

Short Communication

Synthesis of self-doped conducting polyaniline bearing phosphonic acid monoester

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ABSTRACT

Poly(2-methoxyaniline-5-phosphonic acid monoethyl ester) (PMAPE) was synthesized via oxidative polymerization of 2-methoxyaniline-5-phosphonic acid monoethyl ester. This is the first example of the conducting self-doped polymers with phosphonic acid monoester. Self-doping of the polymer was shown by UV–vis–NIR and ESR measurements. The pyridinium salt of the thus-obtained PMAPE was water-soluble and its film exhibited conductivity.

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1. Introduction

Self-doped conducting polymers, which have covalently bound and charged functional groups, are attractive due to the water solubility and their wide applications for polymer-based electronics and biosensors [1]. The most commonly used functional group in self-doped conducting polymers is sulfonic acid, as exemplified by polythiophenes [2], polyanilines [3,4], and polypyrroles [5,6] possessing sulfonic acid. Differing from sulfonic acid, two acidic protons are available in phosphonic acid. The second acid group not used for doping would provide the features, such as acid/base complexation. Furthermore, another functional group would be introduced by the esterification of the second acid group with keeping the doping state. However, self-doped conducting polymers possessing a phosphonic acid group have been very little studied [7–9]. Very recently, we have successfully synthesized a self-doped conducting polyaniline with phosphonic acid attached to the backbone, poly(2-methoxyaniline-5-phosphonic acid) (PMAP, **1a**) (Fig. 1) [10]. Herein, we describe the synthesis of poly(2-methoxyaniline-5-phosphonic acid monoethyl ester)

(PMAPE, **1b**) via oxidative polymerization of 2-methoxyaniline-5-phosphonic acid monoethyl ester. This is the first example of the conducting self-doped polymers with phosphonic acid monoester. The pyridinium salt of the thus-obtained PMAPE was water-soluble and its film exhibited conductivity.

2. Experimental

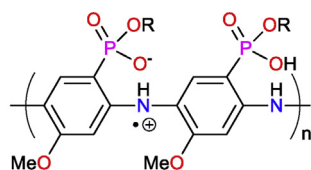
2.1. General

NMR spectra were recorded on a JEOL JNM-ECS 400 spectrometer. Chemical shifts were reported in ppm on the δ scale relative to a residual solvent (CDCl_3 : δ 7.26 for ^1H NMR and 77.0 ppm for ^{13}C NMR, D_2O : δ 4.79 for ^1H NMR) as an internal standard. 3-(Trimethylsilyl)-1-propanesulfonic acid sodium salt (−1.9 ppm) was used as an internal standard for ^{13}C NMR in D_2O . An 85% aqueous phosphoric acid solution (0.00 ppm) was used as an external standard for ^{31}P NMR. Infrared spectra were obtained with a JASCO FT/IR-6200 spectrometer. Mass spectra were measured on a JEOL JMS-DX-303 spectrometer using electron impact (EI) mode. ICP-MS analysis was made on a SHIMADZU ICPS-8100. ESR spectrum was taken on a JEOL X-band spectrometer (JES-RE1XE). UV–vis–NIR spectra were recorded on a JASCO V-670 spectrophotometer. All reagents were purchased from commercial sources. Milli-Q water was used except the synthesis of the monomer.

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Poly(2-methoxyaniline-5-phosphonic acid) (PMAPE) **1a** : R = H

Poly(2-methoxyaniline-5-phosphonic acid monoethyl ester) (PMAPE) **1b** : R = Et

Fig. 1. PMAPE **1a** and PMAPE **1b**.

2.2. Synthesis

(4-Methoxy-3-nitrophenyl)phosphonic acid monoethyl ester (**3**): To a round-bottomed flask were added diethyl (4-methoxy-3-nitrophenyl)phosphonate (**2**) (2.4 g, 8.3 mmol), MeOH (10 mL), and 1 M aqueous NaOH solution (9.1 mL) at room temperature. The mixture was stirred at 70 °C for 3 h. After concentration, 1 M aqueous HCl solution (ca. 10 mL to reach pH 1) was added to the mixture. The mixture was extracted with ethyl acetate. The organic layer was dried with Na₂SO₄ and evaporated in vacuo. The residue was purified by silica-gel column chromatography (1:10 MeOH/CH₂Cl₂, v/v) to give monoester **3** as a yellow solid (1.072 g, 4.1 mmol, 49% yield). Mp 103–104 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ 1.31 (t, J = 6.9 Hz, 3H), 4.00 (s, 3H), 4.06–4.13 (m, 2H), 7.11 (dd, J = 8.7, 3.2 Hz, 1H), 7.91 (ddd, J = 12.7, 8.7, 1.8 Hz, 1H), 8.19 (dd, J = 14.0, 1.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 15.98 (d, J = 6.7 Hz), 56.62, 62.39 (d, J = 5.8 Hz), 113.46 (d, J = 15.3 Hz), 120.97 (d, J = 202.2 Hz), 128.67 (d, J = 13.4 Hz), 137.04 (d, J = 11.5 Hz), 139.07 (d, J = 19.2 Hz), 155.52 (d, J = 2.9 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 16.76; IR(ATR) ν 3069, 2988, 2949, 2908, 2847, 2255, 1699, 1613, 1530, 1352, 1283, 1163, 1023 cm⁻¹; HRMS (EI) m/z calcd for C₉H₁₂NO₆P [(M+H)⁺] 261.0402, found 261.0404.

2-Methoxyaniline-5-phosphonic acid monoethyl ester (**4**): To a three-necked round-bottomed flask were added monoester **3** (873 mg, 3.34 mmol), EtOH (20 mL), and 5% Pd/C (80 mg) under nitrogen. Nitrogen was replaced with hydrogen by evacuation and purging for several times. After stirring under hydrogen at room temperature for 6 h, water (50 mL) was added to the mixture. The mixture was filtered through a filter paper. The filtrate was concentrated in vacuo to give **4** as a gray solid (661 mg, 2.86 mmol, 86% yield). The obtained product **4** was used without further purification. Mp 202–203 °C (uncorrected); ¹H NMR (400 MHz, D₂O) δ 1.19 (t, J = 6.9 Hz, 3H), 3.80–3.89 (m, 2H), 3.99 (s, 3H), 7.26 (dd, J = 8.7, 3.2 Hz, 1H), 7.62 (dd, J = 12.6, 1.8 Hz, 1H), 7.72 (ddd, J = 12.5, 8.7, 1.8 Hz, 1H); ¹³C NMR (100 MHz, D₂O) δ 16.18 (d, J = 5.8 Hz), 56.72, 61.70 (d, J = 4.8 Hz), 112.74 (d, J = 15.3 Hz), 120.72 (d, J = 19.2 Hz), 126.11 (d, J = 184.0 Hz), 126.14 (d, J = 11.5 Hz), 133.17 (d, J = 9.6 Hz), 154.72 (d, J = 2.9 Hz); ³¹P NMR (162 MHz, D₂O): δ 14.6; IR(ATR) ν 2971, 2933, 2840, 2578, 2138, 1637, 1560, 1500, 1308, 1270, 1189, 1037 cm⁻¹; HRMS (EI) m/z calcd for C₉H₁₄NO₄P [(M+H)⁺] 231.0660, found 231.0660.

2.3. Polymerization

2-Methoxyaniline-5-phosphonic acid monoethyl ester (**4**) (540 mg, 2.33 mmol) was dissolved in 2.5 M aqueous pyridine solution (3.0 mL, 7.5 mmol). After the solution was cooled to -5 °C, aqueous solution of (NH₄)₂S₂O₈ (665 mg, 2.91 mmol in 2.6 mL of water) was added over 2.5 h at the same temperature. The reaction mixture was stirred at -5 °C for 5 days. Then, 1 M aqueous HCl solution (10 mL) was added to the mixture. The mixture was stirred for 10 min, and filtered. The resulting residue was successively washed with 0.2 M aqueous HCl solution (60 mL), water (60 mL), and Et₂O (10 mL). The residue was dried at 50 °C under the reduced pressure to give the desired polymer **1b** as a black solid (240 mg, 44%

yield). IR(ATR) ν 2975, 1550, 1496, 1440, 1385, 1257, 1211, 1155, 1073, 1020, 917, 819 cm⁻¹; Anal. calcd. for C₃₆H₄₇N₄O₁₆P₄ based on tetramer in the emeraldine structure: C, 47.22; H, 5.17; N, 6.12; found: C, 44.20; H, 5.46; N, 5.57; composition of P atom was analyzed by inductively coupled plasma-mass spectrometry (ICP-MS), Anal. calcd. for C₃₆H₄₇N₄O₁₆P₄ based on tetramer in the emeraldine structure: P, 13.53; found: 12.71.

2.4. ICP-MS analysis

PMAPE **1b** (11.5 mg) was dissolved in 3 mL of pH 9.0 borate buffer solution, which was diluted with water in measuring flask to 100 mL in total. Quantification was carried out using the calibration curve, which was prepared using four points of the diluted phosphorus standard solution (0, 5, 10, 50 ppm of P).

2.5. GPC analysis

Tandemly arranged two TSKgel α-M (7.8 mm I.D. × 30 cm, TOSOH) columns were used at column temperature 40 °C. A solution of ultrapure water/MeOH (8/2, v/v) containing 20 mmol/L of Na₂CO₃ and 30 mmol/L of NaHCO₃ was used as an eluent at a flow rate of 0.6 mL/min. Sample was diluted to 0.1 wt% with the eluent and filtered through a 0.5 μm cellulose acetate cartridge filter before injection (50 μL). A peak was detected by a UV detector (254 nm). Poly(styrene sulfonic acid)sodium salts (Mw 1260, 4210, 13,500, 29,500, 78,400, 158,000, 2,350,000) were used to make a calibration curve.

2.6. ESR measurement

ESR spectrum of an aqueous PMAPE/pyridine (1:1) solution (4.3 × 10⁻² M based on the monomer unit) was measured at 298 K under non-saturating microwave-power conditions (0.998 mW) operating at 9.0503 GHz.

2.7. Electrical conductivity measurements

The indium tin oxide (ITO)/glass (see the figure in Table 1) and glass substrates (26 × 26 mm) were ultrasonically washed with solvents in order of neutral detergent, water, acetone, ethanol, and desalted water twice for each process. They were stored in desalted water. Before usage they were dried by air duster. The glass substrates were cleaned by UV-O₃ treatment (12 W low pressure mercury lamp, flowing air) for 1 min after drying. The films were formed by drop-casting. The aqueous 1% (w/w) solution of the pyridinium salt of PMAPE **1b** (ca. 4 μL) was dropped onto the ITO/glass substrate, which was dried with hot air from a dryer, or the aqueous 2% (w/w) solution of the pyridinium salt of PMAPE **1b** (ca. 150 μL) was dropped onto the glass substrate, which was baked at 100 °C

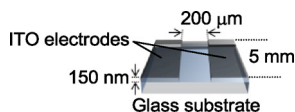
Table 1

Electrical resistance and conductivity for the drop-cast films of the aqueous 1% (w/w) solution of the pyridinium salts of PMAPE **1b**.

Entry	Molar equivalents of pyridine ^a	Electrical resistance (kΩ)	Conductivity (S/m) ^b
1	1	200	1.3
2	2	200	1.3

^a Based on the monomer unit.

^b Conductivity was calculated on the assumption that the gap (see the below figure) was filled with the polymer. Therefore, the obtained values are the minimum value.



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