Highly Conductive Polyaniline Doped with DEHSSA Synthesized in Different Protonic Acids

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Conductive polyanilines doped with di-2-ethylhexylsulfosuccinic acid (DEHSSA) were synthesized in different inorganic acids through emulsion polymerization. A comparison of secondary doping effect by *m*-cresol on the backbone conformation of the polyaniline and electrical conductivity of these samples were performed. The conductivity increases with increasing *m*-cresol and the highest conductivity obtained was 384 S/cm for DEHSSA-doped PANI synthesized in hydrochloric acid (HCl).

Even though polyaniline (PANI) showed promising application as electrochromic devices, photoelectric cells, corrosion protections, light-emitting diode, biosensor, etc.,[1–4] but its applications are still very limited as the electrical conductivity remain as the biggest hurdle to be overcame. When protonic acid-doped PANI were secondary doped with *m*-cresol, their electrical conductivity were improved significantly up to 300 S/cm.[5] Most recently, Lee et al.[6] reported a novel "self-stabilized dispersion polymerization" of highly conductive PANI with conductivity ≈1000 S/cm and the conductivity of this sample showed truly metallic transport property even at low temperature (5 K), as compared to semi-conductor transport of conventionally synthesized PANI. The above-mentioned progresses are accomplished by the so-called 2-steps method: first PANI emeraldine salt (ES) was synthesized and then dedoped into emeraldine base (EB); secondly the EB powder was mixed with dopant (CSA) and dissolved in *m*-cresol and cast into film. In view of the extra cost and time required for this method, our 1-step method is more feasible as PANI is polymerized in the presence of dopant and then "in situ" secondary doped with *m*-cresol by direct addition of *m*-cresol into the PANI solution. This PANI-dopant solution exhibits comparable conductivity (≈300 S/cm) with less gelation, betters solubility, and attractive ease of handling with wider potential applications in different areas.

Through this method, aniline can be polymerized in the presence of structure-directing organic acids, which often are complex acids with bulky side groups, such as camphor sulfonic acid (CSA),[4,5] dodecylbenzenesulfonic acid (DBSA),[7] di-2-ethylhexylsulfosuccinic acid (DEHSSA),[2] and etc. Better thermal stability and solubility could be achieved by replacing typical protonic acids (such as HCl or H_2SO_4) with dopants cum surfactants due to their bulky structure. Even though, there are numerous works reported for highly conductive PANI synthesized in different acids but to our knowledge, no cross-acid type comparison studies were carried out before to compare the effect of type of acid used and secondary doping effect on the electrical conductivity of the resultant PANI synthesized in the presence of DEHSSA as dopant. So, this prompted us to study and try to understand the electrical properties of DESSA-doped PANI synthesized through 1-step method in different protonic acids such as hydrobromic acid (HBr), hydrochloric acid (HCl), sulfuric acid (H_2SO_4), and phosphoric acid (H_3PO_4). The extent of *m*-cresol secondary doping effect has on the electrical conductivities of the respective PANIs was also studied.

15 mmol of DEHSS-Na salt was dissolved in 80 mL of toluene at 0 °C followed by addition of 140 mL of hydrochloric acid (HCl, 1 M) and stirred for 1 h. 15 mmol of aniline was added and stirred for 1 h. A pre-cooled APS solution (in 20 mL HCl) was added in 2 h and the mixture was reacted for 24 h at 0 °C. The reaction mixture was then separated, purified, and concentrated. This procedure was repeated by replacing HCl with HBr, H_2SO_4 and H_3PO_4 under the same synthesis conditions. The ultraviolet–visible–near-infrared (UV–vis–NIR) spectra of the PANI was measured and the change of conductivity with different weight ratio of *m*-cresol from 0 to 5 was investigated for the films dried at 80 °C under dynamic vacuum for 6 h on slide glass. Each film's conductivity was measured thrice using four-point probe method and the average value was given in Table 1.

The UV–vis–NIR spectra of the DEHSSA-doped PANI synthesized in HCl (Figure 1) showed a peak at 350 nm corresponds to transition from π-band to π^*-band of the benzenoid rings (B) along the polymer backbone, where the π electrons of the benzene rings delocalized on the nitrogen atoms. Besides this, the peaks at 440 and ≈760 nm were contributed by the transition from polaron band to π^*-band and from π-band to polaron

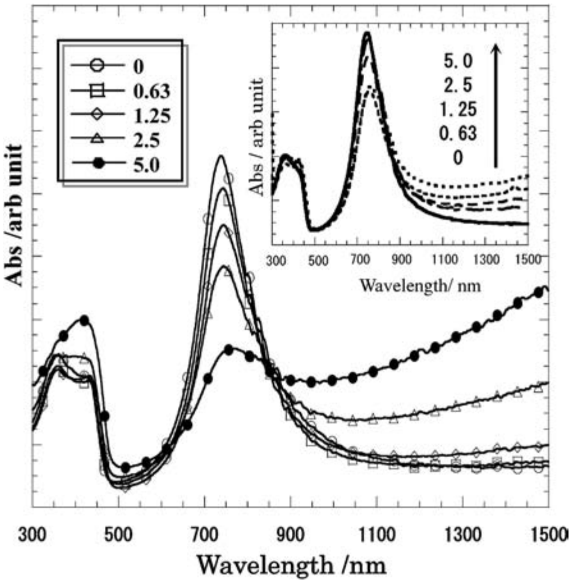

Figure 1. UV–vis–NIR spectra of DEHSSA-doped PANI synthesized in HCl and H_2SO_4 (Inset) with different weight ratio of *m*-cresol secondary doping.

band.[5] Xia et al. proposed that the ≈760-nm peak could be used as a simple characteristic band of PANI backbone in the coil-like conformation. In this conformation, the polarons (in every tetrameric repeating unit) are isolated from each other repeating unit due to the twisting defects between aromatic rings. This explained why the sample with the lowest electrical conductivity has the strongest 760-nm absorption peak.

Due to the bulkiness of the dopant (DEHSSA), the *m*-cresol can fill in the space on top of the PANI rings and the flatness of the *m*-cresol molecules can thus twist the PANI backbone into a more planar and expanded conformation. This leads to better interaction and delocalization of the adjacent polarons along the PANI backbone and hence higher conductivity can be obtained. This is proven by the consistent increase of conductivity with the increase of the % loading of *m*-cresol in our samples. Therefore, the 760 nm band was replaced by the "free-carrier tail" in the near-infrared region due to the intraband transitions within the half-filled polaron.[5] Xia et al. suggested that *m*-cresol induces significant increment of conductivity through counter ions exchange interaction between the positively charged PANI backbone with negative counter ions (dopant) sitting in the vicinity. When counter ions were removed away from the polymer chain, the static repulsive interaction of the positive charges on the polymer backbone tends to extent the polymer chain to form the expanded coil-like conformation.[5] Besides this, Epstein et al. found that the removal of the counter ions has a favorable effect on the electrical conductivity as counter ions can attract the opposite moving charges (polarons) and decreases the conductivity of the DBSA-doped PANI.[8] We believed the same interaction was responsible for the increment of electrical conductivity in our samples.

Generally, the bulk conductivity of DEHSSA-doped PANI films was 25.8, 15.9, 1.39, and 0.25 S/cm synthesized in HBr-, HCl-, H_2SO_4-, and H_3PO_4-doped PANI (Table 1). The higher conductivities exhibited by HBr and HCl samples could be due to solvation effect of Br^- and Cl^- with absorbed water that leads to increased conductivity.[9] The bulk conductivity trend seems to suggest that the pK_a of the acid plays an important role in determining the amount of doping sites or doping level along the polymer's backbone, as the HBr (with lowest pK_a of -9.00) and H_3PO_4 (with highest pK_a of 2.12) exhibited the highest and lowest bulk conductivity, respectively. The conductivity generally increases with increase of *m*-cresol and the highest conductivity obtained was 62.8, 384.0, 55.1, and 85.3 S/cm for DEHSSA-doped PANI synthesized in HBr, HCl, H_2SO_4, and H_3PO_4. The sharp increase of conductivity from weight ratio of *m*-cresol from 1.25 to 2.5 for DEHSSA-doped PANI in HCl showed that this is maybe the percolation threshold for mass transformation of coil-like to expanded coil-like conformation, as shown by the sudden increase of free-carrier tail absorption.

Table 1. Average electrical conductivity of DEHSSA-doped PANI synthesized in different acids

Weight ratio of *m*-cresol	Average conductivity/S·cm^{-1} (±5%)			
	H_2SO_4	H_3PO_4	HBr	HCl
0	1.39	0.25	25.80	15.90
0.63	0.05	0.86	11.60	27.50
1.25	0.55	20.00	43.90	59.40
2.5	4.88	85.30	62.80	366.00
5.0	55.10	79.10	54.90	384.00

Based on the irregular variation of conductivities, we proposed that the bulk electrical property of the PANI was dependent on the ion-exchange of DEHSS/Na salt during the polymerization, in which the doping level and thus the type of acid used during the synthesis, as the amount of added *m*-cresol was disproportional with the increase of conductivity. We deduce that the efficiency was primarily contributed by the number of active doping site of counter ions along the PANI backbone, as the number of counter ions is equal to the number of protonated imine sites along the PANI backbone. This is because the greater the number of counter ions along the backbone that were removed by *m*-cresol, the greater the number of free polarons and better delocalization of charges can be expected. This results in greater transportation of polarons and improved electrical conductivity of the samples. According to our assumption, the DEHSS-doped PANI synthesized in HCl seems to possess the largest number of protonated imine site along the PANI backbone, as suggested by the elevated electrical conductivity obtained. The increase of conductivity seems to reach to a saturation level (at 2.5 wt ratio *m*-cresol for H_3PO_4 and HBr, 5 wt ratio for HCl and H_2SO_4) as most of the DEHSS$^-$ at the protonated imine sites were removed by the *m*-cresol and the maximum transportation of charges along the backbone was achieved.

A 1-step emulsion polymerization of DEHSSA-doped PANI was achieved in different acid (HCl, HBr, H_2SO_4, and H_3PO_4) and a comparison of their electrical conductivity based on secondary doping effect was carried out. The UV–vis–NIR spectra confirmed the conformation changes from coil-like to expanded coil-like conformation based on the free-carrier tail absorption. The bulk conductivities of the DEHSSA-doped PANI synthesized in HBr, HCl, H_2SO_4, and H_3PO_4 were 25.8, 15.9, 1.39, and 0.25 S/cm and the highest conductivities obtained with *m*-cresol secondary doping were 62.8, 384, 55.1, and 85.3 S/cm. The effect of secondary doping is considered to be dependent on the DEHSSA-doping level along the PANI backbone. Based on our results, we suggest that the type of acid used during the polymerization determines the amount of active DEHSS$^-$ sites along the PANI backbone. The future work will be focused on the thermal stability of the conductivity at high temperature.

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