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Azide-assisted self-crosslinking of highly ion conductive anion exchange membranes

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ABSTRACT

Poly(2,6-dimethyl-phenylene oxide)s (PPO)s with thermally crosslinkable azide groups and “side-chain-type” architecture containing quaternary ammonium and triazole groups were synthesized by Cu-catalyzed “click chemistry”. Tough and flexible anion exchange membranes (AEMs) were prepared by solution casting at 70 °C. By simple thermal crosslinking at 135 °C for 18 h, controllably crosslinked PPO AEMs were obtained. Key properties of the crosslinked AEMs, such as ion exchange capacity, thermal stability, water uptake, hydroxide conductivity and alkaline stability were investigated. The crosslinked membranes maintained high hydroxide conductivities despite their extremely low water uptake (up to 57.5 mS cm^{-1} at room temperature, water uptake of 34.5 wt%). The unusually low water uptake and good hydroxide conductivity may be attributed to the crosslinked, “side-chain-type” structures of pendent triazole and cationic groups, which facilitate ion transport. Moreover, the crosslinked membranes exhibited excellent alkaline stability, and retained over 65% of hydroxide conductivity in 5 M or 10 M of NaOH at 80 °C for 400 h. It is assumed that crosslinking decreases the water uptake by polymer chain compaction, thus reducing the nucleophilic attack of water or hydroxide at the cationic center. Thus, triazole-containing AEMs with “side-chain-type” architecture appear to be very promising candidates with good stability as high performance anion exchange membrane.

1. Introduction

Fuel cells are of interest as clean energy power generators that can replace fossil fuel-based generators [1–6]. Among fuel cell types, alkaline fuel cells (AFCs) have been considered as attractive options by virtue of their significant advantage of improved oxygen reduction kinetics and better fuel oxidation kinetics, leading to higher efficiencies and enabling the use of low-cost non-precious metal catalysts [7–11]. Recently, there has been considerable renewed interest in using anion exchange membranes (AEMs) instead of the conventional caustic liquid cells. AEMs not only make the device more compact and lighter, thus raising power density, but also simplify the operation and maintenance of the system by removing the need to handle caustic solutions [8]. One of the major challenges in AEM fuel cells (AEMFC) is identifying suitable hydroxide ion conducting polymeric membranes that maintain robust mechanical properties, chemical stability, and moderate dimensional swelling while providing high hydroxide ion conductivity [9,10]. Generally, the ionic conductivity and chemical stability of AEMs control the performance and lifetime of AEMFCs [10–12]. Thus, high ion-exchange capacities (IEC) are demanded for AEMs in order to achieve sufficient anion conductivity. Unfortunately, increasing IEC is most often accompanied by high water uptake, significant dimensional swelling, or even disintegration of the AEM membrane at elevated temperatures.

Several approaches have been examined to improve anion conductivity, such as the position or distance of quaternary ammonium (QA) or other conducting groups from the main chain (e.g. “side-chain-type”) [13–16], and the control of membrane morphologies by clustered, block or graft/comb-shaped copolymer architectures [17–21], but these approaches have had only partial success. The challenge in materials science continues to be the molecular design of polymeric membranes for efficient anion transport and alkaline stability.

The poor chemical stability of AEMs under high-pH conditions

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at elevated temperatures is another critical issue that limits their practical use in fuel cells. Robust stability above 80 °C is highly desired since the CO_2 solubility in water greatly diminishes above 80 °C, preventing carbonate or bicarbonate formation, and fuel cell operation at elevated temperature also enhances the kinetics of electrochemical reactions. In general, the alkaline instability of AEMs at high pH conditions is instigated either by the degradation of the fixed cationic charge or by the polymer backbones. The known degradation pathways of QA cation by OH^- ions are beta-hydrogen (Hofmann or E2) elimination, direct nucleophilic substitution (S_N2), and ylide formation [22–27]. Polymer backbone degradation commonly occurs by cleavage of C–O bonds in poly (arylene ether sulfone)s [28,29]. Therefore, efficient anion transport combined with alkaline-resistant cationic groups and polymer backbones are critical criteria in the design of advanced AEM materials.

We recently reported methodology for introducing clicked 1,2,3-triazole groups into “side-chain-type” poly(2,6-dimethyl phenylene oxide)s (PPO) to produce highly anion conductive AEMs with good alkaline stability [30–32]. The key findings are that the PPO polymer backbone has good chemically stability under alkaline conditions, and the 1,2,3-triazole could induce the formation of a continuous hydrogen-bonded pathway to sustain efficient ionic conduction. The clicked PPO AEMs also showed a significant improvement in anion conductivity (62 mS cm^{-1} at 20 °C) compared with simple QA-substituted polymers. In particular, these triazole-containing PPO AEMs remained robust and flexible in 1 M NaOH aqueous solution for 2000 h, suggesting that the polymer backbone may have long-term stability in AEMFC. Nevertheless, the clicked PPO AEMs exhibited excessive dimensional swelling in water and alkaline instability of QA cations at the highest IEC values.

Covalent crosslinking of AEMs is considered an effective method for decoupling ionic conductivity and dimensional stability, and improves the alkaline stability of AEMs. The usual chemistries employed for cross-linking include the incorporation of polymerizable [33] or thermal Friedel–Crafts electrophilic substitution [34,35] cross-linkable groups, the introduction of crosslinking agents [36,37], and the application of external stimuli [38–41]. The majority of reported crosslinking methodologies involves the introduction of separate crosslinker molecules or is based on high temperature thermal crosslinking, which increases the process complexity and decreases controllability. Therefore, AEMs possessing high ionic conductivity and dimensional stability, as well as the ability of being crosslinked controllably without the addition of separate crosslinkers are required for practical AEMFC application.

In the present work, we report a unique single step self-crosslinking strategy using azide-assisted low temperature thermal crosslinking, which has the significant advantage that no by-products are formed during the procedure [42,43]. Clicked “side-chain-type” PPO copolymers containing crosslinkable azide groups and with triazole and QA groups were synthesized via Cu-catalyzed alkyne-azide “click chemistry”. Self-crosslinking was achieved readily by simple thermal treatment of the clicked PPO AEMs without the need for a separate crosslinker or catalysts, through the generation of highly reactive nitrenes from azide groups. The properties of the resulting crosslinked AEMs, such as alkaline stability, mechanical strength, dimensional stability, water uptake and hydroxide conductivity, were investigated.

2. Experimental section

2.1. Materials

All reagents and solvents were reagent-grade. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with an average molecular weight of 20,000 was obtained from Sigma-Aldrich. Reagent grade *N*-methylpyrrolidone (NMP), *N*-bromosuccinimide (NBS), 2,2′-azobis-isobutyronitrile (AIBN), *N*,*N*,*N*′,*N*″,*N*″-pentamethyl-diethylenetriamine (PMDETA), copper bromide (CuBr), propargyl, and trimethylamine were purchased from Sigma-Aldrich and used as received without purification. Azidomethyl-substituted PPOs (PPO-N_3) and propargyl trimethylamine (PTMA) bromide salt were prepared according to our previous work [31].

2.2. The synthesis of crosslinkable CA-XxYy copolymers

The copolymers were synthesized by alkyne-azide “click chemistry” in NMP. A typical experiment illustrating ***CA-X40Y10*** is as follows: To a 3-necked flask equipped with a magnetic stirring bar, PPO-N_3 (degree of substitution DS=0.4) (6.5 g, 50 mmol), PTMA bromide salt (2.7 g, 15 mmol), ligand (PMDETA, 10 mmol), CuBr catalyst (5 mmol) were dissolved in 5 mL of NMP. The flask was degassed by three freeze-pump-thaw cycles, left under vacuum, and placed in a thermostated oil bath at 50 °C for 12 h. The reaction mixture was precipitated into water and then the product was washed with water three times. The clicked crosslinkable copolymer ***CA-X40Y10*** (where the 40 refers to the original degree of bromomethylation ***X***, and 10 is the degree of crosslinkable azide groups ***Y***) was obtained after drying in vacuum at 80 °C for 24 h.

2.3. Membrane preparation, evaluation of crosslinking efficiency and ion exchange

The membranes (thickness ~70 µm) having crosslinkable azide groups were prepared by solution casting in NMP at 75 °C. Subsequently, the crosslinking of membranes was carried out in a vacuum oven at 135 °C for 18 h. The gel fraction was employed to determine the degree of crosslinking of the membranes, and was obtained by subjecting the membranes to NMP at 80 °C for 24 h under argon to effect removal of the soluble polymer fraction. The gel fraction value was calculated from the residual mass of the sample by the equation: gel fraction$=(W_d/W_i)\times 100\%$, where W_i is the initial weight of dried membranes and W_d is the weight of the dried insoluble fraction of membranes after extraction.

The crosslinked AEMs ***XxYy*** in the hydroxide form (***x*** refers to the original degree of bromomethylation of PPO, and ***y*** is the degree of crosslinkable sites) were obtained by ion exchange with 1 M NaOH solution at room temperature for 48 h.

2.4. Membrane characterization

All ^1H NMR spectra were recorded on a Bruker AM-400 instrument (400 MHz). Thermal stability of the samples was investigated by using a TA Instruments thermogravimetric analyzer (TGA) model TA SDT Q600. Preheating of the polymer samples was performed at 60 °C for 20 min under argon atmosphere to remove adsorbed moisture. Small amounts of polymer were placed in ceramic cells and the temperature was increased from 30 to 700 °C under nitrogen atmosphere with a heating rate of 10 °C min^{-1}. Fourier transform infrared spectroscopy (FTIR) was recorded on a Perkin-Elmer PE-1710 spectrometer from 4000 to 400 cm^{-1} with a 4 cm^{-1} resolution in 64 scans using polymer thin films. All mechanical properties (tensile strength, tensile modulus, elongation at break, etc.) were measured according to the ASTM D-1708 method. The dog-bone specimens (38 mm × 15 mm overall size