of the second, facilitating spontaneous ground state charge transfer between the blend components. Depending on the composition, miscibility, and molecular and supramolecular order, such a p-type/n-type conducting polymer blend could exhibit metallic behavior. However, few, if any, pairs of currently known conjugated polymers come close to meeting these electronic structure requirements for preparing bipolar conducting polymer systems. Polypyrrole (PPy) is one of the most widely investigated conducting polymers because of its

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⊗ Abstract published in *Advance ACS Abstracts,* February 15, 1997.

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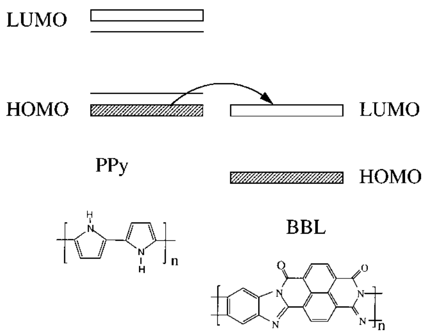

Figure 2. Molecular and electronic band structures of PPy and BBL.

high conductivity (10−1000 S/cm), environmental stability in the p-type doped conducting state, and ease of preparation by chemical and electrochemical methods.[2−4,19] PPy also has a relatively small IP value of ∼3.8−4.0 eV among known p-type conducting polymers.[21] On the other hand, the conducting ladder polymer poly(benzimidazole−benzophenanthroline) (BBL) has n-type conductivity[5−7] of 0.01−100 S/cm, good photoconductivity,[22] large nonlinear optical properties,[23] and the highest EA value (∼4.0 eV)[6,7] among known n-type conducting polymers. The molecular structures and the relative energy band levels of PPy and BBL are shown in Figure 2. Thus, blends of BBL and PPy could represent interesting materials for exploring the concept of a bipolar conducting polymer system.

In this paper, we report the successful preparation of conducting BBL/PPy blends and the initial investigation of their morphology and properties. The binary polymer blends were prepared by chemical template synthesis of polypyrrole in the matrix of BBL films.

Experimental Section

High molecular weight BBL with an intrinsic viscosity of 32 dL/g in methanesulfonic acid (MSA) at 30 °C was synthesized by using the literature method.[24] The reversible Lewis acid coordination complexation method[25] was used to prepare solutions of BBL in nitromethane containing $GaCl_3$. Thin films of BBL were prepared by spin-coating from dilute solutions of the polymer in gallium chloride/nitromethane onto glass substrates and the films were regenerated in deionized water and dried in vacuum. The film thickness of all films was in the range of 30−50 nm. The film thickness was measured with an Alpha Step Profilometer (Tencor Instruments), which has a resolution of 1 nm. BBL/PPy blends were prepared by dipping the BBL films into an aqueous ferric chloride solution of pyrrole monomer whose pH was adjusted to a desired level between 2.0 and 3.0. Typical solutions used in the synthesis of PPy consisted of 0.02 M pyrrole monomer, 0.005 M *p*-toluenesulfonic acid (PTS), and 0.006 M $FeCl_3$. These solutions were generally stable for 2 h after which PPy is formed as a precipitate. Therefore, PPy depositions requiring dipping times longer than 2 h were accomplished by changing the solutions every 2 h. Pure conducting PPy films were formed by dipping blank glass substrates in the same ferric chloride/PTS/pyrrole solution. Before dipping, all the substrates were covered on one side with tape to prevent PPy from depositing on both sides. The resulting BBL/PPy or PPy films were washed thoroughly with deionized water and then dried under reduced pressure at room temperature for 24 h.

The optical absorption spectra of samples were recorded on a Perkin-Elmer Model Lambda 9 UV/vis/near-IR spectrophotometer. The volume fraction composition of PPy in the BBL/PPy blends was estimated from the optical density at 570 nm wavelength before and after the incorporation of PPy. For transmission electron microscopy (TEM), the BBL/PPy films were soaked in water for 2 days and then the films were peeled off the glass substrate using a blade and transferred onto copper grids. TEM images were obtained by using a JEOL Model JEM2000EX instrument at 200 kV accelerating voltage. The dc conductivity of the BBL/PPy films was measured by a four-point probe technique at room temperature. Fourier transform infrared (FTIR) spectroscopy was done by using a Nicolet 20SXC FTIR spectrometer.

The electrochemical properties of films were studied by cyclic voltammetry (CV). The equipment used for the CV experiments was an EG&G Princeton Applied Research Model 273 potentiostat/galvanostat. Data were collected and analyzed by using a Model 270 electrochemical analysis system from the same company. For CV experiments, an electrolyte solution of 0.1 M tetrabutylammonium tetrafluoroborate in acetonitrile was used. Platinum wire electrodes were used as both counter and working electrodes and silver/silver ion (Ag in 0.1 M $AgNO_3$ in the electrolyte solution, from Bioanalytical Systems, Inc.) was used as a reference electrode. The reference electrode was calibrated at the end of each experiment by running cyclic voltammetry on ferrocene as the standard in an identical cell without any polymer on the working electrode. The potential values obtained versus ferrocene were converted to versus saturated calomel electrode (SCE) by adding a constant of 0.1588 to them. The conversion is based on the reduction potential of ferrocenium/ferrocene (Fc^+/Fc) (0.4 V versus NHE) and SCE (0.2412 V versus NHE). Thus, the reduction potential of Fc^+/Fc versus SCE is 0.1588.

Results and Discussion

Template Synthesis of PPy in BBL Matrix. Simultaneous chemical synthesis and deposition of conducting PPy films on substrates dipped into aqueous $FeCl_3$/pyrrole/counterion solutions is well known.[4,8] Similar chemical synthesis and growth of conducting PPy in the matrix of many insulating polymers or nanoporous polycarbonate filtration membranes[26] have been reported. Our "template synthesis" of PPy in the matrix of the conjugated rigid-rod ladder polymer BBL closely followed the approach described by Rubner and co-workers for the deposition of conducting PPy films on glass substrates.[4] Our use of relatively thin (∼30−50 nm) BBL films spin coated on various substrates (glass, fused silica, indium tin oxide (ITO) glass, etc.) as templates allowed us to control the morphology of the starting BBL films and to prepare homogenous BBL/PPy blends of various compositions in relatively short times (15 min to 4 h). This choice also ensured that the BBL/PPy blend samples used in all subsequent experimental characterization (TEM, optical spectra, dc conductivity, electrochemistry, etc.) had comparable film thickness. The dipping time in the aqueous monomer solution served to regulate the amount of PPy incorporated into the BBL films. The actual composition of the BBL/PPy blends (volume fraction of PPy, *f*) was estimated by the optical technique described in the Experimental Section and corroborated by the TEM results discussed below.

Visually, the BBL/PPy blend films were different compared to the pure BBL and PPy films of comparable film thickness. Pure BBL films were purple in transmission and yellowish gold in reflection. After dipping such BBL films into aqueous pyrrole (PTS, $FeCl_3$) solutions, the resulting BBL/PPy films were relatively more transparent (clear to grayish) but their colors in reflection depended on the compositions. At low PPy volume fractions ($f < 0.2$), the BBL/PPy blend films exhibited gold-brown metallic luster in reflection whereas at higher concentrations metallic green luster in reflection was observed. Correspondingly, the BBL/PPy blend films have superior mechanical properties as judged qualitatively from the scratch resistance, strength, and

Figure 3. Transmission electron micrograph of a BBL/PPy blend sample having a PPy volume fraction of 0.10 and a conductivity of 1 S/cm. The white bar scale is 100 nm.

toughness of the blend films compared to either BBL or PPy films.

The chemical synthesis of PPy in the matrix of BBL films is expected to proceed as in the $FeCl_3$-catalyzed chemical polymerization of pyrrole, which is generally believed to follow a radical ion mechanism akin to the electrochemical synthesis of PPy.[19] However, because of the rodlike conformation of BBL chains, the expected rodlike local morphology and void volume in BBL films, and the high electron affinity of BBL, the growing $PPy^{\bullet+}$ chain may strongly interact with the surrounding BBL chains. Such an interaction of $PPy^{\bullet+}$ with BBL could result in an electron transfer from $PPy^{\bullet+}$ to the neutral BBL matrix: $BBL + PPy^{\bullet+} \rightarrow BBL^{-}$ (PPy^{2+}). In this case BBL^{-} serves as the counterion. If such an electron transfer reaction does not occur during the synthesis of PPy inside BBL, however, the BBL/PPy blends of necessity would incorporate the *p*-toluenesulfonate (PTS^{-}) anion.

Morphology. The BBL/PPy blend thin films were examined by transmission electron microscopy (TEM). Figure 3 shows the TEM image of a highly conducting (~1 S/cm) BBL/PPy blend containing 10% volume fraction of PPy. This TEM micrograph shows that the BBL/PPy blend has a two-phase morphology: a dispersed PPy phase consisting of rodlike/ellipsoidal particles of 5−20 nm diameter × 100−180 nm long, with a typical diameter of ~10−15 nm and a typical length of ~140 nm. TEM images at higher magnifications than Figure 3 indicated that these rodlike/ellipsoidal particles are made up of smaller diameter rodlike objects which are likely bundles of PPy chains with extended linear conformations. TEM images of pure BBL films were featureless at all magnification scales and similar to the continuous matrix in which the rodlike particles are randomly dispersed in the micrograph of Figure 3. One of the striking features of the morphology of BBL/PPy blends revealed in the TEM image of Figure 3 ($f = 0.1$) and all TEM images at PPy concentrations of $f \leq 0.17$ is the lack of a connected network structure of the PPy phase. At higher volume fractions of PPy ($f > 0.17$) the nanophase separation and rodlike morphology of the PPy phase are still observed in the BBL/PPy blends, but interconnection between the PPy particles appeared. The morphology of BBL/PPy revealed in TEM is fundamentally different from those of pure PPy thin films[19] or PPy/insulating polymer blends or polyaniline/insulating polymer blends, which generally show globular or fibrillar network structures.[8−11]

The TEM images of the BBL/PPy thin films clearly show that the intended synthesis of polypyrrole in the matrix of BBL has been accomplished and that PPy does not merely deposit on the surface of the BBL film. The rodlike nanoscale morphology of the PPy phase and its random but uniform distribution in these blends reflect the *template effect* of the BBL morphology. A spin-coated BBL film has only local molecular order due to aggregated and highly ordered rodlike BBL chains; globally, the film and its void volume are isotropic or randomly distributed in the plane of the film. These morphological features are remarkably mirrored in the PPy phase of template-synthesized BBL/PPy blends. One implication of these results for future work is that highly ordered films of BBL, for example such as obtained through film extrusion or shear-induced orientation of liquid crystalline solutions, may allow the template synthesis of macroscopically highly ordered BBL/PPy nanocomposites with PPy aspect ratios significantly greater than the 10−20 observed in Figure 3.

If we assume that the 5−20 nm diameter rodlike particles of PPy observed in the TEM images (Figure 3) consist of bundles of the polymer in extended chain conformation, we can estimate the molecular weight of the template-synthesized polypyrrole. If one PPy chain occupies the typical 140 nm length of PPy particles in Figure 3, from the 0.368 nm repeat unit length[27] of a polypyrrole chain having an extended linear conformation with alternate rings rotated by 180°, one obtains a degree of polymerization of 380 monomer units or a number-average molecular weight of ~24 800. Although there is no direct measurement to check this estimate, it seems reasonable and such a molecular weight could explain the marked improvement in mechanical properties of the BBL/PPy blends compared to those of the pure components.

Optical Absorption Spectra. The thin-film electronic absorption spectra of a BBL/PPy blend ($f = 0.5$), a pure BBL, and a pure PPy are shown in Figure 4. The absorption spectrum of BBL has a λ_{max} at 570 nm (2.18 eV) which is due to a $\pi-\pi^*$ transition and an absorption edge at 700 nm (1.77 eV) which defines an optical band gap for the polymer. The only resolved peak in the absorption spectrum of PPy is at 457 nm (2.71 eV); otherwise, a broad free carrier absorption extending from 600 nm to the near-infrared 3200 nm was observed and is similar to reported ones.[3] Clear assignment of the PPy absorption spectrum to either polaron or bipolaron transitions could not be made. The electronic absorption spectrum of the BBL/PPy blend was a superposition of those of the components. The absence of any new features in the absorption spectra of BBL/PPy blends suggests that the BBL in the as-synthesized blends is largely neutral and hence that *p*-toluenesulfonate ions must be incorporated in the blends as a counteranion. Our comparison of the FTIR spectra (not

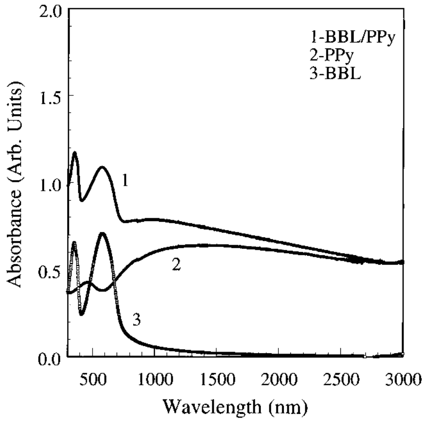

Figure 4. Optical absorption spectra of thin films of BBL/PPy blend ($f = 0.5$) (1), pure conducting PPy (2), and pure insulating BBL (3).

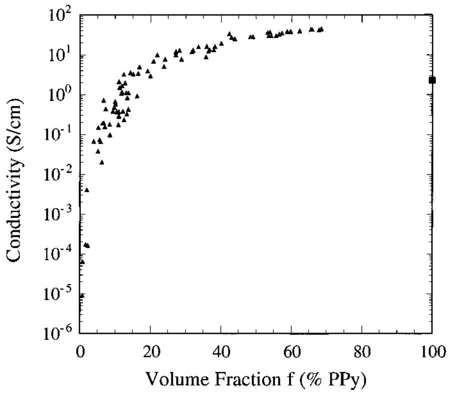

Figure 5. Room temperature conductivity of BBL/PPy blend system as a function of volume fraction (f) of PPy.

shown) of free-standing pure BBL and BBL/PPy blend ($f = 0.32$; $\sigma = 27$ S/cm) thin films and PPy/KBr pellet showed that the FTIR spectrum of the blend was a superposition of those of its components. FTIR spectroscopy of the BBL/PPy blends thus confirmed the optical absorption results which suggest that BBL exists in the blends as a neutral matrix.

Electrical Conductivity. The room temperature dc conductivity (measured by the four-point probe technique) as a function of volume fraction (f) of PPy in the BBL/PPy blends is shown in Figure 5. Conductivity as high as 8×10^{-6} S/cm was observed at f as low as 0.007, which is remarkable considering that pure, undoped, BBL is an insulator with a dc conductivity of order 10^{-12} S/cm or less[7] and that connectivity between the PPy phase was not observed until about $f = 0.17$. At PPy volume fractions of 0.10–0.15, the blend conductivity is already about 2 S/cm, which is identical to that of the pure ($f = 1.0$) PPy films of comparable film thickness and synthesized using the same aqueous monomer solutions and conditions. At higher volume fractions in the 0.5–0.6 range, the conductivity of the BBL/PPy blends reaches 50–70 S/cm, which is over a factor of 25 enhancement compared to the pure PPy films prepared under the same conditions.

The measured electrical conductivity of BBL/PPy blends is dramatically different from the conductivity of previously reported blends of conducting polymers with many insulating polymers[9–11] and from percolation-type effective medium theories.[28–30] Blends of conducting polyaniline (PANI) with polystyrene (PS), poly(vinyl chloride) (PVC), and poly(methyl methacrylate) (PMMA) have been reported to exhibit percolation thresholds as low as $f_c \sim 10^{-4}$, above which high conductivity and connectivity of the PANI phase are observed.[10,11] The ultralow percolation thresholds in these PANI/insulating polymer (PS, PVC, PMMA, etc.) blends arise from the self-organization of PANI chains into an interconnected fibrillar network morphology during liquid–liquid phase separation of blend solutions. The interconnected PANI network above f_c allows normal charge transport and high conductivity in such blends which can be understood in terms of percolation phenomena and effective medium theories.[9,10,28–30] In contrast, attempts to fit the conductivity–volume fraction data of Figure 5 to percolation expressions of the form $\sigma \sim f^{a}$ or $\sigma \sim (f - f_c)^{a}$ failed. Since the morphology of BBL/PPy nanocomposites (e.g. Figure 3) does not show connectivity of PPy particles until about $f = 0.17$ even though the conductivity is already very high (e.g. 1 S/cm at $f = 0.10 < f_c$), we conclude that the conductivity of the BBL/PPy blend system does not mimic normal percolation phenomena[9,10,28–30] and thus a novel mechanism is necessary to explain the underlying charge transport.

Our spectroscopic (UV–vis, FTIR) evidence so far is that the BBL matrix in the as-synthesized BBL/PPy blends is neutral and hence insulating with a conductivity of 10^{-12} S/cm or less. The over 7 and 12 orders of magnitude enhancement of conductivity above that of the BBL matrix in blends with PPy volume fractions of 0.007 and 0.10, respectively, which are far below the connectivity threshold of $f_c \sim 0.17$, cannot be explained by *quantum mechanical tunneling*,[28,29] which is usually the case in percolation systems at volume fractions below the percolation threshold ($f < f_c$). Furthermore, at PPy volume fractions of greater than about 0.15, the conductivity of BBL/PPy blends is higher than that of the pure PPy, reaching over a factor of 25 enhancement at $f \sim 0.50$, which would be impossible for a normal percolation system. The conductivity has its maximum value at $f = 1$ in a normal percolation system of a conducting component and an insulating component.[28,29] We propose that the observed large enhancement of conductivity in BBL/PPy blends originates from *electron transfer mediated bipolar charge transport*. Although BBL in *as-synthesized* BBL/PPy blends is neutral, however, under the electric field used in conductivity measurement, electron transfer from any of the three possible forms of polypyrrole in the blends (PPy^{0}, $PPy^{\bullet+}$, and PPy^{2+}) to BBL most likely occurs. The ionized $BBL^{\bullet-}$ (polaron) can further accept another electron to form BBL^{2-} (bipolaron), facilitating n-type (electron) transport and p-type (hole) transport in the blends that have become largely BBL^{-} (PPy^{2+}) and BBL^{2-}(PPy^{2+}). Such a field-induced electron transfer between PPy and BBL chains in the nanophase-separated blends in effect *amplifies* the number of charge carriers, facilitates bipolar charge transport, and provides a conductive bridge between PPy phases no matter how far apart they are. Underlying this novel mechanism of charge transport and conductivity in BBL/PPy blends is the assumption of *synergistic interaction* (electron transfer) between the two components. Direct evidence supporting such an assumption was obtained from electrochemistry as discussed below.

Cyclic Voltammetry. We have directly probed the electron transfer processes in the BBL/PPy blends by cyclic voltammetry. Figure 6a shows the cyclic voltammogram (CV) of pure BBL thin film. Two quasi-reversible reduction waves with cathodic peaks (E_{pc}) at

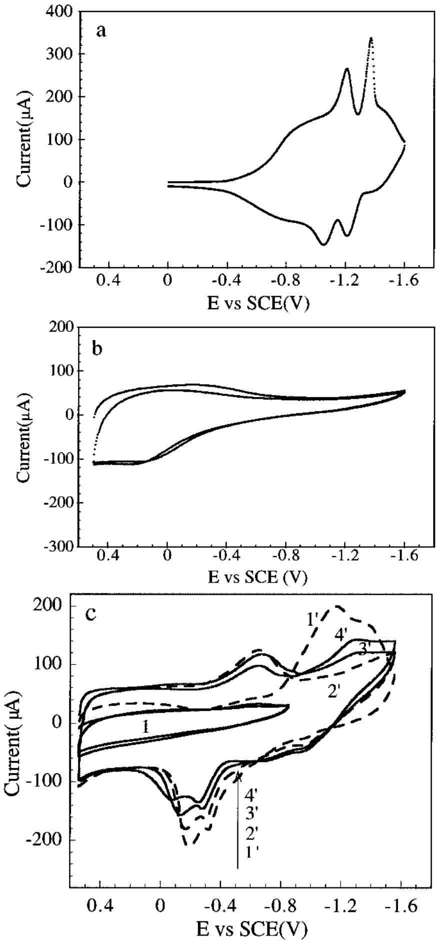

Figure 6. Cyclic voltammograms of (a) reduction of BBL (50 mV/s), (b) reduction of pure conducting PPy (50 mV/s), and (c) BBL/PPy blend ($f = 0.32$) (20 mV/s): initial repeated scans from +0.5 to −0.8 V (1), followed by reduction scan from +0.5 to −1.6 V (1′), and subsequent cyclings (2′ , 3′ , 4′) between +0.5 and −1.6 V.

−1.15 and −1.30 V (vs SCE) are observed and are similar to previously reported[6] CVs for this polymer at neutral pH. This CV of BBL is due to the two-electron electrochemical reaction, which has $BBL^{\bullet -}$ (negative polaron) as an intermediate. It is presumably the

$$BBL + 2e^{-} \leftrightarrow BBL^{2-} \quad (1)$$

product of this electrochemical reaction (negative bipolaron) which is responsible for the reported high (1−100 S/cm) n-type conductivity of chemically and electrochemically reduced BBL.[5−7] The CVs of as-synthesized conducting PPy thin film are shown in Figure 6b and are similar to those reported for this conducting polymer.[31] The cathodic scan from +0.5 to −1.6 V corresponds to the gain of electrons by the oxidized PPy^{2+} and the reverse amodic scan corresponds to loss of electrons by the neutral PPy. It is well known that PPy^{2+} is usually completely converted to the neutral form at −1.0 V (vs SCE) or more negative potentials.

Figure 6c displays several CVs of a BBL/PPy blend thin film ($f = 0.31$). The curves labeled 1 in Figure 6c correspond to initial repeated scans of the blend between +0.5 and −0.8 V, revealing similarity to the CVs of the pure PPy film in Figure 6b. Subsequent CV scans of the same blend over a wider potential range between +0.5 and −1.6 V are also shown in Figure 6c as curves 1′ , 2′, 3′, and 4′. The first reduction (cathodic) scan of the BBL/PPy blend from +0.5 to −1.6 V (curve 1′) is a superposition of the reduction scans of the pure components. However, the subsequent anodic scan from −1.6 to +0.5 V (curve 1′) and repeated complete redox cycling (curves 2′, 3′, and 4′) are dramatically different. Following the first reduction scan from +0.5 to −1.6 V, two large and *new* oxidation (anodic) peaks (E_{pa}) appeared at −0.35 and −0.20 V and a new reduction (cathodic) peak (E_{pc}) appeared at −0.7 V (curve 2′). Subsequent repeated cycling between +0.5 and −1.6 V (curves 3′ and 4′) shows the same redox behavior and persistence of the new CV peaks. It should also be noted that the reduction current between +0.5 and −0.8 V in curves 2′, 3′ , and 4′ is more than twice enhanced compared to the reduction current in the same potential range in curve 1′.

This redox behavior of BBL/PPy blends, particularly the new redox couples, can be best accounted for in terms of electron transfer between the components. Observation of the redox behavior characteristic of PPy when the blend is scanned between +0.5 and −0.8 V indicates that the BBL in the as-prepared blend is neutral and that the polypyrrole is in the oxidized (PPy^{2+} or PPy^{+}) form. This is in accord with the optical absorption and infrared spectroscopies of the blends. However, the first reduction scan between +0.5 and −1.6 V facilitates the dedoping of oxidized polypyrrole and two-electron reduction of BBL, yielding the new blend species BBL^{2-} (PPy^{0}). The expected reoxidation of BBL^{2-} (PPy^{0}) and the expected loss of two electrons at E_{pa} values of −1.20 and −1.05 V as in the pure BBL^{2-} do not occur until much more positive potentials at −0.35 and −0.20 V because as BBL^{2-} loses electrons to the electrode there is simultaneous electron transfer from PPy^{0} to BBL species, forming $BBL^{2-}(PPy^{2+})$ and BBL^{-} ($PPy^{\bullet +}$). The following summarizes the possible species in the electrochemical redox behavior of BBL/PPy blends:

$$BBL(PPy^{2+}) \leftrightarrow BBL^{-}(PPy^{2+}) \leftrightarrow BBL^{2-}(PPy^{2+}) \leftrightarrow BBL^{-}(PPy^{\bullet +}) \leftrightarrow BBL^{2-}(PPy^{\bullet +}) \leftrightarrow BBL^{2-}(PPy^{0}) \quad (2)$$

The cyclic voltammetry results clearly show that under an applied potential the binary BBL/PPy blend system can be transformed to a composite medium which exhibits bipolar charge transport through its two components, in agreement with the electrical conductivity results. These results also suggest that the condition essential for *spontaneous* ground state electron transfer between BBL and PPy, e.g. a BBL LUMO level that is lower than the HOMO level of PPy, is not fulfilled in these blends—hence, the necessity of initial electric field activation of bipolar charge transport in the blend system.

Conclusions

We have demonstrated the novel concept of a bipolar conducting polymer (Figure 1c) through a binary blend of p-type and n-type conjugated polymers. Blends of polypyrrole (p-type) and BBL (n-type) were found to have dc conductivities that are over a factor of 25 enhanced compared to that of the pure conducting polypyrrole component. Furthermore, the volume fraction dependence of the conductivity of BBL/PPy blend system did not exhibit a percolation threshold and could not be described by percolation-type effective medium theories. The synergistic interaction between the blend components which facilitates bipolar charge transport was probed by cyclic voltammetry and evidenced as intermolecular electron transfer.

Although the BBL/PPy blend system has provided the first experimental test of the concept of a bipolar conducting polymer, it is by no means ideal or even optimized. The nanophase separation of this blend system, evidenced by TEM images, appears to preclude metallic behavior and may be the chief factor limiting the conductivity. The absence of *spontaneous* ground state charge transfer between BBL and PPy also means that some novel features of bipolar conducting polymers are yet to be realized. Therefore, future work should aim to achieve π-conjugated polymer pairs with improved molecular miscibility, molecular and supramolecular order, and spontaneous ground state intermolecular electron transfer.

Acknowledgment. This research was supported by the Office of Naval Research and the National Science Foundation (CTS-9311741, CHE-9120001).

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MA961121F