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Understanding ternary poly(potassium benzimidazolid)-based polymer electrolytes

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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 electrolyzers 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, dramatic plasticization and increase of the ion conductivity for the formed poly(potassium benzimidazolid)-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.

Keywords: polybenzimidazole, ionomer, alkaline, ion-solvation, electrolyte

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1 Introduction

Polybenzimidazoles comprise a class of amphoteric polymers used in demanding applications requiring excellent thermo-mechanical stability [1]. Poly(2,2'-(*m*-phenylene)-5,5'-bisbenzimidazole) (*m*-PBI, Figure 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 (Figure 1, top) to give polymer matrices with high proton conductivity [6]. Of the different acids, H₃PO₄ 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 Figure 1 (bottom). Such poly(benzimidazolate)s are strongly nucleophilic and are used as intermediates in the synthesis of Michael addition type crosslinked *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.

Figure 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.

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 electrolyzers [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 physicochemical properties of thin films of *m*-PBI in aqueous KOH of concentrations ranging from 0-50 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 η_{inh} of *m*-PBI (Danish Power Systems ApS), as determined in 96 wt.% H₂SO₄ 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 minutes. 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_α X-ray source with a wavelength λ of 1.5418 Å. The *d*-spacings for the amorphous or crystalline peak maxima were calculated according to the Bragg equation. ¹H-nuclear magnetic resonance (¹H-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 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 σ of the polymer film was calculated according to Equation 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 cm²). The standard deviation for R and R_{blank} was generally well below 3% ($n = 4$).

$$\sigma = t / ((R - R_{blank}) \times A) \quad (\text{Eq. 1})$$

3 Results and discussion

When equilibrated in aqueous KOH, the electrolyte dissolves and evenly distributes in the *m*-PBI matrix as indicated by the homogeneous K and O distribution at a scale of about 1 μm in the cross-sectional EDS maps (Figure 2). In this regard it resembles the ion-solvating polymers (e.g. polyethylene oxide) commonly used as electrolytes in different types of batteries, but is in contrast completely insoluble in water as discussed by Merle et al. [49].

Figure 2 Cross-sectional SEM image (secondary) of *m*-PBI treated in 50 wt.% KOH (left) and corresponding EDS elemental mapping for carbon (C), nitrogen (N), oxygen (O) and potassium (K).

The weight gain of *m*-PBI due to uptake of water and KOH is known to increase with increasing KOH concentration of the bulk solution, but determining individual contribution from water and KOH is far from trivial. The polymer exhibits strong water affinity, absorbing about 3 water molecules per polymer repeat unit through hydrogen bonding with the imidazole moieties. KOH is also highly hygroscopic and form a series of crystalline hydrates in the solid state, which readily dissociate to various hydrated complexes such as $(\text{H}_9\text{O}_5)^-$ or $(\text{H}_{13}\text{O}_7)^-$ when dissolved in water [50]. The degree of ionization of *m*-PBI, i.e. the position of the acid-base equilibrium, depends on the KOH concentration and gravimetric approaches for the composition determination are therefore complicated by the fact that the effective KOH concentration increases during drying [35, 42, 43]. It inevitably shifts the acid-base equilibrium

(Figure 1) towards the poly(benzimidazolidine) resulting in enhanced molar mass per repeat unit. Washing with water reverses the reaction, and the released aqueous KOH can be quantified by acid-base titration. According to this methodology the KOH equivalents per *m*-PBI repeat unit ($m\text{-PBI}_{\text{RU}}$) for samples treated in different concentrations of aqueous KOH were determined, as summarized in Table 1. The KOH content, normalized as KOH equivalents per polymer repeat unit, increased gradually with increasing concentration of the bulk solution reaching 2.6 KOH per repeat unit at 25 wt.% bulk concentration. At the same time the water content was significantly increased from 3.0 H₂O per repeat unit in pure water to 9.7 H₂O per repeat unit in 10 wt.% KOH. The water content further increased to more than 20 H₂O per repeat unit when the KOH concentration of the bulk solution reached 20-25 wt.%. At a bulk concentration of 5 wt.% KOH, the H₂O to KOH molar ratio was 60 and 20 in the bulk solution and in the polymer phase, respectively. At a bulk concentration of 50 wt.% KOH, the H₂O to KOH molar ratio in the bulk solution and polymer phase were 3.2 and 5.5, respectively, apparently showing a concentrating effect of the polymer phase with respect to water in the higher KOH concentration regime. At bulk concentrations around 20-25 wt.%, the H₂O to KOH molar ratio in the bulk solution and in the polymer phase were found to be similar. The compositions were also calculated based entirely on gravimetric measurements as summarized in Figure S1 and were in good agreement with the data obtained from titration and consistent with the data available in the literature [35, 42, 43].

Table 1 Calculated compositions based on acid-base titrations in combination with gravimetric measurements and ion conductivity σ_{rt} at room temperature of the corresponding compositions.

Bulk solution			Polymer phase				
[KOH] / wt. %	H ₂ O per KOH	σ_{rt} /mS cm ⁻¹	Total uptake / wt. %	H ₂ O per <i>m</i> - PBI _{RU}	KOH eq. per <i>m</i> -PBI _{RU}	H ₂ O per KOH	σ_{rt} /mS cm ⁻¹
0	-	-	17.5	3.0	0	-	-
5	60.2	183	23.3	4.0	0.2	20.0	0.2
10	28.5	310	56.5	9.7	0.7	14.9	9
15	17.9	407	108.1	18.5	1.5	12.4	110
20	12.7	491	127.4	21.8	1.8	12.4	130
25	9.5	523	134.2	23.0	2.6	9.0	84
35	5.0	465	99.3	17.0	2.5	6.8	52
50	3.2	324	89.7	15.3	2.8	5.5	13

At room temperature, the ion conductivity of the polymer phase reached as high as 130 mS cm⁻¹ in 20 wt.% aqueous KOH (Table 1). For comparison, the ion conductivity of the bulk solution peaked at a concentration of 25 wt.%, where it reached 523 mS cm⁻¹. Considering practical aspects with respect to the use in electrochemical cells and corrosion of system auxiliary units, it is a clear advantage that lower KOH concentrations can be used without increasing the internal resistance.

An apparent observation after the treatment in aqueous KOH was the anisotropic swelling behavior, as summarized in Figure 3, and as also recently reported Zeng et al. [51] as well as by Couto and Linares [42]. Up to a KOH bulk solution concentration of 15 wt.%, the thickness as well as the surface area increased with increasing concentration. Further increasing the KOH bulk concentration to 20-25 wt.% resulted in a dramatic shrinkage in surface area and a significant thickness increase. For comparison, the swelling behavior of *m*-PBI in H₃PO₄ is practically isotropic [52].

Figure 3 Area, thickness and volume after equilibration in aqueous KOH of different concentrations, expressed relative to the dry pristine material.

Searching for a molecular explanation to the peculiar swelling behavior that was observed on a macroscopic scale, the materials were investigated by X-ray diffraction (XRD), as shown in Figure 4. The broad peak at around $2\theta = 11.5^\circ$ was due to background diffraction from the silicone grease used to protect the sample holder (Si-wafer) from the highly corrosive samples. The *m*-PBI that had been equilibrated in pure water showed a broad amorphous peak around $2\theta = 25^\circ$, in consistence with diffraction data in the literature [19, 53, 54]. The corresponding *d*-spacing was 3.54 Å (Table 2), which is considerably smaller than for many other common polymers and due to the extensive hydrogen bonding network resulting in close chain packing [19]. The intensity of the amorphous peak decreased when the KOH concentration of the bulk solution was increased to 15 wt.%, likely due to the polymer chain separation as a result of the extensive electrolyte uptake. It is obvious that within the layered structure the interlayer molecular force is smaller than the intra-layer one. This explains the observation that the membrane displayed a significant growth in the thickness accompanied with a slow increase of

the surface area in the low KOH concentration range. When equilibrated in 20-25 wt.% KOH full ionization of the polymer is approached (see discussion on FTIR later), resulting in a sudden increase of the thickness accompanied by an area decrease and decreased water content. When the KOH concentration of the bulk solution was further increased to 50 wt.%, sharp reflections at $2\theta = 12.88, 25.83, 32.72$ and 39.14° appeared, corresponding to d -spacings of 6.87, 3.45, 2.74 and 2.30 Å, respectively, which in turn correspond to certain interlayer distances in a lattice structure. The sharp reflections observed after equilibration in KOH in the higher concentration range have previously been assigned to free KOH within the polymer matrix [38, 42]. However, pure KOH and the known KOH hydrates show more complex diffraction patterns and the sharp crystalline reflections are thus more likely due to a crystalline phase of a poly(potassium benzimidazolid) hydrate. The diffraction pattern with only four sharp and intense reflections indicates a symmetric and highly regular structure with crystallite size in the range of 70-120 nm as calculated from the four sharp reflections according to the Scherrer equation. After washing with demineralized water until neutral pH the crystalline reflections vanished (see Figure S2). This phenomenon is similar to the pronounced crystallization observed in the poly(ethylene oxide)-KOH-H₂O system when the concentration of the bulk solution is increased [55].

Figure 4 XRD of *m*-PBI equilibrated in aqueous KOH of concentrations ranging from 0-50 wt.%. The broad peak at around $2\theta = 11.5^\circ$ is due to background diffraction from the silicone grease used to protect the sample holder (Si-wafer) from the highly corrosive samples.

Table 2 Summary of X-ray diffraction data and the corresponding d -spacings and measured densities.

[KOH] / wt. %	$2\theta^\circ$	$d_{sp} / \text{\AA}$	$\rho / \text{g cm}^{-3}$
0	25.16	3.54	1.32
5	25.00	3.56	1.36
10	25.68	3.47	1.47
15	-	-	1.53
20	-	-	1.40
25	-	-	1.46
35	-	-	1.50
50	12.88	6.87	1.53
	25.83	3.45	
	32.72	2.74	
	39.14	2.30	

The *m*-PBI that had been equilibrated in pure water showed typical [35, 43] stress-strain behavior as shown in Figure 5, and engineering tensile strength of around 130 MPa, elongation at break of 80 % and an elastic modulus of 3.0 GPa. The mechanical strength of a polymer is due to attractive intermolecular forces and for pure *m*-PBI, the hydrogen bonding between imidazole moieties are dominating [56]. Introduction of species that interact with the imidazole groups through hydrogen bonding reduces the molecular cohesion. The strong plasticizing effect of water and KOH resulted in a dramatic decay of the engineering tensile strength and elastic modulus and enhanced elongation at break when the KOH concentration of the bulk solution was increased. Ionization of the polymer further promoted this mechanism due to the released intermolecular hydrogen bonding, which is otherwise responsible for the mechanical strength of the pristine material. When the concentration of the bulk solution was increased

to 20-25 wt.%, full ionization of the polymer was reached (see discussion on FTIR later), showing pronounced plastic behavior and permanent deformation at low stress and more than 200% elongation at break. By further increasing the concentration of the bulk solution to 50 wt.%, the elastic modulus increased to 1.4 GPa as compared to 0.3 GPa in 25 wt.% KOH further indicating a high degree of crystallinity [57].

Figure 5 Representative stress-strain curves after equilibration in aqueous KOH of different concentrations.

The *m*-PBI that had been equilibrated in pure water showed the typical FTIR spectral features as reported and assigned elsewhere (Figure 6a) [6, 8, 58, 59]. Of special interest are the characteristic absorption bands at 1440 and 1540 cm^{-1} , which originate from the in-plane ring vibration of the benzimidazole moieties [59]. Equilibration in aqueous KOH strongly reduced the intensity of these absorption bands while new absorption bands at 1550 and 1413 cm^{-1} appeared. Furthermore, new absorption bands at 1315, 1365 and 1602 cm^{-1} appeared at KOH concentrations of 10 wt.% and higher and a new band at

1480 cm^{-1} appeared when the KOH concentration reached 25 wt.%. It clearly shows that the chemical environment of the benzimidazole moieties was strongly affected as a result of the dissociation of the acidic proton. Changes in the fingerprint region were also observed while the low frequency range (2300-3700 cm^{-1}) was dominated by the strong bands from the absorbed water and excess hydroxide ions (not shown).

After drying at 150 °C for 3 h, the strong broad –OH band (2300-3700 cm^{-1}) due to water could no longer be observed and the characteristic absorption band at 3415 cm^{-1} due to free N–H stretching [4, 59] became visible for the pristine *m*-PBI (Figure 6b). At higher KOH concentrations than 15 wt.% the N–H stretching band disappeared. Furthermore, the broad absorption band located around 3100 cm^{-1} assigned to self-associated hydrogen bonded N–H groups [60] disappeared. At the same time, the benzimidazole in-plane vibration band (1440 cm^{-1}) and the imidazole ring breathing at (1282 cm^{-1}) [59] disappeared and a new absorption band at 1375 cm^{-1} appeared.

Altogether the FTIR data indicate a significant change of the chemical environment of the benzimidazole moieties, likely induced by the deprotonation of the imidazole groups as also discussed recently [42]. Based on the FTIR spectral data it seems likely that the fully ionized form of *m*-PBI predominates at KOH concentrations of the bulk solution higher than around 15-20 wt.%, where significant changes in the spectra were observed.

Figure 6 ATR-FTIR spectra of *m*-PBI equilibrated in aqueous KOH of concentrations ranging from 0-50 wt.% before (a) and after (b) drying at 150 °C for 3 h.

The ^1H -NMR spectrum of the pristine *m*-PBI was dominated by signals in the aromatic region as previously assigned in the literature [31, 61] (Figure 7). The signal of the $-\text{NH}$ group (H_a) of the benzimidazole moiety at 13.3 ppm disappeared in the spectrum of the *m*-PBI that had been equilibrated in 50 wt.%, indicating complete ionization. All the signals from the aromatic protons (except the singlet at 9.15 ppm) showed upfield shifts relative to the pristine *m*-PBI, indicating increased shielding. It can be explained by the increased electron density of the aromatic system due to the ionization of the polymer.

Figure 7 ^1H -NMR of pristine *m*-PBI (bottom) and of *m*-PBI equilibrated in 50 wt.% aqueous KOH (top). The peak assignment for pristine *m*-PBI as reported by Thomas et al. [31].

In summary, the spectroscopic data indicate that the deprotonated form of *m*-PBI, poly(potassium(2,2'-(*m*-phenylene)-5,5'-bisbenzimidazolid)), predominates when the KOH concentration of the bulk solution reaches 15-20 wt.%. This is also the concentration region where a sudden increase in thickness and decrease in surface area and a local density minimum can be observed. The full ionization of the polymer releases the extensive hydrogen intermolecular bonding, which in turn allows for extensive swelling of the polymer matrix, extraordinary high water and KOH uptake, and therefore a maximum in ion conductivity, dramatically reduced tensile strength and increased plasticity. Further increasing the KOH concentration to 50 wt.% resulted in decreased water content and increased KOH content, which likely induced the extensive crystallization of the polymer matrix characterized by high density and

dramatically increased elastic modulus. The crystal structure of the poly(potassium (2,2'-(*m*-phenylene)-5,5'-bisbenzimidazolid) or the hydrate thereof remains a subject for further investigation but a schematic illustration of the material is given in Figure 8.

Figure 8 Schematic illustration of poly(potassium (2,2'-(*m*-phenylene)-5,5'-bisbenzimidazolid) hydrate (four polymer repeat units arbitrarily chosen) with the potassium ions located between the planes of the benzimidazole moieties.

4 Conclusions

When poly(2,2'-(*m*-phenylene)-5,5'-bisbenzimidazole) is equilibrated in aqueous potassium hydroxide it undergoes complete ionization when the KOH concentration of the bulk solution reaches 15-20 wt.%. It results in released intermolecular hydrogen bond interactions, which in turn allows for extensive volume swelling causing dramatic plasticization and increase of the ion conductivity. Further increasing the KOH concentration of the bulk solution to 50 wt.% results in reduced water content of the polymer

matrix, inducing significant crystallization of a poly(potassium (2,2'-(*m*-phenylene)-5,5'-bisbenzimidazolidine)) hydrate as evidenced by X-ray diffraction, increased density and enhanced elastic modulus.

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