Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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H. S. O. Chan[a]; T. S. A. Hor[a]; M. M. Tan[a]; K. L. Tan[b]; B. T. G. Tan[b]
[a] Department of Chemistry, National University of Singapore, Kent Ridge, Singapore, Republic of Singapore [b] Department of Physics, National University of Singapore, Kent Ridge, Singapore, Republic of Singapore

To cite this Article Chan, H. S. O. , Hor, T. S. A. , Tan, M. M. , Tan, K. L. and Tan, B. T. G.(1990) 'Characterization of Chemically Synthesized Polyanilines Treated with Tetrafluoroborate Salts: A Comparative Study', Journal of Macromolecular Science, Part A, 27: 1, 41 — 52

To link to this Article: DOI: 10.1080/00222339009351485

URL: http://dx.doi.org/10.1080/00222339009351485

J. MACROMOL. SCI.—CHEM., A27(1), pp. 41-52 (1990)

CHARACTERIZATION OF CHEMICALLY SYNTHESIZED POLYANILINES TREATED WITH TETRAFLUOROBORATE SALTS: A COMPARATIVE STUDY

H. S. O. CHAN,* T. S. A. HOR, and M. M. TAN
Department of Chemistry

K. L. TAN and B. T. G. TAN
Department of Physics

National University of Singapore
Kent Ridge, Singapore 0511, Republic of Singapore

ABSTRACT

A series of polyanilines (PANI) prepared chemically in the presence of different tetrafluoroborates ($NaBF_4$, NO_2BF_4, and Et_4NBF_4) has been characterized by x-ray photoelectron spectroscopy (XPS), infrared spectroscopy (IR), and elemental analysis. The results suggest that only PANI-NO_2BF_4 exhibits conductivity comparable to those PANI's protonated with strong acids. No significant interaction between the tetrafluoroborate salt and the polyaniline was found in the PANI-$NaBF_4$ and PANI-Et_4NBF_4 systems due to the weak hydrolytic ability of the cations. In the case of PANI-NO_2BF_4, the salt rapidly hydrolyzes to give HBF_4 with liberation of NO_2 in the aqueous polymerization medium. This can then act as an effective protonating agent in the same fashion as HCl or HBr normally used for increasing the conductivity of PANI's. We have shown that the differences between a conducting and an insulating polymer can be revealed by IR spectroscopy and XPS. Together, these techniques are very useful in assessing and screening novel chemical agents used to improve conductivity over the existing PANI's.

INTRODUCTION

In the last 10 years, polyaniline (PANI) has been reevaluated as an electrically conducting material [1-4]. This is because of its high electrical conductivity when protonated with acids, low cost compared to other conducting polymers such as polypyrrole and polyacetylene, and its relatively high air stability. It has been thoroughly studied as a novel material used in electrodes and rechargeable batteries as well as field-effect transistors [5, 6]. Polyanilines are normally prepared in an acidic aqueous solution of aniline monomer by means of electrochemical or chemical oxidative polymerization [7-9] to give the linear emeraldine polymer via a radical cation [5, 10], with the resultant formation of polymer chains consisting mainly of 1) benzoid (B) or amine and 2) nitrogen quinone (Q) or imine units. The relative amount of (B) to (Q) depends on the extent of oxidation in the polymerization. Protonation was suggested to occur preferentially on the imine nitrogen sites [11].

While there are reports of the use of a number of tetrafluoroborates as counteranions or as supporting electrolytes in the electrochemical preparation of PANI [12-14], they are seldom cited in connection with chemically prepared PANI's. Most of the chemical polymerizations are conducted in the presence of a strong protonic acid, such as HCl or HBr, to give the corresponding polyaniline-hydrohalide salt (PANI-salt) with conductivity in the region of 5 to 30 S/cm, depending on the acid used. The very corrosive nature of these protonic acids, however, makes the PANI-salt undesirable for certain applications in computers and microelectronics, especially at elevated temperatures where loss of HCl and HBr has been reported [15].

In this communication we report our preliminary results obtained on chemically synthesized polyanilines treated with Et_4NBF_4, $NaBF_4$, or NO_2BF_4. As these polymers are insoluble, solid-state techniques such as XPS [16-19], TG/DTG/DSC [15, 20], IR spectroscopy [13, 21], and elemental analysis [22] have been employed to compare the performance of the PANI-salts prepared. The intrinsic polyaniline (PANI-base) and the very conducting polyaniline hydrochloride (PANI-HCl) prepared previously [19] have also been included for comparison. An attempt was made to study the interaction between the tetrafluoroborate anions and the neutral polyaniline as well as the electronic and chemical structure of the polyaniline salt.

EXPERIMENTAL

Materials

The aniline used was purchased from Aldrich Chemical Co. It was distilled and stored under nitrogen in the dark prior to polymerization. The ammonium persulfate was used as purchased from B.D.H. Nitronium tetrafluoroborate (NO_2BF_4) and sodium tetrafluoroborate ($NaBF_4$) were purchased from Fluka Chemie AG. Tetraethylammonium fluoroborate (Et_4NBF_4) was obtained from Merck. The tetrafluoroborates were used as purchased.

Synthesis of Polyanilines

The chemical procedures employed in the present synthesis of PANI's were based, in modified form, on previously described procedures by Armes and Miller [23]. In the synthesis of PANI-$NaBF_4$, PANI-NO_2BF_4, and PANI-Et_4NBF_4 salts, 1 g aniline (~10.7 mmol) was dissolved in 150 mL of a solution of 2.4417 g $(NH_4)_2S_2O_8$ (~10.7 mmol) containing 0.07 mmol/L of the respective tetrafluoroborate. Polymerization was carried out at room temperature (~28°C) for about 10 h, after which the polymer powder obtained was filtered, washed with a small amount of the corresponding tetrafluoroborate solution, and dried in a desiccator with phosphorus pentoxide (P_2O_5). Interestingly, during the preparation of PANI-NO_2BF_4, brown fumes were observed when NO_2BF_4 was in contact with water. NO_2BF_4 is also by far the least thermally stable of the three tetrafluoroborates, as shown by thermogravimetry.

Elemental Analysis

Elemental analysis was conducted by the Microanalytical Laboratory using a 240C Perkin-Elmer C,H,N analyzer. The fluorine content was measured by the oxygen-bomb flask method and the boron by induced coupled plasma.

Electrical Conductivity

Conductivity measurements were made with a four-point probe connected to a Keithley voltmeter constant-current source system. The samples tested were in the form of compacted disk pellets, 12.7 mm in diameter and ~1 mm thick.

X-Ray Photoelectron Spectroscopy

The vacuum-dried powdered sample was mounted on a standard VG sample holder by using double-sided Scotch tape. Core level spectra were obtained on a VG ESCA/SIMSLAB MKII spectrometer using MgK_α radiation. The binding energies are referenced to the hydrocarbon component in the C_{1s} envelope, defined to be 285.0 eV in order to compensate for the surface charging effects, especially noticeable in the case of less conducting polymers. The surface elemental stoichiometries were obtained from peak area ratios corrected with the appropriate experimentally determined sensitivity factor (based on the sensitivity factor of 1.00 for carbon). An error of ±10% may be expected in the surface stoichiometries.

Infrared Spectroscopy

Infrared spectra were recorded on a Perkin-Elmer 1710 FTIR spectrometer. The spectra were measured at room temperature by scanning from 4000 to 500 cm^{-1} of pressed KBr disks in which the samples were dispersed.

RESULTS AND DISCUSSION

Elemental Analysis

The elemental analysis, electrical conductivity, and XPS stoichiometries are given in Table 1. The structure of the polyaniline chain is confirmed by the C:H:N atomic ratio of about 6:5:1 in all cases, as found by elemental analysis. In general, the higher carbon and lower boron and fluorine content depicted by XPS can be attributed to hydrocarbon contamination at the surface during the XPS analysis. This would have the greatest retarding effect on the least sensitive boron to give a very much lower value than in the bulk. Both the elemental analysis and XPS data

TABLE 1. Elemental Analysis, XPS Stoichiometry, and Conductivity for the Three PANI-Salts

Sample	Elemental analysis	XPS stoichiometries	Conductivity, S/cm
PANI-$NaBF_4$	$C_6H_{4.7}N_1B_{0.075}F_{0.28}$	$C_{6.5}N_1B_{0.057}F_{0.32}$	$<10^{-6}$
PANI-NO_2BF_4	$C_{6.2}H_{4.73}N_1B_{0.35}F_{1.26}$	$C_{7.41}N_1B_{0.21}F_{1.1}$	1.4×10^0
PANI-Et_4NBF_4	$C_{6.0}H_{5.0}N_1B_{0.12}F_{0.40}$	$C_{9.62}N_1B_{0.09}F_{0.30}$	$<10^{-6}$

show that the highest content of boron and fluorine was found in PANI-NO_2BF_4. This suggests that PANI-NO_2BF_4 salt is the most readily formed of the three samples, which explains the high conductivity exhibited by this polymer.

IR Spectroscopy

In Figs. 1 and 2 the IR spectra of the fluoroborate systems are compared with those of the previously prepared PANI-base (insulator) and PANI-HCl ($\sigma \approx 15$ S/cm). In the N–H stretching region from 3500 to 3100 cm^{-1} and the C–H stretching region from 3100 to 2800 cm^{-1}, little information can be gained as the differences between samples are small.

The features in the 1600 to 1450 cm^{-1} region of aromatic ring breathing, N–H deformation, and C=N stretching are more interesting. Jing et al. [24] assigned the band at 1510 cm^{-1} mainly to benzoid ring (B) stretching in PANI. The band at about 1587 cm^{-1} has been related to that of a nitrogen quinone (Q) [25]. In the PANI-HCl and PANI-NO_2BF_4 spectra (Fig. 2), a shift to about 1570 and 1490 cm^{-1} was detected for these two peaks, compared to the PANI-base. This is in accordance with observations by other workers [13, 21, 24]. Interestingly, the nonconductive PANI-$NaBF_4$ and PANI-Et_4NBF_4 show no such shifts (Fig. 1). All the samples exhibit the two bands at around 1313 and 1250 cm^{-1}, which can be attributed to the C–N stretching of the QBB or BBQ and BBB arrangement of the aromatic amines.

In the region of in-plane and out-of-plane bending of C–H bonds on aromatic rings from 1220 to 500 cm^{-1}, a significant difference can be observed for the conductive and nonconductive samples. The two separate bands observed for the three nonconductive samples at about 1160 and 1050 cm^{-1} are due to the intrinsic PANI-base structure. The 1160 cm^{-1}

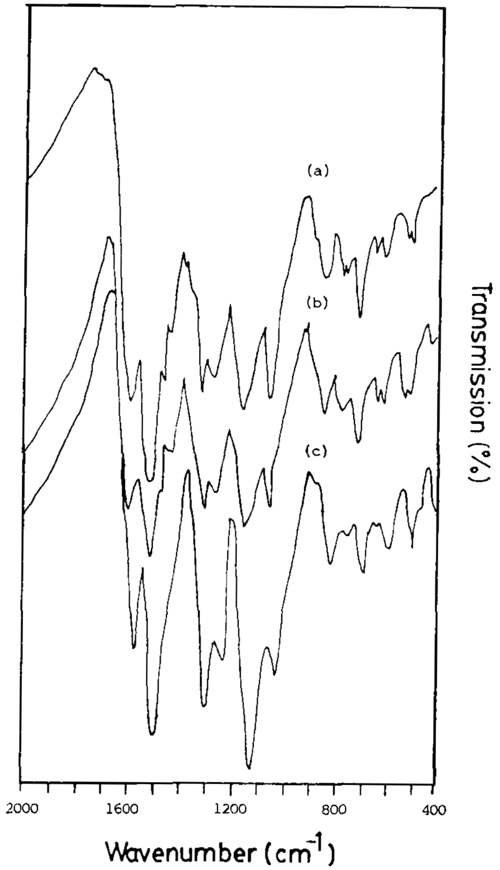

FIG. 1. IR spectra for (a) PANI-$NaBF_4$, (b) PANI-Et_4NBF_4, and (c) PANI-base.

band was referred to by MacDiarmid et al. [26] as a measure of the degree of delocalization of electrons in the intrinsic PANI-base chain. For the conductive samples, the band at 1135 cm^{-1} can be assigned to the PANI-salt structure, similar to that reported for PANI treated with I_2 [24]. This is believed to be the vibrational mode of B−NH−Q or B−N$^+$H−B, which is formed in protonation reactions. This band is very intense and broad for PANI-HCl and PANI-NO_2BF_4, which may be attributed to the existence of the positive charge and the distribution of the dihedral angle between the B and Q rings [27].

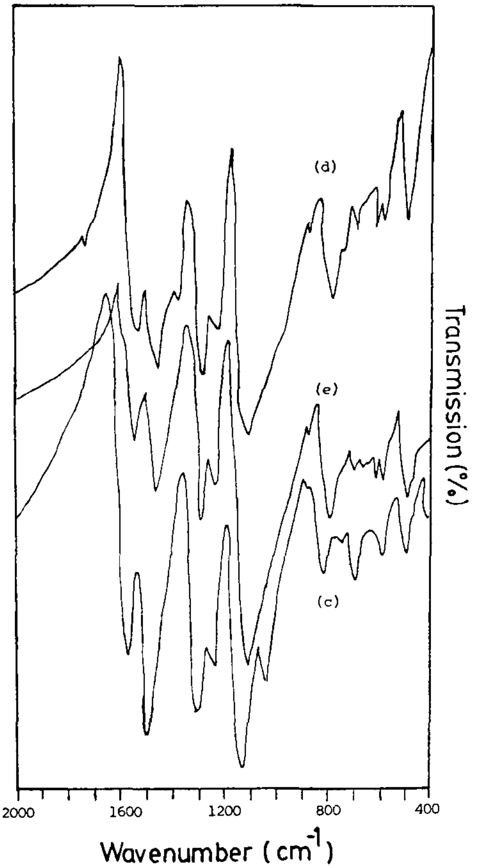

FIG. 2. IR spectra for (d) PANI-HCl, (e) PANI-NO_2BF_4, and (c) PANI-base.

The IR results obtained in this work indicate that protonation of the intrinsic PANI-base occurred to a significant extent only in the PANI-HCl prepared previously and PANI-NO_2BF_4, both of which bear a close resemblance to the highly conductive PANI-HCl reported in the literature [24, 26]. This is in agreement with the elemental analysis, conductivity, and XPS data.

X-Ray Photoelectron Spectroscopy

The N_{1s} spectra for the three PANI-salts are given in Figs. 3, 4, and 5. The high-binding-energy components have been assigned to positively charged nitrogen (N^+) in the N_{1s} envelope [18, 28]. The area percent of N^+ has been used to measure the degree of protonation of PANI's treated with protonic acids [19]. The degree of protonation has been shown to correlate proportionally with the conductivity of PANI's [22]. Table 2 gives a summary of the positions of the N_{1s} component, the percentage of N^+ (degree of protonation), the peak position of the C_{1s} envelope for the present samples, and for the PANI-HCl prepared in previous work, for comparison.

The N^+ percentages indicate that in PANI-NO_2BF_4, about 32% of the nitrogen atoms are charged, and these are likely to be associated with BF_4^- counterions to maintain overall neutrality. Interestingly, the degree of protonation for PANI-HCl is also around 30%. Chiang and MacDiarmid [4] showed that high conductivity can be attained at protonation levels of 25% and above. For PANI-$NaBF_4$, the strong ionic nature of the cation makes it unsuitable as an electron acceptor involving primarily covalent interaction with the nitrogen along the polymer chain. The conventional protonation reaction to form conducting PANI-hydrohalide salt involves covalent interactions between the protonating agent and the PANI-base.

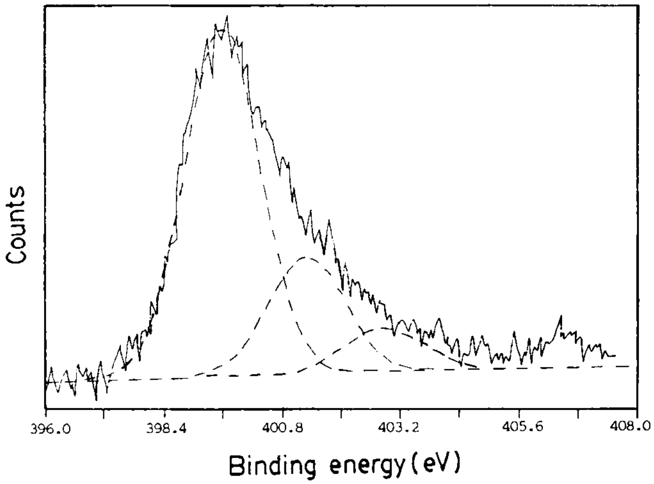

FIG. 3. Curve-fitted N_{1s} spectrum for PANI-$NaBF_4$.

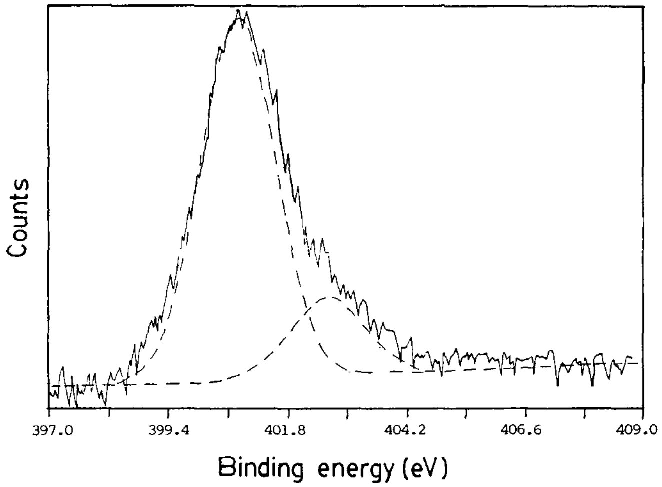

FIG. 4. Curve-fitted N_{1s} spectrum for PANI-Et_4NBF_4.

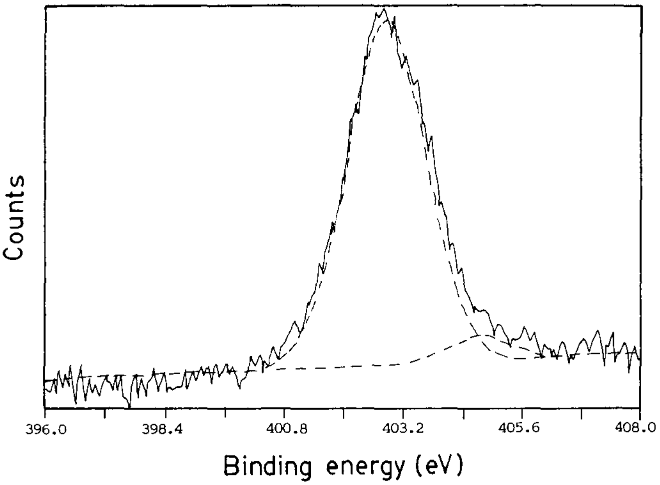

FIG. 5. Curve-fitted N_{1s} spectrum for PANI-NO_2BF_4.

TABLE 2. XPS Results for the Three PANI-BF_4 Salts

Sample	C_{1s} peak position, eV	N_{1s} binding energy, eV	Fraction of N^+
PANI-NO_2BF_4	285.0	399.6, 401.3, 402.8	32.0%
PANI-$NaBF_4$	288.4	402.9, 404.6	6.5%
PANI-Et_4NBF_4	286.2	400.7, 402.5	16.5%
PANI-HCl	285.0	399.7, 401.4, 403.7	30.0%

Although $NaBF_4$ readily dissociates in H_2O, its inability to hydrolyze H_2O makes it unsuitable as a protonating agent. Most of it would have been washed off by the H_2O during the filtering step. The smaller amount of N^+ atoms calculated and the very low conductivity and elemental analysis figures for boron and fluorine for the polymer support this interpretation.

In the case of PANI-Et_4NBF_4, the high-binding-energy component corresponds to the positively charged nitrogen of the ammonium cation and is not due to protonation of the nitrogen atoms in the polymer. The low conductivity found for PANI-Et_4NBF_4 suggests a low degree of interaction between the polymer and the fluoroborate salt, for reasons similar to those outline for $NaBF_4$. The lower solubility compared to $NaBF_4$ means higher retention of the species in the polymer matrix to give a higher boron and fluorine figure in Table 1. The key difference between the three reaction conditions is the change in pH produced by the nitronium salt.

The peak position of the C_{1s} envelope is useful in providing information on the conductivity of the present series of polymers. For PANI-NO_2BF_4 and PANI-HCl this peak is close to 285 eV, indicative of very little sample charging, typical of a conductor. The nonconductive PANI-$NaBF_4$ and PANI-Et_4NBF_4 induced significant amounts of sample charging to increase the binding energy to about 288–289 eV, as shown in Table 2.

CONCLUSIONS

While a number of chemical compounds containing the tetraflouroborate anion are used in electrochemically prepared PANI, the choice is limited in chemically prepared PANI. XPS, IR spectroscopy, and elemental analysis results obtained in this work show that only the PANI treated with NO_2BF_4 exhibits electrical conductivity comparable to those protonated with a conventional strong acid, such as HCl. We have attributed this to *in-situ* decomposition of NO_2BF_4 and formation of HBF_4, which is the effective species in protonating the nitrogen in the polymer chain, an important step toward electrical conductivity. The study has also shown that the performance of a potential protonating agent can be assessed and screened for use in PANI systems by the techniques discussed.

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Received October 21, 1988
Revision received December 19, 1988