

A unidomain membrane prepared from liquid-crystalline poly(pyridinium 4-styrene sulfonate) for anhydrous proton conduction



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ABSTRACT

Liquid-crystalline poly(pyridinium 4-styrene sulfonate) was synthesized through an acid-base reaction between poly(4-styrene sulfonic acid) and a mesomorphic pyridine derivative. Differential scanning calorimetry (DSC) and X-ray diffraction (XRD) measurements revealed that the resultant polymer exhibited a bilayer smectic order with a *d*-spacing of 10.2 nm at temperatures above 193 °C. Thermogravimetric (TG) analysis indicated that the polymer was thermally stable at temperatures up to 288 °C. A solution-cast membrane of the polymer was mechanically sheared in the smectic A phase to obtain a unidomain membrane with a thickness of 0.15 mm. Polarizing optical microscope (POM) and scanning electron microscope (SEM) images confirmed that the smectic bilayers in the unidomain membrane were perpendicularly to the shearing direction. Electrochemical characterization suggested that the uniformly lamellar pathways formed in the uni-domain membrane favored anhydrous proton conduction. The maximum proton transference number and conductivity of the membrane reached 0.46 and $7.0 \times 10^{-6} \text{ S cm}^{-1}$, respectively. The temperature dependence of the proton conductivity followed the Arrhenius law and the estimated activation energy for the anhydrous proton conduction across the membrane was 60 kJ mol^{-1} .

1. Introduction

Proton conductive membranes have attracted much attention due to their potential application in proton exchange membrane fuel cells [1,2]. Commercially available perfluorosulfonic acid membranes, such as Nafion®, are widely used for their considerable proton conductivity and chemical stability. However, their usage is limited to a temperature regime below 80 °C because proton conduction in these materials depends strongly on humidification [3,4]. In order to develop fuel cells working at intermediate temperatures (100–200 °C), a variety of polymers have been proposed for preparing anhydrous proton conductive membranes. Protic salt polymers seem promising due to their facile synthesis together with good processability [5,6]. Brinke et al. have prepared a pyridinium salt polymer by mixing poly(4-vinyl pyridine) with stoichiometric toluene sulfonic acid [7]. Ionic conductivity of $10^{-6} \text{ S cm}^{-1}$ was observed for the salt polymer at 170 °C. Because both protons and the anions contributed to the observed ionic conductivity of the protic salt, the proton current was characterized by proton transference number [8,9]. Yang et al. have prepared an anhydrous proton conducting membrane by casting solution of poly-2-vinylpyridinium dihydrogenphosphate onto a porous polybenzoxazole mat [10]. The estimated proton transference number of the

membrane was 0.17–0.20. The authors ascribed the higher fraction of anionic current to easier migration of the free dihydrogenphosphate ions.

Recently we reported a series of low weight molecular liquid crystals consisting of biphenyl benzoate based pyridinium dihydrogen phosphate (**C₆Py-DHP**) for anhydrous proton conduction [11]. The electrochemical characterization revealed that the smectic phase favored proton conduction greatly in the pyridinium salts. We wondered if anhydrous proton conductive membrane could be constructed by introducing the corresponding pyridine liquid crystals to a host polymer containing Brönsted acids. By this way, protons are expected to be transferred efficiently owing to the liquid crystal order while anions are bound to the polymer backbone to prevent free migration. In addition, the resultant liquid crystal polymer allows macroscopic orientation to further enhance proton conduction. In this research, poly(4-styrene sulfonic acid) (**PSSA**) was employed as a host polymer in this research for the strong acidity. **PSSA** alone has hardly been used as a polyelectrolyte because of high water solubility and poor mechanical properties [12]. We integrated a biphenyl benzoate based pyridine derivative (**C₆Py**) with **PSSA** to obtain a stable protic salt polymer **PSS-C₆Py**. The synthetic route is presented in Fig. 1. The resultant **PSS-C₆Py** exhibited a smectic liquid crystal phase at

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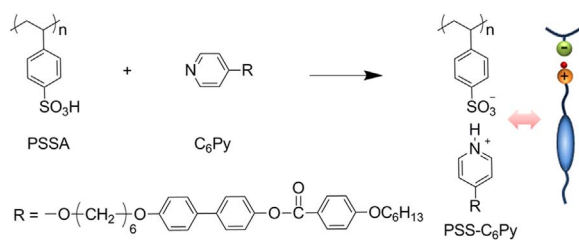


Fig. 1. Synthetic route of PSS-C₆Py.

temperatures above 193 °C. A unidomain membrane was obtained by mechanical shearing the solution-cast PSS-C₆Py membrane in the smectic phase. Electrochemical characterization revealed that both proton transference numbers and conductivities were significantly promoted in the unidomain membrane.

2. Experimental

2.1. Materials

4-(6-(4'-(4-(hexoxy)benzoyloxy)-[1,1'-biphenyl]-4-yloxy)hexoxy)pyridine (C₆Py) was synthesized according to the procedure described previously [11]. PSSA ($M_w=70,000-80,000$, 30 wt% aq.) was obtained from Shanghai Dibo and used as supplied. Solvents were used as received from Chengdu Changzheng.

2.2. Instruments and measurements

The ¹H nuclear magnetic resonance (¹H NMR) spectra were measured on a Bruker AV II-400 spectrometer with DMSO-*d*₆ as the solvent. The Fourier transform infrared (FT-IR) spectra (KBr pellet) were recorded on a NEXUS 670 FT-IR spectrometer at room temperature. The thermal behaviors of the samples were investigated with differential scanning calorimetry (DSC) on a heat flux TA DSC Q20 Modulated instrument (3–5 mg samples, 10 °C min⁻¹ heating and cooling rates and calibrated with indium standards). The thermogravimetric (TG) / differential thermogravimetric (DTG) analysis was performed in a nitrogen atmosphere using a TA instrument Netzsch TGA 209 C at a heating rate of 10 °C min⁻¹. The onset temperature of weight loss during the heating process was reported as the decomposition temperature (T_d). Optical characterizations of the samples were performed by a Weitu XPL-30TF polarizing optical microscope (POM) equipped with a WT-3000 hot-stage (accuracy: ± 1 °C). The X-ray diffraction (XRD) patterns were recorded on an X'Pert Pro diffractometer equipped with an X'Celerator detector and Cu-Kα radiation, operating at 40 kV and 40 mA. The scanning electron microscope (SEM) images were obtained using a Quanta450 environmental scanning electron microscope.

The electrochemical impedance spectroscopy (EIS) measurements were carried out using electrochemical workstation consisted of an EG & G Princeton Applied Research (PAR) potentiostat/galvanostat model 273 A and PAR lock-in-amplifier model 5210 connected to a PC running electrochemical impedance software (Frequency range: 10 mHz–100 kHz, applied voltage: 10 mV) with a WT-3000 hot-stage. The impedance data was processed by a Z View software package. The potentiostatic polarization was measured using the same electrochemical workstation with direct current (DC) power supply (Applied voltage: 850 mV). The vacuum dried sample was sandwiched between two ITO glasses to form an ITO/PSS-C₆Py/ITO blocking cell. A clamping pressure of 300 kPa was applied to the cell to pack the electrodes and the electrolyte closely. The non-blocking cells were prepared according to a literature procedure [13,14]. A mixture of MnO₂, acetylene black and polytetrafluoroethylene (PTFE) in 8:1.5:0.5 w/w ratio was grinded thoroughly. The resulting paste was pressed at 10 MPa onto a nickel gauge and dried for 16 h at 90 °C to form the

MnO₂ electrode assembly. Each electrode contained about 50 mg active MnO₂. The vacuum dried sample was sandwiched between two MnO₂ electrodes to construct a MnO₂/PSS-C₆Py/MnO₂ cell (clamping pressure: 300 kPa). All electrochemical experiments were carried out under a dry nitrogen atmosphere.

2.3. Synthesis of PSS-C₆Py

A solution of C₆Py in methanol/tetrahydrofuran (1/1) (1 wt%) was added drop-wise to a solution of PSSA in methanol/tetrahydrofuran (1/1) (1 wt%) with stirring. The mixture was then stirred at room temperature for 2 h. The resultant precipitate was collected by a suction funnel and washed repeatedly with methanol/tetrahydrofuran (1/1) solvent. The residue was dried in vacuum for 3 days to give PSS-C₆Py in a yield of 94%. The ¹H NMR (400 MHz, DMSO-*d*₆, ppm): δ=9.01 (d, NCH), 8.29 (d, NCHCH), 7.05–8.11 (m, Ar-H), 4.05 (t, OCH₂), 1.28–1.95 (m, CH₂), 0.84 (t, CH₃). FT-IR (KBr): $\nu=2935, 2864, 2772, 1920, 1735, 1639$ (C=N), 1609, 1542, 1510, 1473, 1399, 1317, 1286, 1257, 1204, 1200 (O=S=O), 1170, 1125, 1078, 1036, 1005, 933, 882, 838 cm⁻¹.

2.4. Preparation a solution-cast membrane

PSS-C₆Py was dissolved in *N,N*-dimethylformamide at 50 °C to form a light yellow solution (20 wt%). After that, the solution was allowed to stand at same temperature without stirring for 6 h to get homogeneous and bubble free solution. The viscous solution was then casted onto a clean Teflon plate which was placed on a flat surface. The sample was dried at 80 °C in an oven for 12 h and then cured in the oven for half an hour. Finally, the membrane with a diameter of 20 mm and a thickness of 0.15 mm was peeled off from the Teflon plate. Photograph of the solution-cast membrane is shown in Fig. 2a.

2.5. Preparation of a unidomain membrane

A freshly cast PSS-C₆Py membrane was sandwiched between two indium tin oxide (ITO) coated glass plates and heated to 210 °C on a hot-stage. After annealing at 210 °C for 30 min, the cover plate was slid unidirectionally to shear the sample. The membrane was then cooled quickly to room temperature to preserve the obtained unidomain architecture. Photograph of the unidomain membrane (10×7×0.15 mm) is shown in Fig. 2b.

3. Results and discussion

3.1. FT-IR spectra

The successful preparation of PSS-C₆Py was confirmed by FT-IR spectra as shown in Fig. 3. In the spectrum of PSS-C₆Py, the strong absorption band centered at 1125 cm⁻¹ was ascribed to the asymmetric stretching vibration of the O=S=O unit of PSSA [15,16]. The peak at 1036 cm⁻¹ arose from the vibrations of the phenyl ring attached to the sulfonic group. The band at 1594 cm⁻¹ in the spectrum of C₆Py corresponded to the C=N vibration of the pyridine. After quaternization, the characteristic absorption band at 1639 cm⁻¹ in the spectrum of PSS-C₆Py was assigned to the C=N vibration of the pyridinium ring [17,18].

3.2. Mesomorphism of PSS-C₆Py

TG and DTG curves revealed that PSS-C₆Py had a relatively high thermal stability ($T_d = 288$ °C) with a one-step weight loss event, as shown in Fig. 4a. The glass transition temperature (T_g) of PSS-C₆Py derived from the DSC thermograms during the heating (Fig. 4b) was 139 °C, which was much lower than that of poly(sodium 4-styrene sulfonate) (PSS) (180 °C) [19]. The flexible alkoxy chain of C₆Py may

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