Synthesis and Characterization of Self-Doped Poly(aniline-*co*-aminonaphthalene sulfonic acid) Nanotubes

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ABSTRACT: Self-doped poly(aniline-*co*-aminonaphthalene sulfonic acid) (PANI-ANSA) was synthesized by the copolymerization of 5-aminonaphthalene-2-sulfonic acid (ANSA) and aniline. Scanning electron microscopy and transmission electron microscopy showed that the morphology of PANI-ANSA synthesized at a high molar ratio of aniline to ANSA was nanotubular, but at a low molar ratio, only a granular morphology formed. A possible formation mechanism for nanotubes was proposed. PANI-ANSA had better thermal stability than HCl-doped polyaniline; the highest onset decomposition temperature was as high as 340°C because of —SO$_3$H linked with the polymer backbone by a covalent bond. PANI-ANSA was partially soluble in basic solutions, and its conductivity was between 10^{-2} and 10^{-4} S/cm, depending on the sulfonation degree. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 1297–1301, 2003

Key words: copolymerization; morphology; templates

INTRODUCTION

The investigation of materials with microtubular or nanotubular structures is technologically and scientifically very interesting because of their potential applications in electronic and electrooptical devices,[1,2] molecular wires,[3] drug delivery,[4] and so forth. Moreover, electronically conducting polymers (CPs) have been intensively researched for their one-dimensional conjugated structures and adjustable conductivity,[5] which are desirable properties for molecular wires. Therefore, the synthesis of CP nanotubes is a very interesting project. Numerous chemical methods have been invented to prepare these materials, one of which is called *template synthesis*.[6] It was used by Martin[7,8] to prepare microtubes and nanotubes of CPs, semiconductors, and metals. In the template method, a microporous or nanoporous membrane as a template is required and must be removed after polymerization. Recently, Wan and coworkers[9,10] invented a self-assembled method, termed the *template-free method*, to synthesize microtubes and nanotubes of polyaniline (PANI) and polypyrrole in the presence of β-naphthalene sulfonic acid (β-NSA) as a dopant. The template-free method is very useful for preparing CP microtubes and nanotubes in large amounts because it does not need a complicated posttreatment procedure after polymerization.

Moreover, it is well known that PANI is one of the most important CPs because of its wide range of electrochemical, electrical, and optical properties. However, because of the rigidity of the PANI backbone, its conductive form is insoluble in common organic or aqueous solvents, except in strong polar organic solvents and doped by a suitable functional acid dopant, such as camphorsulfonic acid.[11] For improved processability, many PANI derivatives have been prepared according to various methods: (1) the posttreatment of the PANI base (e.g., sulfonated PANI can be obtained by the treatment of an emeraldine base or lecucoemeraldine base with a sulfonation agent)[12–14] and (2) the homopolymerization of suitable aniline derivatives or the copolymerization of aniline with the derivatives.[15–18] Among these derivatives, sulfonated PANI has attracted much attention because of its better performance, including better processability,[12–18] greater thermal stability,[19–21] and good electrical properties.[22] Recently, Atkinson et al.[15] synthesized a completely sulfonated PANI derivative, poly(5-aminonaphthalene-2-sulfonic acid), by the oxidization of sodium 5-aminonaphthalene-2-sulfonate, which can be soluble in water. However, the conductivity (10^{-3} to 10^{-5} S/cm) was much lower than that of the doped PANI.

Our previous results have shown that β-NSA plays an important role in the formation of PANI microtubes and nanotubes.[9,10,23] Therefore, it is interesting

to use 5-aminonaphthalene-2-sulfonic acid (ANSA) instead of β-NSA as the dopant and a component of a copolymer simultaneously to synthesize self-doped nanotubes, which may enhance their performance.

In this study, self-doped poly(aniline-co-aminonaphthalene sulfonic acid) (PANI-ANSA) was synthesized by the copolymerization of aniline and ANSA. The effect of the molar ratio of aniline to ANSA on the morphology, thermal stability, solubility, and conductivity of resulting PANI-ANSA was studied. A possible formation mechanism of PANI-ANSA nanotubes is discussed.

EXPERIMENTAL

Aniline monomer was distilled under reduced pressure. Ammonium persulfate [APS; $(NH_4)_2S_2O_8$], ANSA, and other reagents were used as received without further treatment. The typical synthesis process of the copolymerization of aniline and ANSA can be described as follows. Aniline (0.912 mL, 10 mmol) and ANSA (aniline/ANSA molar ratio = 50, 10, 4, or 2) were dissolved in 80 mL of deionized water with vigorous stirring at 0–5°C in an ice bath. APS as an oxidant [APS/(aniline + ANSA) molar ratio = 1] in 20 mL of deionized water was added drop by drop for 1 h to the mixed solution. After 24 h, the reaction mixture was poured into a large excess of deionized water and then filtered for the collection of the precipitate. The resulting PANI-ANSA was washed with water, methanol, and diethyl ether several times and finally was dried in a dynamic vacuum at room temperature for 24 h.

For the determination of the formation conditions of the nanotubes of PANI-ANSA, the product morphology was studied as a function of the preparation conditions, including the synthesis method, molar ratio of aniline to ANSA, and reaction time. The morphology of PANI-ANSA was measured with scanning electron microscopy (SEM; Hitachi 530, Tokyo, Japan) and transmission electron microscopy (TEM; Hitachi H-9000). The structure of PANI-ANSA was characterized by Fourier transform infrared (FTIR) spectra (Bruker, EQUINOX55, Ettingen, Germany). The thermal stability of PANI-ANSA was investigated by thermogravimetric analysis (TGA; PerkinElmer TGA7, Wellesley, MA) at a heating rate of 20°C/min. The conductivity of the compressed pellets of PANI-ANSA at room temperature was measured by a four-probe method with a Keithley 196 System DMM digital multimeter (Cleveland, OH) and an Advantest R6142 programmable direct-current voltage/current generator (Tokyo, Japan) as a current source.

RESULTS AND DISCUSSION

Copolymerization of aniline and ANSA

ANSA is sparingly soluble in water and can be polymerized by oxidation in its dilute solutions, but no high molecular weight polymer was obtained. Atkinson et al.[15] converted it into its sodium sulfonate, which could be polymerized in high-concentration water solutions with $Na_2S_2O_8$ or KIO_4 as an oxidant.
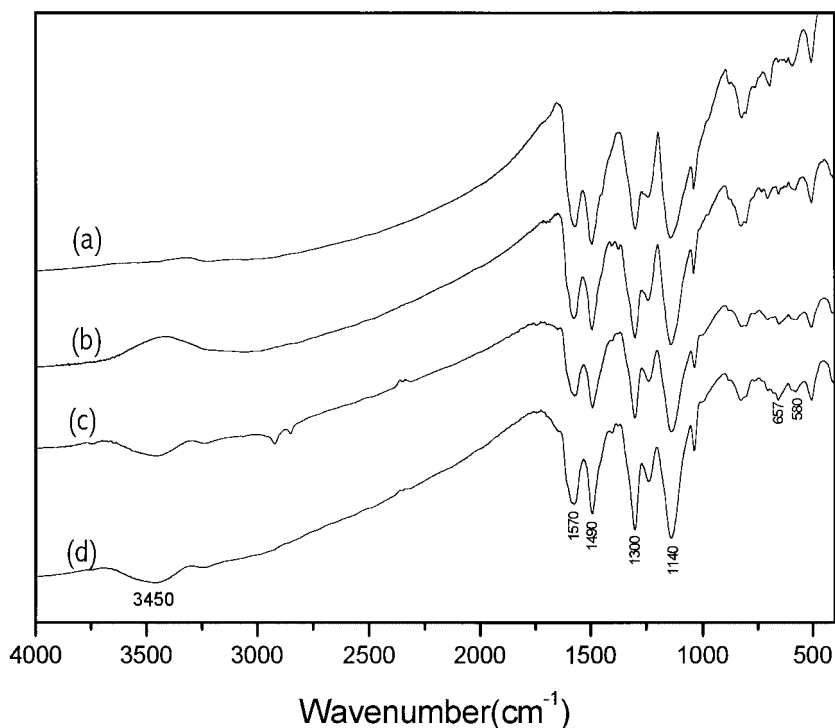

Figure 1 FTIR spectra of PANI-ANSA synthesized at different molar ratios of aniline to ANSA: (a) 50, (b) 10, (c) 4, and (d) 2.

Recently, we found that ANSA was cosoluble with aniline in water when the aniline/ANSA molar ratio was higher than 2 (0.1 mol/L aniline) at 0°C. When an APS solution was added to a solution containing aniline and ANSA, the reaction solution became violet red quickly, and a dark green precipitate was obtained after 24 h. Figure 1 shows FTIR spectra of PANI-ANSA synthesized at different molar ratios of aniline to ANSA. Strong peaks are clearly shown at 1570 (C=C stretching of the quinoid ring), 1490 (C=C stretching of the benzeniod ring), 1300 (C—N stretching), and 1140 cm^{-1} (C—N stretching) for all the samples. The numbers and positions of these peaks are very similar to those of HCl-doped PANI,[24,25] indicating that they all have backbone structures similar to that of doped PANI. However, the intensity of the peak at 1140 cm^{-1}, associated with doped PANI,[26] increased with the decrease in the molar ratio of aniline to ANSA, and this showed an increase in the doping level of PANI-ANSA. Moreover, the stretching vibration of —SO$_3^-$ at 657 cm^{-1},[27] of C—S at 580 cm^{-1},[14] and of —OH of —SO$_3$H at 3450 cm^{-1} increased with the decrease in the molar ratio of aniline to ANSA, indicating that a lower molar ratio of aniline to ANSA resulted in a higher sulfonation degree.
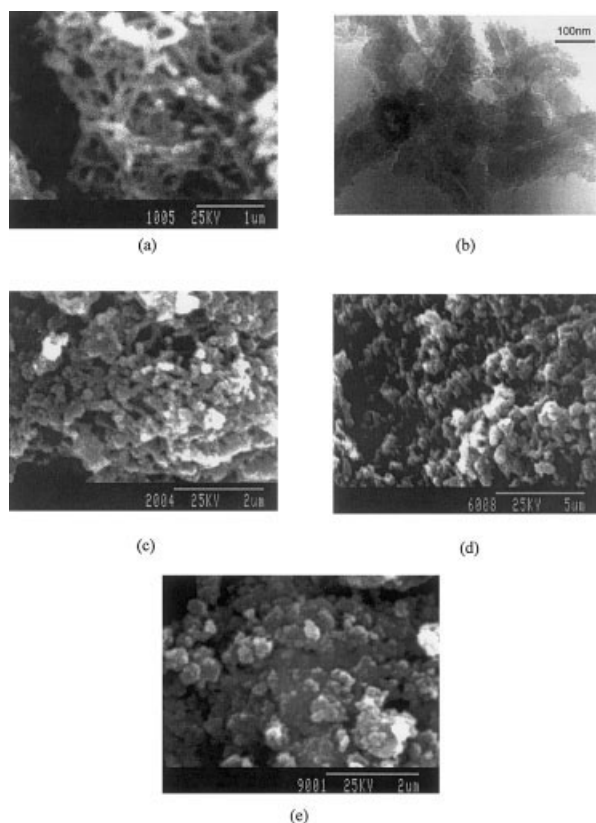

Figure 3 (a,c) SEM and (b,d) TEM images of PANI-ANSA synthesized at an aniline/ANSA molar ratio of 50 at different times: (a,b) precipitate formed after APS was added for half an hour and (c,d) precipitate subsequently formed by another 24 h of reaction.

Morphologies and their formation mechanism

Typical SEM and TEM images of PANI-ANSA with different molar ratios of aniline to ANSA are shown in Figure 2. The molar ratio of aniline to ANSA had a strong influence on the morphologies of PANI-ANSA. At a high molar ratio (aniline/ANSA = 50), for example, fibrous and granular morphologies [Fig. 2(a)] coexisted. The TEM image [Fig. 2(b)] shows that these fibrils were, in fact, hollow, with outer diameters of 60–100 nm. As the molar ratio of aniline to ANSA decreased to 10, however, a very short cylindrical and granular morphology could be observed instead [Fig. 2(c)]. As the molar ratios of aniline to ANSA were further decreased to 4 and 2, only irregular granular structures were obtained [Fig. 2(d,e)].

To understand the formation process of PANI-ANSA nanotubes, we measured the SEM and TEM images of PANI-ANSA synthesized at different reaction times, as shown in Figure 3. After APS was added for half an hour, the precipitate in the reaction solution (violet red) was separated by vacuum filtration. The morphology of the resulting precipitate was spherical with diameters of several micrometers, but the surface was very rough, as shown in Figure 3(a). TEM [Fig. 3(b)] shows that the substructure of the spheres was composed of smaller granular structures. The filtrate continued reacting for another 24 h. The morphology of the subsequently formed precipitate was almost completely nanofibers [Fig. 3(c)]. From the TEM image [Fig. 3(d)], we know that

Figure 2 SEM and TEM images of PANI-ANSA synthesized at different molar ratios of aniline to ANSA: (a) 50, SEM; (b) 50, TEM; (c) 10, SEM; (d) 4, SEM; and (e) 2, SEM.
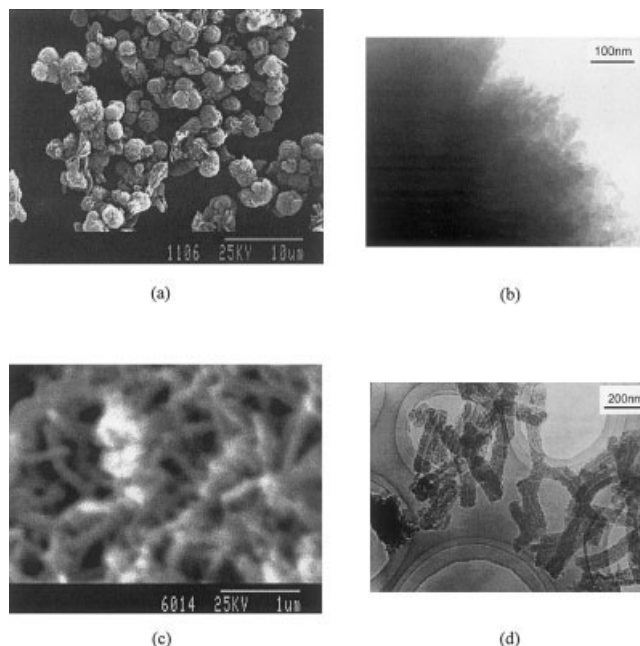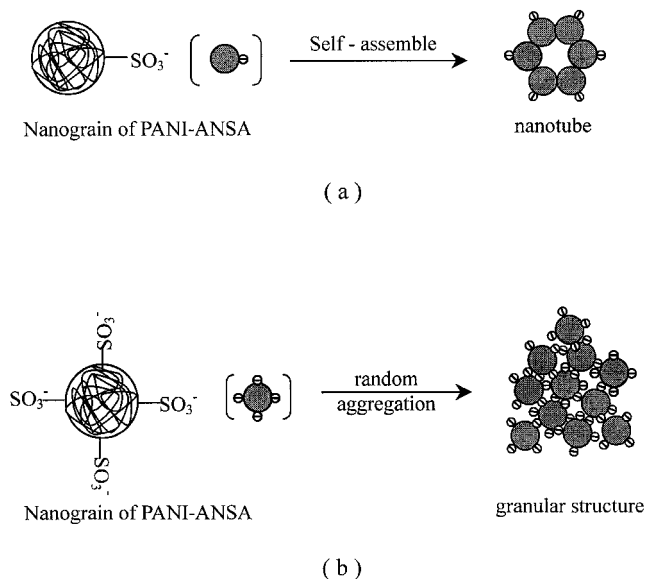
Figure 4 Aggregation model of PANI-ANSA at different molar ratios of aniline to ANSA: (a) self-assembly at a high molar ratio and (b) random aggregation at a low molar ratio.

they were nanotubes with outer diameters of 60–80 nm and inner diameters of less than 10 nm.

From these results, we can conclude that high molar ratios of aniline to ANSA and low reaction rates are favorable for obtaining nanotubes because the reaction rate at the beginning is faster than at other times. Moreover, the nanotubes and spheres were composed of smaller nanograins with diameters of several nano-

meters [Fig. 3(b,d)], and this is similar to the substructure of PANI nanorods obtained by Langer.[28] In PANI-ANSA, each of these nanograins includes many —SO₃H groups on naphthalene units. These —SO_3H groups can be divided into two parts according to their functions. Some of them are used for inter-nanograin doping, including interchain and intrachain doping in nanograins; the others are suspended on the surfaces of the nanograins. The —SO_3H group is hydrophilic, whereas the opposite side of the nanograin is hydrophobic. At a high molar ratio of aniline to ANSA, the distribution of the surface charge of nanograins is asymmetric [Fig. 4(a)]. When PANI-ANSA precipitated from solution, the nanograins formed nanotubes by self-assembly [Fig. 4(a)]. However, a fast reaction rate is disadvantageous for the self-assembly process, so only a spherical structure was obtained at the beginning of the reaction. With a decrease in the molar ratio of aniline to ANSA, the surface charge of the nanograins will gradually become nearly symmetric. The random aggregation becomes dominant, so a granular structure will form [Fig. 4(b)]. This is why a change in the morphology of long nanotube (short cylindrical structure) granular structures was observed when the molar ratio of aniline to ANSA was varied from 50 to 2.

Physical properties

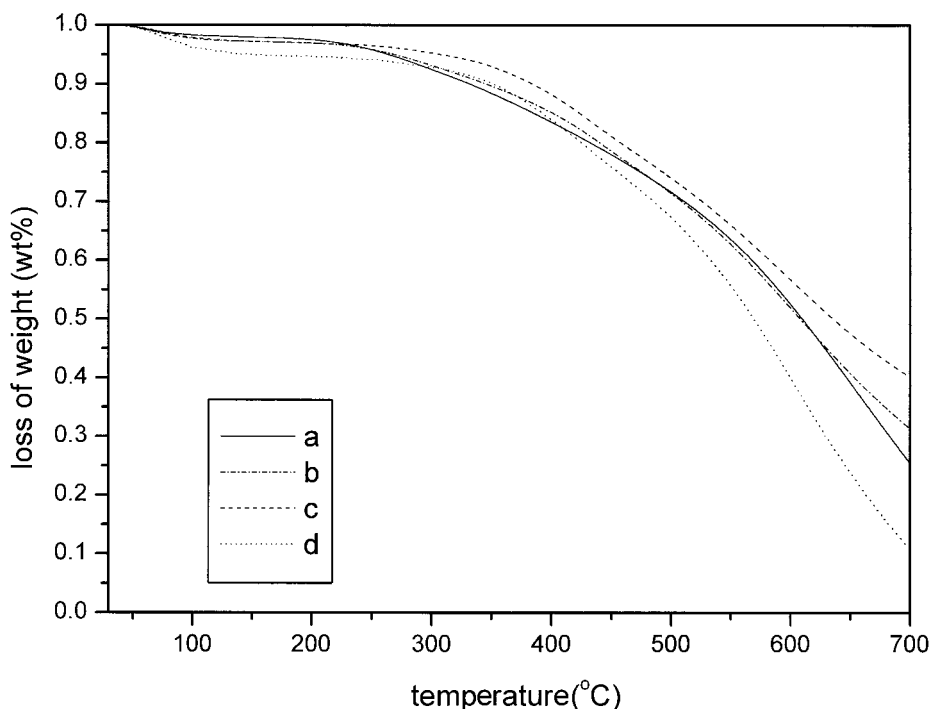One of our aims in synthesizing self-doped conducting PANI-ANSA was to obtain higher thermal stabil-

Figure 5 TGA curves of PANI-ANSA synthesized at different molar ratios of aniline to ANSA: (a) 50, (b) 10, (c) 4, and (d) 2.

TABLE I
The Solubility of PANI–ANSA in 0.2M NaOH Solutions and the
Conductivity at Room Temperature

Aniline/ANSA molar ratio	50	10	4	2
Soluble ratio (wt%)	36	54	65	86
Conductivity (S/cm)	5.7×10^{-4}	2.7×10^{-3}	6.9×10^{-3}	4.4×10^{-2}

ity in the doped state. Therefore, the thermal properties of PANI-ANSA were measured with TGA: typical TGA curves of PANI-ANSA are shown in Figure 5. The decomposition of PANI-ANSA underwent three steps: the loss of the water or solvent, dedoping and decomposition initiated by dopants, and decomposition of the PANI chains. This is consistent with the results of external acid-doped PANI.[27,28] However, for PANI-ANSA synthesized at low molar ratios of aniline to ANSA [Fig. 5(c,d)], the onset temperature of the decomposition of PANI-ANSA (340°C) was higher than that of inorganic or organic acid-doped PANI (often less than 300°C[29,30]) because of —SO$_3$H linked to the polymer backbone by a covalent bond.

In addition, PANI-ANSA is partially soluble in basic water solutions because the —SO$_3$H group can become a water-soluble salt in it. Table I lists the solubility ratio of PANI-ANSA in a 0.2 mol/L sodium hydroxide solution. With the decrease in the molar ratio of aniline to ANSA, the soluble ratio increased because of the greater number of —SO$_3$H groups in the PANI-ANSA backbone.

The conductivity of PANI-ANSA synthesized at different molar ratios of aniline to ANSA was between 10^{-2} and 10^{-4} S/cm (Table I). Moreover, the conductivity increased with the decrease in the molar ratio of aniline to ANSA because of the increasing doping level. However, the conductivity was lower than that for the HCl-doped PANI[24] because of distortion of the π-conjugated polymer chain by the introduction of a naphthalene ring into the polymer backbone.

CONCLUSIONS

Self-doped PANI-ANSA was successfully synthesized by the copolymerization of aniline and ANSA. The morphology, solubility, thermal properties, and room-temperature conductivity of the resulting PANI-ANSA were influenced by the molar ratio of aniline to ANSA. In particular, a change in the long nanotube (short cylinder) grains in the morphology was observed when the molar ratio of aniline to ANSA was varied from 50 to 2. Because the —SO$_3$H group was hydrophilic and the opposite side of a nanograin was hydrophobic, a self-assembly model was used to interpret the observed phenomenon. Moreover, the ther-

mal stability of PANI-ANSA was found to be better than that of an external acid-doped PANI because the —SO$_3$H group was covalently attached to the polymer backbone.

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