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Mechanochemical Route to the Conducting Polymer Polyaniline

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ABSTRACT: A solvent-free mechanochemical route for the synthesis of polyaniline has been developed. Reactions between anilinium salts, such as anilinium chloride, anilinium sulfate, and anilinium camphorsulfonic acid and the oxidant, ammonium peroxydisulfate, result in polyaniline formation on ball-milling the reactants. Spectroscopic studies indicate that polyaniline is formed in its doped, conductive emeraldine oxidation state. By varying the aniline-to-oxidant ratio, a yield of up to 65% can be achieved. The polyaniline has a relatively high surface area of 69.7 m^2/g using the Brunauer−Emmett−Teller method. A typical bimodal molecular weight distribution is observed for the polyaniline product. Resistance measurements indicate that 1 h is sufficient for the solid-state reactions to reach completion.

Introduction

Since the discovery that conjugated polymers can be made to conduct electricity through doping, a tremendous amount of research has been carried out in the field of conducting polymers.[1] The 2000 Nobel Prize in Chemistry recognized the discovery of conducting polymers and over 25 years of progress in this field.[2] Among the family of conjugated polymers, polyaniline is one of the most useful since it is air and moisture stable in both its doped, conducting form and in its dedoped, insulating form.[3] Polyaniline is also unique among conducting polymers in that it has a very simple acid/base doping/dedoping chemistry (Figure 1). It has a great variety of potential applications including anticorrosion coatings,[4,5] batteries,[6−8] sensors,[9−11] separation membranes,[12−14] and antistatic coatings.[15,16]

Polyaniline can be made chemically or electrochemically by oxidative polymerization of the monomer aniline.[3] The electrochemical synthesis generally yields a polyaniline film on the anode, while the chemical polymerization route can make polyaniline in bulk quantities. The classical chemical synthesis of polyaniline is carried out in solution using aniline, an oxidant, and a strong doping acid with either aqueous or organic solvents.[3] By freezing the reaction bath, the polymerization can also proceed in the solid state.[17,18] Since the liquid monomer aniline forms solid salts with doping acids, such as hydrochloric, sulfuric, and camphorsulfonic, room-temperature solid-state polymerization of aniline should be possible using a solid anilinium salt as the precursor. Here, we describe a solvent-free mechanochemical route to polyaniline in which the reaction is induced by ball-milling an aniline salt and an oxidant under ambient conditions. The optical properties, molecular weight distribution, and electrical conductivity of the products are reported. The optimal molar ratio of aniline to oxidant is determined to obtain maximum yield. In-situ electrical resistance measurements of the reaction mixture indicate that 1 h is sufficient for the reaction to reach completion.

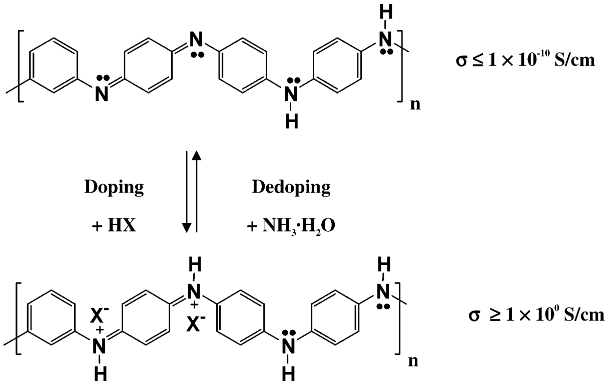

Figure 1. Repeat unit of the emeraldine oxidation state of polyaniline in the undoped, base form (top) and the fully doped, acid form (bottom). HX represents any protonic acid.

Experimental Section

Synthesis. Anilinium hydrochloride, anilinium sulfate, and ammonium peroxydisulfate were of analytical grade and were used as received (Fisher). A salt of aniline and camphorsulfonic acid (CSA) was prepared by the reaction between aniline and CSA in water followed by evaporation. In a typical solid-state reaction to produce polyaniline, a mixture of an anilinium salt and ammonium peroxydisulfate were loaded into a stainless steel grinding bowl of 50 mL capacity. The molar ratio of the anilinium salt to ammonium peroxydisulfate varied from 0.25:1 to 10:1. Six stainless steel grinding balls, four with a diameter of 1 cm and two with a diameter of 0.5 cm, were loaded with the reactants to facilitate grinding. The grinding bowls were then sealed and spun at 600 rpm in a planetary micromill (Pulverizette 7) for 1 h.

Purification. Once the spinning stopped, the product was transferred into a beaker and washed. Rinsing with 1.0 M ammonia yielded dedoped polyaniline, while rinsing with water left the product in the doped state. Approximately 250 mL of ammonia and 1000 mL of distilled water were used for rinsing. The product was then washed with methanol, filtered, and dried in a vacuum oven at room temperature for a period of at least 24 h. The dried product was then weighed to determine the percent yield.

Spectroscopy. Samples for UV−vis spectroscopy were prepared by dissolving a small amount of polyaniline in dimethyl formamide. The absorption spectra of the polyaniline were recorded on a UV−vis spectrometer (HP 8453). Samples for the FT-IR were prepared as a pellets by pressing a mixture

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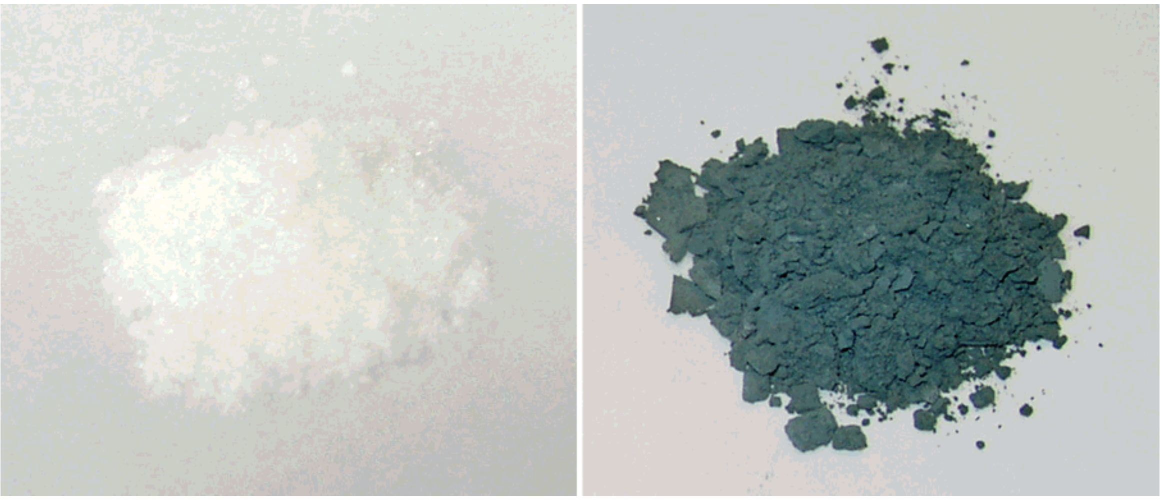

Figure 2. Mixture of anilinium sulfate and ammonium peroxydisulfate before (left) and after (right) ball-milling for 1 h.

of polyaniline and potassium bromide. FT-IR spectra were recorded on a Jasco FT-IR 420 spectrophotometer.

Molecular Weight. Molecular weight distributions of the polyaniline were measured by gel permeation chromatography (Shimadzu GPC), using a Polymer Laboratories guard column (PLgel MIXED-D 5 μm+) and an evaporative light scattering detector (ELSD-LT). The polyaniline was dedoped before dissolving in dimethyl formamide, which was also used as the mobile phase (flow rate: 0.8 mL/min). The solutions were filtered with 0.20 μm syringe filters before injection into the column. The column temperature was maintained at 40 °C. Polystyrene standards were used as the reference.

Surface Area. The surface area of the product was measured by nitrogen adsorption−desorption isotherms using the Brunauer−Emmett−Teller (BET) method (Micromeritics ASAP 2010). Dedoped samples obtained with 4:1 aniline-to-oxidant molar ratios were used in the experiments. The samples were degassed under vacuum at 100 °C before taking measurements.

Scanning Electron Microscopy. Powder samples were loaded onto an aluminum stage using carbon tape. The samples were neither ground nor gold-coated before the experiment. SEM images were taken with a JEOL 6700 field emission scanning electron microscope.

In Situ Resistance Measurements. The anilinium salt and ammonium peroxydisulfate were separately ground into fine powders. Weighed amounts of the two solid precursors were mixed in a glass vial by shaking. A small amount (approximately 0.30 g) of the mixture was then loaded into a hollow insulating tube and sandwiched between two stainless steel rods (0.8 cm in diameter). The setup was attached to a hydraulic press (Carver) and subjected to a pressure of 16 000 psi. Two stainless steel plates were used as contact pads to facilitate the connection to the source meter (Keithley 2400), which was interfaced with a computer. Rubber layers were used to insulate the contact pads from the press. Resistance versus time data were recorded during polymerization.

Sublimation Experiments. Anilinium sulfate and ammonium peroxydisulfate with a 1:1 molar ratio were first ball-milled for 1 h and then transferred to a crucible and heated at 250 °C in air. As a control experiment, the same amount of ammonium peroxydisulfate as that used in the synthesis was place in another crucible and heated with the polyaniline product. The crucibles were heated for 24 h and then cooled to room temperature.

Results and Discussion

The synthesis of polyaniline in a solvent-free environment has been achieved through a mechanochemical route. The process involves ball-milling a solid mixture of an anilinium salt and an oxidant at ambient temperature [Warning: large-scale reactions could produce excessive heat]. Figure 2 shows a mixture of anilinium sulfate and the oxidant ammonium peroxydisulfate before and after ball-milling. The white mixture of starting materials turns green after milling, indicating the formation of polyaniline in its doped emeraldine oxidation state. Note that without milling, little product forms due to limited contact between the reactants.

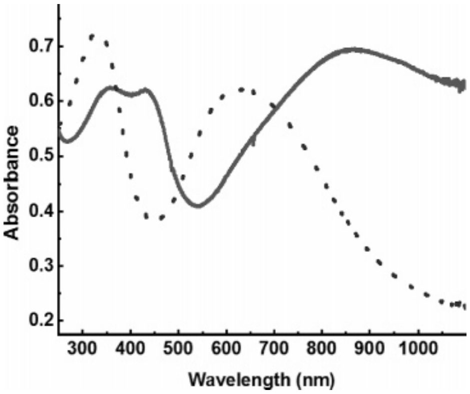

Figure 3. UV−vis spectra of polyaniline synthesized from ball-milling anilinium sulfate and ammonium peroxydisulfate for 1 h. The as-prepared product is in its doped emeraldine salt form (solid line) and can be dedoped (dotted line) by ammonia.

Figure 3 shows a typical UV−visible spectrum (solid line) of doped polyaniline obtained from ball-milling anilinium sulfate and ammonium peroxydisulfate (1:1 molar ratio). The peaks at 389 and 430 nm and the broader absorption at 869 nm correspond to electronic transitions from valence band to polaron band characteristic of the doped emeraldine oxidation state of polyaniline.[19] This is consistent with the green color observed in the product. Rinsing the product with ammonia yields dedoped polyaniline. Its UV−vis spectrum exhibits two absorption maxima at 340 and 638 nm. These peaks represent the $\pi-\pi^*$ transition and charge-transfer excitation-like transition bands of the emeraldine base form of polyaniline, respectively.[20] The FTIR spectra of the samples show characteristic bands at 1589 and 1496 cm^{-1} corresponding to the quinoid and benzenoid rings, respectively, in polyaniline.[21] The results indicate that polyaniline is indeed produced by this mechanochemical route.

The molar ratio of aniline to oxidant was systematically varied in order to optimize the yield of polyaniline.

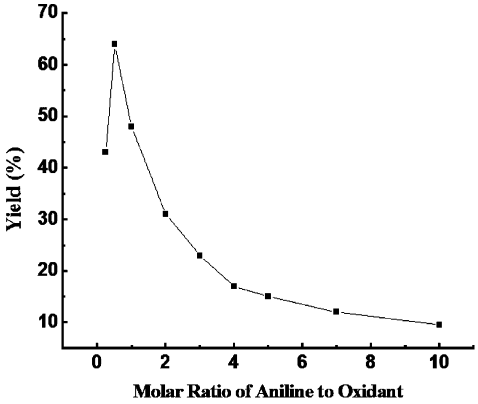

Figure 4. Percent yield of polyaniline made using different molar ratios of anilinium chloride to the oxidant ammonium peroxydisulfate.

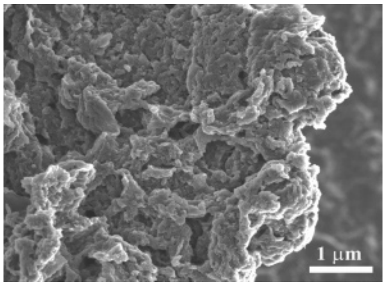

Figure 5. Scanning electron microscopy image showing the polyaniline product obtained with a 4:1 aniline·HCl-to-ammonium peroxydisulfate ratio.

Figure 4 shows the plot of the percent yield of polyaniline made from anilinium chloride and ammonium peroxydisulfate. With the amount of the oxidant kept constant, the molar ratio of aniline to oxidant was varied from 0.25 to 10. The plot shows a trend that higher yields were obtained with lower molar ratios between anilinium chloride and oxidant. A maximum yield of ~65% is obtained when the molar ratio between anilinium chloride and oxidant is 0.5. However, as the molar ratio of anilinium chloride to oxidant is increased, the yield decreases due to the formation of a significant amount of aniline oligomers or overoxidized small-molecular products. The same trend is observed when anilinium sulfate or a salt of aniline and camphorsulfonic acid is used. Since such solid-state reactions are limited by the diffusion of the solid precursors, methods for improving grinding should be helpful to increase the yields. The measured BET surface area of the polyaniline product is 69.7 m^2/g. This is a relatively high value and even exceeds the surface area reported for polyaniline coated on porous silica.[22] Scanning electron microscopy studies reveal that large chunks observed in the product are actually composed of fine particles at the submicrometer scale (Figure 5).

The products prepared from different monomer-to-oxidant ratios appear to be very consistent. Figure 6 shows the UV−vis spectra of dedoped polyaniline prepared with different monomer-to-oxidant ratios from 0.25:1, 1:1, 2:1, 3:1, 4:1, 5:1, 6:1, and 7:1. No significant difference can be observed between the spectra. No significant difference can be observed in their morphology, either (see Figure S1 (Supporting Information), SEM images of the morphologies of products).

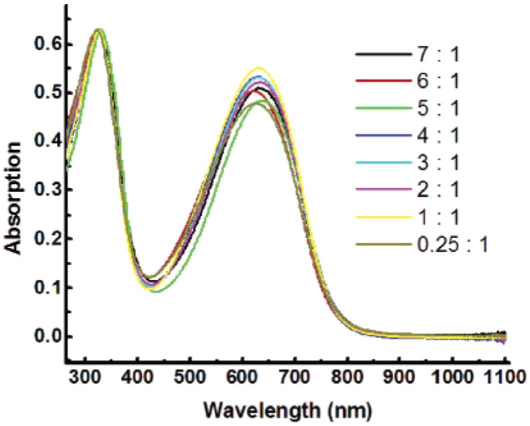

Figure 6. UV−vis spectra of dedoped polyaniline prepared with different aniline-to-oxidant molar ratios. It appears that emeraldine base is obtained in all the reactions.

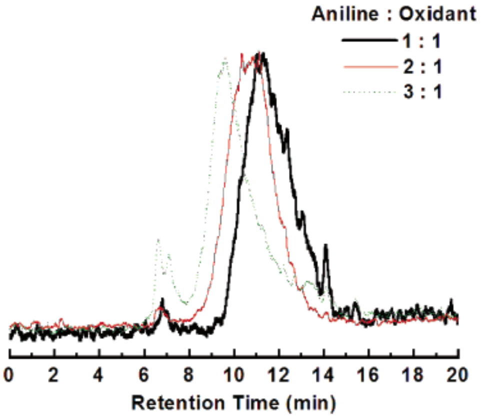

Figure 7. Gel permeation chromatogram showing the molecular-weight distribution of polyaniline made with different molar ratios of aniline to ammonium peroxydisulfate.

However, the molecular-weight distributions of the products are affected by the monomer-to-oxidant ratios. Figure 7 shows the molecular weight distributions of the samples obtained by gel permeation chromatography. Note that lower-molecular-weight samples exhibit a higher retention time. The synthetic process favors the formation of lower-molecular-weight polyaniline, especially at lower molar ratios of anilinium salt to oxidant. For example, the molecular-weight distribution for polyaniline obtained at 1:1, 2:1, and 3:1 ratios of anilinium salt to ammonium peroxydisulfate center around 11 220, 18 200, and 45 700, respectively, on the basis of polystyrene standards. The observed trend can be explained from the fact that, at a lower salt/oxidant ratio, chain growth is limited because of the small number of monomer molecules available for reaction. Conversely, with higher salt/oxidant ratios, the population of the monomer is sufficient to facilitate chain growth, resulting in the formation of higher-molecular-weight polyaniline. There is also a high-molecular-weight peak at around 501 200 found for each polymerization reaction. This bimodal molecular-weight distribution is also observed for polyaniline synthesized in solution.[23]

The changes in resistance of the reactant mixture as the reaction proceeds can be monitored using a simple home-built setup (Figure 8). The two reactants were first ball-milled separately and then mixed thoroughly in a vial by shaking. A small amount (about 0.3 g) of the mixed reactants was then sandwiched between two stainless steel rods inside an insulating tube and pressed at approximately 16 000 psi. The resistance change of the as-formed pellet was then monitored vs

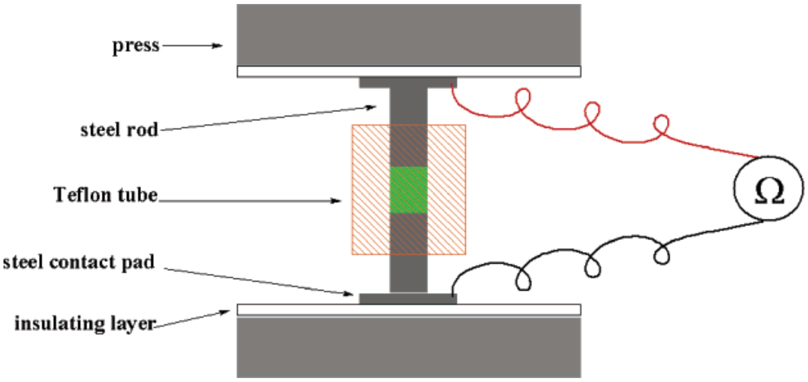

Figure 8. Schematic diagram showing the experimental setup for the in-situ resistance measurements. The resistance of the reaction mixture (green) is measured as the reaction proceeds.

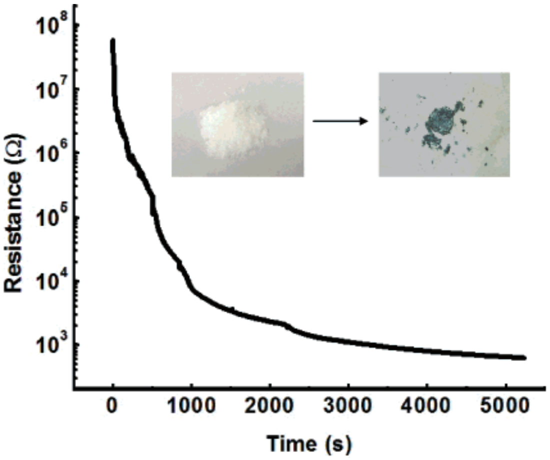

Figure 9. Real-time resistance changes of the reactant mixture, anilinium sulfate, and ammonium peroxydisulfate under 16 000 psi of pressure. The resistance drop from megaohms to kiloohms indicates the formation of the conducting product—doped polyaniline. The inset shows the reactant mixture before and after the measurement.

time (Figure 9). Note that the resistance of anilinium sulfate by itself stabilizes at the 0.1−1 MΩ level within minutes, while the resistance of pure ammonium peroxydisulfate exceeds the upper limit of the source meter (200 MΩ). The initial resistance of the reactant mixture (~70 MΩ) is considerably greater than that of the anilinium sulfate, as expected. Within minutes, the resistance drops significantly, falling below 1000 Ω within an hour. This indicates that the two highly insulating starting materials react to form a reasonably conductive product. Once no further significant change in resistance was observed (5500 s), the pressed sample was removed from the tube. The pellet appeared green and had a conductivity of 10^{-2} S/cm, indicating the formation of polyaniline in its doped, conductive emeraldine oxidation state. From the experiment shown in Figure 9, it appears that 1 h (3600 s) is a sufficient amount of time for the reaction to approach completion. Clearly, any reaction carried out in a ball mill should be complete within an hour since the stirring and mixing during ball-milling is much more dynamic than that occurring in a static press, thus facilitating the diffusion of reactants and increasing the synthetic yield.

The mechanochemical route to polyaniline still involves “wet” processes during the purification steps. If a “dry” purification method can be designed to remove the byproducts, which are mainly ammonium sulfate and aniline oligomeric salts, polyaniline will be obtained in a completely solvent-free system. The most applicable solid-state purification method for polyaniline synthesis seems to be thermal decomposition or evaporation since the byproducts can be sublimed or decomposed before the decomposition temperature of polyaniline. For example, ammonium sulfate decomposes between 230 and 280 °C, while the decomposition temperature of polyaniline is above 280 °C. In a preliminary experiment, anilinium sulfate and ammonium peroxydisulfate were first ball-milled for 1 h, transferred to a crucible, and heated at 250 °C. As a control experiment, the same amount of ammonium peroxydisulfate as used in the synthesis was placed in another crucible and heated with the polyaniline product. The crucibles were heated for 24 h and then cooled to room temperature. The crucible with ammonium peroxydisulfate was empty, and the one with polyaniline product still had dark powder remaining. The yield of the product was ~20 wt% based on anilinium sulfate. The polyaniline obtained is cross-linked and oxidized, as indicated by IR spectra. By lowering the decomposition temperature and applying vacuum, the oxidation of polyaniline should be minimized and yield should be improved.

Conclusions

The conducting polymer polyaniline can be readily synthesized through a mechanochemical route. UV−vis and FT-IR studies confirm the formation of the emeraldine oxidation state of polyaniline. A yield of up to 65% based on aniline can be achieved using a 1:1 molar ratio of anilinium salt to oxidant. Relatively high BET surface areas of up to 69.7 m^2/g are found. A bimodal molecular-weight distribution is observed. Resistance measurements indicate that 1 h is sufficient for reactions to go to completion.

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Supporting Information Available: Scanning electron microscopy images showing the polyanilie product. This material is available free of charge via the Internet at http://pubs.acs.org.

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