Optical and electrical characterization of a conducting polypyrrole composite prepared by *in situ* electropolymerization

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A study of the optical and electrical properties of a conducting polypyrrole–polyoxyphenylene composite, PPy–POP, prepared by *in situ* electropolymerization is presented. Electropolymerization was performed potentiostatically in a solution of pH 9 which contained the monomers pyrrole, allylphenol and sodium 4-hydroxybenzenesulfonate (4HBS), by applying a potential of 1.25 V *vs.* SCE. The films obtained were characterized optically by UV/VIS and IR spectroscopy and electrically by measurements of the temperature dependence of the ac and dc conductivity. FTIR measurements indicated that the polymer blend obtained consists of PPy and the insulating polymer poly-2-allyloxyphenylene (POP), whereas the third monomer, 4HBS, is incorporated into the PPy–POP film as dopant for the conducting PPy. Furthermore, optical characterizations show a light degree of overoxidation of PPy in the PPy–POP composite. In the UV/VIS spectra, the formation of both polaron and bipolaron electronic states of the band structure of PPy can be seen, but the IR spectra demonstrate the transition of the PPy structure from a conducting quinoid to benzoid type with increasing polymerization potential. This is accompanied by the introduction of a carbonyl group into the PPy backbone and a reduction of the conjugation length of the polymer chain, which has a strong influence on the conductivity of the polymer composite. Despite this overoxidation process, the PPy–POP film retains a conductive character which allows the growth of thick films. The temperature dependence of the ac and dc conductivity of PPy–POP was investigated. The total ac conductivity, $\sigma_{tot}(\omega)$, in the frequency range 10^2–10^5 Hz, changes by approximately four orders of magnitude in the range from 77 to 300 K, showing a sub-linear dispersive behavior. The temperature dependence of the dc conductivity of such a polymer composite can be described by Mott's variable range hopping (VRH) model according to $\sigma = \sigma_0 \exp[-(T_0/T)^\gamma]$, with $\gamma = \frac{1}{2}$, which corresponds to a pseudo-one-dimensional conduction process.

1 Introduction

The combination of conventional polymers with conducting polymers allows us to create new polymeric materials with unique electrical properties. In such composites, the insulating polymer provides good mechanical properties and processability and the conducting polymer is responsible for the electrical conductivity. Polypyrrole (PPy) is representative of conducting polymers, with high electrical conductivity, good environmental stability and easy synthesis. The charge carriers of the p-doped semiconductor PPy are generally considered to be radical cations (polarons) or dications (bipolarons) stabilized by counter-ions incorporated into the film during formation.[1]

PPy can be readily electropolymerized in both an aqueous solution of neutral pH and a non-aqueous solution by applying a potential in the range 0.6–0.8 V *vs.* SCE.[2] More positive potentials and a pH greater than 11 leads to overoxidation of the polymer backbone by introducing carbonyl or hydroxy groups, which gives rise to a decrease in the conjugation length and hence to a loss of the conductivity of the polymer.[3] On the other hand, the conductivity and the physical properties of PPy depend on the choice of the counter-ion, often called dopant. Aromatic sulfonic derivatives are known to permit the synthesis of conducting PPy over a broad pH range and at applied voltages moderately higher than 0.8 V *vs.* SCE.[4,5]

For the preparation of PPy blends, several methods have been developed, *e.g.*, the copolymerization method of grafting pyrrole on to a polymer backbone, and the composite method of inclusion of electrochemically or chemically polymerized pyrrole in the matrix of a host polymer. Polymer composites prepared by electrochemical polymerization exhibit high conductivity but require uniform films of the host polymers, which are difficult to prepare on a large scale. Chemically prepared composites are less conductive than the former type, but the reaction time of the preparation is shorter and large-scale production of uniform blends is possible.

Recently, we have demonstrated a new approach to the synthesis of a PPy composite, based on the *in situ* electropolymerization of both the conducting polymer, polypyrrole, and the non-conducting polymer matrix, polyoxyphenylene.[6] The process allows the controlled deposition of conducting polymer composite layers based on pyrrole and phenolic compounds. Owing to the great difference in the polymerization features of the two monomers, a trade-off has to be made in the oxidation potential (1.25 V *vs.* SCE) and the pH of the monomer solution (9) in order to electropolymerize the polypyrrole blend in one process step. Despite the presence of sodium 4-hydroxybenzenesulfonate in the electrolyte, it is assumed that the relatively high oxidation potential and the alkaline medium give rise to a certain degree of overoxidation of PPy in the polymer blend.

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For the evaluation of this effect, vibrational and UV/VIS spectroscopy were used and the results of the optical study of the PPy–POP blend are presented in this paper. Both methods are potentially useful screening techniques because the changes in electron density and distribution that occur in the polymer as it is oxidized and reduced are reflected in changes either in the concentration of the charge carriers or in the bond order and dipole, which in turn give rise to changes in UV/VIS absorption maxima and IR absorption frequencies and intensities. An explanation of the PPy absorption spectra in the UV and visible range is possible within the framework of the polaron/bipolaron structure model[1] used for conjugated conducting polymers that possess a non-degenerate ground state. The degree of oxidation of a thin organic conducting polymer is reflected in the concentration of polaron and bipolaron states which can be identified in optical absorption measurement as electronic transitions.[7–13]

The main question in the context of the electrical properties of the PPy–POP blend, presented in this paper, is how disorder influences the electrical conductivity, and hence the charge transport in the organic semiconductor polypyrrole, due to the introduction of the electrical insulator polyoxyphenylene as matrix.

The electrical conductivity is an inherent property of conjugated polymers and is an important parameter reflecting the structural order of the conjugated polymer. The temperature dependence of the dc conductivity provides first-hand information about the possible charge transfer processes involved in conduction in disordered materials. For the evaluation of the ac and dc conductivity of the PPy–POP polymer blend, Mott's variable-range-hopping (VRH) model was considered, as this is one of the most successful theoretical models to predict the probable transport mechanism operating in disordered materials.[14–16] The theory allows one to distinguish between different dimensionalities, n ($n = 1$, 2 and 3), of the charge transport process by the description of the temperature dependence of the conductivity. The result of the evaluation of the ac and dc conductivity in the framework of the VRH model is presented in this paper. The fitting of the experimental data indicates a quasi-one-dimensional transport mechanism, which allows the determination of the charge carrier density of the polymer blend.

2 Experimental

2.1 Chemicals

Pyrrole (Py), sodium p-toluenesulfonate (TOS) and tetramethylammonium hydroxide (Me_4NOH) from Aldrich and 2-allylphenol (2AP), sodium 4-hydroxybenzenesulfonate (4HBS) and ethylene glycol monobutyl ether (Cellosolve) from Merck were of reagent grade and were used without further purification, except for pyrrole, which was distilled under an N_2 atmosphere and stored in a sealed vessel at 5 °C until required for use. De-ionized water (2 MΩ^{-1} cm^{-1}) (Merck) was used to dissolve the salts and the other components.

2.2 Electrodes and substrates

The working electrodes consisted of sputtered gold films with a thickness between 200 and 1500 Å on different substrates. As glue metal, chromium of thickness between 15 and 500 Å was used. The reference electrode was a saturated calomel electrode (SCE) with a 1 M KCl junction, to which all potentials are referred. As counter electrode we used a platinum foil.

Glass microscope slides, 1.6 and 3.6 cm^2 in area, were used for UV/VIS and IR measurements. The electrical measurements were carried out by using interdigital structures (IDS) realized by photolithographic techniques, which consist of 90 finger pairs each of 10 μm width and with a 5 μm distance

between the electrodes, with a length overlap of about 0.26 cm. The IDS were mounted on a TO-8 header.

2.3 Electrochemical polymerization

Electropolymerization of the polymer composite was performed in a three electrode cell by using a freshly prepared solution containing 0.23 M 4HBS, 0.0023 M 2AP, 0.05 M pyrrole, 0.1 M Me_4NOH and 0.4 M Cellosolve. The solution, with a final pH of 9 as measured with a Metrohm 654 pH meter, was purged with argon for 10 min before use in order to remove traces of oxygen.

The electropolymerization of the PPy–POP films doped with 4HBS was performed potentiostatically at room temperature by using a Princeton Applied Research (PAR) Model 273 potentiostat/galvanostat. A linear ramp from 0.0 to 1.25 V was applied and then held constant during the polymerization time. The synthesized films were kept in the background electrolyte to equilibrate for about 30 min, until the open cell potential reached a stable value (± 1 mV), then the films were rinsed with de-ionized water and dried in a stream of N_2.

Polypyrrole layers doped with either 4HBS or TOS were deposited from an aqueous solution containing 0.05 M pyrrole and either 0.23 M 4HBS or 0.1 M TOS as background electrolyte by applying a constant potential of 1.25 and 0.8 V $vs.$ SCE, respectively, supplied by the PAR Model 273 potentiostat. After preparation, the films were thoroughly washed with de-ionized water and dried in ambient air at room temperature for several hours.

2.4 Visible spectra

Visible spectra of the electrochemical synthesized PPy layers and PPy–POP copolymer films were recorded with a Varian Cary 1 double-beam spectrophotometer in the range 300–900 nm with the resolution set to 1 nm.

2.5 FTIR spectra

FTIR measurements of the polymer films were carried out with a Brucker IFS66 spectrometer, which was continuously purged with dry air without carbon dioxide by using a Zander KEN-15 adsorption dryer system. Spectra were obtained with either a MCT (mercury cadmium telluride) or a DTGS (deuterated tryglycine sulfate) detector, depending on the signal intensity, at 2 cm^{-1} resolution and 200 scans over the range 4000–400 cm^{-1}, in a reflection configuration with a nearly tangential angle of incidence of 83°.

2.6 Conductivity measurements

The low temperature ac conductivity measurements were performed in an Oxford OPTISTAT liquid nitrogen cryostat in the range 77–300 K, under a reduced pressure of 10^{-5} Torr, using N_2 as a gas exchanger. A fully automated Hewlett-Packard HP 4194A Impedance/Gain Phase Analyzer was used to carry out the ac measurements.

The measured total system stray capacitance was <0.8 pF and the in-series resistance, R_s, was about 10 mΩ at room temperature, which could be further reduced by an open–short compensation technique during the measurement.

The measurements were performed by using the four-terminal pair configuration equipped with four 1 m long coaxial shielded cables as outside conductors connected together at their ends[17] and with four stainless-steel coaxial cables, 0.5 m long and 2.18 mm in diameter, as connectors inside the cryostat. The TO-8 holder with the sample was mounted in a large-area thermal contact pressed between two copper blocks.

An open–short zero compensation technique was employed to reduce the effects of the text fixture residual during measurements. The compensation circuit is shown in Fig. 1. With
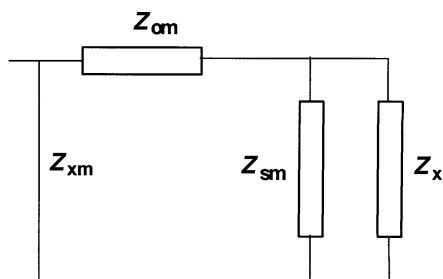
Fig. 1 Compensation circuit of the conductivity measurement system.

this circuit, the impedances on the sample can be calculated from the following equation:

$$Z_x = Z_{om} \frac{Z_{sm} - Z_{xm}}{Z_{xm} - Z_{om}} \qquad (1)$$

where Z_{xm} is the measured value for the unknown sample, Z_{om} the open, stray impedance and Z_{sm} the short impedance. For the blank measurement, a pure IDK was measured in the same way as when the coated sample was in place. The estimated measurement error of the system was less than 1% if the measurement frequency did not exceed 1 MHz. The resistance of the sample was determined from the impedance–phase data, Z and θ, according to the following relationship:

$$R = |Z| \cos \theta \qquad (2)$$

3 Results and discussion

3.1 *In situ* electrochemical polymerization of PPy–POP

According to the literature, the threshold oxidation potential for pyrrole is approximately 0.6 V depending on the deposition conditions (nature of the supporting electrode, solvent, pH, *etc.*), whereas in alkaline media, for each of the selected phenolic monomers (2AP and 4HBS), the onset of the oxidation peak occurs at 0.2 and 0.5 V, respectively.[18]

Fig. 2 shows three successive current potential curves of the voltammogram obtained for a mixture of 2AP, 4HBS and Py by scanning between 0.0 and 1.8 V at a constant sweep rate of 50 mV s^{-1}. After the first cycle, the electrode surface has been mostly coated with a black polymer layer. The polymerization process of this three-component system corresponds to an irreversible oxidation process, which consists of two anodic peaks starting at 0.25 and 0.75 V, peaking around 0.37 and 1.08 V, respectively, whereas no cathodic current can be seen. Each of the peaks present in the voltammogram corresponds to a monomer oxidation. According to ref. 18, the first peak, at 0.37 V, can be attributed to the electropolymerization of 2AP and the second peak, at 1.08 V, the intensity of which is more than five times larger than that of the first peak, is assumed to be due to the deposition of polypyrrole (PPy), which is also responsible for the observed formation of a black film on the working electrode.

The corresponding oxidation peak for 4HBS, which should start at 0.5 V and peak between 1.0 and 1.3 V could not be observed.[18] This is supported by recent electrochemical and optical investigations of the system 2AP–4HBS under the chosen experimental conditions.[6] No film formation of poly-4HBS on the working electrode could be observed, which can be explained by the high solubility of polysulfonic acids in aqueous solutions. For these depositions, in which 2AP monomer was present in addition to 4HBS, the voltammograms show an anodic peak between 0.3 and 0.4 V in the first cycle. This peak was attributed to the polymerization of 2AP according to ref. 18. Furthermore, it has been shown[6] that the reflectance patterns of the polymer film obtained in the presence of 2-AP and 4HBS are almost identical and can
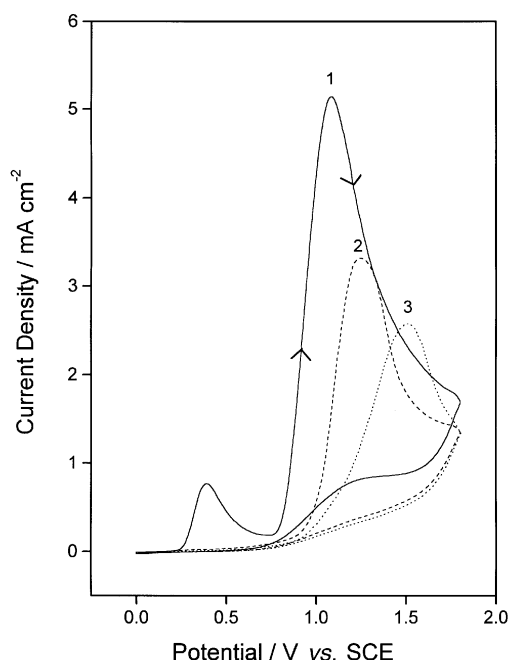

Fig. 2 Cyclic voltammogram (first three cycles) obtained for the potentiodynamic electropolymerization of the PPy–POP composite in the presence of Py, 2AP and 4HBS, synthesized on a gold electrode. $A = 0.5$ cm^2; scan rate, 50 mV s^{-1}; arrows indicate the sweep direction.

be attributed to polyoxyphenylene film, poly-2AP. No absorption bands of 4HBS are visible in the IR spectrum.

It is evident from Fig. 2 that after the first cycle the observed anodic peak potential of the PPy deposition shifts to a more positive potential and the peak current decreases. These effects can be due to both the codeposition of the non-conductive layer of poly-2AP and the PPy overoxidation. A similar behavior was observed by Kaplin and Qutubudin for pure overoxidized polpyrrole films.[19] The resultant polymer, PPy-POP, is subsequently less conductive and the oxidation of new monomer requires a higher potential owing to the increasing potential barrier. As shown previously,[6] polymerization at lower potentials than the PPy peak potential ($E_{pa} \approx 1.15$ V *vs.* SCE) in order to avoid overoxidation of PPy could not be performed because inhomogeneous and porous films with thicknesses of only a few tens of nanometers were obtained.

3.2 FTIR measurement of PPy–POP

The IR spectrum of PPy–POP is shown in Fig. 3 (A) and (B). The former shows the complete spectrum and the latter corresponds to the enlarged fingerprint region, *i.e.*, below 2000 cm^{-1}. It is compared with a vibrational spectrum of a slightly overoxidized PPy–4HBS film, grown at a constant oxidation potential of 1.25 V *vs.* SCE for the respective range of wavelengths. In general, the FTIR spectrum of PPy shows a rich-band fingerprint region, exhibiting seven strong intensity bands. Both the intensity and position of these IR bands are mainly related to the structure of the polypyrrole film.[20–25]

Tian and Zerbi[21,23] proposed the theory of effective conjugation coordinate to explain the correlation between structure and conductivity. Their calculations were based on the concept of a benzenoid structure for reduced (insulating) PPy [Fig. 4(A)] and a quinonoid structure for the conducting (oxidized) form [Fig. 4(B) and (C)]. Seven main IR absorption bands in spectra published by Street *et al.*[24] and Furukawa *et al.*[25] were found to agree well with their concept. These absorption bands were denoted bands A′–G′ for the oxidized state of the polymer. For an as-synthesized (doped) PPy–
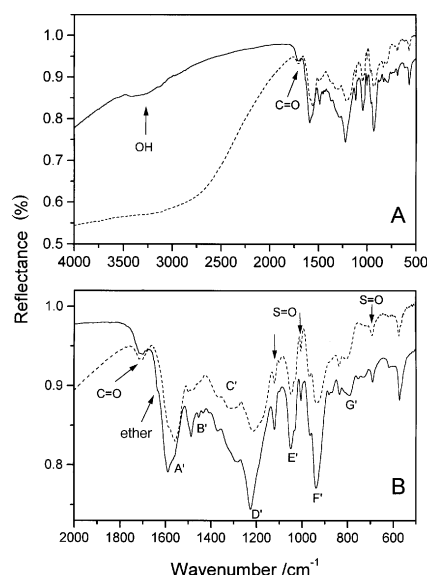
Fig. 3 Infrared spectra of (solid lines) a PPy–POP film and (dashed lines) an overoxidized (grown at 1.25 V) PPy film doped with 4HBS: (A) complete spectrum; (B) fingerprint region. The main band designations are given according to ref. 23.

Fig. 4 Benzenoid insulating (A) and quinonoid polaronic (B) and bipolaronic (C) structures of polypyrrole.

4HBS film (not shown), the characteristic high intensity bands are located around 910, 1040, 1180 and 1550 cm^{-1}, which have been assigned to C–H in-plane bend, C–H out-of-plane bend, ring breathing and C=C/C–C stretch, respectively. They are denoted as F′, E′, D′, A′ bands, according to Tian and Zerbi.[21,23]

The spectrum of PPy–POP resembles the main characteristics of the fundamental bands mentioned above and additional features which are produced mainly by the presence of poly-2AP and 4HBS. The relevant spectral assignments and the vibrational energies associated with the IR spectra in Fig. 3 and those of 4HBS are summarized in Table 1. Considering the vibrational bands of 4HBS and the IR spectrum of 4HBS-doped polypyrrole film grown at a constant potential of 1.25 V, six contributions of 4HBS can be assigned.[26–30] Three of them, located at 1006, 1122 and 693 cm^{-1}, are associated with the symmetric and asymmetric S=O stretch and the C–S stretch vibrations of the sulfonic group, respectively. The bands at 1500, 1031 and 837 cm^{-1} are related to the out-of-
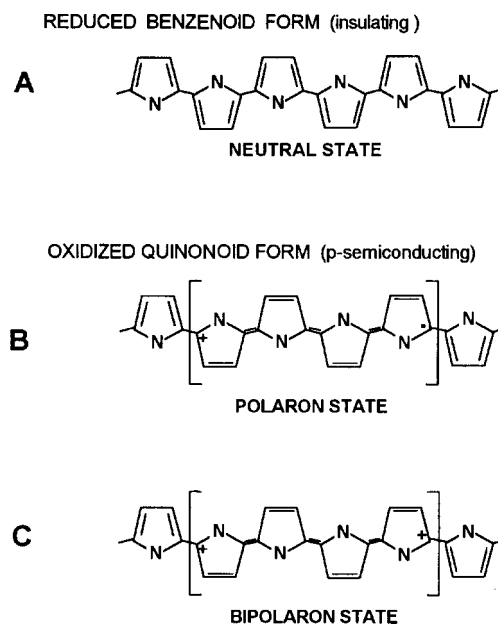
plane C=C bend and the in-plane and out-of-plane C–H bend of the *para*-substituted benzene ring. Other contributions of 4HBS are difficult to assign because they are masked by the polymer vibrations. The six bands mentioned above are also seen in the spectra of PPy–POP (Fig. 3). Owing to the presence of these vibrational bands of 4HBS in the spectra of the PPy–POP composite and the absence of the oxidation peak for 4HBS during the electrochemical preparation of the polymer film (Fig. 2), we assume that in addition to OH$^-$, the component 4HBS, present as an anion in the monomer solution also, is incorporated in the PPy–POP film as a dopant for polypyrrole. This is supported by the fact that, despite the polymerization in alkaline media and at potentials higher than 0.8 V, the composite film obtained exhibits electroactive and semiconducting behavior, as will be shown by the UV/VIS and conductivity measurements (see below). This unusual behavior has been reported for polypyrrole films electrooxidized in the presence of aromatic sulfonic derivatives, such as 4HBS, over a broad range of pH (4–11). Bad quality

Table 1 Spectral assigments and vibrational energies associated with the IR spectra of 4HBS (spectrum not shown), a PPy–POP composite film and an overoxidized PPy film (grown at 1.25 V) doped with 4HBS, both taken from Fig. 3^a

Assignment			Monomer/polymer		
Vibrational mode	Group	PPy/matrix	4HBS	PPy–POP 1.8 V	PPy–4HBS 1.25 V
ν(C=O)	Carbonyl[22]	Overoxidized	–	1700 (w)	1700 (w)
ν(C=C)	Allyl[26]	POP	–	1635 (w)	–
ν(C=C)	Benzene[29]		1592 (m)	1591 (s)	1587 (w)
	Pyrrole[20] (quinonoid structure)	A′ band	–	–	1559 (s)
γ(C=C)	Benzene[27,30]	Dopant	1504 (m)	1498 (m)	1500 (w)
ν(C=C)/ν(CN)	Pyrrole/benzene[23]	D′ band	–	1227 (s)	1214 (s)
ν(Ar–O–Ar)	Ether[26]	POP	–	1193 (w)	–
ν_a(S=O)	Sulfonic acid salt[28]	Dopant	1119 (m)	1122 (m)	1122 (m)
γ(CH)	Pyrrole[20,23]	E′ band	–	1045 (s)	1048 (s)
δ(CH)	*p*-Substituted benzene[26]	Dopant	1033 (s)	1028 (w)	1031 (w)
ν_s(S=O)	Sulfonic acid salt[28]	Dopant	1006 (m)	1006 (m)	1006 (m)
δ(CH)	Pyrrole[23]	F′ band	–	939 (s)	937 (s)
γ(CH)	*p*-Substituted benzene[26]	Dopant	841 (s)	837 (m)	838 (m)
ν(C–S)	Sulfonic acid salt[28]	Dopant	698 (s)	693 (w)	693 (m)

^{a} Vibrational assignments are taken from the literature.[20,22,23,26–30] Intensity descriptions: s, strong; m, medium; w, weak; sh, shoulder. Vibration descriptions: ν, stretching; γ, out-of-plane bending; δ, in-plane-bending. For abbreviations, see text.

films or even insulating films are obtained when aqueous alkaline solutions containing only hydroxide salts as electrolytes are used for electrochemical polymerization.[12,31]

As already mentioned, the five well defined modes denoted G′, F′, E′, D′ and A′ bands are also present in the IR spectrum of both the PPy–POP film and the overoxidized polypyrrole film. For the latter, three of them, bands F′, D′ and A′, showed a shift to higher energies of 938, 1214 and 1559 cm^{-1}, respectively, compared with the corresponding positions of these bands in the spectrum of fully doped PPy–4HBS and those already reported in the literature.[32] A further blue shift of the F′, D′ and A′ bands to energies of 939, 1227 and 1591 cm^{-1} with respect the overoxidized polypyrrole film can be observed for the PPy–POP film. The observed blue shift with increasing deposition potential of the polypyrrole film corresponds mainly to a structure change from the benzenoid to the quinonoid structure (see Fig. 4), which is directly related to the oxidation process according to Tian and Zerbi.[21,23] Davidson and Turner[20] interpreted this change of structure on the principle that an increase in the sp^2 character results in shortening of all bonds. According to this, the absorption bands associated with stretching vibrations can be expected to shift to higher energy. The strong band E′ around 1045 cm^{-1} does not show significant changes either in the position or in intensity.[21]

The bands at 1635 and 1192 cm^{-1}, which do not appear in the spectrum of PPy–4HBS but do in the spectrum of poly-2AP,[6] do not suffer any apparent shift and has been attributed to a pure POP vibration. They are associated with the C=C stretch of the benzene ring and C–O–C stretch vibrations of the ether group, respectively.

Finally, the weak, broad band around 1700 cm^{-1} in the spectrum of PPy–POP and overoxidized PPy–4HBS indicates clearly the presence of a carbonyl group, C=O, in the polymer chain. Kaplin and Qutubudin[19] have demonstrated that the electropolymerization potential affects the chemical structure of polypyrrole films synthesized in aqueous solution at neutral pH. Only for films prepared between 1.0 and 1.5 V was a C=O absorption band observed around 1700 cm^{-1}. When the polymerization potential fell below 1.0 V the absorption band was not visible. This has been recently confirmed for polypyrrole films doped with aromatic sulfonic derivatives prepared from aqueous solution by applying an anodic potential in the range 0.8–1.3 V.[6] Beck et al.[22] ascribed the presence of this band to an overoxidation process of the polymer film. The most acceptable suggestion about the origin of this band is the attack of the nucleophilic hydroxide ion to the radical cation of the PPy unit during electropolymerization in alkaline solution.[33] The formation of this carbonyl group leads to a shortening of the conjugation which is also responsible for the possible inactivation of polypyrrole.

Looking at the high energy region of the spectra in Fig. 3(A) (above 2000 cm^{-1}), a monotonic decrease in transmission can be seen, which is characteristic of systems containing free charge carriers, i.e., conducting polymers, and corresponds to a tail of the electronic transition from the valence band to electronic states in the band-gap region,[32] discussed later. The spectrum of PPy–POP also shows a broad band with a minimum at approximately 3400 cm^{-1}, which could correspond to the overlap of the N–H stretching of the pyrrole ring, usually located at 3300 cm^{-1}, and the OH band arising mainly from poly-2AP.

3.3 UV/VIS measurement of PPy–POP

The absorption spectra of PPy–POP and fully doped PPy–TOS, "as grown" and electrochemically reduced at −0.8 V vs. SCE, are shown in Fig. 5. Electrochemically synthesized PPy–POP films show the main absorption features of fully electroactive PPy, but the ratio of the absorbance maxima of
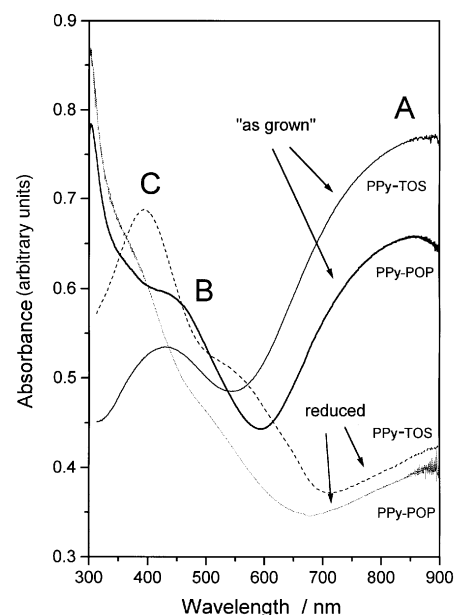

Fig. 5 UV/VIS absorbance spectra of a PPy–POP composite and a fully doped PPy–TOS film: solid lines, "as-grown"; and dashed lines, reduced at −0.8 V vs. SCE.

band A to band B is decreased from ≈1.6 for the fully doped PPy–TOS to ≈1.1 for the PPy–POP composite layer. The two broad absorption maxima, indicated as bands A and B in Fig. 5, are attributed to the transitions of the polaron and the bipolaron/polaron state in the energy band diagram of PPy.[7,9,10] Spectroelectrochemical studies of polypyrrole films have demonstrated that the ratio of the absorbance maxima of band A to band B decreases as both more negative potentials and potentials >1.0 V are applied to the film.[13] The ratio mirrors the doping level of the polymer,[11] which is dependent upon the oxidation degree and the conjugation length of the polymer chain.[12] Hence, the trend of the absorption ratio shown in Fig. 5 suggests that PPy–POP is slightly doped, probably owing to overoxidation which causes a reduction in the conjugation length giving rise to possible changes in the band structure of the polymer. Nevertheless, the polymer composite is electrochemically active and can be reduced to a low doping level, where the contribution of the fully reduced polypyrrole can be seen as a shoulder (band C in Fig. 5) at the high energy side, located around 380 nm. The absorption band C is assigned to the $\pi \to \pi^*$ interband transition, i.e., from valence band to conduction band of the neutral state. It is not well defined as a band, owing to the overlap of the absorption band originated by the benzene components of POP present in the film which have a strong absorption below 320 nm.

The absorption band A, which represents the intraband transition of the polaron state, could spread out beyond 1000 nm, comprising the transition of valence band to the bonding level of the bipolaron state,[8] and it has been also assigned to free carrier effects by Kim et al.[9] However this absorption band is the same bipolaronic band extended to the near-IR region, which has been already confirmed by the IR measurements.

3.4 Temperature dependence of ac and dc conductivity of PPy–POP

The electrical conductivity of PPy–POP films was measured in the temperature range 77–300 K. The electrical conductivity of this doped composite decreases with decreasing temperature, showing semiconductor-like behavior. Fig. 6 shows the frequency dependence of the total ac conductivity, σ_{tot}, of
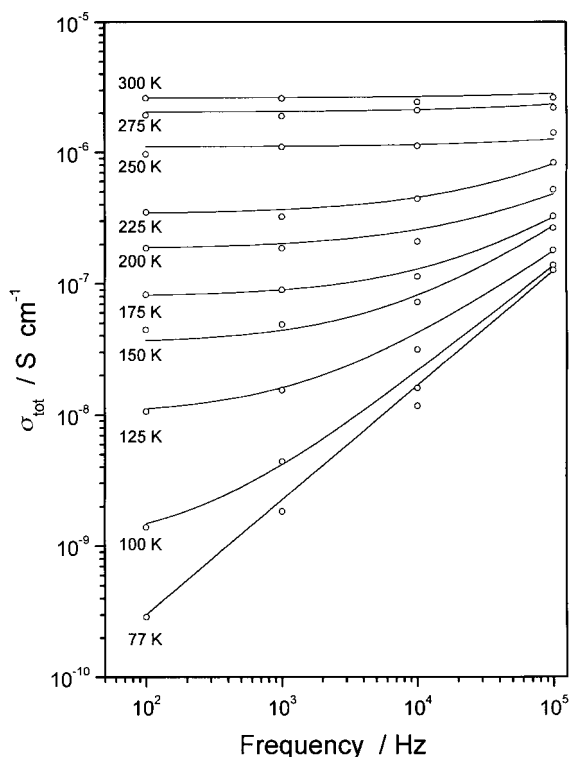
Fig. 6 Frequency dependence of the measured total conductivity, σ_{tot}, of a PPy–POP film at different temperatures.

Fig. 7 Variation of the total conductivity, σ_{tot}, and the dc conductivity of PPy–POP with the reciprocal of temperature at different frequencies.

a PPy–POP film over the whole temperature range considered. It shows a change of approximately four orders of magnitude. Each of these curves shows a frequency behavior which can be described by

$$\sigma_{tot}(\omega) = \sigma_{dc} + \sigma_{ac}(\omega) \qquad (3)$$

where the total measured conductivity, σ_{tot}, at a given frequency is separated into σ_{dc}, static conductivity, and σ_{ac}, which is frequency dependent. The static conductivity is simply the limit of $\sigma_{ac}(\omega)$ when $\omega \to 0$.[14] The conductivity is strongly frequency dependent at low temperatures, but with increasing temperature σ_{tot} becomes independent of frequency, remaining almost constant through the entire frequency range for $T \geqslant 250$ K. By fitting the experimental points to this theoretical model, the values of σ_{dc} can be estimated from the plateau values of each of these curves. The σ_{dc} values are found to be in satisfactory agreement with the corresponding measured σ_{dc} values, as reported for many other systems such polyacetylene,[34] metallophthalocyanines[35] and polypyrrole–poly(vinyl methyl ether) composites.[36] Fig. 7 shows the measured total conductivity σ_{tot} and also the evaluated σ_{dc} conductivity as a function of the reciprocal of temperature at different frequencies. They look similar to the results reported earlier for lightly doped polypyrrole.[37] This is in good agreement with our results obtained with IR and UV/VIS spectroscopy, already discussed, indicating that the PPy–POP composite film is only slightly doped due to a certain degree of overoxidation, which occurred during the synthesis of the composite material.

The log σ_{dc} *vs.* T^{-1} plot (Arrhenius representation, not shown) is markedly curved, indicating that σ_{dc} does not correspond to a single thermally activated process. When the data are replotted as log $\sigma T^{1/2}$ *vs.* $T^{-1/2}$, they fit closely to a straight line, as shown in Fig. 8, indicating that the charge transport mechanism can be explained by using the quasi-one-dimensional variable-range hopping (VRH) model according to the description of the temperature dependence of the con-
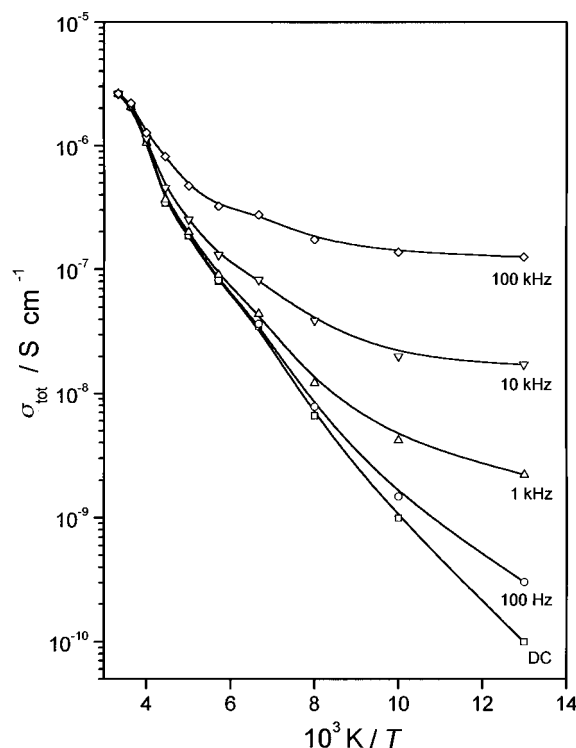
ductivity:

$$\sigma = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^{\gamma} \right] \qquad (4)$$

with $\gamma = 1/(n + 1)$, where σ (S cm^{-1}) is the conductivity, T (K) is the temperature, n is the dimensionality of the charge transport process and σ_0 (S cm^{-1}) and T_0 (K) are material constants. For the quasi-one-dimensional transport process, T_0 is
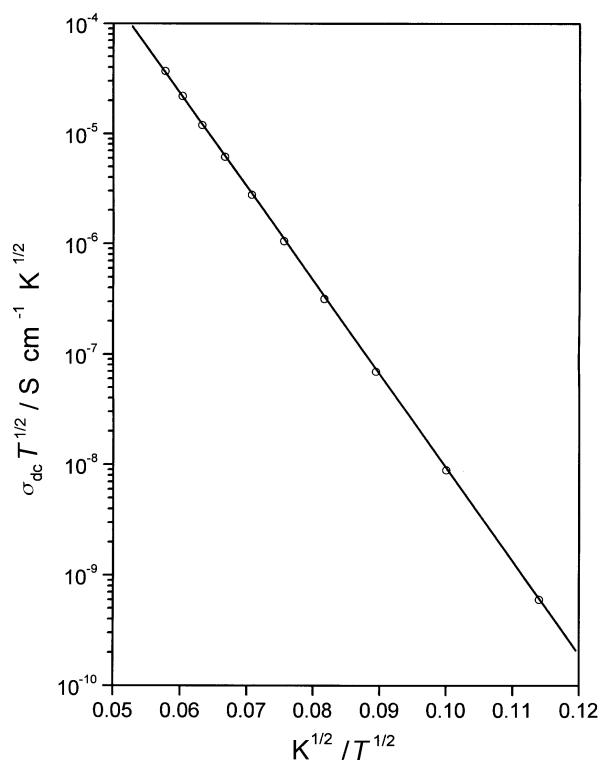

Fig. 8 Plot of $\sigma_{dc} \, T^{1/2}$ as a function of $T^{-1/2}$. The straight line is from the theoretical fits using eqn. (4) for $n = 1$.

given by[38]

$$T_0 = \frac{8}{k\xi N_{E_F} Z} \tag{5}$$

where ξ is the delocalization length of the electron wavefunction considered to be between 3 and 10 Å depending on the disorder of the polymer, k is the Boltzmann constant, N_{E_F} is the density of states and Z is the number of nearest-neighbor chains.

According to Zuo et al.,[39] the size of the conducting areas can be estimated by means of the expression

$$d = \frac{kT_0}{4eE_0} \tag{6}$$

where T_0 is the slope of the straight line of the plot $\log \sigma T^{1/2}$ vs. $T^{-1/2}$ (Fig. 8) and E_0 is the intensity of the electric field in the sample. Typical values for E_0 in polymer composites ranges from 10 to 100 kV cm^{-1}.[39] Considering a typical average value of $E_0 = 50$ kV cm^{-1} inside the composite PPy–POP sample, and with $T_0 = 33781$ obtained from Fig. 8(A), we obtain a size of ≈ 145 nm for the semiconducting areas, after a least-squares fit.

In the case of PPy, contradictory values for n have been published for the charge transport, e.g., $n = 3$,[40–43] $n = 2$[44] and $n = 1$.[45,46] This discrepancy has been attributed to the different preparation conditions of PPy samples.[47] As reported in the literature, many synthesized polymer blends and other composite systems (conducting polymer–insulating matrix) can be built in such a way that their structure consists of either (i) a large number of parallel or (ii) mixed chains of finite length aligned in a preferred direction, allowing in this way the hopping of the charge carriers between them.[48] Moreover, Nakhmedov et al.[49] have shown that when the connections to adjacent aligned chains are successively interrupted and the ends of a single chain are connected to the ends of only a few (one or two) aligned neighboring chains, the dynamics of the carriers should cross over from a three-dimensional transport process to the quasi-one-dimensional transport mechanism, and eqn. (4) holds with $n = 1$ ($\gamma = \frac{1}{2}$). Based on these ideas, we believe that this is the most probable chain formation in the PPy–POP polymer composite, which may explain the transport mechanism as a quasi-one-dimensional hopping process. Furthermore, this coincides with the fact that the size of ≈ 145 nm for the semiconducting areas, estimated by means of eqn. (6), lies among those values reported for other polypyrrole and polyaniline blends (40–400 nm), in which the transport is described by the quasi-one-dimensional VRH model.[50,51]

The fitting of the experimental values in Fig. 8 to the theoretical model of eqn. (4) with $\gamma = \frac{1}{2}$ gives rise to a value $T_0 = 33781$ K. Joo et al.[52] have established that kT_0 can be considered as the effective energy separation between localized states and that this value represents a measure of the conductivity in the amorphous region. Different values of this parameter have been found in the literature for different semiconducting polymer–insulating matrix composites. Depending on the kind of polymer blend, they ranged from the lowest value $T_0 \approx 2500$ for highly conducting blends to $T_0 > 25\,000$ for lightly conducting polymers blends.[51]

Using eqn. (5) and the value obtained for T_0, we calculated the density of states at the Fermi energy by assuming a delocalization length of about 10 Å, which corresponds to three or four monomer units, giving a value of $N_{E_F} = 7.23 \times 10^{21}$ eV^{-1} cm^{-3}. The number of charge carriers per unit volume, n_t, within a range kT of the Fermi energy can be estimated for each temperature according to ref. 53. At room temperature $n_t = 2.95 \times 10^{20}$ cm^{-3}, whereas at 77 K $n_t = 3.82 \times 10^{19}$ cm^{-3}. These values are reasonable and are in good agreement with the values reported by other workers, as has been observed for different disordered materials,[54] and are two

orders of magnitude lower than that of fully doped polypyrrole, indicating that PPy–POP is slightly doped, probably owing to overoxidation which causes a reduction in the conjugation length of the polymer chain.

4 Conclusion

The conducting polypyrrole–polyoxyphenylene composite PPy–POP was optically and electrically characterized. The composite material was prepared by an in situ electrochemical polymerization process in an alkaline medium of pH 9 at 1.25 V vs. SCE, which allows the simultaneous deposition of the conducting polymer (PPy) and the non-conducting polymer backbone (POP). UV/VIS and FTIR spectroscopy indicate that the PPy film obtained is slightly overoxidized, which has been attributed to the relatively high deposition potential and the alkaline medium. Both support the introduction of structural defects in the π-conjugated chain of polypyrrole, namely that of carbonyl groups, which disturb the delocalization length of the π-electrons and cause a change of the quinonoid structure, a feature of the highly doped PPy, to a benzenoid structure, which is characteristic of a lower doping level of PPy. Nevertheless, it exhibits the main characteristics of a pure polypyrrole film polymerized under commonly used preparation conditions (neutral pH and an applied potential of 0.8 V vs. SCE). PPy is electrically conducting and still electrochemically active, which indicates the formation of both polaron and bipolaron electronic states as charge carriers in the polymer backbone during the in situ polymerization of the polymer composite. As dopant, 4-hydroxybenzenesulfonic acid anion, present in the monomer solution, is incorporated in the bulk of the conduction polymer.

The electrical conductivity of doped composite PPy–POP films was measured in the temperature range 77–300 K. It decreases by approximately four orders of magnitude with decreasing temperature, showing a semiconductor-like, sublinear dispersive behavior. The dc conductivity values, obtained from a least-squares fit of the experimental results, were in satisfactory agreement with the corresponding measured σ_{dc} values for other organic semiconductors and conducting polymer composites. They were similar to the results reported earlier for lightly doped polypyrrole, which confirms the results obtained with IR and UV/VIS spectroscopy. The fitting of the temperature dependence of experimental data indicates a quasi-one-dimensional transport mechanism in such polymer composites as can be described by Mott's variable range hopping (VRH) model according to $\sigma = \sigma_0 \exp[-(T_0/T)^\gamma]$, with $\gamma = \frac{1}{2}$.

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