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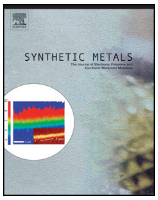

Characterization of self-doped conducting polyanilines bearing phosphonic acid and phosphonic acid monoester

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ABSTRACT

Novel self-doped polyanilines bearing phosphonic acid, poly(2-methoxyaniline-5-phosphonic acid) (PMAP) and poly(2-methoxyaniline-5-phosphonic acid monoethyl ester) (PMAPE) were characterized in the following properties: (1) thermostability, (2) morphology in the solid state, (3) absorption and transparency in the spin-coating film, (4) delocalization of polaron, (5) doping efficiency, and (6) chemical oxidation and reduction. The UV–vis–NIR absorption spectra of the spin-coating films of PMAP/pyridine (1:2) and PMAPE/pyridine (1:1) show the polaron band and free carrier tail, which are characteristic to the conducting polymers. The highly transparent films of them (up to ~90% transparency) were formed by spin-coating. Concerning the property of the polaron in the polymer, the ESR spectra suggest that polaron of PMAP/pyridine (1:2) is more delocalized than that of PMAPE/pyridine (1:1). The XPS experiments indicate that the doping efficiency of PMAP is much higher than that of PMAPE, which is likely to be due to diprotic acid units derived from phosphonic acid of PMAP. Oxidation and reduction of PMAP and PMAPE were demonstrated by treatment with the corresponding oxidant $\{(NH_4)_2S_2O_8\}$ and reductant $(N_2H_4{\cdot}H_2O)$, respectively.

1. Introduction

Polyaniline is one of the most studied conducting polymers because of the availability, stability, and unique redox property [1]. Recently, high conducting polyanilines are applied as conducting thin films, organic solar cell materials, electromagnetic interference shielding, corrosion protection, and so on [2,3]. Polyanilines possessing covalently bound acid moieties can dope themselves without external dopants [4]. Such self-doped polyanilines are attractive due to their water solubility. Among a number of self-doped polyanilines [5–21], a sulfonated polyaniline [6] reported as a first self-doped conducting polyaniline by Epstein et al. in 1990 has been researched and developed widely. Nowadays, it can be commercially available as poly(2-methoxyaniline-5-sulfonic acid) (PMAS) in practical use, which exhibits moderate conductivity and water solubility [15]. PMAS can be used not only as conducting materials but also as a redox mediator in catalytic systems [22–27]. Furthermore, its doping state, electronic state, conformational change [28,29], redox behavior [30], and metal interaction [29] are also attractive.

Quite recently, we focused on the phosphonic acid as a dopant for polyaniline [12,13,31] and synthesized two self-doped polyanilines bearing phosphonic acid, poly(2-methoxyaniline-5-phosphonic acid) (PMAP) [32,33] and poly(2-methoxyaniline-5-phosphonic acid monoethyl ester) (PMAPE) [34] (Fig. 1). These are the first reports for the self-doped polyaniline possessing the phosphonic acid moiety directly attached to the polymer backbone. Self-doping is clearly shown by UV–vis–NIR and ESR spectra in the pyridinium salts of PMAP and PMAPE [32,34], and their conductivity of the drop-casting film is 0.19 and 0.01 S/cm, respectively. As new self-doped polyanilines, further characterization including the properties for the doping and electronic state is required for the materials application. Here, we report the properties for both polyanilines: (1) thermostability, (2) morphology in a solid state, (3) absorption and transparency in the spin-coating film, (4) delocalization of polaron, (5) doping efficiency, and (6) chemical oxidation and reduction. This report also describes the comparison of the self-doped conducting polyanilines in view of monoprotic and diprotic acid derived from phosphonic acid.

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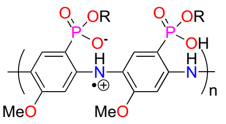

Poly(2-methoxyaniline-5-phosphonic acid) (PMAP) : R = H
Poly(2-methoxyaniline-5-phosphonic acid monoethyl ester) (PMAPE) : R = Et

Fig. 1. Structures of PMAP and PMAPE.

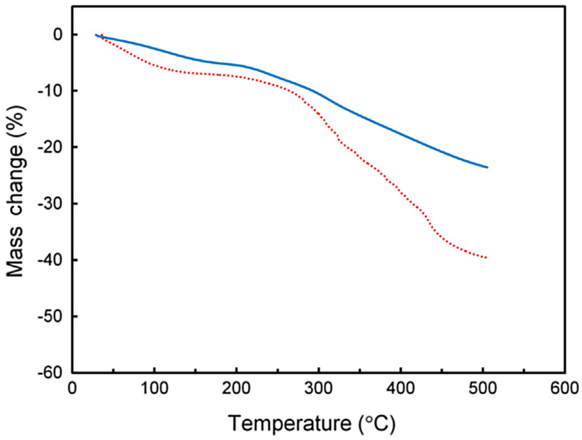

Fig. 2. TGA curves for PMAP and PMAPE under a nitrogen atmosphere. Blue solid line: PMAP, red dotted line: PMAPE. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

2. Experimental

2.1. General

All reagents were purchased from commercial sources and used without further purification. PMAP and PMAPE were prepared by our previously reported procedures [32–34]. The FT-IR spectra of PMAP and PMAPE are shown in Fig. S1. MilliQ water was used for the spectral measurements. pH 9.0 aqueous borate buffer solution was prepared by the following method: $B(OH)_3$ (3.09 g, 0.05 mol) was dissolved in MilliQ water (90 mL). After that, 2 M aqueous NaOH solution was added to the solution to prepare pH 9.0 (0.5 M). UV–vis–NIR spectra were recorded on a JASCO V-670 spectrometer.

2.2. Thermogravimetry analysis (TGA)

TGA was recorded on an SII TG/DTA6200 analyzer. Samples were put in open aluminum pan and measured under a nitrogen atmosphere (flow rate 150 mL/min).

2.3. Scanning electron microscope (SEM) measurements

The powder of PMAP and PMAPE was put on a carbon tape. The SEM images were observed on a JEOL JSM-6335.

2.4. X-ray photoelectron spectroscopy (XPS) measurements

The XPS measurements were carried out with an X-ray photoemission spectrometer (SHIMADZU Corp./Kratos, AXIS-165x) in an ultrahigh-vacuum chamber (2.3–9.3 × 10^{-9} Torr) at room temperature. The monochromatic Al Kα line of 1486.6 eV was employed as an X-ray source. The tube current, tube voltage, and pass energy were set at 12 mA, 15 kV, and 160 eV, respectively. Before recording the spectra, the sample surfaces were cleaned by argon-ion etching. The emission current and argon gas pressure were 15 mA and 1.2–1.7 × 10^{-7} Torr, respectively. The binding energies were calibrated using Ag $3d_{5/2}$ line (368.2 eV) [35]. The intensity (counts/s) was corrected for quantitative analysis using appropriate transmission values supplied by the instrument manufacturer. Peak analysis of the obtained spectra was conducted using an analysis software (Light Stone, OriginPro 9.0J). Background subtraction was performed by subtracting linear function from the data to remove the gradient of the spectra. To deconvolute the N 1s spectra, they were fitted with Voigt functions, where Lorentzian width was fixed to 0.25 eV.

2.5. Redox transformations

i) Oxidation reaction

PMAP (10 mg, 0.049 mmol based on the aniline unit) was dissolved in 1 mL of pH 9.0 aqueous borate buffer solution under air at room temperature. $(NH_4)_2S_2O_8$ was added to the stirring solution in three parts {1st: 3 eq. (33 mg, 0.15 mmol), 2nd: 7 eq. (79 mg, 0.34 mmol), 3rd: 10 eq. (112 mg, 0.49 mmol)}. After every addition, 40 µL of solution was sampled by micropipette and then diluted with 4 mL of pH 9.0 aqueous borate buffer solution. The UV–vis–NIR spectra for the solutions were measured to monitor the reaction. The similar procedure was employed for PMAPE, where the amount of PMAPE (10 mg, 0.043 mmol based on the aniline unit) and the molar equivalents of $(NH_4)_2S_2O_8$ are same {1st: 3 eq. (29 mg, 0.13 mmol), 2nd: 7 eq. (67 mg, 0.29 mmol), 3rd: 10 eq. (96 mg, 0.42 mmol)}, but the solution was further diluted by half for the UV–vis–NIR measurements.

ii) Reduction reaction

The similar procedure to the oxidation reaction was employed for PMAP and PMAPE by use of $N_2H_4{\cdot}H_2O$ instead of $(NH_4)_2S_2O_8$. In the reduction reaction of PMAP, $N_2H_4{\cdot}H_2O$ was added in four parts {1st: 8 eq. (20 µL, 0.41 mmol), 2nd: 42 eq. (99 µL, 2.04 mmol), 3rd: 50 eq. (119 µL, 2.45 mmol), 4th: 50 eq. (119 µL, 2.45 mmol)}. In the reduction reaction of PMAPE, $N_2H_4{\cdot}H_2O$ was added in two parts {1st: 10 eq. (21 µL, 0.43 mmol), 2nd: 40 eq. (84 µL, 1.73 mmol)}.

3. Results and discussions

3.1. Thermal stability

TGA was performed to examine the thermal stability of PMAP and PMAPE. Fig. 2 shows the TGA curves for both polymers measured under a nitrogen atmosphere. The weight loss at a low temperature (~100 °C) is attributed to volatilization of water contained in polymer [36,37]. Almost 10% weight loss was observed in PMAP and PMAPE at 300 °C. In the case of PMAP, the weight was decreased with increasing the temperature, which is likely to be due to the cleavage of the phosphonic acid moiety. On the other hand, a significant weight loss occurred on PMAPE in the temperature range higher than ~300 °C, which could be caused by decomposition of the ethyl group.

3.2. Morphology

In recent years, much attention has been paid to control morphology of polyanilines and many nano-structurally characteristic polyanilines (i.e. fiber, wire, rod, tube, etc.) have been reported [1,2,38]. To investigate the morphology, the SEM analysis was carried out for the powder of PMAP and PMAPE (Fig. 3a–c and d–f), respectively. Such powders were obtained by crushing the hard solids with a spatula, which were prepared by drying the wet clayey pastes with water after the work-up in the oxidative polymerization [32,34]. Fig. 3a and d shows the SEM images of 100 times