



Polysulfones with highly localized imidazolium groups for anion exchange membranes



E. Annika Weiber, Patric Jannasch*

Department of Chemistry, Polymer & Materials Chemistry, Lund University, P.O. Box 124, Lund SE-221 00, Sweden

ARTICLE INFO

Article history:

Received 20 December 2014

Received in revised form

29 January 2015

Accepted 3 February 2015

Available online 11 February 2015

Keywords:

Cationic polyelectrolytes

Ionomers

Poly(arylene ether sulfone)s

Ion conductivity

Fuel cells

ABSTRACT

In order to promote phase separation and properties of anion-exchange membranes (AEMs) we have prepared polysulfones with an exceptionally high local concentration of imidazolium groups. Statistical copolymers containing single dioxyphenylene rings directly functionalized with four cationic groups were synthesized by polycondensations of 4,4'-dichlorodiphenylsulfone, 4,4'-isopropylidenediphenol and tetramethylhydroquinone, followed by complete benzylic bromination and quaternization using *N*-methylimidazole, as well as trimethyl amine for reference. In contrast to the quaternary ammonium (QA) containing materials, the thermal stability of the imidazolium (Im) functionalized AEMs increased with the cationic content and only decomposed above 290 °C at high ionic contents. Small angle X-ray scattering of polysulfone AEMs showed distinct ionomer peaks indicating a characteristic separation distance of ~ 7 nm. At an ion exchange capacity of 2.2 mmol g⁻¹, the Br⁻ conductivity at 60 °C reached 6 and 29 mS cm⁻¹ for the QA and Im functionalized AEMs, respectively, despite a similar water content. Thus, the water in the latter membranes was utilized more efficiently for ion transport, possibly because the conjugated Im groups provided a higher degree of ion dissociation than the QA groups.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Various durable anionic and cationic polymers are currently studied and developed for use as proton- (PEMs) and anion-exchange (AEMs) membranes for use in water treatment [1] and different energy-related electrochemical applications such as fuel cells [2–4] and flow batteries [5]. Consequently, the ion and water transport characteristics of these membranes are critical to their performance. In PEMs functionalized with sulfonic acid groups the formation of a distinct and percolating hydrophilic phase domain is seemingly crucial in order to reach high proton conductivity, particularly at low water contents [6,7]. Because of their charged and highly polar nature, the sulfonate groups typically phase separate from the polymer backbone to form ionic clusters [6]. These nanosized clusters are typically observed by transmission electron microscopy and small angle X-ray scattering (SAXS), and several studies have shown that an efficient clustering of sulfonate groups during membrane preparation contributes to the formation of a percolating and highly conductive hydrophilic phase domain in the hydrated state [8–11]. The formation of ionic clusters in AEMs is hampered by the nature of the organic cation, typically

quaternary ammonium (QA), which is quite compatible with the polymer backbone [7]. Usually the QA groups do not phase separate efficiently when attached directly and randomly along the polymer backbone, as indicated by the absence of scattering maxima in SAXS profiles [12]. Ionic clusters in AEMs have recently been observed in AEMs where QA groups have been concentrated to specific chain segments in the backbone polymer [13,14], attached to short side chains in statistical copolymers [15,16], and when utilizing QA groups with long alkyl chains [17] to facilitate phase separation. A further strategy to promote phase separation is to prepare hydrophilic–hydrophobic multiblock copolymers in which blocks highly functionalized with ionic groups are combined with hydrophobic non-ionic ones [18,19]. Although requiring complex synthetic procedures, these copolymers can be tailored to form percolating hydrophilic phase domains. These are normally larger than the ionic clusters formed by statistical copolymers and provide a high conductivity through the membrane. In particular, sulfonated block copolymers have been extensively studied with the goal to prepare PEMs with high proton conductivity at low relative humidity [20]. Still, from an industrial point of view it may still be more appealing to prepare statistical copolymers containing a high local concentration of ions to provide membranes with the necessary phase separation.

In a previous work we prepared poly(arylene ether sulfone)s (PAESs) with different local concentrations of QA groups [14].

* Corresponding author. Tel.: +46 46 2229860.

E-mail address: patric.jannasch@chem.lu.se (P. Jannasch).

This was achieved by attaching precisely two, three or four QA groups to single dioxyphenylene rings along the polymer backbone. The ionic clustering was found to be most efficient in the AEMs based on the copolymer containing the tetra-functionalized rings. However, at a given ion exchange capacity (IEC, mmol g⁻¹) the anionic conductivity was observed to decrease with increasing number of QA groups per ring. Kreuer et al. have previously concluded that a close proximity of the ionic groups may give limitations in ion dissociation, and thus a reduction in the concentration of charge carriers [21]. One strategy to enhance the ion dissociation while retaining a high local ion concentration to facilitate ion clustering may be to employ conjugated cations where the charge is delocalized. There have been several reports where polymers functionalized with conjugated cations, such as imidazolium [22–24], guanidium [25] and pyridinium [26,27] have been studied as AEMs.

The aim of the present work was to investigate the ionic clustering and conductivity of AEMs densely functionalized with imidazolium groups, and to compare the results with corresponding AEMs carrying non-conjugated QA groups. Consequently we synthesized and studied a series of PAESs containing dioxyphenylene rings substituted with four *N*-methylimidazolium (Im) groups. As far as we know, these copolymers have the highest local concentration of Im groups in an aromatic polymer structure reported so far. A series of statistical copolymers with different IEC values were successfully prepared in polycondensations of mixtures of bisphenol A, tetramethylhydroquinone and 4,4'-dichlorodiphenyl sulfone, followed by benzylic bromination and functionalization using *N*-methylimidazole. Properties such as water uptake, ionic clustering and ion conductivity of AEMs based on these copolymers were compared with AEMs derived from the corresponding copolymers functionalized with trimethylammonium groups. In addition, two AEMs based on poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) functionalized with Im and QA groups, respectively, were included in the study as state-of-the-art benchmark materials.

2. Experimental

2.1. Materials

Bisphenol A (BPA, 97%, Acros), and tetramethylquinone (4MHQ, 95%, TCI) were recrystallized from toluene, and 4,4'-dichlorodiphenyl sulfone (DCDPS, 97%, Acros) was recrystallized from *N,N*-dimethylformamide. K₂CO₃ (99%, Acros) was dried overnight at 120 °C prior to use. *N*-Bromosuccinimide (NBS, 99%, Acros), azobisisobutyronitrile (AIBN, 98%, Acros), trimethylamine (7.3 M aq. solution, Acros), *N*-methylimidazole (99%, Acros), PPO ($M_n=20$ kg mol⁻¹, $M_w/M_n=2.3$, Sigma-Aldrich), toluene (HPLC grade, Honeywell), dimethylacetamide (DMAc, 99+%, Acros), 2-propanol (IPA, HPLC grade, Honeywell), chlorobenzene (99.5+%, Labscan analytical sciences), 1,2-dichlorobenzene (99+%, Fluka Analytical) and *N*-methyl-2-pyrrolidinone (NMP, reagent grade, Acros) were all used as received.

2.2. Condensation polymerization

The precursor copolymers were prepared by polycondensation via nucleophilic aromatic substitution reactions as previously reported [14]. Here, the preparation of sample c4PAES-25 is presented as an example. 4MHQ (0.3722 g, 2.24 mmol), BPA (1.4859 g, 6.51 mmol) and DCDPS (2.5116 g, 8.75 mmol) were placed in a two-necked round bottom flask equipped with a nitrogen inlet and a Dean-Stark trap. Next, K₂CO₃ (6.04 g), DMAc (28 mL) and toluene (28 mL) were added and the reaction mixture was initially kept at 130 °C for 4 h under constant nitrogen flow to

azeotropically remove the water and toluene. The polycondensation was subsequently carried out at 165 °C during 20 h. The viscous reaction mixture was diluted by adding 50 mL DMAc and the product was then precipitated in IPA. Finally the precipitate was washed several times in IPA and water, followed by drying under vacuum at 60 °C. The total polymer yield was above 94% in all the polycondensations. The copolymers were designated as c4PAES-*x*, where *x* is the targeted mol percentage of 4MHQ-containing units in the copolymer, i.e., the mol percentage of 4MHQ in the 4MHQ-BPA mixture used in the polycondensation (Scheme 1).

2.3. Benzylic bromination and preparation of cationic polymers

The benzylic positions on the c4PAES-*x* copolymers were selectively brominated in a radical mediated reaction. For example, sample c4PAES-25 was modified by first dissolving 0.775 g of the polymer in 1,2-dichlorobenzene (30 mL) in a two-necked round bottom flask. Degassing was achieved by bubbling N₂ through the solution during 45 min before adding NBS (1.34 g, 7.55 mmol) and AIBN (0.0186 g, 0.113 mmol). The reaction mixture was heated to 110 °C and after 2 h a second portion of NBS (1.43 g, 8.02 mmol) and AIBN (0.0178 g, 0.108 mmol) was added. After 4 h reaction in total, the dark-orange solution was poured into IPA and the precipitated polymer was subsequently washed repeatedly in IPA and water. The degree of benzylic bromination reached ~100% by ¹H NMR analysis. The brominated polymers were named c4PAES-*y*Br where *y* was the degree of bromination, corresponding to the number of benzylic bromide groups per unit in the copolymer (i.e., per sulfone bridge). A 500% excess of *N*-methylimidazole was added to 5 wt% solutions of the benzylic brominated polymers in NMP. After 72 h at room temperature, the polymers were precipitated in IPA, washed and dried at room temperature under vacuum. The functionalization with trimethylamine was performed in the same way as described above, however with a 300% excess. The cationic polymers carrying Im and QA groups were designated as c4PAES-*z*Im and c4PAES-*z*Q, respectively, where *z* was the IEC evaluated by Mohr titrations (IEC_{titr}) as described below.

Two PPO samples were also prepared and studied as benchmark materials. PPO (1.5 g) was dissolved in chlorobenzene (30 mL) and degassed. Precise amounts of NBS (0.6070 g, 3.4 mmol) and AIBN (0.0342 g, 0.21 mmol) were added to target 27% bromination of the benzylic positions. The reaction mixture was kept at 110 °C for 4 h, followed by precipitation of the polymer in IPA and washing in water. In the resulting polymer, 10% of the methyl groups were brominated as evaluated by ¹H NMR spectroscopy. The brominated PPO was further reacted with *N*-methylimidazole and trimethylamine, respectively, in solution as described above. The resulting polymers and AEMs were designated as PPO-1.0Im and PPO-0.9Q, respectively, where the numbers indicate the IEC value evaluated via Mohr titrations.

2.4. Polymer characterization

All polymers were characterized by ¹H NMR spectroscopy employing a Bruker DRX400 instrument at 400.13 MHz using chloroform-*d* (δ 7.26 ppm) or DMSO-*d*₆ (δ 2.50 ppm) solutions. Molecular weights and polydispersity indices (M_w/M_n , PDIs) were determined by size exclusion chromatography (SEC) using a series of three Shodex columns (KF-805, -804, and -802.5) and a refractive index detector. The samples were measured at room temperature in chloroform at an elution rate of 1 mL min⁻¹. Four polystyrene standard samples ($M_n=650$ kg mol⁻¹ from Water Associates, 96 and 30 kg mol⁻¹ from Polymer Laboratories, and 3.18 kg mol⁻¹ from Agilent Technologies) were used for calibration.

Download English Version:

<https://daneshyari.com/en/article/7021512>

Download Persian Version:

<https://daneshyari.com/article/7021512>

[Daneshyari.com](https://daneshyari.com)