Solid-State Reduction of Silver Nitrate with Polyaniline Base Leading to Conducting Materials

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ABSTRACT The polyaniline (PANI) base was ball-milled with silver nitrate in the solid state. Samples were prepared at various mole ratios of silver nitrate to PANI constitutional units ranging from 0 to 1.5 for three processing times, 0, 5, and 10 min. The emeraldine form of PANI was oxidized to pernigraniline, and the silver nitrate was reduced to metallic silver. Nitric acid is a byproduct, which may protonate the residual emeraldine and pernigraniline. The changes occurring in the structure of PANI are discussed on the basis of Fourier transform IR and Raman spectroscopies. Raman spectra revealed the formation of pernigraniline salt. The reaction between the two nonconducting components, emeraldine base and silver nitrate, produced a mixture of two conducting components, emeraldine or pernigraniline nitrate and metallic silver. The accompanying conductivity changes were determined. The increase in the conductivity of the original base, 10^{-9} S cm^{-1}, up to 10^{-2} S cm^{-1} was found to depend on the mole ratio of silver nitrate to PANI base and on the processing time of the components in the ball mill.

KEYWORDS: polyaniline • conducting polymer • conductivity • FTIR spectroscopy • Raman spectroscopy • oxidation • emeraldine • pernigraniline • silver

INTRODUCTION

Polyaniline (PANI) chemistry involves three basic types of reactions (a): (1) The preparation of PANI or its ring-substituted derivatives by oxidation of the corresponding monomers (2). The reactions of the thus-prepared PANI (emeraldine) salt are further represented (b) by the deprotonation of PANI, which manifests itself in reversible salt—base transition, and the well-known conversion from a conducting to a nonconducting state. Finally, (c) redox processes, such as the oxidation of emeraldine to pernigraniline or its reduction to leucoemeraldine, are subsequently important reactions. This brief list can be extended to ring substitution, degradation, hydrolysis, cross-linking, heterocycle formation, etc. An aqueous medium is most commonly used in the preparation of PANI, as well as in many applications based on the individual forms of PANI and their interconversions. Reactions proceeding in the absence of solvents, however, are of special interest in understanding PANI chemistry.

In solid-state *polymerizations*, the reactants, aniline salts and peroxydisulfate, enter the mechanochemical reaction as solids and are pulverized with a pestle and mortar (3—8) or they are ball-milled (9). In fact, one of the components (e.g., aniline or a substituted aniline) may actually be a liquid, which may eventually solidify after reaction with acids,

which converts them into salts (6, 7). Alternatively, aniline could be frozen at −20 °C to produce a solid before the oxidation reaction started (3). Some procedures have used the addition of water (5) or of an aqueous acid solution (10), provided the reaction mixture remained in the solid state. An interesting variation of such a polymerization is the oxidation of aniline in frozen aqueous mixtures, i.e., in ice (11—14). This reaction proceeds spontaneously without the need for mechanical processing.

Solid-state *protonations*, i.e., reactions between the PANI (emeraldine) base and solid acids, also proceed easily by the mechanochemical route (15, 16). This approach has been used in the preparation of PANI, which is soluble in organic solvents, and its subsequent processing is then easier (17—20).

Similar solid-state *oxidations*, i.e., reactions between the PANI base and a solid oxidant, have been reported only rarely (16). The formation of a PANI—fullerene complex by solid-state blending (21) also belongs to this type of experiment. In the present communication, the PANI (emeraldine) base was oxidized with silver nitrate with the object of advancing the understanding of the solid-state reactions involving PANI and of preparing conducting polymer—metal nanocomposites. The composite materials of this type may exhibit the high level of electrical conductivity afforded by metals along with the properties characteristic of polymers while maintaining a very simple way of preparation. The fact that these composites combine the metallic conductivity of silver with the semiconducting character of PANI may be of additional interest in the design of components having a low sensitivity of conductivity on temperature.

Simple electronic components and electron-ion conductivity transducers are the next fields of potential application.

MATERIALS AND METHODS

PANI and Its Solid-State Oxidation. PANI was prepared by the standard oxidation of 0.2 M aniline hydrochloride (Fluka; Zurich, Switzerland) with 0.25 M ammonium peroxydisulfate (APS; Lach-Ner, Czech Republic) in an aqueous medium (22). The produced PANI (emeraldine) salt was deprotonated with an excess of 1 M ammonium hydroxide, collected on a filter, and dried in air. A dry powder of PANI (emeraldine) base was mixed with silver nitrate at various mole ratios of oxidant to PANI constitutional units, [AgNO$_3$]/[PANI] = 0.25, 0.5, 0.75, 1.0, 1.25, and 1.5, and processed in a vibration ball mill (Wig-L-Bug C32-003A; Dentsply International, Inc., York, PA) for times up to 10 min. For the purpose of the calculation of the number of PANI moles involved, the PANI constitutional unit was regarded as being composed of two aniline units, with its molar mass being (15) 181.22 g mol^{-1} for emeraldine base. A reference sample of PANI (emeraldine) base without silver nitrate was also prepared, as well as samples in which PANI base was simply mixed with an oxidant, without any milling; for these samples, the ball-milling time was regarded as being equal to zero. A sample of PANI (emeraldine) nitrate, used as a reference in the spectroscopic characterization, was prepared by reprotonation of the PANI (emeraldine) base with 1 M nitric acid (23).

Spectroscopic Characterization. Fourier transform infrared (FTIR) spectra of the samples dispersed in a potassium bromide matrix were recorded in the wavenumber range of 400−4000 cm^{-1} at 64 scans per spectrum at 2 cm^{-1} resolution using a fully computerized Thermo Nicolet NEXUS 870 FTIR spectrometer with a DTGS TEC detector. Spectra were corrected for the moisture and carbon dioxide in the optical path.

Raman spectra excited in the visible range with a HeNe 633 nm laser or an Ar$^+$-ion 514 nm laser on compressed sample pellets were collected on a Renishaw inVia Reflex Raman spectroscope. A research-grade Leica DM LM microscope with an objective magnification of 50× was used to focus the laser beam on the sample. The scattered light was analyzed by the spectrograph with a holographic grating with 1800 lines mm^{-1} for a 633 nm excitation line or 2400 lines mm^{-1} in the case of a 514 nm excitation excitation line. A Peltier-cooled CCD detector (576 × 384 pixels) registered the dispersed light. To avoid degradation of the samples by the laser beam, a reduced beam power was always used.

Conductivity. The conductivity was measured by a four-point van der Pauw method on pellets of 13 mm diameter and ∼1 mm thickness compressed at 700 MPa with a manual hydraulic press, using a current source SMU Keithley 237 and a Multimeter Keithley 2010 voltmeter with a 2000 SCAN 10-channel scanner card. For low-conducting samples, a two-point method using a Keithley 6517 electrometer was applied. Before such measurements, circular gold electrodes of 10 mm diameter were deposited on both sides of the pellets.

RESULTS AND DISCUSSION

The PANI (emeraldine) base is composed of oxidized quinonediimine units and reduced phenylenediamine units in equimolar proportions (Figure 1). Reaction with an oxidant, such as silver nitrate, converts the reduced amine units in the emeraldine structure to the oxidized imine type, and pernigraniline is produced (Figure 1). Metallic silver is the next product of the reaction. Nitric acid, a byproduct arising during the reaction, protonates the residual emeraldine base or its oxidation products, pernigraniline, or both.

The conductivity of the PANI (emeraldine) base was 1.8 × 10^{-9} S cm^{-1}, close to that of silver nitrate, 1.2 × 10^{-9}
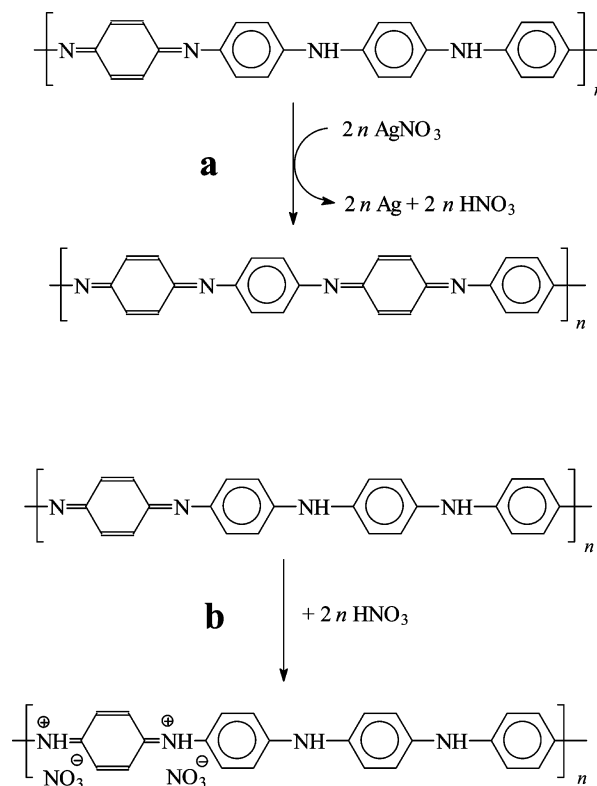
FIGURE 1. (a) Reaction of PANI (emeraldine) base with silver nitrate yielding a pernigraniline base. Metallic silver and nitric acid are byproducts. (b) Quinonediimine units in a residual emeraldine base (and possibly also in produced pernigraniline base) and subsequently protonated with produced nitric acid.

S cm^{-1}. Both reactants are thus regarded as nonconducting. The products, the protonated emeraldine and silver, are conducting and, consequently, an increase in the material conductivity indicates the progress of the reaction. We assume that, as the initial insulating mixture becomes conducting, the redox reaction can proceed not only at the interface between the emeraldine base and the silver nitrate crystals but also at interfaces of these reactants with the produced protonated PANI. The newly produced conducting material enables transport of electrons and protons between the PANI (emeraldine) base and silver nitrate molecules, and direct contact is not necessary for them to react (14, 24−26). By using this concept, the reaction between two solids, PANI (emeraldine) base and silver nitrate, is feasible without the need for any reactant molecules to diffuse to each other.

Conductivity. When nonconducting PANI (emeraldine) base was ground together with silver nitrate, the emeraldine base was converted to pernigraniline (Figure 1), which is also expected to be nonconducting in its base form. There are two byproducts, however, that are responsible for the resulting conductivity: (a) nitric acid, which reacts with residual PANI (emeraldine) base to give semiconducting emeraldine nitrate (Figure 1), and (b) metallic silver. The reaction between the emeraldine base and silver nitrate proceeds easily, and a brief manual blending is sufficient to provide the essential homogenization of the mixture; a "zero" processing time is all that is necessary for a marked increase in the conductivity to 10^{-4}−10^{-3} S cm^{-1} (Figure 2). Ball-
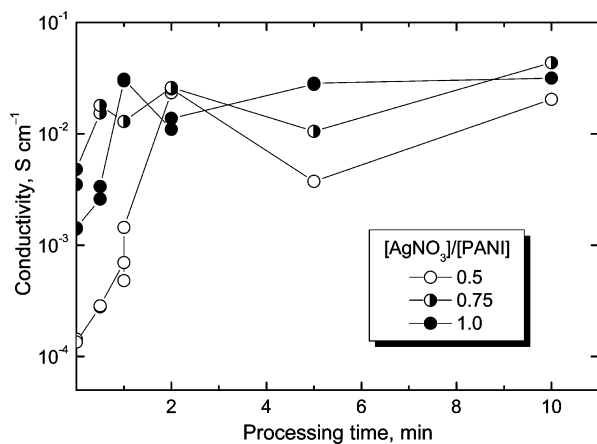
FIGURE 2. Dependence of the conductivity of the PANI (emeraldine) base blended with silver nitrate in various mole ratios of [AgNO₃]/[PANI] = 0.5, 1.0, and 1.5, on the time of processing in a ball mill.
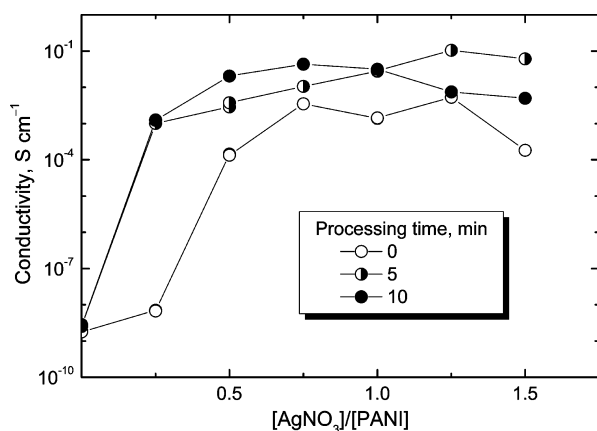

FIGURE 3. Dependence of the conductivity of the PANI (emeraldine) base blended with silver nitrate in a ball mill for 0, 5, and 10 min in mole ratios of [AgNO₃]/[PANI].
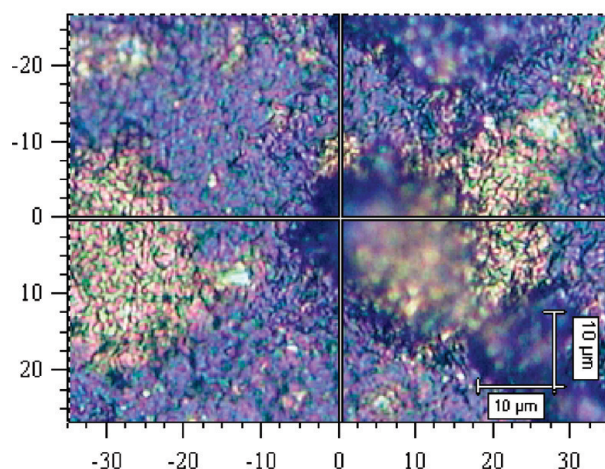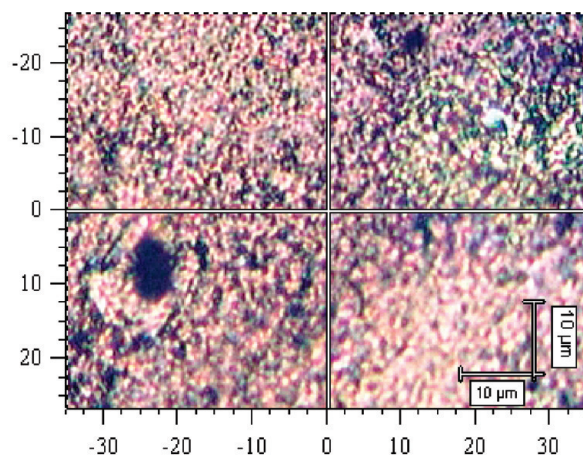

FIGURE 4. Surface of PANI pellets prepared from a mixture of silver nitrate and PANI (emeraldine) base by blending for 0.5 min (top) or 10 min (bottom) in a mole ratio of [AgNO₃]/[PANI] = 0.5.

milling for 2–3 min improved the conductivity to the level of 10^{-2} S cm^{-1}, and extended processing did not have any additional effect on the electrical properties. It should be noted that milling of the PANI base alone did not result in any changes in the conductivity, which fluctuated randomly between 1.8×10^{-9} and 2.7×10^{-9} S cm^{-1} for various processing times. The increase in the conductivity thus sensitively reflects the progress of the reaction between the PANI base and silver nitrate. The reproducibility of the preparation has been tested and is shown in Figure 2 by three pairs of points (full circles) for processing times 0, 0.5, and 2 min at a ratio [AgNO₃]/[PANI] = 1. The figure shows that the differences in the conductivity of reproduced samples are much lower than those generally observed between the samples prepared under various reaction conditions.

The dependence of the conductivity on the mole ratios of the reactants, [AgNO₃]/[PANI], has an unpronounced maximum between 0.75 and 1.25 (Figure 3). The contribution of protonation to the increase in conductivity can manifest itself only when the conversion of emeraldine to pernigraniline is incomplete. Whether or not pernigraniline can be protonated in a similar manner and whether such a product is conducting, as some studies suggest (27), is still open to discussion. The silver is responsible for the conductivity especially when silver nitrate is used in excess. It should be stressed that the general correlation between the content of silver and the conductivity of PANI–silver composites is not straightforward. The conductivity of the composites can differ widely at comparable silver contents (28–30), depending on the morphology of the silver and its distribution within the sample.

Morphology. The surface of the pellets obtained by the processing of PANI (emeraldine) base and silver nitrate in a ball mill for various times, at various mole ratios, has been visualized by optical microscopy (Figure 4). The presence of bright (violet) domains of $10-20\ \mu$m size in the dark (blue) field is observed. The bright domains, visible in both figures, are present in all of the samples. They obviously correspond to both the white silver nitrate and silver metal, while the dark regions correspond to PANI. The surface of the domains increases with the time of blending, as well as with the mole fraction of silver nitrate. The distribution of the domains in samples prepared at a fixed mole ratio of silver nitrate to PANI (emeraldine) base, [AgNO₃]/[PANI], varies with the milling time. The bright domains on the surface of the pellets are dominating when the times are longer, in comparison with samples prepared with shorter processing times.
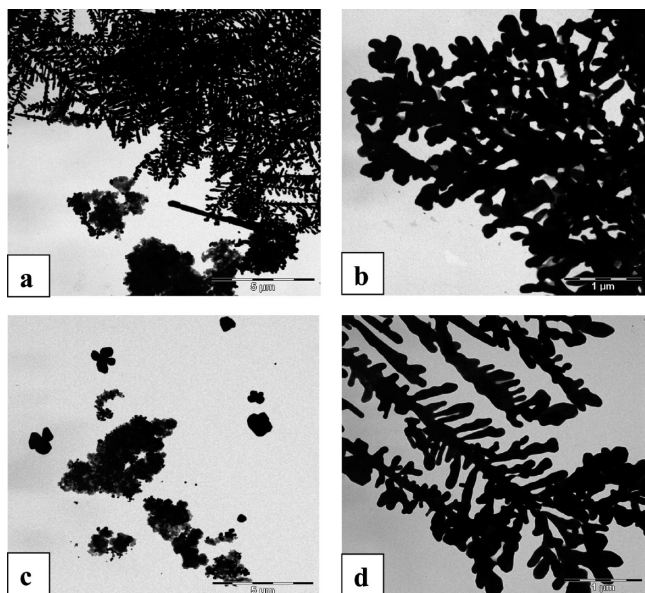
FIGURE 5. TEM images of silver in the composites prepared from silver nitrate and PANI (emeraldine) base by blending of the reactants for 2 min (a and b) or 5 min (c and d) in a mole ratio of [AgNO₃]/[PANI] = 1.
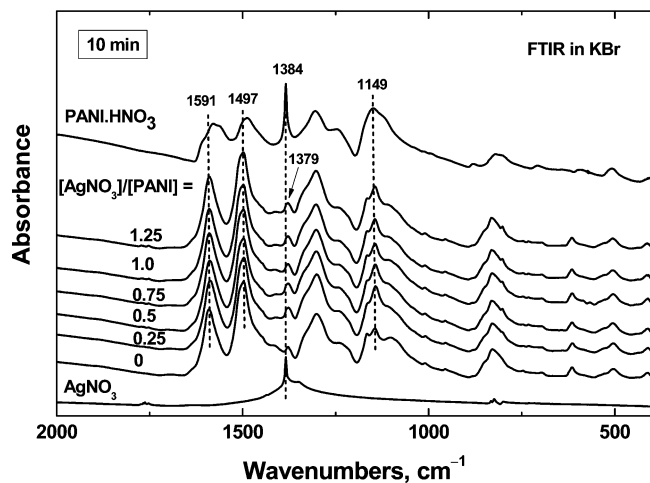

FIGURE 6. FTIR spectra of the PANI (emeraldine) base processed in a ball mill with silver nitrate at various mole ratios for 10 min.

The morphology of the silver can be observed by transmission electron microscopy (TEM; Figure 5). The dendritic structure, with branches having about 100 nm diameter, is typical for this type of sample. It should be noted that, with PANI−silver composites prepared in various ways, globular silver nanoparticles of approximately 50 nm size and their clusters are usually found (28−30).

FTIR Spectra. The spectrum of the original PANI (emeraldine) base (Figure 6) displays bands connected with quinonoid and benzenoid ring vibrations of 1591 and 1497 cm^{-1} (31). The band at 1379 cm^{-1}, attributed to a C−N stretching vibration in the neighborhood of a quinonoid ring, is characteristic of the PANI (emeraldine) base. The band at 1302 cm^{-1} is assigned to the C−N stretching vibrations in secondary aromatic amines. The region of 1010−1170 cm^{-1} corresponds to the aromatic C−H in-plane bending modes. Three maxima are observed in this region: 1167, 1145, and 1103 cm^{-1}. The band at 1167 cm^{-1} is typically observed in

the spectrum of the PANI (emeraldine) base. The presence of the maximum at 1149 cm^{-1} signifies that deprotonation was not complete (31). It is observed in the spectrum of doped PANI nitrate. Out-of-plane C−H deformations on substituted aromatic rings are located in the region of 800−880 cm^{-1} (32, 33). A single band at 832 cm^{-1} and a very small peak at 695 cm^{-1}, also typical of the PANI base, are observed in this region.

The FTIR spectra of samples prepared by mixing of the PANI (emeraldine) base with silver nitrate in various proportions, but without using a ball mill, indicate that the molecular structure of the PANI (emeraldine) base is only slightly (if at all) influenced by mixing with silver nitrate. The positions of the bands in the spectra and their shapes remain unchanged. Because the samples were inhomogeneous, in some cases, only one strong peak of nitrate anions was present in the spectrum. We have excluded such spectra.

Ball-Milling. The processing of a pure PANI (emeraldine) base in a ball mill, without any addition of silver nitrate, has no significant influence on the molecular structure, as reflected by FTIR spectra (the corresponding spectra are not shown). However, the molecular structure was changed when the PANI (emeraldine) base and silver nitrate were sealed in the capsule of the ball mill and ground there for at least 0.5 min. The evolution of the spectra for the PANI (emeraldine) base processed with silver nitrate at various mole ratios for 10 min is plotted in Figure 6. A small shift of the main bands of quinonoid ring vibrations at 1591 cm^{-1} is detected in the spectra. Changes are also observed in the region from 1200 to 1020 cm^{-1}. Three bands with a maximum at about 1145 cm^{-1}, with a sharper side maximum at 1165 cm^{-1} and a broader one at 1102 cm^{-1}, preserve the triplet structure, but the shape is significantly influenced by the grinding (Figure 6). The integral absorption of the central band increases and the side maxima are suppressed (or the absorption of the peak at 1146 cm^{-1} increased) by a comparison with the spectrum of the original PANI base. All of these changes may correspond to protonation of the PANI (emeraldine) base after reaction with silver nitrate (31).

It is surprising that the presence of silver nitrate in the samples is not obvious from the spectra; the sharp peak of NO₃$^-$ vibrations observed at 1384 cm^{-1} in the spectrum of pure silver nitrate (Figure 6) is missing. This peak, however, is well observed in the spectrum of the PANI (emeraldine) base redoped with nitric acid to PANI nitrate (23). A peak in this region is also found with the oxidized pernigraniline form of PANI (34, 35).

We suppose that the solid-state reaction is mainly limited only to a thin interface between the surface of the PANI granules and powdered oxidant. The IR spectra of the product dispersed in KBr pellets correspond to the volume inside the PANI (emeraldine) base granules, and so they provide little evidence of the doping process in PANI and nothing about their oxidized surface. For this reason, we have decided to record Raman spectra, which are surface-sensitive.
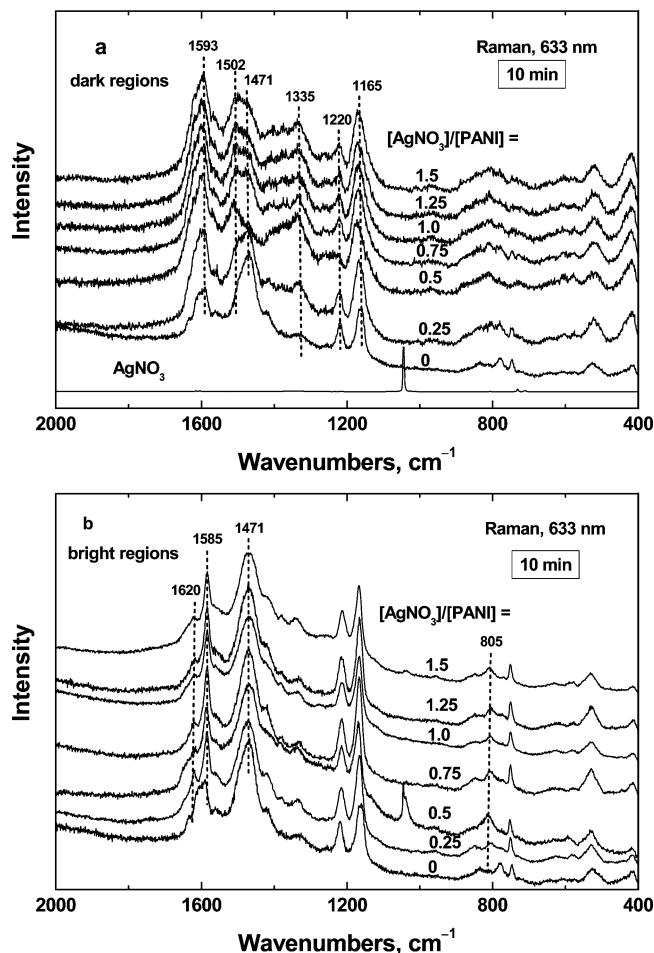
FIGURE 7. Raman spectra of the PANI (emeraldine) base processed in a ball mill with silver nitrate at various mole ratios for 10 min and measured as pellets with excitation at 633 nm. The spectra were separately recorded in (a) dark and (b) bright regions of the samples.
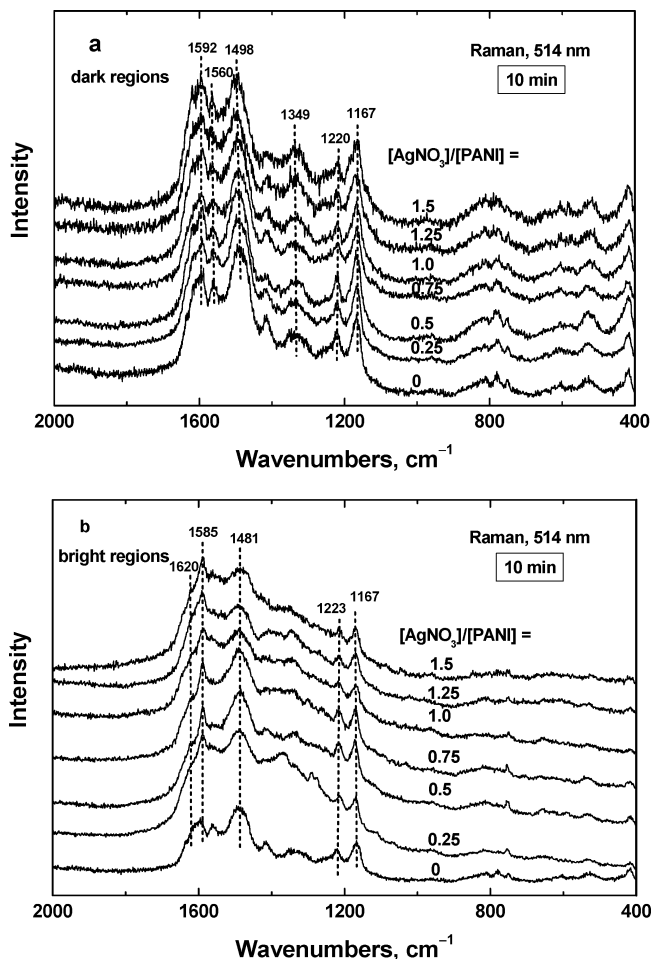

FIGURE 8. Raman spectra of the PANI (emeraldine) base processed in a ball mill with silver nitrate at various mole ratios for 10 min and measured as pellets with excitation at 514 nm. The spectra were separately recorded in (a) dark and (b) bright regions of the samples.

Raman Spectra. The bright domains in the dark field observed by optical microscopy (Figure 4) were studied by using Raman spectroscopy. The Raman spectra of the surface of the pellets obtained by pressing the PANI (emeraldine) base processed in a ball mill for 5 or 10 min, and measured with excitations at 633 and 514 nm, exhibit much more pronounced changes in comparison with the spectrum of a pure original PANI (emeraldine) base than in the case of FTIR spectroscopy. The spectra were recorded separately in the dark and bright regions of the samples (Figures 7 and 8). It is well-known that the benzenoid or quinonoid constitutional units are often resonance-enhanced depending on the laser excitation wavelength (36−38). On the basis of UV−visible spectra of various forms of PANI (39−41), it is to be expected that the vibrations originating from quinonoid units in the polymeric products should be resonance-enhanced with both the 514 and 633 nm laser excitation wavelengths but more so with a 633 nm laser excitation.

The Raman spectrum of the original PANI (emeraldine) base obtained using a 633 nm excitation line (shown in Figure 7 for comparison) contains the peak connected with the C−C and C═C vibrations in benzenoid and quinonoid rings observed at 1593 cm^{-1} and the band at 1471 cm^{-1}

assigned to the C═N vibration in quinonoid units, which dominates the spectrum. A band of C−N stretching vibrations at 1220 cm^{-1} and a band of C−H bending vibrations of quinonoid rings at 1165 cm^{-1} are clearly observed in the Raman spectrum using a 633 nm excitation line (42−50).

Ball-milling. The evolution of Raman spectra employing an excitation line at 633 nm, for various mole ratios of oxidant to PANI (emeraldine) base for 10 min of grinding in a ball mill, is plotted in Figure 7. The spectra are different in the dark and bright regions of the samples. In the spectra measured in the *dark regions* (Figure 7a), the band connected with the C−C and C═C vibrations in benzenoid and quinonoid rings is observed at 1593 cm^{-1} (broadened) and a small shoulder at 1620 cm^{-1} is detected in the spectra of the samples mixed with silver nitrate. The last peak is observed in the spectrum of PANI (emeraldine) salt and belongs to the stretching vibrations of C−C bonds in benzenoid rings (42−50). The intensity of the dominant band of the C═N stretching vibrations in quinonoid units observed at 1471 cm^{-1} in the spectrum of the PANI (emeraldine) base is relatively decreased, and a new maximum at about 1502 cm^{-1} appeared on this band, which may be assigned to C═N and N−H deformation vibrations associated with the semi-

quinonoid structures (42–50). In addition to these changes, a relatively strong band at 1335 cm^{-1}, related to the vibration of the protonated semiquinonoid segments C–N$^{•+}$, with side peaks at 1375 and 1415 cm^{-1}, observed in cross-linked structures, appeared in the spectra (36, 37). The intensity of the peak at 1220 cm^{-1} (corresponding to C–N stretching vibrations) has decreased, and a new peak at 1258 cm^{-1} has appeared in the spectrum. The C–N stretching vibrations of various benzenoid, quinonoid, or polaronic forms and the benzene ring deformation vibrations are connected with this band. The position of the peak for the C–H bending vibration of quinonoid rings has moved from 1165 to 1168 cm^{-1}. The changes are more pronounced in the spectra of ground samples for a higher concentration of silver nitrate. All of these described changes are characteristic of the protonated state of PANI and correspond to the formation of delocalized polaronic structures (42–50). At the same time, the presence of the relatively intense band at 1471 cm^{-1} of the C=N vibration in quinonoid units corresponds to the oxidized form of PANI. A similar situation has been demonstrated during interaction of the PANI (emeraldine) base with transition-metal cations (48). The Raman spectrum of Zn-PANI measured with excitation 633 nm contains the characteristic bands of quinonoid segments of the PANI (emeraldine) base and also bands observed in (emeraldine) salt and assigned to the protonated semiquinonoid segments C–N$^{•+}$. The formation of a protonated PANI (pernigraniline) due to partial oxidation of the PANI (emeraldine) base by the metal ions has been confirmed by an increase of the band at ca. 900 nm in the UV–visible spectrum (48). The stabilization of conducting PANI (pernigraniline) salt and the absence of deprotonation of the oxidative structure of PANI in ionic liquids have also been recently demonstrated (27). This means that the reaction described in Figure 1 indeed proceeds so that the final product is PANI (pernigraniline) protonated with nitric acid produced and present in the dark regions of the samples.

The Raman spectra excited with the 633 nm line in the *bright regions* differ from the spectra measured in the dark regions (Figure 7b). First of all, their intensity is several times enhanced. A new intensive peak of the C=C stretching vibration in quinonoid structures at 1585 cm^{-1} with a sharp shoulder at about 1620 cm^{-1} corresponding to the C–C stretching vibration in benzenoid structures is well detected in the spectra. The band at 1471 cm^{-1} assigned to the C=N vibration in quinonoid units is preserved with unchanged intensity, which is close to the intensity of the band observed at 1585 cm^{-1}. Small new bands at 1378 and 1332 cm^{-1} are present in the spectra; a new peak at 805 cm^{-1} has also appeared. The spectra are virtually independent of the silver nitrate content. Similar bands are present in the surface-enhanced Raman spectra (SERS) of colloids obtained after oxidation of the PANI (emeraldine) base after adsorption on the silver nanoparticle surface (49) and in the SERS spectra of PANI thin films (50). They are characteristic of the pernigraniline state of PANI. We suppose that the bright regions reflect the traces of oxidized PANI (emeraldine)

present on the surface of the reduced silver granules. Interfacial contact between the reaction products, pernigraniline and metallic silver, gives rise to SERS (49, 50).

The evolution of the Raman spectra excited with a 514 nm excitation line in both the dark and bright regions is shown in Figure 8. The UV–visible spectrum of PANI (pernigraniline) salt exhibits a band near 530 nm, so we suppose that it will be resonantly enhanced with this excitation line (27). The spectra measured in the *dark regions* of the samples exhibit bands at 1592, 1560, 1498, 1349, 1220, and 1167 cm^{-1}. In comparison with the spectrum of the original PANI (emeraldine) base (Figure 8a), the ratio of the intensity of the band of the C–C and C=C vibrations in the benzenoid and quinonoid units (1592 cm^{-1}) and the intensity of the C=N vibrations in the quinonoid units (1498 cm^{-1}) relatively increased with an increase in the content of the oxidant; a small shoulder at about 1620 cm^{-1} appeared in the spectrum. The presence of the band of quinonoid vibrations, together with the features of the protonated structure in the spectra of the samples ground in the ball mill with silver nitrate, supports the finding obtained from the Raman spectra excited with a 633 nm line, that the spectra of the dark regions correspond to the resonantly enhanced Raman spectra of protonated PANI (pernigraniline) (48–50).

The spectra measured with a 514 nm excitation line in the *bright regions* exhibit enhanced intensity in comparison to the original PANI base. The bands at 1585, 1481, 1384, 1340, 1223, and 1169 cm^{-1} are present in the spectra of the samples obtained after 10 min of processing with silver nitrate (Figure 8b). The intensity of the band of the C–C and C=C stretching vibrations in benzenoid and quinonoid structures at 1585 cm^{-1} relatively increased with an increase of the silver nitrate content, and the band of the C=N stretching vibrations in quinonoid units at 1481 cm^{-1} remains in the spectra. We observe a higher background in comparison with the spectra measured with a 633 nm excitation line. It may be connected with absorption of the excitation light followed by fluorescence. We conclude that, similarly to the excitation at 633 nm, the spectra correspond to the formation of PANI (pernigraniline) salt deposited on the silver particles (48–50).

CONCLUSIONS

The nonconducting PANI (emeraldine) base reacts with silver nitrate in the solid state. The emeraldine form of PANI is oxidized to pernigraniline, and silver ions are reduced to metallic silver. Quinonediimine units in a residual emeraldine base are subsequently protonated with produced nitric acid. The conductivity increased from 10^{-9} to 10^{-2} S cm^{-1} during this reaction. Even a simple mechanical blending in a mortar leads to a marked increase in the conductivity, which sensitively reflects the progress of the reaction. The conductivity is enhanced after processing in a ball mill for several minutes; extending the processing time to over 5 min had no additional effect. FTIR spectroscopy of powdered samples mixed with potassium bromide and then pressed in pellets reveals only small changes in the PANI, viz., the conversion of emeraldine to pernigraniline and the proton-

ation caused by nitric acid, which is a byproduct. The samples pressed in pellets for Raman spectroscopic analysis are microscopically heterogeneous, with microseparated organic and inorganic phases. Raman spectroscopy can identify the "bright" areas composed of silver coated with pernigraniline and "dark" areas represented by PANI (pernigraniline), which becomes gradually protonated by nitric acid. SERS scattering was observed because of the presence of a pernigraniline—silver interface in the "bright" regions. The ease of the reaction between the PANI (emeraldine) base and silver nitrate is explained by the transfer of electrons and protons from the reductant, a PANI (emeraldine) base, to the oxidant, silver nitrate, assisted by the conducting PANI (pernigraniline) nitrate (14, 25, 27), which is generated in situ during the reaction.

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