



Preparation and characterization of self-suspended tetraaniline with liquid crystal texture



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ABSTRACT

A simple and effective approach is used to obtain the amino-capped tetraaniline, which can be doped by the nonylphenol polyoxyethylene ether sulfate to acquire self-suspended tetraaniline through a common dialysis. The synthetic self-suspended tetraaniline was flowable at or near room temperature. Furthermore, the tetraaniline fluid could directly present the liquid crystal property without any solvent. Also the self-suspended tetraaniline exhibited a high electrical conductivity, which reached up to 0.1 S/m.

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1. Introduction

Intrinsically conducting polymers still remain the subject of intense research by many groups worldwide [1]. Polyaniline (PANI) is one of the most promising conducting materials due to its facile synthesis, low cost, remarkable environmental stability and relatively high conductivity [2]. It has been applied to many aspects such as organic lightweight batteries, microelectronics, electrorheological fluids, and chemical sensors [3–5]. However, because of its rigid and highly conjugated backbone, PANI suffers from poor processability.

Aniline oligomers have similar structures and electrochemical properties with polyaniline [6,7]. Aniline oligomers have been furthermore proved very helpful in the so-called oligomer approach for calculating and predicting properties of polymers [8]. So they could be regarded as model compounds for studying the chain structure and functional properties of polyaniline by analog of aniline oligomers [9].

The different degree of polymerization for aniline oligomers had been synthesized successfully by researchers [10–13]. Among these oligomers, the chain structure of tetraaniline is the most appropriate for the research of polyaniline. For instance, the

conductivity of phenyl-capped tetraaniline could switch followed by the order-disorder transition [14], and the DBSA doped tetraaniline had a better thermal stability than pure tetraaniline [15]. But all of them were in powder at the pure condition. In this work, the liquid tetraaniline was obtained at the natural state after secondary doping with a special long-chain protonic acid, which exhibited novel properties, such as a special liquid crystal texture. We had already reported the synthetic techniques of some self-suspended nanoparticles [16–19]. The man-made self-suspended tetraaniline is flowable at or near room temperature without any solvent. And it exhibits high conductivity, which reaches up to 0.1 S/m. The unique electronic, magnetic, and luminescent properties of various nanostructures have made the self-suspended tetraaniline a promising alternative to conducting lubricants, heat-transfer fluids, batteries, and printing electronics [20–22].

2. Experimental

2.1. Materials

N-phenyl-*p*-phenylenediamine (dimer), ammonium persulfate (APS), dimethyl formamide (DMF), acetone, *N*-methyl pyrrolidone (NMP), ammonium hydroxide and hydrochloric acid (HCl, 37%) were obtained from Sinopharm Chemical Reagent Co., Ltd, China. Nonylphenol polyoxyethylene ether sulfate (NPES, C₉H₁₉C₆H₄O

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(CH₂CH₂O)CH₂CH₂CH₂SO₃H) was purchased from Aladdin (Shanghai, China). All the reagents were used as received in this study.

2.2. Synthesis of amino-capped tetraaniline (TANI) and self-suspended TANI

Typically, 1.84 g of *N*-phenyl-*p*-phenylene-diamine was dissolved in 10 mL of DMF, and followed by adding 25 mL of HCl and 100 mL of deionized water. Then an aqueous solution of 4.56 g ammonium persulfate (25 mL) was gradually dropped into the mixed solution at 0 °C under stirring. After 3 h of vigorous stirring, the suspension was filtered and repeatedly washed with 0.6 M HCl and acetone. Finally, the precipitate was treated with an excess of 0.5 M ammonium hydroxide to be neutral and dried in a vacuum at 60 °C for 48 h.

To obtain the self-suspended TANI, 3.65 g (0.01 mol) of the as-synthesized TANI was added into a mixed solution of 15.64 g (0.02 mol) of NPES and 120 mL of NMP. The mixture was kept stirring at 0 °C for 8 h. Then the suspension was filtered and dialyzed with a cellulose dialysis membrane with a cutoff molecular weight of 1000 for 72 h. Finally, the product was collected and dried in a vacuum at 60 °C for 48 h.

2.3. Characterization

Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) was used to determine the mass spectrum of the as-synthesized TANI. XRD patterns were acquired by a D/Max-III A (Rigaku) diffractometer using Cu K α radiation ($\lambda=1.54\text{ \AA}$). IR measurements were made on a FTIR spectrometer (Thermo Nicolet Nexus) using KBr powder. UV–vis spectra were recorded using a Shimadzu UV-2250 Spectrophotometer. Morphologies of TANI and TANI-NPES were examined using the scanning electron microscope (SEM, HITACHI S-4800) and transmission electron microscope (TEM, JEOL JEM-2010), respectively. Rheological properties were studied using an ARES-RFS rheometer (TA) at an angular frequency of $\omega=1\text{ s}^{-1}$ and with a strain amplitude of 10% in the temperature range from 20 to 80 °C. TANI-NPES was spin-cast onto a glass slide and then observed on an OLYMPUS BH-2 polarized light microscope at room temperature. The conductivity was measured using a HIOKI3532-50 LCR HITESTER meter (HIOKI, Japan) in the range from 100 Hz to 5 MHz, at room temperature with a relative humidity of 50–70%.

3. Results and discussion

First the molecular structure of the as-synthesized TANI was characterized by MALDI-TOF and XRD, as shown in Fig. 1(a) and (b),

respectively. It can be observed from Fig. 1(a) that a distinct protonation peak appears at around 365.5, corresponding to the molecular weight of the as-synthesized TANI. The value is consistent with the theoretical molecular weight of TANI. Besides, the spectrum shows no additional peak. This suggests that the TANI was successfully obtained as the target product in this study. Fig. 1(b) shows the XRD pattern of the as-synthesized TANI. It can be seen that the TANI has a certain degree of crystallinity. The most intense peaks are centered around 20° and 25°, which is mainly ascribed to the periodicity parallel to the tetramer chain and corresponding to the periodicity perpendicular to the chain direction, respectively [23–25].

The transition in oxidation state of TANI and TANI-NPES was monitored by UV–vis spectra (Fig. 2(a)). The spectrum of TANI has two absorption peaks at 310 nm and 590 nm. The former is attributed to $\pi \rightarrow \pi^*$ transition of benzene ring while the latter belongs to $\pi_B \rightarrow \pi_Q$ transition of benzene ring and quinone ring. The two peaks reveal the TANI is in the emeraldine oxidation state. After the TANI was doped by NPES, the protonation band of the TANI backbone increased the conjugation length leading to the delocalization of polaron [15]. Just due to this reason, the characteristic peak at 590 nm disappears while a new peak appears at 430 nm.

Fig. 2(b) shows the FTIR spectra of the TANI, TANI-NPES and NPES. For the TANI, the curve exhibits mainly the bands at 1596, 1496, 1305, 1218 and 1167 cm^{-1} . The intense band at 1596 cm^{-1} is due to the skeleton of benzoquinone ring. The bands corresponding to C–N stretching vibrations are observed at 1305 and 1218 cm^{-1} . We can easily assign 3379 cm^{-1} to (Q) =NH stretching vibration. In the fingerprint, the bands observed at 745 and 693 cm^{-1} in the spectra of oligomer correspond to the C–H out-of-plane bending and the ring out-of-plane deformation of a mono-substituted benzene ring, respectively. Comparison of the TANI and TANI-NPES shows that differences between them are the absorption peaks at around 2900 and 1110 cm^{-1} , which origin from the –SO₃H group vibration of NPES. The result clearly shows the NPES has been successfully doped in the backbone of the TANI.

The SEM photograph of the as-synthesized TANI is shown in Fig. 3(a). It is clear that the morphology of TANI is powder-like and irregular, which consists of particles with different sizes. It is noted that the TANI-NPES is liquid in the ambient temperature (Fig. 3(b) inset), so the morphologies are characterized by TEM as shown in Fig. 3(b). It is clear that TANI-NPES has a two-phase structure with a granule size of 20–30 nm. We believe that the dispersed phase is made up of the rigid TANI fragment of the TANI-NPES while the continuous phase consists of the flexible NPES fragment.

TGA measurements of TANI, TANI-NPES and NPES were carried out ranging from room temperature to 700 °C under nitrogen to

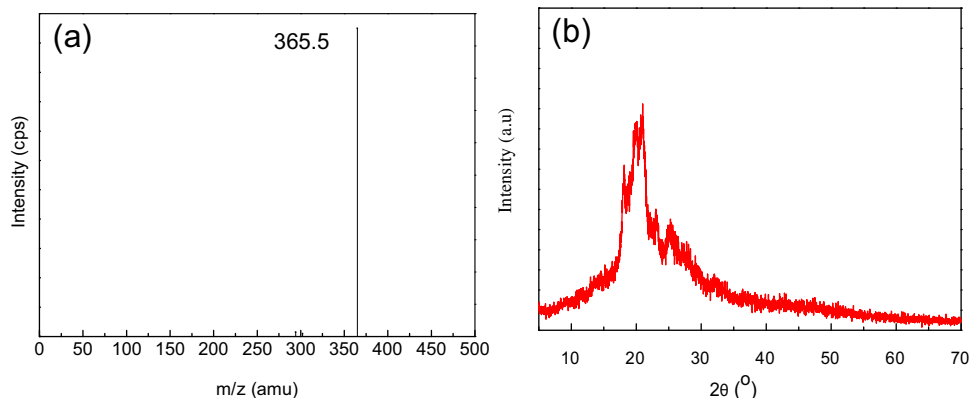


Fig. 1. (a) Mass spectrum and (b) XRD profile of the as-synthesized TANI.

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