

SYNTHESIS AND CHARACTERIZATION OF A NOVEL DOPANT (C3-ABSA) FOR SYNTHESIZING TUBULAR POLYANILINE*

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Abstract 4-(3-(4-((4-Nitrophenyl)azo)phenoxy)propyl)aminobenzene sulfonic acid (C3-ABSA) was synthesized by the reaction of 3-bromo-1-(4-((4-nitrophenyl)azo)phenoxy)propane (B3) with sodium *p*-aminobenzene sulfonic acid (ABSA) and acidification with hydrochloric acid. The C3-ABSA was characterized by FTIR, ¹H-NMR and second ion mass spectrum (SIMS). The molecular formula of dehydrated C3-ABSA was estimated to be ca. C₂₁H₂₀O₆N₄S by SIMS. Its decomposition temperature was measured by TGA to be ca. 232°C. It was found that tubular polyaniline (PANI) with a conductivity of 1.1 S/cm at room temperature was successfully synthesized by *in-situ* doping polymerization in the presence of C3-ABSA as a dopant.

Keywords Polyaniline microtubules, Sulfonic acid dopant, Conductivity

INTRODUCTION

Polyaniline (PANI) is a typical conducting polymer and it has been extensively studied in recent decades due to its environmental stability, low cost and ease of synthesis^[1-5]. It has been demonstrated that the emeraldine base form of PANI (EB) could be doped with proton acid as a dopant by using chemical and electrochemical polymerization^[6]. Unlike other conducting polymers, such as polypyrrole (PPy), polyacetylene (PA) and polythiophene (PTH), there is no change in the number of electrons on the backbone chain after protonation, although one can change the density of electrons on the polymer chain through the control of its oxidation state^[7]. Thus, the dopant plays an important role in controlling the molecular structure and the physical properties. Recently, for instance, Wan *et al.* reported that microtubules of PANI^[8] and PPy^[9] were successfully synthesized by *in-situ* doping polymerization in the presence of β -naphthalene sulfonic acid (β -NSA) as a dopant. It was found that β -NSA dopant plays an important role in forming tubular PANI. Thus, designing and searching for a new type of dopant are necessary in order to prove the reliability and practicability of the new method to synthesize tubular PANI. As we know that the *p*-nitrophenylazophenyl group with *cis-trans* isomerization as mesogen was used to synthesize side chain liquid crystal (LC) polymers^[10, 11] because of its typical characteristics of larger π -flowing field consisting of donor and acceptor electricity group in backbone^[12]. This asymmetric electricity backbone with a charge transferring character can easily be induced to polarize and orient in the extra electric field^[13, 14]. Thus, it is expected that such sulfonated materials may be used as a dopant for PANI doping, resulting in new physical properties. We designed and synthesized 4-(3-(4-((4-nitrophenyl)azo)phenoxy)propyl)aminobenzene sulfonic acid (C3-ABSA) as a novel dopant to synthesize tubular PANI.

In this article, synthetic method and characterization of the molecular structure of C3-ABSA dopant are reported for the first time. The tubular PANI with conductivity of 1.1 S/cm at room temperature was successfully

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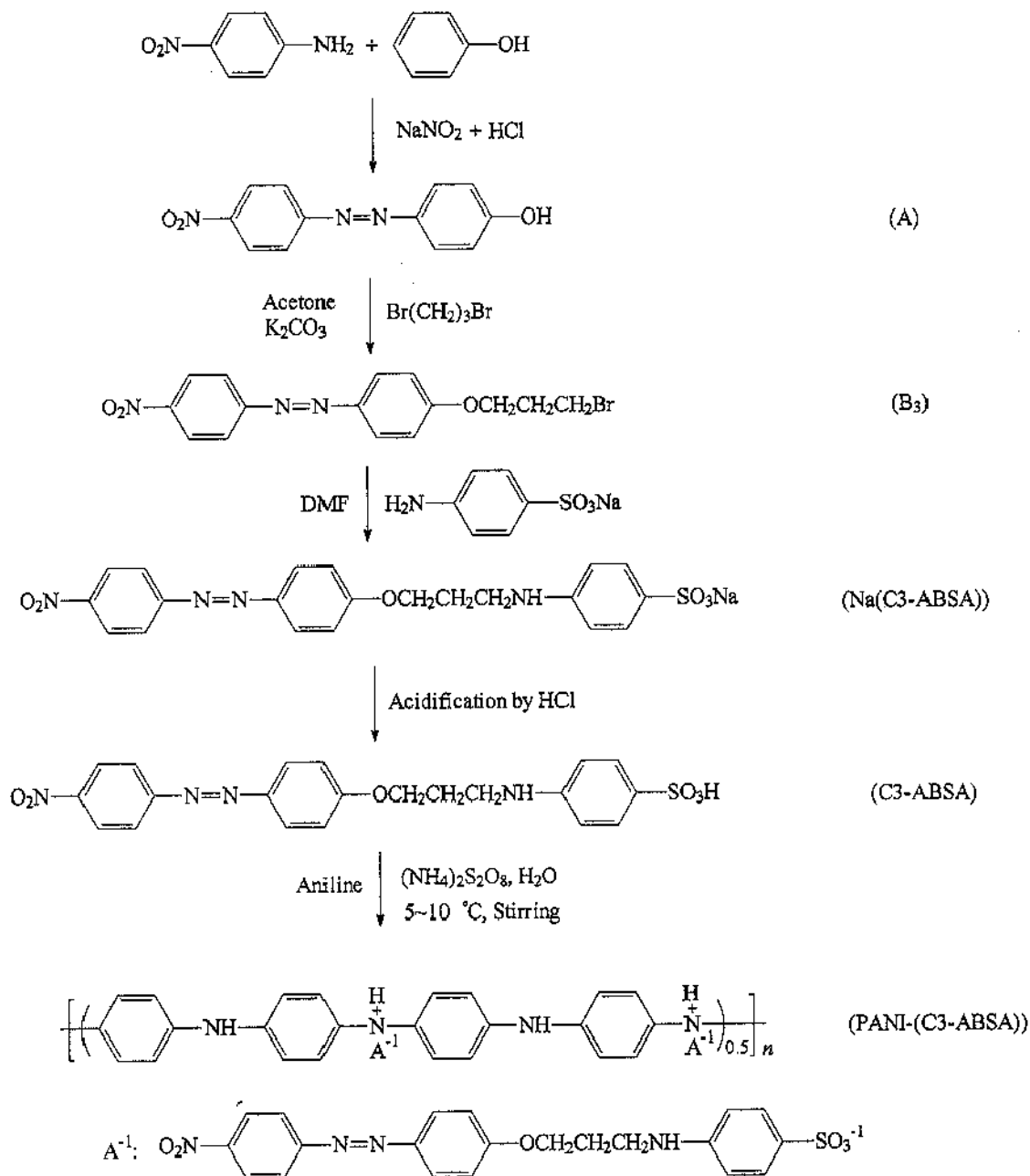
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synthesized by *in-situ* doping polymerization in the presence of C3-ABSA as a dopant.

EXPERIMENTAL

Preparation of C3-ABSA

The synthesis of C3-ABSA dopant was shown in Scheme 1. 4-((4-Nitrophenyl)azo) phenol (A) was synthesized by a method reported by Furniss *et al.*^[15], the melting point of which is 219°C. 3-Bromo-1-(4-((4-nitrophenyl)azo) phenoxy) propane (B3) was successfully synthesized by the Williams etherification method as described in reference^[11]. B3 reacted with sodium *p*-aminobenzenesulfonic acid [Na(ABSA)] to form C3-ABSA. A typical synthetic



Scheme 1

procedure is as follows: 1.95 g Na(ABSA) (10 mmol) was dissolved in 25 mL DMF containing less than 5 mL deionized water and heated to 80°C for 0.5 h under magnetic stirring. 1.82 g B3 (5 mmol) was added to the mixture which was kept at a given temperature for 24 h. Upon cooling to room temperature, a solid was formed on rotary evaporation. It was then washed three times with deionized water and recrystallized from methanol to obtain a brownish-yellow powder. Acidification of the powder with approximately 40 mL of concentrated hydrochloric acid resulted in the precipitation of an orange-yellow solid (yield: 37% after acidification). The fine C3-ABSA powder was obtained by recrystallization from 95% ethanol. Its decomposition temperature determined by TGA was ca. 232°C.

¹H-NMR (300 MHz, DMSO); (δ , from TMS): 2.07–2.12 (*m*, 2H, $-\text{C}-\text{CH}_2-\text{C}-$), 3.1 (*s*, 1H, $-\text{NH}-$), 3.33–3.37 (*m*, 2H, $-\text{CH}_2-\text{N}-$), 3.54 (*s*, 3H, $-\text{SO}_3\text{H}_3^+\text{O}$), 4.23–4.28 (*m*, 2H, CH_2-O), 6.83–6.86 (*d*, 2H, Ar-H, *o*-to-NH) 7.19–7.21 (*d*, 2H, Ar-H, *o*-to-O-), 7.51–7.54 (*d*, 2H, Ar-H, *o*-to- SO_3^-), 7.96–8.05 (*m*, 4H, Ar-H, *o*-to-N=N-), 8.40–8.43 (*d*, 2H, Ar-H, *o*-to- NO_2); Negative SIMS: 455 and $\text{C}_{21}\text{H}_{20}\text{N}_4\text{O}_6\text{S}$.

FTIR (KBr pellet, cm^{-1}): 3434, 2996, 2768, 1601, 1522, 1502, 1403, 1345, 1255, 1160, 1142, 1110, 1033, 1011, 859, 839, 755, 639, 606, 565 and 458

Preparation of PANI-(C3-ABSA)

The microtubules of PANI doped with C3-ABSA were synthesized by a similar method for PANI- β -NSA^[8], as shown in Scheme 1. A typical synthetic procedure for PANI-(C3-ABSA) is as follows: 0.2 mL aniline monomer was mixed with 5.0 mg C3-ABSA under ultrasonication. 1.0 mL $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (APS, 2.0 mol/L) dissolved in deionized water was added into the above mixture, and stirred ultrasonically at 6–12°C for 1.0 h. The product obtained after filtration was washed several times with 95% ethanol and deionized water and then dried under vacuum for 24 h to obtain the blue-black powders.

The molecular structure of C3-ABSA dopant was characterized by ¹H-NMR, FTIR and SIMS. ¹H-NMR spectra were measured on a DMX-300 (BRUKER) spectrometer, using deuterated dimethyl sulfoxide (*d*₄-DMSO) as solvent and tetramethylsilane (TMS) as the internal chemical shift reference. Negative/positive SIMS was performed on APEXII (USA, BRUKER) with glycerol as substrate. FTIR spectra were recorded using a IFS-113V, (BRUKER) spectrometer. The samples were pelleted with KBr. Thermal stability of C3-ABSA dopant was measured by a TGA (PERKIN ELMER TGA7) instrument with a heating rate of 10 K/min and with indium and zinc as calibration sample.

The tubular morphologies of PANI-(C3-ABSA) were proved by a Scanning Electron Microscope (S-530 Toshiba). The room-temperature conductivity was measured by a four-probe method, using ADVANTEST R6142 programmable DC voltage/current generator and KEI THLEY 196 system DMM.

RESULTS AND DISCUSSION

The FTIR spectrum of C3-ABSA is shown in Fig. 1, and the assignments of absorption bands are given in Table 1^[16]. The characteristic absorption peaks of B3^[17], such as the asymmetric and symmetric stretching vibration of the nitro group appear at 1522 cm^{-1} and 1345 cm^{-1} , the stretching vibrations of $\text{C}-\text{NO}_2$, $\text{Ar}-\text{O}-\text{C}$ and the benzene ring appear at 859, 1142, 1601 cm^{-1} respectively. 1502 and 839 cm^{-1} (1,4-substitution on the ring) can be observed in the spectrum of C3-ABSA dopant. Compared with the FTIR spectrum of B3, however, it was found that the absorption peak of C3-ABSA at 1254 cm^{-1} become broad and a shoulder peak appears at 1160 cm^{-1} , which is attributed to the strong asymmetric stretching vibration of SO_2 . The symmetrical stretching vibration of SO_2 at 1068, 1033 and 1011 cm^{-1} is also obviously observed. Moreover, the absorption peak of $\text{C}-\text{Br}$ vibration (686 cm^{-1}) of B3 obviously disappears. These results only showed that B3 reacts with Na(ABSA). But it did not confirm that acidification of Na(ABSA) with HCl took place due to the absence of assignment of $-\text{OH}$ of benzenesulfonic acid. In Fig. 1, a broad absorption peak at 3434 cm^{-1} assigned as $-\text{OH}$ associated with $-\text{SO}_2$ is indeed observed. For C3-ABSA, however, definite assignment is hard because of the overlapping of $-\text{NH}$ and $-\text{OH}$ absorption bands. In order to solve this problem, the negative SIMS spectrum (Fig. 2) of C3-ABSA was measured, in which a main peak appears at *m/z* 455 corresponding to the negative-ion molecular

Table 1. FTIR vibration bands of C3-ABSA and their assignment⁽¹⁶⁾

Bands (cm ⁻¹)	Assignment*	Bands (cm ⁻¹)	Assignment*
3434	Str. of associated OH and sym. Str. of -NH-	1033	Str. of SO ₂
2996~1700	Hydrated ion absorption	1011	
1601	Str. of C=C of aromatic rings	859	Str. of C-N and op of bending of N-H
1521	Asym. str. of NO ₂	839	Op str. of -H on 1,4 ring
1402	Bending of CH ₂ in -CH ₂ -N	755	Ip bending of C-NO ₂
1345	Sym. str. of NO ₂	722	Rock of -CH ₂
		693	
1254	Str. of C-O-C in Ar-O-C	606	Ar. ring deformation
		565	
1160	Sym. str. of SO ₂	458	
1142	Str. of C-O		
1109	Str. of C-S in Ar-S-		

*Asym: asymmetric; Sym: symmetric; Str: stretching; Ip: in-plane; Op: out-plane; Ar: aromatic ring

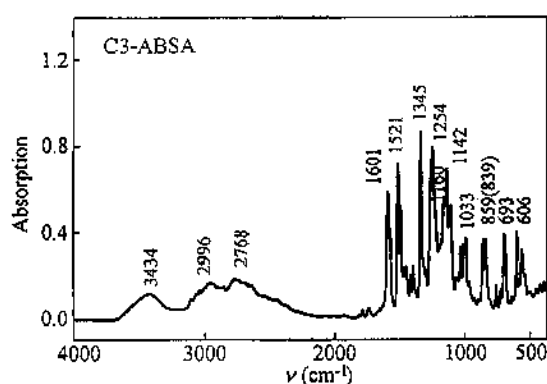


Fig. 1 FTIR spectrum of C3-ABSA

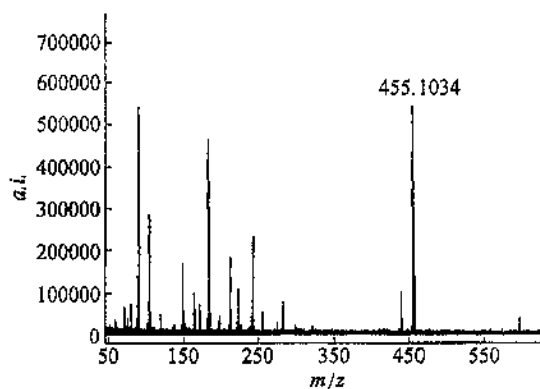
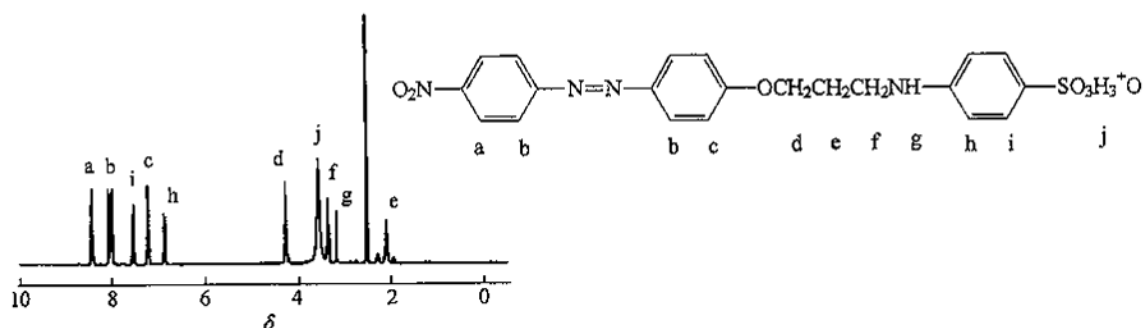
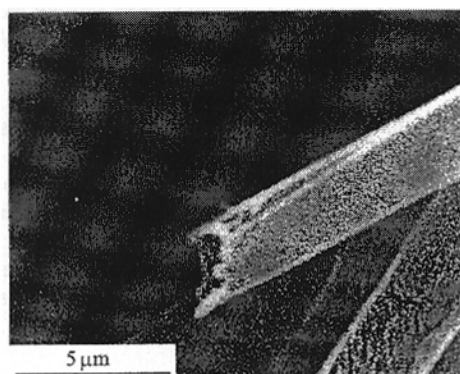


Fig. 2 SIMS spectrum of C3-ABSA

weight of C3-ABSA. In the positive SIMS spectrum, the Na⁺ peak is absent. These results indicated that the product obtained in this study was C3-ABSA, instead of Na (C3-ABSA). Moreover, it is noted that an IR absorption peak at 900 cm⁻¹ usually assigned as the bending vibration of S-O in S-OH disappears. This is a typical characteristic vibration of S-O in hydrated benzenesulfonic acid. Therefore, C3-ABSA is suggested as a hydrated species. This is indicated by the fact that there is a very broad peak (1700~2960 cm⁻¹), and centering at 2768 cm⁻¹ as shown in Fig. 1. In the ¹H-NMR spectrum of C3-ABSA (Fig. 3), the presence of a broad chemical shift centered at $\delta = 3.55$ and a sharp chemical shifts at $\delta = 3.1$ suggest the existence of water and -NH in the C3-ABSA backbone. No proton chemical shift of S-OH is observed due to the formation of S-H₃O⁺. So the proposed hydrated C3-ABSA was further confirmed by ¹H-NMR results. Combination with SIMS analysis, the molecular formula of dehydrated C3-ABSA was estimated to be ca. C₂₁H₂₀N₄O₆S. The decomposition temperature of C3-ABSA is ca. 232 °C. As we expected, PANI-(C3-ABSA) microtubules with a diameter of the order of several micrometers and a length up to 200 μ m could be synthesized by *in-situ* doping polymerization in the presence of C3-ABSA as the dopant. It was proved by SEM images (Fig. 4) that PANI-(C3-ABSA) is hollow. Room-temperature conductivity of the resulting PANI-(C3-ABSA) microtubules is in the range of 1.0×10^{-6} ~1.1 S/cm as measured by a four-probe method. It was found that the molecular structure, tubular size and room-temperature conductivity of PANI-(C3-ABSA) tubules strongly depend on the concentration of C3-ABSA used.

Fig. 3 ^1H -NMR spectrum of C3-ABSAFig. 4 Typical SEM image of PANI-(C3-ABSA) tubules synthesized by *in-situ* doping polymerization of aniline in the presence of C3-ABSA as a dopant

In conclusion, a novel sulfonic acid of C3-ABSA as the dopant of PANI was synthesized for the first time. FTIR, ^1H -NMR and SIMS spectra characterized the molecular structure of C3-ABSA dopant. The molecular formula of C3-ABSA was estimated by SIMS analysis to be ca. $\text{C}_{21}\text{H}_{20}\text{N}_4\text{O}_6\text{S}$. By using C3-ABSA as a dopant, tubular PANI with maximum conductivity of 1.1 S/cm at room temperature can be obtained by *in-situ* doping polymerization. Thus, C3-ABSA designed and synthesized by us can be considered as a novel dopant for PANI with a tubular morphology and unique physical properties.

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