



## Effect of morphology on anion conductive properties in self-assembled polystyrene-based copolymer membranes

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### ABSTRACT

Polystyrene (PS) based random and block copolymers with trimethylammonium and azide side groups are synthesized via nitrogen mediated living radical polymerization. Anion exchange membranes (AEMs) are fabricated from the synthesized copolymers with hydrophobic and hydrophilic dialkyne crosslinkers using Click reaction. Morphological analysis by SAXS and TEM reveals the formation of ordered spherical nanostructure in the block copolymer membranes. In comparison with AEMs from the random copolymer, the block membranes show superior conductivity in higher KOH solutions despite their lower original IEC. The highest conductivity is obtained in 3 M KOH. No significant increase of water absorption or swelling is observed at elevated temperatures for any of the membranes, indicating their good mechanical integrity. No physical degradation is observed for the block membranes after 63 days in 8 M KOH at 60 °C. Fuel cell testing reveals that the block copolymer membranes with well-ordered nanostructure maintained better performance after 10 polarization curves compared to the commercially available AEM (A201).

### 1. Introduction

There has been a resurgence of interest in anion exchange membrane fuel cells (AEMFCs) in recent years as these systems combine the advantageous characteristics of both proton exchange membrane (PEM) fuel cells and traditional alkaline fuel cells [1,2]. AEMFCs can circumvent some of the shortcomings of PEM fuel cells, such as use of costly catalysts and instability of membranes due to an acidic medium [3–7], while avoiding the electrolyte management issues experienced with alkaline fuel cells [8]. However, anion exchange membranes (AEMs) still face a number of developmental challenges before they can be commercially viable. These challenges include low conductivity compared to PEMs and chemical instability of the cationic group. AEMs also need to meet the required mechanical strength and durability for extended use in harsh alkaline conditions. The real challenge for developing an ideal AEM is to balance sufficient mechanical properties with high ion exchange capacity and water content, which maximize conductivity.

Amphiphilic block copolymers are of particular interest for ion exchange membranes as a hydrophilic block can promote ion conduction while a hydrophobic block maintains the mechanical integrity of the

membrane. Depending on the segregation strength and degree of polymerization, microphase separation of block copolymers results in nanostructured membranes with a wide range of morphologies. The microphase separation helps to generate well-defined ion conduction paths. This characteristic of block copolymers is extensively applied in the development of PEMs. Multiple research groups have demonstrated that well-ordered and continuous conductive hydrophilic channels effectively enhance the proton conductivity of the membrane while maintaining adequate mechanical properties [9–18]. Recently, block copolymers were also used for AEM fabrication, and similar morphological effects on the membrane properties were observed. Poly(arylene ether)-type multiblock aromatic AEMs have been reported by several groups [19–24]. High IEC up to 1.93 meq/g and high conductivity (144 mS/cm) at 80 °C were achieved by Watanabe et al. [19] Knauss et al. and Xu et al. reported poly(phenylene oxide) (PPO) based block and graft AEMs with good mechanical strengths together with remarkable anion conductivities [25–27]. Examples of other block copolymers used for AEM include poly(arylene ether ketone) and poly(methyl methacrylate) [28–31]. All of these block copolymer membranes have shown promising conductivities.

Styrenic block polymers can be readily synthesized by controlled

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polymerization (living anionic/radical polymerization), which is necessary for the development of well-defined morphologies. Sequential addition of monomers in living radical polymerization enables the synthesis of copolymers with beneficial features such as controlled molecular weight, defined block composition, and selective block functionalization. Polystyrene (PS)-based imidazolium and ammonium block copolymers were synthesized by Elabd et al. Their investigation of anhydrous materials demonstrated that the morphologies, including the connectivity and long-range order, significantly affected conductivity [32]. Balsara et al. also synthesized PS block copolymers and investigated the bound ion effect in lamellar morphologies [33,34]. Coughlin et al. used atom transfer radical polymerization to prepare poly(styrene-*b*-vinylbenzyltrimethylammonium) (PS-*b*-PVBTMA) and observed ordered lamellar and hexagonal morphologies [35].

Although PS-based block copolymers are attractive for AEMs, their deficient mechanical properties, particularly their brittleness, limit their potential. Several groups have attempted to resolve this problem by introducing a soft segment into the polymer, e.g., polyethylene-*b*-poly(vinylbenzyl trimethylammonium bromide) (PE-*b*-PVBTMA) and triblock copolymer polystyrene-*b*-poly(ethylene-co-butylene)-*b*-polystyrene (SEBS) with benzyltrimethylammonium groups [36–40]. These membranes showed adequate ionic conductivity and improved mechanical properties, but the results were highly dependent on the water content. In some cases excessive swelling was also observed.

Chemical crosslinking is a remedy for the high degree of swelling, enhancing the mechanical strength of the membranes. Various bi- and multifunctional chemicals such as dialdehyde [41,42], dithiol [43], 2-methylimidazole [44], and tetraepoxy [45] have been used as crosslinkers in AEMs. Specifically, crosslinking is crucial for PS-based AEMs to resolve their drawback of brittleness due to the stiffness of the polymer backbone. Diamines such as DABCO [46–49] and alkyl diamines [50,51] are effective crosslinkers in preparing PS-based AEMs. Recently, the PS-based block copolymer AEM prepared by crosslinking using olefin metathesis has demonstrated improved strength and satisfactory ion conductivity [52]. In our previous work, relatively stable and conductive AEMs were prepared from PS-based random copolymers using click chemistry as an effective crosslinking method [53]. In this paper, we report AEMs prepared from PS-based random and block copolymers fabricated via click chemistry using different hydrophilic and hydrophobic crosslinkers. The interrelationship of membrane morphology, hydrophilicity, and transport properties is studied and cell performance of PS-based block copolymer AEMs is evaluated.

## 2. Experimental

### 2.1. Materials

All chemicals and reagents were purchased from Sigma-Aldrich and used as received unless specifically mentioned. The inhibitor in styrene and 4-vinylbenzyl chloride (VBC) (90%) was removed through the column packed with a commercial product, named ‘inhibitor remover’ (Sigma-Aldrich #311332) prior to polymerization. Benzoylperoxide (BPO) was recrystallized from chloroform followed by drying under vacuum at 30 °C. Tetrahydrofuran (THF) and dimethylformamide (DMF) were dried by a VAC solvent purifier before using.

### 2.2. Synthesis of poly(vinylbenzylchloride) (PVBC), polystyrene (PS), and poly(styrene-block-vinylbenzylchloride) (PS-*b*-PVBC)

Synthesis of PVBC was performed using the previously reported method [53]. PS and PS-*b*-PVBC were synthesized by slight modification of PVBC synthesis. Detailed procedures and spectroscopic data of all polymers are described in [Supplementary material](#).

### 2.3. Functionalization of PVBC and PS-*b*-PVBC

Azidation of backbone polymers and quaternization of azide-functionalized polymers were performed by modification of the previously reported method [53] and described in [Supplementary material](#).

### 2.4. Synthesis of crosslinkers

A solution of diol (octanediol, trimethylene glycol (TEG), or polyethylene glycol (PEG-400, average DP = 8–9)) (13.6 mmol, 1 equiv) in THF (40 mL) was added to a mixture of NaH (0.80 g, 2.5 equiv) in THF (30 mL) with stirring over 30 min. The mixture was stirred for 1 h at room temperature and then a solution of propargyl bromide (4.0 equiv) in THF (30 mL) was added by syringe over 45 min. After stirring the resulting mixture at room temperature for another 1 h, the temperature was increased to 60 °C. The mixture was quenched with 3% HCl (100 mL) after overnight reaction and then the organic layer was removed by rotary evaporation. The crude product was extracted from the acidic aqueous layer with dichloromethane, DCM (100 mL). The organic layer was washed with brine (100 mL), dried over MgSO<sub>4</sub> and filtered. The product was purified by removing the organic solvent via rotary evaporator. The three types of crosslinkers produced, 1,8-bis-propargyloxy-octane, bispropargyl-TEG, and bispropargyl-PEG(400) are labeled as OG, 3EG, and 8EG, respectively. Yield: 80–90%. <sup>1</sup>H NMR: (499.7 MHz, CDCl<sub>3</sub>) [OG: δ 4.14 (alkyne-CH<sub>2</sub>-OCH<sub>2</sub>-, 4H), 3.51 (-OCH<sub>2</sub>-alkyne, 4H), 2.42 (alkyne terminal-CCH, 2H), and 1.29–1.42 (internal -CH<sub>2</sub>-CH<sub>2</sub>-, 8H). 3EG: δ 4.2 (alkyne-CH<sub>2</sub>-OCH<sub>2</sub>-, 4H), 3.68–7.2 (internal -OCH<sub>2</sub>-CH<sub>2</sub>O-, 8H), 3.67 (OCH<sub>2</sub>-alkyne, 4H), 2.44 (alkyne terminal-CCH, 2H). 8EG: δ 4.2 (alkyne-CH<sub>2</sub>-OCH<sub>2</sub>-, 4H), 3.58–7.2 (internal -OCH<sub>2</sub>-CH<sub>2</sub>O-, 32H and -OCH<sub>2</sub>-alkyne, 4H), 2.44 (alkyne terminal-CCH, 2H)]

### 2.5. Casting membrane and in-situ click reaction

*N,N*-dimethyl sulfoxide (DMSO) solutions (8 wt%) of quaternized and azide-functionalized polymer were prepared and the required amount of crosslinker was added to the solution. The mixture was stirred for 10 min to obtain a homogeneous solution and then poured on a pre-heated glass plate (110–120 °C). Within 5–6 h, the majority of the solvent was evaporated which resulted in the formation of a thin membrane on the glass plate. The casting plate was allowed to cool down to room temperature and immersed in DI water before the membrane was removed from the glass plate. Solubility of all block copolymers was different from that of the homopolymer. Therefore, *N,N*-dimethyl sulfoxide (DMSO) and *N,N*-dimethyl acetamide (DMAc) were used in a 1:1 ratio for preparing the casting solution (8 wt%) of a block copolymer and the general casting procedure was followed to prepare membranes. The thickness of obtained membranes was in the range of 55–110 μm with average of 76 μm.

### 2.6. General instrumentation

Nuclear magnetic resonance (<sup>1</sup>H NMR) spectroscopy was performed on a Varian NMR 500 MHz spectrometer using CDCl<sub>3</sub> and DMSO-*d*<sub>6</sub> as solvents and tetramethylsilane (TMS) proton signal as an internal standard. Solid-state <sup>13</sup>C NMR experiment of powder and membrane samples was performed through CP/MAS method on JEOL-ECZ 400 MHz spectrometer with a <sup>13</sup>C operating frequency of 100 MHz and a spin rate of 10 kHz. Fourier transform infrared spectroscopy (FT-IR) was performed on a Nicolet 380 spectrometer with an attenuated total reflection (ATR) setup equipped with a diamond crystal and a Germanium plate. Gel permeation chromatography (GPC) was performed on a Shimadzu LC-20AD with two Jordi DVB Mixed Bed columns (250 × 10 mm) calibrated against polystyrene standards with a flow rate of 1.0 mL/min using a THF eluent at 35 °C. Thermal gravimetric analysis (TGA) was done using a TA Instrument Q50 under a

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