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Influence of different types of acidic dopant on the electrodeposition and properties of polyaniline films

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The effect of different types of acidic dopant namely, poly(vinyl sulfonic) (PVS), camphor sulfonic (CSA) and hydrochloric acids on the electrodeposition of polyaniline (PANI) films by cyclic voltammetry has been investigated and correlated with the morphology and properties of the polymers produced. The polymer films were studied by cyclic voltammetry, electron microscopy, u.v.–visible spectroscopy, X-ray diffraction and conductivity measurements. The nucleation step of the electrodeposition of PANI depends on the counter-ion of the dopant and significantly affects polymer growth as well as the morphology of the polymers produced. The properties of the polymeric films were also greatly influenced by the type of acid dopant used in the electrodeposition. Although all dopants used were protonic acids the conductivity of the polymer was affected by the counter-ion and could be enhanced by exposition to *m*-cresol due to secondary doping effects. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polyaniline; electrodeposition; doping)

INTRODUCTION

Conducting polymers have been prepared by different methodologies[1–13] and widely studied since their discovery. One important feature of these materials is the great dependence of the final properties on the polymer morphology and structure, which is determined during polymer synthesis and preparation. This is particularly true when one uses electrochemical techniques, since many parameters can be varied, such as, potential, charge, time, temperature, pH, ionic strength and supporting electrolyte.

Several studies[1–11] have been carried out to characterize the morphology, structure and properties of the polymers produced. One of the first studies on this subject was done by Diaz[1] who obtained a fairly smooth surface forming a continuous PANI film. Later, MacDiarmid et al.[3] showed that a fibrillar morphology is usually obtained for electrochemically prepared PANI. Wei et al.[6] observed that the presence of the dimer *p*-aminodiphenylamine increases the electrodeposition rate and produces a more uniform PANI films with a similar fibrillar morphology. Other studies[4–11] were made as an attempt to correlate different synthesis conditions to the polymer morphology and properties. It has also been found that the molecular weight of electropolymerized polyaniline can be significantly increased by the addition of neutral salts to the supporting electrolyte[11].

The possibility of synthesizing and doping polyaniline (PANI) with protonic dopants containing different types of counter-ion is one of the key factors responsible for the versatility of this class of polymers. Recently, new types of protonic acids have been used, such as polyacids and functionalized acids, to dope chemically synthesised polyanilines in order to improve selected properties, in particular, solubility, processibility and electrical conductivity[12,13]. One of the key achievements was to enable the solubilization of polyaniline, in the doped state, in organic solvents, reaching conductivity values above 100 S cm^{-1}. Several other physical studies of the properties of polyanilines prepared with different dopants can be found in the literature[14–17].

Besides all the work done in this field, a comparison between acidic dopants of different types on the growth and properties of the PANI films produced had not yet been systematically studied. In this paper the influence of different types of dopant acid used in the electrodeposition, namely polyvinylsulfonic acid (PVS, polyacid), camphorsulfonic acid (CSA, functionalized organic acid), and hydrochloric acid (inorganic acid), in the presence and absence of a neutral salt (high ionic strength), on polymer growth and on the electronic properties, morphology and structure of PANI has been investigated.

EXPERIMENTAL

Polymeric films growth

The electrodeposition of polyaniline films was performed by cyclic voltammetry onto square platinum electrodes with geometric area of 0.50 cm^2, using a sweep rate of 50 mV s^{-1}. A three-electrode cell was used with a platinum counter electrode and a hydrogen reversible electrode (HRE) as reference. The experiments were carried out at room temperature under nitrogen atmosphere, in the

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potential range from 0.1 V to 1.24 V (HRE), for the first three cycles, and then for the subsequent cycles the highest potential was limited to 1.0 V in order to minimize the overoxidation and the degradation of the polymer. The cycles were stopped at 0.6 V to ascertain the emeraldine oxidation state for all polymers produced. The electrolyte aqueous solutions, prepared with milli-Q water, consisted of 0.1 M aniline and polyvinylsulfonic acid (PVS, Aldrich), camphorsulfonic acid (CSA, Aldrich) or hydrochloric acid (HCl, Merck) at a concentration of 1.0 M. To observe the influence of the addition of salts on the film growth, 2.0 M calcium chloride ($CaCl_2$, Reagen) was added to a solution containing HCl. The electrochemical response measurements were performed using the same apparatus as used for the electrodeposition but without the presence of the monomer. The voltammetric apparatus employed was an EG and G/PARC model 273A potentiostat controlled by a personal computer and the EG and G/PARC M270 software.

Polymer characterisation

The u.v.–vis electronic absorption spectra were obtained by use of a Varian cary spectrophotometer model 2315 for the polymers dissolved in organic solvent solutions, as indicated in Results Section. Electrical conductivity measurements were performed by using the four-probe technique. X-ray diffraction patterns were taken on a Rigaku RU-200B diffractometer, using Cu k-α radiation and a Ni filter. Scanning electron micrographs of samples coated with a thin layer of gold were obtained with a Zeiss microscope model DSM 960 operated at 20 kV.

RESULTS AND DISCUSSION

Influence of the dopant on the polymer growth

The supporting electrolyte plays an important role in the growth of conducting polymer. In the case of PANI this is more intense, since the supporting electrolyte commonly used, an aqueous acidic medium, also promotes the protonic acid doping of the polymer. Furthermore, the counter-ions of the dopant remain in the final structure of the polymer. The results showing the effect of the acid dopant on the electrodeposition and properties of PANI films will be presented below. *Figure 1a*, *1b*, *1c* and *1d* show the first three cycles of the electrodeposition by cyclic voltammetry in the presence of supporting electrolytes containing different types of acid, namely PVS, CSA and HCl, as well as, in high ionic strength media, HCl + $CaCl_2$. It is interesting to note the great influence of the counter-ion, as well as the ionic strength of the media, on the initial stages of the polymer growth, mainly in:

1. the magnitude of the current in the inversion potential;
2. the potential of monomer oxidation;
3. the intensity and shape of the polymer redox peaks; and
4. the current and charge increase upon cycling.

In the first three cycles the current associated with the monomer oxidation increases for PVS (monomer oxidation current of the first cycle $I_1 = 2.0$ mA and for the third cycle $I_3 = 2.9$ mA) and HCl + $CaCl_2$ ($I_1 = 2.0$ mA, $I_3 = 6.8$ mA), whereas it decreases for CSA ($I_1 = 6.1$ mA, $I_3 = 2.6$ mA) and HCl ($I_1 = 5.1$ mA, $I_3 = 1.4$ mA) upon cycling. Such behaviour is associated with differences in the nucleation step of the film growth, which, according to Córdova et al.[18], depends on the monomer electrooxidation, oligomerisation, monomer diffusion and formation of polymer-growing sites

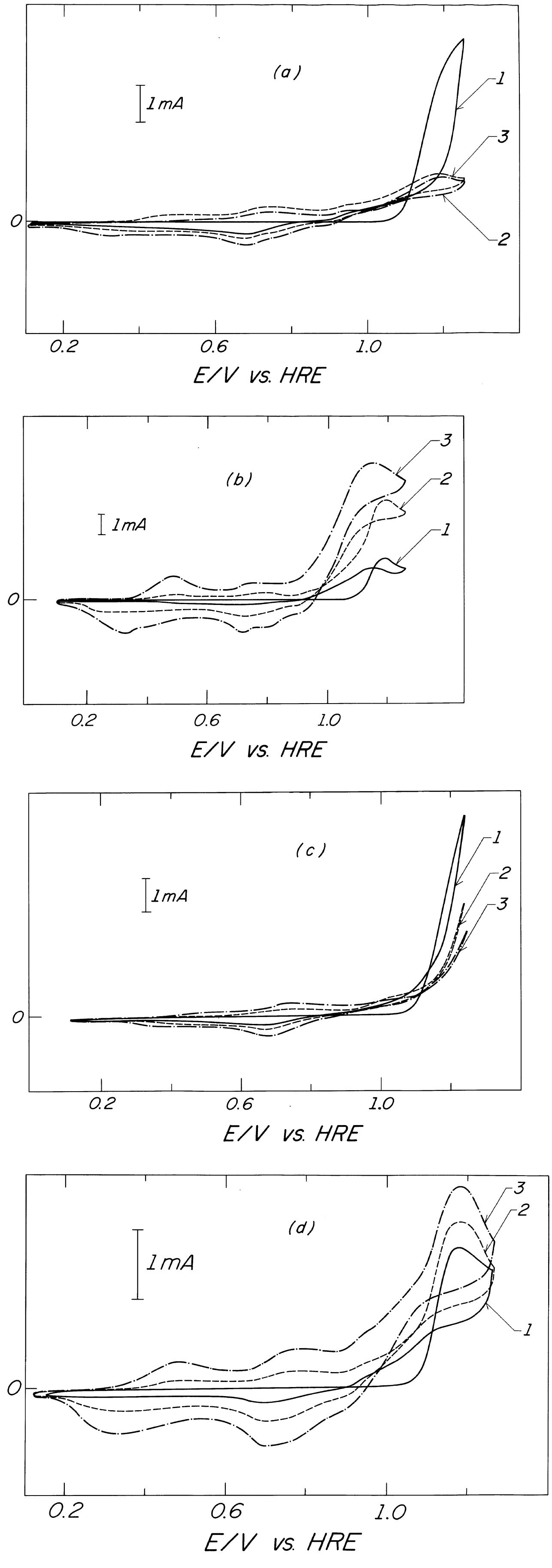

Figure 1 Cyclic voltammograms of the first three cycles for the electrodeposition of PANIs on Pt in the presence of different acidic media: (a) 1 M HCl; (b) 1 M HCl + 2 M $CaCl_2$; (c) 1 M CSA; (*d*) 1 M PVS. Aniline concentration = 0.1 M. $V = 50$ mV s^{-1}

on the electrode. These results suggest that an instantaneous nucleation occurs in the case of PVS and HCl + $CaCl_2$, for which the current in the inversion potential always increases since the first cycles upon cycling. *Figures 2 and 3* present the current in the inversion potential and the charge of the voltammogram, respectively, showing the evolution of film growth up to 25 cycles. It can be observed that films grown in PVS and HCl + $CaCl_2$ media present a fast growth in the first 10 cycles, which is consistent with the three-dimensional compact morphology observed for these systems, as will be discussed later. Differently, the films grown in HCl and CSA media (*Figure 1a* and *1c*) present a decrease of the inversion current in the first cycles indicative of progressive nucleation[18], which is consistent with the two-dimensional porous morphology. Also, in this case the evolution of film growth (*Figures 2 and 3*) showed an induction period in the first cycles, after which a considerable film growth was observed after the 8th cycles indicated by the large current increase.

Another interesting aspect is the fact that the film growth is considerably greater for the high ionic strength media, HCl + $CaCl_2$ (*Figure 2b* and *Figure 3b*), when compared with media used without salt. This was previously observed for the electrodeposition of PANI at constant potential[11], in which case a remarkable increase in the average molecular weight of the polymer was also found. The explanation given was that the reaction rate between positively charged ions was increased by the presence of dissolved salts, due to charge screening effects. So, in the present case, one can conclude that the reaction of the radical cation of aniline dimers formed and the polymer growing chains positively charged will be also increased in the presence of salts.

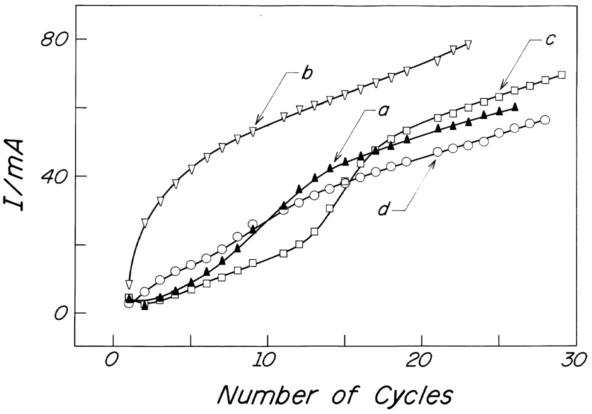

Figure 2 Current of inversion curves as a function of the number of cycles for PANIs electrodeposited in the presence of different acidic media: (a) 1 M HCl; (b) 1 M HCl + 2 M $CaCl_2$; (c) 1 M CSA; (d) 1 M PVS

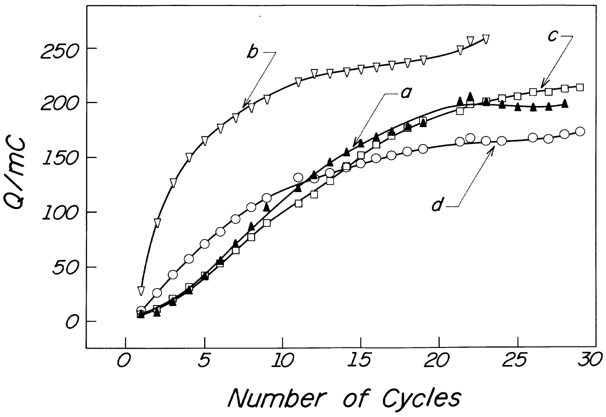

Figure 3 Charge curves as a function of the number of cycles for PANIs electrodeposited in the presence of different acidic media: (a) 1 M HCl; (b) 1 M HCl + 2 M $CaCl_2$; (c) 1 M CSA; (d) 1 M PVS

Influence of the dopant on the polymer properties

Electrochemical response. The effect of the supporting electrolyte used in the electrodeposition on the electrochemical response of the films (in 1.0 M HCl) is presented in *Figure 4*. It can be observed that all films studied present, in general, the same pattern characteristic of PANI chemically or electrochemically synthesised in common HCl media[13], i.e. two redox couples at 0.6 V and 1.10 V *versus* HRE. These redox processes have been assigned to the interconversion between the different oxidation states of polyanilines and accompanied by an electrochromic effect. The first one, at low potential values, has been associated with the interconversion between leucoemeraldine and emeraldine (accompanied by a colour change from yellow to green) and the second one, to the interconversion between emeraldine to pernigraniline (green to violet). The same electrochromic behaviour was observed for the others films obtained in this study independent of the electrolyte used.

However, an intermediate redox process appears at around 0.70 V *versus* HRE, which is dependent on the electrolyte nature. Such peaks have been associated with degradation[19–21] on the polymer structure caused by

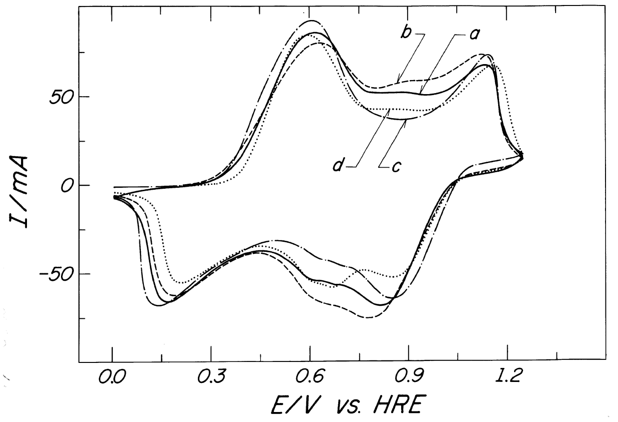

Figure 4 Electrochemical response by cyclic voltammetry in 1.0 M HCl of PANI as-electrodeposited in the presence of different acidic media: (a) 1 M HCl; (b) 1 M HCl + 2 M $CaCl_2$; (c) 1 M CSA; (d) 1 M

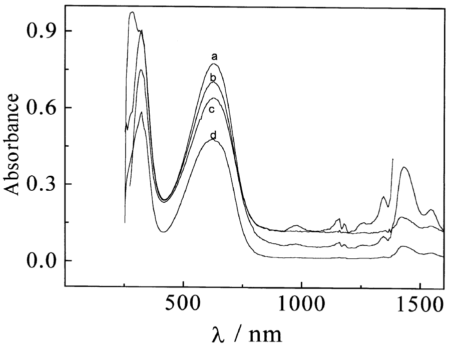

Figure 5 u.v.–vis spectra of dedoped PANIs as-electrodeposited in the presence of different acidic media: (a) HCl; (b) HCl + $CaCl_2$; (c) CSA; (*d*) PVS. Solvent used: NMP

undesirable reaction such as hydrolysis, chain scission and/or crosslinking. All voltammograms of *Figure 4* correspond to the second scan for comparison, since these redox peaks increase upon cycling. PANI films electrodeposited in the presence of high-molecular-weight dopants, i.e. CSA and PVS, present a low degradation peak, when compared to those obtained in HCl. The largest intensity of the intermediate peak was observed for the highest ionic strength media. Previous work by Genies et al.[19] suggests that the rate of side reactions increases when PANI is produced at high polymerization rates, which could also be an explanation for the present observation, being in agreement with results presented in *Figures 2 and 3*.

u.v.–vis absorption. The electronic absorption of conducting polymers is useful in investigating the oxidation and doping state of the polymer backbone. The u.v.–vis analysis of films show that after deprotonation, with 0.1 M, NH_4OH, all films present the same spectra in NMP (blue solution) characteristic of the PANI in the emeraldine base oxidation state, i.e. two bands at 300 and 635 nm (*Figure 5*) assigned respectively to π–π^* and excitonic transitions[22,23]. Such observation occurs because the dopant and its counter-ion are absent after dedoping. In the case of PVS, which is a polyacid, the dedoping process was particularly difficult, taking a long period of time, due to the polymeric nature of the counter-ion. It was also observed that for such dopant, the dedoping process practically did not occur at low pH, as expected when donnan phenomena effects are involved[24].

The electronic transition at low energy (635 nm) can be associated with charge carriers, namely polarons, which are responsible for the conductivity of this polymer. It is interesting to note that only doped PANI as-electrodeposited in CSA (*Figure 6*) was soluble in chloroform, *m*-cresol and NMP (green solutions), similar to what happens to the chemically synthesised PANI doped with CSA. Such behaviour is due to the organic and bulky nature of the counter-ion of the dopant which induces solubility[12]. Such effect does not occur when other dopants are used. Furthermore, the combination of CSA with *m*-cresol significantly affects the electronic transition and conductivity of PANI[25,26], due to a secondary doping effect, as will be discussed later. This leads to the formation of a free-carrier tail characteristic of a delocalised polaronic band, which is closely related to the electrical conductivity of polyanilines. Such band is also present but in a much less extent in the case of chloroform and NMP (*Figure 6b* and *6c*). One can also observe that an electronic absorption band around 770 nm (880 nm for *m*-cresol), indicative of localised polarons (primary doping), still remains for these solvents.

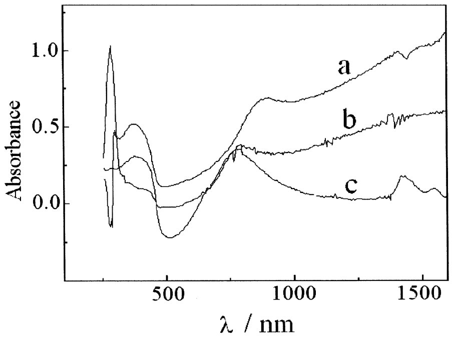

Figure 6 u.v.–vis spectra of doped PANIs as-electrodeposited in CSA medium and dissolved in: (a) *m*-cresol; (b) chloroform and (c) NMP

Electrical conductivity. The conductivity values of the films electrodeposited in the presence of different acidic dopants, before and after exposure to *m*-cresol, are presented in *Table 1*. Although in all cases the primary dopant is the protonic acid, these results show that the counter-ion plays an important role in determining the PANI conductivity. Also, previous work[25,26] showed that certain solvents such as *m*-cresol may act as a secondary dopant. Indeed, in the present case one can observe that *m*-cresol acts as a secondary dopant, promoting an increase in conductivity which is more or less intense depending on the primary dopant present. Such secondary doping processes have been assigned to a conformational change in the polymer backbone from a coil-like to a more expanded conformation. It is expected that the counter-ion of the primary dopant affects the interaction of PANI with *m*-cresol and its structure and morphology, affecting, consequently, the conductivity of the PANI film. The conductivity of the film electrodeposited in the presence of $HCl + CaCl_2$ is slightly higher than that in HCl, since a polymer with higher molecular weight is produced, as mentioned before. This effect is reflected in the conductivity after exposition to *m*-cresol, since the dopant counter-ion is the same and the salt is not incorporated in the PANI structure. Conversely, after exposition to *m*-cresol, the conductivity of PANI–CSA film is considerably higher than PANI–HCl film, although, before exposition to *m*-cresol, their conductivity are the same. Such behaviour demonstrates that the counter-ion plays an important role in determining the interaction of doped PANI with *m*-cresol. These results are consistent with those obtained by MacDiarmid[25,26] for chemically synthesised PANI. The explanation of such effect, given by Ikalla[27], is the existence of specific interactions between the sulfonic acid protonated polyaniline and the phenolic solvents. Such a concept, called molecular recognition, is a new theory applied to polyaniline. In this case, the carbonyl group in CSA forms a hydrogen bond with the hydroxyl group of *m*-cresol, whereby the phenyl ring becomes coplanar with one of the PANI rings thus enabling enhanced van der Waals interaction.

Morphology. The supporting electrolyte has a great influence on the morphology of electrodeposited PANI, as shown in *Figure 7a*, *7b*, *7c* and *7d*. It can be observed that an interconnected porous fibrillar-like morphology was obtained in the cases of HCl and CSA media. Such fibrillar morphology has been previously obtained for polyanilines prepared using several other conditions[6–10]. It is interesting to point out that the morphology is less porous and the fibrils are larger (diameter 700–1000 nm, *Figure 7c*) for the PANI obtained in CSA medium than those produced in the presence of HCl (350–450 nm, *Figure 7a*). This fibrillar-like morphology was obtained for those polymers that exhibited

Table 1 Electrical conductivity (S cm^{-1}) of polyaniline electrodeposited in the presence of different types of acid dopant, before and after exposition to *m*-cresol (24 h)

	HCl	$HCl + CaCl_2$	PVS	CSA
As-deposited	1.0	2.0	0.1	1.0
After exposure to *m*-cresol	40	80	10	120

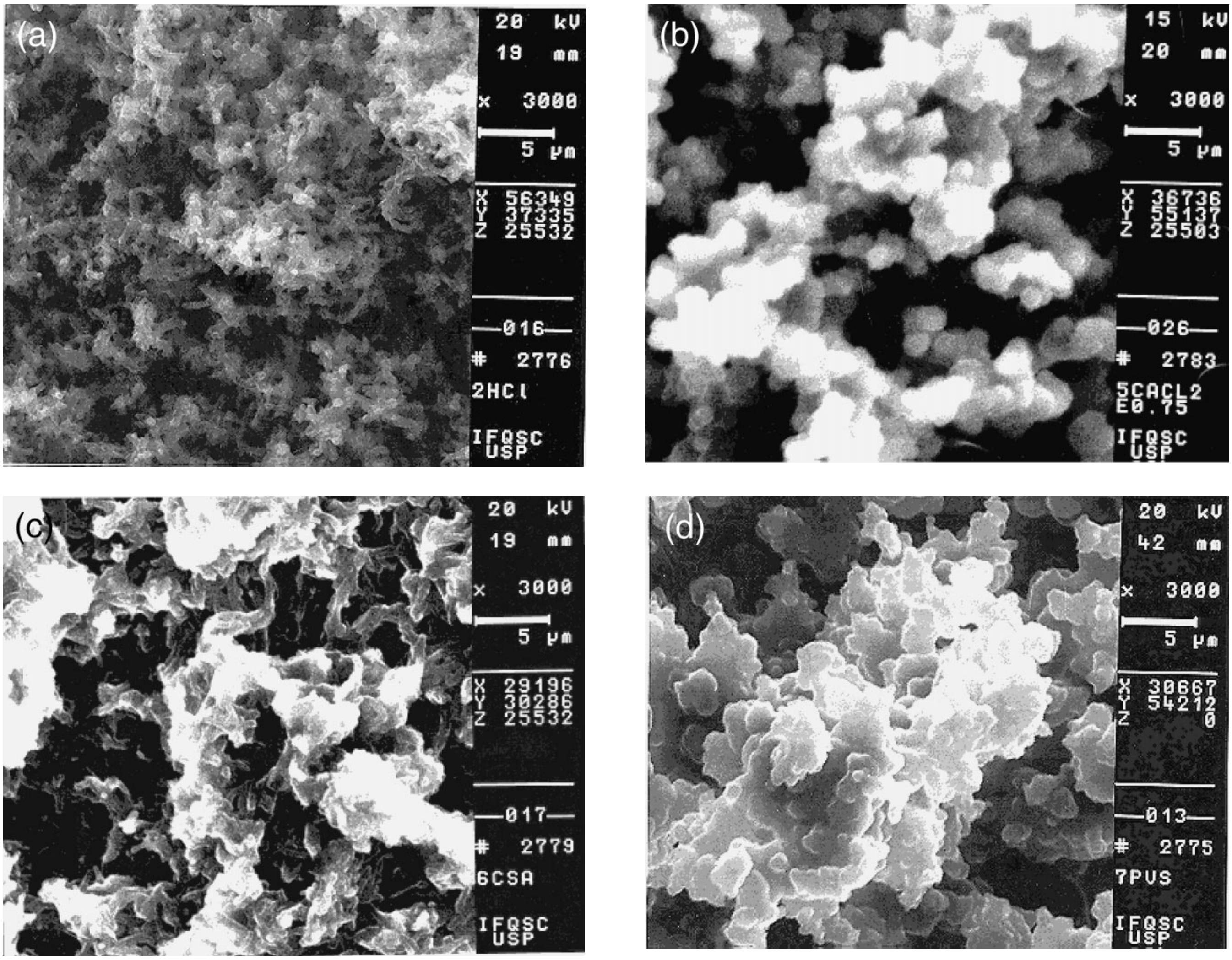

Figure 7 Scanning electron microscopy images of PANIs electrodeposited in the presence of different acidic media: (a) HCl; (b) HCl + $CaCl_2$; (c) CSA; (d) PVS. Aniline concentration = 0.5 M; $V = 50$ mV s^{-1}

a progressive nucleation. Unexpectedly, if the ionic strength of HCl medium is increased by adding a salt having the same anion, $CaCl_2$, the morphology is much more compact with a globular-like aspect. One should recall that in the latter case the polymer growth occurs by instantaneous nucleation which increases significantly in the presence of the salt. Similarly, PANI–PVS also presents a more compact morphology consistent with the instantaneous nucleation observed. These results indicate that the initial step of electrodeposition influences not only the behaviour of the polymer growth but also the final morphology of the polymer.

X-ray diffraction analysis. In the X-ray patterns shown in *Figure 8* the role of the counter-ion in determining the structure of doped PANI films can be observed. The PANI films synthesised, and therefore doped with CSA and PVS, present no well-defined crystallinity peaks in the diffractogram. This occurs since the bulky counter-ion, camphor sulfonic and poly(vinyl sulfonic) anions, located inside the PANI structure to maintain the eletroneutrality of the protonic doped polymer chains, hinders the packing of the polymer chains and consequently the crystallization. On the other hand, PANI–HCl presents a crystalline diffraction pattern ($2\theta \cong 25°$), even when synthesised in the presence of salt, which is not incorporated in the polymer structure, at

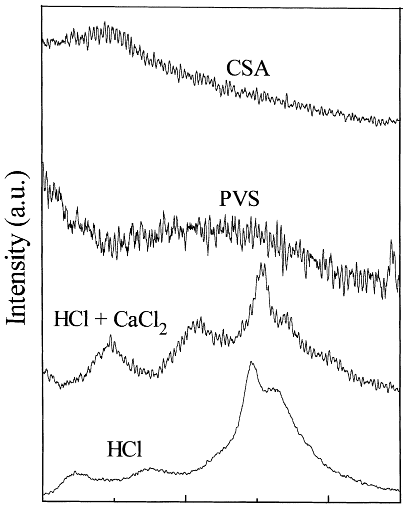

Figure 8 X-ray diffraction patterns of PANIs electrodeposited in the presence of different acidic media, as indicated

least not to a great extent. Interestingly, the crystallinity can be destroyed by undoping the polymer, and restored by redoping it with HCl. Previous studies have demonstrated[28] that doping chemically synthesised PANI with HCl leads to a more crystalline polymer than its undoped powder form, which is in agreement with our results.

CONCLUSIONS

The nucleation step of the electrodeposition of PANI depends on the counter-ion of the dopant and significantly affects the polymer growth as well as the morphology of the polymers produced. Instantaneous nucleation leads to a more compact morphology whereas progressive nucleation to a porous fibrillar-like morphology. The properties of the polymeric films are also greatly influenced by the type of acid dopant used in the electrodeposition. Solubility in the doped state was obtained only for PANI–CSA. The intermediate degradation peak observed in the polymer electrochemical response by cyclic voltammetry was less intense for PANI with larger size counter-ion dopant such as CSA and PVS. A semi-crystalline X-ray pattern was observed for PANI doped with dopants containing small size counter-ions. Although all dopants used were protonic acids the conductivity of the polymer was affected by the counter-ion and could be enhanced by exposition to *m*-cresol due to secondary doping effects.

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