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Preparation and characterization of fully oxidized form of polyaniline

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Summary

The oxidation state of polyaniline (PANI) can be varied from the fully reduced leucoemeraldine base (LEB) to the half oxidized emeraldine base (EB) and to the fully oxidized form pernigraniline base (PNB). In this work, the synthesis and properties of the highest oxidation state of polyaniline, pernigraniline, in the base as well as the corresponding salt form are discussed.

Introduction

Throughout the literature, the PNB and LEB forms are considered to be insulating, whereas the half oxidized form, after protonation, has been found to be conducting [1-3]. The PNB form has recently attracted significant interest because it is the only known polymer besides polyacetylene that is known to exhibit a two-fold degenerate ground state [4-6].

A preparation method for the fully oxidized PNB form was first suggested by Green and Woodhead [7]. Early work of these authors reports that the fully oxidized state of polyaniline is rather unstable and that it cannot be isolated in the dry form. However, in 1990, MacDiarmid et al. have reported the first synthesis and isolation of PNB as an analytically pure powder, and demonstrated the production of free-standing, flexible films of this material [8]. The method reported by these authors for the synthesis of pernigraniline base is based on the controlled oxidation of EB with m-chloroperbenzoic acid [8]. Leclerc et al. [9] were the first to show that the fully oxidized PANI can exist in two different forms, i.e., the uncharged pernigraniline base (PNB), and the protonated pernigraniline salt (PNS), as shown in Figure 1.

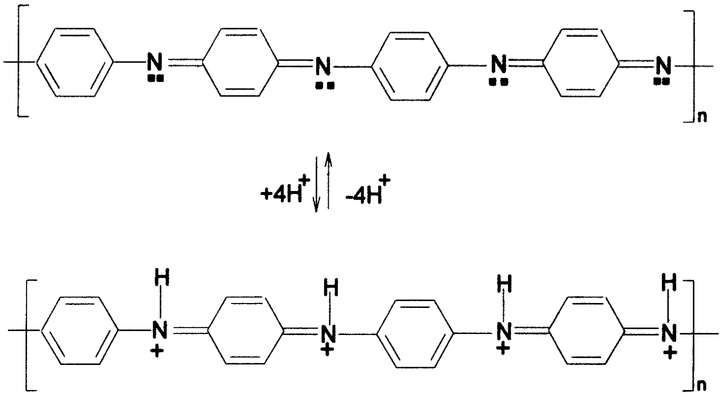

Figure 1 **Molecular structures of pernigraniline base (top) and pernigraniline salt (bottom) forms of polyaniline.**

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Based on the assumption that pernigraniline can be transformed in a stable protonated form, we presumed that its conductivity should be significantly higher than that of emeraldine base because of a significantly higher charge carrier density. Consequently we have investigated the preparation of a chemically stable, protonated pernigraniline form. We have devoted significant efforts to the qualitative investigation of the new materials prepared in this work by spectroscopic methods, employing FTIR and UV absorption spectroscopy as primary tools. In addition, we report our first measurements of the electric conductivity of these protonated pernigraniline salts.

It is important to note already here that an important postulate was considered for all experimental aspects of the present work, namely that H_2O and other nucleophiles have a pronounced effect on the chemical integrity of PNB and PNS and, as will be shown later, lead to the chemical degradation of these polymers.

Experimental Section

Materials and methods

All chemicals were obtained from Fluka and used as received unless otherwise indicated. EB was obtained from Neste Chemicals and dried at room temperature under vacuum for 24 h prior to use for all experiments. m-Chloroperbenzoic acid was purified according to reference [10]. Camphorsulfonic acid (CSA) was dried at 50°C under vacuum of 10 mbar for 24 h. Formic acid was obtained from Aldrich and was purified by fractional distillation. All solvents used were of spectrograde quality and experiments were done under N_2 atmosphere. Pernigraniline base was synthesized according to the previously published method [8].

Protonation of pernigraniline base

Camphorsulfonic acid (CSA) and methanesulfonic acid (MSA) were used as protonating agents for PNB; formic acid, hexafluoroisopropanol, m-cresol, and NMP were used as solvents. Pre-dried PNB powder was mixed with CSA in a nitrogen atmospheric glove box using an agate mortar with the following molar ratios of CSA per aniline unit (CSA/PhN): 0.25, 0.5, 1.0 (these mixtures are in the following abbreviated as $PN.CSA_x$, where x = CSA/phN). In order to produce solutions, these mixtures were subsequently added to the respective solvent and magnetically stirred for 48 h to yield a 2% (w/w) salt solution. The resulting solutions of protonated pernigraniline were filtered through a 1µm Teflon® filter. Solutions based on emeraldine base and CSA ($EB.CSA_x$ where x is the molar ratio of CSA/PhN of 0.25, 0.5, 1.0) were also prepared using the above method.

$PN.CSA_x$ as well as $EB.CSA_x$ films prepared from formic acid solutions were cast onto glass substrates and dried under a vacuum of 10^{-4} mbar at room temperature for approximately 48 h; films prepared from m-cresol solutions were dried in air at 60°C for 24 h on a hot plate. These films could be easily peeled off the glass substrate. Films cast from hexafluoroisopropanol were covered by a Petri-dish in order to allow for a slow evaporation of the solvent at room temperature.

Deprotonation process

Several methods were used to deprotonate the $PN.CSA_{1.0}$ and $PN.MSA_{1.0}$.

* $PN.CSA_{1.0}$ was treated with pyridine for 24 h.

- PN.$CSA_{1.0}$ was treated with pyridine for 24 h and subsequently washed with ethanol.
- PN.$MSA_{1.0}$ was treated with NH_4OH for 24 h and subsequently washed with ethanol.

After the deprotonation process, all powder samples were dried at room temperature under vacuum (10^{-4} mbar) for 24 h.

DC electrical conductivity was measured by the standard four-point method. Since PN-salt films are hydroscopic, films were stored under dynamic vacuum until the conductivity measurements. The thickness of the films was measured by a Tencor Instruments (Alpha step 200) profilometer. FTIR spectra were performed using a Bruker IFS66v on the press pellets of the sample in KBr. The spectra were based on over 32 scans over the range of 400 – 4000 cm^{-1}. A Perkin Elmer Lambda 900 spectrometer was used to collect the absorption spectra of solutions in the wavelength range of 280 to 900 nm with a scan speed of typically 375 nm/min. Prior to spectroscopic measurements, all solutions were diluted with an appropriate amount of solvent in order to adjust the absorption of the sample to a level of between 0 and 2. Absorption spectra were obtained using quartz cuvettes and pure solvents were used as the reference.

Results and Discussion

Characterization of PNB

FTIR spectroscopy has been previously used to measure qualitatively the various intrinsic oxidation states of PANI [12], and was also applied in the present work. IR spectra display several characteristic peaks that are associated with the reduced, half oxidized, and fully oxidized form of PANI respectively. Figure 2 shows the FTIR transmission spectra of the PNB prepared in this work, in comparison with the one of EB, which was used as the starting material.

Major differences in the spectra of PNB and EB are observed in the region between 1000 cm^{-1} and 1600 cm^{-1}. The IR transmission spectrum of PNB exhibits a high intensity ratio of the peaks at 1600 cm^{-1}/1500 cm^{-1}, consistent with the presence of predominantly quinoid units [8,13,14]. The same feature was observed previously for oxidized aniline oligomers [12,13]. Earlier studies have also suggested that the IR absorption modes at about 1500 cm^{-1} and 1600 cm^{-1} are associated with aromatic ring stretching. Tang et al. [17] have assigned the 1600 cm^{-1} peak to ring stretching of N=Q=N (Q-quinoid ring) and the 1500 cm^{-1} peak to the ring stretching of N-B-N (B-benzenoid ring). Furthermore, these two bands in PNB are slightly shifted (about 10 cm^{-1}) to lower frequency when compared to EB. A similar shift has been previously observed for the aniline oligomer of B-N=Q=N-B-N=Q=NH.

Another informative peak in the IR spectra of PNB is the weak C-N stretching absorption of the QB_cQ (B_c-cis benzenoid unit) units at about 1380 cm^{-1}. Leucoemeraldine does not absorb at this frequency, in contrast to the emeraldine and pernigraniline forms. However, this absorption in PNB is split into two peaks at 1370 cm^{-1} and 1411 cm^{-1}; additionally a broad band centered at 1315 cm^{-1} appears. These peaks can be assigned to a combination of several stretching forms of C-N bonds in QB_cQ, QBB and BBQ.

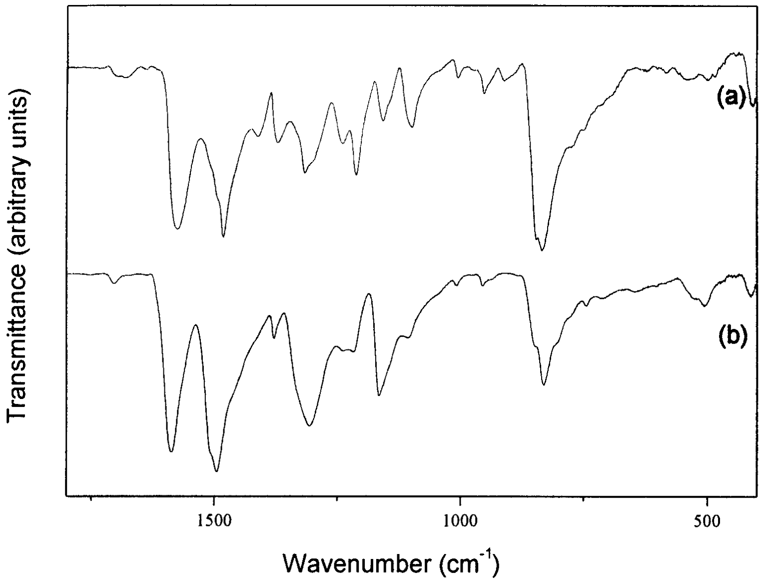

Figure 2 FTIR transmission spectra of (a) PNB and (b) EB in KBr pellets.

A peak at 1164 cm^{-1}, which is interpreted as a mode of N=Q=N stretching [18] remains unchanged in PNB spectrum. A new peak appears at around 1088 cm^{-1} that is interpreted as the C-H in plane bending of the ring [17]. In summary, the spectrum of the PNB prepared in the present work is in good agreement with the one reported by Epstein et al. [8] and also compares well with that of the fully oxidized analogous octamer [15,16].

The optical absorption spectra of freshly prepared PNB and EB in NMP solutions are shown in Figure 3. The spectrum of PNB shows absorption bands centered around 545 nm (2.2 eV) and 327 nm (3.8 eV) and an additional transition appearing below 280 nm (4.4 eV). For EB, only two peaks are observed at 637 nm (1.9 eV) and 327 nm (3.8 eV). These values are in close agreement with the results of MacDiarmid et al. (530 nm, 327 and 283 nm) [19] and with the fully oxidized capped-octaaniline (COA) octamer (525 nm and 320 nm) [16].

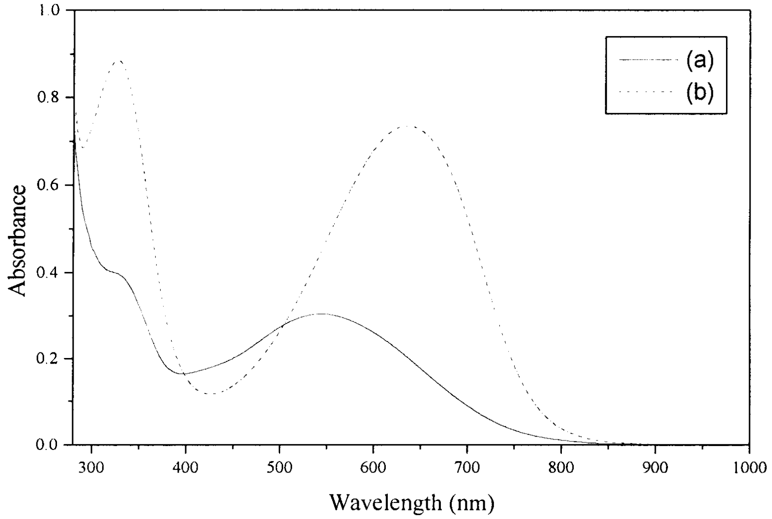

Figure 3 UV/Vis spectra of (a) PNB and (b) EB in NMP solution.

Conductivity of protonated pernigraniline

Fully protonated EB ($EB.CSA_{0.5}$) and PN ($PN.CSA_{1.0}$) films prepared from HFIP were used to measure DC conductivities. $PN.CSA_{1.0}$ was found to exhibit a significant conductivity (0.01 S/cm), while $EB.CSA_{0.5}$ showed a conductivity of 47 S/cm. Fully protonated PN films prepared from m-cresol showed a significantly higher conductivity (28 S/cm) than the $PN.CSA_{1.0}$ films prepared from HFIP and roughly matches the conductivity of protonated EB films prepared from m-cresol (107 S/cm). However, both films are green and exhibited identical absorption spectra, characteristic of the protonated EB form. These results suggest that PN.CSA 1.0 actually reacts with m-cresol since processing from m-cresol does not result in the protonated form of PN, but instead a protonated derivative of EB is formed.

However, when cast from formic acid, $PN.CSA_{1.0}$ films exhibit one order of magnitude higher conductivity than that of the protonated EB equivalents (Table 1); the conductivity of the latter is in agreement with data published for similar samples [20]. We also noted that PNB and PN salt films prepared from formic acid have a semicrystalline character, as clearly evidenced by the wide angle X-ray diffractograms of these films. Table 1 summarizes the room temperature electrical conductivity data for protonated forms of EB and PN.

Table 1 Conductivity of films of EB and PN protonated with CSA; all films prepared from formic acid solutions.

CSA/PhN molar ratio	DC conductivity (S/cm)	
x	$EB.CSA_x$	$PN.CSA_x$
0.25	0.004	0.006
0.5	0.038	0.02
1.0	0.004	0.23

It should be pointed out that, as previously reported [21], the conditions of film preparation strongly affect the final conductivity. In accordance with the work of others [13,22] we observed that protonated PN is unstable under ambient conditions and seems to undergo chemical conversion. However, it is presently not clear whether the latter form is another oxidation state or some degradation of the polymer. The conductivity of those degraded films is somewhat lower than that of protonated emeraldine salt, and their optical absorption spectra are similar to those of the emeraldine salt indicating that the mechanism of this decomposition might in fact include the reduction to the emeraldine form. We also should note that solutions of $PN.CSA_{1.0}$ in formic acid exhibited a limited stability. We observed a color change from blue to green when such solutions were kept for a time of about 12 h and interpret this color change with the reduction of the PN salt to EB. The limited stability of these PN solutions also stifled the casting of PN films with a thickness of more than about 20 µm, due to the slow evaporation of the solvent.

Deprotonation process

In order to investigate the stability of the pernigraniline upon doping with CSA, PN.CSA salts were neutralized under different conditions and the recovered material was analyzed and compared with the original PNB material. When the PN.CSA$_{1.0}$ was treated with pyridine, it deprotonated to the PNB form, as evidenced by the UV/Vis absorption spectra shown in Fig.4.

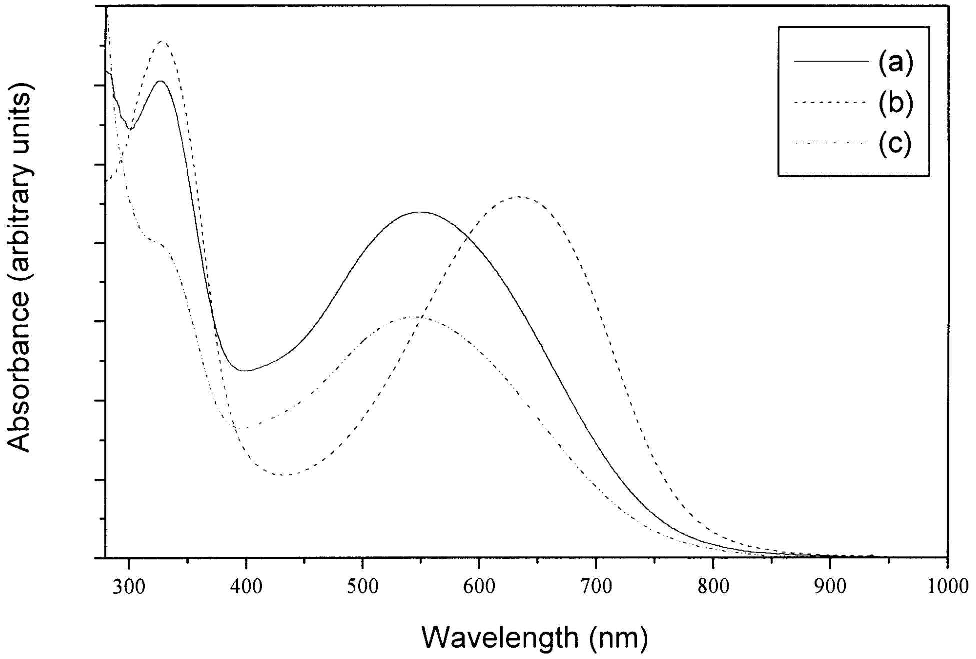

Figure 4 UV/Vis absorption spectra (recorded in NMP as the solvent) of deprotonated PN.CSA$_{1.0}$ (a) using pyridine (b) using pyridine and ethanol, and (c) untreated PNB; spectra were measured on NMP-solution of the recovered polymer.

However, we found that if the deprotonated form is additionally washed with ethanol before dissolution in NMP, the absorption maximum changed from 550 nm to 633 nm where the EB-form has its prominent absorption band (cf. Fig. 3). Thus, we assume that treatment with ethanol leads to the immediate reduction to the EB form. FTIR spectra also evidence this behavior (Fig. 5) which is also in well agreement with the above discussed instability of PNB salts in the presence of m-cresol.

As shown in Figure 5(a), the IR spectrum of PN.CSA$_{1.0}$ which was deprotonated exclusively with pyridine is essentially similar to that of pristine PNB (fig. 5(c)). Upon treatment with ethanol, the relative intensity of 1590 to 1490 cm^{-1} band decreases and the small peak around 1160 cm^{-1} disappears, indicative for the reduction of PNB by the presence of ethanol (fig. 5(b)). It is evident from Fig. 5 that after treatment with ethanol the spectrum substantially exhibits the original features of EB.

It is found that also the deprotonated process of PN.MSA$_{1.0}$ with using NH$_4$OH was unsuccessful; the dedoped forms of EB.MSA$_{1.0}$ and PN.MSA$_{1.0}$ obtained after neutralization with NH$_4$OH show similar UV absorption spectra. Similar results were obtained when deprotonated PNB was washed with H_2O. Cao has also observed the same behavior for deprotonation process of PN salt form [23]. Based on above observations we conclude that PN salt degrades in the presence or nucleophiles such as water and ethanol.

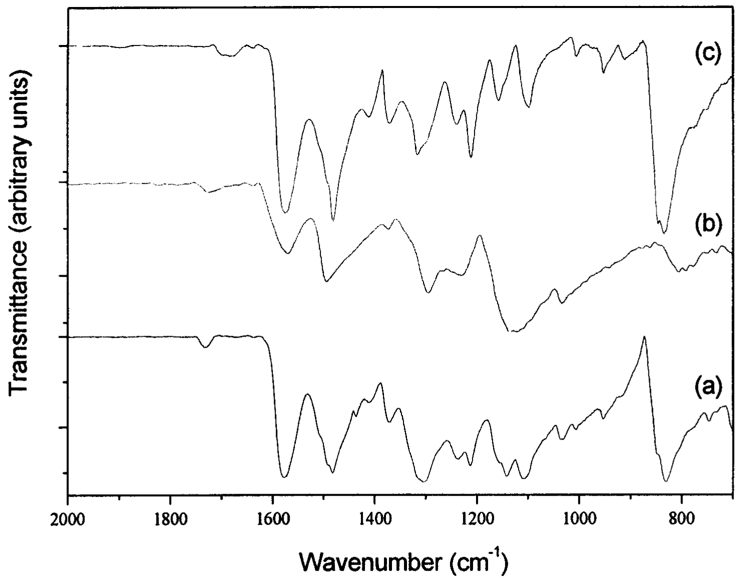

Figure 5 FTIR spectra of deprotonated PNB.CSA$_{1.0}$ (a) using pyridine (b) using pyridine and ethanol, and (c) untreated PNB; spectra were measured using KBr pellets of the recovered polymer.

Conclusion

Fully oxidized form of polyaniline, pernigraniline can be prepared as a pure powder in nitrogen atmosphere. Protonated form of PNB, called "Pernigraniline salt", can be obtained in highly acidic media with control the method of processing such as solvent, temperature, drying procedure, etc. Conductivity measurements revealed DC electrical conductivities of up to 0.23 S/cm. These experiments unequivocally demonstrate that the fully oxidized, protonated form of polyaniline indeed represents a material which can exhibit significant electrical conductivity.

Acknowledgments

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