# Understanding ternary poly(potassium benzimidazolide)-based polymer electrolytes

David Aili[*], Katja Jankova, Junyoung Han, Niels J. Bjerrum, Jens Oluf Jensen, Qingfeng Li

*Department of Energy Conversion and Storage, Technical University of Denmark, Kemitorvet 207, DK-2800 Kgs. Lyngby, Denmark*

ABSTRACT

Poly(2,2′-(*m*-phenylene)-5,5′-bisbenzimidazole) (*m*-PBI) can dissolve large amounts of aqueous electrolytes to give materials with extraordinary high ion conductivity and the practical applicability has been demonstrated repeatedly in fuel cells, water electrolysers and as anion conducting component in fuel cell catalyst layers. This work focuses on the chemistry of *m*-PBI in aqueous potassium hydroxide. Equilibration in aqueous KOH with concentrations of 15–20 wt.% was found to result in ionization of the polymer, causing released intermolecular hydrogen bonding. This allowed for extensive volume swelling, high electrolyte uptake, dramatic plasticization and increase of the ion conductivity for the formed poly(potassium benzimidazolide)-based structure. Further increasing the concentration of the bulk solution to 50 wt.% resulted in dehydration and extensive crystallization of the polymer matrix as evidenced by X-ray diffraction, increased density and enhanced elastic modulus.

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## 1. Introduction

Polybenzimidazoles comprise a class of amphoteric polymers used in demanding applications requiring excellent thermomechanical stability [1]. Poly(2,2′-(*m*-phenylene)-5,5′-bisbenzimidazole) (*m*-PBI, Fig. 1) is the most widely used derivative and it is synthesized by melt condensation polymerization [2] or more commonly by homogenous solution polymerization in polyphosphoric acid [3] from 3,3′-diaminobenzidine and isophthalic acid. It is a highly hygroscopic polymer, showing water uptake typically around 15 wt.% [4], corresponding to about 3 water molecules per polymer repeat unit. It strongly interacts with ionic species [5], and the imidazole moieties are readily protonated in the presence of protic acids (Fig. 1, top) to give polymer matrices with high proton conductivity [6]. Of the different acids, $H_3PO_4$ is of particular interest as dopant due to its low vapor pressure and high intrinsic proton conductivity at temperatures well above 100 °C [7]. During the last two decades this electrolyte system has been thoroughly characterized with respect to e.g. the chemistry of acid uptake and proton transport [8–14], thermal [15] and chemical stability [16,17], nanostructure [18] as well as gas permeability [19]. Furthermore, many new polybenzimidazole chemistries [20] and polymer blend systems [21] have been developed.

The weakly acidic imidazole protons of *m*-PBI can be subtracted if a strong base (such as an alkali metal hydroxide, alkoxide or hydride) is used to form a polyanion, as shown in Fig. 1 (bottom). Such poly(benzimidazolide)s are strongly nucleophilic and are used as intermediates in the synthesis of Michael addition type cross-linked *m*-PBI [22] or poly(alkyl/aryl benzimidazolium) ionomers [23–26]. The *N*-functionalized polybenzimidazoles have recently been explored as potential anion conductors [27–29] or as a component in phosphoric acid doped polymer blends [30]. In this connection, significant chemical stability improvements have been achieved by means of steric [31,32] or electronic [33] optimization of the polymer backbone.

Alternatively, the pristine form of *m*-PBI can be equilibrated in aqueous solutions of alkali metal hydroxides to form apparently homogenous ternary systems composed of the hydroxide salt and water dissolved in the polymer matrix. Such semi-solid materials exhibit remarkably high ion conductivity [34], excellent chemical stability at low alkali concentrations [35] and have been tested as electrolytes in hydrogen [34,36,37] and direct alcohol [38–42] fuel cells, water electrolysers [43,44] and as anion conducting phase in alkaline fuel cell catalyst layers [45–47]. Despite the recent efforts to develop electrochemical systems around this electrolyte system, the physicochemical chemistry of polybenzimidazoles in alkaline environment remains unexplored to a large extent. In this work, a combination of techniques was employed to study the

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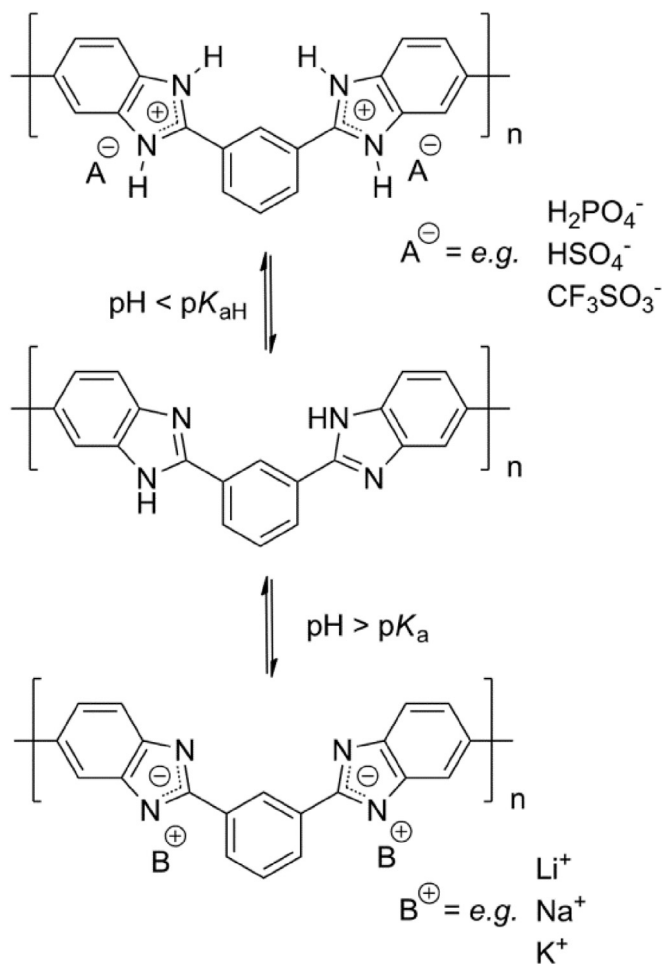
**Fig. 1.** Schematic illustration showing the amphoteric nature of *m*-PBI and the protonation and deprotonation of the benzimidazole moieties in acidic (top) and basic (bottom) environment, respectively.

physicochemical properties of thin films of *m*-PBI in aqueous KOH of concentrations ranging from 0 to 50 wt.%. The ionized form of the polymer was found to predominate at KOH concentrations higher than 15–20 wt.%, which resulted in released intermolecular hydrogen bonding, high swelling, significant plasticization and enhanced ion conductivity. Further increasing the concentration of KOH in the bulk solution resulted in dehydration and crystallization of the polymer matrix.

## 2. Experimental

### 2.1. Materials

The inherent viscosity $\eta_{inh}$ of *m*-PBI (Danish Power Systems ApS), as determined in 96 wt.% $H_2SO_4$ at 30.0 °C (solid content 500 mg dL$^{-1}$) using an Ubbelohde capillary viscosimeter, was 0.95 dL g$^{-1}$. The polymer was dissolved in *N,N*-dimethylacetamide (DMAc) (6.1 wt.% solid content) and cast on partly covered Petri dishes (11 cm diameter) from room temperature to 120 °C at 7 °C h$^{-1}$. The *m*-PBI films were delaminated from the glass substrates in demineralized water and further treated with demineralized water for 4 h at 95 °C and dried at 150 °C for at least 4 h. The aqueous KOH solutions with concentrations of 5, 10, 15, 20, 25, 35 and 50 wt.% (corresponding to 0.9, 1.9, 3.0, 4.2, 5.5, 8.4 and 13.4 mol L$^{-1}$, respectively) were prepared by dissolving KOH pellets

(Sigma−Aldrich) in demineralized water and the concentrations were confirmed by density measurements at room temperature (1.04, 1.08, 1.13, 1.18, 1.25, 1.36 and 1.52 g mL$^{-1}$, respectively) which were compared with literature data [48].

### 2.2. Characterization

The weight and dimensional changes were recorded for a total of 8 square-shaped samples per KOH concentration (initial area 15−20 mm × 15−20 mm, initial thickness 30−40 μm), in 2 separate series of experiments. The samples were individually marked and dried at 150 °C for at least 4 h before the weight and dimensions were recorded. The samples were subsequently kept in sealed poly(tetrafluoroethylene) (PTFE) bottles filled with aqueous KOH for about 16 h at 90 °C. The solutions were cooled to room temperature and the weight and dimensions of the individual samples were recorded after careful blotting with tissue paper. The weight and dimensional changes were calculated on the basis of the dry pristine material. The compositions were determined gravimetrically as described elsewhere [35,43] and by pH titration with a 0.01 mol L$^{-1}$ HCl (aq.) standard solution (Sigma−Aldrich) on approximately 30 mg of the KOH doped *m*-PBI after stirring in 30 mL demineralized water for at least 15 min. The samples were washed extensively with demineralized water after the titration, dried at 110 °C *in vacuo* for 2 h for the determination of the polymer weight fraction.

The Fourier transform infrared (FTIR) spectra were recorded using a Perkin Elmer Spectrum Two equipped with an attenuated total reflectance (ATR) accessory. X-ray diffraction (XRD) was carried out using a Rigaku MiniFlex 600 using a Cu K$_\alpha$ X-ray source with a wavelength $\lambda$ of 1.5418 Å. The *d*-spacings for the amorphous or crystalline peak maxima were calculated according to the Bragg equation. $^1$H nuclear magnetic resonance ($^1$H-NMR) spectra were recorded on a Bruker Ascend at an operating frequency of 400 MHz. Deuterated dimethylsulfoxide (DMSO-$d_6$) was used as solvent and the solvent residual signal at 2.50 ppm was used as reference. The stress-strain curves were recorded using a Testometric Micro 350 at a crosshead speed of 10.00 mm min$^{-1}$, using dog-bone shaped specimens (30 mm between the shoulders and 2.0 mm wide) prepared by die-cutting in a hydraulic press. Scanning electron microscopy (SEM) was carried out on a Carl Zeiss EVO MA10 equipped with an INCA EDS system from Oxford Instruments. The samples were prepared by sandwiching the polymer films between two pieces of non-woven carbon cloth followed by ion-milling using a Hitachi E−3500, and subsequently sputter-coated with carbon.

The ion conductivity was measured in a tubular (inner diameter 0.9 cm) cell composed of two separate blocks made of PTFE. Electrodes made of nickel mesh with point-welded wires for electrical connections were fixed using PTFE gaskets, which also fixed the distance between the electrodes in the cell assembly to 2.0 mm. The resistance between the electrodes, taken as $Z_{re}$ at $Z_{im} = 0$, was recorded by electrochemical impedance spectroscopy, using a VersaStat 3 from Princeton Applied Research. The cell was calibrated using a set of KCl (aq.) conductance standards from Sigma−Aldrich. The ion conductivity $\sigma$ of the polymer film was calculated according to Eq. (1), where *t* is the thickness of the polymer film, *R* is the measured resistance with the polymer film mounted between the electrodes, $R_{blank}$ is the resistance of the electrolyte filling up the gap between the polymer film and electrode (1.0 mm on each side) and *A* is the cross-sectional area of the cell (0.636 cm$^2$). The standard deviation for *R* and $R_{blank}$ was generally well below 3% (4 measurements).

$$\sigma = t/((R - R_{blank}) \times A) \tag{1}$$