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Solvoconductivity of Polyconjugated Polymers: The Roles of Polymer Oxidation Degree and Solvent Electrical Permittivity

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The solvoconductive properties of low-defect anodically coupled polypyrroles and polythiophenes, made so they are able to be solvated by organic vapors with suitable substituents, have been studied. The investigation was performed by contemporary conductivity and electrochemical quartz crystal microbalance analysis of the polymer films as a function of the solvent vapor partial pressure. Solvoconductivity was measured at two doping levels (lightly and heavily doped) of the polymers and for a series of solvents in a wide range of dielectric constants. Lightly doped polymers are responsive to vapors whereas heavily doped polymers do no respond at all. For the sensitive polymers the response follows the electrical permittivity of the solvent ϵ_s with respect to that of the polymer ϵ_p, in the sense that conductivity increases for $\epsilon_s > \epsilon_p$ and decreases for $\epsilon_s < \epsilon_p$. A redox-type conduction model accounts for the responsive behavior of lightly doped polymers whereas a metal-like conduction model accounts for the absent responsivity of heavily doped polymers.

1. Introduction

In recent times there has been a huge demand for sensors, which has resulted in corresponding production. In particular, the request for sensors for volatile organic compounds (VOC) has been addressed with a polymer array sensor based mainly on the conductivity change upon solvent swelling. In particular, the threshold percolative conduction of nanometer-size conductors in an insulating matrix has produced sensors based on carbon particles[1−4] or gold colloids.[5,6]

The use of π-conjugated polymers in sensor devices for VOC detection has resulted in much research and several products have reached the marketplace.[7] Electrical conductivity has been, in general, considered as the parameter to follow in this kind of device. We will hereafter use the term solvoconductivity to define this type of phenomena and positive (negative) solvoconductive effect to define the increase (decrease) of conductivity produced by the VOC vapor.

Both positive and negative effects are commonly found in the literature. Considering positive effects, previous studies have evidenced the (reversible) water[8] and (irreversible) alcohol (methanol and ethanol)[9] dependence of conductivity of polyaniline. The vapor causes an increase of conductivity of several orders of magnitude, which was attributed to solvent-induced solid-state ionic conductivity and structural ordering (crystallization) of the polymer, respectively. Positive effects up to a factor of ≈10^6 were observed in iodine-doped commodity polymers and oligothiophene-terminated dendrimers, as well as in protonated polyaniline, after exposure to organic polar solvents.[10] A similar positive effect of

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humidity (from 10^{-2} to 18 S cm^{-1}) was previously observed in a redox dendrimer.[11]

Polypyrrole has often been the workhorse and in those cases mostly negative effects have been encountered. In one case it was reported to sense vapors of different alcohols with a linear increase of resistance with solvent uptake.[12] The result was attributed to the different work functions of the polymer and the solvent molecule.[13] More recently,[14] the use of polypyrrole with different counteranions in an array has been suggested. A polypyrrole dodecyl sulfate conductivity-based electrode was found to sense methanol with an increase of resistance of $\approx$30%[15] and other polypyrrole devices have been developed as sensors of a variety of vapors.[16,17]

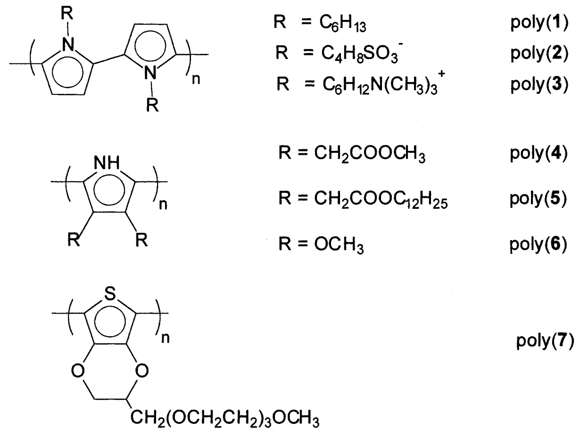
A highly negative solvoconductive effect was found in poly(3,4-dimethoxypyrrole) films.[18] Even higher negative effects were previously recorded on a redox ladder polymer in which the dry conductivity was decreased 10^4 times compared to the acetonitrile wet state.[19]

Despite such a large amount of research, the reason for the occurrence of either positive or negative effects in the solvoconductivity of conducting polymers is still unknown.

A second unclear aspect of the solvoconduction in such polymers is its dependence on the doping (oxidation) level of the polymer. This feature, which is linked to the electroactive properties of polyconjugated polymers, is a difficult matter since the oxidation level of the polymer may be easily changed by changing the environmental conditions. Previous investigations were simply performed on as-prepared doped polymer deposits.

To shed some light on these points, it appeared to us of the most importance the use of polymers with a reasonable level of regularity. Defects such as those produced by overoxidation, with an irregular introduction of carbonyl and hydroxyl moieties in the polymer chain,[20] may in fact change unpredictably both the conductive and the solvating properties of the polymer. A practical way of producing low-defect polymer films is the anodic coupling of monomers functionalized with the appropriate substituent. *N*-Substitution of pyrrole leads to particularly defective and poorly conducting materials due to the introduction of carbonyl groups into the polymer structure (at the β positions) by the high voltage required for polymerization. Much less defective materials may be obtained from oligomers that are oxidized at less positive potentials,[21] and in fact 2,2′-bipyrroles *N*-substituted with alkyl, alkylsulfonate, or alkylammonium moieties have been recently coupled anodically to low-defect polymers.[22]

Chart 1



3,4-Disubstitution with the required substituent does not present this kind of problems since the β-positions are capped and we have accordingly considered also some of these pyrrole and thiophene monomers. We have previously reported that heavily doped poly(3,4-dimethoxypyrrole) displays an impressive reversible drop of conductivity when exposed to vapors of different chemicals from ethanol to hexane.[18] In the same investigation we reported that an analogous polythiophene poly(3,4-ethylenedioxythiophene) (PEDT) is not sensitive to vapors, which was attributable to its lack of solvating ability. A PEDT substituted with ethyleneoxy chains would have presumably been able to solvate and then act as a solvent sensing material.

Following these suggestions, we have exploited the behavior of polymers from the *N*-substituted 2,2′-bipyrroles, 3,4-disubstituted pyrroles, and thiophenes shown in Chart 1. Among *N*-substituted 2,2′-bipyrroles we selected the dihexyl-substituted one to provide a neutral lypophilic polymer whereas alkylsulfonate- and alkylammonium-substituted dipyrroles where chosen as typical polyanionic and polycationic polymers able to solvate polar VOC. 3,4-Disubstituted pyrroles provide examples of different polar ends at the other side of the pyrrole ring whereas the thiophene is a typical highly conducting polythiophene with a polar side chain. This paper reports their solvatoconductive behavior, both in the lightly doped (LD) and heavily doped (HD) forms, toward a series of solvents of different polarity.

2. Experimental Section

Chemicals and Reagents. Acetonitrile was reagent grade (Uvasol, Merck) with a water content <0.01%. The supporting electrolytes tetrabutylammonium perchlorate (Bu_4NClO_4) and tosylate (Bu_4NTos) were previously dried under vacuum at 70 °C. All other chemicals were reagent-grade and used as-received.

The dipyrrole monomers 1,1′-dihexyl-1*H*,1′*H*-[2,2′]bipyrrole (**1**), 4-[1′-(4-sulfobutyl)-1′*H*-[2,2′]bipyrrol-1-yl]butanesulfonic acid tetrabutylammonium salt (**2**), and {6-[1′-(6-trimethylam-

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monium-hexyl)-1′*H*-[2,2′]bipyrrol-1-yl]-hexyl]}-trimethylammonium ditetrafluoborate (**3**),[22] the pyrrole monomers 3,4-bis-[(methoxycarbonyl)methyl]pyrrole (**4**) and 3,4-bis[(dodecyloxycarbonyl)methyl]pyrrole (**5**),[23] 3,4-dimethoxypyrrole (**6**),[24] and 2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxymethyl}-2,3-dihydro-thieno-[3,4-b][1,4]dioxine (**7**)[25] were prepared as reported in the literature.

Polymer films were electrodeposited by potentiostatic oxidation at 0.5 V (for **1**−**3**), 0.9 V (for **4** and **5**), and 1.0 V (for **7**) of 10^{-2} M monomer solutions in acetonitrile + 0.1 M Bu_4NClO_4. Poly(**6**) films were synthesized as the tosylate salt according to the literature.[18]

Apparatus and Procedure. *General Electrochemistry.* Experiments were performed at 25° C under nitrogen in three electrode cells. The counter electrode was platinum; the reference electrode was a silver/0.1 M silver perchlorate in acetonitrile (0.34 V vs SCE). The working electrode for cyclic voltammetry was a platinum microdisk electrode (0.003 cm^2). The voltammetric apparatus (AMEL, Italy) included a 551 potentiostat modulated by a 568 programmable function generator and was coupled to a 731 digital integrator.

Conductivity Sensor. The apparatus and procedures used for conductivity experiments were previously described in detail.[26] The electrode for conductivity measurements was a microband array platinum electrode (5-μm bandwidth, 100-nm thick) with interband spacing of 5 μm. The polymer deposit, produced with a deposition charge of 20 mC, was thick enough to ensure minimum resistance, under which condition the conductivity σ is given by $\sigma = k/(R - R_0)$, where R is the measured resistance, R_0 the lead resistance (was 100 ohm), and k the cell constant (0.2 cm^{-1}). Though the conductivity device is a two-probe one, contact effects are minor as proven by the identical results obtained with a more complex four-probe device.

EQCM Sensor. Electrochemical quartz crystal microbalance (EQCM) analysis was performed with a platinum-coated AT-cut quartz electrode (0.2 cm^2), resonating at 9 MHz, onto which the polymers were deposited. The oscillator circuit was homemade and the frequency counter was Hewlett-Packard model 5316B. Data were collected by a microcomputer with a homemade analyzing software by which frequency changes were monitored as mass changes Δm.

Vapor Generation to EQCM and Conductivity Sensors. Vapors were generated from bubblers at 15 °C, diluted with dry nitrogen to desired concentrations, and delivered to the sensor cells (at 25 °C) by a computer-driven mass-flow controller (MKS, Andoven MA, model 1179 A equipped with model PR 4000 F two-channel power supply). A total mass flow of 200 mL min^{-1} was routinely used, partial vapor pressures ranging from 5 to 100%. As a final test of the validity of these conditions, the spectrophotometric analysis of toluene generation (in the range 50−500 mL min^{-1}) has given vapor concentrations in perfect agreement with published vapor pressures.

3. Results and Discussion

3.1. Electrochemical and Conductive Properties of the Polymers.

This first section illustrates the relationship between the oxidation state of the polymers and their conductivity.

The CV of the polymer films in acetonitrile + 0.1 M Bu_4NClO_4 displays a reversible response at redox potentials $E°$ given in Table 1. It may be observed that the values for the poly(**1**)−poly(**5**) series are in the narrow and positive range 0.13−0.25 V, corresponding to a substantial stability of the undoped (or lightly doped) state in the air. In contrast, poly(**6**) and poly(**7**) with their quite negative $E°$ values (−0.60 V) are presumably stable in the heavily doped state only.

Table 1. Polymer Oxidative Redox Potentials ($E°_p$) and Maximum Conductivity (σ) in Acetonitrile + 0.1 M Bu_4NClO_4

monomer	$E°_p$ (V)	σ (S cm^{-1})	monomer	$E°_p$ (V)	σ (S cm^{-1})
1	0.25	0.02	**5**	0.21	0.001
2	0.15	0.001	**6**	−0.60	15
3	0.13	0.005	**7**	−0.60	70
4	0.16	0.002			

The reversible charge Q_r involved in the redox process of the poly(**1**)−poly(**5**) series, measured at 0.8 V and related to the mass, corresponds to 0.5 electrons per pyrrole ring;[22] in poly(**6**) one electron is exchanged per pyrrole unit[18] and in poly(**7**) 0.6 electrons per thiophene ring, as for PEDT itself.[18]

In situ conductivity measurements of the polymer films in acetonitrile + 0.1 M Bu_4NClO_4 show the oxidation-driven transition from a low-conductivity state to a conductive state usual in polyconjugated polymers. Conductivities are listed in Table 1 whereas conductivity plots for two representative members of the two series, that is, poly(**1**) and poly(**7**), are shown in Figure 1 along with their relevant CVs.

3.2. Stability of the Doping Level.

The stability of the polymers (both in the undoped and the doped forms) to the environment was determined by measuring the open-circuit voltage (OCV) of ≈1-μm-thick films in acetonitrile + 0.1 M Bu_4NClO_4 after potential-controlled full reduction or oxidation. The decay curves are shown in Figure 2 for poly(**1**) and poly(**7**) as representative of the two series of polymers. The curves were obtained under stirring in aerated solutions.

The OCV of the poly(**1**)−poly(**5**) series after being doped at the fully oxidized form (0.7 V) decays progressively due to the reducing action of moisture. The neutral form of the polymer after reduction (−0.5 V) attains quickly (within a few minutes) a stable OCV of 0.05 V. The OCV of a platinum electrode gives the same value which corresponds to the redox level of the solution (and of its environment). This potential, which is stable for hours, corresponds to a low level of doping (≈1% of the doping level measured at 0.8 V).

The OCV of the poly(**6**)−poly(**7**) series after oxidation at 0.7 V decays in a fashion similar to that of the poly(**1**)−poly(**5**) series. At difference the undoped form of these polymers is extensively oxidized in the air with a progressive decay of the OCV. In any case, as Figure 2 clearly shows, the decay to the onset of the polymer redox potential requires only a few seconds whereas the subsequent decay is slow. In this connection we could observe that the spontaneous aerial oxidation is fully reversible since reduction regenerates the pristine material completely.

It is therefore confirmed that only the neutral form (or better its lightly doped form) of the poly(**1**)−poly(**5**) series may be considered stable in the environment. Anyway, all the investigated polymers after oxidation at 0.7 V attain within 5 min a potential close to 0.6 V. Within the same time lag the undoped form of the poly(**6**)−poly(**7**) series attains an OCV close to the redox potential of the polymer (ca. −0.7 V) and a quite low level of doping (ca. 1−2% of the doping level at 0.8 V at most).

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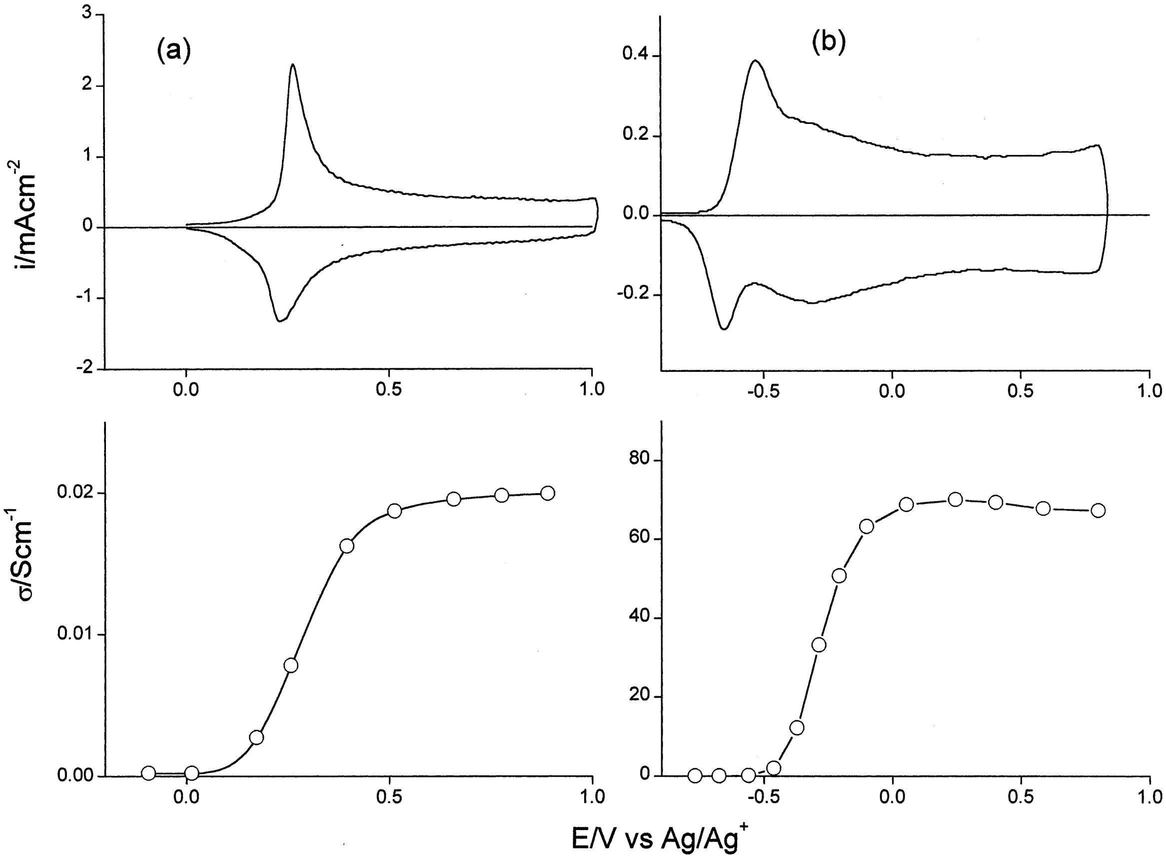

Figure 1. Cyclic voltammograms (upper) and in situ conductivity plots (lower) of (a) poly(**1**) and (b) poly(**7**) in acetonitrile + 0.1 M Bu_4NClO_4.

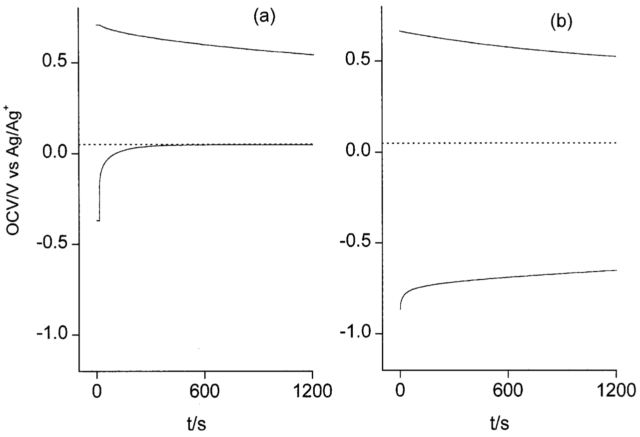

Figure 2. Open-circuit voltage (OCV) vs time of (a) poly(**1**) and (b) poly(**7**) films in aerated acetonitrile + 0.1 M Bu_4NClO_4 under stirring after (upper) anodic or (lower) cathodic polarization. Dashed line: OCV value at a platinum electrode.

Following these results, the polymer films for solvoconductive tests were previously potentiostatically driven to −1.0 and 0.7 V for the lightly doped (LD) and heavily doped (HD) forms, respectively. Subsequently, the HD forms were equilibrated for 5 min (maximum) in the washing acetonitrile solution; the LD forms were first electrochemically doped at a 1% level and then briefly washed. We have checked that the OCV potential of these films was unchanged after the solvoconductive tests (performed under nitrogen) so that reliable solvoconductive measurements could be performed in any case.

3.3. Solvent Uptake. The solvent uptake by the polymer films was measured by EQCM. The uptake was in any case reversible since nitrogen fluxing restored the starting weight completely. A linear dependence of the amount of adsorbed solvent and partial pressure is generally obeyed. Solvation may be impressive, such as, for example, for poly(**6**) and poly(**7**), which display a massive $CHCl_3$ uptake for both the HD and the LD state (Figure 3).

The absorption isotherms of the polymers were calculated and the relevant constants (ratio of concentrations in the solid and in the gas phase, both given as mol L^{-1} and assuming that the polymer density is 1 g cm^{-3}) are summarized in Tables 2 and 3.

From Table 3, in which several solvents are considered, it may be observed that the values reflect the expected affinity of the solvents to the polymer phase. Thus, the polar poly(**4**) is better solvated by polar solvents where its homologue with an alkyl spacer poly(**5**) is better solvated by apolar solvents. Similarly, poly(**1**) is better solvated by apolar solvents, different from poly(SOPD) and poly(NRDP), which are much better solvated by polar solvents.

3.4. Conductivity Changes. The change in conductivity with solvent partial pressure is shown by the experimental plots in Figure 3. Also these changes were reversible since nitrogen fluxing restored the starting conductivity values.

The highly surprising result is that the conductivity response of the HD state is flat (Figure 3a) and this occurs for all the polymers. Only at vapor pressure values close to saturation (not shown in the figure) does

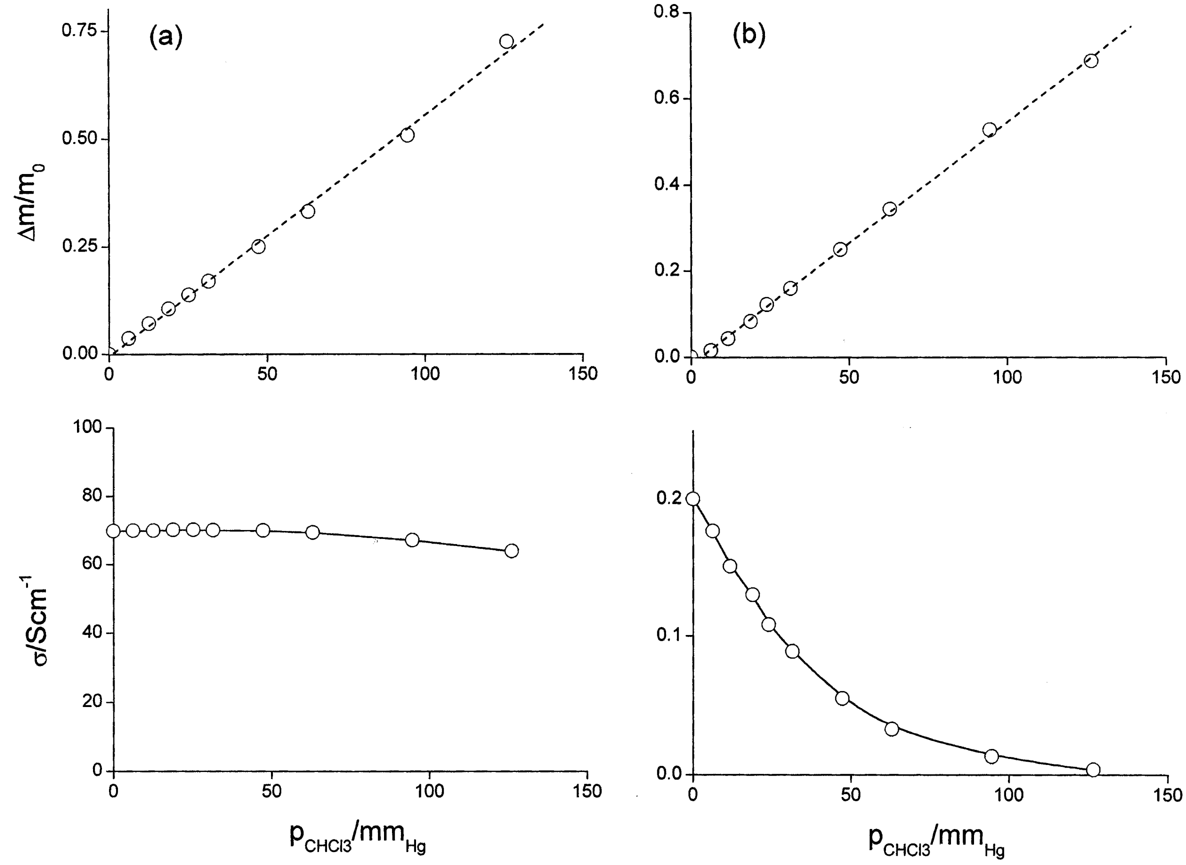

Figure 3. EQCM mass increase of adsorbed vapor (upper) and conductivity (lower) vs partial pressure of $CHCl_3$ vapors for poly(**7**) film (a) in the HD state and (b) in the LD state.

Table 2. Partition Constants *K* and Relative Conductivity Change per Mole of Adsorbed $CHCl_3$ ($\Delta\sigma/\sigma_0$)/*X* for Some LD and HD Polymers

monomer	polymer state	K	$(\Delta\sigma/\sigma_0)/X$
1	LD	680	1.25
1	HD	380	0.0
4	LD	700	6
4	HD	675	0.0
6	LD	300	−5.0
6	HD	600	0.0
7	LD	2200	−1.5
7	HD	2200	0.0

Table 3. Partition Constant of Solvents[a] for the LD Polymers

monomer	CH_3CN(36)	EtOH(24)	$CHCl_3$(4.9)	CH_3Ph(2.4)	C_6H_{14}(1.9)
1	280	250	680	1500	2700
2	880	1500	530	30	110
3	750	370	100	20	0
4	1200	900	700	240	30
5	430	270	1000	2700	330

[a] Dielectric constant in parentheses.

conductivity decrease appreciably. The massive conductivity changes previously observed for poly(**6**)[18] are in fact obtained for most of the polymers only under vapor pressures close to saturation. Under these conditions solvent molecules aggregate in clusters both in the vapor phase and presumably also in the framework of the polymer, with the consequence of an anomalously huge change of conductivity.

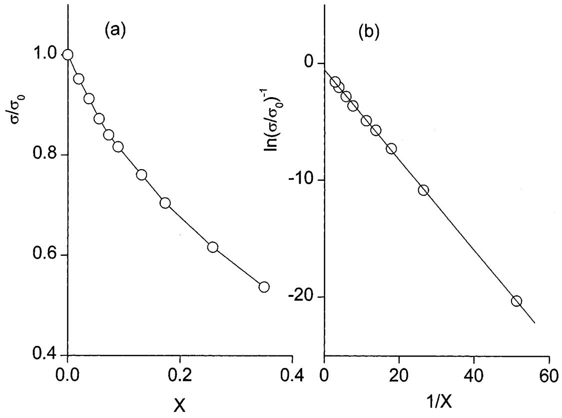

Figure 4. (a) Relative conductivity σ/σ_0 vs molar fraction X of adsorbed *n*-hexane for neutral poly(*N*,*N′*-dihexyldipyrrole) and (b) plot of inverse $\ln(\sigma/\sigma_0)$ vs inverse X.

It is in the LD state that the polymer responds to the solvent uptake with an appreciable change of conductivity (Figure 3b). The change of conductivity with solvent partial pressure may be alternatively expressed as the relationship between the relative conductivity (as the ratio σ/σ_0 of conductivity over conductivity under nitrogen) and the adsorbed solvent (as molar fraction X of solvent molecules). We will hereafter follow this way of presenting the results since it allows a direct correlation of conductivity and solvent uptake. It may then be observed that the (σ/σ_0) vs X relationship (Figure 4a) approximates linearity for X approaching zero. The relevant slopes $(\Delta\sigma/\sigma_0)/X$ ($\Delta\sigma = \sigma - \sigma_0$) for both HD and LD states of some selected polymers are summarized in Table 2.

3.5. Solvoconductivity and Electrical Permittivity. The solvoconductivity of the responsive LD forms have been investigated at different VOCs, particularly

Table 4. Relative Conductivity Change per Mole Fraction of Adsorbed Solvent[a] ($\Delta\sigma/\sigma_0$)/X for the LD Polymers

monomer	CH_3CN(36)	EtOH(24)	$CHCl_3$(4.9)	CH_3Ph(2.4)	C_6H_{14}(1.9)
1	20	5.5	1.25	-0.9	-2
2	0.5	0.8	0.2	0.0	-0.2
3	2	0.4	-0.5	0.0	-
4	2.2	1.8	6	-0.7	-2
5	18	4	1.3	-0.55	-0.7

[a] Dielectric constant in parentheses.

with the poly(**1**)−poly(**5**) series due to their stability in the LD state. The ($\Delta\sigma/\sigma_0$)/X values are summarized in Table 4. From inspection of this table it may be observed that the ($\Delta\sigma/\sigma_0$)/X values are positive for solvents with high dielectric constant and negative for low values. In practice, hexane and toluene always display negative slopes whereas these are always positive for acetonitrile and ethanol.

After the previous consideration the conductivity response appears to be determined by the dependence of the hopping probability on the relative permittivity of the solvent ϵ_s and of the polymer ϵ_p.[27] According to Mott's variable-range hopping (VRH) conductivity applied to a model based on clusters[28] and following the procedure shown in the Appendix, we have evaluated the equations relating σ/σ_0 and X. The experimental results do in fact follow the relationship

$$[\ln(\sigma/\sigma_0)]^{-1} = [B(\epsilon_s - \epsilon_p)/\epsilon_p]^{-1}X^{-1} + 1/B$$

(where B is a constant, see eqs 8 and 9 in the Appendix) as shown in Figure 4b.

The relationship

$$\Delta\sigma/\sigma_0 = [B/(1 - B)][(\epsilon_s - \epsilon_p)/\epsilon_p]X$$

(from eqs 8 and 10 in the Appendix) accounts for the linear response of conductivity with solvent partial pressure at low levels of pressure. The ($\Delta\sigma/\sigma_0$)/X vs ϵ_s plots are linear (see e.g. Figure 5) with the x-axis intercept at $\epsilon_s = \epsilon_p = 2-5$. This range of values corresponds in fact to that of conjugated polymers.[29]

The clear conclusion is that the responses follow the electrical permittivity of the solvent ϵ_s with respect to that of the polymer ϵ_p, in the sense that conductivity increases (positive solvoconductivity) for $\epsilon_s > \epsilon_p$ and decreases (negative solvoconductivity) for $\epsilon_s < \epsilon_p$.

3.6. The Solvoconductive Mechanism. Conducting polymers at a low doping level may be assumed to be essentially constituted by polymer chains with weak van der Waals interactions between them. The scarce oxidative charges are dispersed within this matrix and move according to a hopping mechanism similar to that of redox conduction, as shown for, for example, lightly doped polypyrrole.[30] In this state the solvent molecules enter the polymer matrix modifying the energetics of the hopping charge separation in the sense of decreasing the activation energy as the electrical permittivity is increased.

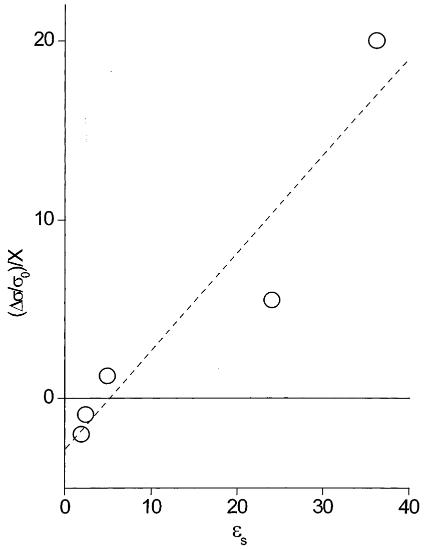

Figure 5. Ratio of change of relative conductivity $\Delta\sigma/\sigma_0$ and molar fraction X of adsorbed solvent ($\Delta\sigma/\sigma_0/X$) vs solvent dielectric constant ϵ_s for poly(**1**) film in the LD state.

In the heavily doped ("metallic") regime the interactions among the polymer chains are enormously increased with three-dimensional delocalization of the electronic states[31] and the polyconjugated chains form well-packed and highly conducting domains[32] in which respect the substituents are laterally disposed. Solvation may be supposed to be localized at the side substituents without interposing between the conductive pathways. The result is that no significant solvent effect is observed in the conductivity unless the swelling is so heavy that the polymer grains separate grossly into large insulated domains.

A similar mechanism has been previously invoked. The distribution of adsorbed molecules in polypyrrole decyl sulfate was investigated by neutron reflectivity.[33] It was found that the solvents molecules do not insert in void spaces but swell the polymer. The fact that resistance changes are much lower with chloroform than with methanol, despite the similar solvent content, has been attributed to different location of the solvation, that is, at the side alkyl chains of the counteranion for chloroform and at the polypyrrole backbone for the polar methanol. The resistance changes (increases with solvation) were in any case thereby attributed to increased distance of the hopping sites.

Finally, it should be mentioned that a different mechanism has been invoked to explain the solvent dependence of the conductivity in several I_2-doped polymers.[10] A solvent-dependent mobility of the sites has been suggested since the redox conduction increases with solvation apparently following the plasticizing ability of the solvent.

Conclusions

The solvoconductive properties of low-defect polypyrroles and polythiophenes were evaluated at two doping

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levels (lightly and heavily doped) of the polymers and for a series of solvents encompassing a wide range of polarity. Heavily doped polymers are not sensitive to vapors whereas lightly doped polymers do in fact respond. Their response follows the difference of electrical permittivity between the solvent and the polymer. The result is that if the solvent is more permittive, conductivity increases and vice versa. A VRH conduction model accounts for the responsive behavior of lightly doped polymers whereas pseudo-metallic conduction may account for the absence of responsivity of heavily doped polymers.

These results make it clear that conducting polymers are not good candidates for VOC conductivity sensors when used in the heavily doped state. Appreciable and (depending on the substitution pattern) selective responses are instead obtained with only slightly doped polymers. This indication and the requirements of environmental stability in practice indicates low-doped alkyl-substituted polypyrroles as the best candidates in the role of solvoconductive polyconjugated polymers.

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Appendix

According to Mott's VRH model, the conductivity is given by the equation

$$\sigma = K \exp(-2\alpha R)\exp(-E_a/kT) \qquad (1)$$

where R is the separation of the hopping sites, α the inverse localization length, and E_a the activation energy of hopping. With clusters with diameter d, E_a is given by

$$E_a = e^2/(2\pi K d) \qquad (2)$$

$$K = \epsilon_0\epsilon(1 + d/2R) \qquad (3)$$

If E_{a0} is E_a in the vacuum ($\epsilon = 1$), eq 1 turns to

$$\sigma = A \exp(-E_{a0}/kT\epsilon) \qquad (4)$$

Assuming that the relative permittivity ϵ is the sum of the molar fraction X of the permittivity of each component (ϵ_s for the solvent and ϵ_p for the polymer),

$$\epsilon = \epsilon_s X + \epsilon_p(1 - X) \qquad (5)$$

eq 4 may be simplified as

$$\sigma = A \exp[-B/(1 + CX)] \qquad (6)$$

where

$$B = E_{a0}/(kT\epsilon_p) \qquad (7)$$

$$C = (\epsilon_s - \epsilon_p)/\epsilon_p \qquad (8)$$

Calling σ_0 the conductivity at $X = 0$, eq 6 turns into

$$[\ln(\sigma/\sigma_0)]^{-1} = (1/BC)X^{-1} + 1/B \qquad (9)$$

and for X approaching zero,

$$(\sigma/\sigma_0) - 1 = \Delta\sigma/\sigma_0 = [BC/(1 - B)]X \qquad (10)$$

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