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Facile Preparation of Soluble and Conductive Polyaniline in the Presence of Lignosulfonate and a Constant Magnetic Field (0.4 T)

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ABSTRACT: A convenient and economical method for preparing soluble conductive polyaniline nanoparticles is introduced in this article. Polyaniline (PANI) was prepared by utilizing a renewable resource calcium lignosulfonate (LS) as dopant in the presence (PANI-LS-M) and absence (PANI-LS-A) of a constant magnetic field (MF). Their structures and properties were systematically studied. Compared with PANI-LS-A, the PANI-LS-M exhibited a much higher conductivity, solubility, and thermo stability, which was due to the effective doping of the LS caused by the stretching and orientation effects of the MF. The conductivity of the PANI-LS-M (20.2 S/cm), which was prepared in the presence of a MF (0.4 T) with a polymerization yield of as much as 96%, was increased by four times compared with that of the PANI-LS-A (4.9 S/cm). Meanwhile, the solubility of the PANI-LS-M was two times higher than that of the PANI-LS-A in solvents such as NMP, dimethyl sulfoxide, dimethyl formamide, formic acid, and acetidin. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2014, 131, 40467.

INTRODUCTION

As one of the most promising conductive polymer, polyaniline (PANI) has attracted much attention because of its easy synthesis, excellent environmental stability, attractive redox, and simple acid/base doping/dedoping.[1–5] However, PANI is inherently insoluble and infusible due to its strong intermolecular interactions and has seriously restricted its applications.[6] To solve these problems, numerous efforts have been made, such as introducing alkyl groups[7,8] or hydrophilic groups (e.g., sulfonic groups)[9,10] to the molecular chains of PANI.

Sulfonates have been used as a dopant in the in situ polymerization of aniline (An) to afford PANI with high conductivity and good solubility.[11] However, most studies just focus on the sulfonic acids such as camphor sulfonic acid,[12] dodecylbenzenesulfonic acid,[13] and para-toluene sulfonic acid.[14] These dopants are not cost-effective and not environmental in terms of renewability of materials. Recently, polymeric dopants have also been used for the synthesis of soluble, electroactive polymers.[15–19] Among them, lignosulfonate (LS), an inexpensive byproduct from pulp industries, is a highly water-soluble polysulfonic product composed of crosslinked phenylpropane units and functional groups such as sulfonic, phenolic, hydroxyl, and hydrophobic groups.[20] As a polymeric dopant, LS has gained more and more attention and has been used to synthesize water-dispersible PANI.[19–23]

However, there exist great steric hindrance between the polymeric sulfonate and the conducting polymer during the polymerization, which can cause the torsion of the PANI backbone, thus making it difficult for the effective doping of LS into the PANI chains.

Chemical reactions with free radicals are dramatically affected by a magnetic field (MF) and the most important MF effect on diamagnetic molecules is magnetic orientation and concentration.[24–26] Uniform MFs tend to align molecules in the polymerizing medium, which can indeed accelerate the polymerization and can be favorable for increasing conductivity of the reaction products.[27,28] Therefore, the aim of this article is to obtain a soluble and high conductive PANI doped with LS (PANI-LS) under the presence of a constant MF.

EXPERIMENTAL

Materials

An was supplied by Chengdu Kelong Chemical Reagents Co. and was purified by distillation under reduced pressure prior to use. Calcium lignosulfonate (LS) was purchased from Tianjin Yeats Chemical Reagent Co. Ammonium persulfate (APS) was purchased from Chuandong Chemical Reagent Company (Chengdu, China). Carbon paper (25 S/cm) was obtained from Shanghai Hesen Electronics Co. All the other chemicals were of analytical grade and used as received.
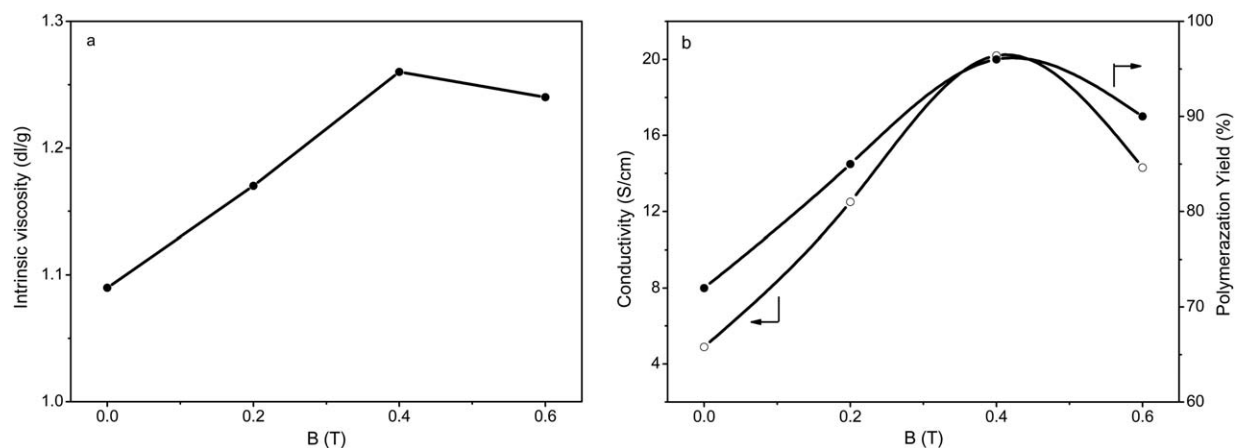
Figure 1. Effects of the MF on the intrinsic viscosity (a) and polymerization yield and conductivity (b) of the PANI-LS.

Preparation of PANI-LS

A representative polymerization for synthesizing PANI-LS was as follows: Firstly, LS (1.58 g) was added to an HCl (1.0 M, 70 mL) aqueous solution in a 250-mL glass flask and stirred for 30 min. Then, An (1.82 mL) was added to the LS solution and stirred vigorously for 30 min to obtain a brown emulsion, and some pieces of carbon papers were added in. APS (4.56 g) was dissolved in HCl (1.0 M, 30 mL) aqueous solution and then added dropwise to the above emulsion. After that, the emulsion was stirred for 5 h in the presence or absence of a MF. When the reaction was completed, ethanol (25 mL) was added in for de-emulsification, then the resulting mixture was filtered and the filter cake was washed with distilled water repeatedly until the filtrate was colorless. The carbon papers loaded with PANI-LS were taken out and used as a working electrode for electrochemical tests. Finally, the filter cake was dried in a vacuum oven at 60°C for 24 h to obtain PANI-LS. The product of 1.68 g was obtained with the yield of approximately 90% referring to the amount of An.

Characterization

All electrochemical tests were carried out on electrochemical workstation system (CHI660). A three-electrode cell was used, in which a piece of carbon paper (2 cm × 0.3 cm) loaded with PANI-LS was used as working electrode, a platinum foil as counter electrode, and a saturated calomel electrode as reference electrode. The electrolyte was 1 M HCl aqueous solution. Cyclic voltammetry (CV) tests were performed by scanning the potential from −0.2 to 1.0 V at a scan rate of 20 mV/s. Electrochemical impedance spectroscopy (EIS) spectra were acquired in the frequency range from 10^5 Hz to 10^{-2} Hz with ac amplitude of 5 mV.

Viscosity tests of the PANI-LS solution were carried out with an Ubbelohde capillary viscometer. A certain amount of PANI-LS powder was dissolved in 98% H_2SO_4 to prepare PANI-LS solutions with concentration of 2.5, 3.3, 5, 6.7, and 10 mg/mL. The viscosities of PANI-LS solutions in different concentrations were determined in a thermostated water bath of 30°C. Flow times were recorded with a stopwatch with reproducibility ±0.2 s. All the viscosity tests were repeated at least three

times to ensure the reliability of the data. The solubility of PANI and PANI-LS samples were qualitatively evaluated using the following method: 0.2 g of fine polymer powders were added into the solvent of 10 mL in a small glass container and ultrasonic oscillation for 10 min at room temperature. Then, the solutions were filtrated and washed with distilled water until the filtrates were colorless, then dried, and the solubility obtained.

FTIR spectra were recorded on a Nicolet FTIR 5700 spectrophotometer in KBr pellets. X-ray diffraction pattern of the PANI-LS were taken with a 94 Shimadzu6000 X-ray diffractometer using Cu Kα radiation in the 2θ range of 10–40°. The thermogravimetric analysis (TGA) of the samples was performed on SHIMADZU DTG-60H analyzer under a nitrogen atmosphere from 30°C to 600°C at a heating rate of 10°C/min. Scanning electron microscopy (SEM) images of the samples were obtained using Hitachi S-4700(II) SEM. A pellet of PANI-LS (diameter: 10 mm, thickness: 3 mm) was prepared by compression at 10 MPa at 25°C for conductivity measurement using a four-point probe (VEECO FPP-5000) meter.

RESULTS AND DISCUSSION

Selection of MF Intensity for the Synthesis of PANI-LS

Intrinsic Viscosity, Conductivity, and Polymerization yield. Figure 1(a) illustrates the effects of the MF on the intrinsic viscosity of the PANI-LS. As could be seen in Figure 1(a), the value of intrinsic viscosity increased with increasing intensity of MF and then decreased when a MF of 0.6 T was applied, indicating the variation tendency of molecular weight (MW).

The conductivity and the polymerization yields of the PANI-LS at different MF intensities (0-0.6 T) were also calculated and shown in Figure 1(b), which have similar variation as that of intrinsic viscosity. The conductivity increased with the increasing intensity of MF and reached a maximum of 20.2 S/cm at 0.4 T, which was much higher than that of PANI-LS prepared under common polymerization conditions.[19,22,23] Meanwhile, the yields increased monotonically from 72% (0 T) to as much as 96% (0.4 T) when a reaction time of 5 h was adopted, which was higher than that of Roy S reported.[19]
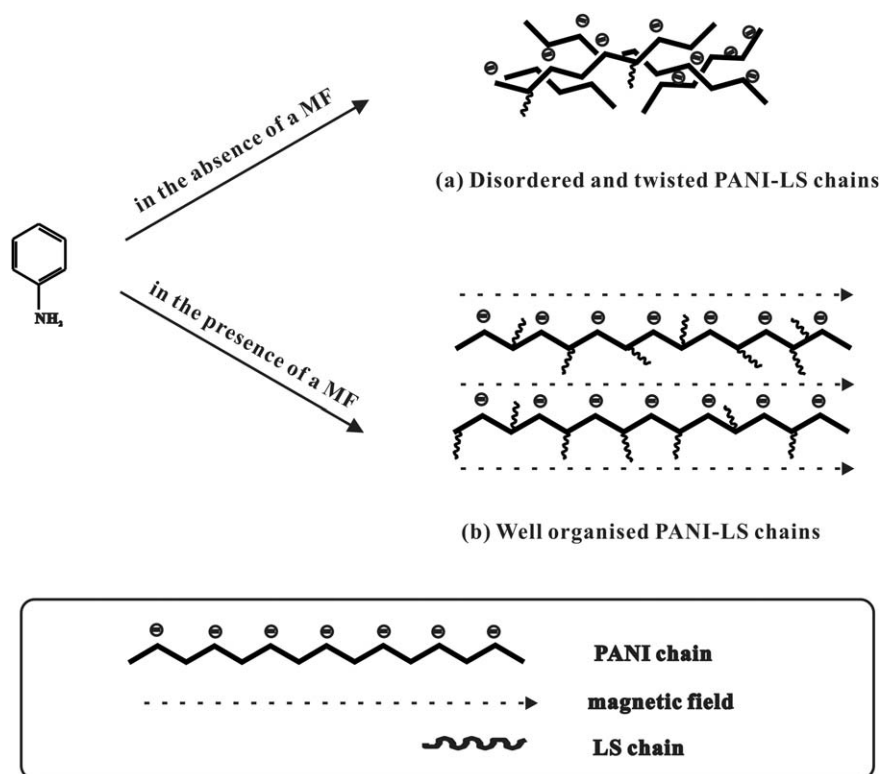
**Scheme 1.** Synthesis of PANI-LS in the presence and absence of a MF.

For an illustrative purpose, the polymerization and doping mechanism were presented and are shown in Schemes 1 and 2. An applied MF could initiate level splitting of radicals in triplet state (Zeeman effects), restraining the radical's intersystem crossing from triplet state to singlet state, thus increasing the concentration of radicals in triplet state, which initiate the polymerization.[26] Moreover, MF can induce orientation to most organic polymer molecules, which makes the molecular chains aligned more orderly.[28]

In the process of An polymerization, the stretch and orientation effects of MF caused prior arrangement and growth of molecular chains, chain segments, and micro-fiber in a certain direction and extended conformation of molecules (see Scheme 1). Therefore, the chains of both PANI and LS were alternatively rearranged under the electrostatic force and hydrogen bonding as shown in Scheme 2. More dopants were compactly linked to PANI with the increase of MF intensity. In addition, LS in turn as a template could take a conformation with more extended chains,[23] consequently forming a

large conjugated system. The coplanarity of the molecular chains was also improved, and thus the conductivity of PANI-LS was increased owing to the free motion of charges in the large conjugated system.

However, a high reaction rate may bring about an early termination reaction. Oligomers and byproduct were produced at 0.6 T due to the anabatic collision of free radicals, which could induce a low degree of polymerization and yield; the conductivity was also decreased as shown in Figure 1(b).

CV and EIS Analysis. Figure 2(a) illustrated the CV curves of the PANI-LS synthesized at different MF intensity (0–0.6 T). It was apparent that all the curves were the same profile, a typical CV of the samples showing the typical oxidation and reduction peaks in good agreement with PANI. The peaks located at ~0.25 V should be ascribed to the transition from the leuco form to the emeraldine form, whereas the peaks at ~0.8 V were the transition from emeraldine to pernigraniline. The middle peaks (at ~0.6 V) were assigned to the degradation of the
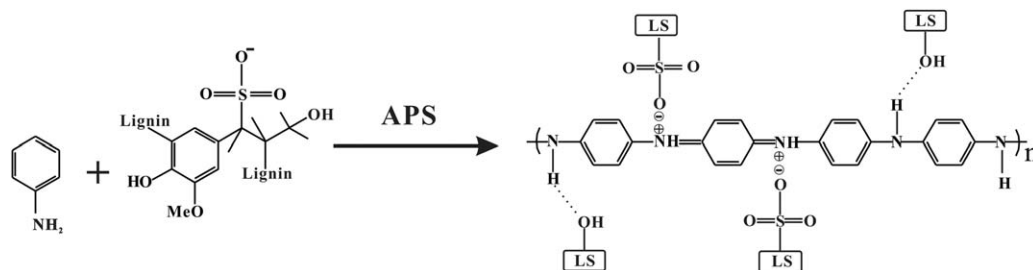
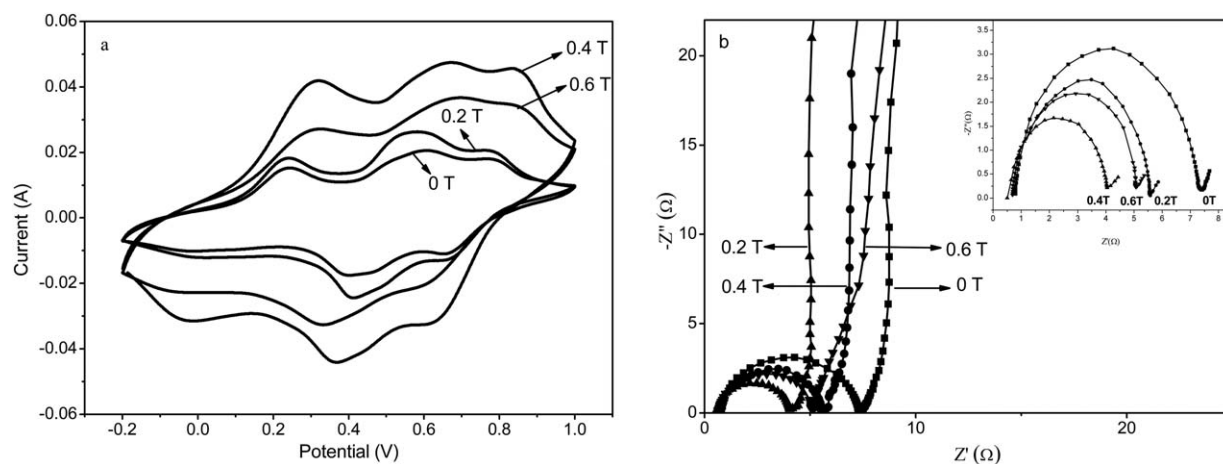**Scheme 2.** Proposed interaction between PANI chains and LS.

Figure 2. CV curves (a) and EIS curves (b) of PANI-LS synthesized at different MF intensity.

PANI.[29] As could be seen in Figure 2(a), the anodic peak current increased with the increase of MF intensity and attained a maximum at 0.4 T, then decreased with further increasing intensity of MF, which was in line with the conductivity.

Figure 2(b) showed the EIS curves of PANI-LS synthesized at different MF intensity. It can be observed that all of the EIS curves display similar characteristics; the impedance response of the PANI-LS system at all potentials consist of three distinct regions, and the top right corner in Figure 2(b) is a larger view of the higher frequency region. The semicircles at higher frequency region are related to the charge transfer resistance (Rct),[30] which had the same variation with CV plots. As could be seen in Figure 1(b), the Rct of the PANI-LS films reduced from 7.5 Ωm^2 to 4 Ωm^2 when increasing the MF intensity, and reached a minimum at 0.4 T, indicating the decreasing resistance, which was consistent with results obtained in CV tests.

According to the above results, the MF intensity of 0.4 T was optimal for the synthesis of conductive PANI-LS. Therefore, the PANI-LS prepared in the presence of a MF (0.4) T was used for the following study.

Fourier Transform Infrared Spectroscopy
The Fourier transform infrared spectroscopy (FTIR) spectra of PANI-LS synthesized in the absence of a MF (PANI-LS-A) and in the presence of a MF (PANI-LS-M) is as shown in Figure 3. The spectra of PANI and LS are included for comparison. The main characteristic peaks of PANI can be clearly observed: two peaks at 1,562–1,578 cm^{-1} and 1,482–1,491 cm^{-1} were associated with the stretching of quinoid and benzenoid rings of PANI chains, respectively.[19,23] The peak at 1,297–1,303 cm^{-1} should be due to C—N stretching vibration in an alternative unit of quinoid–benzenoid–quinoid (secondary aromatic amine). The peaks at 1,245–1,247 cm^{-1} and 1,130–1,150 cm^{-1} could be assigned to a C—N+• stretching vibration in the polaron structure[31,32] and a vibration mode of the —NH+= structure, respectively, which confirmed the formation of protonated conductive PANI-LS.[23] The peaks occurring at 820–823 cm^{-1} were assigned to C—H out of plane bending vibration mode. All the main peaks of LS were found in agreement with previous reports.[23,33] The peaks at 1,026–1040 cm^{-1} should be

attributable to S=O symmetric stretching of the —SO_3 group on the LS chains,[22] which indicates the $NH^+ \dots SO_3^-$ interaction between the PANI chain and LS groups, and this band was slightly weak because of the low mass ratio of LS used. And the peak at 510–521 cm^{-1} was ascribed as shear vibration modes of sulfonic acid (O=S=O group deformation). Compared with the bands of PANI-LS-A, the main characteristic peaks of PANI-LS-M shifted to a lower frequency to some extent, which indicated that the delocalization of electron in the PANI-LS-M was more extended than that in the PANI-LS-A, consequently a higher conductivity was obtained.

Solubility. Solubility of pure PANI and PNAI-LS samples was investigated in five different solvents including NMP, dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), formic acid (HCOOH), and acetidin, respectively, and are shown in Table 1. Compared with the pure PANI, the PANI-LS samples presented better solubility in polar solvents such as NMP, DMSO, and DMF, especially in NMP. Meanwhile, as can be seen in Table 1, the solubility of PANI-LS-M was almost twice that of PANI-LS-A. The significant improvement of the solubility was due to the effective doping of the LS in the presence of MF; a great number of large-sized sulfonic acid molecules increased the
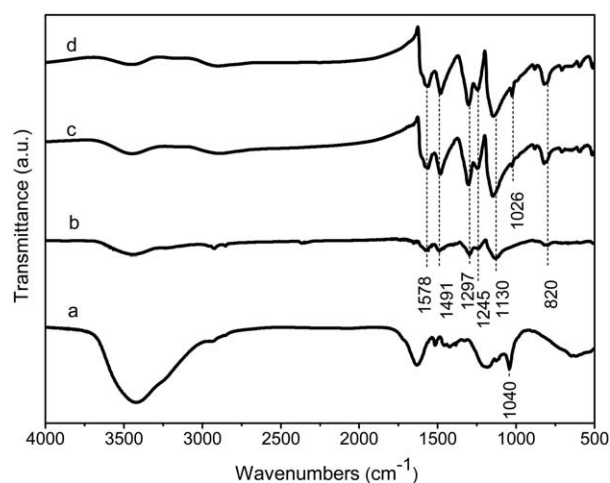

Figure 3. FTIR of LS (a), PANI (b), PANI-LS-A (c), and PANI-LS-M (d).
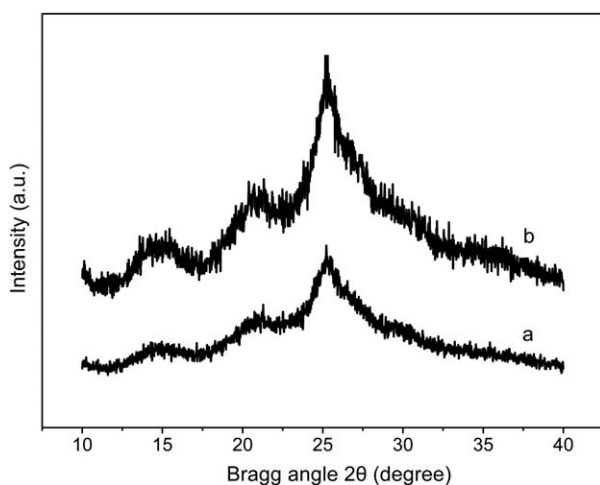
Table 1. Solubility of PANI and PNAI-LS Samples

Samples	Solubility in different solvents (mg/mL) and solution colors				
	NMP	DMSO	DMF	HCOOH	acetidin
PANI	1.78 (B)	1.64 (BR)	1.55 (DP)	1.47 (B)	0.89 (B)
PANI-LS-A	2.12 (DB)	2.03 (B)	2.02 (B)	2.01 (DP)	1.13 (BL)
PANI-LS-M	4.27 (DB)	4.12 (B)	4.16 (B)	3.66 (DP)	2.58 (BL)

Solution colors: B, blue; DB, dark blue; BR, brown; DP, dark purple, BL, black;

interplanar distance and the solvent molecules could be easily entered into the lattices to dissolve the polymer chain in solvents. Moreover, the polarity of PANI-LS was enhanced by the introduction of sulfonic groups in LS, which has good compatibility with solvents.[35,36] Thus, the sulfonic groups should be responsible for the significant variation of the solubility.

In addition, the color of the PANI-LS solution depended on the solvents. This reveals that the samples exhibit solvatochromic properties, as the PANI-LS chains may have different conformations in different solvents.[37,38] The presence of MF and LS can greatly improve the poor solubility of PANI, and thus soluble PANI-LS possess significant potential applications in various fields, such as conductive nanocomposite films, corrosion protection, and electrochemical devices.[19]

X-Ray Diffractograms. X-Ray diffractograms (XRD) patterns of PANI-LS-A and PANI-LS-M are as shown in Figure 4. The two strongest peaks centered at about 20° and 25° should be ascribed to the periodicity parallel and perpendicular to the polymer chains, indicating that PANI-LS samples were both partial crystallization.[39,40] As could be seen in Figure 4, the peak intensity of PANI-LS-M is significantly higher than that of PANI-LS-A, also with wider width, indicating a higher regularity and crystallinity of PANI-LS-M molecular chains. This was due to the obvious microscopic orientation of PANI-LS-M, its molecular chain-preferred arrangement in a certain direction and extended conformation, leading to the enhancement of the regularity and symmetry of PANI-LS-M samples, eventually obtaining the improvement in crystalline material performance.

Thermal Analysis. Figure 5 illustrated the TGA curves of PANI-LS-A and PANI-LS-M. The initial loss below 150°C was assigned to gradual evaporation of moisture. The second loss around 250°C was due to the thermochemical decomposition of LS from PANI, that is, the breaking of $NH^+\ldots SO^{3-}$ interaction between PANI and LS. For the PANI-LS-A, a severe weight loss 27% from about 250°C while PANI-LS-M showed a slight weight loss of 23%. When heated to 600°C, the weight loss of PANI-LS-A and PANI-LS-M was 46.2% and 36%, respectively. Free sulfonate groups are, in general, thermally active, and they possibly weaken the thermal degradation of the PANI-LS-M. Moreover, the sulfonate group becomes much more thermally stable when it forms a complex with a counteraction[33] and LS could interact with PANI through the formation of hydrogen bonds as shown in Scheme 2, although these hydrogen-bonded interactions were slightly labile. Thus, in comparison, the TGA curve of the PANI-LS-M clearly demonstrated an increased thermal stability, which in turn offers thermal processing advantages.

Morphologies. Figure 6 shows the morphologies of the PANI-LS-A and PANI-LS-M. As shown in Figure 6(a), an irregular mixture of granular particles and a larger range of aggregates were observed, suggesting the disorder and stacks of PANI-LS-A chains. Figure 6(b) exhibited an orderly morphology of laminated structure with a diameter of 100 nm, indicating the well-extended one-dimensional nanostructure of PANI-LS-M. The polymerization in the MF greatly enhanced the anisotropic diamagnetic susceptibility of PANI-LS-M particles,[41,42] leading to

Figure 4. XRD patterns of PANI-LS-A (a) and PANI-LS-M (b).
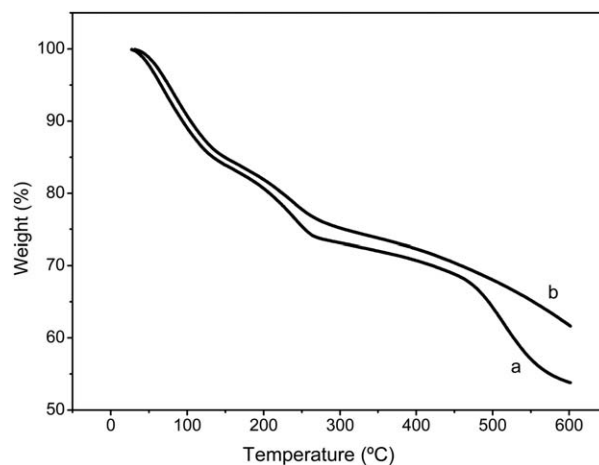
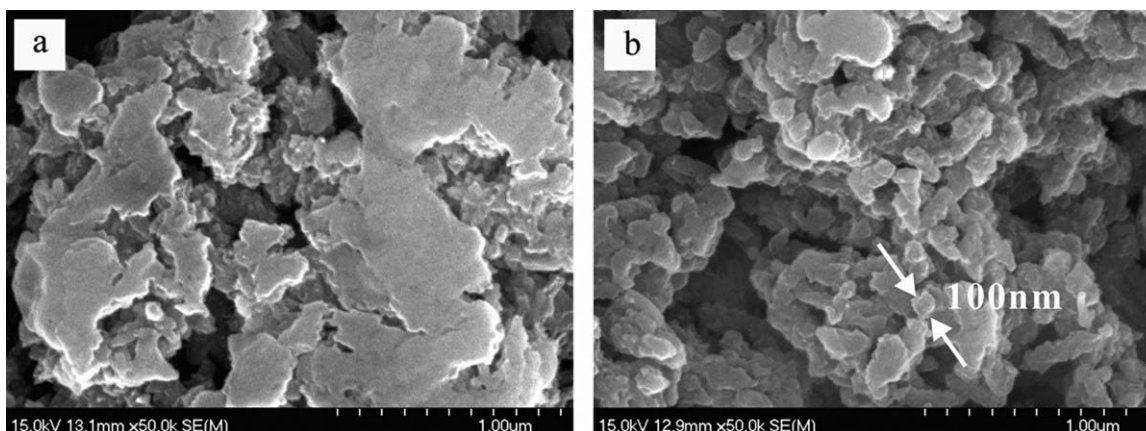**Figure 5.** TGA curves of PANI-LS-A (a) and PANI-LS-M (b).

Figure 6. Morphologies of PANI-LS-A (a) and PANI-LS-M (b).

an obvious differentiation in the characteristics of response to MF in different directions; the particles underwent rotation or rearrangement and achieved a high degree of orientation when aggregated.

CONCLUSION

Soluble conductive PANI-LS was successfully prepared by utilizing a renewable resource LS as dopant in the presence of MF. The morphology of PANI-LS-M indicated the orientation effect of the MF. The resultant PANI-LS-M with a highly yield up to 96% exhibited an improved regularity and thermal stability, and the solubility has doubled and the conductivity increased up to as high as 20.2 S/cm when a MF of 0.4 T was applied, which was four times that of PANI-LS-A. Moreover, the present approach has many advantages: (i) a renewable resource anionic lignosulfonate was utilized for producing ordered PANI nanoparticles, and it is very cheap and can be easily obtained from pulp processing; (ii) the introduction of MF accelerate the monomer conversion rate, orientating and stretching the flexural molecular chain, which not only saved the polymerization time but also made the doping of LS effectively; the polymerization yield and the conductivity were dramatically improved; and (iii) the presence of MF and LS greatly improved the poor solubility of PANI. Compared with the traditional method, this method for the preparation of soluble conductive PANI material is much more convenient and economical and has great potential applications.

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