The Influence of Aniline to Acid Composition on the Electrical Conductivity of PANI-PAAMPSA

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In this study, the influences of aniline to acid composition were investigated on the electrical conductivity of PANI-PAAMPSA. The ratio of aniline to sulfonic acid groups was optimized for the maximum conductivity of PANI-PAAMPSA. The conductivity is strongly correlated with the electronic structure of PANI-PAAMPSA; the highest conductivity of PANI-PAAMPSA was observed when PANI has the longest conjugation length.

Key Words : Polyaniline, Poly(2-acrylamido-2-methyl-1-propanesulfonic acid), Conductive polymer

Introduction

Polyaniline (PANI) has been subjected to intense researches due to its unique physical and chemical properties. In the early years, PANI was doped with small molecule acids, such as hydrochloric acid.[1] The problem with these systems, however, is their insolubility in any common solvents, which limits processibility of the final material. Recently, aqueous dispersions of conductive PANI have been demonstrated through the synthesis of aniline in the presence of polymer acid templates.[2-4] In these systems, PANI is protonated by the acid pendant groups and excess acid groups in the polymer acid render the final material water-dispersible. Compared to small-molecule acids for dopants, these polymer acid templates also have the advantages of increased chemical stability while preserving the electrical conductivity. We chose poly(2-acrylamido-2-methyl-1-propanesulfonic acid), or PAAMPSA, as the polymer acid template to dope PANI due to its strong acid property and capability to enhance the water dispersibility of PANI-PAAMPSA.[5] To increase the conductivity of PANI-PAAMPSA, it is important to understand the factors that govern its electrical conductivity. Herein, we report the influences of aniline to acid composition on the conductivity of PANI-PAAMPSA.

Experimental

We first synthesized PAAMPSA *via* conventional free-radical polymerization. We refer to the polymer as PAAMPSA-45 where 45 is the poly(ethylene oxide)-, PEO-, equivalent number-average molecular weight of the polymer in kg/mol. To synthesize PANI-PAAMPSA,[6,7] PAAMPSA was first dissolved in deionized water. Aniline monomer was then added to the PAAMPSA solution and stirred at room temperature. The oxidizing agent, ammonium peroxydisulfate, was dissolved separately in deionized water. The molar ratio of monomer to oxidizing agent was fixed at 1:0.9. The solutions were purged with nitrogen for 30 min. The ammonium per-oxydisulfate solution was added dropwise to the PAAMPSA–aniline solution cooled in an ice-water bath. The reaction medium was kept at ice-water temperature for 6 h and proceeded overnight to complete the reaction. To obtain PANI-PAAMPSA, the polymer suspension was precipitated by acetone.

Results and Discussion

We investigated the influence of the composition of PANI-PAAMPSA, as probed by the aniline to acid molar ratio, on the electrical conductivity of the resulting material. For this study, we varied aniline to sulfonic acid group molar feed ratios of 1:0.5, 1:1, 1:1.5, 1:2, and 1:3 to synthesize PANI. We refer to these polymers as PANI-PAAMPSA n:m where n:m is the aniline to sulfonic acid group molar ratio determined by x-ray photoelectron spectroscopy (XPS). Dedoped PANI-PAAMPSA n:m is denoted PANI n:m where n:m again denotes the aniline to sulfonic acid group molar ratio obtained by XPS.

To determine the structure of PANI-PAAMPSA in this series, ^{13}C solid-state NMR was performed on PANI-PAAMPSA samples. Figure 1 shows the ^{13}C NMR spectra of PANI-
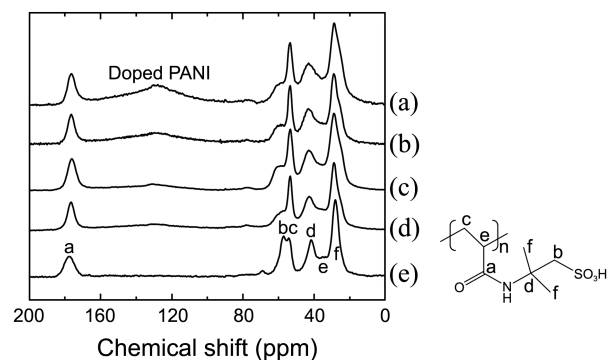

Figure 1. ^{13}C NMR spectra of (a) PANI-PAAMPSA 1:0.72, (b) 1:0.83, (c) 1:1.26, (d) 1:1.91, and (e) PAAMPSA-45. The chemical shifts of PAAMPSA-45 are labeled accordingly.

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PAAMPSA 1:0.72, 1:0.83, 1:1.26, and 1:1.91, as well as PAAMPSA-45. The ratios shown in Figure 1 are different from the prescribed molar feed ratios because a portion of unreacted aniline monomers is washed away during precipitation. The peaks for PAAMPSA-45 are assigned in Figure 1(e) in accordance to the chemical structure.[8,9] In addition to the polymer acid peaks between 10 and 70 ppm, as well as that at 175 ppm, a broad bump due to charge delocalization along the PANI backbone[10,11] appears between 100 and 160 ppm in the PANI-PAAMPSA spectra (Figure 1(a)-(d)), and its intensity increases with decreasing PAAMPSA content. This observation indicates that PANI content increases in PANI-PAAMPSA samples as the PAAMPSA content decreases.

To resolve the peaks associated with PANI, we carried out ^{13}C solid-state NMR on all the dedoped PANI-PAAMPSA samples. To obtain the non-conductive emeraldine base form of PANI, we deprotonated PANI-PAAMPSA through the addition of excess ammonium hydroxide. Figure 2 shows the ^{13}C NMR spectra on the dedoped form of PANI-PAAMPSA with varying aniline to acid molar ratios. The peaks in Figure 2 are assigned in accordance to the chemical structure of the base form of PANI. The chemical shifts shown in Figure 2 are similar to those from all the previous PANI-PAAMPSA samples analyzed, indicating that aniline is polymerized in a para-directed, head-to-tail fashion in the presence of PAAMPSA. This structure results in PANI that is linear and defect-free.[12,13] Very similar carbon environments are observed in all the ^{13}C NMR spectra of PANI-PAAMPSA samples in this series. Despite changes in composition, all the PANI-PAAMPSAs are structurally very similar.

To determine the nitrogen environments of PANI-PAAMPSA, we performed the ^{15}N solid-state NMR on PANI-PAAMPSA samples. Figure 3 contains the ^{15}N NMR spectra of (a) PANI-PAAMPSA 1:0.72, (b) 1:0.83, (c) 1:1.26, and (d) 1:1.91. In all the ^{15}N NMR spectra of PANI-PAAMPSA samples, we do not observe any peaks at ~320 ppm, which are associated with residual imine nitrogens.[14,15] This observation indicates that all the PANI-PAAMPSA samples in this series are completely doped as-synthesized. A single peak is observed at 115 ppm in all the ^{15}N NMR spectra of PANI-PAAMPSA in this series (Figure 3). This peak is assigned to the protonated amines whose charges are delocalized along the PANI-PAAMPSA backbone.[11,14,16] We
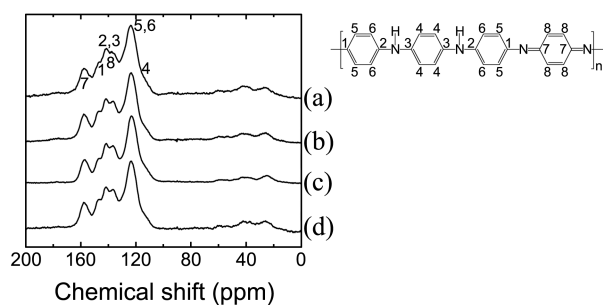
Figure 3. ^{15}N NMR spectra of (a) PANI-PAAMPSA 1:0.72, (b) 1:0.83, (c) 1:1.26, and (d) 1:1.91.

also observe a sharp and intense peak at 26 ppm in all the ^{15}N NMR spectra of PANI-PAAMPSA, and its intensity increases with increasing PAAMPSA content in PANI-PAAMPSA. This peak arises from residual anilinium monomers.[15] To examine the influence of such anilinium monomers on the conductivity of PANI-PAAMPSA, we remeasured the conductivity of PANI-PAAMPSA 1:0.83 after we removed the residual anilinium monomers by multiple precipitations. The conductivities were generally the same between the as-synthesized sample (1.09 S/cm) and the reprecipitated sample (1.01 S/cm). This observation indicates that the presence of anilinium monomers does not impact the conductivity of PANI-PAAMPSA. Our ^{15}N NMR experiments show that all the PANI-PAAMPSA samples in this series are fully doped as-synthesized and have large extents of charge delocalization along the backbone.

The XRD spectra of PANI-PAAMPSA with varying aniline to acid molar ratios are shown in Figure 4. The ionic association peak between aniline and sulfonic acid group is observed at $2\theta = 26°$ in all the PANI-PAAMPSA samples.[5] The number of Bragg reflections and the intensity of the reflections appear to decrease as the PAAMPSA content increases, indicating a decrease in crystallinity with increasing PAAMPSA content in PANI-PAAMPSA.[15] This observation is expected because PAAMPSA is amorphous; larger amount of amorphous polymer acid chains would make ordering of PANI chains difficult.

The UV-vis-NIR spectra of PANI-PAAMPSA samples are

Figure 2. ^{13}C NMR spectra of (a) dedoped PANI-PAAMPSA 1:0.72, (b) 1:0.83, (c) 1:1.26, and (d) 1:1.91. The chemical shifts are labeled accordingly on the accompanying chemical structure.
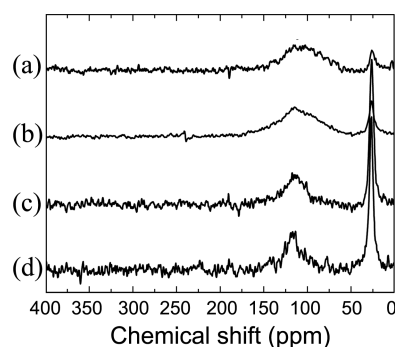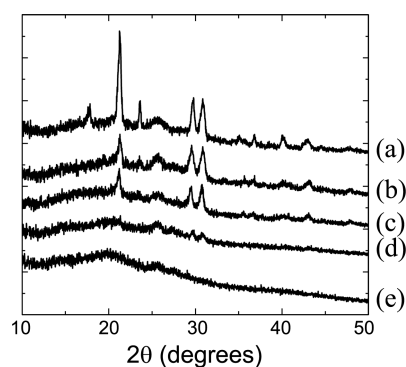
Figure 4. X-ray diffraction patterns of (a) PANI-PAAMPSA 1:0.72, (b) 1:0.83, (c) 1:1.05, (d) 1:1.26, and (e) 1:1.91.
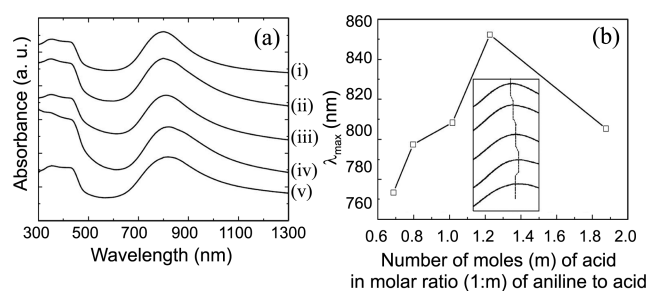
Figure 5. (a) UV-vis-NIR spectra of (i) PANI-PAAMPSA 1:0.72, (ii) 1:0.83, (iii) 1:1.05, (iv) 1:1.26, and (v) 1:1.91. The individual spectra have been shifted along the y axis for clarity. The location of peak maximum, λ_{max}, of each spectrum is quantified in (b). Inset: a magnified figure showing each peak position in (a).

Figure 6. The bulk conductivity of PANI-PAAMPSA with varying aniline to acid molar ratios.

shown as a function of aniline to acid molar ratio in Figure 5(a). The peaks corresponding to π-π^* transition of benzenoid, polaronic shoulder, and polaron interband transition[18-20] are observed in the spectra. As the PAAMPSA content increases in PANI-PAAMPSA, the polaron interband transition of PANI-PAAMPSA red shifts. The polaron interband transition blue shifts again with further increasing PAAMPSA content in PANI-PAAMPSA. The position of polaron interband transition peak (λ_{max}) is quantified in Figure 5(b). The shift of λ_{max} to higher wavelengths typically indicates an increase in conjugation length of the material. As the content of sulfonic acid group increases, it is expected to increase the number of sites for doping PANI. The conjugation length of PANI therefore increases with increasing the amount of PAAMPSA. However, PAAMPSA is inherently insulating. Having excess PAAMPSA can thus hinder charge hopping and macroscopic conduction. Therefore, the conjugation length of PANI-PAAMPSA decreases with further increasing the PAAMPSA content.

To examine the structure-conductivity relationships of PANI-PAAMPSA as a function of aniline to acid ratios, we measured the electrical conductivities of PANI-PAAMPSA films in this series. The measured conductivities are shown in Figure 6. As the sulfonic acid group content increases relative to that of aniline, the conductivity of PANI-PAAMPSA increases by approximately 6-fold. PANI-PAAMPSA at an aniline to sulfonic acid group ratio of 1:1.26 has the highest conductivity of 2.6 S/cm in this series of polymer examined. Further increasing the PAAMPSA content, however, results in a decrease in the conductivity of PANI-PAAMPSA. This conductivity trend is directly correlated with the changes in conjugation lengths of PANI with compositions as observed in the UV-vis-NIR spectra (Figure 5(b)). However, the structural changes of PANI-PAAMPSA with compositions observed from solid-state NMR and XRD studies are not correlated with the observed conductivity trend. These experiments indicate UV-vis-NIR to be a very sensitive measure of conductivity.

Conclusion
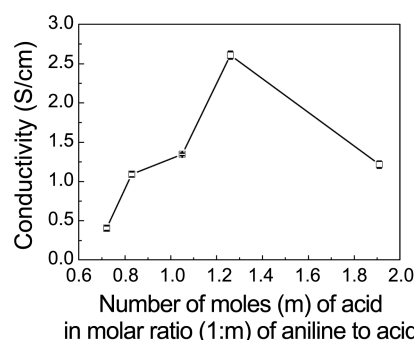
In conclusion, we observed that an optimum ratio of aniline to sulfonic acid groups exists for the maximum conductivity of PANI-PAAMPSA. The specific origin of this conductivity change with compositions requires further study. The electrical conductivity is, however, strongly correlated with the electronic structure of the material; PANI-PAAMPSA with the highest conductivity contains the least electronic defects along the polymer backbone and has the longest conjugation length of PANI. The position of polaron peak maximum, λ_{max}, is thus a good indicator for the conductivity of PANI-PAAMPSA in this series.

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