

Proton conductive polymers obtained by in-situ polymerization of a mesomorphic benzimidazole monomer in smectic A, nematic and isotropic phases



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ABSTRACT

Side-chain polymers with different microstructures have been prepared by in-situ ultra-violet (UV) photopolymerization of a liquid crystal monomer bearing a terminal benzimidazole moiety. The molecular weights of **PBI_S**, **PBI_N**, and **PBI_I** obtained from the smectic A (*S_A*), nematic and isotropic liquid phases were 1.53, 1.40 and 1.38×10^4 g mol⁻¹, respectively. In-situ UV polymerization of the monomer aligned by mechanical shearing in the *S_A* phase resulted in a macroscopically layered polymer **PBI_{als}**. **PBI_{als}** exhibited higher glass transition temperature than **PBI_S**, **PBI_N**, and **PBI_I**. Electrochemical impedance spectroscopy (EIS) measurements suggested the anhydrous proton conductivity of **PBI_{als}** parallel to the aligned layers was more than one order of magnitude higher than those of **PBI_S**, **PBI_N** and **PBI_I**. At the same temperature, proton conductivity of **PBI_S** was higher than those of **PBI_N** and **PBI_I**. The results suggested that the architecture of the benzimidazole polymer, which could be tuned by the mesomorphoses of the monomer, had a profound impact on the anhydrous proton conduction.

1. Introduction

The proton exchange membrane fuel cells working at medium temperatures (100–200 °C) have been received increasing interests owing to improved carbon monoxide tolerance and higher energy efficiency [1–3]. Commercially available perfluorosulfonated membranes, such as Nafion®, would suffer from the elevated temperatures because proton conduction in these membranes depends strongly on humidification [4]. Therefore, a number of efforts have been devoted to develop anhydrous proton conductors based on non-perfluorosulfonated polymers [5–10]. Hydrogen bonding networks are regarded as pathways for proton transportation through the hopping mechanism [11]. Self-assembled materials with hydrogen bonding networks, such as comb polymers, have been prepared for anhydrous proton conduction [12–14]. Macroscopically anisotropic polymers with well-defined proton pathways exhibited advantages in anhydrous proton conduction. For example, partially sulfonated poly(styrene-*b*-methylbutylene) formed lamellar structures under normal stress and exhibited an anisotropy of 75 in the proton conductivity [15]. Macroscopic layers developed in the mechanically sheared sulfonic liquid crystal polymer and the proton conductivity approximately increased 10 folds after shearing [16]. In the case of liquid crystal polymer, the induced regular structures would disappear when the polymer was heated to the

isotropic state. It was suggested that in-situ photopolymerization of mesomorphic monomers could decrease the thermal fluctuation and fix the anisotropic assembly [17–19]. Kato et al. reported anisotropically ion-conductive films obtained by in-situ photopolymerization of aligned ionic liquid crystal monomers bearing imidazolium ions [20,21]. However, ordered proton conductive polymers have hardly been prepared by in-situ polymerization of liquid crystals owing probably to absence of proper monomer.

Recently we reported proton conductive benzimidazole liquid crystals exhibiting *S_A* and nematic phases [22]. In this research, benzimidazole polymers with different architectures were prepared by in-situ polymerization a mesomorphic monomer in different phases. A mesomorphic monomer bearing a terminal benzimidazole moiety (**mBI**) was first prepared for polymerization, as shown in Scheme 1. Then polymers **PBI_S**, **PBI_N**, and **PBI_I** were prepared by in-situ ultra-violet (UV) photopolymerization of **mBI** in the *S_A*, nematic and isotropic phases, respectively. In-situ UV polymerization of the monomer aligned by mechanical shearing in the *S_A* phase resulted in a macroscopically layered polymer **PBI_{als}**. The polymer resulted from the state with more well-defined order had higher molecular weight and glass transition temperature. The observed anhydrous proton conductivities of **PBI_I**, **PBI_N** and **PBI_S** increased in turn at the same temperature. Owing to the oriented conducting pathways, **PBI_{als}** exhibited

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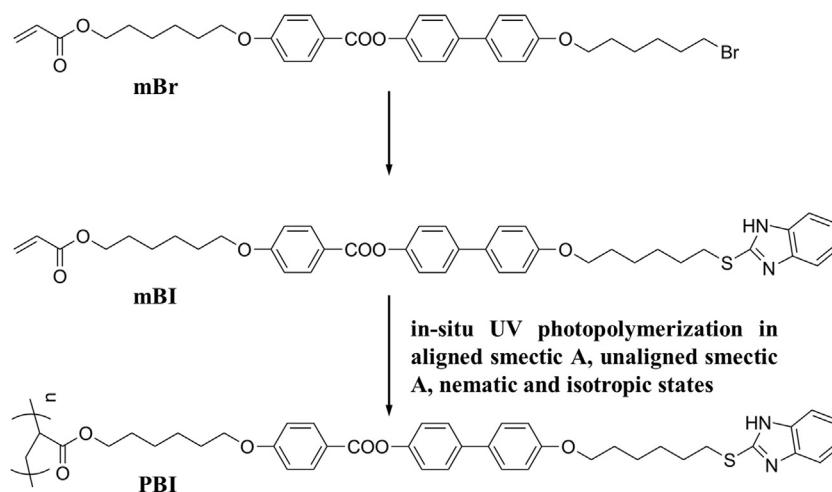
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Scheme 1. Synthetic route of the benzimidazole polymers.

enhanced and anisotropic proton conduction. The results revealed that proton conductivity of the benzimidazole polymers depended strongly on molecular arrangement, which could be tuned by in-situ UV photopolymerization of the mesomorphic monomer in different phases.

2. Experimental

2.1. Instrumentation

The ^1H nuclear magnetic resonance (NMR) spectra were obtained using a Bruker AV II-400 spectrometer. The Fourier transform infrared (FT-IR) spectra were measured with the use of a Perkin Elmer Spectrum Two Li10014 spectrometer. Elemental analyses were done by using a Euro EA3000 CHNS/O Elemental Analyzer. Polarized optical micrographs of the samples were observed using a Weitu XPL-30TF polarizing optical microscope (POM) equipped with a WT-3000 hot-stage. The differential scanning calorimetry (DSC) measurements were performed by a TA DSC Q20 modulated instrument at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. The thermogravimetric (TG) analyses were conducted on a TA instrument Netzsch TGA 209C at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. The onset temperature of weight loss was reported as the decomposition temperature. The UV irradiation was carried out using a high-pressure mercury lamp (500 W) as an irradiation source. The X-ray diffraction (XRD) analyses were carried out by a Bruker AXS D8 discovery diffractometer equipped with a Hi-Star 2D detector, using $\text{Cu-K}\alpha$ radiation filtered by cross-coupled Göbel mirrors at 40 kV and 40 mA. Sample's temperature was controlled by an Anton Parr hot-stage. The scanning electron microscope (SEM) observations were performed by a Nova NanoSEM450 field emission SEM at an accelerating voltage of 5 kV. The molecular weights and polydispersity indexes (PDIs) of the polymers were determined on a gel permeation chromatography (GPC) systems with Tosoh HLC-8320 high-speed liquid chromatograph system using THF as an eluent at $40\text{ }^\circ\text{C}$ at a flow rate of 0.6 mL min^{-1} with two TSK gel Super HM-H column ($6 \times 150\text{ mm}$). The impedance spectra of electrochemical impedance spectroscopy (EIS) measurements were recorded on an EG & G Princeton Applied Research P4000 + electrochemical workstation connected to a PC running electrochemical impedance software (Frequency range: 100 kHz–0.1 Hz, applied voltage: 10 mV).

2.2. Materials

All commercially-available starting materials, reagents and solvents were used as supplied and were obtained from TCI and Acros. All reactions were carried out under a dry nitrogen atmosphere. mBr was synthesized according to the procedures described previously [16].

2.3. Synthesis of 4'-((6-(benzimidazolethio)hexyloxy)phenyl)oxy) biphenyl-4-yl 4-(6-(acryloyloxy)hexyloxy) benzoate (mBI)

2-mercaptobenzimidazole (1.0 g, 6.7 mmol) in aqueous NaOH solution (3.4 mL , 2 mol L^{-1}) was stirred at room temperature for 30 min. mBr (4.2 g, 6.7 mmol) dissolved in tetrahydrofuran (25 mL) was then added dropwise into the solution. The mixture was stirred at reflux for 10 h. After cooling, the solvent was evaporated under reduced pressure and the residue was washed with water. The crude product was recrystallized from ethanol and purified by flash column chromatography (silica) using dichloromethane as an eluent to give mBI (4.2 g) as a white solid. Yield: 90%. $^1\text{H NMR}$ (400 MHz CDCl_3) 8.15, 7.59, 7.57, 7.23, 6.98, 6.91(m, 16H, Ph), 6.40, 6.13, 5.82 (m, 3H, $\text{CH}_2=\text{CH}$), 4.21, 4.01(m, 6H, OCH_2), 3.37(t, 2H, CH_2S), 1.75–1.24(m, 16H, CH_2CH_2). FT-IR(KBr) ν : 3070(hydrogen-bonding), 2932, 2861, 1725, 1636(C=C), 1606, 1513, 1498, 1470, 1440(C–S), 1389, 1344(C=N), 1288, 1258, 1212, 1163, 1072, 996, 880, 846, 791, 761, 735, 682, 651, 519 cm^{-1} . Elemental analysis calcd (%) for $\text{C}_{41}\text{H}_{44}\text{N}_2\text{O}_6\text{S}$ requires: C, 71.07; H, 6.40; N, 4.04; S, 4.63; Found: C, 71.09; H, 6.38; N, 4.07; S, 4.52.

2.4. In-situ photopolymerization of mBI

Photoinitiator (2,2-dimethoxy-2-phenylacetophenone, 1.3% weight to mBI) and inhibitor (4-methoxyphenol, 0.1% weight to mBI) were added to mBI in THF. The solution was stirred for 10 min and the solvent was removed under reduced pressure to give a white powder. After dried under vacuum overnight, the powder was sandwiched between two indium tin oxide (ITO) coated glass slides. The sample was heated to $170\text{ }^\circ\text{C}$ and then cooled to $130\text{ }^\circ\text{C}$ (corresponding to the S_A phase) at a cooling rate of $5\text{ }^\circ\text{C min}^{-1}$. The monomer was macroscopically aligned at $130\text{ }^\circ\text{C}$ via mechanically shearing between the slides as the procedures reported previously [16]. In-situ polymerization of the aligned monomer was immediately carried out at $130\text{ }^\circ\text{C}$ under the exposure to UV light (365 nm , 35 mW cm^{-2}) for 40 min. After that, the polymer was cooled to room temperature and peeled off to give PBI_{als} . In the similar way, PBI_{S} was obtained by photopolymerization of mBI without shearing at $130\text{ }^\circ\text{C}$. PBI_{N} and PBI_{I} were prepared by in-situ polymerization at $155\text{ }^\circ\text{C}$ (corresponding to the nematic phase) and $170\text{ }^\circ\text{C}$ (corresponding to the isotropic phase), respectively.

2.5. Electrochemical characterization

All the polymers were dried under vacuum overnight for electrochemical characterization. Anhydrous proton conductivities of all the polymers were determined by EIS measurements. Impedance responses

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