

Multi-block poly(arylene ether)s containing pre-chloromethylated bisphenol: anion conductive ionomer†

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We report a simple method for the preparation of anion conductive ionomers (ACIs) using chloromethylated bisphenol A, without the use of chloromethyl methyl ether (CMME) (carcinogenic). Aminated multi-block poly(arylene ether)s (AMBPEs) were obtained by nucleophilic aromatic substitution, followed by polymer condensation then amination. The reported ACIs exhibited a 2.74 milliequivalent per g ion-exchange capacity (IEC) and hydroxide ion conductivity of 56 mS cm⁻¹.

Fuel cells have been considered as a source for clean or renewable energy, because of their low emission levels with high efficiency and promising stationary, automotive and mobile applications.¹ Most research efforts have been directed toward the development of polymer electrolyte fuel cells (PEFCs) using proton conducting ionomers (PCIs) (preferentially perfluorosulfonic acid polymers such as Nafion). Significant drawbacks of PEFCs such as fuel loss, low durability, and costly electro-catalysts restricts their wide spread commercialization.²⁻⁴ As an alternative, there is a growing interest in alkaline membrane fuel cells (AMFCs) that utilize ACIs which show facile fuel oxidation in alkaline media, better oxygen reduction at the cathode and with less precious transition metal based electro-catalysts (Co, Ni, Pd, *etc.*).^{5,6} Thus, ACIs with good ion conductivity are urgently required.

A variety of ACIs based on polystyrenes,⁷ poly(phenylene oxide)s,⁸ poly(ether-imide),⁹ poly(arylene ether)s,¹⁰⁻¹³ radiation-grafted fluorinated polymers,¹⁴ and organic-inorganic hybrid composites,¹⁵ have been investigated. These ACIs are typically prepared by chloromethylation using CMME. Recently, Watanabe *et al.*, reported ACIs based on poly(arylene ether sulfone ketone)s containing quaternized fluorenyl groups.^{10,11}

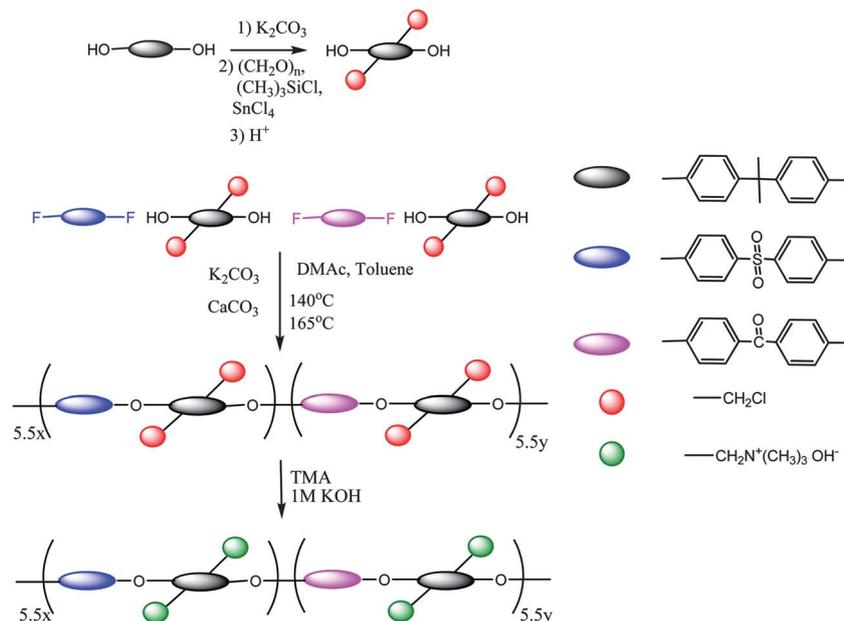
Chloromethyl groups were introduced at the specific positions of the fluorenyl groups by the Friedel-Crafts reaction by using CMME. However, the carcinogenic and potentially harmful to human health nature of CMME is a serious drawback of the reported method.¹⁶⁻¹⁹ These ACIs were achieved by chloromethylation of a block co-polymer, while functionalization of the monomer is expected to result in a relatively higher degree of functionalization. To avoid this problem, we report a method for the synthesis of aminated multiblock poly(arylene ether)s by using a functionalized (2,2'-bischloromethyl) bisphenol A (CMBPA) monomer as a novel ACI forming candidate.

The CMBPA monomer was prepared by introducing the chloromethyl groups by the *in situ* chloromethylation of bisphenol A (BPA). The BPA monomer was treated with potassium carbonate such that it underwent an electrophilic substitution reaction through the formation of two phenoxide anions, which act as electron donating groups. The formed phenoxide monomer was treated *in situ* with the chloromethylating agent, which was a mixture of paraformaldehyde, trimethylchlorosilane and a Lewis acid (SnCl₄).²⁰

The AMBPE was synthesized by a nucleophilic substitution polymerization of 4,4'-difluorophenyl sulfone (5.5 mmol), 4,4'-difluorobenzophenone (5.5 mmol) and (2,2'-bischloromethyl) bisphenol A (11.5 mmol), in the presence of potassium carbonate in dry *N,N'*-dimethylacetamide (DMAc). The amination was achieved by treating with trimethylamine solution (35%) for 24 h at room temperature (Scheme 1). This method avoids the gelation of poly(arylene ether)s as reported previously.¹⁰ The functionalized CMBPA monomer was prepared by using optimised conditions, which ruled out the possibility of self-crosslinking (which is due to excess addition of paraformaldehyde and SnCl₄ in the Friedel-Crafts alkylation reaction). We optimised the conditions to avoid the unwanted Friedel-Crafts alkylation reaction leading to self-crosslinking by using a mixture of paraformaldehyde (185 mmol), trimethylchlorosilane (185 mmol) and anhydrous stannic chloride (0.183 mmol) at 80 °C, as the chloromethylation reagent. AMBPE membranes are named as AMBPE-*X*, where *X* is the degree of chloromethylation (DCM).

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Scheme 1 Synthesis of aminated multi-block poly(arylene ether)s containing functionalized bisphenol A groups.

^1H NMR spectra of the BPA and CMBPA (D_2O exchange) are compared in (Fig. 1(a) and (b)). A new peak at 4.70 ppm for CMBPA was attributed to the presence of the $-\text{CH}_2\text{Cl}$ group (denoted as d), in addition to the new broad peak at 4.98 ppm (attributed to D_2O exchange). If a $-\text{CH}_2\text{OH}$ group was formed then the peak at 4.70 ppm would have disappeared with exchange of D_2O . After the chloromethylation, the chemical shift values for the aromatic protons shifted from the range of 6.8–7.2 ppm to 6.6–7.06 ppm (assigned as a, b and c in Fig. 1(b)). The peak at 1.58 ppm corresponds to the $-\text{C}(\text{CH}_3)_2$ (gem-dimethyl) group (denoted as e in Fig. 1(b)).

AMBPE copolymer was confirmed by the peaks with chemical shift values 1.71 and 1.65 ppm, which correspond to $-\text{C}(\text{CH}_3)_2$ (denoted as b and b' in Fig. 1(c)). The peak at 2.94 ppm (assigned as a in Fig. 1(c)) corresponds to the methyl protons of the trimethyl ammonio groups and the peak at 4.77 ppm (assigned as c, d and e in Fig. 1(c)) corresponds to the four methylenes of the trimethyl ammonio groups. The aromatic protons of the diphenyl sulfone, CMBPA and benzophenone moieties correspond to the peaks with chemical shift values between 6.76–7.80 ppm (denoted as f to o in Fig. 1(c)).

Under optimised reaction conditions, 76% DCM (estimated by the integral peak ratio of d and e using eqn (1)) was obtained.

$$\text{DCM} = \frac{2A(H_d)}{A(H_e)} \quad (1)$$

where $A(H_d)$ is the integral area of the H_d peak ($-\text{CH}_2\text{Cl}$), and $A(H_e)$ is the integral area of the H_e peak ($-\text{C}(\text{CH}_3)_2$ group) (Fig. 1(b)). For the CMBPA monomer, varied DCMs of 60%, 45% and 32% were achieved under various conditions. For the AMBPE membranes, ion exchange capacities (IEC) were obtained as 2.74, 2.28, 1.86 and 1.19 milliequivalent per g,

which correspond to DCMs of 76%, 60%, 45% and 32%, respectively.

The molecular weight of the ionomers was measured by GPC. The number average molecular weight (M_n) ranged between 4.5 and $8.7 \times 10^4 \text{ g mol}^{-1}$, while the weight average molecular weight (M_w) varied from 1.1×10^5 to $2.0 \times 10^5 \text{ g mol}^{-1}$, for different ACIs with respective IEC values. In spite of the high molecular weight, ACIs showed high solubility in many organic solvents due to the highly functionalized bisphenol moieties.

Water uptake (WU) and ion conductivity (σ) (summarized in Fig. 2) are important properties for fuel cell applications. The WU values were estimated from the weight of dry and wet membrane (immersed in water at 30 °C for 48 h). The membrane with the highest IEC value showed maximum water uptake (approximately 170%) (Fig. 2(a)). Furthermore, IEC and WU values are comparable with other ACIs based on the aminated ammonio groups, reported in the literature.^{10,21,22} WU and IEC values varied proportionally, depending on the overlapping of hydrated regions caused by the distribution of the ion conducting groups in the matrix. In spite of the 170% water uptake value, gel-like properties were not observed and the membranes were mechanically robust due to the high molecular weights of the ionomers.²¹

AMBPE membranes are considered to contain hydrophilic morphology, where hydrophilic domains contribute toward the IEC/conductivity. The hydroxide ion conductivity of the AMBPE membranes were measured in deionized water at 30 °C by an impedance technique discussed in the ESI.† Hydroxide ion conductivity for different AMBPE membranes were found to be 56, 40, 25, and 12 mS cm^{-1} corresponding to 2.74, 2.28, 1.86 and 1.19 milliequivalent per g IEC values. To the best of our knowledge, the AMBPE-76 membrane

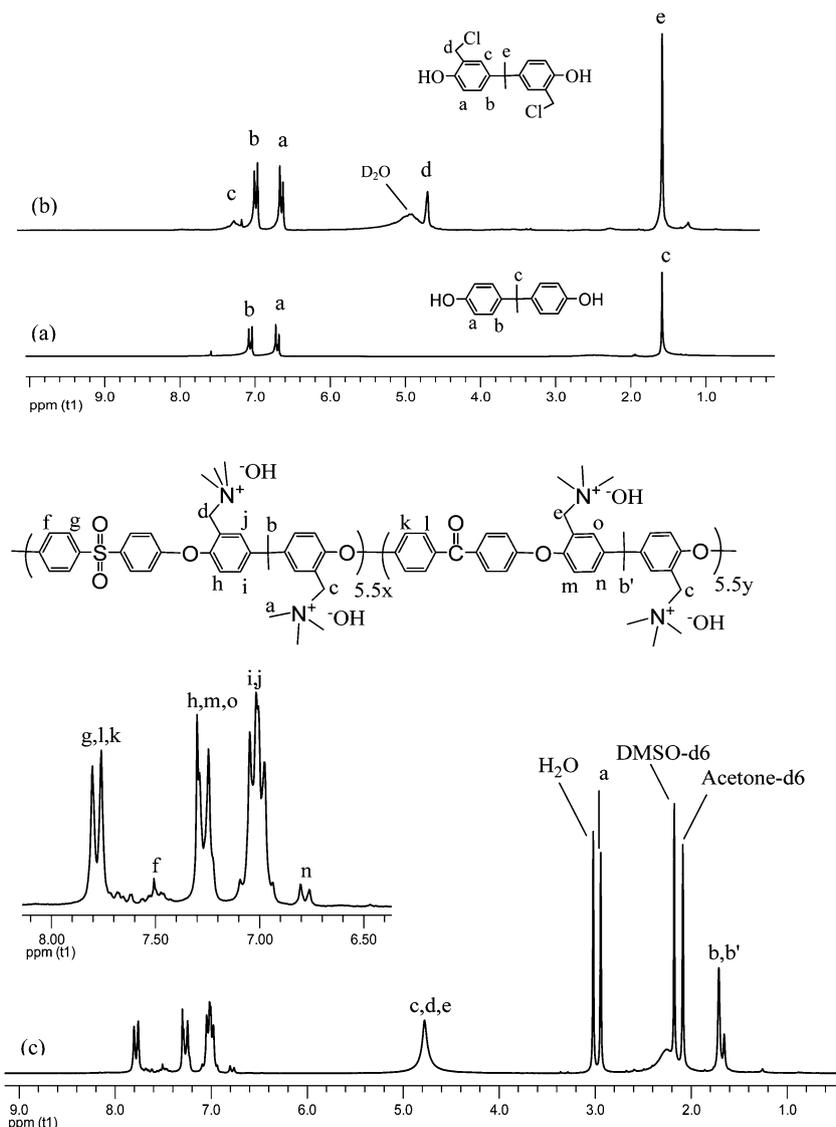


Fig. 1 ^1H NMR spectra of (a) BPA, (b) CMBPA (76% DCM, D_2O exchange) and (c) AMBPE-76 (IEC = 2.74 milliequivalent per g).

(IEC = 2.74 milliequivalent per g) showed the highest hydroxide ion conductivity (56 mS cm^{-1} at 30°C) reported thus far for anion conducting ionomers in the literature.^{8–10,12,13,19,23} While the conductivity for AMBPE-76 was measured at about 85 mS cm^{-1} at 70°C . Moreover, hydroxide ion conductivity for the AMBPE membranes followed Arrhenius-type temperature dependent behaviour at elevated temperatures (except at 70 and 80°C) (Fig. 2(b)). The apparent activation energy estimated from the slope was between 5.9 – 12.2 kJ mol^{-1} and depended on the IEC. The activation energy of AMBPE was similar to or slightly lower than those of reported anion exchange membranes. These membranes exhibit much higher conductivity possibly due to highly functionalized blocks which exhibit more ion exchangeable sites. These results suggest a multi-block structure with highly ionized hydrophilic blocks is effective for improved hydroxide conductivity and IEC.

In summary, multi-block poly(arylene ether)s containing functionalized BPA were synthesized *via* an *in situ* chloromethylation, followed by polymer condensation then amination. The proposed reaction route avoided the use of CMME (carcinogenic and hazardous), which is a commonly used reagent in the chloromethylation reaction. By cleverly optimising the reaction conditions, a DCM of up to 76% was achieved, which corresponded to 2.74 milliequivalent per g IEC after amination, resulting in the development of highly charged ACIs. High hydroxide ion conductivities of up to 56 – 85 mS cm^{-1} at temperatures 30 – 70°C were obtained, which also revealed an Arrhenius-type temperature dependent behaviour for AMBPE membranes and activation energies of 5.9 – 12.2 kJ mol^{-1} . The design concept of ACIs is based on a multi-block copolymer structure with highly functionalized hydrophilic blocks. This enabled the introduction of more functional groups, which were responsible for high conductivity and IEC.

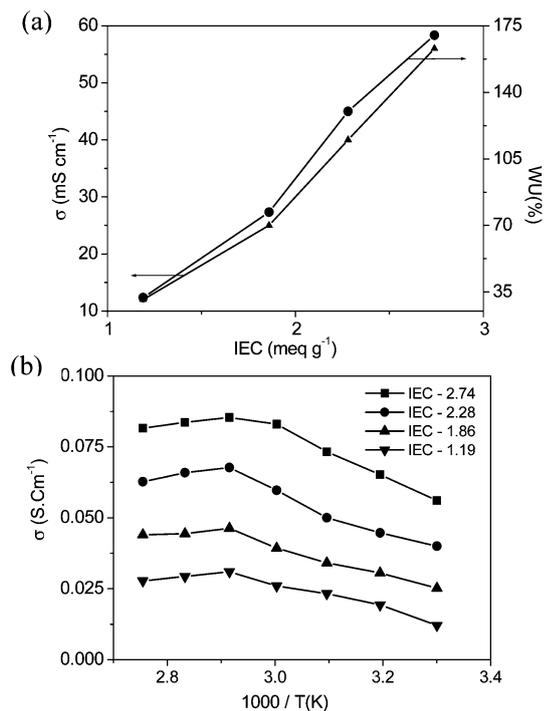


Fig. 2 (a) Hydroxide ion conductivity and water uptake as a function of IEC at 30 °C: (\blacktriangle) conductivity; (\bullet) water uptake. (b) Temperature dependence of hydroxide ion conductivity for AMBPE membranes bearing various IECs.

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