

Synthesis and optical, electrical, and thermoelectric properties of sodium salts of polyaniline sulfonic acid



Isao Yamaguchi*, Yusuke Sada

Department of Chemistry, Interdisciplinary Graduate School of Science and Engineering, Shimane University, 1060 Nishikawatsu, Matsue 690-8504, Japan

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ABSTRACT

Sodium salts of poly(aniline-5-sulfonic acid) (PAS), The **PAS(Na)s**, were obtained by the reaction of PAS with NaOH in water. The degree of sodium sulfonation of the **PAS(Na)s** depended on the feed amount of NaOH. The absorption peak of the **PAS(Na)s**, corresponding to an exciton transition generated by self-doping in the polymer backbone, decreased with the number of sodium sulfonated units. The **PAS(Na)s** were subjected to electrochemical oxidation, and the two oxidation peaks shifted to a lower potential as the degree of sodium sulfonation increased. The electrochemical reaction was accompanied by electrochromism. Thermoelectric measurements of the **PAS(Na)s** suggested that the majority of carriers were holes. The Seebeck coefficients (S 's) of the **PAS(Na)s** increased as the degree of sodium sulfonation of the polymers increased.

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1. Introduction

Thermoelectric materials have attracted significant attention as simple, automatic, and eco-friendly means of achieving energy conversion owing to their unique capability to directly convert heat to electricity [1]. The performance of thermoelectric materials is determined by a dimensionless quantity called the figure of merit, ZT , which is defined by the following equation,

$$ZT = S^2 \sigma T / \kappa$$

where S is the Seebeck coefficient (thermoelectric power, the change in voltage per unit temperature difference in a material), σ is the electrical conductivity, T is the temperature in Kelvin at which the properties are determined, and κ is the thermal conductivity. Materials with $ZT > 1$ are expected to be competitive with refrigeration and electric power generation methods.

Bismuth telluride, with a ZT value of approximately 1.0 at room temperature, is commercially available as a raw material for Peltier coolers [2]. However, inorganic thermoelectric materials suffer from issues such as toxicity, shortage of natural resources, and expensive, complex manufacturing processes. On the other hand, organic and polymeric semiconductors (OPs) could serve as materials with potentially high ZT values because of their low κ values, which are 2–3 orders of magnitude less than those of inorganic

semiconductors and metals [3]. Thus, OPs could result in light-weight, low-cost, large-area, flexible, and non-toxic thermoelectric modules. π -Conjugated polymers such as poly(alkylthiophene)s [4,5], poly(ethylenedioxythiophene)s [6–9], poly(carbazolenevinylene)s [10], and poly(phenylenevinylene)s [11,12] have been investigated as thermoelectric materials because they exhibit high electric conductivities after doping. It has been reported that the Seebeck coefficient is inversely proportional to the c value (c = carrier (hole) concentration) of a sample [13]. Hence, controlling the doping level in π -conjugated polymers is important in achieving a high ZT value. However, it is usually difficult to control the doping level in π -conjugated polymers.

Polyanilines with sulfonic acid side groups (SPANs) have attracted significant attention due to their self-doping behavior that results in high electrical conductivities and interesting electrical and optical properties [14–20]. The sulfonic acid proton in SPANs is considered to play an important role in self-doping. Thus, the substitution of other ions such as those of alkaline metals for the sulfonic acid proton in SPAN can control the self-doping level in SPANs. It was reported that the degree of lithium sulfonation in SPANs depended on the feed ratio of LiOH to SPANs in reactions of SPANs with LiOH [21]. Elucidation of relationship between the thermoelectric properties and the level of doping in alkaline metal salts of SPANs will provide fundamental information for the development of new OPC thermoelectric materials.

Herein, we report the synthesis of sodium salts of poly(aniline-5-sulfonic acid) (PAS) and their optical, electrochemical, electric, and thermoelectric properties. To the best of our knowledge, this

* Corresponding author. Tel./fax: +81 852 32 6421.

E-mail address: iyamaguchi@riko.shimane-u.ac.jp (I. Yamaguchi).

is the first report concerning the thermoelectric properties of conducting polymers with controlled doping levels.

2. Experimental

2.1. General

PAS was synthesized according to the reported method [22]. Other reagents were purchased and used without further purification.

IR spectra were recorded on a JASCO FT/IR-660 PLUS spectrophotometer with a KBr pellet. Elemental analysis was conducted on a Yanagimoto MT-5 CHN corder. GPC analysis was carried out on a TOSOH HLC-8120 system with polystyrene gel columns (K-803 and K-804) with a RI detector using *N,N*-dimethylformamide (DMF) containing 0.006 M LiBr as an eluent. The M_n and M_w values of **PAS(Na)-5** were 5450 and 7800, respectively. GPC measurements of the other polymers were not conducted because they contain sulfonic acid groups that may interact with polystyrene gels. pH measurements were carried out with a Sato Shouji PH-SD. UV–vis spectra were obtained using a JASCO V-560 spectrometer. Cyclic voltammetry was performed with a Hokuto Denko HSV-110. Electric conductivity measurements were conducted using an Advantest R8340A ultra high resistance meter with a two-probe method. The S values were determined by measuring electrical potential differences with a Keithley 2182A nanovoltmeter when a temperature gradient was established between two ends of the molded sample pellet. The S value of Ni at 300 K was measured as a reference sample, and the measured value of $-19 \mu\text{VK}^{-1}$ is in good agreement with the value of $-19.24 \mu\text{VK}^{-1}$ reported in the literature.

2.2. Synthesis of **PAS(Na)**s

Representative procedure: To an aqueous solution (2 mL) of PAS (0.085 g, 0.5 mmol aniline unit) was added 5 mL of NaOH(aq) (0.1 M, 0.5 mmol). After the reaction solution was stirred at room temperature for 1 h, the solvent was removed under vacuum and dried under vacuum at 80 °C to yield **PAS(Na)-5** (0.076 g, 78%). Anal. Calcd for $(\text{C}_6\text{H}_4\text{NSO}_3\text{Na} \cdot 1.5\text{H}_2\text{O})_n$: C, 32.73; H, 3.20; N, 6.36. Found: C, 32.51; H, 3.63; N, 6.00.

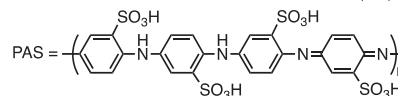
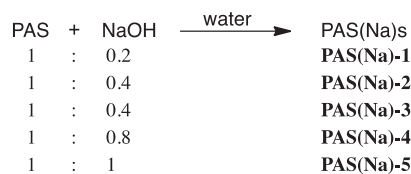
PAS(Na)-1, **PAS(Na)-2**, **PAS(Na)-3**, and **PAS(Na)-4** were prepared analogously. Data of **PAS(Na)-1**. Yield = 94%. Anal. Calcd for $\{(\text{C}_6\text{H}_4\text{NSO}_3\text{Na})_{0.2}(\text{C}_6\text{H}_5\text{NSO}_3)_{0.8} \cdot 2\text{H}_2\text{O}\}_n$: C, 36.84; H, 4.53; N, 7.16. Found: C, 36.79; H, 4.88; N, 6.90. Data of **PAS(Na)-2**. Yield = 96%. Anal. Calcd for $\{(\text{C}_6\text{H}_4\text{NSO}_3\text{Na})_{0.4}(\text{C}_6\text{H}_5\text{NSO}_3)_{0.6} \cdot 2\text{H}_2\text{O}\}_n$: C, 36.03; H, 4.33; N, 7.00. Found: C, 36.14; H, 4.57; N, 6.69. Data of **PAS(Na)-3**. Yield = 87%. Anal. Calcd for $\{(\text{C}_6\text{H}_4\text{NSO}_3\text{Na})_{0.6}(\text{C}_6\text{H}_5\text{NSO}_3)_{0.4} \cdot 1.8\text{H}_2\text{O}\}_n$: C, 33.24; H, 3.72; N, 6.46. Found: C, 33.07; H, 4.12; N, 6.88. Data of **PAS(Na)-4**. Yield = 74%. Anal. Calcd for $\{(\text{C}_6\text{H}_4\text{NSO}_3\text{Na})_{0.8}(\text{C}_6\text{H}_5\text{NSO}_3)_{0.2} \cdot 1.5\text{H}_2\text{O}\}_n$: C, 33.40; H, 3.36; N, 6.49. Found: C, 33.25; H, 3.64; N, 6.06.

3. Results and discussion

3.1. Synthesis and solution properties

Treatment of PAS with NaOH in molar ratios of 1:0.2, 1:0.4, 1:0.6, 1:0.8, and 1:1 in water afforded sodium salts of PAS, **PAS(Na)-1**, **PAS(Na)-2**, **PAS(Na)-3**, **PAS(Na)-4**, and **PAS(Na)-5** in yields of 74–96% (Scheme 1). The synthesis results are summarized in Table 1. The polymers were soluble in water and polar organic solvents such as methanol, DMF, and dimethyl sulfoxide (DMSO).

The degrees of sodium sulfonation of the **PAS(Na)**s were estimated by titration of the intact sulfonic acid groups of **PAS(Na)**s



Scheme 1. Synthesis of **PAS(Na)**s.

with NaOH. Fig. 1 shows the pH changes in the aqueous solutions of PAS, **PAS(Na)-1**, and **PAS(Na)-5** with the addition of NaOH(aq) to the solutions. The titration curves indicate that neutralization of PAS and **PAS(Na)-1** proceeded normally; organic sulfonic acids have pKa values of approximately 4, and the acidity of polymeric acids usually becomes weaker as titration proceeds. A smaller volume of NaOH(aq) was required to neutralize the sulfonic acid groups of **PAS(Na)-1** compared to that required for PAS because **PAS(Na)-1** has fewer sulfonic acid groups than PAS. The titration curve of **PAS(Na)-5** began at approximately pH = 7. This result suggests that all sulfonic acid protons were replaced by Na⁺ in **PAS(Na)-5**. The titration analysis revealed that the degrees of sodium sulfonation of **PAS(Na)-1**, **PAS(Na)-2**, **PAS(Na)-3**, **PAS(Na)-4**, and **PAS(Na)-5** were nearly consistent with the feed molar ratios of NaOH/PAS. Analytical data also supported these results.

The reduced viscosities (η_{sp}/c) of PAS and **PAS(Na)-3** in DMSO were 0.14 and 0.22 g⁻¹ dL ($c = 0.10$ g dL⁻¹), respectively. The η_{sp}/c values of the polymers in DMSO increased when their concentrations, c , were reduced. The η_{sp}/c values of PAS and **PAS(Na)-3** changed from 0.29 and 0.24 g⁻¹ dL ($c = 0.083$ g dL⁻¹) to 0.55 and 0.52 g⁻¹ dL ($c = 0.050$ g dL⁻¹) through values of 0.37 and 0.27 g⁻¹ dL ($c = 0.063$ g dL⁻¹). These results suggest that the polymers behaved as polymeric electrolytes in dilute solutions [23]. The η_{sp}/c values of the DMSO solutions ($c = 0.10$ g dL⁻¹) of **PAS(Na)-1**, **PAS(Na)-2**, **PAS(Na)-4**, and **PAS(Na)-5** were 0.16, 0.17, 0.24, and 0.28 g⁻¹ dL, respectively. These data suggested that the **PAS(Na)**s adopted more rigid structures than PAS did in DMSO.

3.2. IR spectra

Fig. 2 shows the IR spectra of PAS, **PAS(Na)-1**, **PAS(Na)-2**, **PAS(Na)-3**, **PAS(Na)-4**, and **PAS(Na)-5**. The main features of the IR spectra of the polymers are similar, whereas some of the relative intensities vary appreciably. The peaks at 1070 and 1040 cm⁻¹ were assigned to aryl-S linkages, aromatic ring vibrations exhibiting some characteristics of C–S stretching. It has been reported that SPANs exhibit two peaks corresponding to aromatic ring vibrations in aryl-S linkages [16]. These wavenumbers are comparable to those of SPAN. The peak intensity ratio, I_{1070}/I_{1040} , increased as the degree of sodium sulfonation increased. These observations suggest that sodium sulfonation significantly affected the aryl-S linkages.

3.3. UV–vis spectra

Fig. 3 shows the UV–vis spectra of PAS, **PAS(Na)-1**, **PAS(Na)-2**, **PAS(Na)-3**, **PAS(Na)-4**, and **PAS(Na)-5** in H₂O. The peaks at 478 nm and 330 nm were assigned to the exciton and benzenoid π – π^* transitions, respectively [15,21]. The peak at approximately 478 nm decreased and that at approximately 330 nm increased with the increase in the degree of sodium sulfonation. These observations are comparable to the case in which LiOH(aq) was added to a

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