

Aqueous Dispersions of DBSA-Doped Polyaniline: One-Pot Preparation, Characterization, and Properties Study

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ABSTRACT: Aniline was polymerized in the presence of dodecylbenzene sulfonic acid (DBSA) as a functionalized protonic acid, in an aqueous medium to directly synthesize polyaniline (PANI)-DBSA particles. DBSA acted as a dopant and a surfactant with stabilizing PANI-DBSA dispersions by formation of strong hydrogen bonds. The $\text{NH}^+ \dots \text{SO}_3^-$ interactions between the PANI chains and the DBSA appeared at 1026 cm^{-1} in Fourier transform infrared (FTIR) spectrum. Elemental analysis was used to determine the degree of sulfonation (S/N ratio) of PANI chains and resulted that the sulfur-to-nitrogen ratio is 0.35. Thermogravimetric analysis (TGA) technique was used to analyze thermal properties of the particles and resulted that the synthesized PANI-DBSA particles have high thermal stabil-

ity. The moisture, DBSA and PANI contents of the PANI-DBSA were estimated from TGA curve, and then the number of aniline repeating units doped with one DBSA molecule was approximately calculated. X-ray diffraction (XRD) analysis confirmed that a chemical crosslinking reaction occurs between the PANI chains during thermal treatment of PANI-DBSA. The morphology of PANI-DBSA powder was investigated by scanning electron microscopy technique and showed that the PANI particles develops from round particles to a smooth surface. © 2009 Wiley. Periodicals, Inc. *J Appl Polym Sci* 113: 3980–3984, 2009

Key words: aqueous dispersions; thermal stability; polyaniline; dodecylbenzene sulfonic acid; polymerization

INTRODUCTION

The discovery of conducting polymers has opened up a new promising field in material science and engineering. Among them, polyaniline (PANI) is one of the most promising conducting polymers because of its unique properties, its ease of preparation, and excellent environmental stability. PANI has the utilization potential in a large number of applications, such as rechargeable batteries,¹ corrosion protections,² sensors,³ electronic devices,⁴ and light-emitting diodes.⁵ The major problem in applying these polymers is their poor processability, which several methods have been used to overcome this problem including *N*-substitutions,⁶ block copolymers,⁷ and doping PANI with a functionalized protonic acid.⁸

Undoped PANI can be schematically represented by Figure 1. The value of y represents the oxidation state and can be varied continuously from $y = 1$ (leucoemeraldine) to $y = 0$ (pernigraniline). When $y = 0.5$, the PANI is in the emeraldine oxidation form and so-called emeraldine base (EB). The imine

atoms in any of the species can be protonated in whole or in part to give the corresponding salt.⁹

MacDiarmid et al.¹⁰ found that pernigraniline is formed at the initial stage of oxidative polymerization of aniline, followed by reduction to emeraldine oxidation state. However, the exact mechanism of chemical polymerization of aniline is not yet fully known.^{11,12}

The EB form of PANI cannot be dissolved in common organic solvents, however, it can be dissolved in 1-methyl-2-pyrrolidinone (NMP) solvent. Therefore, freestanding EB form of PANI films can be cast from the NMP solution.¹³ The EB form of PANI can be doped by a protonic acid such as HCl, HNO₃, or H₂SO₄ and transferred to emeraldine salt (ES) form of PANI with a moderately high electrical conductivity.¹⁴ Cao et al.¹⁵ suggested a postdoping process, which involves the neutralization of the ES form to the EB form of PANI and the protonation of the EB form with the functionalized protonic acids. The results showed that the EB form redoped with dodecylbenzene sulfonic acid (DBSA) is soluble in various organic solvents, such as chloroform and xylene solvents.

This research work describes a direct one-pot method for aniline polymerization in an aqueous solution in the presence of the DBSA as a functionalized

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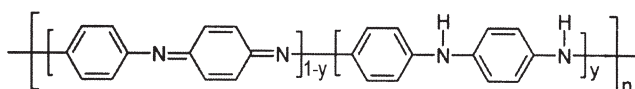


Figure 1 The structure of undoped polyaniline.

protonic acid. This method provides a simple, inexpensive, and convenient synthesis route for preparation of a stable polymer. Thermal stability and number of DBSA attached to each aniline unit of PANI-DBSA were calculated by the related thermogravimetric analysis (TGA) curve. Also, X-ray diffraction (XRD), and scanning electron microscopy (SEM) techniques were used to study of the crystallinity and morphology of the doped PANI, respectively.

EXPERIMENTAL

Materials

Aniline (99.5%) was purchased from Sigma-Aldrich (St. Louis, MO) and purified by distillation under vacuum. DBSA and ammonium persulfate (APS, 98.5%) were purchased from Merck (Darmstadt, Germany) and used as received. Other chemicals were also used as received without further purification. The used water in this study was deionized water.

Preparation of EB form of PANI

In a three-necked flask, 25 mL (275 mmol) of distilled aniline was dissolved in 500 mL of HCl (1M) and cooled to 0°C using ice bath. A total of 78.1 g (343 mmol) of APS was dissolved in 250 mL of HCl (1M) and added slowly into flask solution (exothermic reaction). The pink color appeared immediately and turned into deep blue. After 5 min, green colored polyaniline-HCl ES was started to precipitate from the solution. The polymerization was further preceded by stirring at 30°C for 24 h. The precipitate was filtered, washed with HCl (1 M) for several times, and stirred in a flask containing aqueous ammonia solution (1M). The blue precipitate was stirred for 3 h at room temperature to ensure the completion of de-doping. The resultant blue EB was filtered, washed with water, methanol, and acetone to remove the unreacted starting materials and oligomers. Finally, the blue EB was collected and dried in a vacuum oven at 80°C for 12 h to give 21 g (84.5%) of PANI.

Preparation of the PANI doped with DBSA (PANI-DBSA)

In a 1000 mL-flat bottom flask as a reactor, 8.3 g (90 mmol) of aniline was mixed with 29.3 g (90 mmol) of DBSA and 400 mL of distilled water to form a homogeneous milky white dispersion of anilinium-

DBSA complex. The flask was placed into an ice bath containing salt, equipped with a thermometer and cooled to 0–5°C. Then, 20.5 g (90 mmol) of APS was dissolved in 200 mL of distilled water and added into the flask during 2 min at the mentioned temperature. After 24 h, the dark green suspension of the doped PANI powder was precipitated with 600 mL of acetone. The precipitant was filtered off and washed with deionized water for several times until the filtrate was colorless and its pH value was the same as that of the deionized water. Then the product was collected and dried at 60°C for 48 h. The yield of product has been given in Table I.

Measurements

Infrared spectra of the pure PANI and PANI-DBSA were recorded on a Shimadzu 4300 FTIR spectrophotometer by the use of KBr pellets. Elemental analysis of C, H, N, and S atoms was performed in a Fisons Elemental Analyzer EA-1108. Perkin Elmer thermogravimetric analyzer model TGA-7 was conducted to measure the weight losses of the PANI-DBSA and pure DBSA in the temperature range of 30–700°C at a heating rate of 10°C/min in air. XRD measurements were made with a Rigaku XRD model D-MAX-2B to analyze four different samples of the PANI-DBSA powder in the range from 5 to 50° at a scan rate of 4°/min. One sample was without thermal treatment, and others were isothermally heated at 100°C, 200°C, and 300°C for 1 h, respectively. The surface morphology of the PANI and PANI-DBSA powders were studied using a Jeol 5400 scanning electron microscope.

RESULTS AND DISCUSSION

Synthesis of PANI-DBSA

A stable doped PANI aqueous dispersion was obtained from aniline polymerization in the presence of DBSA. The obtained dark green suspension was precipitated by acetone at the end of the polymerization reaction. Acetone not only decreased the viscosity of the reaction solution, but also cleaned out the residual DBSA. The obtained PANI-DBSA particles were soluble in common organic solvents such as chloroform, *m*-cresol, dimethylsulfoxide, toluene, and xylene. The molar ratio of aniline: DBSA into the flask was 1 : 1, but excess amount of DBSA remains in the flask at the end of the polymerization.

TABLE I
The Yield and Elemental Composition of the PANI Doped With DBSA

Polymer	Yield (%)	C (%)	H (%)	N (%)	S (%)
PANI-DBSA	61	76.9	4.26	10.11	3.54

This excess DBSA forms micellar structures and acts as a surfactant, with stabilizing dispersion of PANI-DBSA particles (Fig. 2). Also, the presence of excess DBSA molecules stabilizes the aqueous PANI-DBSA dispersion by forming strong hydrogen bonding with the PANI-DBSA particles. The hydrophobic tails of free and bonded DBSA molecules are arranged in a way that they all turn to each other, whereas the hydrophilic groups of the free DBSA turn to the aqueous phase.¹⁶

Infrared spectra

The FTIR spectra of pure PANI and PANI-DBSA are shown in Figure 3. The C=C stretching vibrations of quinoid and benzenoid rings are seen at 1587 and 1485 cm^{-1} , respectively. The peaks at 1317 and 830 cm^{-1} are corresponding to C-N stretching and C-H out-of-plane vibrations of 1,4-disubstituted benzene ring, respectively. The symmetric and unsymmetric stretching vibrations of O=S=O and S-O groups in PANI-DBSA sample appear as two new peaks at 1317 and 670 cm^{-1} , respectively. The peak at 1026 cm^{-1} is due to $\text{NH}^+\dots\text{SO}_3^-$ interaction between the PANI chain and the DBSA dopant.

Elemental analysis

To further investigation of the PANI-DBSA structure, elemental analysis was used to determine the degree of sulfonation (S/N ratio) of PANI chains. Table I shows the elemental composition of the PANI doped with DBSA. The results show that the sulfur-to-nitrogen ratio is 0.35. Based on the S/N ratio, it was found that approximately one sulfur atom per 6.6 aniline units exists in the polymer structure.

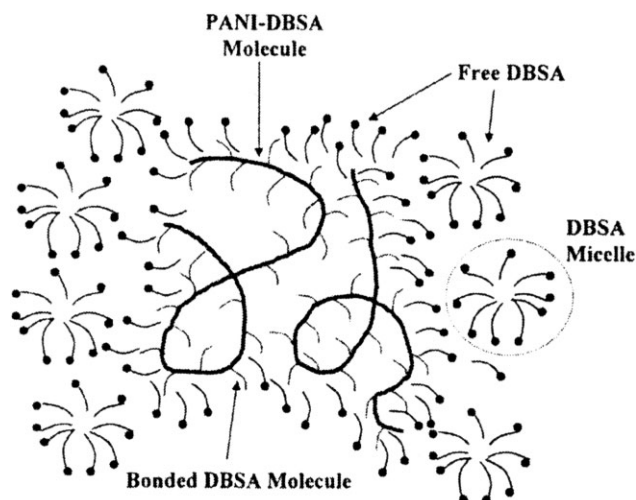


Figure 2 A schematic model of aqueous dispersions of PANI-DBSA.

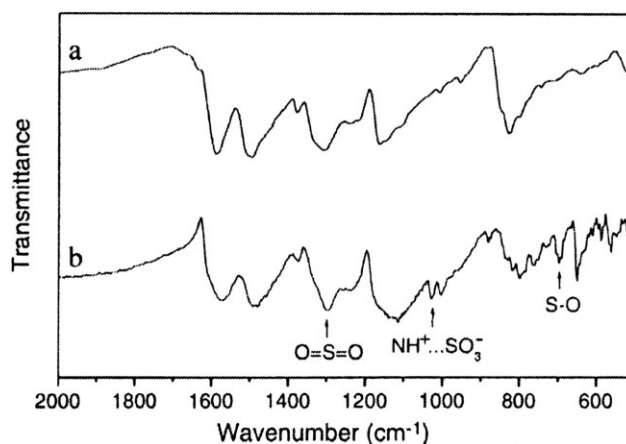


Figure 3 The FTIR spectra of the pure PANI (a) and the PANI-DBSA (b).

Thermal properties of PANI-DBSA

The TGA curves of pure DBSA and the PANI-DBSA powder are shown in Figure 4. Pure DBSA is degraded at around 250°C, but PANI-DBSA shows three major stages for the weight losses. The first weight loss is due to evaporation of moisture at $\sim 100^\circ\text{C}$. The second weight loss starting at $\sim 300^\circ\text{C}$ is attributed to destroy of the $\text{NH}^+\dots\text{SO}_3^-$ interaction between the PANI chain and the DBSA dopant with degradation of DBSA. This result shows that the starting degradation temperature of the PANI-DBSA is higher than that of the pure DBSA. The third weight loss of PANI-DBSA happens at the higher temperature (450°C) with decomposition of the chemical structure of the PANI backbone. Figure 4 shows that the doped PANI material is highly stable and can be used for various high temperature applications.

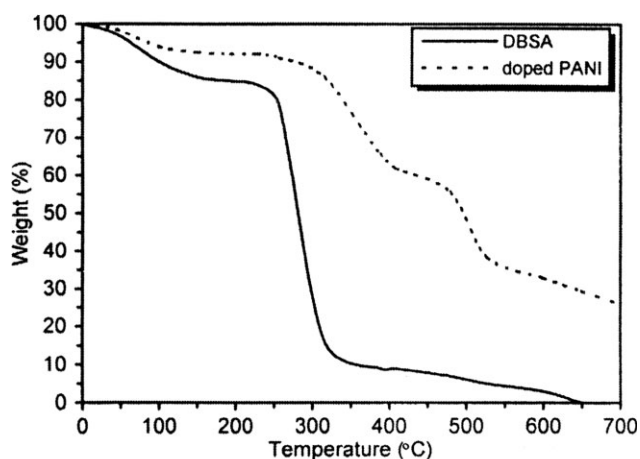


Figure 4 The TGA curves of the pure DBSA and the PANI-DBSA.

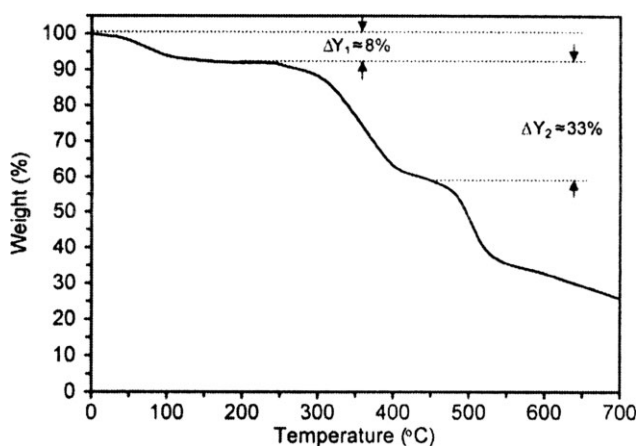


Figure 5 The TGA curve of PANI-DBSA showing the moisture (ΔY_1) and DBSA (ΔY_2) contents.

Calculation of the moisture and DBSA contents

The TGA curve of the PANI-DBSA was used for calculation of the moisture and DBSA contents of PANI-DBSA sample. As shown in Figure 5, the moisture and DBSA contents are $\sim 8\%$ (ΔY_1) and 33% (ΔY_2), respectively. Therefore, the weight percentage of PANI should be $\sim 59\%$. The aniline repeating units doped with one DBSA molecule were calculated by eq. (1).

$$\frac{100 - \Delta Y_1 - \Delta Y_2}{\Delta Y_2} = \frac{M_1 \times X}{M_2 \times 1} \quad (1)$$

The weight loss of moisture (ΔY_1), the weight loss of DBSA (ΔY_2), the molecule weight of aniline (M_1), and the molecule weight of DBSA (M_2) were substituted with 8, 33, 92, and 326, respectively. Then the value of the number of aniline repeating units (X) was calculated by eq. (1) and obtained at ~ 6.65 . It means that there are ~ 6.65 aniline repeating units doped with one DBSA molecule. Similarly, the obtained results showed that ~ 1.5 aniline repeating

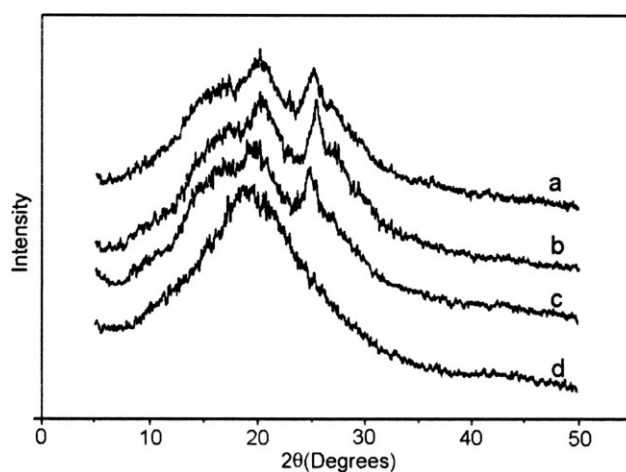


Figure 6 The XRD spectra of four PANI-DBSA samples. (a) Unheated, (b) heated at 100°C for 1 h, (c) heated at 200°C for 1 h, and (d) heated at 300°C for 1 h.

units contain one water molecule. Therefore, the obtained results from elemental analysis and TGA about doping level of PANI are fully compatible.

XRD spectra

Figure 6 shows four XRD analysis spectra of PANI doped with DBSA samples. For the doped PANI powder without thermal treatment (curve a), the resulted XRD indicated a broad amorphous diffraction peak $\sim 20^\circ$ and two weak crystalline peaks $\sim 15^\circ$ and 25° . Curves (b) and (c) represent the XRD spectra of the doped PANI samples heated isothermally at 100 and 200°C for 1 h. These spectra are almost similar to curve (a). Curve (d) shows the doped PANI powder heated isothermally at 300°C for 1 h. This XRD curve indicates that it is completely amorphous. Therefore, these obtained results confirmed that a suggested chemical crosslinking reaction by Scherr et al.¹⁷ happens during the

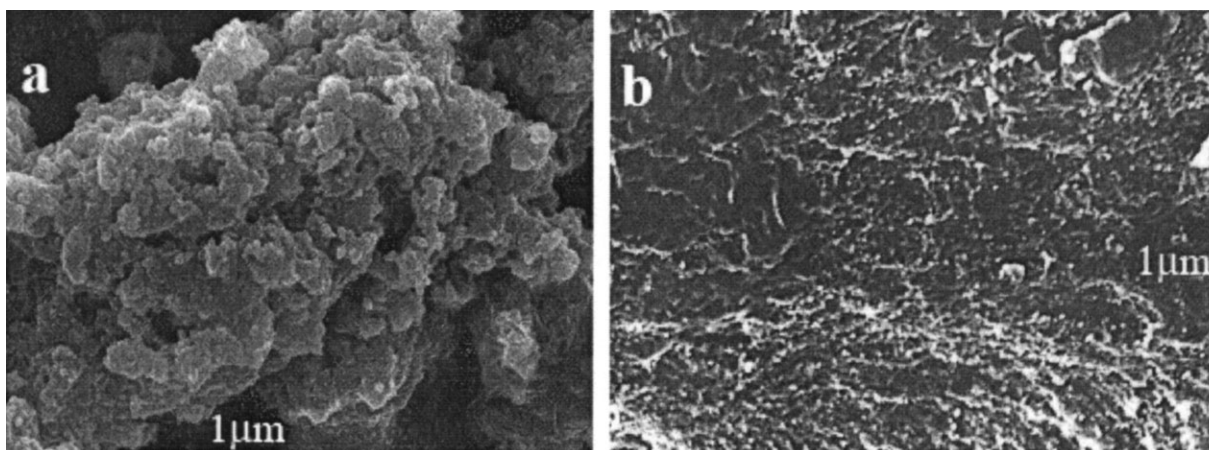


Figure 7 The SEM images of pure PANI (a) and PANI-DBSA sample (b).

thermal treatment process. A three-dimensional chemical structure decreases the crystallinity and increases the amorphous state apparently.

SEM images

The morphology of the pure PANI and the PANI-DBSA were analyzed by SEM and their photographs are shown in Figure 7. It is very clearly observable that pure PANI has spherical particles and the obtained PANI-DBSA powder has only a smooth surface. These photographs show that with doping PANI by DBSA, the surface morphology of PANI particles develops from round particles to a smooth surface area.

CONCLUSION

This article describes a process for polymerization of aniline in the presence of DBSA to obtain stable PANI-DBSA aqueous dispersions. Thermal properties study of the obtained material by TGA instrument showed that the PANI-DBSA is stable and can be used for various high temperature applications. Also, the TGA results and elemental analysis illustrated that 6.6 aniline repeating units have been approximately doped with one DBSA molecule, and 1.5 aniline repeating units have absorbed one water molecule. The XRD results showed that the PANI-DBSA (at 300°C for 1 h) has only a broad amorphous diffraction peak and the chemical crosslinking

reaction occurs among the PANI chains. The SEM images showed that the doped PANI has a smooth and homogeneous surface.

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