Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A
This journal is © The Royal Society of Chemistry 2013

Electronic Supplementary Information (ESI)

Multi-block poly(arylene ether)s containing pre-choloromethylated bisphenol: Anion conductive ionomers

Amaranadh Jasti, and Vinod K. Shahi,*
Electro-Membrane Processes Division,
CSIR-Central Salt and Marine Chemicals Research Institute,
G.B. Marg, Bhavnagar-364002 (Gujarat), India
Tel.: +91-278-2567760 (ext. : 7340); fax: +91 278 2567562/6970; E-mail address: vkshahi@csmcri.org

1. Materials.

4,4'-Difluorophenyl sulfone, 4,4'-difluorobenzophenone, andbisphenol A (BPA) were purchased from Aldrich, Inc., and crystallized fromtoluene/ethanol. Paraformaldehyde, trimethylchlorosilane, anhydrous zinc chloride, trimethylamine aqueous solution (35wt %), *N*,*N*'-dimethylactamide, toluene and methanol were purchased from Spectrochem, India. and used as received. Chloroform,potassium carbonate, sodium hydroxide,ethanol, andacetone were (AR grade; SD Fine Chemicals, India) used as received. Nitrogen, Argon gases were purchased from Ultra Pure Gases (I) PVT. LTD., India.

2. Synthesis of (2,2'-bischloromethyl) bisphenol (CMBPA) monomer.

Charge 40mmol of BPA into250 mL three necked round bottom flask containing 100 mL N,N'-dimethylactamidehaving inert atmosphere. 68 mmol of potassium carbonate was added to above solution and stirred for 4 h. After stirring the excess potassium carbonate was filtered and the filtrate was used as reaction mixture.185 mmol of paraformaldehyde, 185mmol of trimethylchlorosilane, and 0.183mmolanhydrous stannic chloride mixture has been prepared, added slowly to the above reaction mixtureunder stirring conditionat 80°C for 12 h. The product was obtaining by precipitating of reaction mixture indilute HCl followed by washing in hot DI water. The obtained product was dried overnight in a vacuum oven at

60°C. The obtained CMBPA monomer was used for further reaction process. Different degree of chloromethylation (DCM) 76%, 60%, 45% and 32% of CBPA monomer were prepared.

3. Synthesis of chloromethylated multiblock polyether (CMMBPE) ionomer.

4,4'-difluorophenyl sulfone (5.5 mmol), 4,4'-difluorobenzophenone (5.5 mmol), (2,2'-bischloromethyl) bisphenol (11.5 mmol), potassium carbonate (6.0 mmol), calcium carbonate (60 mmol), *N*,*N'*-dimethyl acetamide (80 mL), and toluene (20 mL) were charged into three necked round bottom flask equipped with Dean-Stark trap and nitrogen inlet. The reaction mixture was heated to 140°C for 3h and after complete evaporation of toluene;the temperature was slowly increased to 165°C for another 6h. The reaction mixture was precipitated indeionized water and washed with chilled methanol. The obtained product was purified by dissolving in *N*,*N*-dimethyl acetamide followed by precipitation in acetone andwhite solid polymer was dried in vacuum oven at 90°C.

4. Membrane Preparation

CMMBPE (1.0 g) was dissolved in 7 mL *N*,*N'*-dimethylacetamide (DMAc) and then cast on a clean glass plate. For getting of 55 μm thick and transparent film, the glass plate was dried under reduced pressure at 90°C for 12 h.

5. Amination and Ion Exchange Reactions

The obtained transparent thin film was aminated by treating with 35 wt% of trimethylamine aqueous solution for 24 h at room temperature. After amination the thin film was washed with water and converted to hydroxide form by dipping in 1M KOH solution for 24 h at room temperature. The obtained AMBPE copolymer was used for the further characterizations.

6. Measurements.

The ^{1}H NMR was recorded by NMR spectrometer (Bruker, 200& 500 MHz for ^{1}H NMR) in $CDCl_3$ (deutrated chloroform) or DMSO-d_6 (deutrated dimethylsulfoxide) with reference to tetramethylsilane. The Molecular weight of ionomers were measured by gel permeation chromatography (GPC, Waters 2695, Waters HPLC Alliance model) equipped with Styragel HR 5, HR 4E and HR 0.5 columns coupled with Water 2996 DAD detector (Empower 2 Software) with THF as eluent after the calibration with standard polystyrene samples.

7. Conductivity.

Membrane hydroxide conductivity of AMBPE membranes were measured by potentiostat/galvanostat frequency response analyzer (Eco Chemie, B.V. Utrecht, The Netherlands Auto Lab, Model PGSTAT 302N). The membrane was sandwiched between two in-house made stainless steel circular electrodes (4.0 cm^2). Direct current (dc) and sinusoidal alternating currents (ac) were supplied to the respective electrodes for recording the frequency at 1 μA/s scanning rate within 10^6 to 1 Hz. The membrane resistance was determined from Nyquist plots using Fit and Simulation method. Membrane resistance (R^m) was measured in equilibration with deionised water and membrane conductivity (σ) was estimated by the following equation,

$$\sigma_{-} = \frac{\Delta x}{A R^{m}} \qquad (1)$$

Where $\Delta x$and $A$are the membrane thickness and membrane conducting area respectively.

Membrane conductivity data at different temperatures under 100% relative humidity (RH) was used for the estimation of activation energy (E_a) by following expression:

$$E_a = -b \times R \qquad (2)$$

This journal is © The Royal Society of Chemistry 2013

Where b is the slope of the regression line of ln σ (S cm^{-1}) vs 1000 T^{-1} (K^{-1}) plot and R is the gas constant (8.314 J K^{-1} mol^{-1}).

8. Water Uptake.

The membrane water uptake *(WU)* was determinedby dipping the membrane in distilled water for 24 h and the wet weight was recorded afterremoving surfacial water. Then the wet membranes were dried under vacuum at 80°C until to get a constant weight and thus dryweight of the membranes were recorded. The water uptake (*WU*) ofthe membranes was determined using the following eq.

$$WU = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100$$

Where W_{wet} and W_{dry} are the masses of the membrane under wetand dry conditions.