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Protonation of Polyaniline with 3-Nitro-1,2,4-triazol-5-one

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The preparation of materials combining the features of conducting polymers and energetic compounds is demonstrated. The protonation reaction between two nonconducting compounds, polyaniline (PANI) base and 3-nitro-1,2,4-triazol-5-one (NTO), an insensitive explosive, yields conducting products. Three ways of preparation have been tested: the interaction of PANI base with NTO dissolved in water, the polymerization of aniline in a medium containing NTO, and solid-state blending of both components. The increase in conductivity and density after protonation is assessed. The FTIR spectra are used to examine changes in the molecular structure of PANI and NTO occurring during the protonation.

Introduction

Protonation of polyaniline (PANI) base with acids is of fundamental importance in exploiting the electrical properties of this polymer.[1] In such a process, the conductivity of PANI base, $10^{-10}-10^{-9}$ S cm^{-1}, increases by several orders of magnitude to the level of $10^{-1}-10^{0}$ S cm^{-1}. Besides the preparation of polymer materials of defined conductivity, the response in the conductivity and color to the change in the degree of protonation has been proposed for the sensing of ammonia,[2] optical monitoring of acidity,[3] and in the detection of free halogens.[4]

Various types of acids have been used in the protonation of PANI. These are introduced directly during the polymerization of aniline or they react with a priori prepared PANI base. Inorganic acids are the most common, hydrochloric and sulfuric acids being typical examples. Organic acids have often been tested for improving the processibility of PANI. Sulfonic acids, especially camphorsulfonic[5−7] and dodecylbenzenesulfonic acids,[8,9] have frequently been used, while carboxylic acids, e.g. formic,[10] maleic,[11] or tartaric[12] acids, have been applied in a limited number of studies. Lewis acids have also been demonstrated to yield conducting PANI after interacting with PANI base.[13,14]

Besides the typical acids mentioned above, there are other organic compounds that can provide a proton and thus participate in the protonation of PANI. Picric acid[15] (2,4,6-trinitrophenol) and *m*-cresol,[16] each of which contains a sufficiently acidic hydrogen in an hydroxyl group, may serve as examples. Picric acid has been demonstrated to react with PANI base even in the solid state to yield a conducting PANI picrate.[15,17] The films cast from PANI picrate solution in *m*-cresol were

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reported[18] to have a conductivity of 150 S cm^{-1}. The solid-state protonation of poly(*o*-toluidine) with picric acid was used to prepare conducting composites with ABS rubber.[19]

The structure and properties of 2-nitro-1,2,4-triazol-5-one (NTO) have been studied in connection with its use as an insensitive explosive.[20−24] It is a weak organic acid ($pK_a = 3.7$). In this paper we demonstrate that NTO is able to protonate PANI in a controlled manner and can be used for the preparation of PANI of varying conductivity. This is a new type of material that combines the electric properties of a conducting polymer with that of an energetic compound. In the systems comprising such material, the ignition could possibly be achieved by the Joule heat evolved by passing electric current.

Experimental Section

PANI Base. Aniline hydrochloride (0.20 mol, 25.9 g; Fluka, purum) and ammonium peroxydisulfate (0.25 mol, 57.1 g; APS; Fluka, purum) were separately dissolved in water (500 mL in each case). The solutions were then mixed at room temperature, and the aniline was left to polymerize. The next day, the precipitated PANI hydrochloride was collected on a filter and washed copiously with 1 M ammonium hydroxide. The resulting PANI base was dried at 60 °C in vacuo.

Protonation of PANI Base with NTO. NTO was obtained from the University of Pardubice (Czech Republic). Solutions of varying concentration of NTO in water (up to 30 mM) were prepared. The dependence of optical absorption at wavelength of 320 nm, recorded with a UV−Vis spectrophotometer Lambda 20 (Perkin-Elmer, UK), on NTO concentration was linear. Portions of PANI base (20 mmol, 362 mg) were suspended in 100 mL of NTO solutions for 24 h. The residual concentration of NTO in the supernatant liquid after the reaction of NTO with PANI base was determined from the corresponding decrease in the optical absorption. The degree of protonation was calculated from the amount of NTO consumed in the protonation. The partly protonated PANI was collected on a filter and dried in vacuo at 60 °C.

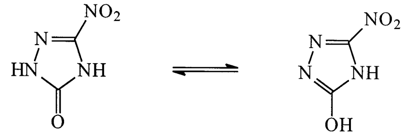
Preparation of PANI in the Presence of NTO. Aniline (20 mmol) was oxidized in the presence of NTO (20 mmol) with APS (25 mmol) in 100 mL of aqueous medium. The collected precipitate was washed with a saturated aqueous solution of NTO and with acetone and dried as above.

Solid-State Protonation. In another approach, the protonation of PANI in the solid state was used.[15] PANI base was mechanically blended for 15 min with an equimolar amount of NTO in a mortar.

Infrared Spectra. Fourier transform infrared (FTIR) spectra were recorded with a Nicolet IMPACT 400 FTIR spectrometer in an water-purged environment. All spectra in the range 400−4000 cm^{-1} with 2 cm^{-1} spectral resolution were obtained from compressed KBr pellets in which the PANI−NTO powders were evenly dispersed. Two hundred scans were collected for each FTIR spectrum. The spectra were corrected for the moisture and carbon dioxide in the optical path.

Conductivity and Density. Conductivity was measured at room temperature by a four-probe method on compressed pellets, 13 mm in diameter and 1 mm thick, using a Keithley 237 current source and Keithley 2010 low-noise multimeter. Conductivities below 10^{-3} S cm^{-1} were determined using a two-probe technique with a Keithley 6517 electrometer after deposition of gold electrodes on both sides of the pellets. The Archimedes method was used to determine the density by weighing the pellets without electrodes in air and in decane at 20 °C with a Sartorius Research R160P balance.

Scheme 1. Keto−Enol Forms of 3-Nitro-1,2,4-triazol-5-one (NTO)



Results and Discussion

Precautions for the Handling of Dangerous Materials. NTO (Scheme 1) is an energetic compound. Even though NTO is an *insensitive* explosive, the appropriate safety regulations should be obeyed. The careful handling of gram quantities has never caused any problems. The metallic salts of NTO, however, can be highly sensitive to external stimuli.

Protonation of PANI with NTO. The keto−enol tautomeric structure of NTO (Scheme 1) reveals, in the enol form, the presence of an hydroxyl group that is sufficiently acidic to react with bases. The salts of NTO containing an inorganic cation are well-known and exploited as explosives.[25] It was thus expected that NTO will also form a "salt" with a PANI base. The reaction of nonconducting blue PANI base with an acid generally leads to a conducting green protonated PANI[26] (Scheme 2). The rearrangement of electrons in PANI produces cation-radicals that act as charge carriers and are responsible for the electrical conduction. The extent of conductivity is dependent on the balance of the individual PANI forms (Scheme 2).

PANI base was suspended in the aqueous solutions of NTO. The use of various mole ratios of NTO per mole of PANI base (calculated per two aniline units), $(n_{NTO}/n_{PANI})_0 = 0-1.5$, allowed for the control of the degree of protonation in the polymer, expressed similarly as n_{NTO}/n_{PANI}. The formula of a hypothetical PANI fully protonated with NTO, $n_{NTO}/n_{PANI} = 1$, is depicted in Scheme 3. The consumption of NTO by PANI base from the supernatant liquid proved that the protonation indeed takes place. The degree of protonation increases with increasing content of NTO used for the protonation (Figure 1). The maximum degree of protonation that was achieved in this way was $n_{NTO}/n_{PANI} \sim 0.3$.

The protonation is well-documented by the conductivity measurements. The conductivity of PANI base, 3.5×10^{-9} S cm^{-1}, increased after a 30% protonation to 3.4×10^{-3} S cm^{-1}, i.e., by 6 orders of magnitude (Figure 2). This is a level of conductivity that may be of practical interest. The additional support has also been obtained from the determination of density, which also increases with the increasing fraction of NTO incorporated into

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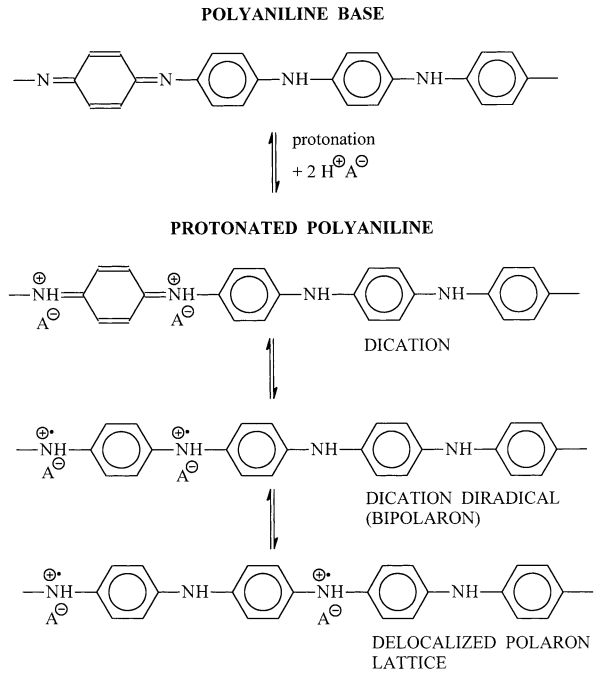
Scheme 2. Nonconducting PANI Base Reacts with an Acid (HA) to Give a Conducting Protonated PANI[a]



[a] The resulting "salt" may have a dication structure that is partly transformed by redistribution of electrons to dication diradicals or delocalized cation radicals or both. Unpaired electrons are responsible for the conduction in protonated PANI.

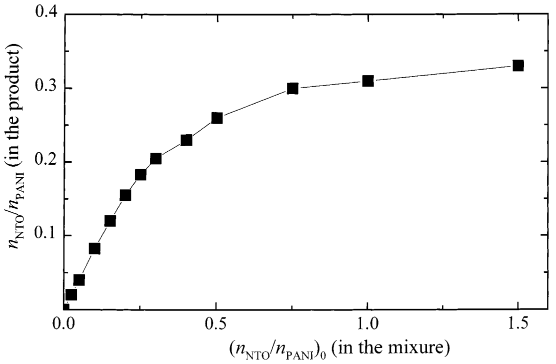
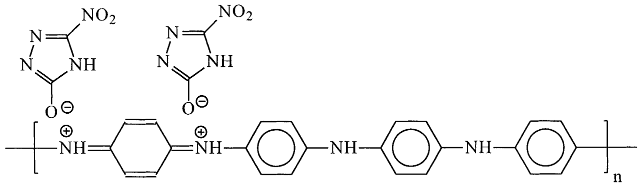


Figure 1. Dependence of the degree of PANI protonation, n_{NTO}/n_{PANI}, on the initial molar ratio of NTO and PANI base in the protonating medium, $(n_{NTO}/n_{PANI})_0$.

Scheme 3. PANI Protonated with NTO



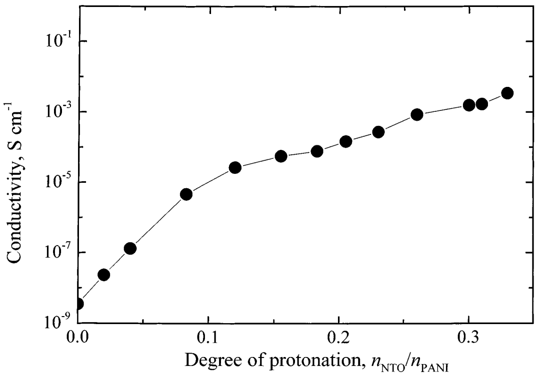


Figure 2. The dependence of the conductivity on the degree of protonation, n_{NTO}/n_{PANI}.

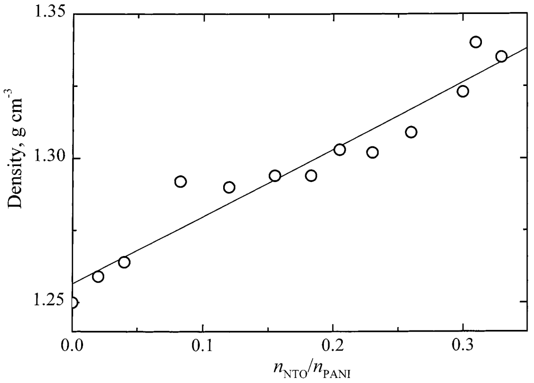


Figure 3. The dependence of density on the degree of protonation, n_{NTO}/n_{PANI}.

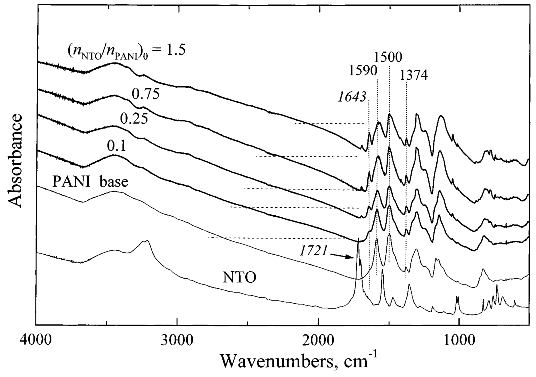


Figure 4. The FTIR spectra of PANI base protonated with various proportions of NTO, $(n_{NTO}/n_{PANI})_0$ (shown at the individual spectra). The spectrum of pristine NTO is shown for comparison.

PANI (Figure 3), as expected: the density of PANI base at 20 °C is[27] 1.25 g cm^{-3} and that of NTO 1.93 g cm^{-3}.

FTIR Spectroscopic Evidence of Protonation. A deeper insight into the process of protonation is achieved by analysis of the FTIR spectra. The absorption spectrum of PANI base (Figure 4) is in a good agreement with previously reported results.[28-30] The main peaks at 1590 and 1500 cm^{-1} correspond to stretching deformations of quinonoid and benzenoid rings, respectively (Scheme 2). The band at 1374 cm^{-1} is attributed to C−N stretching in the neighborhood of a quinonoid ring. The 1308 cm^{-1} band is assigned to the 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. In the region of 800−880 cm^{-1}, the out-of-plane deformations of C−H in a 1,4-disubstituted benzene ring are located.

The spectrum of polycrystalline NTO dispersed in KBr pellets (Figure 4) is close to the spectrum of the thin NTO film presented by Sorescu et al.[21] The peaks at 3478, 3248, and 3210 cm^{-1} correspond to the N−H stretching vibrations (cf. Scheme 1). The peak at 1721

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cm^{-1} in the spectrum of NTO has been interpreted as a carbonyl-stretching vibration,[21] with a secondary peak at 1698 cm^{-1} corresponding probably to the N–O asymmetric-stretching mode. The absorptions at 1548 and 1476 cm^{-1} belong to the N–H bending vibrations. The broad band at about 1356 cm^{-1} is related to the $C{-}NO_2$ stretching vibrations. The bands at about 1010 cm^{-1} can be assigned to the in-plane vibrations of the ring, and the region from 900 to 600 cm^{-1} corresponds to the out-of-plane torsion ring vibrations.

When the PANI base reacts with NTO, the appearance of a broad band at wavenumbers higher than 2000 cm^{-1}, characteristic of the conducting form of PANI,[31] is the significant feature (Figure 4). The metallic polaron energy band is responsible for the broad absorption.[32] The horizontal dashed lines in Figure 4 are placed at a level of absorption at 1590 cm^{-1}. The intersection of these lines with an absorption tail at wavenumbers >2000 cm^{-1} has a trend to move to lower wavenumbers as the degree of protonation increases. The increasing absorption in the region >2000 cm^{-1} is in good correlation with the increasing conductivity of the samples (Figure 2).

The band at about 1590 cm^{-1} in the spectrum of PANI base is red-shifted to 1581 cm^{-1} as NTO content increases, and a shoulder at about 1608 cm^{-1} corresponding to the protonated form of PANI[31] appears. The absorption band at 1308 cm^{-1} is strengthened during the protonation,[33] and the band characteristic of the conducting protonated form at about 1240 cm^{-1} increases. The latter peak has been interpreted as a $C{-}N^{+\bullet}$ stretching vibration in the polaron structure.[30] A band at about 1116 cm^{-1} appears, belonging to the vibration mode of $-NH^{+}{=}$, formed after protonation (Scheme 2). This indicates the presence of positive charges on the chain and the distribution of the dihedral angle between the quinonoid and benzenoid rings[34] (Scheme 3). All these features give evidence of the progressing protonation of PANI. On the other hand, the peak at 1374 cm^{-1}, typical of PANI base, is observed in all spectra (Figure 4). This indicates that the protonation, although well-documented, is not complete.

Even more straightforward evidence is obtained from NTO absorption peaks. The band at 1721 cm^{-1}, corresponding to the carbonyl-stretching vibration, disappeared after interaction of NTO with PANI base (Figure 4), and a new band at 1643 cm^{-1}, corresponding to the OH-deformation vibration, has been found instead. This is consistent with the fact that NTO interacts with PANI in the enol form (Scheme 3). The additional peaks of pristine NTO at 3248 and 3210 cm^{-1} (Figure 4) and at 1019 and 1008 cm^{-1} and the peaks in the region of 830–600 cm^{-1} are shifted, which also indicates a more intimate interaction between the PANI and NTO.

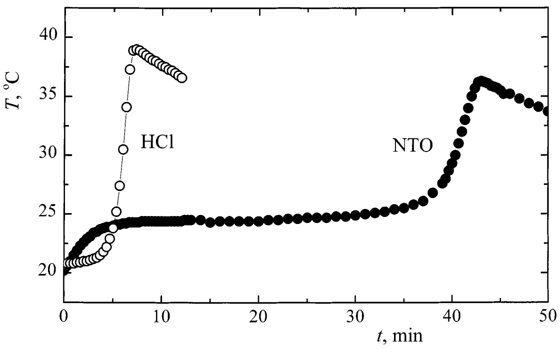

Figure 5. Temperature profile of the aniline polymerization; 0.2 M aniline was oxidized with 0.25 M ammonium peroxydisulfate in the presence of (a) 0.2 M HCl or (b) 0.2 M NTO.

Table 1. Elemental Composition of PANI

	C	H	N	S
Calculated				
PANI–NTO[a]	54.0	3.6	27.0	
PANI sulfate	62.6	4.4	12.2	6.7
Found				
PANI[b]	57.5	4.1	12.0	6.3

[a] Based on the formula shown in Scheme 3. [b] Aniline (0.2 M) oxidized with 0.25 M ammonium peroxydisulfate in the presence of 0.2 M NTO.

Polymerization of Aniline in the Presence of NTO. PANI is produced by the oxidation of aniline in aqueous acidic media. In combining the conducting polymer with energetic compounds, it is logical to propose the introduction of NTO directly into the reaction mixture. The oxidation of aniline is exothermic and can be thus followed by the changes of temperature (Figure 5). If instead of aniline hydrochloride we oxidize an equimolar mixture of aniline and NTO with ammonium peroxydisulfate, the polymerization, reflected by an increase of temperature, is considerably delayed. This is, at least partly, caused by a lower acidity of the medium. Nevertheless, NTO provides the acidity that is sufficient for the progress of polymerization. The conductivity of PANI produced in this way is 0.21 S cm^{-1}, lower than that of PANI hydrochloride,[27] 4.4 S cm^{-1}, but still reasonably high. This optimistic result, however, should be subjected to a critical assessment. During the oxidation of aniline, ammonium peroxydisulfate is decomposed to ammonium sulfate and at the same time protons are released.[35] The sulfuric acid thus produced may compete with NTO in the protonation of PANI.[36] The results of elemental analysis (Table 1), especially the content of nitrogen and sulfur, show that the composition of PANI prepared in the presence of NTO corresponds to PANI sulfate and that the content of NTO in a product is only marginal. The same conclusion is reached on the basis of FTIR spectra (Figure 6, spectrum a), where the peak at 1643 cm^{-1} corresponding to NTO is completely missing. The shifts of 1500 and 1590 cm^{-1} peaks of PANI base to lower wavenumbers, however, clearly prove that we are dealing with a protonated form of PANI. The incorporation

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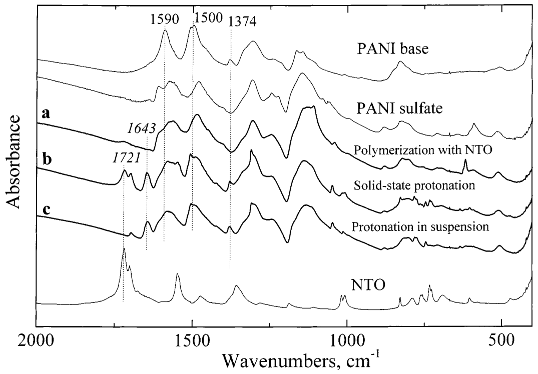

Figure 6. FTIR spectra of PANI base, PANI sulfate, PANI prepared in the presence of NTO (a), the product of solid-state protonation (b), and PANI protonated with NTO in aqueous suspension, $(n_{\mathrm{NTO}}/n_{\mathrm{PANI}})_0 = 1.5$ (c). The spectrum of NTO is included for comparison.

of NTO into PANI during the preparation of the polymer is thus ineffective and the observed protonation is afforded by sulfuric acid rather than NTO.

Solid-State Protonation. It has earlier been reported that PANI base can be protonated by mechanical blending with a solid acid.[15,18] If the PANI base (conductivity of 3.5×10^{-9} S cm^{-1}) is treated in a mortar with NTO (conductivity of 7.6×10^{-15} S cm^{-1}) in equimolar proportions (Scheme 3), product with a conductivity of 1.9×10^{-3} S cm^{-1} is obtained. This demonstrates that the protonation depicted in Scheme 2 takes place. A similar blending of PANI base with picric acid yielded a product having a conductivity[15] of 0.12 S cm^{-1}, the picric acid, however, being a considerably stronger acid (p$K_a \sim 1$) compared with NTO (pK_a = 3.7). Solid-state blending thus offers an alternative to the treatment of PANI base with the solutions of NTO in producing the materials that might be of potential use in the modification of energetic compounds.

The FTIR spectra again support this conclusion and the spectrum of PANI (Figure 6, spectrum b) corresponds to the conducting form of PANI. As expected, the protonation reaction between PANI base and NTO is not been complete. The presence of residual NTO (keto form, 1721 cm^{-1}) is confirmed by spectra along with the NTO incorporated into PANI (enol form, 1643 cm^{-1}). The peak 1374 cm^{-1}, typical of PANI base, also suggests incomplete interaction between PANI base and NTO. Both reactions in the solid state (Figure 6, spectrum b) and in the suspension (Figure 6, spectrum c) thus lead to a partial protonation of PANI with NTO. In a suspension process, the residual NTO remains in the liquid phase and the product after drying thus does not contain any free NTO (Figure 6, spectrum c; the absorption at 1721 cm^{-1} is missing).

Conclusions

Nonconducting polyaniline base reacts with 3-nitro-1,2,4-triazol-5-one to yield a new type of material combining the electrical properties of conducting polymers and the energetic character of the compound used for protonation. The reaction of PANI base suspended in aqueous solutions of NTO provides a product with a ~30% degree of protonation. The conductivity increases after protonation by 6 orders of magnitude. Besides common acids, organic compounds that comprise an acidic hydrogen are thus capable of protonating PANI base. The protonation is also accompanied by a density increase. FTIR spectra prove that NTO is incorporated into PANI in the enol form. The solid-state protonation is an alternative way to obtain a conducting material from nonconducting components. Also in this case the protonation reaction is not complete and part of free NTO remains in the product. On the contrary, the polymerization of aniline in the presence of NTO yields PANI sulfate, a conducting product that does not contain any significant amount of NTO.

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