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# Anion-Assisted Anodic Coupling of 2,2′-Bipyrrole. Role of Tosylate Anion in the Electrochemical Synthesis of Polypyrrole

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Cyclovoltammetric analysis has shown that anodic coupling of 2,2′-bipyrrole in acetonitrile is influenced by the electron-donor properties of the anion of the supporting electrolyte. 2,2′-Bipyrrole oxidation in the presence of poor electron-donor anions ($ClO_4^-$, $PF_6^-$, $BF_4^-$, $CF_3SO_3^-$) occurs in a one-electron process at a potential independent of the anion, yielding the dimer whereas with more electron-donor anions (tosylate, benzenesulfonate, methanesulfonate, camphorsulfonate, chloride, and nitrate) the oxidation process is shifted to lower potentials according to the anion type and concentration, requires 2.5 electrons/bipyrrole unit and results in polypyrrole formation. The results are explained by ion pairing and hydrogen bonding of the electron-rich anion with the initially produced radical cation to form a highly reactive radical species. As a consequence, the well-known favorable action of tosylate in promoting polypyrrole formation may be satisfactorily accounted for by a chemical homogeneous process rather than by morphological factors.

## Introduction

The effect of the counteranion on structure and conductivity properties of polypyrrole is well documented.[1−9] In particular it was recognized that tosylate anion promotes the electrooxidation of pyrrole to a polypyrrole of greatly improved conductivity and mechanical properties.[10] This effect, which we will hereafter call the "tosylate effect", was attributed to morphological factors, and a great deal of structure analysis was performed by SEM,[11] X-ray diffraction,[12] and neutron scattering.[13] It was formerly assumed that the planar moiety of the tosylate anion can act as a template,[14] favoring a regular stacking of the polymer chains in an anisotropic manner. However it was later recognized that also bulky aliphatic anions, such as the camphorsulfonate anion, do yield anisotropic structures.[15]

From our side we did not observe the tosylate effect when the N-position of the pyrrole is substituted: the polymerization of *N,N*′-dimethybipyrrole shows no difference between perchlorate and tosylate.[16] Moreover, we have checked the tosylate effect in several cases of electrodeposition of bipyrroles and bithiophenes,[17] and we have observed that it is displayed only with heteroaromatic monomers containing the NH pyrrole moiety. In all the other cases the action of tosylate was not dissimilar from that observed with the usual counteranion perchlorate.

Several mechanisms have been proposed for electrodeposition of pyrrole and its derivatives.[18] However, it is generally agreed that the electrodeposition involves two stages, a homogeneous process to form oligomers and a heterogeneous one, their precipitation on the electrode. We focused on the first one, analyzing the electrochemical response (cyclovoltammetric analysis) of pyrrole oxidation in the presence of tosylate anion. Since in any case the investigation of pyrrole is com-

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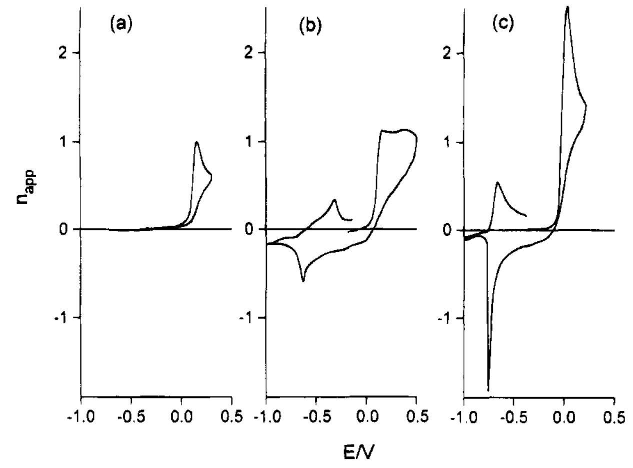

**Figure 1.** CV of 2,2′-bipyrrole $1 \times 10^{-3}$ M in AN in the presence of 0.1 M tetrabutylammonium perchlorate (a) before and (b) after addition of 1% water; (c) in AN in the presence of 0.1 M tetrabutylammonium tosylate.

plicated by side reactions and electrode fouling due to the high oxidation potential of pyrrole, we addressed to the more easily oxidizable 2,2′-bipyrrole.

In this paper we report the effects of tosylate and other anions on the electrochemical oxidation of 2,2′-bipyrrole in acetonitrile.

## Experimental Section

**Chemicals and Reagents.** 2,2′-Bipyrrole was synthesized according to the literature.[19] Acetonitrile (AN) was distilled twice over $P_2O_5$ and once over $CaH_2$. The supporting electrolytes (tetrabutylammonium salts), when not commercially available, were prepared by reaction of a 0.1 M solution of tetrabutylammonium hydroxide in 2-propanol with the stoichiometric amount of the suitable acid followed by removal of the solvent under reduced pressure; in any case before use they were dried under vacuum at 70 °C. All other chemicals were reagent grade.

**Apparatus and Procedure.** Experiments were performed at 25 °C temperature under nitrogen in three-electrode cells. The counterelectrode was platinum; reference electrode was a silver/0.1 M silver perchlorate in AN (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 (CV) was a platinum microdisk electrode (0.003 cm$^2$). For UV−vis spectroscopy a 0.8 × 2.5 cm indium−tin−oxide (ITO) sheet (ca. 20 Ω/square resistance, from Balzers, Liechtenstein) was used. A platinum sheet (15 cm$^2$) was used in electrolyses.

UV−vis spectra were taken with a Perkin-Elmer Lambda 15 spectrometer. The apparatus and procedures used in the in situ conductivity experiments were previously described in details.[20] Electrochemical quartz crystal microbalance (EQCM) measurements were performed with the apparatus and procedure described previously.[21]

## Results and Discussion

**Anodic Coupling of 2,2′-Bipyrrole with Perchlorate as Anion.** 2,2′-Bipyrrole is oxidized in AN in the presence of 0.1 M tetrabutylammonium perchlorate at a one-electron irreversible peak ($E_p = 0.17$ V at 0.1 V/s in $10^{-3}$ M solution, a in Figure 1). No polymer is produced with potential cycling, as previously reported.[22] The shape of the CV peak ($E_p - E_{p/2} = 40$ mV) and the dependence of $E_p$ on concentration $C$ ($\Delta E_p/\Delta(\log C) = -20$ mV) and scan rate $v$ ($\Delta E_p/\Delta(\log v) = 20$ mV) clearly indicate that the one-electron transfer is followed by a second-order irreversible reaction.[23] The reaction is very likely to be the dimerization of the initially formed radical cation, as reported for pyrrolic radical cations which couple to dimer directly, i.e., without interposed steps such as, e.g., proton release.[24]

Electrolysis at the peak potential confirms the suggested formation of the dimer. Analysis of the current−charge relationship and of the electrolysis products indicates that 1 electron/molecule is effectively consumed for dimer formation at the early stages of the oxidation (exhaustive electrolysis causes degradation of the products). Typically the partial electrolysis (0.1 F/mol) of a $5 \times 10^{-3}$ M solution, followed by reduction of the released protons, gives a $2.5 \times 10^{-4}$ M light yellow solution of tetrapyrrole, identified on the basis of its maximum absorption wavelength (343 nm) and reversible oxidation potential ($E_0 = -0.18$ V).[22]

The shift of $E_p$ for 2,2′-bipyrrole oxidation from its $E_0$ value of 0.23 V[22] allows the evaluation of the dimerization rate constant[23] which results to be ca. $10^8$ M$^{-1}$ s$^{-1}$. This value is compatible with the lifetime of the radical cation, which could be detected in $10^{-4}$ M solutions only at scan rates higher than 1000 V s$^{-1}$.[22]

Addition of water (1%) does not significantly change the CV peak height for 2,2′-bipyrrole oxidation nor its potential and polymer is formed only to a negligible extent at the peak potential. The fact that the number of exchanged electrons apparent from the peak current ($n_{app}$) is practically unaffected by water is unusual; in fact $n_{app}$ is known to be increased in oxidation of pyrroles by the proton-scavenging action of water.[25] In this case water addition causes the appearance of a further oxidation process beyond $E_p$, at ca. 0.4 V (b in Figure 1). Potential cycling over this potential causes easy polymer deposition. The charge yield (ratio of the reversible charge over the deposition charge at the neutral state) is ca. 30%. The CV of the deposited polymer shows a reversible oxidation process at $E_0 = -0.45$ V. The UV−vis spectrum of the neutral polymer displays a maximum at 395 nm; the in situ conductivity is 20 S cm$^{-1}$.

**Anodic Coupling of 2,2′-Bipyrrole with Tosylate as Anion.** In a $10^{-3}$ M 2,2′-bipyrrole solution in AN containing 0.1 M tetrabutylammonium tosylate the $n_{app}$ of the oxidation peak rises from 1 to 2.5 electrons (c in Figure 1). Furthermore $E_p$ shifts to a less positive potential, while the shape of the peak is unchanged ($E_p - E_{p/2} = 40$ mV). Potential cycling at the peak makes the polymer develop easily (charge yield = 20%). In monomer-free solution the CV of the polymer shows a single neat process at $E_0 = -0.70$ V with a long and flat capacitive range (Figure 2). The UV−vis spectrum shows a maximum absorption at 405 nm; the conductivity is 70 S/cm. These data indicate that tosylate favors the deposition of a long-chain conjugated polymer.

Disregarding the good quality of the produced polypyrrole, the remarkable result is that tosylate anion

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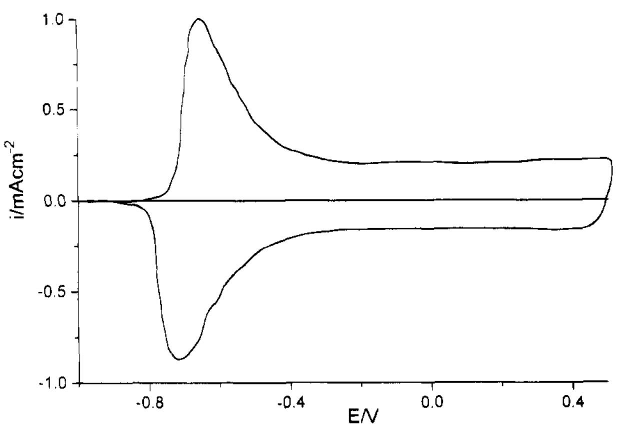
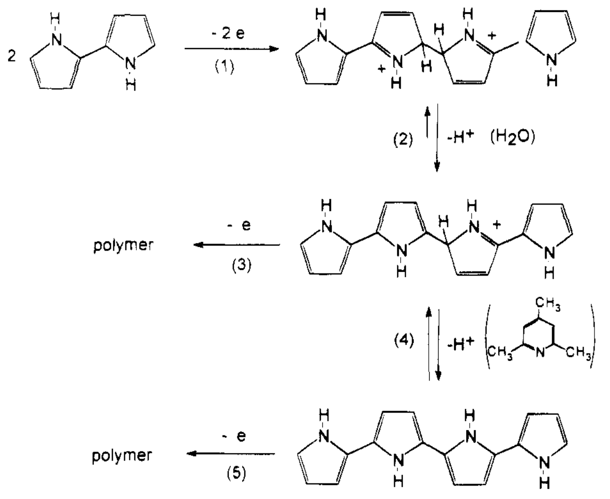


**Figure 2.** CV of polypyrrole film produced from 2,2′-bipyrrole in AN in the presence of 0.1 M tetrabutylammonium tosylate and recorded in monomer-free solution. Scan rate 0.1 V/s; reversible charge 4 mC cm$^{-2}$.

**Scheme 1**



changes both the number of exchanged electrons and the peak potential of the CV electrochemical oxidation of 2,2′-bipyrrole, suggesting that the role of this anion is chemical rather than structural.

**The "Tosylate Effect".** Before discussing the action of tosylate in the polymerization process of 2,2′-bipyrrole, we must reconsider the action of water. As previously reported,[25] the presence of water makes the one-electron oxidation of pyrroles increase to $n_{app} = 2.5$, which has been explained by the fact that water, a base stronger than pyrrole, subtracts the protons produced in the coupling process preventing the protonation of pyrrole itself. In the case of 2,2′-bipyrrole, a molecule more basic than pyrrole, water does not appear to be an efficient proton scavenger since the oxidation is still a one-electron process. In any case it has been observed that further oxidation processes appear at higher potentials accompanied by polymer formation. To explain this behavior, we suggest a reaction pathway (Scheme 1) in which the one-electron oxidation of the 2,2′-bipyrrole (eq 1) leads to the diprotonated tetrapyrrole, which is not further oxidizable. Water deprotonates it to the monoprotonated tetrapyrrole (eq 2) which is now oxidizable to polymer though at a higher potential than for dipyrrole (eq 3).

This mechanistic hypothesis is supported by the results of electrooxidation experiments carried out in the presence of collidine (2,4,6-trimethylpyridine), a base strong though inert to oxidation and radical attack. Under these conditions the deprotonation of protonated tetrapyrrole would be pushed to completion (eq 4) and polymerization would forcedly involve the neutral tetrapyrrole (eq 5). As a matter of fact, upon addition of collidine in 1:1 or higher collidine:substrate ratio, the one-electron oxidation peak of 2,2′-bipyrrole in the presence of 0.1 M tetrabutylammonium perchlorate turns to $n_{app} = 2$ without any $E_p$ shift nor display of further oxidation processes. Oxidation at the peak produces polypyrrole, though the material is scarcely conjugated ($E_0 = -0.35$ V) probably due to an oligomeric nature.

Within this frame the role of tosylate cannot be limited to that of an efficient proton scavenger. Its base properties are even lower than those of water itself (the p$K_a$ of *p*-toluenesulfonic acid in water is ca $-7$ vs $-2$ for $H_3O^+$ [26] ). The proton-scavenging action is undoubtedly present but must be only one step of a more complex reaction pathway. Since no chemical step is interposed between the electron transfer to radical cation and the rate determining step of dimerization, the fact that the peak potential for 2,2′-bipyrrole oxidation is shifted to lower values by tosylate ion (but not by water nor collidine) leads us to conclude that the anion must exert its action on the primary electrode product, namely, the radical cation (water and collidine operate downhill of the coupling step). We suggest that this action develops trough ion pairing, a phenomenon often invoked in ionic organic reactions in aprotic dipolar solvents such as acetonitrile. It is well-known how dramatically different anions may influence the kinetics of reactions involving free carbonium ions or ion-pairs such as $S_{N1}$ nucleophilic substitutions. In such reactions the perchlorate anion yields free ions while more electron-donor anions stabilize intimate or solvent-separated ion pairs.[27,28] In our case the tosylate anion would be also oriented and held in place in the ion-pair by hydrogen bonding with the NH moiety of the pyrrole ring. As a matter of fact, hydrogen bonding to NH groups greatly increases the association constants of ion pairs;[29] moreover, it may account for the fact that the tosylate effect is specific of NH-containing pyrrole systems.[16,17]

As shown in Scheme 2, we suggest that the radical cation of 2,2′-bipyrrole forms an ion pair with the tosylate anion (eq 1); the resulting ion pair may dimerize (eq 2) at a faster rate than the free-radical cation due to the shielding of the positive charge and the consequent elimination of coulomb repulsion; the tetrapyrrole, generated from the protonated species (eq 3), is further oxidized at the applied potential and couples to give polymer (eq 4). Equation 3 accounts for the proton-scavenging action of the anion and the increase of $n_{app}$ to a value compatible with an efficient polymerization, namely 2 electrons/bipyrrole unit for the coupling and 0.25 electron/pyrrole ring for polymer oxidation.

To check this hypothesis, we investigated the system in more detail by performing CV of a $10^{-3}$ M solution of

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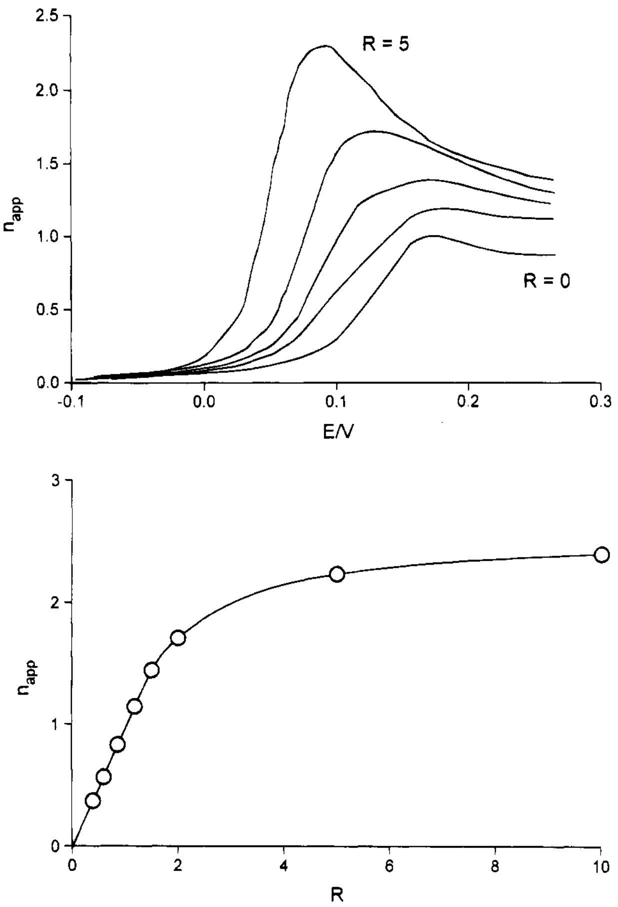
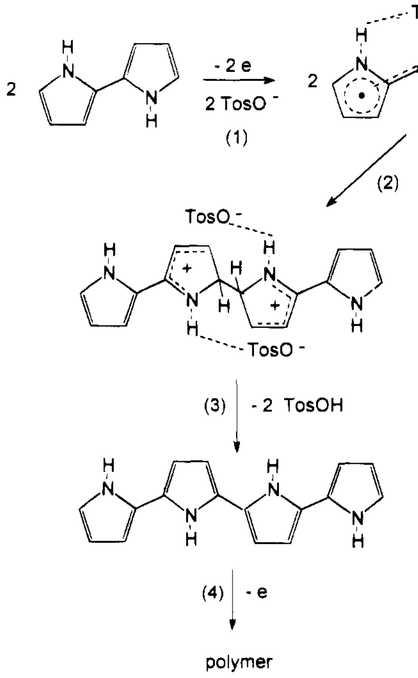


**Figure 3.** (a, top) CV of 2,2′-bipyrrole $1 \times 10^{-3}$ M in AN in the presence of 0.1 M tetrabutylammonium perchlorate with progressive addition of tetrabutylammonium tosylate in ratio *R* to 2,2′-bipyrrole (*R* = 0.0, 0.4, 0.8, 1.5, 5.0). (b, bottom) Plot of $n_{app}$ for the anion induced oxidation process vs *R* for tosylate.

**Scheme 2**



2,2′-bipyrrole in AN containing 0.1 M tetrabutylammonium perchlorate with progressive additions of tosylate salt. Upon addition a slope develops on the cyclic voltammogram at ca. 0.12 V, close to the initial peak at 0.17 V (Figure 3a). The processes are of comparable height when the molar ratio *R* of tosylate to 2,2′-bipyrrole is 1:1. When $R \geq 10$, only a single peak is displayed with $n_{app} = 2.5$. The plot of the current at the generated peak (as $n_{app}$) vs *R* (Figure 3b) is initially linear with slope unity and then bends going asymptotically to the limit value of 2.5. Further addition of the anion causes only a negative $E_p$-shift linear with the logarithm of the anion concentration (slope ca. 60 mV).

Thus it appears that the reaction of tosylate with the radical cation of 2,2′-bipyrrole is stoichiometric in the sense that each exchanged electron involves one tosylate anion. In other words, the tosylate anion quantitatively pairs with the radical cation. When $R > 2.5$ the dimerization (and subsequent polymerization) occurs between neutral ion pairs only. The 60 mV negative shift of $E_p$ for a 10-fold increase of the anion concentration reflects the equilibrium of ion-pair formation.

The favorable competition of tosylate over perchlorate anion is kept from the first chemical step to the final product as shown by EQCM analysis. Polymer films were produced from $10^{-2}$ M 2,2′-bipyrrole solution in the presence of 1.0 M perchlorate and $5 \times 10^{-2}$ M tosylate salt: the deposit is formed with the ratio of mass increase over polymerization charge $\Delta m/Q$ expected for ingress of tosylate salt solely.[21] Moreover the mass of the deposit decreases when the deposit is dipped in 1.0 M $NaClO_4$ aqueous solution: exchange of perchlorate for tosylate produces a 23% decrease of mass vs the 25% value expected for a complete exchange. These results indicate that the counteranion in the polymer is essentially tosylate, despite its low ratio to perchlorate (5%) in the polymer-forming solution.

The fact that tosylate is so able to promote the coupling reaction to obscure the presence of perchlorate is attributable to unability of the latter to form ion pairs,[30] which is related to its poor electron-donor properties. Therefore, it might be expected that other electron-donor anions could be as efficient as the tosylate anion in promoting polymerization. We have explored this possibility as reported in the following section.

**The "Anion Effect".** The effect of several anions, both inorganic ($Cl^-$, $Br^-$, $BF_4^-$, $PF_6^-$, $NO_3^-$) and organic ($CF_3SO_3^-$, $CH_3SO_3^-$, $PhSO_3^-$, $NO_2PhSO_3^-$) was checked following the same procedure used with the tosylate anion. The anions were selected on the basis of their nonoxidizability in the potential range used for 2,2′-bipyrrole oxidation (strongly basic anions were therefore excluded) and differ in electron-donor properties. At a first instance and in consideration of the suggestion of hydrogen-bonding formation, we have associated the electron-donor properties and the ion-pair ability of the anions to their basicity. A more sophisticated correlation between ion-pairing aptitude and hardness parameters (in terms of the HSAB formalism[31] ) would be probably more correct, but the lack of literature data do not allow this interpretation for the moment. The results are summarized in Table 1 along with the $pK_a$ values of the conjugated acids.

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**Table 1. Peak Potential Shift $\Delta E_p$ and Limiting Number of Exchanged Electrons $n_{app}$ for Oxidation of $10^{-3}$ M 2,2′-Bipyrrole in AN in the Presence of 0.1 M Tetrabutylammonium Perchlorate upon Addition of Different Anions ($C = 10^{-2}$ M) (Acidity of the Related Acids Is Given as p$K_a$ in AN)**

| anion | $\Delta E_p$/V | $n_{app}$ | p$K_a$ |
|---|---|---|---|
| $ClO_4^-$ | 0 | 1 | 1.6[32] |
| $BF_4^-$ | 0 | 1 | |
| $PF_6^-$ | 0 | 1 | |
| $Br^-$ | 0.13 | 1.2 | 5.5[33] |
| $NO_3^-$ | 0.11 | 2.5 | 8.9[33] |
| $Cl^-$ | 0.18 | 2.5 | 8.9[33] |
| $CF_3SO_3^-$ | 0 | 1 | 2.6[32] |
| $NO_2PhSO_3^-$ | 0.05 | 1.8 | 6.9[34] |
| $PhSO_3^-$ | 0.09 | 2.5 | 7.9[34] |
| $CH_3PhSO_3^-$ | 0.10 | 2.5 | 8.0[32] |
| $CH_3SO_3^-$ | 0.12 | 2.5 | 8.4[32] |
| CS[a] | 0.14 | 2.5 | |

[a] CS = (1*S*)-(+)- or (1*R*)-(−)-10-camphorsulfonate anion.

In some cases ($PF_6^-$, $CF_3SO_3^-$, and $BF_4^-$) anion addition was ineffective, but in others it induced the same effects observed with the tosylate anion, namely, a negative shift of the oxidation peak potential, an increase in $n_{app}$ (see Table 1) and easy polymerization. The latter anions shift the 2,2′-bipyrrole oxidation potential according to their basicity, thus confirming that the anion effect, though comprehensive of other electronic effects, is essentially due to basicity. From the table it appears also that a p$K_a$ value (for the conjugated acid) higher than ca. 5−6 is required to observe the favorable effect on polymerization. Figure 4 illustrates the case of the very efficient chloride anion.

The cases of $Br^-$ and $NO_2PhSO_3^-$ anions are borderline as the peak potential shift is low, the slope in the plot of $n_{app}$ vs $R$ is lower than unity (0.5 and 0.2), and the $n_{app}$ value is only 1.2 and 1.8. This indicates a lower ion-pairing and/or lower coupling rates. The nitrate anion deviates from the series of inorganic anions since from its basicity it is expected to behave like the chloride anion, but the peak shift is lower. This result evidences the abovementioned participation of effects other than basicity.

In light of these results, it is expected that the camphorsulfonate anion, which produces anisotropic polypyrrole,[15] displays the "anion effect". We have found that this anion produces the more marked peak potential shift within the series of sulfonate anions (Table 1) and that, as expected, this shift is the same independently from the stereoisomerism of the anion.

Since the peak potential shift by efficient anions is up to 0.18 V, the corresponding apparent dimerization rate constant of the 2,2′-bipyrrole radical cation is increased from $10^8$ up to $10^{17}$ $M^{-1}$ $s^{-1}$. These values are much higher than those expected for a diffusion controlled reaction ($10^{11}$ $M^{-1}$ $s^{-1}$) supporting the idea that a fast dimerization step is preceded by a ion-pairing equilibrium with a high formation constant. In fact ion-pair formation constants in aprotic solvents are commonly higher than $10^4$ $M^{-1}$.[29]

Further evidence for the intervention of ion pairing was given by measurements carried out in other media with different dielectric properties. The use of 1,2-dichloroethane ($\epsilon = 10.4$) promoted ion pairing with the ions which proved to be borderline cases in AN ($\epsilon = 36.2$). Thus the $n_{app}$ of a $10^{-3}$ M 2,2′-bipyrrole solution was increased by addition of $10^{-2}$ M bromide salt from 1.2 to 2.2 and the $E_p$ shift from 0.13 to 0.17 V.

## Conclusions

This investigation has shown that anions promoting the electrodepostion of good-quality polypyrrole in acetonitrile also lower the potential and increase the current of 2,2′-bipyrrole oxidation. The formation of an ion pair between the initially formed radical cation and the assisting anion opens a fast route to the polymer. In this view the good properties of the material are the outcome not of a solid state effect but of a faster coupling rate in solution; in other words, the assistance of the anion develops at the molecular level of the first coupling step. Of course we cannot rule out ion pairing also at the further steps to polymer and eventual structural effects but these would be a consequence of the ion-pair mechanism and not of an ill-defined and extraneous template assistance.

It is must be remarked that the anion effect, first shown by tosylate but now found for anions having similar basic properties, operates only on N-unsubstituted pyrroles, due to the intervention of the pyrrole NH moiety in directing the ion-pairing process. We have recently explained the different electrolyte-exchange properties of N-unsubstituted and -substituted polypyrroles through an analogous hydrogen-bonding intervention.[21]

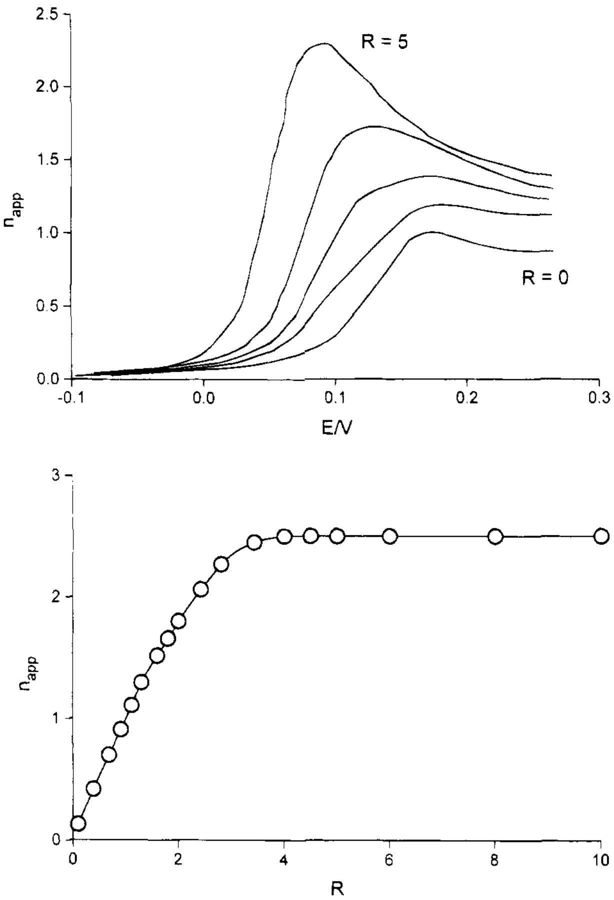

**Figure 4.** (a, top) CV (current as $n_{app}$) of 2,2′-bipyrrole $1.6 \times 10^{-3}$ M in AN in the presence of 0.1 M tetrabutylammonium perchlorate with progressive addition of tetrabutylammonium chloride in ratio $R$ to 2,2′-bipyrrole ($R$ = 0.0, 0.2, 0.4, 1.0, 2.0, 4.0). (b, bottom) Plot of $n_{app}$ for the anion induced oxidation process vs $R$ for chloride.

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