Lewis Acid Doped Polyaniline: Preparation and Spectroscopic Characterization

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It is demonstrated that polyaniline can be solubilized in nitromethane via complexation with $SnCl_4$. The solutions of PANI−$SnCl_4$ complex show UV−vis−NIR spectral features distinctly different from those reported for Brönsted acid doped PANI. The removal of the solvent results in the formation of a free-standing film of $SnCl_4$-doped PANI. The solid-state complex shows the stoichiometry of $PANI(SnCl_4)_{1.0}(CH_3NO_2)_{1.0}$, which means that both types of polyaniline nitrogens (imine and amine) participate in the complexation reaction and one solvent molecule is introduced in the polymer matrix per one Lewis acid molecule. Mössbauer parameters of the complex (IS = 0.43 mm/s vs SnO_2, QS = 0.49 mm/s) are consistent with hexacoordinated Sn(IV) in an environment of nonequivalent ligands. XPS studies are in good agreement with Mössbauer spectroscopy, giving Sn3d XP spectra characteristic of $SnCl_4 \cdot 2L$ complexes. Similar complexation can be achieved in dried PANI-$(HCl)_{0.5}$; however, in this case, $SnCl_4$ is complexed only on nonprotonated nitrogen sites.

Introduction

Polyaniline belongs to the most intensively studied polymers in the last 15 years. This research effort is stimulated by the fact that emeraldine, the partially oxidized form of polyaniline, is conductive and processible. It also shows good environmental stability. Processible conductive polyaniline can be obtained from emeraldine base by its doping with an appropriately functionalized protonic acid. Such dopant must possess sufficiently strong Brönsted acid centers capable of polyaniline protonation together with suitable functional groups which, when introduced to the polymer matrix upon doping, induce the solubilization of its stiff conjugated backbone. Several processibility inducing polyaniline dopants have been proposed, for example, functionalized sulfonic acids[1,2] or phosphoric acid diesters.[3,4] Although the exact nature of protonated polyaniline solutions is still the subject of a scientific debate (are they true solutions or colloidal dispersions?),[5] it is now obvious that polyaniline can be solution processed.

As clearly seen from the above discussion, the studies of polyaniline doping have been dominated by the Brönsted acid−base chemistry. The Lewis acid−base chemistry of this polymer has been somehow neglected, and to our knowledge, no detailed studies of Lewis acid doped polyaniline have been published to date. We have undertaken such research for two important reasons:

(1) Successful solubilization of stiff backbone polymers, such as aromatic polyazomethines, via complexation with a Lewis acid ($GaCl_3$) have been reported.[6] A similar effect is expected for polyaniline, taking into account the basicity of this polymer and its similarity to aromatic polyimines. Moreover, doping with a Lewis acid should render polyaniline soluble in different types of solvents than in the case of Brönsted acid doping.

(2) The spectroscopic properties of Lewis acid doped polyaniline both in a solution and in the solid state should be significantly different from those of Brönsted acid doped polymer due to different types of chemical interactions in both systems.

In this paper we report the results on $SnCl_4$-doped polyaniline. We have selected this dopant because, in addition to Lewis acid properties, it possesses a Mössbauer nucleus ([119]Sn) that facilitates the elucidation of the doping process by Mössbauer spectroscopy.

Experimental Section

(a) Chemicals. Aniline (POCh) was distilled and stored under nitrogen prior to polymerization. Nitromethane (Aldrich) was dried with $CaCl_2$ and vacuum distilled. $SnCl_4$ (POCh), HCl (POCh), $(NH_4)_2S_2O_8$, (Aldrich), LiCl (Aldrich) were used as received.

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(5) Wessling, B. *Handbook of Organic Conductive Molecules and Polymers,* Nalwa, H. S., Ed.; Wiley & Sons: New York, 1997, Vol. 3, p 497.

(6) Yang, C. J.; Jenekhe, S. A. *Chem. Mater.* **1991**, *3*, 878.

(b) Synthesis of Polyaniline. Polyaniline was synthesized using a modification of the method described by Beadle et al.[7] In a typical synthesis, 10 mL (0.1097 mol) of aniline was dissolved in the mixture of 85 mL of 3 M HCl, 95 mL ethanol, and 16 g of LiCl. The mixture was cooled to −23 °C in a frozen CCl_4 bath. Then precooled solution containing the oxidizing agent [6.25 g (0.0274 mol) $(NH_4)_2S_2O_8$ and 8 g LiCl in 60 mL of 2 M HCl] was slowly added with vigorous stirring in order to keep the temperature constant. The polymerization was carried out at −23 °C for 1 h, then the reaction mixture was allowed to warm to room temperature. The precipitated polyaniline powder was filtered and washed with 1 M HCl until the filtrate became colorless. The resulting polyaniline hydrochloride was converted into the base form of the polymer by treatment with a 0.3 M NH_3(aq) solution. After drying to constant mass, the low molecular weight fractions were removed by extraction with chloroform. FTIR of PANI: 1587, 1495, 1378, 1301, 1215, 1162, 1103, 827 cm^{-1}. The inherent viscosity of the obtained polymer measured at 25 °C in $0.1\%_{w/w}$ solution in sulfuric acid was 1.4 dL/g. Elemental analysis of PANI base: Calcd for $C_6H_{4.5}N$: C, 79.56; H, 4.97; N, 15.47. Found: C, 76.01; H, 4.97; N, 14.71, which corresponds to the formula $C_{6.03}H_{4.68}N_{1.0}$.

(c) Doping of Polyaniline with $SnCl_4$. The general method for preparing solutions and the doping procedure can be briefly described as follows: 2 mL (17.1 mmol) of $SnCl_4$ was placed into the sidearm of the doping reactor and carefully degassed. Then 30 mL of freshly dried nitromethane was vacuum distilled to the same arm of the reactor. After distillation the sidearm was closed and 100 mg of emeraldine powder was placed into the main body of the apparatus. Polyaniline was dried by dynamic pumping in a vacuum line for 6−8 h with constant heating at 90 °C. Then the doping solution was distilled over from the sidearm to the main body of the reactor containing PANI base. The doping was carried out overnight with constant stirring. Polyaniline was quickly solubilized by the doping with the Lewis acid, which manifested itself as a deep dark blue coloration of the doping medium and the gradual disappearance of the PANI base powder.

Solutions of PANI doped with $SnCl_4$ have film forming properties. Free-standing films were obtained by evaporation of the solvent. Such films were pumped in a vacuum line till constant mass in order to remove the excess of the dopant and finally sealed off with a torch. Selected samples were additionally cryogenically pumped for 6 h after sealing.

In addition to the studies of PANI base doping with $SnCl_4$, we have tested whether protonic acid doped polyaniline, namely $PANI(HCl)_{0.45}$, can be additionally complexed with tin tetrachloride. Since $PANI(HCl)_{0.45}$ is strongly hydrated (approximately two water molecules solvate each chloride anion introduced to the polymer matrix), it is necessary to carefully dry the sample in order to avoid the hydrolysis of $SnCl_4$. The sample was dried with $SOCl_2$, which is a convenient drying agent since both the solvent and its hydrolysis products are highly volatile and can easily be removed by pumping in a vacuum line. The doping of $PANI(HCl)_{0.45}$ with tin chloride was carried out exactly in the same manner as the doping of PANI base (vide supra). Similarly as PANI base, $PANI(HCl)_{0.45}$ dissolves in $SnCl_4$/nitromethane and free-standing films can be prepared by casting from this solution.

Elemental Analysis. All samples studied were subjected to elemental analysis. C, H, and N were determined by combustion analysis. Cl was determined using Hg^{2+} in the presence of diphenylcarbazone (mercurometric determination) after Pt-catalyzed combustion of the sample in an oxygen atmosphere. Sn was determined by atomic absorption on previously mineralized samples.

UV−Vis−NIR Spectroscopy. UV−vis−NIR measurements were carried out in an atmosphere of dry argon using two types of spectrometers: Lambda 2 (Perkin-Elmer) covering the

Table 1. Elemental Analysis of $SnCl_4$ Doped Emeraldine, $(C_6H_{4.5}N)_x$

	%C	%H	%N	%Cl	%Sn
(a) Sample Pumped in Dynamic Vacuum Till Constant Mass					
calcd for $(PANI)(SnCl_4)_{1.2}(NM)_{1.0}$[a]	18.08	1.62	6.02	36.66	30.64
found	17.91	1.76	5.85	34.03	30.10
(b) Sample Additionally Cryogenically Pumped for 6 h					
calcd for $(PANI)(SnCl_4)_{1.0}(NM)_{1.0}$[a]	20.36	1.82	6.79	34.42	28.85
found	19.74	1.89	5.67	34.02	29.20

[a] PANI denotes one polyaniline structural unit involving one ring and one nitrogen, i.e. $C_6H_{4.5}N$, since in the emeraldine base form there exist equal numbers of imine and amine nitrogens (4.5 is the average number of hydrogen atoms per structural unit). NM denotes the nitromethane molecule, CH_3NO_2

spectral range of 200−1100 nm and CARY 2315 (Varian) working in the range 200−2000 nm. Solutions were tested in quartz cuvettes, whereas for the solid-state spectra, thin films of $SnCl_4$-doped PANI were deposited on quartz substrates by casting in an inert atmosphere.

XP Spectroscopy. XPS measurements were performed on an ESCALAB-210 (Fisons Instruments, VG Scientific) spectrometer with a Mg Kα X-ray source (1253.6 eV photons). The X-ray source was run at 12 kV and 20 mA. The pressure in the analysis chamber during the scans was kept below 10^{-8} Torr. Thin films of doped PANI were deposited on aluminum substrates by casting and then transferred to the spectrometer chamber. All casting and transfer operations were carried out in an inert atmosphere. The binding energies were referenced to the C1s graphite carbon peak at 284.6 eV. The spectra were deconvoluted into suitable components of a Gaussian line shape with a Lorentzian function. All fitting parameters were freely adjustable and determined for each spectrum with an iterative, least-squares routine.

Mössbauer Spectroscopy. Mössbauer spectra were recorded for free-standing films of doped PANI. The samples were loaded in a drybox in to a tight polyamide container prior to the experiment and immediately transferred to the cryostat of the spectrometer.

The spectra were recorded at 77 K in a transmission geometry using a constant acceleration spectrometer coupled to a 0.12 mcurie $^{119}mSn/CaSnO_3$ source. The transmitted 23.875 keV g radiation was detected with a pure Ge detector using a 0.05 mm Pd foil in order to filter the 24.35 keV K X-ray. The velocity scale was calibrated by a $^{57}Co/Rh$ source and α-Fe and sodium nitroprusside absorbers. The values of isomer shift (IS) are given with respect to the center of the 295 K SnO_2 spectrum.

The spectra were analyzed in a least-squares procedure by full diagonalization of the Hamiltonian describing quadrupolar interactions.[8] Although quadrupole splittings are not resolved, the computer analysis of the shape of the broadened line enables a good estimation of the quadrupolar splitting, with a full width at half-maximum of the resonant Lorentzian line equal to 0.84(2) mm/s in all cases.

Results and Discussion

Emeraldine has two types of basic sites capable of coordinating Lewis acids: amine and imine nitrogens. In the polymer chain they are present in equal numbers. Thus, the maximum amount of tin tetrachloride molecules which can be inserted in to the polymer matrix via Lewis acid−base coordination equals one molecule per repeat unit of emeraldine, i.e., one phenylene ring and one nitrogen atom. However, the results of elemen-

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Table 2. Elemental Analysis of SnCl$_4$-Doped Emeraldine Hydrochloride, [(C$_6$H$_4.5$N)(HCl)$_{0.45}$]$_x$

|	%C	%H	%N	%Cl	%Sn
calcd for (PANI)(HCl)$_{0.45}$(SnCl$_4$)$_{0.55}$(NM)$_{0.55}$[a]	27.67	2.34	7.64	33.12	23.04
found	25.48	2.59	6.555	33.15	20.90

[a] PANI denotes one polyaniline structural unit involving one ring and one nitrogen, i.e. C$_6$H$_{4.5}$N, since in the emeraldine base form there exist equal numbers of imine and amine nitrogens (4.5 is the average number of hydrogen atoms per structural unit). NM denotes the nitromethane molecule, CH$_3$NO$_2$

tal analysis show a 20 mol % excess of SnCl$_4$ in the dynamically pumped sample (see Table 1). This excess dopant must be strongly adsorbed on the surface of the sample, because the results of ESCA, which probes only the surface, show a Sn/N molar ratio of 1.65. Physically adsorbed SnCl$_4$ can, however, be removed by extended cryogenic pumping. One more feature of the elemental analysis must be pointed out. The amount of nitrogen is roughly twice higher than expected for a simple PANI(SnCl$_4$)$_{1.0}$ complex. This means that each tin tetrachloride enters the polymer matrix solvated with one nitromethane (NM) molecule. Such an assumption leads to a very good agreement between the calculated and experimentally determined analytical data (Table 1). Thus for cryogenically pumped samples, the following chemical formula can be postulated: (PANI)(SnCl$_4$)$_{1.0}$-(NM)$_{1.0}$, which means that the doped product is a simple adduct of a Lewis base and a Lewis acid. The solvation of SnCl$_4$ inserted in the polymer with one nitromethane molecule changes the coordination number of tin from 5 to 6, which is preferable for tin tetrachloride complexes.[9]

Doping of emeraldine hydrochloride with SnCl$_4$ is slightly different. In this case two types of basic sites coexist: Cl$^-$ anions, which are weaker bases, and nonprotonated nitrogens, which are stronger bases. In principle, both basic centers can coordinate tin chloride. However, the results of elemental analysis seem to indicate that only nitrogen atoms form chemical bonds with SnCl$_4$. Analytical results can be reasonably well fitted only if one assumes that tin tetrachloride dopant molecules are complementary to Cl$^-$ ions, i.e., the sum of SnCl$_4$ and Cl$^-$ must give 1 (Table 2). This assumption, based solely on analytical data, is further corroborated by the close similarity of the ^{119}Sn Mössbauer spectra of emeraldine base doped with tin tetrachloride and emeraldine hydrochloride doped with tin tetrachloride (vide infra). Again, as in the previous case, solvation of each dopant molecule by nitromethane molecule must be postulated.

Lewis acid doping of PANI base results also in a significant increase of its conductivity, which shows the value of 10^{-3} S/cm at room temperature. This value is however more than 5 orders of magnitude lower than the conductivity of the best Brönsted acid doped samples.

The verification of the exact chemical nature of the dopant and its coordination sphere in the polymer matrix is a difficult task. Among spectroscopic methods available, Mössbauer effect spectroscopy seems to be best suited for this purpose. There are several advantages to this method:
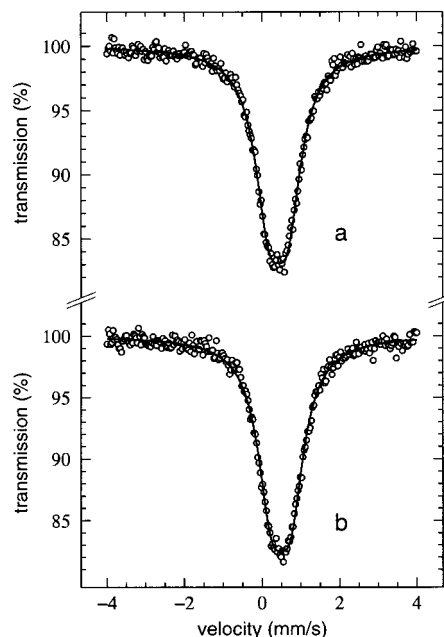
Figure 1. Mössbauer spectra registered at 78 K of (a) (PANI)-(SnCl$_4$)$_{1.0}$(CH$_3$NO$_2$)$_{1.0}$ and (b) (PANI)(HCl)$_{0.45}$(SnCl$_4$)$_{0.55}$(CH$_3$NO$_2$)$_{0.55}$.

Table 3. ^{119}Sn Mössbauer Parameters of Lewis Acid (SnCl$_4$) Doped Polyaniline Measured at 78 K

sample	IS (mm/s)[a]	QS (mm/s)[b]
(PANI)(SnCl$_4$)$_{1.0}$(NM)$_{1.0}$	0.43(2)[c]	0.49(2)
(PANI)(HCl)$_{0.45}$(SnCl$_4$)$_{0.55}$(NM)$_{0.55}$	0.49(2)	0.49(2)

[a] IS relative to SnO$_2$. [b] QS = 1/2 $e2qQ$. [c] Errors are given in parentheses, in units corresponding to the last digit of quoted values.

First, the observed isomer shifts are large with respect to the line widths of the registered peaks, which allows for a precise and unequivocal determination of the oxidation state of tin in the compound under investigation.

Second, for a given oxidation state, significant variations of the isomer shift are reported, depending on the ionicity of the tin−ligand bond and the type of the closest coordination sphere. This makes possible precise differentiation between different forms of tin in nominally the same oxidation state.

Third, although quadrupole interactions are not resolved in the case of ^{119}Sn, Mössbauer spectroscopy they contribute to the broadening and shape of the spectral lines. The analysis of these changes is analytically very useful, since it corroborates the conclusions drawn on the basis of the isomer shift values and in addition may provide information concerning the nonequivalency of the coordinated ligands.

In Figure 1a and b, Mössbauer spectra of (PANI)-(SnCl$_4$)$_{1.0}$(NM)$_{1.0}$ and (PANI)(HCl)$_{0.45}$(SnCl$_4$)$_{0.55}$(NM)$_{0.55}$ are presented, whereas the calculated Mössbauer parameters are listed in Table 3.

The value of IS in tin halide compounds depends on the coordination number. It usually decreases in a series SnX$_4$ > SnX$_5^-$ > SnX$_6^{2-}$.[10] For six-coordinated neutral tin halide complexes of the type SnX$_4$·2L (where L =

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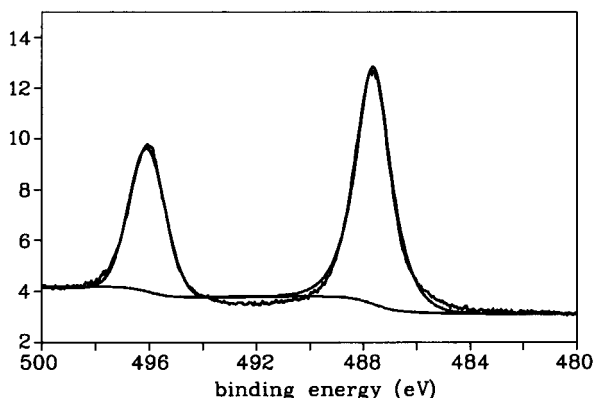
Figure 2. Sn3d XP spectrum of $PANI(SnCl_4)_{1.0}(CH_3NO_2)_{1.0}$.

Lewis base ligand), the isomer shift is even lower than in the case of SnX_6^{2-}.[11]

The IS of tetracoordinated $SnCl_4$ is 0.84 mm/s.[12,13] Thus a decrease of this Mössbauer parameter to 0.43 mm/s upon the insertion of $SnCl_4$ to polyaniline matrix strongly suggest the change in the coordination sphere of tin. The IS values measured for $(PANI)(SnCl_4)_{1.0}$-$(NM)_{1.0}$ and $(PANI)(HCl)_{0.45}(SnCl_4)_{0.55}(NM)_{0.55}$ are very close to those reported for $SnCl_4$ complexes with bidentate basic ligands such as pyridine, bipyridine, and ethylenediamine (IS = 0.42, 0.43, and 0.49 mm/s, respectively).[11] The Mössbauer parameters are therefore consistent with 6-fold coordination of tin in a polyaniline matrix.

The isomer shift values of $SnCl_4$ complexes with basic polyaniline and partially protonated polyaniline are slightly different (0.43 and 0.49 mm/s). This may be caused be a small alteration of the electron density on the complexing nitrogen atom via the protonated nitrogen atom which is adjacent to it.

The observed quadrupole interactions in both types of complexes studied (0.49 mm/s in both cases) seem to reflect the nonequivalency of the ligands coordinated by the tin chloride molecule (polymer chain via nitrogen atom and nitromethane).

Although XPS Sn spectroscopy provides less structural information than Mössbauer effect studies, it is interesting to compare the results obtained by both methods. In Figure 2. the Sn3d XP spectrum of PANI-$(SnCl_4)_{1.0}(NM)_{1.0}$ is shown. A doublet corresponding to the Sn3d3 and Sn3d5 spectrum is clearly observed. The spectrum can be interpreted as originating from Sn(IV) sites. The measured Sn3d5 binding energy (487.6 eV) is very similar to E_b determined for hexacoordinated tin complexes of the following type: $SnCl_4 \cdot 2L$ (E_b= 487.3 eV for $SnCl_4 \cdot 2Py$ and E_b = 487.1 eV for $SnCl_4 \cdot 2DMSO$, where Py = pyridine and DMSO = dimethyl sulfoxide).[14,15] Thus XPS results are in good agreement with the Mössbauer effect ones. Both methods indicate that the doping of PANI with $SnCl_4$ is purely acid–base in nature, not perturbed by side redox reactions since tin

does not change its oxidation state upon insertion in the polymer matrix. It should be however stated here that Sn core binding energies are fairly insensitive to their coordination environment. The results of Sn3d XPS can therefore be considered, at most, as supporting the Mössbauer effect spectroscopic data, which provide much more precise information. The advantage of the application of Mössbauer spectroscopy is clearly seen here. The observed Mössbauer parameters of both complexes studied in this research are similar but mesureably different, whereas the Sn3d XP spectra of these complexes are indistinguishable.

Undoped conjugated polymers usually exhibit electronic transitions in the visible range of the spectrum. Upon doping, new electronic states are created within the energy gap which give rise to electronic transitions in the near-infrared part of the spectrum. Thus UV−vis−NIR spectroscopy is a very convenient tool for studying doping-induced changes in the electronic structure of conductive polymers.

Before discussing the solution and solid-state spectra of $SnCl_4$-doped polyaniline, it is instructive to review the spectra obtained for protonic acid doped polyaniline. Protonic acid doping results in the formation of so-called polaron lattice. According to Xia et al.,[16] the UV−vis−NIR spectra reflect the degree of the delocalization of the charge carriers created upon protonic acid doping (polarons). Solution spectra obtained in inert solvents exhibit three relatively narrow absorption peaks at 360, 430, and ca. 800 nm. This last absorption peak is characteristic of localized polarons. In solvents strongly interacting with protonic acid doped polyaniline, such as *m*-cresol or hexafluoro-2-propanol,[17] instead of an 800 nm peak, a featureless increase of the absorption extending toward the NIR is recorded. This absorption tail can be treated as a spectroscopic manifestation of charge carrier (polarons) delocalization.

The insertion of $SnCl_4$ in to the polymer matrix via complexation must lower the electron density on the nitrogen atoms. Thus a partial positive charge is imposed on the polymer chain that, depending on the chain conformation, may be more or less delocalized:
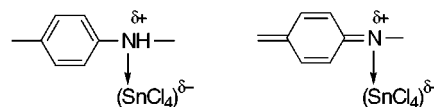
In Figure 3 the solution spectrum of $PANI(SnCl_4)_{1.0}$ in nitromethane is presented. In addition to a localized peak at 370 nm, a broad intense absorption with the maximum at ca. 1530 nm is observed. It strongly resembles the solution spectrum of $PANI(CSA)_{0.5}$ in hexafluoro-2-propanol.[17] As in the case of protonic acid doping, the broad absorption can be attributed to charge delocalization. The removal of the solvent causes a small hypsochromic shift of the maxima of both observed peaks; however, the main features of the spectrum remain the same (Figure 4a).

Solution and solid-state spectra of $(PANI)(HCl)_{0.45}$-$(SnCl_4)_{0.55}$ also show a broad peak due to charge delo-

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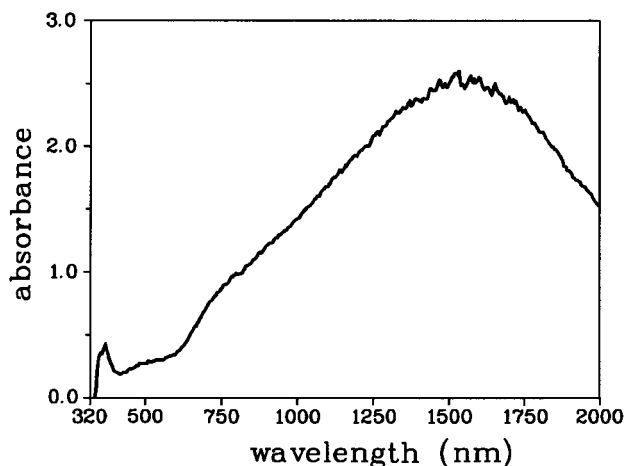
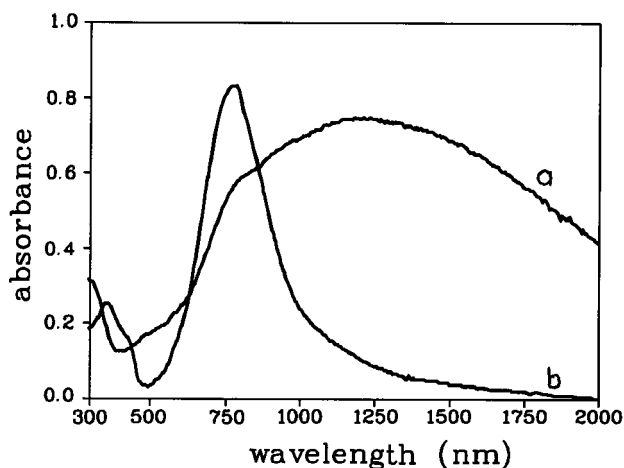**Figure 3.** Solution UV−vis−NIR spectrum of PANI(SnCl₄) in nitromethane.

Figure 4. UV−vis−NIR spectra of PANI(SnCl₄)$_{1.0}$(CH₃NO₂)$_{1.0}$ film cast from nitromethane: (a) freshly prepared film and (b) film exposed to water vapor for 10 min.

calization with the maxima at 1360 and ca. 1000 nm, respectively.

Thus, UV−vis−NIR spectra strongly suggest that partial charge is imposed on the polymer chain as a result of Lewis acid complexation. The lowering of the electron density should also be evidenced in N1s XPS spectra. Usually such complexation results in a shift of the line corresponding to the complexed nitrogen toward higher binding energies (E_b). The N1s XP spectrum of PANI base can be deconvoluted into two components, corresponding to imine (398.4 eV) and amine (399.3 eV), of approximately equal intensity.[18,19] In Figure 5 the N1s XP spectrum of (PANI)(SnCl₄)$_{1.0}$(NM)$_{1.0}$ is presented. The spectrum of (PANI)(HCl)$_{0.45}$(SnCl₄)$_{0.55}$-(NM)$_{0.55}$ is similar. In both cases, Lewis acid doping gives rise to significant changes in the observed spectral lines. The deconvolution leads to three lines at higher binding energies than those characteristic of undoped
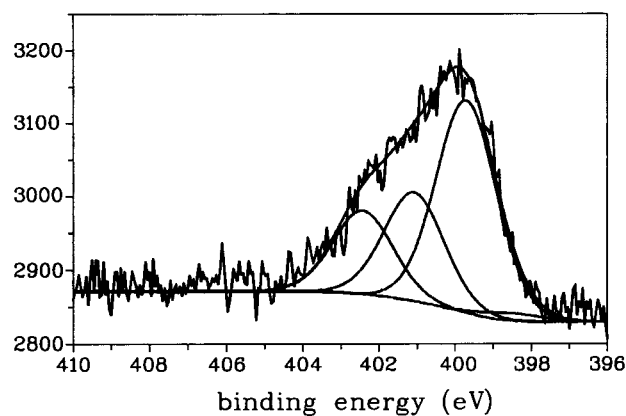

Figure 5. N1s XP spectrum of PANI(SnCl₄)$_{1.0}$(CH₃NO₂)$_{1.0}$.

PANI. This is consistent with the complexation concept.[20] The lines at 399.7 eV (51% of the total integrated intensity) and 401.0 eV (27% of integrated intensity) may originate from the imine and amine nitrogens involved in SnCl₄ complexation; they are blue-shifted by 1.5 eV with respect to the E_b of uncomplexed atoms. The origin of the third line at E_b = 402.4 eV is not clear at the present time. It closely resembles the signal observed for protonic acid doped PANI.[21,22] One is tempted to propose a trivial explanation of this phenomenon. XPS is a surface probe and PANI(SnCl₄)$_{1.0}$ is very unstable with respect to decomposition of the hydrolytic type. In such case, reaction with minute amounts of water results in the evolution of HCl, which immediately converts Lewis acid doped PANI into Brönsted acid doped PANI. Thus, at the surface of the sample regions of protonated PANI may exist. The lower intensity of the 401.0 eV line as compared to the 399.7 eV one implies that the Lewis acid complexes at amine sites are decomposed preferentially. We have studied this decomposition in greater detail. The exposure of a freshly cast film of (PANI)(SnCl₄)$_{1.0}$(NM)$_{1.0}$ to water vapors causes quick transformation of its UV−vis−NIR spectrum into the one characteristic of Brönsted acid doped PANI (compare parts a and b of Figure 4). Similarly, upon exposure to water vapors, the Mössbauer spectrum characteristic of tin in (PANI)(SnCl₄)$_{1.0}$-(NM)$_{1.0}$ complex transforms into the spectrum of SnOCl₂, which is the first product of SnCl₄ hydrolysis (IS = 0.28(2)).

Conclusions

To summarize, we have discovered a new route to polyaniline solubilization by its complexation with Lewis acids. Thus Lewis acid doped PANI is solution processible and has film-forming properties. It can also be easily transformed into Brönsted acid doped PANI.

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