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Comparison of different quaternary ammonium groups on desalination performance of BPPO-based anion exchange membranes

Muhammad Imran Khan[a,b]

[a]*School of Chemistry and Material Science, University of Science and Technology of China, Hefei 230026, Anhui, China, emails: raoimranishaq@gmail.com*
[b]*Fujian Institute of Research on Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, Fujian, China*

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ABSTRACT

In this work, brominated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) backbone was quaternized with four different amines such as pyridine (PYR), dimethylethanolamine (DMEA), trimethylamine (TMA) and methylpyrrolidine (MP) for preparing anion exchange membranes (AEMs). The successful reaction between BPPO and amines was confirmed by Fourier transform infrared (FTIR) spectroscopy. The influence of quaternary ammonium groups on the membranes properties such as ion-exchange capacity, water uptake (W_R), linear expansion ratio, thermal stability, mechanical stability, transport number and area resistance of prepared AEMs was investigated in details. The morphology of prepared AEMs was observed by scanning electron microscopy. The effect of quaternary ammonium groups on performance of AEMs in the desalination of NaCl from aqueous solution was evaluated at a lab-scale electrodialysis stack under same experimental conditions and compared with each other in term of current efficiency, energy consumption and flux of salt. The results showed that pyridinium-based membrane (BPPO-PYR$^+$) exhibits higher desalination performance than other membranes under identical experimental conditions.

Keywords: BPPO; Quaternary ammonium groups; Anion exchange membrane; Water uptake; Electrodialysis

1. Introduction

To fulfill the requirement for a more reliable high quality water supply and other basic needs due to increased population and pressure for both consumptive and nonconsumptive uses, desalination is a technique of interest in many countries. But desalination technique alone cannot deliver optimum quantity of clean water supply. The capacity to make the best use of desalination is a concerning matter at present time for a number of water-related researchers. The most common desalination process employed is distillation and membrane-related processes [1]. Historically, though distillation technologies have dominated the seawater desalination market in the past decades, due to its disadvantages such as high cost, the newest desalination plants are using membrane technologies instead of distillation technique now. The quality of feed water is one of the determining factors in deciding the type of membrane process to employ [1,2]. In membrane-based desalination technology, the used electric energy consumption is almost the same or lower than distillation and it needs not any thermal energy. The membrane-based electrodialysis (ED) process was mostly employed for production of quality water through desalination process. The energy consumption employed for the process depends on the salinity of the feed water. Membrane-based ED processes have considerable advantages in desalting brackish water and are used over a wide range salinity concentration levels from brackish to seawater [1,3].

Ion-exchange membranes (IEMs) are one of the most advanced separation membranes which play an important role in an increasing number of processes in both chemical and biochemical industry. They are widely studied and utilized as active separators in various electrically driven processes such as ED for desalting brackish water reconcentrating brine from seawater and production of table salt. In such processes,

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the ion interactions with membranes, water and with each other occur in complex fashions. Therefore, the knowledge of physico/chemical properties of IEMs is a major contributing factor behind decisions about their applicability in specific separation processes at different operating conditions [4–9]. They are usually divided into anion/cation exchange membranes based on the functional groups. Anion exchange membranes (AEMs) permit only the transportation of anions instead of cations and thus they play an important role in processes including electrodialysis, electro-membrane reactor, diffusion dialysis and chloralkali [10–13]. However, their permselectivity is important to investigate the efficiency of AEMs in electro-membrane-based separation process [13–15]. Hence highly selective and chemical/thermal/oxidative stable AEMs are required for above mentioned processes.

Several polymers backbones such as polystyrene [16–18], polysulfone [19], polyether imide [20], poly(arylene ether) [21], poly(phthalazinone ether ketone) (PPEK) [22] and poly(phthalazinone ether sulfone ketone) (PPESK) [23] have been employed in the development of AEMs. First, the chloromethylation of these polymers was carried out and thereafter converted for distinct AEMs applications such as in fuel cell [24], biomedical devices [25,26], pervaporation [27], solid-state polypeptide synthesis [28], etc. Chloromethylation process was carried out by using chloromethyl ether (CME) as main reagent. However, CME is highly dangerous for human health and is a banned chemical [15,29,30]. Much attention has been paid for the development of AEMs without employing CME to remove the above discussed issues. Bromination of benzylmethyl and chloroacetylation of phenyl are known to be favorable method for the elusion of CME [31–33]. Polymers namely benzylmethyl-containing polysulfone [33,34], poly(phenylene) [35] and poly(arylene ether ketone) [36] have been utilized to get AEMs via bromination and subsequent quaternization. This approach has, however, not been misused in the development of intermolecular AEMs which have outstanding strength and magnificent for discrete applications [37,38].

In the view of above discussed issues, we have selected brominated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) as polymer backbone for the present research work because it is free from chloromethylation reaction to develop AEMs. The hydrophobic surface of BPPO membranes can be easily modified by grafting hydrophilic materials to get hydrophilic surface. AEMs developed from BPPO backbone exhibited excellent thermal, chemical and mechanical stability which is essential for ED applications [13,39]. Compared with other polymers such as poly (ether sulfone), polysulfone and poly (vinylidene) fluoride, BPPO contains abundant –CH_2Br functional group which can react easily with amines without penetrating base membrane and use of cross-linkers [13,40]. Moreover, BPPO is well known to be a stable polymer and very much susceptible for the nucleophilic attack [13].

In the present work, a series of AEMs were prepared from BPPO with different quaternization reagents such as pyridine, dimethylethanolamine, trimethylamine and N-methylpyrrolidine. The physico-chemical properties of developed AEMs were studied in detail. The major aim of this work is to find the optimum tertiary ammonium group for BPPO-based AEMs in term of desalination performance. The effect of quaternary ammonium groups on the desalination performance of AEMs was investigated carefully and compared with each other in term of current efficiency, energy consumption and flux of salt.

2. Experimental

2.1. Material

BPPO with aryl substitution degree of 0.48 and benzyl substitution degree of 0.52 was supplied by Tianwei Membrane Co. Ltd., Shandong, China. Its degree of bromination was proved by ^{1}H NMR as represented in Fig. 1. Pyridine, dimethylethanolamine, trimethylamine, N-methylpyrrolidine, N-methyl-2-pyrrolidone (NMP), silver nitrate ($AgNO_3$), potassium chromate (K_2CrO_4), sodium chloride (NaCl) and sodium sulphate (Na_2SO_4) were kindly supplied by Sinopharm Chemical reagent Co. Ltd, Shanghai, China. These chemicals were used as received. Deionized (DI) water was used throughout the work.

2.2. Fabrication of anion exchange membranes

The polymer membranes were prepared by solution-casting method as reported in our previous work [13,39,41,42]. In a typical procedure, BPPO was dissolved into N-methyl-2-pyrrolidone (NMP) solvent to obtain 8% solution. Measured amount of pyridine, dimethylethanolamine, trimethylamine and methylpyrrolidine was added into casting solution according to Table 1 to achieve AEMs with different quaternary ammonium groups. The mixed solution was stirred overnight at 40°C. After that it was poured onto glass plate and dried at 60°C in air for 1 d. The membranes were peeled off from glass plate, washed with DI water, and then stored in water. The prepared membranes are named as BPPO-PYR$^+$, BPPO-DMEA$^+$, BPPO-TMA$^+$ and BPPO-MP$^+$. Chemical structure of the prepared AEMs is also shown in Fig. 2.

2.3. Characterizations

2.3.1. Instrumentations

Fourier transform infrared (FTIR) analysis of dried membranes was carried out by using attenuated total reflectance (ATR) with FTIR spectrometer (Vector 22, Bruker, Massachusetts, MA, USA) in the range of 4,000–400 cm^{-1}. The morphology of membranes was investigated by field emission scanning electron microscope (Sirion200, FEI Company, USA). Thermal stability of membranes was studied by using TGA-50H analyzer (Shimadzu) under nitrogen flow with a heating rate of 10°C/min within temperature range of 25°C–700°C. A tensile test by Q800 dynamic mechanical analyzer (TA Instruments, Kyoto, Japan) was used to investigate mechanical stability of membrane in wet state. This test was carried out 3–4 times for each sample in wet state and average values have been reported.

2.3.2. Ion-exchange capacity

Ion-exchange capacity (IEC) of prepared membranes was calculated by classical Mohr's method as reported in our previous work [13,39,41–43]. In this typical procedure, first-dried membrane samples were immersed in 1 M NaCl solution for

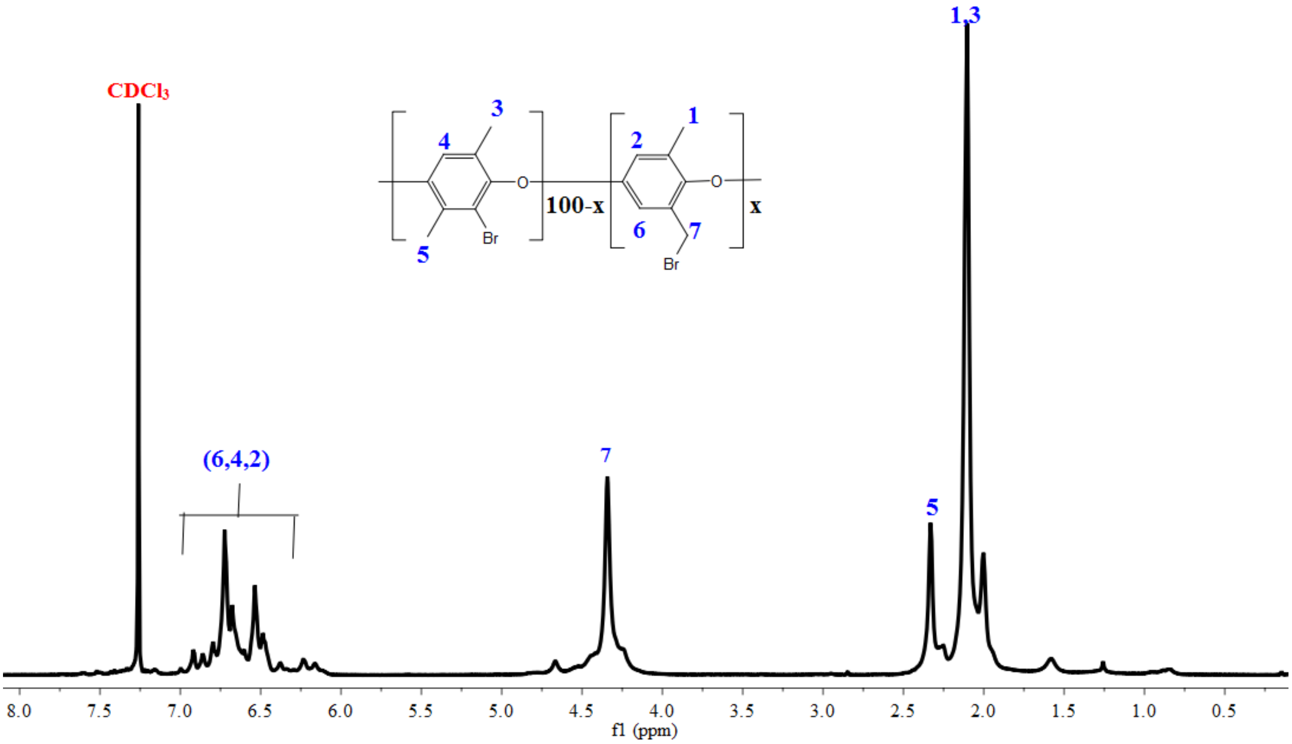

Fig. 1. ^{1}H NMR spectra of BPPO.

Table 1
Composition of AEMs with different tertiary ammonium groups

Membranes	BPPO (g)	Amine (g)
BPPO-PYR$^+$	0.8	0.108
BPPO-DMEA$^+$	0.8	0.124
BPPO-TMA$^+$	0.8	0.078
BPPO-MP$^+$	0.8	0.117

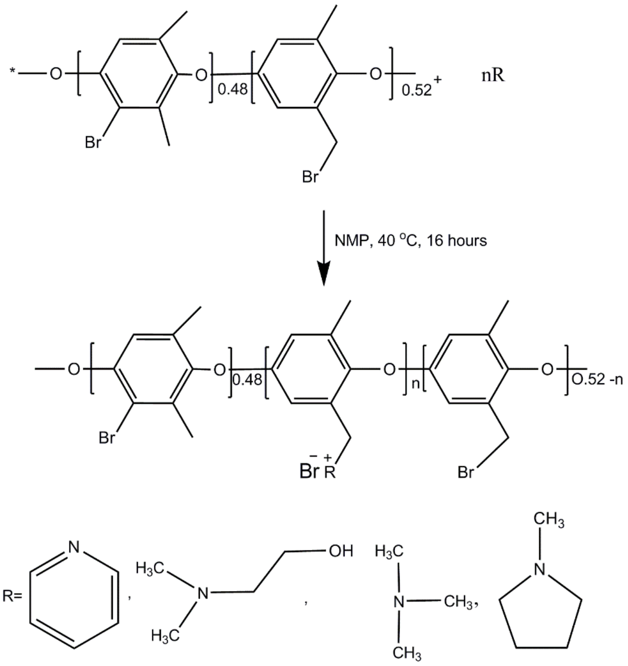

Fig. 2. Preparation of anion exchange membranes.

48 h to change charge site from Br$^-$ to Cl$^-$. After that membrane samples were washed with DI water to remove excess NaCl from them. Then, the washed samples were put into 0.5 M Na_2SO_4 for 48 h. The released Cl$^-$ was measured by titration with $AgNO_3$ solution employing potassium chromate as an indicator. It was measured using following equation:

$$\mathrm{IEC} = \frac{VC}{W_{dry}} \tag{1}$$

where W_{dry} is the weight of membrane sample in dry state, V and C are the volume and concentration of $AgNO_3$, respectively.

2.3.3. Water uptake and linear expansion ratio

Water uptake refers to the amount of water per unit weight of membrane sample. It was measured through the weight difference of dry and wet membrane sample. Membrane was dipped into DI water for 24 h and wet weight was measured after removal of surface water by absorbing paper. After drying at 60°C for 12 h, the weight of dry membrane was again recorded. Water uptake was measured by using the following equation [13,39,41–43]:

$$W_R = \frac{W_{WET} - W_{DRY}}{W_{DRY}} \times 100\% \tag{2}$$

where W_{WET} and W_{DRY} are the weights of wet and dry membranes, respectively.

The linear expansion ratio (LER) of prepared membranes was recorded at room temperature. For this, the membrane sample was cut into a (2*2) cm^2 pieces and LER was measured from the following equation [13,41]:

$$\mathrm{LER} = \frac{(L_{\mathrm{WET}} - L_{\mathrm{DRY}})}{L_{\mathrm{DRY}}} \times 100\% \tag{3}$$

where L_{WET} and L_{DRY} are the lengths of wet and dry membranes, respectively.

2.3.4. Ionic resistance of membrane

The ionic resistance of prepared membrane was measured according to our previous reported method [13,39]. In a typical procedure, it was measured by commercial cell-assembly (MEIEMP-I, Hefei Chemjoy Polymer Material Co., Hefei, Anhui, PR. China) composed of five cells under a constant current mode. The effective area of membranes was 7.07 cm^2. Prior to the measurement of ionic resistance, the prepared membrane was equilibrated in 0.5 M NaCl solution for 24 h at ambient temperature. The membranes were taken out from solution and viscid solution was wiped off. The membrane was tightly sandwiched between electrodes. After this, 0.3 M Na_2SO_4 solution was given to the electrodes cell whereas 0.5 M NaCl solution was given to the central electrode. The ionic resistance of membrane was measured by DC power supply (Shekonic, Yangzhou Shuanghong Co., Ltd.) provide constant current and digital multimeter (model: GDM 8145, Good Will Instrument Co. Ltd., Taiwan) measure potential between the electrodes at room temperature.

2.3.5. Membrane transport number

The transport number of AEMs was measured by two compartment cell made of Perspex sheet of effective membrane area 7.07 cm^2 as reported in previous work [13,39]. The concentrations of NaCl into two compartments were 0.01 M and 0.05 M, respectively. The transport number was calculated from the following equation [11,44,45]:

$$E_m = \frac{RT(2t^- - 1)}{nF} \ln\left(\frac{C_1}{C_2}\right) \tag{4}$$

where n is the electrovalence of counterion ($n_i = 1$ in this case), R is the gas constant (8.314 J/K mol), F is the Faraday constant (96,487 C/mol), t^- is the transport number, T is the absolute temperature (K), C_1 and C_2 are concentrations of NaCl solution in the testing cell.

2.3.6. Desalination by electrodialysis

The desalination performance of prepared AEMs was investigated according to the previous reported method [13,39]. The setup employed here is depicted in Fig. 3. It is made up of an anode and a cathode of stainless steel sheets coated with platinum. It has six electrode compartment separated by two CEMs and three AEMs. Each electrode compartment provides an effective area of 7.0 cm^2 to the membrane. Prepared AEMs were used in desalination experiments. This experiment was performed under constant current density of 28.60 mA/cm^2. The feed solution of NaCl with starting concentration of 0.1 M was circulated at 25 mL/min through each compartment. The electrode compartment were circulated with 0.3 M Na_2SO_4 solution at 25 mL/min to prevent

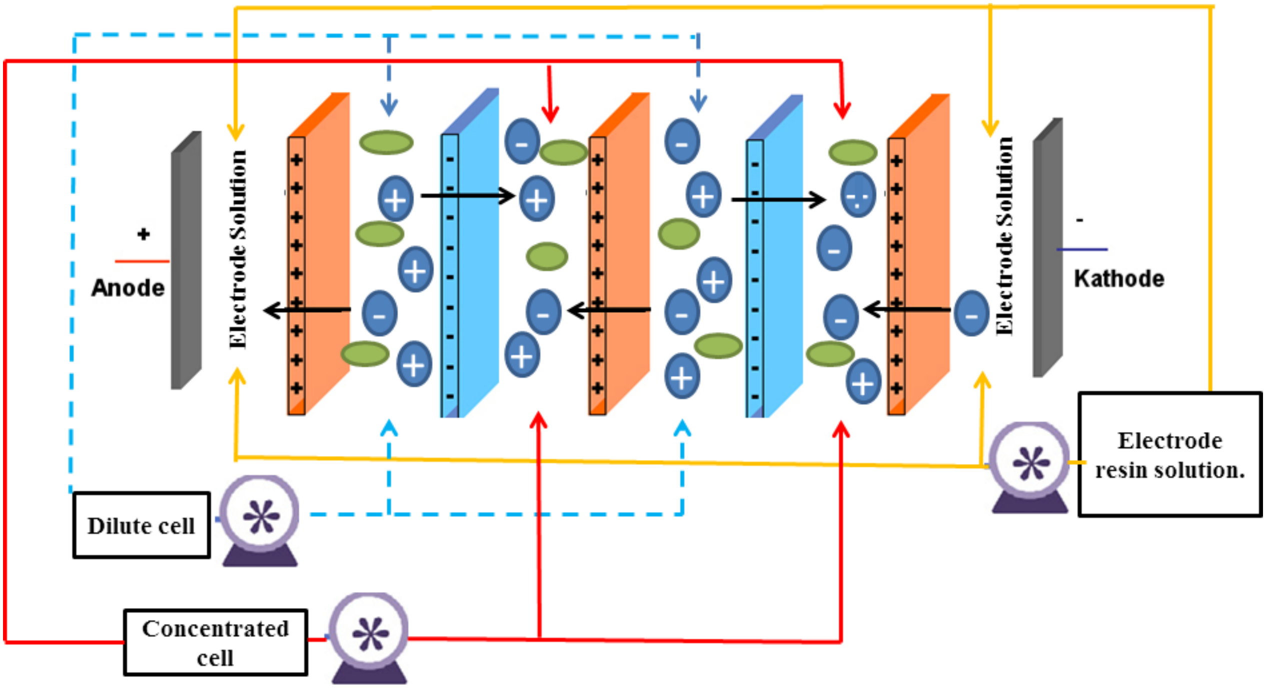

Fig. 3. Schematic setup of ED stacks.

pH change. The salt concentration was measured by conductivity meter after specific time interval. The performance of developed AEMs was compared with each other in terms of flux of salt, current efficiency and energy consumption calculated by the following equations [29]:

$$\text{Flux} = \frac{\Delta N}{At} \tag{5}$$

$$\eta = \frac{Fz\Delta N}{n_c It} \tag{6}$$

$$P = \frac{U\int I dt}{m} \tag{7}$$

where η = current efficiency of dilute (%), $\Delta N = C_d^{n-1}V_d^{n-1} - C_d^n V_d^n$ (mole), C_d^n and C_d^{n-1} are the concentration of dilute cell (M) at time 0 and t, respectively, V_d^n and V_d^{n-1} are volume of dilute cell (L) at time 0 and t respectively, P = energy consumption of NaCl (KW h kg^{-1}), n_c = number of cell pair, I = current (A), U = applied potential (V), m = mass of removed salt (kg) and t = time (s).

3. Results and discussion

3.1. Chemical structure

The successful synthesis of AEMs with different amines was investigated by FTIR analysis. The ATR-FTIR spectrums of pristine BPPO as well as prepared AEMs with different tertiary ammonium groups are shown in Fig. 4. The adsorption peaks of symmetrical and asymmetrical stretching vibration of C–O are at 1,200 and 1,306 cm^{-1} and those of phenyl group are at 1,470 and 1,600 cm^{-1}, respectively [13,41]. After the reaction with different amines, the characteristic band at 1,110 cm^{-1} appeared in all AEMs is associated C–N stretching vibration which is absent in pristine BPPO membrane representing the successful reaction between BPPO and amines. The band appeared at 750 cm^{-1} was attributed to C–Br stretching vibration in BPPO membrane [39,46]. After reaction with amines, this band was disappeared in ATR-FTIR spectra of prepared AEMs [39,46,47]. This all proves successful introduction of different ion-exchange groups into polymer matrix.

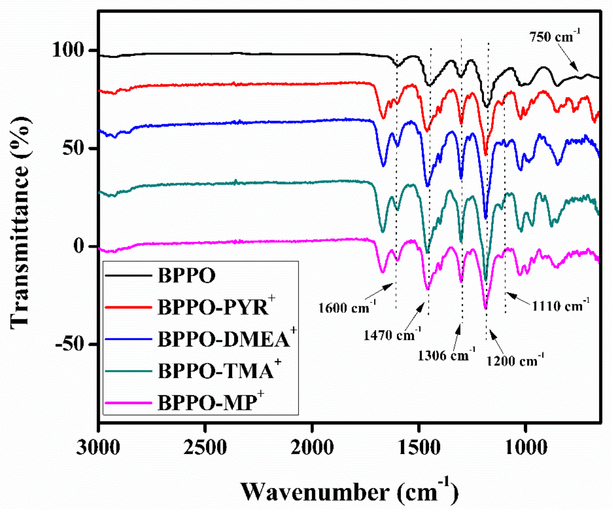

Fig. 4. IR spectrum of pristine BPPO and prepared AEMs.

3.2. Morphology

Here, a morphological investigation of prepared AEMs bearing different tertiary ammonium groups was carried out by scanning electron microscopy (SEM). Fig. 5 depicts the SEM micrograph of surface and cross-section of developed membranes. It reveals that the surfaces and cross-sections of all fabricated AEMs possess compact, homogeneous and uniform morphology. It can be seen that surfaces of all prepared AEMs are free from any obvious defects or cracks on it. Hence dense and homogeneous morphology of prepared membranes is successfully achieved here. This observed

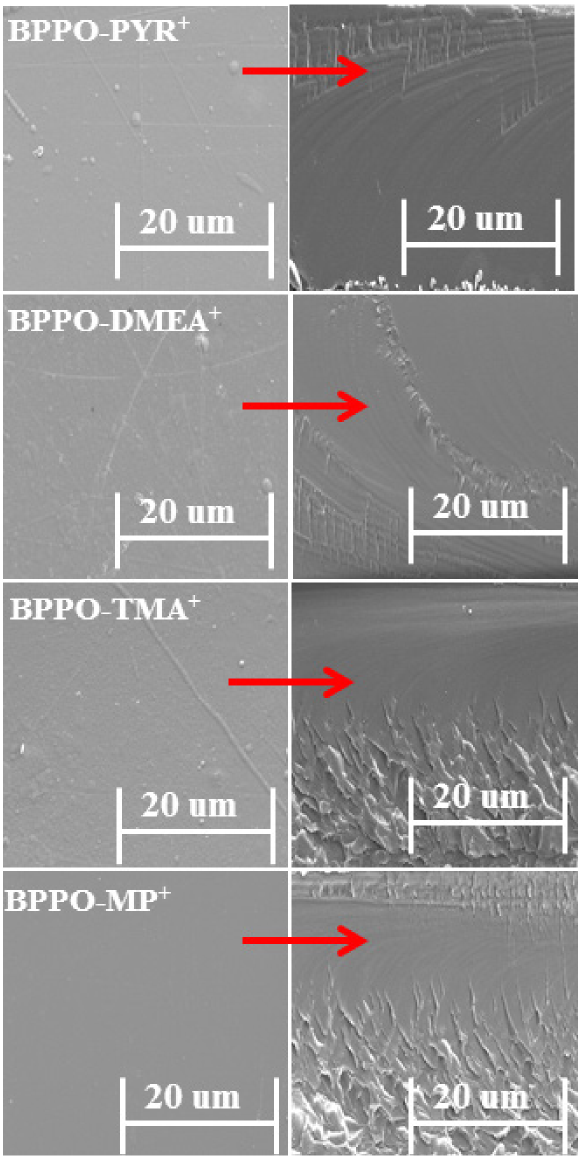

Fig. 5. Surface (left) and cross-section (right) of prepared AEMs.

morphology of prepared AEMs is useful for the desalination of NaCl from aqueous solution via ED process.

3.3. Ion-exchange capacity, water uptake, linear expansion ratio and thickness

IEC gives useful information about charge density of a functionalized membrane and it is also a crucial factor which governs conductivity and transport properties of any membrane [48,49]. It was measured by classical Mohr's method and is given in Table 2. It has been observed that BPPO-TMA$^+$ exhibits higher IEC (1.45 mmol/g) than other prepared AEMs as the mass ratio of all amines is same. It is due to smallest size of TMA than other amines. Therefore, the nucleophilic reactivity of TMA is higher than other amines which results in the higher IEC of BPPO-TMA$^+$. On the other hand, developed membrane BPPO-DMEA$^+$ represents lower IEC (1.34 mmol/g) because DMEA is larger and bulkier amine than other studied amines. Moreover, pristine BPPO membrane shows no IEC due to lack of ion-exchange contents into the membrane matrix. The IEC values of prepared membranes follow the order: BPPO-TMA$^+$ > BPPO-PYR$^+$ > BPPO-MP$^+$ > BPPO-DMEA$^+$ > BPPO. Thus, the prepared AEMs are highly charged which indeed required for electro-membrane separation process.

The water content of an IEM is stated as, "the weight of water included in one gram of swelled membrane soaked in pure water" [49,50]. The water uptake of IEMs has high influence on electrochemical applications. In order to investigate the effect of quaternary ammonium groups, water uptake of each membrane was measured at room temperature. As expected, the general trend should be that water uptake increases with increasing IECs as a result of increase in hydrophilicity [51]. Table 2 summarizes water uptake of prepared AEMs as well as pristine BPPO membrane. BPPO-PYR$^+$ is found to have higher water uptake than all other membranes because pyridinium is of larger size generate larger free volume in membrane matrix. Similar behavior was observed in previously published works [47]. On the other hand, prepared membrane BPPO-MP$^+$ possess lowest water uptake among all the prepared membranes because of its smallest size which induce lowest free volume in membrane. From BPPO-DMEA$^+$ and BPPO-TMA$^+$ membranes, the membrane BPPO-TMA$^+$ possesses lower water uptake than BPPO-DMEA$^+$ due to smaller molecular size of TMA groups providing less free volume in the membrane. Moreover, pristine BPPO membranes exhibit lower water uptake (3.2%) than the developed AEMs due to the lack of ion-exchange group into the polymer matrix. From water uptake results, it could be concluded that the water uptake of prepared AEMs is found to be decreased in the order: BPPO-PYR$^+$ > BPPO-DMEA$^+$ > BPPO-TMA$^+$ > BPPO-MP$^+$ > BPPO.

Table 2
Theoretical ion-exchange capacity, experimental ion-exchange capacity, water uptake, linear expansion ratio and thickness of prepared AEMs

Membranes	IEC_T (mmol/g)	IEC_{Exp} (mmol/g)	W_R (%)	LER (%)	Thickness (nm)
BPPO-PYR$^+$	1.50	1.39	52.8	16.1	71
BPPO-DMEA$^+$	1.50	1.34	47.4	11.4	64
BPPO-TMA$^+$	1.50	1.45	27.7	9.6	69
BPPO-MP$^+$	1.50	1.36	13.7	4.0	62
BPPO	–	–	3.2	1.2	64

Table 2 depicts the LER of pristine BPPO membrane and AEMs bearing different quaternary ammonium groups at room temperature. It is found to be 16.1%, 11.1%, 9.6% and 4.0% for prepared AEMS BPPO-PYR$^+$, BPPO-DMEA$^+$, BPPO-TMA$^+$ and BPPO-MP$^+$, respectively. On the other hand, LER of pristine BPPO membrane is found to be 1.20%. From this, it could be concluded that developed AEMs have good swelling resistance which is essential for long time running in desalination via ED process.

3.4. Thermal and mechanical stability

Thermal stability of prepared membranes bearing different tertiary ammonium groups (BPPO-PYR$^+$, BPPO-DMEA$^+$, BPPO-TMA$^+$ and BPPO-MP$^+$) was studied by thermo-gravimetric analysis (TGA) in the temperature range of 40°C–800°C at a heating rate of 10°C/min under nitrogen atmosphere. Fig. 6 represents the TGA curves of prepared AEMs bearing different tertiary ammonium groups. Thermal stability of membranes can be assessed from decomposition temperature and remaining weight percentage [52]. All prepared AEMs represented three distinct thermal degradation stages: (1) the initial weight loss around 80°C–140°C is attributed to the evaporation of residual solvent (NMP) and absorbed water. (2) The second weight loss stage observed around 250°C–300°C is associated to the degradation of functional group within the studied membranes. (3) The third weight loss step observed around 470°C–500°C is ascribed to the degradation of polymer backbone. Thus the maximum degradation rate of polymer backbone of studied membranes (470°C–500°C) is higher than previously reported AEMs (430°C–470°C) [13]. Moreover, it can be observed that BPPO-PYR$^+$ is much stable than other developed AEMs. The possible reason could be higher stability of membrane structure. Even after attack of pyridine moiety on BPPO, the aromaticity of pyridine ring remains

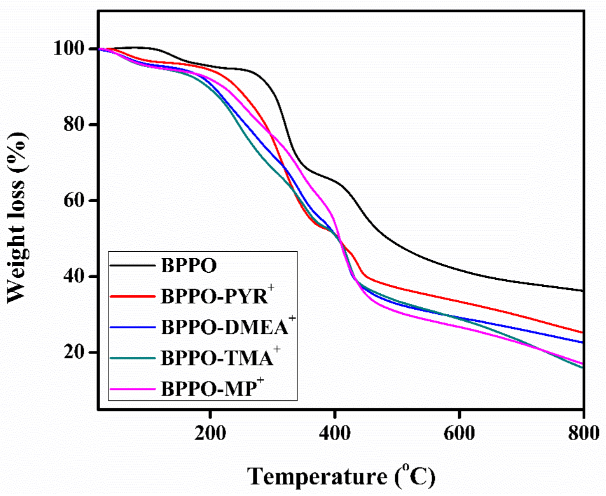

Fig. 6. TGA thermograms of pristine BPPO and different anion exchange membranes.

intact. Hence membrane becomes much stable and is evident from Fig. 6. On the other hand, BPPO-TMA$^+$ is found to exhibit lesser stability than other membranes. Due to the small size and less stable membrane structure, the degradation of this membrane happened fast than other membranes.

The mechanical properties of AEMs are of great significance for their application in desalination of NaCl via ED process. The mechanical properties of pristine BPPO membrane and prepared membranes (BPPO-PYR$^+$, BPPO-DMEA$^+$, BPPO-TMA$^+$ and BPPO-MP$^+$) were studied in wet state at room temperature. Table 3 summarizes the tensile strength (TS) and elongation at break (E_b) of AEMs and pristine BPPO membrane. TS value of pristine BPPO membranes was found to be 2.02 MPa whereas E_b value was 2.86% [39]. Similarly, it can be observed that all AEMs possess reasonable mechanical stability with tensile strength of 15.27 to 32.52 MPa and elongation at break of 9.10% to 55.85%. In case of membrane BPPO-TMA$^+$, after the incorporation of TMA inside BPPO backbone, the membrane structure gets rigid and this can be verified with the reported E_b value in Table 3. The polymer chain in case of BPPO-TMA$^+$ become very stiff and hence the flexibility of membrane was least than other membranes [51]. On other hand, for prepared membrane BPPO-DMEA$^+$, the polymer structure is much flexible compared with other membranes due to the pendent side chain containing amine DMEA. It has been observed that BPPO-DMEA$^+$ showed highest E_b than other prepared membranes.

3.5. Transport number and ionic resistance

The transport number of an IEM is the selectivity with which it transports a specific ionic species to pass through it. It depends on membrane characteristics such as water uptake, ion-exchange capacity, morphology, thickness, etc. There are several methods to measure transport number of an IEM namely Hittorf's method, Lodge's moving boundary method and EMF method [53]. Here, it was measured by EMF method [13,39] and obtained results are given in Table 4. It has been observed that transport number of BPPO-PYR$^+$ is higher (0.98) as compared with other prepared membranes. This is related to the higher water uptake of membrane BPPO-PYR$^+$ which make it suitable for NaCl desalination via ED process.

Ionic resistance of prepared AEMs with different quaternary ammonium groups (BPPO-PYR$^+$, BPPO-DMEA$^+$, BPPO-TMA$^+$, BPPO-TMP$^+$ and BPPO-MP$^+$) was measured in 0.5 M NaCl at room temperature. It is dependent on membrane properties such as ion-exchange capacity, water uptake, morphology binder characteristics, thickness, etc. [39]. The obtained ionic resistance for all AEMs is given in Table 4. The ionic resistance of prepared AEMs is found to be decreased in the following order: BPPO-PYR$^+$ > BPPO-DMEA$^+$ > BPPO-TMA$^+$ > BPPO-MP$^+$. It has been observed that ionic resistance of BPPO-PYR$^+$ is lowest (0.88 Ω cm^2) than all prepared membranes. This is associated to the higher water uptake of BPPO-PYR$^+$ than all other prepared membranes. The lowest ionic resistance of BPPO-PYR$^+$ is beneficial for higher desalination performance. On the other hand, BPPO-MP$^+$ (2.98 Ω cm^2) exhibits higher ionic resistance because it possess lower water uptake than other membranes.

Table 3
Tensile strength (TS) and elongation at break (E_b) of prepared AEMs

Membranes	TS (MPa)	E_b (%)
BPPO-PYR$^+$	15.27	27.26
BPPO-DMEA$^+$	32.52	55.85
BPPO-TMA$^+$	18.84	9.10
BPPO-MP$^+$	17.18	29.71
BPPO	2.02	2.86

3.6. ED performance of developed membranes

After the detailed characterization of all prepared AEMs, they were used for desalination of NaCl from aqueous solution via ED process. The desalination test was carried out under conditions mentioned in section 2.3.6. The variation in conductivity of NaCl in dilute compartment for all AEMs is depicted in Fig. 7. It is found to be decreased with increasing desalination time for all investigated AEMs. Pyridinium-based membrane showed better desalination performance than other AEMs under identical experimental conditions. It is correlated with different water uptake of the prepared AEMs. Water uptake of prepared AEMs was in following order: BPPO-PYR$^+$ > BPPO-DMEA$^+$ > BPPO-TMA$^+$ > BPPO-MP$^+$. Water content plays a decisive role in conduction of ions through increase of the hydrophilic domains which provide larger ionic pathways and increased percolation of ion-conductive channels within the membrane [53]. BPPO-PYR$^+$ exhibits higher water uptake than other AEMs reported in this work. As expected, the

Table 4
Ionic resistance and transport number of prepared AEMs

Membranes	Ionic resistance (Ω cm^2)	Transport number
BPPO-PYR$^+$	0.88	0.98
BPPO-DMEA$^+$	1.40	0.98
BPPO-TMA$^+$	1.93	0.95
BPPO-MP$^+$	2.98	0.90

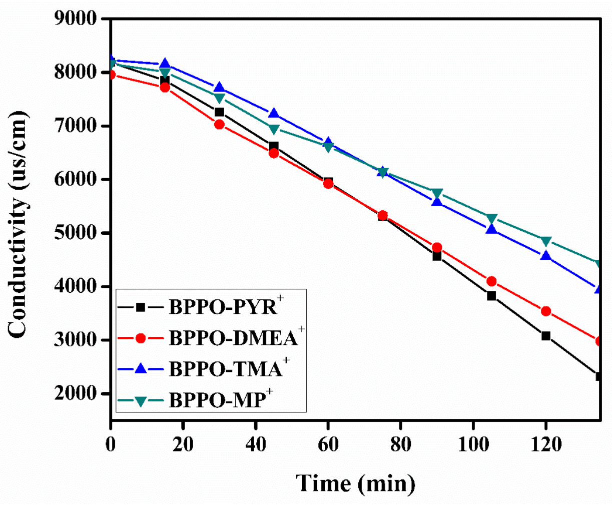

Fig. 7. Change in conductivity of NaCl with time.

Table 5
ED performance of prepared AEMs

Membranes	Operating current		
	0.2 A		
	η (%)	*P* (kWh/kg)	Flux (mole/m^2 h)
BPPO-PYR$^+$	47.0	32.29	5.01
BPPO-DMEA$^+$	32.50	48.53	3.47
BPPO-TMA$^+$	26.40	51.41	2.81
BPPO-MP$^+$	10.80	123.52	1.15

general trend was that water uptake increased with increasing IECs for all membranes as a result of an increase in the hydrophilicity. BPPO-TMA$^+$ membranes exhibited smaller water uptake than those of BPPO-PYR$^+$ and BPPO-DMEA$^+$ membranes probably because of the smaller molecular size of TMA groups providing less free volume in the membrane. The water uptake was as high as 52.8% and 47.4% for BPPO-PYR$^+$ (IEC= 1.39 mmol/g) and BPPO-DMEA$^+$ (IEC = 1.34 mmol/g), respectively, while that for BPPO-TMA$^+$ (IEC = 1.45 mmol/g) was 27.7%. The higher water uptake of BPPO-PYR$^+$ leads to lower area resistance and higher transport number which is responsible for its better desalination performance than other prepared membranes. Table 5 summarizes the desalination performance of all prepared AEMs under same experimental conditions. It can be observed that BPPO-PYR$^+$ with higher water uptake exhibits higher flux (5.01 mole/m^2 h) and lower energy consumption (32.29 kWh/kg salt) than other prepared membranes. From this, we have concluded that BPPO-PYR$^+$ exhibited higher desalination performance than other prepared AEMs under same experimental conditions.

4. Conclusions

AEMs with different quaternary ammonium groups have been prepared from BPPO by solution-casting method. The successful synthesis of prepared AEMs was confirmed by FTIR analysis. They exhibited excellent thermal and mechanical stability. The morphology of AEMs has been observed by SEM analysis. BPPO-PYR$^+$ showed higher water uptake than all developed membranes. The present study indicated that BPPO-PYR$^+$ showed higher transport number and lower area resistance than other membranes. Therefore, BPPO-PYR$^+$ showed higher desalination performance than all other reported membranes under similar experimental conditions. From present investigations, pyridinium group proves to be a promising tertiary ammonium group for BPPO-based AEMs to achieve higher desalination performance.

Symbols

AEM	—	Anion exchange membrane
BPPO	—	Brominated poly(2,6-dimethyl-1,4-phenylene oxide)
CMX	—	Commercial cation exchange membrane
CC	—	Concentrated compartment
DMEA	—	Dimethylethanolamine
E_b	—	Elongation at break
ED	—	Electrodialysis
F	—	Faraday constant
IEC	—	Ion-exchange capacity
IEM	—	Ion-exchange membrane
IECT	—	Theoretical ion-exchange capacity
LER	—	Linear expansion ratio
MP	—	Methylpyrrolidine
NMP	—	N-Methyl-2-pyrrolidone
PYR	—	Pyridine
R	—	Gas constant
SEM	—	Scanning electron microscopy

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