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Brominated Polyaniline

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Polyaniline base and polyaniline hydrobromide were reacted with bromine in aqueous medium. The content of bromine in the modified polymer increased with the amount of bromine introduced into the reaction mixture. The enhanced conductivity of polyaniline base after reaction with bromine was explained by the protonation with hydrobromic acid originating during the bromination. FTIR and optical spectra were used to discuss the chemical changes in polyaniline (PANI). The density of brominated PANI was also determined.

Introduction

In 1977, Shirakawa et al.[1] discovered that halogenation of *trans*-polyacetylene increased its conductivity by several orders of magnitude. *trans*-Polyacetylene films that were reacted with bromine attained a maximum conductivity of 0.5 S cm^{-1}, and a similar reaction with iodine vapors led to a product with a conductivity of 38 S cm^{-1}. Charge-transfer complexes between halogens and *trans*-polyacetylene were proposed to be responsible for the enhanced conduction. This breakthrough study stimulated further interest in conducting polymers. Similar research on polyaniline (PANI) and polypyrrole is represented by the papers reporting the interaction of PANI with iodine.[2−4] An increase in the conductivity, observed with these polymers also, was explained by the oxidative doping. In this paper, we discuss the physicochemical changes observed after the reaction of PANI with bromine.

Experimental Section

Bromination of PANI. Protonated PANI was prepared by the oxidation of 0.2 M aniline hydrochloride with 0.25 M ammonium peroxydisulfate in aqueous medium at ambient temperature. The product was deprotonated in an excess of 1 M ammonium hydroxide. Polyaniline base was washed with acetone and dried at 60 °C in vacuo.

A halogenation procedure used by Zeng and Ko[3] was followed. Polyaniline base (5 mmol, 905 mg) was suspended in 40 mL portions of water. An increasing amount of bromine (2.5, 5, ..., 20 mmol Br_2) was added to the suspension at room temperature. The ratio of elemental bromine per each nitrogen in PANI thus varied as $[Br_2]/[PANI\ (two\ rings)] = [Br]/[N] = 0.5, 1, ..., 4$. After 2 weeks, brominated PANI was collected on a filter, washed with water, and dried. In another series of experiments, water was replaced with 1 M HBr.

Conductivity. Electrical conductivity was measured at room temperature by the four-probe method on compressed pellets, 13 mm in diameter and 1 mm thick, using a Keithley 237 high-voltage source measure unit as a current source and a Keithley 2010 low-noise multimeter. Conductivity below 10^{-3} S cm^{-1} was measured by the two-probe technique with a Keithley 6517 electrometer.

FTIR and Visible Spectra. Brominated PANI was dispersed in potassium bromide and compressed into pellets. IR measurements in the range of 400−4000 cm^{-1} were recorded with a fully computerized Nicolet Impact 400 FTIR spectrometer (200 scans per spectrum at a resolution of 2 cm^{-1}). The spectra were corrected for the presence of moisture and carbon dioxide in the optical path. UV−vis spectra of brominated PANI dissolved in *N*-methylpyrrolidone were recorded with a Lambda 20 (Perkin-Elmer) spectrophotometer.

Other Characterization. The Archimedes method was used to determine density by weighing the compressed pellets in air and in decane at 20 °C with Sartorius Research R160P balances. The bromine content was determined by Schöniger analysis.[5]

Results and Discussion

In textbooks of organic chemistry, we learn that the chemical reaction between aniline and bromine proceeds so easily even at high dilutions that it has been proposed for the collection of bromine from seawater. The polymer-

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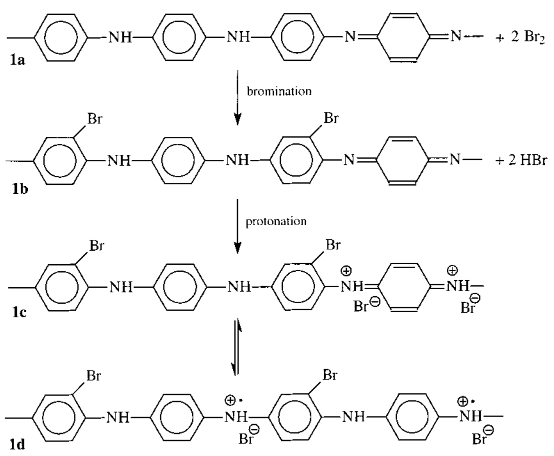
Scheme 1. Reaction of the PANI Base with Bromine



analogous bromination of the PANI (emeraldine) base (Scheme 1, formula 1a) is expected to take place in the benzene rings (1b). The substitution of hydrogen with bromine yields hydrobromic acid. The produced acid subsequently protonates imine nitrogens in the PANI base producing polyaniline hydrobromide (PANI•HBr) (1c). The protonation reaction is of fundamental importance for the increase in the conductivity of the PANI base after bromination as discussed below. The coexistence of a dication (1c) with a cation radical (1d) gives rise to the formation of charge carriers, polarons.

When the bromination proceeds in a solution of HBr instead of water, PANI is present in its protonated form as PANI•HBr from the very beginning. The substitution of hydrogen in the aromatic ring with bromine produces HBr as in the preceding case. The acidity of the medium thus increases. The mechanism of bromination is expected to be the same both in water and in HBr.

Degree of Bromination. The situation depicted in Scheme 1 corresponds to the reaction of one bromine molecule with two aromatic rings, $[Br_2]/[PANI\ (two\ rings)] = [Br]/[N] = 1$. On an average, each second aromatic ring becomes brominated and, at the same time, a corresponding amount of bromine becomes incorporated into the PANI chains as HBr. Brominated PANI having one bromine atom per benzene ring would be produced at $[Br]/[N] = 2$. A polymer with the same bromine content could be, in principle, obtained by the polymerization of 2-bromoaniline. For $[Br]/[N] > 2$, a multiple bromination of the aromatic rings has to occur assuming that all bromine had been consumed in the reaction. An excess of HBr liberated during the bromination cannot participate in the further protonation of PANI, and it increases the acidity of the medium.

The bromination is well documented by elemental analysis (Figure 1). The content of bromine increased from a zero value for the PANI base to 56.7 wt % for the brominated product at the degree of bromination $[Br]/[N] = 4$. Under the same conditions, the content of bromine in PANI•HBr increased from 29.4 to 59.1 wt %. In this case, the found bromine content follows well the theoretical prediction (Figure 1) calculated on the assumption that the reaction with bromine proceeds quantitatively and that one molecule of HBr is produced per each bromine atom introduced onto the aromatic rings of PANI. The content of bromine in the samples of the brominated PANI base is systematically lower. This may indicate that PANI is protonated with the liberated HBr only incompletely, and the protonation is complete when the reaction proceeds in an excess of HBr.

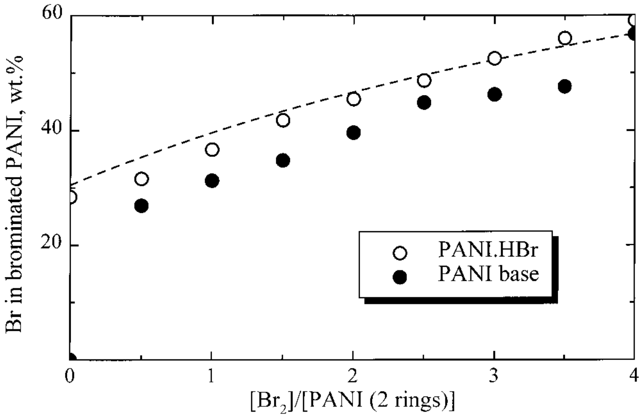


Figure 1. Content of bromine in the PANI base treated with various proportions of bromine, [Br]/[N], in water (full circles) and in 1 M HBr (open circles). Dashed line shows a theoretical prediction of bromine content in brominated PANI•HBr (corresponding to open circles).

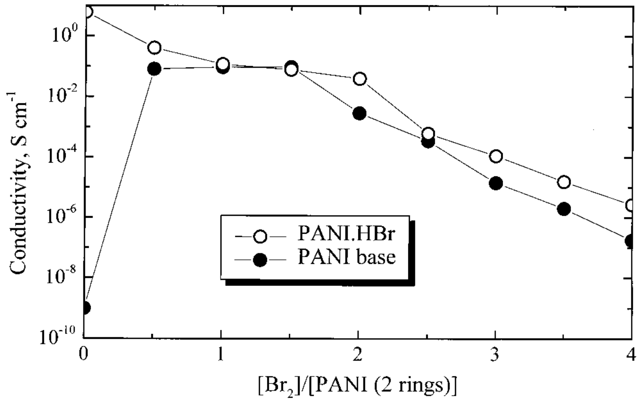


Figure 2. Conductivity of polymers produced after bromination of the PANI base in water (full circles) and in 1 M HBr (open circles) with various amounts of bromine, [Br]/[N].

Conductivity. Electrical properties of modified PANI are of primary interest. When the PANI base was treated with bromine, the conductivity increased from 1.0×10^{-9} to 8.3×10^{-2} S cm^{-1} at a low degree of bromination (Figure 2). The protonation of the PANI base with HBr, liberated during the bromination (Scheme 1), is responsible for this impressive change. Any additional bromination leads to the reduction of conductivity.

The conductivity of brominated PANI•HBr decreased from 4.6 to 2.6×10^{-6} S cm^{-1} with an increasing degree of bromination (Figure 2). The conductivity of the product at the degree of bromination $[Br]/[N] = 2$ was 4.0×10^{-2} S cm^{-1}. Poly(2-bromoaniline), prepared by the oxidation of 2-bromoaniline under the same conditions as PANI, only allowing for a longer polymerization time, had a conductivity[6] of 3.9×10^{-5} S cm^{-1}, which is close to the value of 1.3×10^{-6} S cm^{-1} reported in the literature.[7] This clearly confirms that the bromination

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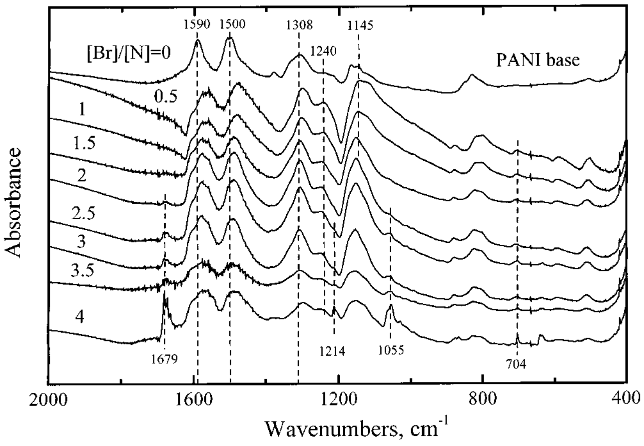

Figure 3. FTIR absorption spectra of the PANI base brominated in water to various degrees, [Br]/[N].

of PANI and the polymerization of 2-bromoaniline do not lead to structurally identical products. The difference in the conductivity of the brominated PANI base and PANI·HBr becomes negligible at high bromination degrees (Figure 2).

FTIR Spectra. The absorption spectrum of the PANI base alone (Figure 3) is in good agreement with previously reported results.[3,8,9] The main peaks at 1590 and 1500 cm^{-1} correspond to stretching deformations of quinone and benzene rings, respectively. The band at 1374 cm^{-1} is attributed to C−N stretching in the neighborhood of a quinoid ring. The 1308 cm^{-1} band is assigned to C−N stretch in a secondary aromatic amine, whereas in the 1010−1170 cm^{-1} region, the aromatic C−H in-plane bending modes are observed. The out-of-plane deformations of C−H in the 1,4-disubstituted benzene ring are located in the region of 800−880 cm^{-1}.

Spectral changes in the samples with low degrees of bromination, [Br]/[N] = 0.5−1, are typical of the protonation of the emeraldine base with acids. First, the spectra exhibit a broad absorption band at wavenumbers higher than 2000 cm^{-1} (only a part of this band is shown in Figure 3). This is characteristic of the conducting form of PANI,[10] the metallic polaron energy band being responsible for the broad absorption.[11] After more extensive bromination, [Br]/[N] > 1, absorption in this region is again reduced. These changes correlate well with the conductivity of the samples, which reaches a maximum at moderate bromination degrees (Figure 2, full points). Similarly, the main peaks of the PANI base at 1590 and 1500 cm^{-1} are red-shifted to 1570 and 1480 cm^{-1}, exactly as observed in the spectrum of protonated PANI. For highly brominated samples, a smaller shift is observed, in accordance with the decreasing conductivity of samples.

The band at 1603 cm^{-1} is attributed to the Raman active −C=C− ring-stretching vibration. These normally IR-inactive modes become active when protonation induces conformation changes in the polymer chain, i.e., when polarons or bipolarons are produced, resulting in the breakage of symmetry along the chain. The 1140 cm^{-1} band can be assigned to a vibration mode of the $-NH^{+}=$ structure, which is formed by protonation (Scheme 1, formula 1c). This indicates the presence of positive charges on the chain and the distribution of the dihedral angle between the quinone and benzenoid rings. The band increases with the degree of protonation of the PANI backbone.[12] The same shifts and changes in the absorption spectra have been observed in the bromination of the emeraldine base, especially for the samples where [Br]/[N] = 0.5−1 (Figure 3).

The band at 1374 cm^{-1} (C−N stretching in the neighborhood of a quinoid ring) shows a decrease in intensity with increasing bromine content. The absorption band at 1308 cm^{-1} (C−N stretching of secondary aromatic amine) is strengthened during the protonation. It may correspond to π-electron delocalization in the polymer induced by protonation or to the positive charge on a polymer chain due to a $-NH^{+}=$ structure leading to a strong increase in the molecular dipole moment.[8] Because of various configurations of polymer chains, the C−N bonds have a different chemical environment[13] and, consequently, different frequencies of the C−N stretching vibration band. The band characteristic of the conducting protonated form is observed at about 1240 cm^{-1}. It has been interpreted as the $C-N^{\bullet+}$ stretching vibration in the polaron structure.[9] All these features have been observed at moderate degrees of bromination (Figure 3).

Chemical changes expected after the reaction with bromine are supported by the spectra in the region of 900−700 cm^{-1} corresponding to aromatic out-of-plane C−H deformation vibrations. Their frequencies are mainly determined by the number of adjacent hydrogen atoms in the ring but are not very much affected by the nature of the substituents.[14] Before the reaction with bromine, the band at 840 cm^{-1} in the spectrum of the PANI base corresponds to the 1,4-disubstituted benzene ring. After bromination, two new bands at about 800 and 880 cm^{-1} and a band at about 706 cm^{-1} related to the 1,2,4-trisubstituted benzene ring are observed.

Besides the spectral features of PANI alone, there are some new peaks found after bromination. This is the band at 1679 cm^{-1} for [Br]/[N] > 1 (corresponding most probably to a quinone structure which is absent in the spectra[6] of poly(2-bromoaniline)), 1214 cm^{-1} (found in the spectra[6] of poly(2-bromoaniline)), 1055 cm^{-1} (most probably in-plane ring deformation), 1030 cm^{-1} (present in the spectra[6] of poly(2-bromoaniline)), and 704 cm^{-1} (probably the C−Br stretching vibration).

Visible Spectra. Spectra in the visible region also reflect the chemical changes associated with the chemical transformation of PANI (Figure 4). All samples were soluble in *N*-methylpyrrolidone at the simultaneous deprotonation and loss of HBr. The spectra recorded in this solvent thus correspond to the bases. The absorption spectrum of the PANI base has two characteristic peaks.[15,16] The first, at 300−330 nm, is connected with

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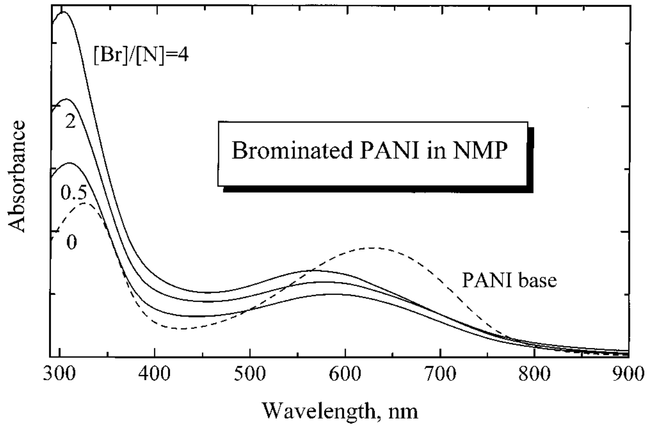

Figure 4. Visible spectra of PANI base brominated to various degrees, [Br]/[N], dissolved in *N*-methylpyrrolidone.

a $\pi-\pi^*$ transition centered on the benzenoid rings and distorted by the presence of amine groups. The other, at 600−630 nm, is due to the transition from a localized benzenoid highest occupied molecular orbital to a quinoid lowest unoccupied molecular orbital. The absorption in the $\pi-\pi^*$ transition band region increases with increasing bromine content. The bromine in the benzene ring absorbs in the region of 300 nm, and therefore, the position of the peak is blue-shifted from 330 to 300 nm. The position of excitonic peak shifts from 630 to 560 nm. It is well-known that the position of this peak is sensitive to the nature of the counterions[16] and solvent[17] and to the chemical structure of the polymer.[18] In the present case, the observed shift is associated with the latter factor.

Density. Another property, which is affected by the introduction of bromine into PANI macromolecules, is the polymer density (Figure 5). As the extent of bromination increases, density grows from that of the PANI base,[19] 1.23, to 2.30 g cm^{-3}. At higher bromination degrees, the products have comparable densities regardless of the reaction medium, water or 1 M HBr. Density is an important parameter in the design of colloidal PANI particles,[20] and halogenation may thus be of advantage in the preparation of the particles of variable density.

Potential Applications. A dramatic increase in the conductivity of the PANI base exposed to halogens could be exploited in their detection. Clearly, the response is not specific, and a similar conductivity change would be observed after the contact of a PANI-based sensor with various acids. Moreover, the change induced by halogenation may be irreversible. However, when used in a sensor array in combination with other conducting polymers, the reaction of the PANI base with halogens could be used in the monitoring of long-term exposure to halogens or in early-warning devices for toxic hazards.

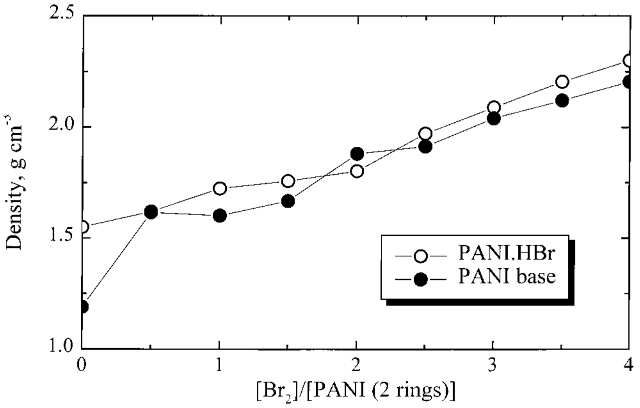

Figure 5. Density of polymers produced by the bromination of the PANI base in water (full circles) and in 1 M HBr (open circles) with various amounts of bromine, [Br]/[N] at 20 °C.

Conclusions

The reaction of PANI with bromine yields brominated PANI. The content of bromine in PANI is proportional to the concentration of bromine introduced in the reaction mixture; it increased to 59.1 wt % of bromine for the highest used bromination ratio [Br]/[N] = 4. In the bromination, HBr is released; it participates in the protonation of PANI. This is manifested by an increase in the conductivity of the PANI base from 1.0 × 10^{-9} to 9.5 × 10^{-2} S cm^{-1} after treatment with an equimolar amount of bromine. FTIR spectra reveal a correlation between the conductivity and the protonated structure of brominated PANI. As a consequence of HBr release, the bromination of the PANI base in water and of PANI·HBr in hydrobromic acid yields the same product, a brominated PANI·HBr. Extensive bromination reduces the conductivity of ring-substituted PANI. The bromination of PANI can be thus used for controlling conductivity over a broad range. The changes in the conductivity of PANI after contact with bromine could be used in the nonselective detection of free halogens. The density of brominated PANI increases with increasing bromine content.

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