Electrochemical Synthesis of Polypyrrole within Poly(4-butanesulfonate−cyclopentadithiophene) Films. A 1:1 Polypyrrole−Polythiophene Composite

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Anodic coupling of dipyrrole on thin films of poly(4-butanesulfonate−cyclopentadithiophene) in acetonitrile produces polypyrrole within the polythiophene structure. Cyclic voltammetry, UV−vis spectroscopy and impedance measurements show that the polypyrrole chains are interwoven with the polythiophene chains in a polymeric composite with a pyrrole:thiophene ratio close to 1.

Introduction

Polypyrrole (PP) and polythiophene (PT) have been the object of several investigations aiming at the production of pyrrole−thiophene copolymers.[1−9] In some cases statistical copolymers were produced from pyrrole and thiophene,[1] bithiophene,[4] or terthiophene.[2] A statistical copolymer was produced from 2-(2-thienyl)-pyrrole with the either moiety being engaged in coupling reactions.[3] Regularly alternating copolymers were produced from 2,5-bis(*N*-methyl-2-pyrrolyl)thiophene[5] and from 2,5-bis(2-thienyl)pyrrole,[6−8] while well-defined oligomers alternating *N*-methylpyrrole and thiophene units have been reported recently.[9]

The homopolymers have been also combined in heterogeneous structures such as polythiophene−polypyrrole bilayers.[10] The potential interest of these materials in electronic applications, such as those based on quantum wells, is well documented.[11] In the course of our recent investigations aiming at the production of a well-behaved self-doped polythiophene,[12] we synthesized a regular sulfonate-substituted polythiophene by anodic coupling of tetrabutylammonium 4-butanesulfonate−cyclopentadithiophene (4-(4*H*-cyclopenta[2,1-*b*:3,4-*b*′]-dithienyl)butanesulfonte, CPDTSO; Figure 1a).

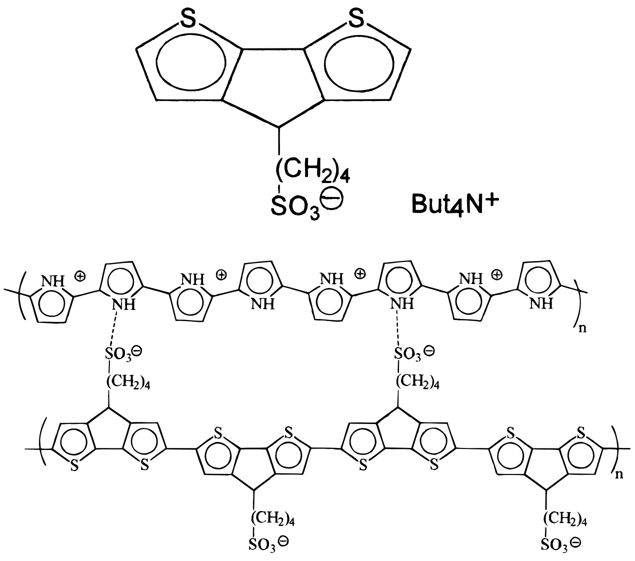

Figure 1. Formulas of (a, top) the dithiophene monomer and (b, bottom) of the polythiophene−polypyrrole molecular composite.

Since we had also previously ascertained that the sulfonate group assists the anodic coupling of dipyrrole to polypyrrole,[13] we realized that the sulfonate-substi-

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tuted thiophene monomer and polymer we had prepared might be used for the production of "molecular bilayer" conducting polymers. These materials are intended as PT–PP composites in which the cationic sites on oxidized PP are associated with anionic sites in PT, so that (i) the different polymers are mixed on the molecular scale and (ii) the relative amounts of PT and PP are ruled by a well-defined stoichiometry.

Therefore we explored two routes to create template PT–PP molecular assemblies of a PT–polyanion chain with a PP–polycation chain (Figure 1b), which we describe in the present paper. In the first route (route 1) the PT chain is produced via coupling of the thiophene monomer CPDTSO and subsequently the PP chain is formed on the PT chain by coupling of dipyrrole driven by the PT–sulfonate groups; the supporting electrolyte may be a perchlorate salt which is ineffective in dipyrrole polymerization.[14]

In the second procedure (route 2) a PP film is deposited as CPDTSO salt by coupling dipyrrole in a solution containing CPDTSO as the supporting electrolyte; subsequently the CPDTSO counteranions are coupled to PT chains within the PP matrix.

Experimental Section

Chemicals and Reagents. The monomer tetrabutylammonium 4-(4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithienyl)butanesulfonate (CPDTSO) was synthesized as described previously.[12] Acetonitrile (AN) was reagent grade (Merck) with a water content <0.01%. 2,2′-Dipyrrole was synthesized according to the literature.[15] The supporting electrolyte tetrabutylammonium perchlorate (Bu_4NClO_4) was previously dried under vacuum at 70 °C. All other chemicals were reagent grade and used as received.

Apparatus and Procedure. Experiments were performed at 25 °C under nitrogen in three-electrode cells. The counterelectrode was platinum; the reference electrode was a silver/0.1 M silver perchlorate in acetonitrile (0.34 V vs SCE). The voltammetric apparatus (AMEL, Italy) included a 551 potentiostat modulated by a 568 programmable function generator and coupled to a 731 digital integrator.

The working electrode for cyclic voltammetry and ac impedance was a platinum minidisk electrode (0.003 cm^2). For UV–vis spectroscopy a 0.8 × 2.5 cm indium–tin oxide (ITO) sheet (ca. 80% transmittance, ca. 20 Ω/square resistance, from Balzers, Liechtenstein) was used.

UV–vis spectra were taken with a Perkin-Elmer Lambda 15 spectrometer. The ac impedance experiments were performed with a Solatron 1250 frequency response analyzer and a Solartron 1286 electrochemical interface; both of them were controlled by a commercially available software (FRACOM). The frequency range between 0.5 Hz and 10 kHz was covered with 6 points/decade.

Results and Discussion

Template Deposition of Polypyrrole within Poly(CPDTSO) (Route 1). The procedure followed in this case consists in depositing a thin (ca. 0.1 μm) film of poly(CPDTSO) on the electrode, immersing the electrode in a solution of dipyrrole and oxidizing the dipyrrole to polypyrrole on the poly(CPDTSO) film. The template action of the sulfonate group would produce the polymer within the film, whereas other oxidation products of the dipyrrole will be soluble species.[14]

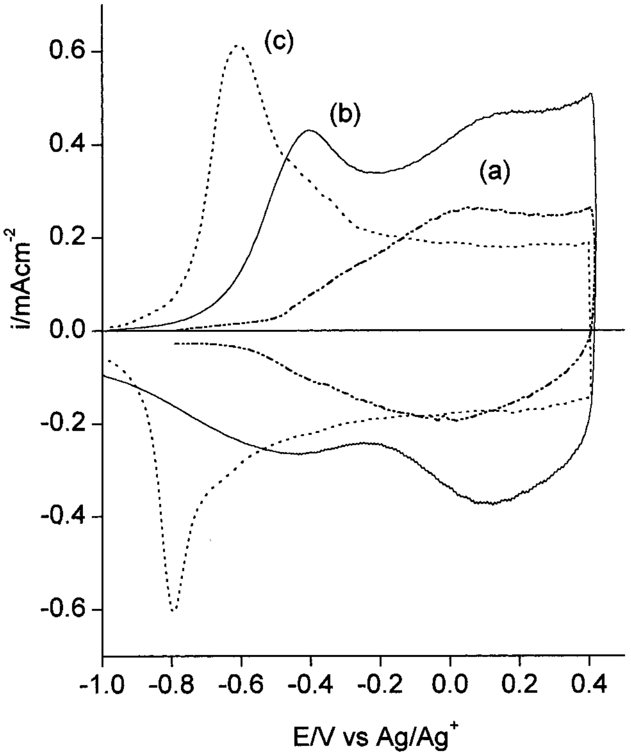

Figure 2. Cyclic voltammetry for poly(CPDTSO) in AN + 0.1 M Bu_4NClO_4: (a) before and (b) after PP deposition ((c) PP tosylate for comparison). Scan rate: 0.1 V s^{-1}. Reversible charge (before PP deposition) Q_{r0}: 1.7 mC cm^{-2}.

Films of poly(CPDTSO) were deposited as previously reported[12] by anodic coupling of the monomer typically 2 × 10^{-3} M in AN + 0.1 M Bu_4NClO_4 via potential cycling over the oxidation peak at 0.6 V. Cycling the potential of a thin film of poly(CPDTSO) (storing a reversible charge $Q_{r0} = 1-2$ mC cm^{-2} at 0.4 V) in a 2 × 10^{-3} M solution of dipyrrole in AN + 0.1 M Bu_4NClO_4 up to 0.3 V (i.e., right beyond the peak of dipyrrole oxidation) produces in the CV the appearance of an additional response, due to the deposited polypyrrole, until a steady state profile is attained after a few (two–three) CV cycles at a scan rate of 0.1 V s^{-1}. This indicates that polymerization occurs initially but stops after a few cycles; in further cycles dipyrrole oxidation continues, but only soluble species (pyrrole tetramers[14]) are formed. The poly(CPDTSO)–PP films display in monomer-free solution the CV of the polythiophene at $E° = 0.1$ V imposed over the CV response of the polypyrrole at $E° = -0.4$ V (b in Figure 2). The latter potential appears to be anodically shifted by ca. 0.3 V from that of polypyrrole tosylate, which may be explained by a lower stabilization of the oxidized (polycationic) PP by the polyanionic poly(CPDTSO) in comparison with the (nonpolymeric) sulfonate since the latter does not suffer the constraints of a rigid polymeric structure.

The total reversible charge Q_{rt} (measured between −0.8 and 0.4 V) is significantly increased from Q_{r0}, particularly for $Q_{r0} < 2$ mC cm^{-2}, whereby the ratio Q_{rt}/Q_{r0} is ca. 2.5. For a 1:1 ratio of pyrrole:thiophene rings in the composite, it is expected that the ratio Q_{rt}/Q_{r0} is 2.6, given that 0.25 electron/thiophene ring is exchanged

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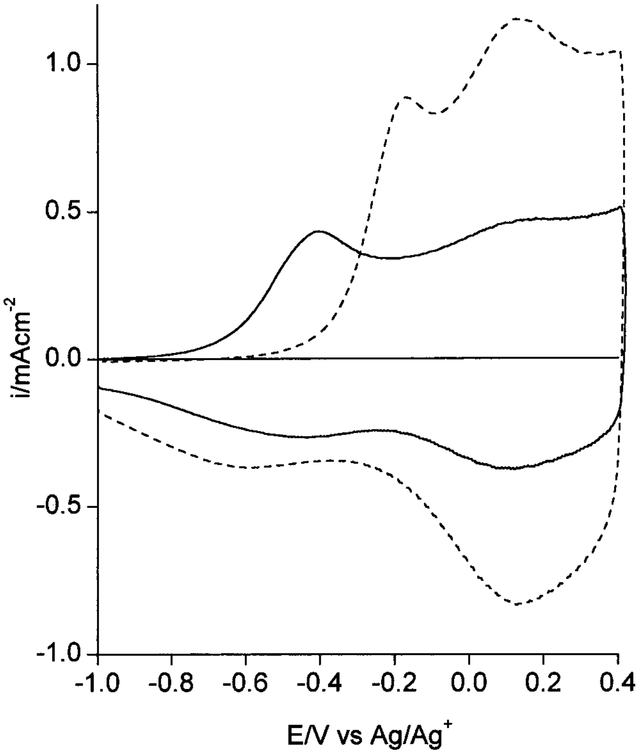

Figure 3. Cyclic voltammetry for poly(CPDTSO)−PP composite films of different thickness in AN + 0.1 M Bu_4NClO_4. Scan rate: 0.1 V s^{-1}. Reversible charge (before PP deposition) Q_{r0}: (—) 1.7; (- - -) 5.2 mC cm^{-2}.

in PT perchlorate[12] and 0.4 electron/pyrrole ring is used in PP sulfonate.[16] Thus PP appears to be polymerized within PT with a pyrrole:thiophene ratio close to 1.

This occurs for the lower film thicknesses. As the thickness is increased, the ratio Q_{rt}/Q_{r0} decreases and the CV response of the polypyrrole is gradually distorted, i.e., the separation between the forward and backward peak potentials increases, whereas that of the polythiophene keeps its symmetrical aspect (Figure 3). At thicker films the sulfonate groups located far from the polymer/electrolyte interface cannot exert their templating action and PP is formed only at the outer regions. Under these conditions in the undoped film the connection between the inserted PP and the underlying electrode becomes mediated by an insulating PP-free PT layer. This is the reason the CV response of PP in the thicker films is distorted.

The production of a PT−PP composite with pyrrole:thiophene ratio close to 1 is confirmed by the UV−vis spectrum. The composite film in the undoped state shows comparable absorption maxima at 440 and 520 nm attributable to PP[14] and poly(CPDTSO),[12] respectively (Figure 4a). Since the two polymers absorb quite similarly, as shown by a comparison of the extinction coefficients of terpyrrole (2.6 × 10^4 M^{-1} cm^{-1} [17]) and terthiophene (2.3 × 10^4 M^{-1} cm^{-1} [18]), the comparable intensity of the bands is in agreement with the equimolar presence of the components.

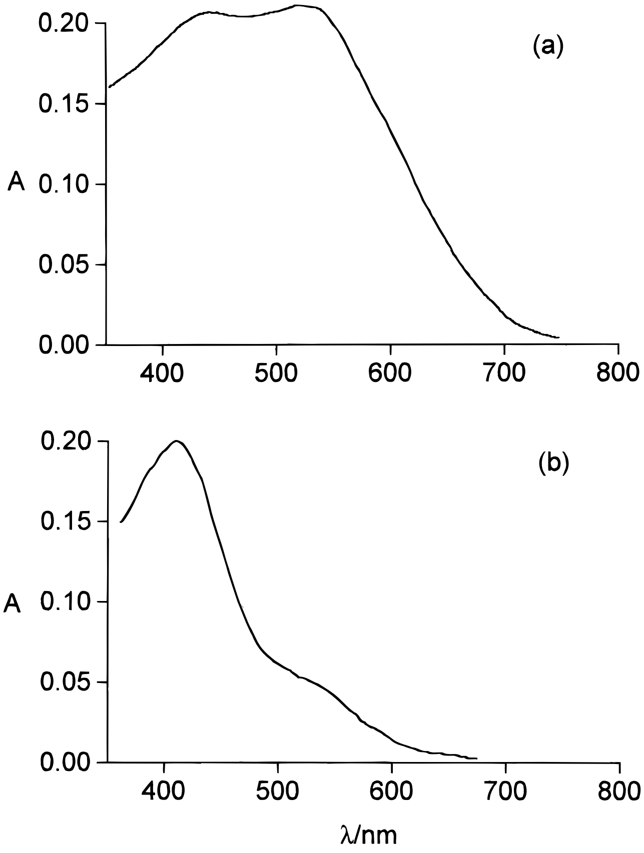

Figure 4. UV−vis spectrum of poly(CPDTSO)−PP composite in the undoped state produced according to (a) route 1 and (b) route 2.

Deposition of Polypyrrole with CPDTSO as Anion and Subsequent Coupling of CPDTSO to Polythiophene (Route 2). A different approach to produce PT−PP molecular assembly was that of polymerizing dipyrrole using CPDTSO as the counteranion and subsequently coupling the intercalated CPDTSO anion to polythiophene.

The CV of a 10^{-3} M solution of dipyrrole in AN containing 10^{-2} M CPDTSO as supporting electrolyte shows the oxidation peak of the dipyrrole at 0.1 V (as in the presence of tosylate[13]). Continuous cycling up to 0.2 V shows the deposition of the polypyrrole (the same product is obtained by potentiostatic deposition at 0.2 V). The polymer displays a conductivity of 0.2 S cm^{-1}, which is lower than that for PP tosylate (100 S cm^{-1} [16]) but is compatible with a large interchain spacing introduced by the CPDTSO anion. The presence of the sulfonate anion is already evidenced by the ratio of the reversible charge, measured in AN + 0.1 M Bu_4NClO_4 up to 0.4 V, to that used for the deposition, a ratio that corresponds to a content of 0.4 anion/pyrrole unit in the oxidized polymer as in PP tosylate,[16] and by the shape and peak potentials of the CV, which are the same as for PP tosylate. In the perchlorate electrolyte the sulfonate anion is strongly bound also to undoped polypyrrole since only a negligible amount of the CPDTSO anion (less than 10% by spectrophotometric analysis) is released in solution upon polypyrrole reduction.

The potential of the film is then cycled in AN + 0.1 M Bu_4NClO_4 solution up to 0.7 V (i.e., beyond the oxidation of CPDTSO). The CV (Figure 5) shows in the first oxidative sweep the reversible oxidation of the polypyrrole at ca. −0.3 V followed by an irreversible one

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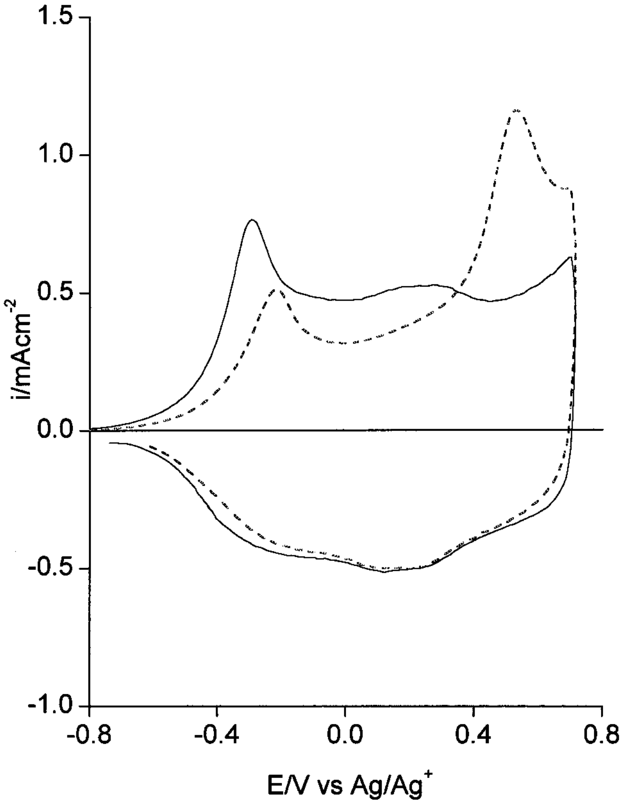

Figure 5. Cyclic voltammetry for PP–CPDTSO in AN + 0.1 M Bu_4NCl_4 up to the CPDTSO oxidation. (···) first and (—) subsequent cycles. Scan rate: 0.1 V s^{-1}; final reversible charge Q_{rt}: 5 mC cm^{-2}.

of the incorporated CPDTSO anion at 0.5 V; the following CV shows the reversible oxidation of the polypyrrole and that of the intercalated poly(CPDTSO) as a redox couple at ca. 0.2 V. The reversible charge increases by 20% at most, whereas the ratio expected from a 100% compensation of the doping positive charge of PP by the CPDTSO anion is 50% (0.25 electron/thiophene ring) so that it is clear that the efficiency of the process is not high. The UV–vis spectrum of the film confirms the low content of polythiophene in the polypyrrole (Figure 4b). These results are independent of the film thickness from 0.3 to 0.03 μm.

The low level of polymerization cannot be accounted for by expulsion of the CPDTSO anion from PP during anodic coupling of CPDTSO itself, as indicated by spectrophotometric analysis of the solutions after coupling. Therefore we attribute the result to an incomplete coupling of the CPDTSO units in the polymer. This may be explained by the long distance between the dithiophene anions and by their low mobility due to pinning of their negative charge to the polypyrrole polycationic chain. Under these conditions reaction routes alternative to coupling are open to the produced radical cations, mainly nucleophilic attack by water. On the contrary the successful template polymerization of dipyrrole on the sulfonate polythiophene film (route 1) is due to the fact that monomers are rapidly fed from the solution to polymerize with the radical cations engaged by the sulfonate groups in the solid matrix.

Impedance of Poly(CPDTSO)–PP Composite Films. Electrochemical impedance spectroscopy has become a popular method for the characterization of electroactive polymer films. In recent years, a large amount of theoretical[19–26] and experimental work (see, e.g., refs 27–33) has been performed with the aim of determining the transport properties of the most interesting materials.

We have measured the impedance of poly(CPDTSO), PP, and poly(CPDTSO)–PP composite films in AN + 0.1 M Bu_4NClO_4 between −0.8 and 0.4 V, i.e., in a potential domain where switching from an insulating to a conducting behavior occurs. The poly(CPDTSO)–PP composite was prepared following the procedure previously described as route 1 onto the same poly(CPDTSO) film submitted to impedance experiments. Reversible charges for poly(CPDTSO) (Q_{r0}) were ≤2 mC cm^{-2} in order to operate with equimolar PT–PP composite films. Homopolymeric PP tosylate films were prepared as reported in the literature.[13]

Figure 6 shows the impedance plots obtained at −0.8 (a) and 0.0 V (b). Besides the diagrams of the three polymers, Figure 6a shows the response of a bare platinum electrode. The insert in Figure 6b shows an idealized impedance diagram for an electrode/conducting polymer/electrolyte system in which the charge-transfer resistance of both charge carriers at the relevant interfaces (i.e., electrons and ions at the electrode/polymer and polymer/electrolyte interface, respectively) is negligible. Such a diagram, which is predicted by both kinetic models[19–22,25,26] and transmission line equivalent circuits,[23,28–32] consists of two straight lines forming 45° and 90° angles with the real axis. Both approaches ascribe similar meaning to the limiting values of the real part of the impedance: the high- and low-frequency limits, hereafter called R_{hf} and R_{lf}, respectively (while R_s represents the uncompensated resistance of solution), may be related to the rate of transport of electrons and counterions. In terms of electronic and ionic resistance (R_E and R_I), one may write $R_{hf}^{-1} = R_E^{-1} + R_I^{-1}$ and $R_{lf} = (R_E + R_I)/3$.

At the negative potential limit (Figure 6a) the response of poly(CPDTSO) almost coincides with that of bare platinum: the polymer, in the undoped state, is electrochemically inert. As there is no increase of the real component, it may be concluded that its ionic resistance is negligibly small, a not surprising result considering the film thickness (ca. 0.1 μm) and the large concentration of ionic (sulfonate) groups in the polymer.

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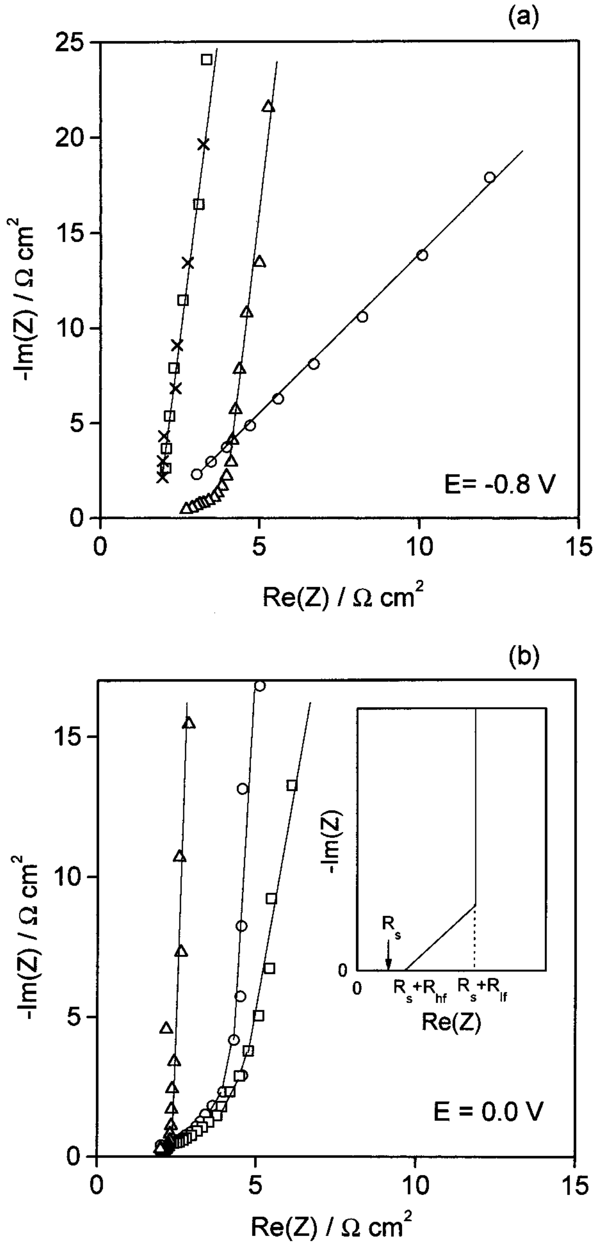

Figure 6. Nyquist plots for the ac impedance of a 0.003 cm^2 Pt electrode either bare (×) or coated with poly(CPDTSO) (□), PP (△), or poly(CPDTSO)−PP composite (○) in AN + 0.1 M Bu_4NClO_4 at $E = -0.8$ (a, top) and 0.0 V (b, bottom). Reversible charge: (□) 1.7; (△) 3.3; (○) 3.7 mC cm^{-2}. Insert: idealized impedance diagram for an electrode/conducting polymer/electrolyte system (R_s is the uncompensated resistance of solution).

Also the effect of the poly(CPDTSO) film on the electrode capacitance is small: the capacitance at 1 kHz is 8 and 6.5 μF cm^{-2} for bare and poly(CPDTSO)-coated platinum, respectively. At the same potential, PP is partially doped, as testified by the presence of a 45° region at high frequency and a fairly large capacitance (see below). The poly(CPDTSO)−PP composite behaves in an intermediate way; its impedance at each frequency is lower than that of poly(CPDTSO) but larger than PP. For PP and poly(CPDTSO)−PP composite too, there is no shift of the high-frequency limit.

At $E = 0.0$ V (Figure 6b), where all polymers are in the doped state, all diagrams conform to the theoretically predicted shape, though the extension of the 45° region is much smaller for PP than for poly(CPDTSO) and poly(CPDTSO)−PP composite, which are comparable. The high-frequency limit always corresponds to R_s, so that one must conclude that for each polymer either R_E or R_I is negligibly small. If so, R_{lf} directly provides the value of the other, nonzero resistance. The point is, therefore, that of identifying which is which. The electronic resistivities of PP and poly(CPDTSO) are known, since they can be estimated from independent measurements in a metal/polymer/metal geometry (10^{-2} and 2 Ω cm for PP[16] and poly(CPDTSO),[12] respectively). Therefore, the R_E of 0.1 μm thick films must be $<10^{-5}$ Ω cm^2 and the values of resistivity calculated from R_{lf} (8×10^4 and 6×10^5 Ω cm for PP and poly(CPDTSO), respectively) must be ascribed to R_I. The fact that in the case of poly(CPDTSO) the ionic resistance is much lower in the undoped than in the oxidized state is not too surprising if one considers that in the undoped state this polymer may be viewed as a cation exchanger and that the cation-exchanging ability is progressively lost when the sulfonate groups become paired with positively charged thiophene groups formed upon oxidation.

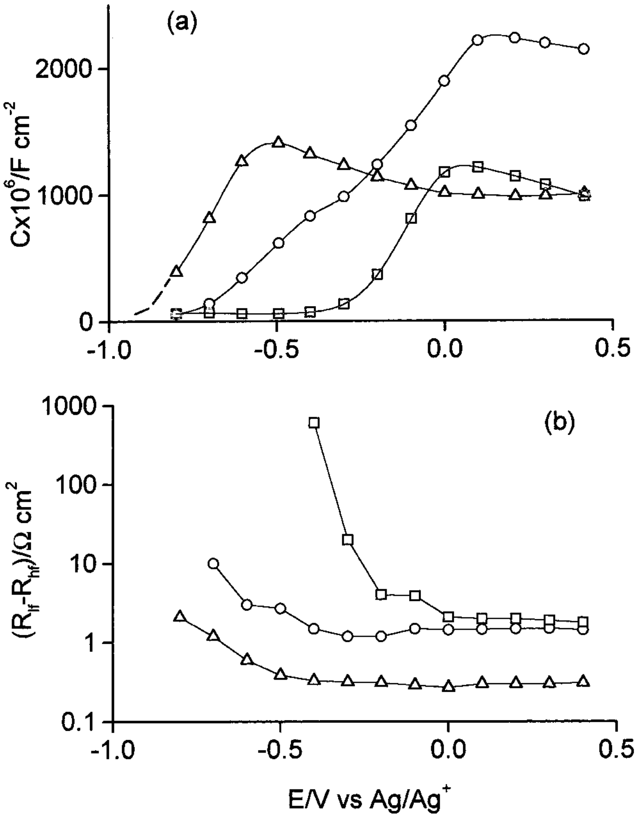

Figure 7. Potential dependance of (a) the capacitance and (b) the real part of the charge transport impedance of poly(CPDTSO) (□), PP (△), or poly(CPDTSO)−PP composite (○) films in AN + 0.1 M Bu_4NClO_4. Reversible charge: (□) 1.7; (△) 3.3; (○) 3.7 mC cm^{-2}.

Figure 7a shows the potential dependence of the capacitance of the different films. The sharp increase in capacitance corresponding to doping occurs at potential progressively more positive for PP, poly(CPDTSO)−PP composite, and poly(CPDTSO), in agreement with the cyclic voltammograms in Figure 2. In the potential domain where both PP and poly(CPDTSO) are doped, the poly(CPDTSO)−PP composite capacitance in close to the sum of the capacitances of the components.

Moreover in the same potential domain the capacitance of poly(CPDTSO) doubles after transformation into the poly(CPDTSO)–PP composite, which constitutes an additional indication that polypyrrole and polythiophene chains are present in a 1:1 ratio in the composite.

The dependence on potential of the difference $\Delta R = (R_{\mathrm{lf}} - R_{\mathrm{hf}})$ is shown in Figure 7b. Taking into account the above-mentioned relationships among R_{hf}, R_{lf}, R_{E}, and R_{I}, ΔR cannot be simply identified with either R_{E} and R_{I}. If, upon increasing E, R_{E} decreases and R_{I} increases in such a way that their relative size is inverted, ΔR is essentially determined by R_{E} at low E and R_{I} at high E. This is in our opinion the case of poly(CPDTSO). In the case of PP, ΔR represents in the whole potential range, in which the polymer is oxidized, an ionic resistance. The poly(CPDTSO)–PP composite behaves similarly with PP in the whole potential range. At the positive potential limit, where both the component polymers are doped, it has an ionic resistance very close to that of poly(CPDTSO) and 5–10 times higher than for PP. At less positive potentials, where the poly(CPDTSO) component is undoped and electronically resistive, the composite keeps its ΔR value almost unchanged, which suggests that the ionic resistance is still dominating or in other words, that the electronic conductivity is still high. Only at the lower potential limit, where the PP component starts to be dedoped ΔR starts to increase, as in PP.

The above impedance data allows us to draw some conclusions on the structure of the poly(CPDTSO)–PP composite. They contribute to rule out the possibility that PP is deposited as a top layer on poly(CPDTSO). In such a case, which is that of the thick composite films tested by CV (see above), an inner insulating poly(CPDTSO) film would hinder PP from feeling the electrode potential until the poly(CPDTSO) film is not switched to the conductive state. Also the hypothesis that poly(CPDTSO) and PP exist as a leopard-skin assembly of patches of each material disagrees with the data: in such a case, the impedance of the poly(CPDTSO)–PP composite would be roughly given by a parallel combination of the individual impedances, i.e., capacitances would add (but they do only in a limited potential range) and the composite resistance would approach that of the most conductive component (while it approaches that of the less conductive one). In our opinion these data support the idea of interwoven polymer networks: the poly(CPDTSO) matrix, while allowing pyrrole polymerization, seems to limit the PP ionic conductivity and affect its ability to become doped.

Conclusions

The use of a sulfonated bithiophene has allowed the production of polypyrrole–polythiophene composite with interwoven polymer chains. Cyclic voltammetry, UV–vis, and impedance spectroscopy have shown that the copolymer is in fact a compound of the two polymers with a pyrrole:thiophene ratio close to 1. The molecular composite has been obtained by the template polymerization of dipyrrole on the sulfonate polythiophene film. This has proven to be the most favorable deposition method for the composite as dipyrrole coming from the solution is assisted in the polymerization by the sulfonate groups in the solid matrix. On the contrary, oxidation of sulfonated bithiophene molecules present as counteranions in polypyrrole polycation opens up pathways alternative to coupling so that only partial polymerization is produced. This result does not rule out the possibility of an efficient polymerization of monomers inserted in a polymeric matrix but suggests that disorder in the matrix hinders this process. The fact that ordered structure, such as self-assembled layers of pyrroles[34–36] and thiophenes[37] are amenable to be efficiently polymerized, indicates that an ordered sequence of monomers, i.e., an ordered polymeric structure, is a necessary prerequisite for polymerization within a polymer matrix.

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