Polymer Chemistry

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MINIREVIEW

Anion exchange membranes (AEMs) based on Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and its derivatives

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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Polymeric anion exchange membranes (AEMs) attract increasing attention, because they have prominent roles in various energy and environment-related fields. The most important prerequisite toward high performance AEMs is to search for an appropriate base polymeric material, which should be chemically stable and easily handled for fabricating AEMs. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is considered to be a promising candidate since it enables versatile routes to obtain high performance AEMs. Furthermore, the properties of these AEMs can be feasibly adjusted and controlled to meet various application requirements. In this review, recent progresses in PPO based AEMs are comprehensively presented. Herein, we highlight the strategies used for designing PPO based AEMs and hope to provide promising principles, concepts, and routes into the synthesis of other polymers based AEMs.

1. Introduction

Ion exchange membranes (IEMs) play significant roles in numerous fields. Current research focuses on the development of IEMs for separation processes and energy conversion devices,[1-4] which can be applied to electrodialysis and diffusion dialysis for industrial wastes treatment.[5] More recently, there are increasing interests in various electrochemical energy generation and storage systems, including polymer electrolyte membrane fuel cells,[6-11] redox flow batteries (RFBs),[12,13] reverse electrodialysis cells (REDs),[14,15] microbial fuel cells (MFCs),[16] and hydrogen production (water electrolysis and artificial photosynthesis based membrane).[17,18] These technologies rely upon IEMs that separate and transport ions between the anode and cathode.[19] These IEMs should meet several requirements: reasonable ionic conductivity, good chemical and dimensional stability, long-term durability in the actual operating environment, mechanical toughness, and sufficient heat tolerance.[20,21]

IEMs for practical applications are broadly divided into cation exchange membranes (CEMs) and anion exchange membranes (AEMs). AEMs provide an environment for electrochemical reactions at high pH that may reduce the need for platinum catalysts in electrochemical devices such as fuel cells.[22-25] However, the investigations about AEMs based systems are still in their infancy, which is mainly due to the development lag of AEMs. To date, there are no readily available AEMs that serve as the standard-bearer, while commercially available Nafion (Dupont) membranes as state-of-the-art CEMs have driven the progresses of CEMs related process.[26]

There have been significant advances in preparing AEMs from a variety of polymer main chains ranging from poly(olefin)s, poly(styrene)s, poly(phenylene)s, poly(ether sulfone)s, poly(ether imide)s, and poly(arylene ether)s to organic–inorganic hybrid composites. [27-31] The AEMs can be obtained by chloromethylation of these polymers and followed by reaction with trimethylamine (TMA) to form benzyltrimethylammonium groups. Although it contributes to the progresses of AEMs, this route is especially environmental unfriendly and relatively complicated. In the chloromethylation, the commonly used chloromethyl methyl ether (CME) and bis-chloromethylether (BCME), are considered to be carcinogens. Their usage have been restricted since the 1970s and thus large-scale production is limited.[32-34]

To overcome this hurdle, poly(2,6-dimethyl phenylene oxide) (PPO) as a potential candidate has been extensively studied to produce AEMs by both our group and other researchers. Apart from its excellent physicochemical properties, the most attractive advantage lies on the easy and controlled preparation procedures to obtain AEMs. The original route is as follows: PPO is brominated to access benzylhalide groups for subsequent quaternization as an alternative to chloromethylation.[35] Consequently, studies about PPO and its derivative AEMs are moving forward all the time.

In this review, key developments in PPO-based AEMs are discussed: (1) AEMs prepared from bromination of PPO (BPPO), (2) AEMs prepared from PPO through Friedel-Crafts acylation, (3) AEMs prepared from PPO derivatives through in-situ polymerization, (4) inorganic-organic AEMs prepared from PPO derivatives through sol-gel processes, (5) AEMs prepared from PPO derivatives through atom transfer radical polymerization (ATRP). Apart from studies into these diverse preparation methods, recent investigations with an emphasis on the different applications of PPO based AEMs have also been comprehensively presented. Based on these achievements, the value of PPO for the development of AEMs will be demonstrated. This minireview provides commonly available strategies for deriving AEMs from other polymers using PPO, a model example as a starting material.

2. Characterization of AEMs

To evaluate the performance of an AEM, ion exchange capacity (IEC), and water uptake (WU) are important parameters to be considered. IEC is the number of cationic groups (molar equivalents per gram dry membrane), and the Mohr method is highly recommended to determine it for AEMs.[36] WU is calculated on the basis of the weight difference between the wet membrane and the dry membrane.[37]

Besides, to satisfy various application requirements, the AEMs' conductivity (or area resistance), mechanical strength, thermal and chemical stability are also major concerns. The conductivity is generally determined by using electrochemical impedance spectroscopy (EIS) through the four-point probe technique.[38] In this method, the membrane resistance is measured in the in-plane direction to aid assessing the conductive properties of the membrane to be used in electrochemical devices.[39] It is a common method to compare different AEMs' conductive behaviour, while the resistance in the through-plane direction will affect the electrochemical performances. In other applications, such as for separation processes, the membrane resistance in the through-plane direction is measured by sandwiching the membrane between two electrodes.[40]

Good mechanical strength under various conditions is a basic requirement of AEMs. Examining the tensile properties in both the dry and wet state is commonly done to assess the mechanical properties.[41] Thermal and chemical stability are key factors in affecting the long-term performance of an AEM. Normally, thermogravimetric analysis (TGA) measurements are performed to address the membrane' thermal stability. While examining the chemical stability, a sample is usually exposed to a concentrated alkaline solution (alkaline stability is the biggest challenge for an AEM) for a controlled period of time. Subsequently, changes in chemical structure, mechanical and electrical properties are then recorded.[42]

Characterization as mentioned concentrate on the membrane macroscopic properties, which in principle are influenced by the membrane micro-morphology. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), tapping mode atomic force microscopy (AFM), and small angle X-ray scattering (SAXS) are usually employed to probe micro-morphology.[19]

Characterization about chemical structures and compositions are essential to provide more information about membrane materials at a molecular scale. Nuclear magnetic resonance (NMR), Raman and Fourier transform infrared spectroscopy (FT-IR) techniques are commonly used.

In this review, these common characterizations will assist in the understanding of PPO-based AEMs produced by diverse routes.

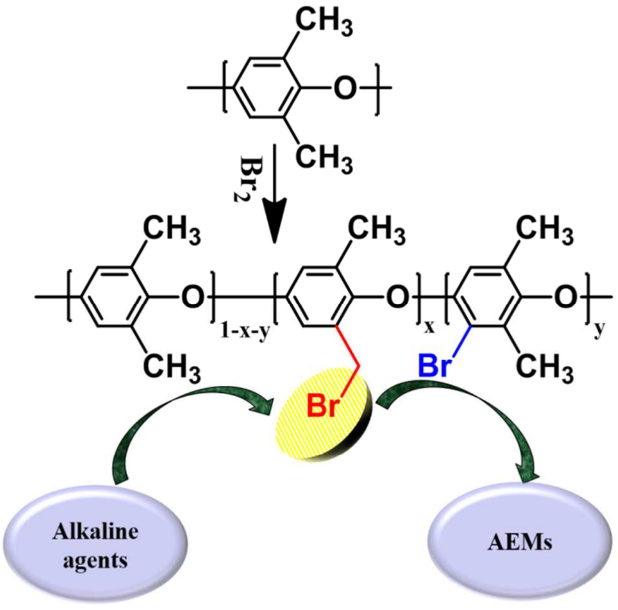

Fig. 1. Schematic illustrations for brominated PPO.

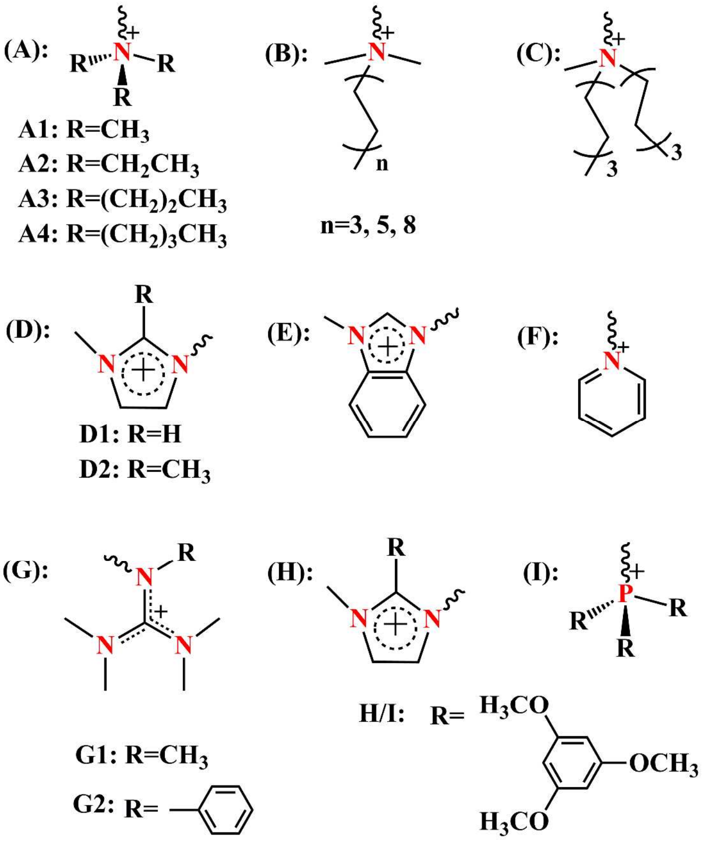

Fig. 2. Common cationic head-groups for AEMs.

3. AEMs directly prepared from bromination of PPO (BPPO)

PPO possesses a high glass transition temperature (Tg = 210 °C), and displays excellent mechanical strength.[43] As an aromatic polymer, the basic structure unit of PPO contains an aromatic ring, two methyl groups, and an end-hydroxyl (phenol) group. Although the structure of PPO is simple compared with other aromatic polymers, it allows many modifications in both the aryl and benzylic positions. The main modifications to PPO have been carefully listed in our prior review about proton exchange membranes (PEMs) prepared from PPO.[44]

Recently, PPO has been explored as a suitable matrix for AEMs via bromination, followed by quaternization reactions. Generally, the bromination can occur either at the benzylic position or directly on the aromatic rings, depending on the bromination agents and reaction conditions.[45] This method leads to the idea that the properties of the membranes can be quantitatively controlled not only by bromination process (the substitution position and content) but also by the subsequent amination processes.[46,47] The scheme for preparing AEMs from BPPO is illustrated in Fig. 1.

Table 1 Properties of trimethyl amine functionalized and ethylenediamine crosslinked BPPO based AEMs (data collected from Ref. 47)

Membrane series	AS[a]	BS[a]	IEC (mmol/g)	WU (%)
1	0.16	0.12	0.89	41.8
2	0.16	0.17	1.27	50.0
3	0.16	0.29	1.94	59.3
4	0.16	0.31	2.08	74.0
5	0.16	0.33	2.18	77.0
6	0.10	0.29	1.94	67.3
7	0.28	0.29	1.95	47.8
8	0.38	0.29	1.94	44.2
9	0.42	0.29	1.93	38.7
10	0.54	0.29	1.92	30.2

[a] AS: aryl substitutions, BS: benzylic substitutions. Both are assumed Mono-substituted.

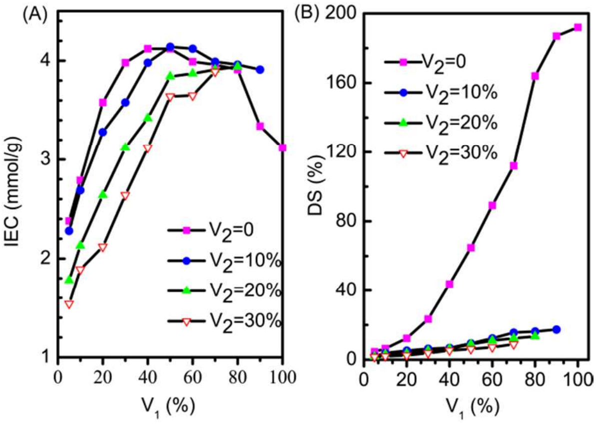

Fig. 3. Effect of volumetric ratios of trimethyl amine (V_1) and ethylenediamine (V_2) on both membrane IEC (A) and membrane dimensional stability (B) with time=10 h, temperature=35 °C, benzylic substitution of PPO=0.992. (data from Ref. 46).

Functionalized by trimethylamine (TMA) and subsequent crosslinking

The quaternary ammonium (QA) cationic head-group (Fig. 2(A)) is a common functional group for AEMs. , QA-type AEMs can be readily obtained by immersing the BPPO base membrane into a properly proportional aqueous solution such as trimethylamine (TMA) (alkaline functional agents) and ethylenediamine (EDA) (crosslinkers). The properties of these AEMs can be feasibly adjusted by varying the contents of benzylic and aromatic substitutions (Table 1).[48,49] As expected for the first membrane series, IEC increases with increasing benzylic substitution. Nevertheless, fixed group concentration (CR), which is expressed as the ratio of IEC to WU, initially decreases and then remains approximately unchanged when increasing WU. While for second membrane series, IEC remains approximately unchanged by the aryl substitution but the CR increases with increasing aryl substitutions due to decreasing WU of the membrane. Therefore, adjusting the ratio of benzylic to aryl substitutions can help to synthesize a membrane with both the desired IEC and an appropriate WU for desired applications.

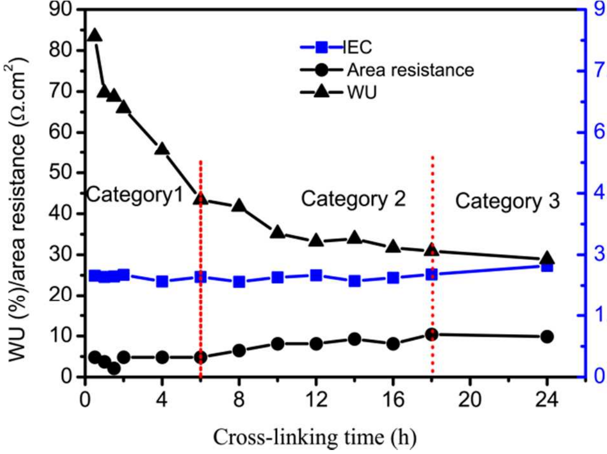

Fig. 4. Effect of surface crosslinking time on the main properties of AEMs (data from Ref. 50).

Furthermore, the resultant AEMs' properties can be regulated by changing the relative contents of TMA and EDA.[46] Obviously, the IEC and dimensional stability (DS) vary with the ratio of TMA and EDA reagents (Fig. 3). Using EDA as a surface crosslinker is another way to adjust the AEMs' properties. In this method, the CR can be changed by controlling the crosslinking time, while maintaining constant IEC (Fig. 4).[50] In Fig. 4, the resulting AEMs can be divided into three categories of membranes, as separated by the dashed line. The first category of AEMs show high WU and thus can be used in diffusion dialysis for processing wastes containing strong acid and cations with high valence. The second category of AEMs with moderate WU and area resistance, can potentially be applied in electrodialysis and fuel cells. The last category of AEMs with low WU and high area resistance is applicable to situation where both the acid recovery ratio and the selectivity are less important but with purpose to decrease the acid concentration of waste containing a relatively low concentration acid and valuable metal ions.

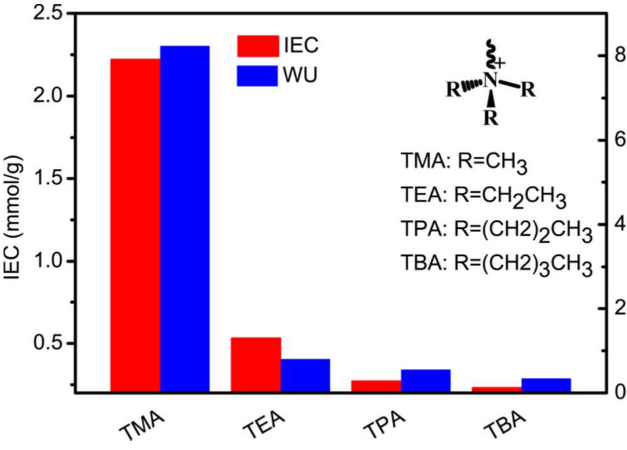

Fig. 5. Effect of amine agents on the main properties of anion exchange membranes (data from Ref. 51).

Functionalized by amine with long alkyl chains

Apart from the bromination and crosslinking procedure, the kinds of tertiary amines used for quaternization also play crucial roles in determining the resulting AEMs' properties. QA groups bearing long alkyl chains were successfully introduced onto BPPO to provide more options for BPPO based AEMs.[51,52] From the resulting properties of AEM functionalized by different amines shown in Fig. 5, it is observed that the IEC decreases in the following order: trimethylamine (TMA)< triethylamine (TEA)< tripropylamine (TPA)< tributylamine (TBA). This trend implies that with an increase in alkyl length of the amines, the quaternary amination reaction become more difficult due to increasing steric hindrance.[53] These studies focused on adjusting the AEMs' IEC and WU while ignoring other properties, especially hydroxide conductivity and alkaline stability.

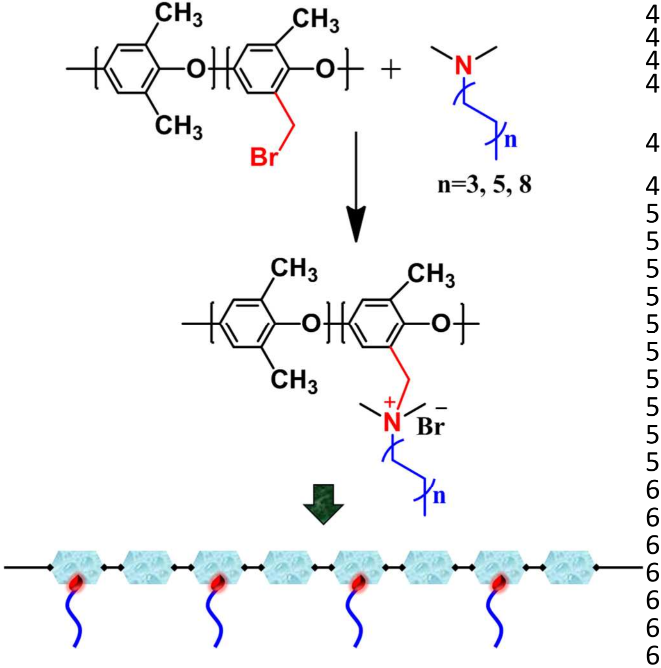

Fig. 6. Schematic illustrations for comb-shaped anion exchange membranes.

Li *et al.* continued to increase the length of the alkyl chains and aimed to obtain high performance AEMs, which can be used in alkaline polymer electrolyte fuel cells (APEFCs).[54] This class of functional group is illustrated in Fig. 2(B), and the resulting AEMs were termed comb-shaped AEMs. As shown in Fig. 6, the authors prepared a series of AEMs with varied alkyl chain length and IECs.[55] They found that the hydroxide conductivity increased with increasing alkyl chain lengths; the AEMs with an alkyl chain of 16 carbon atoms exhibited the highest conductivity (35 mS/cm at 20 °C).[56] The significant point was that the AEMs achieved such high hydroxide conductivity while retaining low WU levels (20.4% at 20 °C). The authors explained that the incompatibility between the hydrophilic polymer main chain and the hydrophobic aliphatic chain drove the AEM to form QA-ion rich nano-scale domains, facilitating ion transport and the degree of phase separation increased as increasing length of alkyl chain.[57] These AEMs also presented outstanding alkaline stability because the large volumetric aliphatic chains protected the AEMs from being attacked by hydroxide ions.[58] These studies suggest that BPPO with comb-shaped structure can achieve high performance AEMs.

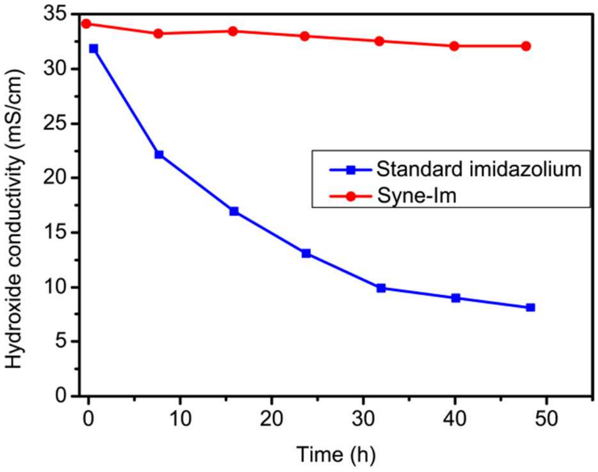

Fig. 7. Hydroxide conductivity of AEMs based on 1,4,5-trimethyl-2-(2,4,6-trime-thoxyphenyl) (syne-IM) and 1-methylimdazole (standard imidazolium) during an alkaline stability test at 80 °C 1 mol/L KOH,[59] Copyright 2013. Reproduced with permission from John Wiley and Sons.

Functionalized by alternative cationic head-groups

Although QA-type BPPO based AEMs have been successfully prepared and applied, they usually suffer from a number of disadvantages stemming from the intrinsic nature of QA groups. The two main disadvantages of QA groups are low stabilities in hydroxide form and low conductivities.[60,61] The poor stability of QA head-groups in high pH environments is caused by the strong nucleophilic OH^- anions via direct nucleophilic displacements, Hofmann elimination reactions (when β hydrogens present), and/or minor side-reactions involving ylide-intermediates.[62-64] On the other hand, the low hydroxide conductivity is mainly attributed to the relatively weak alkalinity of QA hydroxides and resultant poor self-dissociation capability (*e.g.* TMA has a pKa =10.8).[65]

As a consequence, the development of BPPO based AEMs has been directed towards alternative cationic head-groups. Pyridine cation (Fig. 2(F)) is a common cationic head-group and has been introduced onto various polymers for the preparation of AEMs.[66-69] Bromomethyl groups can feasibly react with pyridine for the synthesis of pyridinium type AEMs.[70,71] Unfortunately, pyridine may cause the decomposition of PPO backbone during the functionalization process. Ultimately, the pyridinium AEMs cannot be well applied due to the weak mechanical strength.

With the progress in extending the use of cationic chemistry, various alkaline agents for AEMs have been synthesized and reacted with BPPO. Cationic head-groups including imidazolium (Fig. 2D, 2E, 2H), guanidinium (Fig. 2G), and stabilized phosphonium (Fig. 2I) used with BPPO as base materials have been recently investigated by our group and other researchers.

Imidazolium (Im) is a promising candidate for the synthesis of thermally and chemically stabilized AEMs, due to the presence of steric hindrance and the π-conjugated structure of the five-member heterocyclic ring.[72] Firstly, 1-methylimidazole (MIm) has been attached onto PPO main chains (Fig. 2(D1)).[73] The obtained AEMs displayed conductivities up to >100 mS/cm at 80 °C with improved short-term thermal as well as chemical stability compared with classic QA-type AEMs. However, the long-term chemical stability of the membranes was still not high enough. The MIm-containing AEMs tended to degrade in KOH (2 mol/L) solution at only 25 °C. This instability was mainly caused by the weakly acidic proton bound to the C2 position (R=H, Fig. 2D), which easily suffer from strong attack by OH- anions.[74] In order to eliminate the influence of the acidic protons, *1,2*-dimethylimidozole (DIm) has been linked to the PPO main chains (Fig. 2(D2)).[75] The C2 position of DIm cations contains a methyl group; this replacement of the acidic C2 protons weakened the attack by OH^- and improved the alkaline stability of the resulting AEMs.[76] It was observed that the IECs of DIm-PPO (IEC=2.16 mmol/g) did not change much (KOH (2 mol/L) solution at 25 °C) even after 9 days of ageing, suggesting the enhanced alkaline stability. As to the Im cations stability, further studies have indicated that the electron-donating and steric hindrance of the substituent groups at C2 position will contribute to the stability of Im.[74,77] 1,4,5-trimethyl-2-(2,4,6-trime-thoxyphenyl) imidazolium (syne-Im) combining electron and steric effects was designed by Yan *et al.* to functionalize BPPO (Fig. 2H).[59] The resulting membrane presented much more stability compared to standard MIm (100 °C vs. 40 °C temperature tolerance in 1 mol/L NaOD/D_2O for 48 h), as shown in Fig. 7.

Another candidate cationic head-group is the guanidinium group, which is a superbase (PKa=13.8) and highly tolerant to alkaline environments.[78,79] High performance AEMs were prepared by reacting BPPO with 1,1,2,3,3-pentamethylguanidine (PMG) (Fig. 2(G1)).[80] The resultant AEMs exhibited high hydroxide conductivity (up to 71 mS/cm at room temperature) and excellent thermal and alkaline stability. Recently, a novel guanidine, 2-benzyl-1,1,3,3-tetramethylguanidine (BTMG), with an additional bulky benzyl group was synthesized and used for functionalizing BPPO (Fig. 2(G2)).[81] By evaluating the corresponding model small molecules in 1 mol/L NaOH/D_2O solution at 60 °C using ^1H NMR technique, the BTMG in this work was stabilized compared to the most common PMG.

In regard to P-based AEMs, an novel class of highly alkaline head-groups-phosphonium cations were also introduced into BPPO main chains via a feasible reaction (Fig. 2I).[82,83] The optimized ionomeric AEM exhibited good performance because the efficient decentralization of the positive charge of the phosphorus atom by the electron- donating triple 2,4,6-trimethoxyphenyl groups simultaneously enhances both the stability and basicity.

The above work demonstrates that non-QA type alkaline functional groups displayed several advantages, mainly alkaline stability. However, the studies cannot be compared to each other due to different testing conditions used. To date, the best method for such testing is still in debate. On the other hand, most of these studies ignored the effects of alkaline groups on the polymer backbone, which will determine the AEMs' degradation behavior. These issues have to be addressed in future research. In addition, more optimized alkaline functional groups have been reported, and then deserve to be introduced into the PPO.

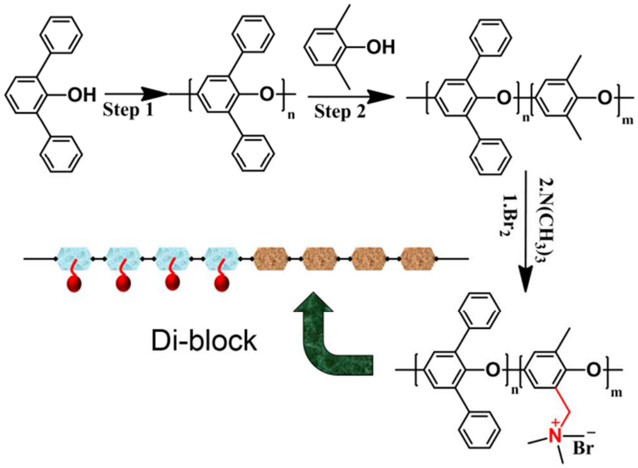

Fig. 8. Schematic illustrations for PPO based di-block AEMs.

AEMs prepared by PPO based copolymers

Apart from developing novel alkaline anion-exchange groups, the control of macromolecular structure is another effective strategy in enhancing AEMs' properties. Copolymers with additional compositions may produce extraordinarily high performances. Particularly, block copolymers with hydrophilic and hydrophobic segments, have the ability to produce well-defined phase aggregation micro-morphology due to the thermodynamic incompatibility between disparate blocks.[84] For PPO based copolymers, the attainment of PPO based block copolymers is a challenging task. Because the synthesis of PPO polymers involves a copper-amine complex catalyzed oxidative mechanism and macromolecular chains rearrangement easily occurs during the polymerization process.[85] Knauss et al. carefully designed the synthetic route by firstly polymerizing the more reactive monomer 2,6-diphenylphenol followed by 2,6-dimethylphenol (as depicted in Fig. 8).[86]

Table 2 Properties of PPO based di-block AEMs (data collected from Ref. 86)

Sample	P content (%)[b]	IEC (mmol/g)	WU (%)	Br^- Conductivity (mS/cm)		
				30 °C	50 °C	65 °C
P-b-M[a]	21	0.40	7.9	0.1	0.2	0.4
P-b-M	49	1.27	44	7.0 (47)[c]	15 (65)[c]	20 (74)[c]
P-r-M	21	0.15	19	0.1	0.3	0.6
P-r-M	48	1.35	34	0.4	1.6	2.6

[a] P: 2,6-diphenylphenol; M: 2,6-dimethylphenol.
[b] Calculated by mole percent of methyl substituted backbone protons relative to the total backbone protons by ^1H NMR.
[c] Hydroxide conductivity.

This study aimed at elucidating the influences of the second component and copolymer' structure on the resulting AEMs' performances. Both random and block copolymers with varied IECs were compared. As illustrated in Table 2, the block copolymers show higher conductivities than the random copolymers. In the block copolymers, the ion exchange groups are closely associated and potentially form more connective ion conducting channels.[87] The highest conductivity (in OH^- form) is 84 mS/cm at the following fabricating conditions: methyl substituted ratio=0.49, bromination degree=1.16, theoretical IEC=2.49 mmol/g.

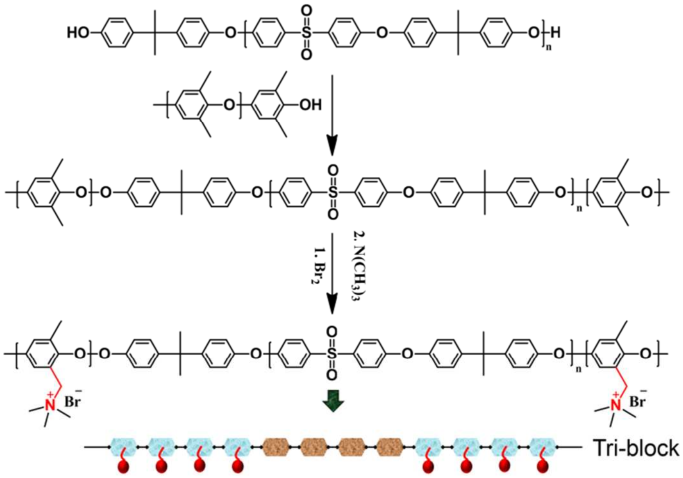

Fig. 9. Schematic illustrations for PPO based tri-block anion exchange membranes.

Tri-block copolymers are endowed with richer characteristics comparing to di-block copolymers.[88] PPO is sole among the aromatic polymers having a mono-functional end-chain, and this feature renders the preparation of fully aromatic tri-block copolymer possible.[89] Bai *et al.* developed a tri-block PPO based copolymer using hydroxy-terminated poly(arylene ether sulfone) (HO-PAES-OH) as the middle hydrophobic block and quaternized BPPO as the hydrophilic blocks (Fig. 9).[90] By SAXS techniques, a clear peak at around 0.2 nm^{-1} for the tri-block AEMs with different IECs was observed, indicating the existence of phase separation morphologies. Naturally, the AEM (IEC=2.43 mmol/g) attained a high hydroxide conductivity of 104 mS/cm at 60 ^{o}C.

Copolymers employing QA-type BPPO as a hydrophilic block is a promising strategy in promoting hydroxide conductivity. However, this research is still in the initial stages and thus further studies in depth such as adjusting the length of block are worth conducting. On the other hand, non-QA type block AEMs also need to be studied because the alkaline stability is still a major concern in most AEMs based electrochemical systems.

Thermal sensitive AEMs prepared from BPPO

For AEMs directly prepared from BPPO, further modification will enrich the membranes' functions. For example, a typical thermal sensitive monomer, N-isopropylacrylamide (NIPAAm) can be easily grafted onto BPPO base membranes using radiation-induced grafting.[91] During grafting stage, -CH$_2$Br groups produce radicals to initiate polymerization when exposed to ^{60}Co γ-ray radiation source. The residual -CH$_2$Br groups can be further functionalized using amine agents to form AEMs.[92] This study provides a new research direction where stimuli-responsive AEMs will be prepared to expand the scope of application involving the use of AEMs.

4. AEMs prepared from PPO derivatives through Friedel-Crafts acylation

AEMs prepared from chloroacetylation of PPO (CPPO)

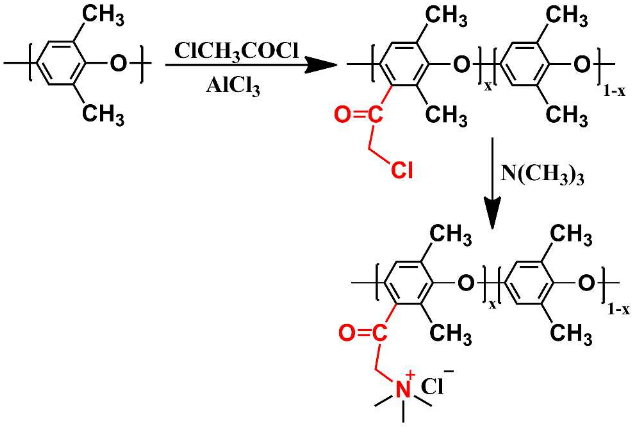

Fig. 10. Schematic illustrations for PPO based AEMs via chloroacetylation reation.

As discussed above, the bromination reaction provides a convenient and environmentally friendly method for the preparation of PPO-based AEMs without using hazardous materials such as CME. To continue the development of AEMs from the linear engineering plastic PPO, another novel method that is free of CME was explored to prepare AEMs in our lab as presented in Fig. 10. Chloroacetyl groups rather than chloromethyl groups linked onto the aromatic rings of PPO; the chloroacetylation of PPO (CPPO) was converted into QA-type AEMs by amination.[93] Chloroacetylation of aromatic polymers, acting as a simple and controllable way of preparing AEMs, is not restricted by the structure of aromatic polymers (side methyl groups are definitely not needed) and crosslinking side reaction can be avoided.[94,95]

Table 3 Chloroacetylation of PPO under Friedel–Crafts condition (data collected from Ref. 93)

Membrane series	PPO:CAC^{a}:AlCl$_3$ (mol:mol:mol)	Reaction Temp (^{o}C)	Substi -tution degree ^{b}(%)	Visual observation
1	1.00:1.00:0.50	40	22.3	cracked
2	1.00:1.00:0.75	40	31.2	cracked
3	1.00:1.00:1.25	40	63.2	good
4	1.00:0.50:0.50	40	32.9	cracked
5	1.00:0.75:0.75	40	33.2	cracked
6	1.00:1.50:1.50	40	71.8	fragile
7	1.00:1.00:1.00	20	37.5	cracked
8	1.00:1.00:1.00	30	44.9	Excellent
9	1.00:1.00:1.00	40	50.3	Excellent
10	1.00:1.00:1.00	50	70.6	fragile
11	1.00:1.00:1.00	60	83.5	fragile

a: 1,3-bis-chloroacetyl.
b: Determined by ^{1}H NMR.

To chloroacetylate PPO, PPO was treated with 1,3-bis-chloroacetyl (CAC) in the presence of a Friedel-Crafts catalyst. The chloroacetylation process depended largely on the quantity of the catalysts (anhydrous AlCl$_3$) and the reaction temperature. As shown in Table 3, at a given temperature, the substitution degree grows as the quantity of the increasing catalyst in the cases of equal molar ratio of PPO to CAC (1-3 in Table 3) or that of CAC to AlCl$_3$ (4-6 in Table 3). At a given ratio of reactants and catalyst (7-9 in Table 3), the substitution degree increases significantly with increased reaction temperature. However, not all the substitution degrees achieved are suitable for AEMs preparation. The results of membrane formation are qualitatively evaluated visually in the last column of Table 3. The subsequent amination process may also affect the properties of resulting AEMs. The optimal conditions of amination time=48-50 h, amination concentration=1.5 mol/L, and amination temperature=35-45 °C were established to obtain novel AEMs with satisfactory properties.

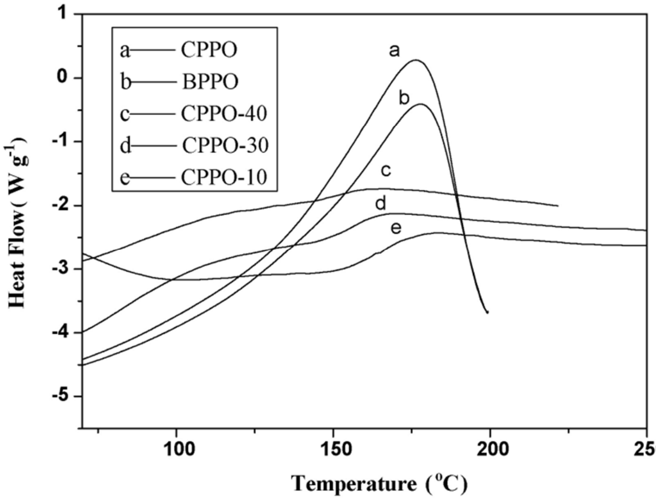

Fig. 11. DSC curves of CPPO/BPPO blend membranes. Ref. 96.

The AEMs directly prepared from CPPO often possess an extremely low WU due to the hydrophobic nature of the chloroacetyl groups. For CPPO based AEMs, the conductivity is usually low because the ion transport is assisted by water molecules and thus low WU generally leads to low conductivity.[97,98] Hence, it is necessary to ensure sufficient conductivity by blending CPPO with other highly hydrophilic materials. Owning to the identical backbone of BPPO and CPPO, functionalized BPPO can be expected to be a good choice for blending due to exceedingly high water sorption of QA type BPPO. BPPO with a benzylic substitution of 100% and CPPO with a phenylic substitution of 50.3% were mixed and then the base membranes were aminated with TMA.[96] Fig. 11 shows the glass transition temperatures (Tg) of the materials. It was reported that these blend membranes exhibited only one broad Tg peak regardless of CPPO contents, indicating the good compatibility between CPPO and BPPO.

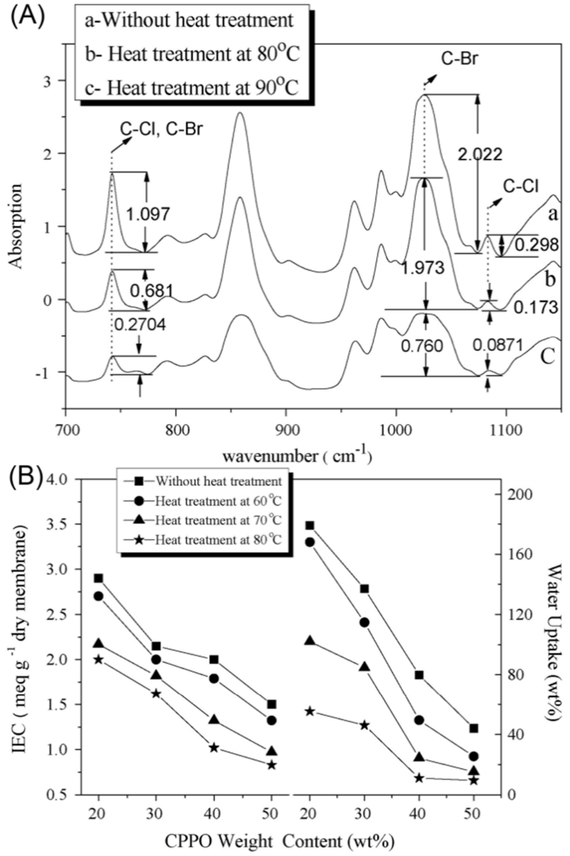

Fig. 12. (A) FT-IR spectra of (a) unheated CPPO-20 base AEM, (b) CPPO-20 base AEM heated at 80 ◦C for 1 h, and (c) CPPO-20 base AEM heated at 90 ◦C for 1 h; (B) IEC and water uptakes of CPPO/BPPO blend AEMs with different heat treatments. Ref. 100.

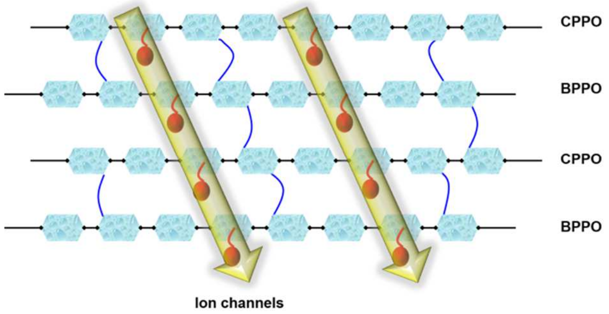

Fig. 13. Schematic for ordered hydroxide ion channels from CPPO/BPPO blending membranes with partial crosslinked structure.

Besides high conductivity, highly thermal and DS stability are required for practical applications. For this system, a partially crosslinked structure formed via a Friedel-Crafts reaction between the chloroacetyl groups and neighboring phenyl groups.[100] The crosslinking reaction was confirmed by using FT-IR spectra. When compared with the untreated AEMs, the intensities of peaks at 741 and 1082 cm^{-1} assigned to the C-Cl band and the overlapping bands related to C-Cl and C-Br respectively, decrease significantly after heat treatment (Fig. 12(A)).[101] The crosslinked structure formed via heating reaction can also be proved by IEC and WU measurements as shown in Fig. 12(B). Generally speaking, membrane conductivity normally decreases with crosslinking. However, the crosslinked membrane can maintain as high conductivity as that of untreated one. This can be explained by the inter-crosslinking leading to the ordered distribution of chloroacetyl groups and bromomethylated groups in the matrix, which will lead to a more ordered distribution of anion exchange groups (Fig. 13). According to the above studies, chlorocetylate PPO can also be functionalized by non-QA type groups.

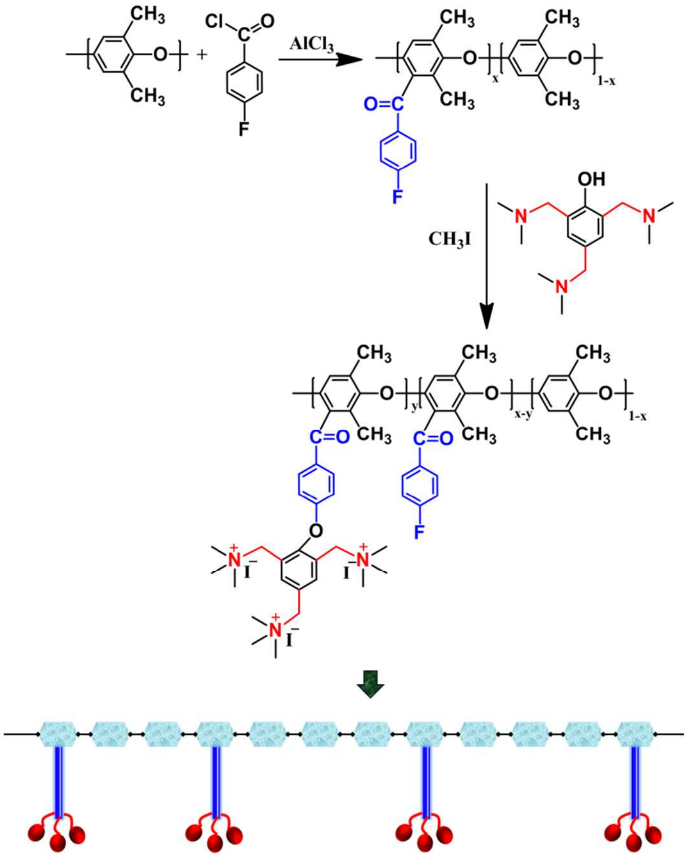

Fig. 14. Schematic illustrations for PPO based AEMs with tri-functional cations.

AEMs with tri-functional cations prepared from PPO derivatives

Apart from synthesizing typical AEMs, Friedel-Crafts acylation also plays roles in designing AEMs with novel structures. For most AEMs, one unit of polymer main chains generally links one functional group. IEMs with highly localized and dense ionic groups show more developed phase-separated morphology with well-interconnected ion transporting pathways, which has been well-documented in PEMs.[102] Recently, this design was realized with PPO polymers (Fig. 14). PPO reacted with 4-fluorobenzoyl chloride through Friedel-Crafts acylation reaction to obtain 4-fluorobenzoylated PPO. Then a novel tri-functional moiety, 2,4,6-tri(dimethylamineomethyl)-phenol (TDAP), was synthesized and grafted onto the PPO main chains by means of the 4-fluorobenzoyl units. The resulting AEM (IEC=1.50 mmol/g) displayed about 4 times higher conductivity than that of conventional quaternized PPO AEMs at 60 °C, suggesting tri-functional ammonium moieties can act as an advanced concept in designing AEMs . Moreover, alkaline stability was slightly improved. However, a clear mechanism explanation about alkaline stability was not given in this work. Future study on this system is worthwhile.

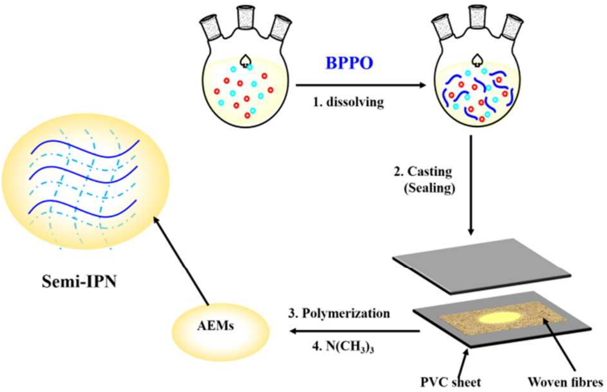

Fig. 15. Schematic for the solvent free strategy.

5. AEMs prepared from PPO derivatives through in-situ polymerization

For AEMs, a research objective is to prepare high performance AEMs via a simple, rapid, and non-toxic process. Although great efforts have been devoted to avoiding the use of carcinogen chloromethylation reagents to decrease the risks of producing AEMs, suitable fabrication strategy is urgently needed for large-scale industrial production. A non-solvent strategy for AEMs synthesis was explored by in-situ polymerization in our group.[103] As illustrated in Fig. 15, this method consists of four main steps: 1. dissolving aromatic polymers in proper monomers, 2. casting the solution on a substrate (non-woven fabrics), 3. polymerization, and 4. quaternization. Consequently, this route is especially environmental friendly because a large excess of solvent is not needed for polymer solubility and can be completely removed.

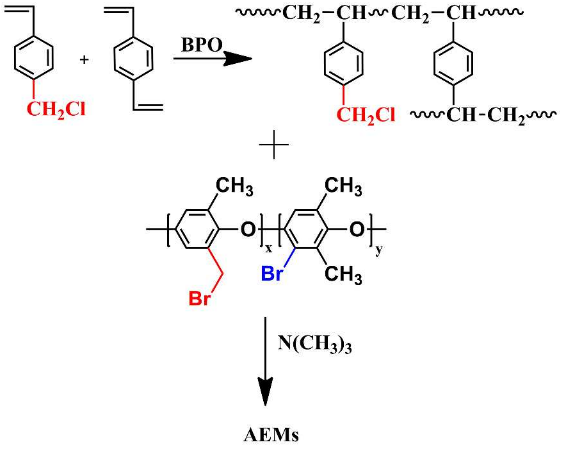

Fig. 16. Schematic illustrations for AEMs prepared from VBC and BPPO in-situ polymerization.

This new method has been proved feasible by using BPPO (polymer) - 4-vinylbenzyl chloride (VBC, monomer) - divinylbenzene (DVB, crosslinker). The BPPO was dissolved in a monomer mixture of VBC and DVB, and then in situ polymerization was conducted to incorporate BPPO into the network of poly(VBC–DVB) (Fig. 16), and formed a semi-interpenetrating polymer network (IPN).[103] Quaternization yielded the final AEMs. It should be stressed that this route is not only green but also controllable. The ratio of VBC and DVB can be adjusted. Generally, the quaternary amination process become harder with increasing crosslinking degree and thus IEC, WU, and hydroxide conductivity decrease. [104,105]

This green route for developing AEMs is not restricted to the BPPO-styrene system, that can be widely used for other (aromatic) polymers-(aromatic) monomers.[106,107] Hence, applying this method to PPO, CPPO, and BPPO deserves further research.

6. AEMs prepared from PPO derivatives by the sol-gel process

Organic-inorganic hybrid membranes combined the features of inorganic materials with those of organic ones.[108,109] A number of polymers can be incorporated with various functionalized inorganic meso-structured particles or an inorganic network.[110] The resulting membranes intrinsically possess the physical and chemical properties of both the inorganic and organic components. The sol-gel process allows a relatively easy incorporation of pure inorganic phase into an organic matrix with fine tuning of the inorganic network.[111] A sol is defined as a stable suspension of particles or polymers in a liquid, whereas a gel is obtained when interactions between species in the sol become extensive enough to immobilize the liquid.[112] This process allows tailoring of the materials by adjusting parameters such as the nature of the precursors, the ratio of the concentrations of precursor to organic solvent and water, and the final pH of the sol.[113] Originally, the method was used to prepare nanostructured organic-inorganic composite materials. Currently, it has been used to prepare inorganic-organic (hybrid) IEMs, including AEMs.

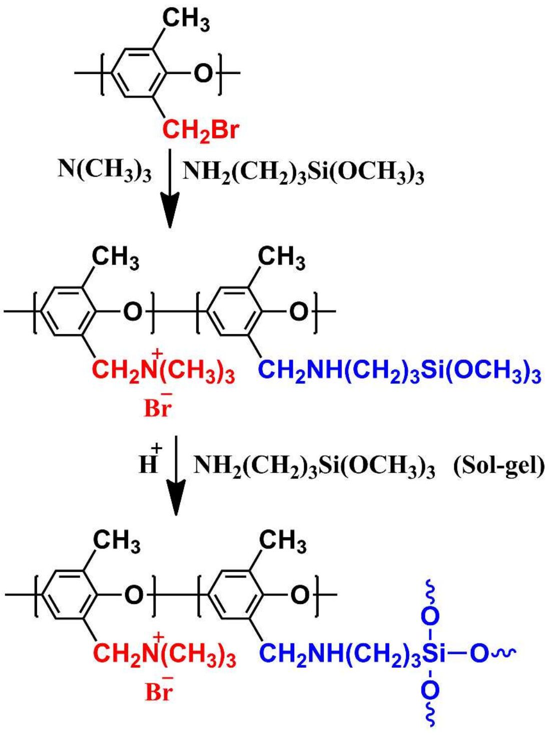

Fig. 17. Schematic for PPO based hybrid AEMs involving small molecule alkoxysilane.

As described above, the modification of PPO is well conducted for obtaining polymeric IEMs. [45,114] As shown in Fig. 17, a new hybrid membrane was obtained by introducing 3-aminopropyl-trimethoxysilane (APTS), together with TMA, into BPPO and then forming silica networks via the sol-gel process through further condensation and hydrolysis reactions with APTS. The AEM contained both weak base and strong base groups with total IEC values ranging from 2.5 to 3.0 mmol/g. Such AEMs may be applied in devices at higher temperature because the TGA curves indicated that the first decomposition temperature occurred at more than 300 °C.

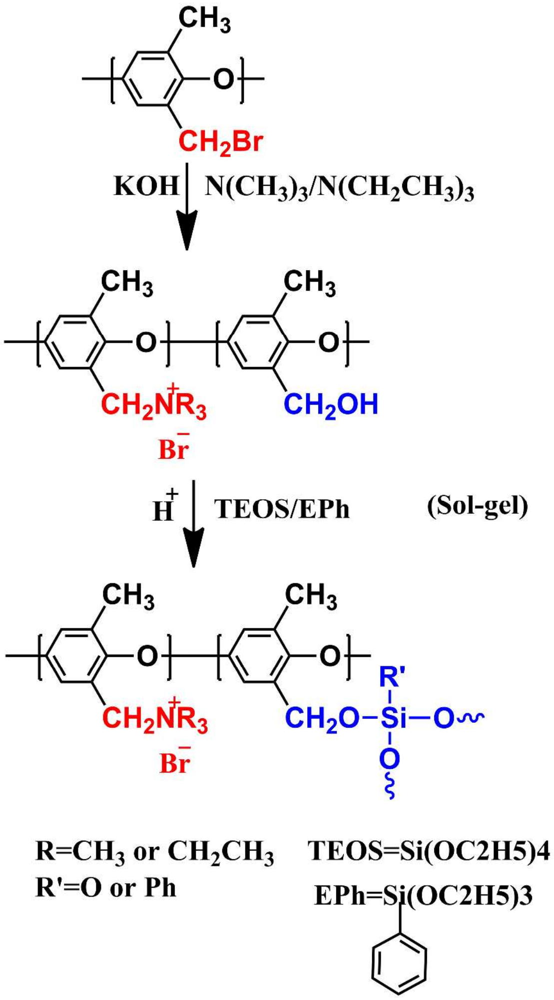

Fig. 18. Schematic of PPO based hybrid AEMs through hydroxylation treatment.

Another route for the preparation of PPO-based hybrid AEMs consists of three steps: partial hydrolysis, quaternization and a final sol-gel process (Fig. 18).[115,116] The sol-gel reaction was performed by addition of monophenyltriethoxysilane (EPh), tetraethoxysilane (TEOS), and H_2O at a controlled temperature.[117,118] The hybrid AEMs' properties, especially conductivity, can be adjusted by changing the inorganic silica component. The crosslinked Si-O-Si network may limit the mobility of the conductive ions and hinder the formation of connected hydrophilic ionic clusters and channels.[119,120] On the other hand, the Si-bound hydroxyl groups (-SiOH) bond strongly to the H_2O molecules and are thus favorable for water retention and ions transport.[121] By detailed comparisons, the

AEMs with 2.8-7.8% silica contents show the best performances with a hydroxide conductivity of up to 11 mS/cm at room temperature. In order to further increase the crosslinking degree and stability of hybrid AEMs, polyvinyl alcohol (PVA) was used and blended with the pre-quaternized BPPO; the -OH of PVA participated in the sol-gel process to form hybrid IEMs.[122] Apart from constructing a denser network, the incorporation of PVA increased the hydrophilicity and extended the range of applications.

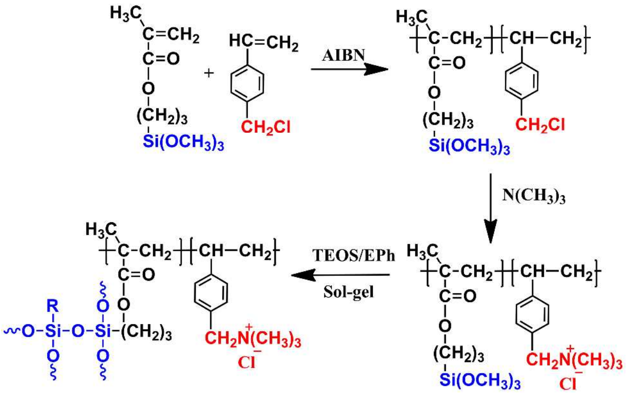

Fig. 19. Schematic illustrations for synthesis of multi-alkoxy silicon crosslinking agents.

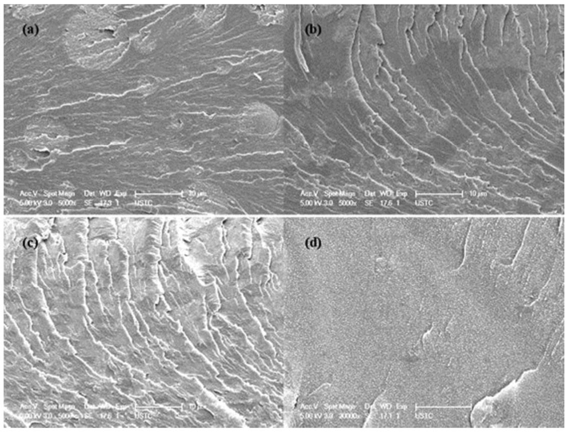

Fig. 20. SEM images of the BPPO and multi-alkoxy silicon crosslinking agent blended hybrid AEMs Ref. 123, Copyright 2012. Reproduced with permission from John Wiley and Sons.

Besides small molecule alkoxysilanes, hybrid precursors with reactive pendant alkoxy silane groups are also promising candidates for the sol-gel process.[124,125] Such hybrids are usually derived from the copolymer of organic monomer and organically modified alkoxysilane.[126] The multi-alkoxy silicon groups combined with the advantages of flexible polymers can be used for crosslinking during sol-gel reaction. Consequently, hybrid AEMs with enhanced compatibility between the organic phase and inorganic phase can be obtained. As illustrated in Fig. 19, hybrid AEMs were prepared by quaternizing the copolymer of VBC and γ-methacryloxypropyl trimethoxy silane (γ-MPS) (poly(VBC-co-γ-MPS)) and then reacting the copolymer with EPh or TEOS via the sol-gel process. However, the resulting hybrid IEMs were very brittle and thus woven fibers such as polyethylene terephthalate (PET), must be used as supporting materials. The resulting hybrid membranes displayed relatively low hydroxide conductivities of 0.227 to 0.433 mS/cm due to the incorporation of the hydrophobic supporting materials. With the aim of preparing free-standing hybrid AEMs, BPPO was mixed with poly(VBC-co-γ-MPS).[123] The blends were then quaternized prior to the sol-gel process. These hybrid AEMs possess the tensile strength (TS) and the elongation at break (E_b) in the range of 29.2-34.2 MPa and 7.7-11.1% respectively. They were flexible enough to be self-supporting membranes. From the SEM images of the blended hybrid AEMs (Fig. 20), homogenous membrane morphologies, without phase separation, were observed, suggesting the excellent miscibility between BPPO and poly(VBC-co-γ-MPS). As a result, these free-standing AEMs, produced from the blend of hybrid precursors and BPPO displayed higher hydroxide conductivities of 6.7-12 mS/cm, that are comparable to other reported polymeric AEMs.[128]

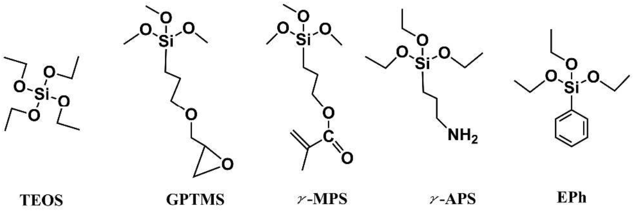

Fig. 21. Chemical structures of the organic silanes.

It is well known that hollow fiber membranes (HFMs) need to be self-supported without reinforcing materials.[129] For PPO-based hollow fiber AEMs, a heterogeneous sol-gel process can be employed to embed inorganic components into organic base materials.[130,131] The heterogeneous sol-gel process is similar to the above described homogeneous reaction. The special point is that the membranes' properties are closely related to the types of added silanes. BPPO was modified by five kinds of organic silanes: TEOS, γ-(2,3-epoxy propoxy)propyl-trimethoxylsilane (GPTMS), γ-aminopropyl triethoxysilane (γ-APS), EPh and γ-MPS.[129] The chemical structures of the five silanes, shown in Fig. 21, are diverse: TEOS has four alkoxy groups while the others have three; EPh has a phenyl group which is hydrophobic and γ-APS has a hydrophilic amino group; the epoxy or methacrylate group in GPTMS or γ-MPS is reactive and can be easily modified using a ring-opening or polymerization process.[132,133] Finally, the recommended choices are TEOS, EPh and γ-MPS, because the AEMs prepared from them presented more desirable properties: IEC (1.69-1.76 mmol/g), WU (63-72%) and TS (2.54-3.01 MPa).

It is widely accepted that achieving homogeneity is a main challenge in the development of hybrid membranes. However, there are few investigations about the micro-morphologies of as-prepared AEMs. The compatibility on the molecular level is not well proven. On the other hand, the interface between organic and inorganic phases should also be studied in detail, as it is crucial for the characteristics of hybrid membranes.

7. AEMs prepared from PPO derivatives through ATRP reaction

Recent efforts have been devoted to developing functional membranes by employing the ATRP technique.[134] Compared with conventional polymerizations, this technique shows a potential in designing materials with well-defined structures to achieve optimal properties. The essential characteristic of ATRP is the equilibrium between propagating radicals and dormant species, predominately in the form of initiating alkyl halides and macromolecular species.[135] BPPO is an effective macroinitiator for ATRP reaction, and has been applied for initiating the polymerization of 4-styrenesulfonic acid sodium salt (SSS) for the fabrication of PEMs.[136] The resulting poly(phenylene oxide)-*graft*-4-styrenesulfonic acid sodium salt (PPO-*g*-PSSS) membranes possess relatively low WU and high proton conductivities. The high performances can be explained by the architecture consisting of one hydrophobic main chain and several hydrophilic side chains.

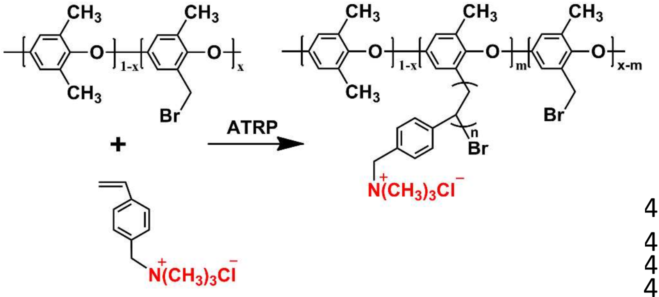

Fig. 22. Schematic illustrations for PPO based AEMs via ATRP.

Motivated by the molecular design of PEMs, well-defined poly(phenylene oxide)-*graft*-quaternary ammonium functionalized 4-vinylbenzyl chloride (PPO-*g*-QVBC) graft copolymers were synthesized for use as AEMs. The procedures are described below and the synthetic scheme is shown in Fig. 22.[137] The macroinitiator BPPO and quaternary ammonium functionalized 4-vinylbenzyl chloride (QVBC) were dissolved in the solvent before $CuBr_2$, ascorbic acid and 2, 2'-dipyridyl were added. The reaction temperature was controlled at 110 °C in a sealed tube for 24 h; the resulting PPO-*g*-QVBC copolymers were obtained by precipitating into anhydrous diethyl ether. Finally, the membrane was obtained by casting the copolymer solution. It is possible to control the number of grafts per PPO chain and the molecular weight of the graft by adjusting the bromination degree and ATRP conversion rate. Additionally, the macromolecular design can be expected to enhance alkaline stability, and can be used to adjust the membranes' properties by the careful selection of the graft copolymers.

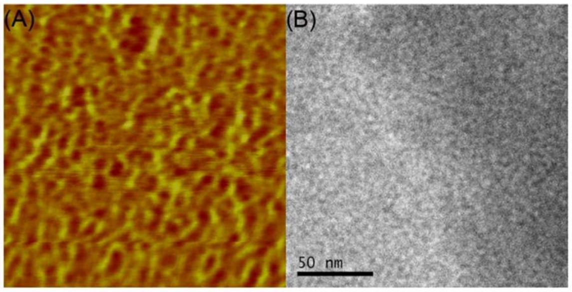

Fig. 23. (A) The AFM tapping phase images and (B) TEM images of PPO-*g*-QVBC AEMs. Ref. 137.

The resulting AEM (IEC=1.99 mmol/g) shows a considerably high conductivity of 39 mS/cm at 20 °C, and this value was well above that of a QPPO AEM with similar IEC. The interconnected ion conducting pathways, derived from the graft architecture, is responsible for the attainment of the high conductivities. The hydrophobic-hydrophilic phase separation micro-morphology of the AEM designated B-*g*-Q-1.5 was detected by AFM (Fig. 23(A)) and TEM techniques (Fig. 23 (B)); a wormlike and inter-connected hydrophilic network nano-channels, spreading over the overall field of view was clearly observed.

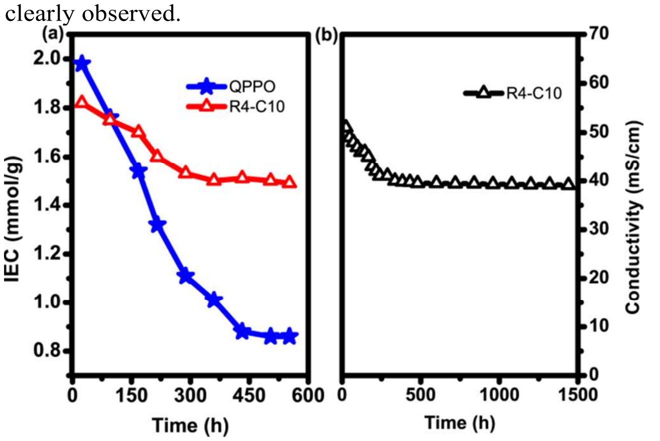

Fig. 24. (a) The changing trend in IEC values of QPPO and PPO-*g*-QVBC (rod-coil type) membrane, and (b) hydroxide ion conductivities of PPO-*g*-QVBC (rod-coil type) AEM after immersion in 2 mol/L NaOH at 60 °C. Ref. 138.

For AEMs, alkaline stability is of particular importance. The chemical stability of AEM originating from the 'grafting from' BPPO copolymers was comparable to main-chain-type AEMs bearing QA group, but was not as elegant as expected. The improvement in alkaline stability from the viewpoint of molecular design is an effective strategy. It has been reported that when a QA cation is affixed to the benzyl position, the degradation of the polymer backbone is triggered at the ether position.[139] It was deduced from the above finding that using low graft density as possible will reduce the adverse influences of the functionalized grafts on the backbone. PPO-*g*-QVBC copolymers with a low graft density and long side chains (rod-coil type) were obtained.[138] As shown in Fig. 24, the IEC of PPO-*g*-QVBC remains at ~80% of the initial value after 550 h testing in 2 mol/L NaOH at 60 °C, while the IEC of QPPO declines to about 40% of the initial value under identical stability testing conditions. More importantly, QA-type AEMs are more readily obtained relative to AEMs containing other stronger alkaline groups.

In fact, the study of PPO-based graft AEMs represents a novel direction in the field of AEMs. To date, this structure has not been widely used for other polymers. It is predicable that many efforts will be devoted to this topic in the future.

8. Applications of AEMs through PPO derivatives

Interests in the synthesis of materials containing alkaline functional groups, an increasingly important theme in the development of AEMs, are being driven by the desire to prepare advanced AEMs with high performances, such as high conductivity, and high thermo-chemical stability. For AEMs, the combination of polymer and cationic group chemistries usually play vital roles in determining the final AEMs' properties. PPO has been used to form AEMs using the strategies discussed in the above section. Similar to existing AEMs, PPO-based AEMs can be applied to separation, energy conversion, and other processes. The following section is a review of current studies on the application of PPO-based AEMs.

Diffusion dialysis (DD)

Diffusion dialysis (DD), using IEMs is a separation process driven by concentration gradients.[140] AEMs are usually employed in DD for acid recovery. For example, waste solution containing acid ($FeCl_2$/HCl) is placed on one side of the AEMs, while pure water is on the other side. The anions transport to the water side due to the concentration difference between the two sides separated by the AEM. Meanwhile, according to the principle of electrical neutrality, positively charged ions also pass through the AEM along with the anions. The H^+ ions diffuse more easily compared with Fe^{2+} ions, ascribing to their small size, high mobility and low valence state.[141] For such DD processes, AEMs must exhibit high flux and selectivity, which are reflected by the dialysis coefficient of acid (U_H) and separation factor (S), respectively.

PPO based AEMs have been successfully used for DD process and act as candidates for providing progressive insights into the relationships of the intrinsic characteristics of the AEM and DD performances. The PPO was brominated to varied degrees at the benzylic and aryl positions, and subsequently treated with amine agents.[49] The DD results indicate that WU and C_R, - are two significant parameters influencing the DD process - a higher WU favors the diffusion of ions, while a lower C_R decreases electrostatic repulsion of the AEM to the cations.

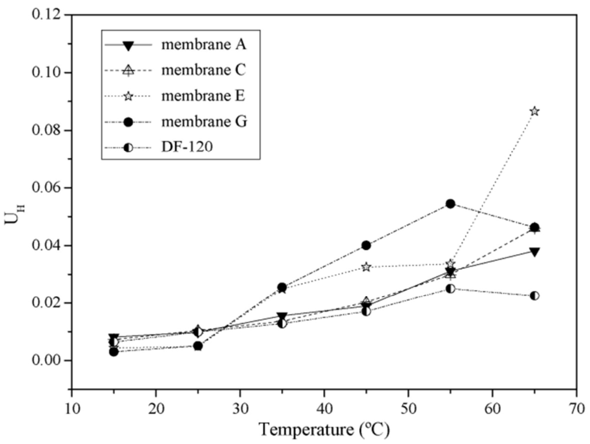

Fig. 25. Dialysis coefficients for the DD of hydrogen chloride (HCl) with hybrid membranes A, C, E, G and commercial DF-120 membrane vs temperature. Ref. 116.

PPO hybrid membranes have been successfully applied to DD.[116] The DD results of these silica containing AEMs were similar to those of the commercial membrane DF-120 at low temperature. However, the advantages of using the PPO-SiO_2 hybrid membranes were particularly obvious when testing temperatures were increased gradually. The micro-phase separation between the silica and BPPO components was the principle reason for this phenomenon. The interphase between the two phases gradually developed at higher temperatures, which strongly supported H^+ ions transport. The effect of phase separation is also evident from DD results of AEMs containing different silica contents. As illustrated in Fig. 25, the silica contents increase gradually from AEM A to G (PPO-SiO_2 hybrid membranes, which are produced from hydroxylation, quaternization and sol-gel reaction of BPPO), and the AEMs with more silica seemed more prone to be affected by temperature. For this system, the DD properties are further improved by adding PVA, because the -OH groups can interact with H^+ to assist its transport.[122] With the variation of PVA contents, the U_H values of HCl were in the range of 0.021 m/h - 0.049 m/h, while the S values were in the range 39-26. This result suggests the potential of PPO based hybrid AEMs for DD application.

Table 4 The properties of AEMs and related fuel cell data (collected from Ref. 73, 75, 81, 142)

Membrane	IEC (mmol/g)	Conductivity (mS/cm)	Testing Temperature (°C)	OCV[a] (V)	PPD[b] (mW/cm^2)
DIm-PPO	2.38	40 (30 °C)	35	0.99	40
MIm-PPO	2.40	32 (20 °C)	50	0.89	30
BIm-PPO	2.21	37 (25 °C)	35	0.82	13
GPPO	2.69	71 (r.t.)	50	0.95	16

a open circuit voltage.
b peak power density.

Alkaline polymer electrolyte fuel cells (APEFCs)

Alkaline polymer electrolyte fuel cells (APEFCs) using a hydroxide conducting polymer as a solid electrolyte is expected to be one of the more promising clean energy conversion techonology.[97] For APEFC technology, several challenges identified are caused by two key fuel cell components: electrocatalysts and AEMs. Two main disadvantages of AEMs are low hydroxide conductivity and low chemical stabilities in hydroxide form.[143] To address the above issues, BPPO based AEMs have been widely developed for APEFCs applications. The design strategies mainly lie on the cationic chemistries and the macromolecular architecture, with the aim of improving OH^- conductivity and chemical stability. By assessing fuel cell properties, these BPPO-based materials display potential in APEFs applications.

As described in part 3.3, alternative cationic groups render the enhancements of OH^- conductivity and alkaline stability. The fuel cell related properties of AEMs with different cationic groups are summarized in Table 4. As shown in this table, DIm-PPO membrane with an IEC value of 2.38 mmol/g in a H_2/O_2 fuel cell test exhibits an open circuit voltage of 0.99 V and a peak power density of 56 mW/cm^2. However, this performance does not do justice to the high ex-situ properties reported. Besides the AEM's properties, the cell behavior is also affected by the activity of catalysts, the performance of the ionomer in the electrodes' catalyst layers, and the MEA fabrication procedure. The alkaline ionomers used during these tests are QA-type and so not expected to be chemically compatible with the imidazolium head-group chemistry of the AEM. In addition, comparisons among AEMs with different head-groups are currently meaningless due to inconsistent testing methods used in different studies. Even so, the fuel cell performances achieved to date indicates the BPPO is a good choice for preparing AEMs for fuel cell applications.

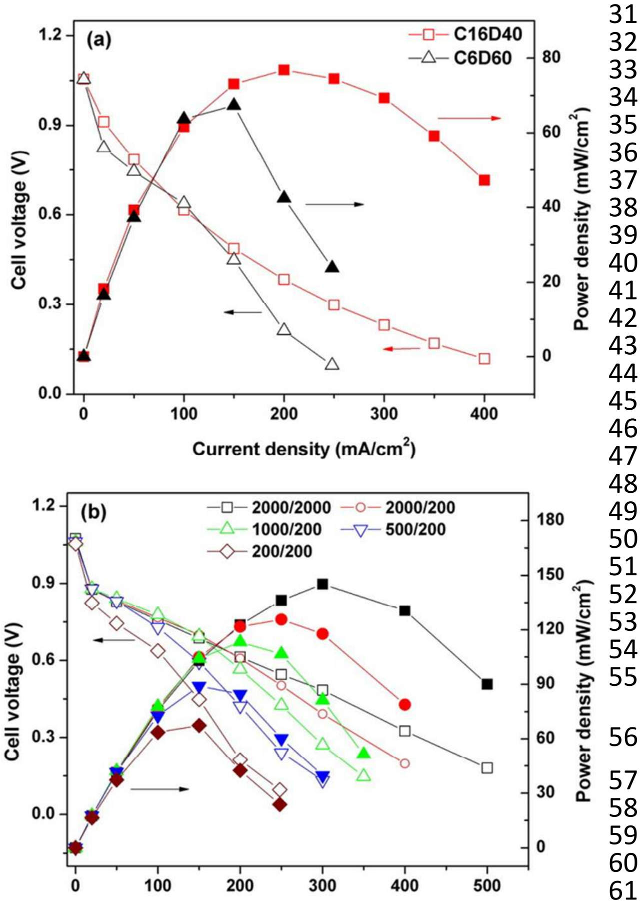

Fig. 26. Polarization curves and power density curves of an AEMFC at 60 °C: (a) with the CyDx ionomer with H_2/O_2 flow rate of 200/200 cm^3/min and (b) with the C_6D_{60} ionomer with different H_2/O_2 flow rates Ref. 55, Copyright 2013. Reproduced with permission from the American Chemical Society.

Another limitation for APEFCs is the lack of a soluble ionomer that can be used in the catalyst layer to construct an efficient three-phase boundary.[144] There is no doubt that the ionomer should be of high hydroxide conductivity and alkaline stability. Recently, good fuel cell results have been obtained by using PPO-based comb-shaped polymers as alkaline ionomers. In Fig. 26, the open circuit voltages (OCVs) are close to the theoretical value at about 1.1 V, and the highest peak power density was 77 mW/cm^2 and 67 mW/cm^2 when using $C_{16}D_{40}$ and C_6D_{60} ionomers respectively. These results suggest the importance of structure design, where the difference in length of the pendant alkyl chains lead to disparate properties. More fuel cell systems using this kind of ionomers should be assembled to evaluate the universality of the application of such ionomers. It is anticipated that PPO based ionomers can be developed as standard ionomers for APEFCs.

Drug delivery

IEMs have been successfully explored for controlling ionized drug delivery, and are especially beneficial for rate-limiting delivery due to their permselectivity.[145] The ion containing HFMs exhibit low toxicity, large effective surface area, and high IEC, which are particularly attractive for drug delivery. PPO was chosen as the base material for the preparation of anion exchange HFMs, since it is easy to be handled and to be charged. As described in section 6, the hybrid HFMs from BPPO and γ-MPS aiming at controlling the release of sodium salicylate (NaSA) were prepared.[131] The membranes lead to a high drug loading efficiency (28.4%) and a relatively low release rate (drug delivery in 7 days under physiological condition: 51.9%). This system was proposed for the study of the possible mechanism by using four model drugs which displayed different physicochemical characteristics such as molecular weight, pKa, and hydrogen bonding capacity. The results suggest that apart from the electrostatic interactions, the non-electrostatic interactions (hydrophobic interactions and hydrogen bonding) are also key factors influencing the controlled delivery of drugs.

Apart from conventional release, AEMs can also be used for a thermally controlled drug delivery system. The controlled delivery process can be achieved by using a PPO-based AEM endowed with grafted PNIAAm chains, as depicted in section 3.5. At temperatures below 32 °C, PNIPAAm chains extend due to the hydrogen bond formation between the hydrophilic segments in the side chains of the polymer and water. Above the 32 °C, the hydrogen bonding decomposes, and the intrinsic affinity of PNIPAAm chains dominates, causing an abrupt collapse.[146] When using thermal responsive AEMs, the permeability coefficient of the drug showed an obvious temperature dependency for the controlled delivery of NaSA.[92]

Adsorption

Cationic HFMs are usually efficient in absorbing charged biomacromolecules, drugs and industrial wastes, due to the high surface-to-volume ratio in comparison to flat membranes.[147] In this area, PPO-based hybrid HFMs present excellent performances. When using bovine serum albumin (BSA) as a model protein, they exhibited adsorption-washing-elution cyclic behaviour in the permeation mode, while the elution percentage can reach about 95%.[126]

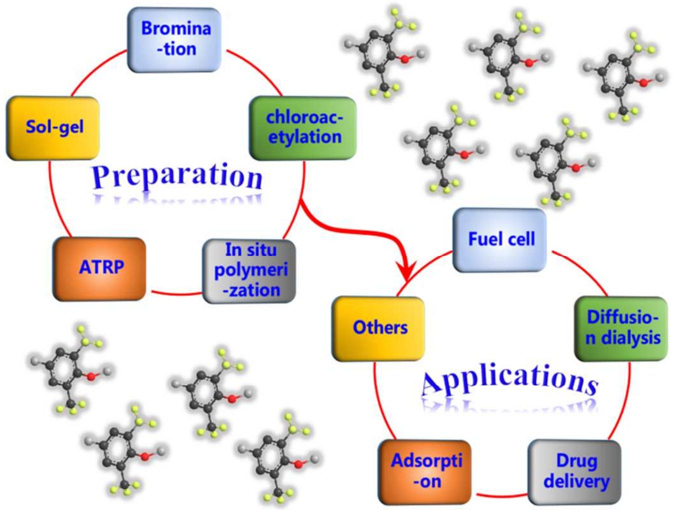

Fig. 27. Schematic illustration for the summary of this review.

Conclusions

We have focused on the design, synthesis and properties of PPO based AEMs (Fig. 27). This min-review demonstrates that the use of PPO opens up opportunities for designing versatile AEMs. Effective synthesis strategies currently employed include: (1) Bromination, (2) Friedel-Crafts acylation, (3) In situ polymerization, (4) Sol-gel, (5) ATRP.

The studies facilitate the better understanding of the relationship between structures on the micro-scale and properties on the macroscopic scale for developing PPO based AEMs. On this basis, it is possible to obtain novel PPO based AEMs by utilizing the reported designs or developing other routes to meet the various requirements. What should be emphasized is that such strategies are not restricted to PPO and can be extended to other aromatic polymers.

The PPO-based AEMs have successfully applied in various membrane relevant systems such as fuel cells, diffusion dialysis, and adsorption. More extensive applications using the PPO-based AEMs should be investigated. It is reasonable to expect that such AEMs will play significant roles in the broad range of energy-related technologies including redox flow batteries, reverse electrodialysis cells, and biological electrochemical systems.

In summary, PPO is a valuable polymer system in the field of AEMs. Studies into preparing and applying PPO based AEMs deserve further efforts. We hope that advanced PPO AEMs with properties comparable to Nafion will be completed in the future.

Acknowledgements

We thank the financial supports from the National Basic Research Program of China (No. 2012CB932802), the National Natural Science Foundation of China (Nos. 21490581, 51273185, 21106140) and National High Technology Research, Development Program 863 (2012AA03A608), and the Fundamental Research Funds for the Central Universities (WK 2060190038). The special thanks will be given to Erigene Bakangura for his kind proof-reading the manuscript.

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