Wittig reaction constructed an alkaline stable anion exchange membrane

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ABSTRACT

Pendant type anion exchange membranes are currently believed to the state of the art membrane due to enhanced stability. Yet, challenge lies in the limited strategy to construct such structure. Herein, pendant type anion exchange membranes with flexible quaternary ammonium groups attached to poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) backbone via length-tunable spacers were successfully prepared by mild and one-pot Wittig reaction. The as-prepared membranes show restricted water swelling, high hydroxide conductivity and low methanol permeability at low ion exchange capacity due to spacer induced microphase separation. Among them, QPPO-SC6 exhibits highest hydroxide conductivity (from 37.6 mS/cm at 20 °C to 99.5 mS/cm at 80 °C) and good chemical stability in alkaline environment at 80 °C. The mechanical and thermal properties of these membranes were also investigated. Results prove that our strategy in preparing anion exchange membranes with flexible spacers has great application potential in anion exchange membrane fuel cells.

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1. Introduction

Fuel cells have attracted great attention recently due to their ability to convert chemical energy directly and efficiently into electrical energy without emission of polluting chemicals [1]. Among various fuel cell types, proton exchange membrane fuel cells (PEMFCs) and anion exchange membrane fuel cells (AEMFCs) offer the greatest potentiality in overcoming the current energy dilemma and climatic variation. AEMFC has gained more and more attention due to its advantages over PEMFC. The advantages include (a) facilitated oxygen reduction kinetics in an alkaline environment; (b) the opposite transfer direction of hydroxide ions and fuels cause much lower fuel permeability; (c) the use of inexpensive, non-precious metal catalysts. However, lack of anion exchange membrane (AEM) with high hydroxide conductivity and long-term stability limits the application of AEMFC [2].

The deterioration of anion exchange membrane fuel cell performance is mainly attributed to the decline of hydroxide conductivity of anion exchange membrane. The conductivity decline is due to the cationic functional groups degradation or polymer chain degradation. They are caused by the attack of hydroxide ions in alkaline media [3]. Systematic studies on cationic functional groups such as ammonium [4], phosphonium, imidazolium [5]

etc., reveal that the quaternary ammonium (QA) functional groups with alkyl chains exhibit the highest chemical stability. Besides, the cationic functional group induced degradation of polymer backbone could be minimized by incorporating alkyl spacers between the cationic groups and the polymer backbone [6].

Consequently, strategies need to be established to construct such structure. Zhuang et al. incorporated pendant quaternary ammonium groups to decrease the cation-induced backbone degradation [7]. The membrane showed enhanced chemical stability and high water swelling. Jannasch et al. attached QA groups to PPO via flexible heptyl side chains by lithium chemistry. Hydroxide conductivity and alkaline stability of the membranes were both enhanced [8]. However, harsh reaction condition (−78 °C with BuLi) limited the extended application of this method. The same goal was fulfilled with facile and safe Suzuki-Miyaura coupling reaction nearly at the same time. The polymers showed high hydroxide conductivity and suppressed water swelling due to good phase separation [9]. Bae et al. prepared poly(biphenyl alkylene)s based anion exchange membrane with tethered QA groups via acid-catalyst polycondensation. Results proved that without alkaline labile C–O bonds, the membranes showed excellent alkaline stability at 80 °C in 1 mol/L NaOH [10]. Although anion exchange membranes prepared by catalytic coupling or condensation reaction showed much better performance in contrast to conventional AEMs, the application of these methods is limited due to the utilization of noble metal catalyst.

Herein, we present a strategy to prepare anion exchange membranes with quaternary ammonium groups connected to the

polymer backbone via flexible spacers of different chain-length. The spacers were attached to the polymer backbone via mild and one-pot Wittig reaction without using any expensive catalyst or extreme conditions. The resultant double bond in the side chain provides the possibility for cross-linking which could be utilized to increase swelling resistance and mechanical strength.

2. Experimental

2.1. Materials

Bromomethylated (2, 6-dimethyl-1, 4-phenylene oxide) (BPPO) was synthesized according to previous report [11]. Triphenyl phosphine and tetrabutyl ammonium bromide were purchased from Alfa Aesar (Shanghai, P. R. China). Sodium sulfate, sodium chloride, sodium hydroxide, potassium carbonate, sodium ethoxide, 1-methyl-2-pyrrolidinone (NMP), dimethyl formamide (DMF), petroleum ether (60–90 °C), ethyl acetate, methanol, trimethylamine alcohol solution (TMA) were purchased from Sinopham Chemical Reagent Co. Ltd. (Shanghai, P. R. China). 4-hydroxybenzaldehyde, 1,4-dibromobutane, 1,6-dibromohexane, 1,10-dibromodecane were purchased from Energy Chemical (Shanghai, P. R. China). All reagents were of analytical grade and used as received.

2.2. Synthesis of brominated poly(phenylene oxide) (BPPO)

PPO (6 g, 50 mmol), N-bromosuccinimide(NBS) (4.5 g, 25 mmol), and 2,2′-azobis-isobutyronitrile (0.25 g, 1.5 mmol) were dissolved in chlorobenzene (50 mL) with vigorously stirring. The solution was refluxed for 3 h. Upon cooling, the polymer was precipitated with ethanol (400 mL) and filtered. It was then washed with ethanol, redissolved in chloroform (60 mL) and precipitated into ethanol (400 mL). The purified product was dried under vacuum overnight. The degree of bromination can be determined by ^{1}H NMR or by titrating the bromide content in quaternized BPPO membranes. ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.72–6.64 (t, 2H), 6.52–6.47 (m, 4H), 4.34 (s, 2H), 2.09 (s, 7H). The degree of benzyl bromination calculated by this ^{1}H NMR result is 33%.

2.3. General procedures for preparing 4-(n-Bromoalkanes) benzaldehyde

4-Hydroxybenzaldehyde (1.0 g, 8.2 mmol), K$_2$CO$_3$ (2.2 g, 15.9 mmol) and α,ω-dibromoalkane (16.4 mmol) were dissolved in DMF (20 mL). The mixture was stirred for overnight at 60 °C. On cooling, the reaction was quenched with water (50 mL) and extracted with ethyl acetate (30 mL). The organic phase was dried over Na$_2$SO$_4$. The crude product was further purified by silica gel chromatography and confirmed via NMR spectroscopy.

2.3.1. 4-(4-Bromobutoxy)benzaldehyde
4-Hydroxybenzaldehyde was reacted with 1,4-dibromobutane according to the general procedure. Pure product was obtained by silica gel chromatography with petroleum ether/ethyl acetate (10:1, v/v) as eluting agent, yield 83.5%. ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.88 (s, 1H), 7.84 (d, 2H), 7.00 (d, 2H), 4.07 (t, 2H), 3.50 (t, 2H), 2.12–2.04 (m, 2H), 2.03–1.95 (m, 2H).

2.3.2. 4-((6-Bromohexyl)oxy)benzaldehyde
4-Hydroxybenzaldehyde was treated with 1,6-dibromohexane according to the general procedure to give a crude product. Then it was purified using silica gel chromatography with petroleum ether/ethyl acetate (15:1, v/v) as eluting solvent to obtain the desired product, yield 50.5%. ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.88 (s, 1H), 7.84 (d, 2H), 7.00 (d, 2H), 4.05 (t, 2H), 3.43 (t, 2H), 1.94–1.80 (m, 4H), 1.54–1.52 (m, 4H).

2.3.3. 4-((10-Brodecyl)oxy)benzaldehyde
4-Hydroxybenzaldehyde was treated with 1,10-dibromodecane according to the general procedure to give a crude product. Then it was purified using silica gel chromatography with petroleum ether/ethyl acetate (20:1, v/v) as eluting solvent to obtain the desired product, yield 47.5%. ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.88 (s, 1H), 7.85 (d, 2H), 7.00 (d, 2H), 4.06 (t, 2H), 3.43 (t, 2H), 1.84 (m, 4H), 1.45 (m, 4H), 1.31 (m, 8H).

2.4. Wittig reaction

The general procedure for the one-pot Wittig reaction is as follows. To a stirred solution of BPPO (1 g, 5.0 mmol) in NMP (50 mL), triphenylphosphine (2.6 g, 10 mmol) was added. The resulting solution was heated at 80 °C overnight. On cooling, the derivative of benzaldehyde, which were synthesized previously (Section 2.3, 8.3 mmol), were added and stirred for 10 min. EtONa (2.5 g, 36.8 mmol) was slowly added to the mixture, and the mixture was stirred at room temperature for 3 h. The crude product was precipitated in methanol (300 mL) and filtered. It was then washed with methanol and further purified by precipitation from chloroform into n-hexane. Finally it was dried under vacuum overnight. The obtained polymers were named as PPO-SC4, PPO-SC6 and PPO-SC10 respectively.

2.5. Membrane preparation

PPO-SC4, PPO-SC6 or PPO-SC10 was dissolved in NMP to form a homogeneous solution (10 wt%). Excess trimethylamine alcoholic solution was slowly added to this solution. The resulting solution was stirred at room temperature for 12 h. It was then cast on a clean glass plate and heat at 60 °C to remove all of solvent. The obtained membrane (namely QPPO-SC4, QPPO-SC6 and QPPO-SC10 membrane) was peeled off and immersed in NaOH (1 mol/L) aqueous solution to change the membrane into OH$^-$ form. The membranes were thoroughly washed with deionized water to remove residual NaOH prior to characterization.

2.6. Characterization

2.6.1. Water uptake and linear expansion ratio
Membrane samples (1 cm × 4 cm, OH$^-$ form) were immersed in deionized water for 48 h. They were then taken out and the surface of the samples was quickly wiped with tissue paper. The weight and length of wet membranes were recorded. Water uptake (Wu) of membranes was calculated as follows.

$$Wu = \frac{Wwet - Wdry}{Wwet} \times 100\% \tag{1}$$

where W_{wet} is the weight of swelled membrane sample and W_{dry} is the weight of dry membrane sample. Linear expansion ratio (LER) was calculated in a similar way.

$$LER = \frac{Lwet - Ldry}{Ldry} \times 100\% \tag{2}$$

where L_{wet} is the length of wet membrane sample and L_{dry} is the length of dry membrane sample.

2.6.2. Ion exchange capacity (IEC)
IEC value was measured by elemental analysis (Vario EL cube) with CHN mode at 950 °C. The absolute error of machine is less than 0.1%. The IEC value was calculated according to the content of