# A series of poly(butylimidazolium) ionic liquid functionalized copolymers for anion exchange membranes

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## HIGHLIGHTS

- High conductive b-VIB based DPEBI as AEM.
- Low water uptake, swelling ratio and activation energy.
- Drastically alkaline stability in 2M KOH.
- Thermally stable up to 250 °C.
- Well distinguished hydrophilic/hydrophobic nanophase separation.

## GRAPHICAL ABSTRACT
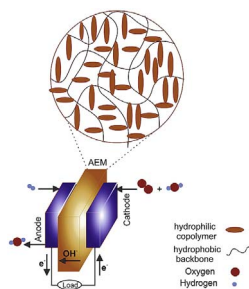


## ARTICLE INFO

## ABSTRACT

A new series of ionic liquid functionalized copolymers for anion exchange membranes (AEM) is prepared. Poly(butylvinylimidazolium)(b-VIB) is copolymerized with para-methyl styrene (p-MS) by the radical polymerization formed block copolymers b-VIB/p-MS, which is crosslinked with poly(diphenylether bibenzimidazole) (DPEBI) providing the desired materials b-VIB/p-MS/DPEBI. Structures are characterized via H$^1$NMR, FTIR spectra and elemental analysis. The b-VIB blocks offer the anion conduction function while DPEBI moieties contribute to enhancing other properties. The prepared membranes display chloride conductivity as high as 19.5 mS/cm at 25 °C and 69.2 mS/cm at 100 °C-higher than that of the commercial membrane tokuyuama A201-. Their hydroxide conductivity reaches 35.7 Scm$^{-1}$ at 25 °C and 73.1 Scm$^{-1}$ at 100 °C. The membranes showed a linear Arrhenius behavior in the anion conduction, low activation energies and distinguished nanophase separation of hydrophilic/hydrophobic regions by the transmission electron microscopy (TEM) studies. Thermal investigations using TGA and DSC confirm that the membranes are stable up to 250 °C. Particularly, drastically alkaline stability due to no decrease in the hydroxide conductivity after 168 h of treatment with 2M KOH.

## 1. Introduction

Nowadays, Fuel cell industry is attracting more attention because of its ability to produce more energy, its efficiency and friendly environment technique compared to combustion engines [1] and the high energy conversion for wearable devices [2–4].

Alkaline anion exchange membranes fuel cell (AAEMs) are widely known as a good alternative to the proton exchange membranes fuel cell (PEMs) [5,6]. AAEMs have got tremendous attention this last decade [7–9], they seem to be the perfect candidate since they enable the use of non noble metals as catalysts [10] e.g. silver, cobalt and nickel [11,12]. and lead to a great solution for high power density [13];

They provide a more efficient environment for the catalyst's stability than the acidic one [13,14]. Also, both the fuel oxidation and oxygen reduction have better kinetic in the alkaline environment [5,15,16]. Add to these advantages, they have very low cost compared to proton exchange membrane [17,18].

Technically good AAEM should at the same time provide high conductivity and ion exchange capacity, good thermal and chemical stability and low swelling ratio and gases permeation [8,19]. However, AEMs still have limitations; their dramatically low conductivity compared to proton exchange membranes [20–22], physically due to the low mobility of hydroxide ions compared to protons [15,22]; and the alkaline stability of their organic cations toward the nucleophile attack [20]. Here in, various researches have been done as example Boncella and co-workers have figured out that ammonium cations degradation is very speed in an alkaline environment which limits the practical use and presents the chemical stability of AAEM as the main criterion [1].

The elaboration and synthesis of novel AEM possessing at the same time high conductivity, good dimensional and alkaline stability are the target of researches and a real challenge in this field [23]. For the improvement of the conductivity, a very direct method adopted in applications is increasing the density of conductive groups including quaternary ammonium, imidazolium, guanidinium, and phosphonium [24]. Another method was successfully achieved via controlling the membrane morphology thanks to better positioning the quaternary ammonium (QA) groups (such as "side chain type"), or a new cluster, block design, and graft/comb shaped copolymer structure. The dimensional stability is normally controlled by covalent crosslinking [23].

Among ionic liquids based AEMs, polymers containing imidazolium were found to be of great interest for device applications [25]. They present some potential benefits: 1) the five heterocyclic ring of imidazolium delocalizes the positive charge, helping to prevent nucleophilic attack of the alkaline environment via Hofmann or $SN_2$ elimination [26], 2) they may have better morphology with more distinguished hydrophilic hydrophobic phase separation [27], 3) imidazolium chemistry avoids the negative chemical environment caused by trimethylamine, and 4) thermal stability of imidazoliums is so far better than the ammonium cation [28–30].

Here we present a new membrane series displaying a good conductivity and a very low cost. The backbone poly(4,4'-diphenylether-5,5'-bibenzimidazole) (DPEBI) is used in the present framework for anion exchange membrane to rise the mechanical and chemical stability of the pendant imidazoliums.

## 2. Experimental

### 2.1. Materials

Polyphosphoric acid, 1-vinylimidazole, and 2,2'-azobisisobutyronitrile (AIBN) were purchased from HEOWNS (Tianjin, China), p-methyl styrene (p-MS) from Xilong Chemical (China), 1-bromobutane from Energy Chemical (China), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP) from Tianjin Fuyu Fine Chemical (China), and N-bromosuccinimide (NBS) and 4, 4'- oxybis (benzoic acid)benzoyl peroxide, 3, 3', 4, 4'- tetraaminobiphenyl, (BPO) from Beijing OUHE Technology (China). p-methyl styrene was passed through a column of alumina to eliminate the inhibitor. The BPO was purified; 10 g of BPO totally dissolved in 40 ml of chloroform has been poured into 100 ml of methanol cooled in an ice bath. The solid was filtered under pressure to obtain the pure BPO. Other chemicals have been used without purification.

### 2.2. Synthesis of poly (4,4'-diphenylether-5,5'-bibenzimidazole) (DPEBI)

The polymer poly (4,4'-diphenylether-5,5'-bibenzimidazole) - has been synthesized in our laboratory following the method reported in
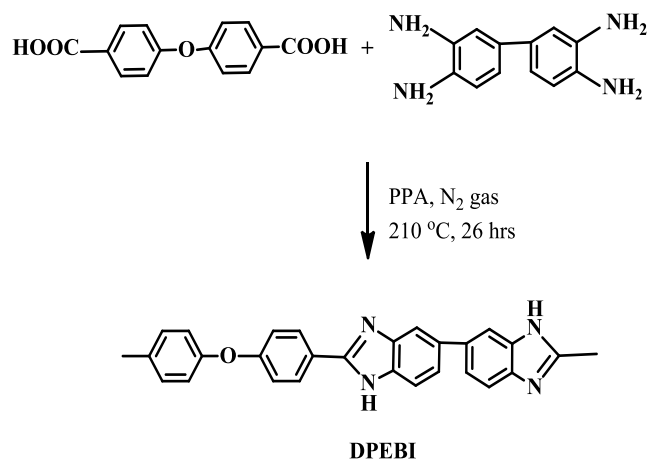


**Scheme 1.** Synthesis procedure of poly (4,4'-diphenylether-5,5'-bibenzimidazole).

the literature [31]. To resume the process an equivalent mole number of 4, 4'- oxybis (benzoic acid) and 3, 3', 4, 4'- tetraaminobiphenyl were mixed in a three necked flask in presence of polyphosphoric acid. The reaction of polymerization was carried out under a mechanical stirring (an overhead was placed in one neck of the flask), nitrogen and high temperature reaching 210 °C. The reaction has been held for 26 h. Once the reaction is over, the polymer is obtained by pouring the viscous solution into cold deionized water and the OPBI in the form of fibers appears in the beaker and further neutralized using sodium bicarbonate solution and washed with deionized water to remove the excess of bicarbonate. In the last step, the polymer is dried at 60 °C in an oven. The reaction is described in Scheme 1.

### 2.3. Synthesis of copolymer butylvinylimidazolium/p-methyl styrene (b-VIB/p-MS)

In a two necked round bottom flask, 1-Vinylimidazole (2.5 ml, 27.57 mmol) with an excess of 1-bromobutane (4 ml, 37.08 mmol) were mixed under nitrogen and stirred at 40 °C for 48 h. After reaction, the excess of 1-bromobutane is removed via evaporation and the resulted butylvinylimidazolium bromide (b-VIB) has been dried.

A mixture of synthesized b-VIB (1 g, 4.32 mmol) is dissolved in 2 ml of DMSO and an appropriate amount of p-MS has been added drop wise. The initiator AIBN (30 mg, 0.183 mmol) was added and the mixture was stirred under nitrogen at 80 °C for 48 h. The obtained copolymer (b-VIB/p-MS) was poured drop wise into acetone and the collected solid is dried in the oven at 60 °C (Rate 99.5%).

### 2.4. Bromination of copolymer b-VIB/p-MS

The calculated amount of b-VIB/p-MS was dissolved in 2 ml of DMSO, NBS and BPO were added to the solution. The bromination is held for 3 h and stirred at 80 °C under reflux and nitrogen. The resulting brominated mixture of b-VIB/p-MS (b-VIB/p-MSBr) was filtered first and then precipitated in THF. After that, the mixture has been centrifuged at least 3 times in order to get the entire solid.

### 2.5. Membrane preparation

The copolymer b-VIB/p-MSBr is mixed with DPEBI in DMSO and stirred until a homogeneous solution. The solution mixture has been poured into a Teflon plate and placed in an oven at 80 °C. First the plate has been covered for 48 h so the copolymerization of the DPEBI with b-VIB/p-MSBr can be achieved; then the cover has been taken off to evaporate the solvent. The entire process of synthesis from 1-Vinylimidazole to the resulted membrane is described in Scheme 2.