Anion-conducting polysulfone membranes containing hexa-imidazolium functionalized biphenyl units

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ABSTRACT

Poly(arylene ether sulfone)s containing randomly distributed biphenyl units tethered with precisely six imidazolium cations are designed and prepared with the aim to facilitate ionic clustering and conductivity of anion exchange membranes (AEMs). A series of statistical copolymers with different cationic contents are synthesized via K_2CO_3-mediated polycondensations of 2,2′,3,3′,5,5′-hexamethyl-4,4′-dihydroxybiphenyl, bisphenol-A and 4,4′-dichlorodiphenylsulfone. After near quantitative benzylic brominations, the copolymers are functionalized with N-methylimidazolium (NIM), 1,2,4,5-tetramethylimidazolium (4IM) and trimethylammonium (QA) cations, respectively. Small angle X-ray scattering of AEMs cast from solution shows that all the different hexa-functionalized moieties induce distinct phase separation. This is especially efficient in the NIM materials, which may be because the less bulky nature of this cation in comparison with 4IM. Thus, at a given water uptake the AEMs containing NIM reach a significantly higher conductivity than those with 4IM ions. In addition, AEMs containing any of the two hexa-imidazolium moieties reach higher conductivities than corresponding materials with hexa-QA moieties, which probably results from the delocalized charge of the former cations which promotes ionic dissociation despite the very high local ionic concentrations. Introducing biphenyl units tethered with precisely six imidazolium cations along a copolymer backbone may be a viable synthetic strategy towards efficient AEMs for different electrochemical energy applications.

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1. Introduction

The function and performance of many emerging electrochemical energy conversion and storage technologies such as fuel cells, electrolyzers and flow batteries rely critically on durable polymeric ion-exchange membranes with efficient and selective transport properties [1–3]. Typically, these membranes consist of high-performance polymers with fluorinated or aromatic backbones carrying ion exchange groups that require water for ion solvation and conductivity in order to provide sufficient device performance [4,5]. Up until recently, most research was focused on proton-exchange membranes (PEMs) for use in proton-exchange membrane fuel cells. However, today most attention is given to the development of anion-exchange membranes (AEMs) for use in alkaline fuel cells [6,7] and vanadium redox flow batteries [8]. In general, AEMs have to meet several application-specific sets of requirements, such as high ionic conductivity, sufficient chemical, hydrolytic and dimensional stability, mechanical toughness, adequate heat endurance, and low permeability to gases or liquids [1].

High ion conductivity in both AEMs and PEMs is to a large extent dependent on efficient clustering of the ions to induce phase separation in order to form a distinct percolating conducting water-rich ionic phase [9–11]. In its simplest form, the membrane consists of a statistical copolymer prepared by combining an ionic monomer with a non-ionic one. Normally, the level of ionic clustering is quite limited in membranes based on copolymers where the ionic groups have a random or statistical placement directly on an aromatic backbone, which usually leads to inferior properties [9,10]. Block copolymers in which the ionic groups are exclusively concentrated to one of the polymeric blocks will typically microphase separate and self-organize into various morphologies with hydrophilic and hydrophobic nano-domains [9–11]. This synthetic approach enables the formation of membranes that contain a percolating phase domain with a high local ionic concentration in which the proton conductivity can be maintained, even at low water contents. The success of this approach have been confirmed for both PEMs [12–14] and AEMs [15–18]. However, the preparation of block copolymers is generally very complex and tedious in comparison to statistical copolymers, and will most certainly not be the first choice for commercial applications. Alternatively, efficient phase separation can be achieved in a more straight-forward manner by preparing statistical copolymers which allow the

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introduction of a high local concentration of ionic groups. This has been successfully demonstrated for PEMs [19–25] and more recently also for AEMs [26–34]. For example, Hickner and Chen prepared and studied polyketones with quaternary ammonium (QA) groups concentrated to triphenyl moeties along the backbone [27]. They found that AEMs based on these copolymers had a much higher Br$^-$ conductivity than randomly functionalized copolymers, and explained this by the formation of distinct ionic clusters in the former membranes. Moreover, Kim et al. have investigated polysulfones with four QA groups attached to fluorene units in the backbone and reported high OH$^-$ conductivity [28]. Meng and Jiang and their respective coworkers have separately prepared and studied aromatic polymers carrying QA groups concentrated to tetraphenyl units in the main chain [29] and on side chains [30], respectively. Recently, we have reported on the preparation of polysulfones containing single phenyl rings in the backbone functionalized with precisely two, three and four QA groups, respectively [31]. At moderate ion exchange capacities (IECs), the Br$^-$ conductivity of the densely functionalized copolymers was found to exceed that of a corresponding copolymer with randomly placed QA groups, despite a significantly higher water content of the latter. In addition, Kim et al. prepared polysulfones containing moeties of seven aromatic rings functionalised with six imidazolium groups and reported high alkaline stability and OH$^-$ conductivity, which was attributed to a clear hydrophilic-hydrophobic phase separation of the AEMs [32].

In the current work, we prepared a series of poly(arylene ether sulfone)s (PAESs) containing various concentrations of biphenyl units functionalized with precisely six imidazolium groups. This resulted in copolymers with an exceptionally high local concentration of aromatic cations having a delocalized positive charge to promote phase separation and ionic dissociation to enhance ion conductivity. Statistical copolymers were synthesized via polycondensations involving a hexamethyl biphenol. After complete benzylic bromination, the bromine atoms were displaced in Menshutkin reactions to form *N*-methylimidazolium (NIM) and 1,2,4,5-tetramethylimidazolium (4IM) cations, respectively. The latter cation is sterically bulky and was selected because it was expected to have a high stability towards nucleophilic attack of an anion due to the many electron donating methyl groups [35,36]. However, it is not yet known how sterically bulky cations will affect the ionic clustering and transport properties. Solvent cast AEMs were characterized with regard to their morphology, water uptake and conductivity to establish their structure-property relationships. The results obtained with the imidazolium materials were compared with those obtained with corresponding copolymers functionalized with quaternary ammonium (QA) groups.

2. Experimental method

2.1. Materials

Bisphenol A (BPA, 97%, Acros) and 2,2′3,3′5,5′-hexamethyl-4,4′-dihydroxybiphenyl (6MBP, > 98%, Acron Polymer Systems) were recrystallized from toluene prior synthesis. 4,4′-Dichlorodiphenyl sulfone (DCDPS, 97%, Acros) and 4,4′-Difluorodiphenyl sulfone (DFDPS, 98%, Fluorochem) were recrystallized from *N,N*-dimethylformamide and K$_2$CO$_3$ was dried at 120 °C overnight before use. *N*-Bromosuccinimide (NBS, 99%, Acros), azobisisobutyronitrile (AIBN, 98%, Acros), trimethylamine (7.3 M aq. solution, Acros), 1-methylimidazole (99%, Acros), 1,2,4,5-tetramethylimidazole (> 98.0%, TCI), toluene (HPLC grade, Honeywell), dimethylacetamide (DMAc, 99+%, Acros), 2-propanol (IPA, HPLC grade, Honeywell), 1,2-dichlorobenzene (99+%, Fluka Analytical) and *N*-methyl-2-pyrrolidinone (NMP, reagent grade, Acros) were all used as received.

2.2. Polymerization and bromination

Statistical copolymers were synthesized by polycondensations of DCDPS, BPA and 6MBP, according to Scheme 1. The reaction was performed in DMAc with anhydrous K$_2$CO$_3$ as catalyst and toluene as azeotropic agent for water removal. The preparation of the copolymer containing 33 mol% 6MBP in relation to BPA is described as an example. 6MBP (0.4246 g, 1.57 mmol), DCDPS (1.4336 g, 4.99 mmol) and BPA (0.7811 g, 3.42 mmol) were placed in a two necked round bottom flask. Next, K$_2$CO$_3$ (2.09 g, 15.1 mmol), DMAc (26.2 mL) and toluene (26.2 mL) were added. The reaction mixture was heated to 130 °C and kept at this temperature under a constant flow of nitrogen during 4 h. After the dehydration step, the temperature was increased to 165 °C and the toluene was removed. After 20 h reaction the highly viscous, purple reaction mixture was diluted with DMAc (60 mL) and precipitated in IPA under vigorous stirring. The white precipitate was repeatedly washed with IPA followed by washing in water. The polymer was finally dried in vacuo at 50 °C over night (yield: 96.5%). The statistical copolymers were designated as c6-PAES-*x* where *x* was the percentage of 6MBP repeating units present in the copolymer, as determined from ^{1}H NMR data.

Bromination of the benzylic positions in the copolymers was performed in accordance with previously reported methods [31]. NBS and AIBN were added in two portions to a 5 wt% degassed solution of the copolymer in 1,2-dichlorobenzene, one at the very start of the reaction and one after 2 h reaction (see Table 1). The total reaction time was 4 h and the reaction temperature was 110 °C. A slightly yellow product was obtained after precipitation in IPA. The precipitate was repeatedly washing in IPA and water, and dried in a vacuum oven overnight at 50 °C. The benzyl brominated statistical copolymer samples were designated as c6PAES-*x*Br.

2.3. Preparation of anion exchange polymers and membranes

The cationic groups were introduced by displacing the bromine atoms of the benzyl brominated copolymers in Menshutkin reactions with trimethylamine, *N*-methylimidazole and 1,2,4,5-tetramethylimidazole, respectively. The copolymers were dissolved in NMP (5 wt% solutions) and an excess of 300 mol% of trimethylamine, or 500 mol% of *N*-methylimidazole, or 500 mol% of 1,2,4,5-tetramethylimidazole was added. The reaction proceeded for 72 h at room temperature. Purification of the materials was done by precipitation in IPA, followed by washing in the same solvent and drying under vacuum. The copolymers containing QA, NIM and 4IM functionalities were designated as c6PAES-QA-*IEC*, c6PAES-NIM-*IEC* and c6PAES-4IM-*IEC*, respectively, where *IEC* represented the ion exchange capacity (IEC) determined by Mohr titrations as described below.

Transparent and tough AEMs with a thickness in the range 30–60 μm were cast from 5 wt% copolymer solutions in NMP at 80 °C under N$_2$. The membranes were first detached from the glass substrate by immersion in deionized water and then further washed in deionized water prior to further analysis.

2.4. Structural analysis

All copolymers were analysed by ^{1}H NMR spectroscopy using a Bruker DRX400 instrument operating at 400.13 MHz. Chloroform-*d* (δ: 7.26 ppm) or DMSO-*d$_6$* (δ: 2.50 ppm) solutions of the samples were used for the characterisation. Size exclusion chromatography (SEC) was employed to evaluate the molecular weights (M_ns) and polydispersity indices (PDIs, $M_n M_w^{-1}$) of the non-functionalized copolymers. Samples were dissolved in chloroform and passed through a series of three Shodex columns (KF-805, −804, and