Fundamental studies on a new series of anion exchange membranes: effect of simultaneous amination-crosslinking processes on membranes ion-exchange capacity and dimensional stability

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Abstract

The effects of amination time and temperature, the compositions of amination medium on membrane stability and ion-exchange capacity (IEC) are reported in this paper. It is revealed that the membrane's IEC increases with the amination time and attains to a plateau value after some time which is dependent on the temperature, e.g. 56 h at 10 °C, and 4 h at 45 °C. To consider both the dimensional stability and the amination rate, it is recommended that the amination be conducted at 35 °C for 10 h in most cases. Addition of some ethylenediamine (EDA) to the amination medium is favorable to the membrane stability due to the formation of crosslinking structure in the membrane bone but it will cause a slight decrease in IEC. From both the IEC and the stability points of view, the content of saturated EDA should be controlled within 10% of the whole amination agent.

To compare with the previous paper [1], the effect of base membranes on IEC and stability is also investigated. It is shown that the membrane dimensional stability can be improved by aryl substitutions without the change of the membrane IEC. Therefore, there are some alternative ways to increase the membrane stability or mechanical strength, e.g. by an increase in the content of EDA (crosslinking agent) or aryl bromine content, a decrease in amination time and temperature and the content of trimethyl amine, etc. By properly balancing them, a series of anion exchange membranes can be obtained to meet different industrial requirements, such as in diffusional dialysis, electrodialysis and water splitting processes. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Ion-exchange membranes are now widely used in the electrodialysis for the desalination of brackish water, the production of table salt, recovery of valuable metals from the effluents of metal-plating industry, recovery of acid and base from the spent leach-

ing solutions, and for many other purposes [2]. For the preparation of those membranes, two alternative routes are conventionally adopted: one is prepared from monomers and the other directly from polymers or copolymers. If an anion exchange membrane is prepared from a monomer, the most commonly used neutral starting material is styrene and divinylbenzene, which are copolymerized into a strongly basic anion exchange membrane by following chloromethylation and quaternary amination processes [3]. Several

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disadvantages have resulted from this technology. In the chloromethylation, the used chloromethyl methyl ether is a carcinogen and potentially harmful to human health [4]. In addition, to improve the mechanical stability, the membranes will suffer to crosslinking, and thus, this will result in limitation of molding of the membrane with intricate shape and also cause an increase in manufacturing cost. If it is prepared from polymer or copolymer, such as polyethersulfone [5], block copolymers [6,7], the same chloromethylation and quaternary amination processes will be conducted. To avoid the use of chloromethyl methyl ether, sometime chloromethylated polymers or copolymers are directly used to prepare such membranes [4,8–10]. Though, this technology causes a decrease in manufacturing cost compared to the first route, these anion exchange membranes are likely to undergo a dimensional change during flocculation and tend to have defects. Especially, as the ion-exchange capacity increases, the affinity to water increases and leads to a decrease in both the mechanical strength and the dimensional stability. Hence, it appears difficult to obtain a membrane with both sufficient dimensional stability and excellent electrochemical properties [6,11]. Fortunately, a new series of anion exchange membranes with both good electrochemical properties and excellent dimension stability have been initiated in our laboratory [1], which were also directly made from engineering polymer poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) by bromination and simultaneous amination-crosslinking processes but no chloromethyl methyl ether is used. The preparation process and its effect on the membrane fundamental properties and performances were investigated in the previous papers [1,12], thus, the main purpose of this paper is to investigate the simultaneous amination-crosslinking processes and its effect on membrane dimensional stability and ion-exchange capacity (IEC) which will decide the other membrane properties including water content, membrane area resistance, transport number, permeability, etc.

2. Experimental descriptions

2.1. Preparation of base membranes [1,12]

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO, with an intrinsic viscosity equal to 0.57 dl/g in chloroform at 25 °C) was dissolved in chlorobenzene to form an 8% solution and this solution was subjected to bromination by adding cholorobenzene-diluted bromine. The extent of bromination was controlled by the amount of bromine being added, while the substitution position (benzyl or aryl) was controlled by temperature [1]. The final solution was precipitated with methanol, washed and dried at 80 °C for at least 20 h to get the brominated polymers. Then the brominated polymers were dissolved in dimethyl formamide (DMF) to form a casting solution of about 15 wt.% and cast onto a clean glass plate to form a base membrane of 0.1–0.2 mm dried thickness.

2.2. Amination

The base membranes were accurately cut into pieces with proper dimensions about 30 mm × 30 mm and subjected to simultaneous amination and crosslinking process by immersing them into an amination medium. In most cases, this amination solution is prepared by mixing certain amount of saturated trimethyl amine (TMA) aqueous solution, saturated ethylenediamine (EDA) aqueous solution and water. So, two volumetric ratios are defined for the composition of an amination agent for the latter analysis. One is V_1 defined by the volumetric ratio of the saturated TMA aqueous solution to the whole amination solution and the other one V_2 defined by the volumetric ratio of the saturated EDA aqueous solution to the whole amination solution. The total amount of both TMA and EDA contained in the amination solution are excess for the reaction. After a proper time, the membranes were extracted from the solution, then washed with distilled water and equilibrated with 1 M NaCl solution to be transformed into the chloride form. The degree of amination and crosslinking was controlled by temperature, composition of amination solution and amination time, which will be discussed in the main text.

2.3. Membrane characterizations

Both the base membranes and the final membranes (functionalized membrane) were checked with the FTIR analysis (Bio-Rad FTS 135 FT infrared spectrometer) to view the structure of the membranes. In addition, the base membranes were checked with the ^{1}H NMR (unity plus 400) measurements for

precise determination of the bromine contents in aryl and benzyl position, respectively. The FTIR spectra were taken directly from the membrane shape and the ^{1}H NMR spectra were taken using solvents deuterium-substituted chloroform. As the final membrane are crosslinked, adequate ^{1}H NMR spectra are impossible to obtain. The final membranes were conducted to the measurements of ion-exchange capacity (IEC) as described in the previous paper [1,12] and dimensional stability as described below.

The dimensional stability is evaluated by the dimensional change ratio, which is calculated from the geometrical average value of linear change ratios in both x and y directions as shown in the following equation:

$$\eta = \sqrt{\left(\frac{x - x_0}{x_0}\right)\left(\frac{y - y_0}{y_0}\right)}$$

where η is the final dimensional change ratio, x, y and x_0, y_0 are, respectively the lengths of a base membrane and a final membrane in x and y directions which are determined by a digital micrometer (0–150 mm, Shanghai, China).
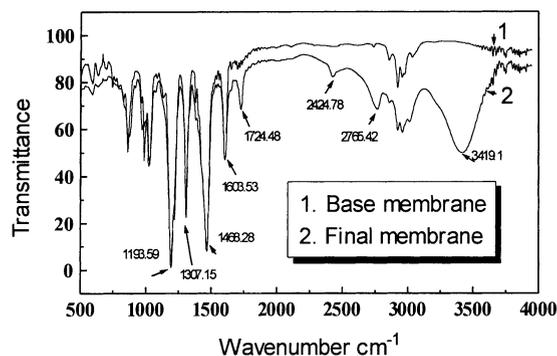

Fig. 1. FTIR spectra of base and final membranes.

stretching vibrations of NH, NH$_2$ and N≡C, the peak at 2765 cm^{-1} is attributed to the vibration of –CH$_2$– while peak at 1724 cm^{-1} is due to vibration of C–N–H or C=N. Therefore, the appearance of these characteristic peaks gives the evidence of the existence of N(CH$_3$) and –NHCH$_2$CH$_2$NH$_2$ or =NCH$_2$CH$_2$NH$_2$ in the final membrane.

The above FTIR spectra analysis conform to the structures of the base membrane and final membrane as shown in the following:

Base membrane
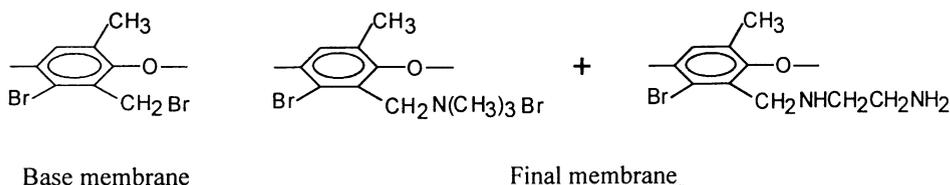
Final membrane

3. Results and discussion

3.1. The FTIR analysis

Fig. 1 shows the spectroscopy of a base membrane and a final membrane. FTIR spectroscopies indicate the appearance of absorption peaks of C–O (oxide ether) and phenyl group, because it has been known that the symmetrical and asymmetrical stretching vibrations of C–O and phenyl group appear at 1193 and 1307 cm^{-1}, and 1468 and 1603 cm^{-1}, respectively. It is observed that four new absorption peaks appear at 1724, 2425, 2765 and 3419 cm^{-1} due to amination. In contrast to the standard spectra [13], we know that the peaks at 3419 and 2425 cm^{-1} are resulted from the symmetrical and asymmetrical

3.2. Effect of time and temperature on IEC

To investigate the effect of time, temperature and composition of the amination medium on the amination process, a base membrane with benzyl bromine content 99.2% (without aryl substitution) is used. The relationship between the IEC and amination time was depicted in Fig. 2. It is observed that IEC increases fast with amination time initially. However, after experiencing some time, IEC attains a plateau value and remains nearly constant at most cases with an exception at temperature 45 °C. The time attaining the maximum IEC value depends on the temperature. The higher the temperature, the shorter the time. For example, if the amination is conducted at 25 °C, the time attaining the maximum value is about 32 h, implying
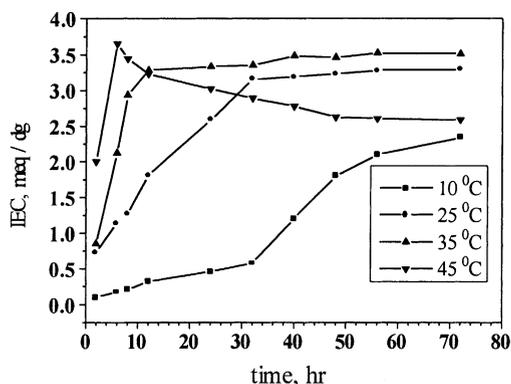
Fig. 2. Effect of time and temperature on IEC of the membranes with $V_1 = 20\%$, $V_2 = 10\%$, BBC = 0.992.

Fig. 3. Effect of time and temperature on dimensional change ratio of the membranes with $V_1 = 20\%$, $V_2 = 10\%$, BBC = 0.992.

that 32 h time is enough for this amination because an additional time only causes a very slight increase in IEC. However, even if the time is long enough, the final IECs at all temperatures are less than the theoretical value 4.33 that is calculated from benzyl bromine content (BBC). [1] This is possibly due to the formation of other aminated polymers as will be discussed later.

The effect of temperature on IEC can be observed by comparing the time-IEC curves at different temperatures. Obviously, with the fixed time, the amination rate is enhanced by temperature. For example, if the amination is conducted at 25 °C, it will take about 32 h to get the plateau IEC; while it will take only 10 h to get this IEC at 35 °C and 4 h at 45 °C. But if the reaction is conducted at 10 °C, it will at least take more than 56 h to get the maximum IEC value. Therefore, an increase in temperature is favorable to the amination reaction. This result is coincided with theoretical fact that amination reaction is endothermic. However, a fast reaction will cause a relatively large dimensional change due to penetration of amination agents and thus, affect the membrane mechanic strength as discussed in the next section.

3.3. Effect of time and temperature on dimensional stability

Fig. 3 demonstrates the effect of amination time and temperature on linear dimensional change of the

membranes. It is shown that the dimensional change ratio increases with amination time and at the same time it will increase with both amination temperature. As mentioned above, with an increase in amination time, IEC of a membrane increases and thus leads to an increase in water content [1]. When the membrane contains certain amount of water, a change in dimension is finally resulted. This dimensional change is not only related to time, but related to temperature as well. As shown in Fig. 3, below 35 °C, the dimensional change ratio is within 8%. As soon as the temperature increase up to 45 °C, this ratio rises to more than 80% and the membrane becomes even swellable and tends to have defects at the final period of amination. This is because at this time, the amination reaction is very quick and causes a rapid penetration of amination agents and water into the polymer chains and thus speeds up further the amination reaction. So at high temperature, amination can be conducted at the depth of the membrane and cause a change in dimension. On the other hand, an increase in membrane dimension can also be caused by the above mentioned degradation reaction. The membrane stability is dependent on its dimensional change. In practical applications, a membrane with small dimensional change and thus high strength is strongly desired. To consider both dimensional stability and amination rate, 35 °C and 10 h will be the proper temperature and time. If not specifically indicated, the following amination reactions are conducted under such a condition.

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[1] IEC = 1000BBC$/((1 - BBC)^*M_1 + BBC^*M_2)$, where IEC is in unit: meg/dg, $M_1 = 120$ (the molecular weight of PPO) and $M_2 = 213.6$ (the molecular weight of final membrane in chloride form), respectively.
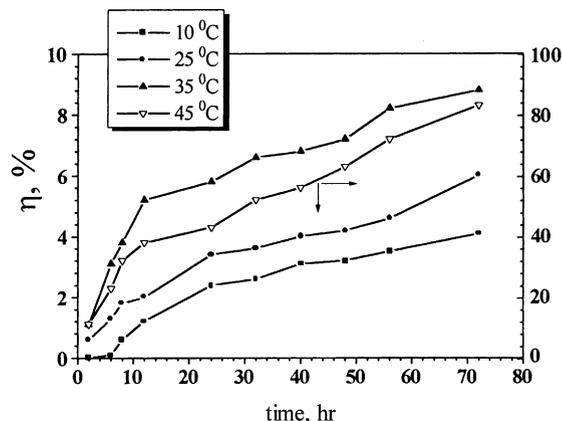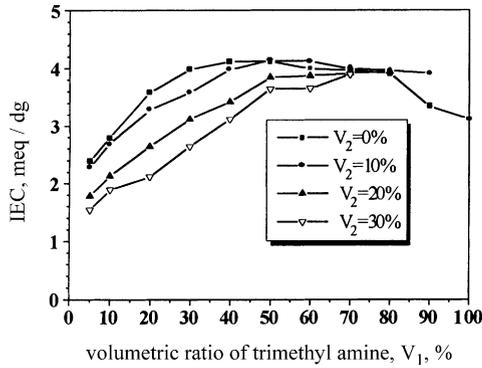
Fig. 4. Effect of volumetric ratios of trimethyl amine (V_1) and ethylenediamine (V_2) on membrane IEC with time = 10 h, temperature = 35 °C, BBC = 0.992.

Fig. 5. Effect of volumetric ratios of trimethyl amine (V_1) and ethylenediamine (V_2) on membrane dimensional stability with time = 10 h, temperature = 35 °C, BBC = 0.992.

3.4. Effect of compositions of amination agents on the membrane's IEC and dimensional stability

It is demonstrated in Fig. 4 that the composition of the amination agents has a significant effect on the membrane's IECs. The IEC of a membrane increases with the content of TMA or the volumetric ratio V_1 until a plateau region is reached at $V_1 = 40\%$, implying that IEC will not increase with content of TMA after $V_1 = 40\%$. An exception is that for $V_2 = 0$, i.e. the case without EDA, IEC will decrease a little after this plateau value. On the other hand, if V_1 keeps unchanged, the IECs will decrease with V_2, i.e. the concentration of ethylenediamine in the amination solution. Theoretical interpretation to these trends can be based on the following amination reactions possibly occurring in the system.
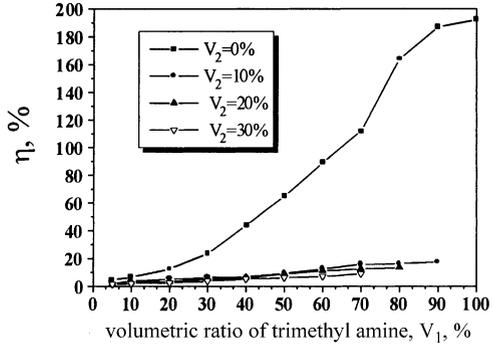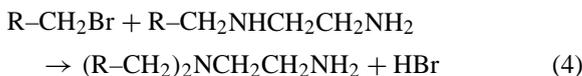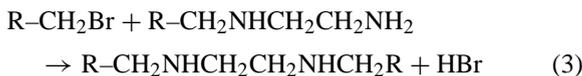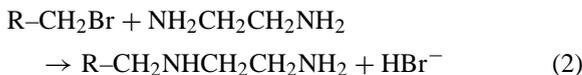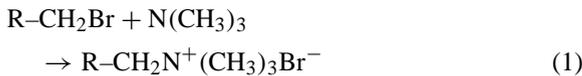
$$R–CH_2Br + N(CH_3)_3$$
$$\rightarrow R–CH_2N^+(CH_3)_3Br^- \qquad (1)$$

$$R–CH_2Br + NH_2CH_2CH_2NH_2$$
$$\rightarrow R–CH_2NHCH_2CH_2NH_2 + HBr^- \qquad (2)$$

$$R–CH_2Br + R–CH_2NHCH_2CH_2NH_2$$
$$\rightarrow R–CH_2NHCH_2CH_2NHCH_2R + HBr \qquad (3)$$

$$R–CH_2Br + R–CH_2NHCH_2CH_2NH_2$$
$$\rightarrow (R–CH_2)_2NCH_2CH_2NH_2 + HBr \qquad (4)$$

Formula (1) is a conventional quaternary amination reaction, which forms an anion exchanger with strong basic group, and thus contribute most of the fixed groups, i.e. IEC. With an increase in the amount of TMA, i.e. the concentration of one reactant in formula (1) increases, the reaction rate correspondingly increases resulting in a membrane with a relatively high IEC. However, if the amination agent is far beyond the amount required for a given membrane to be aminated, an increase in V_1 will not cause any appreciable increase in IEC based on the chemical kinetics.

Formula (2) is also a typical amination reaction forming an anion exchanger with weak basic groups. Since the formed product can react with the brominated polymers and produce high-grade amination groups as shown in formulae (3) and (4), these reactions will exhaust some amount of brominated polymer and reduce the formation of strong basic groups and thus decrease the IEC as shown in Fig. 4. Comparing the curve $V_2 = 0$ with the other three ones, it is interesting to note that some addition of EDA can stabilize the membrane's IEC at the plateau region due to the introduction of the crosslinking structure in the membrane bone.

Fig. 5 shows the effect of composition of aminated agents on the membrane stability. As can be seen, if no EDA is used, the dimensional changes ratio increases with the concentration of TMA. The resultant membranes do not have any mechanical strength and even at some time tend to be swelled into pieces. Nevertheless, as long as some amount of EDA is added in the aminated solution, the situation is completely

Table 1
The base membrane considered in amination process[a]

Base membrane number	M_1	M_2	M_3	M_4	M_5
Aryl substitution (%)	99.2	49.2	39	9.8	0
Benzyl substitution (%)	0	49.8	58	90	99.8

[a] Reactant molar ratio; PPO:bromine = 1 : 1.

different. Even at the case of high concentration of TMA ($V_1 = 0.9$, $V_2 = 0.1$), the dimensional change ratio has not exceeded to 20%. The theoretical analysis for the membrane stability can also be done based on the above formulae. As we know, a strong basic group has a strong hydrated ability and thus can cause a high value in swellable ratio, while a weak basic group has the weak ability to be hydrated and little tendency to be swelled. So some addition of ethylenediamine leads to the formation of weak basic groups as shown in formula (2), especially these weak basic groups can react further with the halogen polymer and introduce a crosslinking structure as shown in formulae (3) and (4), and thus, increase significantly the membrane stability or mechanical strength.

3.5. Effect of the type of base membranes on IEC and dimensional stability

As mentioned in the previous paper [1], by controlling the temperature in the bromination process, a series of brominated polymers with different substitution degrees and positions can be obtained and thus give rise to preparation of different base membranes. To investigate this effect, five base membranes are prepared with different bromine contents and positions as listed in Table 1. These membranes have been aminated in the same medium, which is diluted directly from TMA. As can be seen from Fig. 6, IECs increase with the order of base membranes $M_1 < M_2 < M_3 < M_4 < M_5$ because BBC of these membranes increases with this order. Just described in the above formulae, the amination agents can only react with a benzyl substitution group, forming the functional groups and contributing to the active point or IEC. Therefore, the membrane aminated from M_1 nearly has no IEC, while the membrane aminated from M_5 has an IEC close to the theoretical value. Though the aryl substitutions contribute little to the IECs, their existences cause an increase in the rigidity of the polymers, and
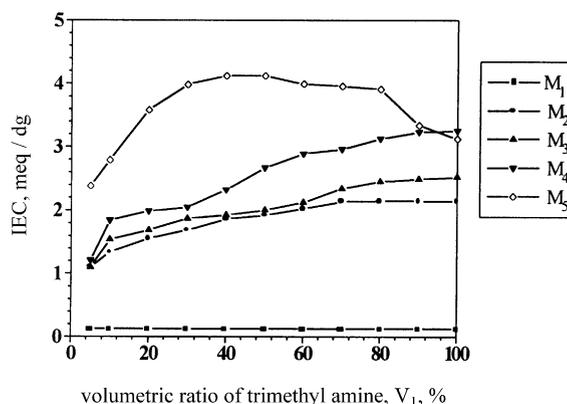

Fig. 6. Effect of the type of base membrane on IEC when the membrane is aminated in absence of ethylenediamine ($V_2 = 0$) with time = 10 h, temperature = 35 °C.

thus slow down the amination reaction and increase the hydrophobicity of the final membranes. This can be observed from Fig. 6 by comparing the profiles of different types of base membranes.

The dimensional change ratio of the final membranes prepared from different base membranes is shown in Fig. 7. Obviously, the introduction of aryl substitution group can significantly reduce the dimensional change and increase the membrane stability. The dimensional change ratios of the membranes prepared from both aryl and benzyl brominated polymer are within 7%. But those of the membranes prepared from benzyl brominated polymer are as high
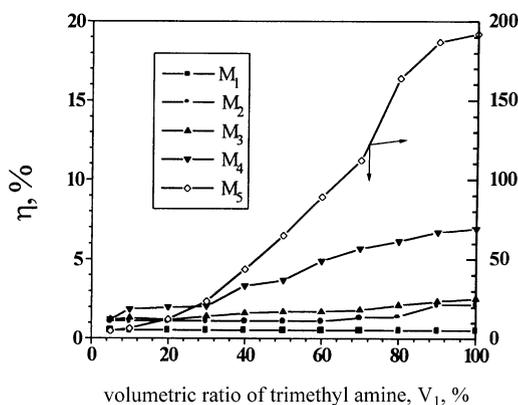

Fig. 7. Effect of the type of base membrane on membrane stability with the conditions as shown in Fig. 6.

as 200% in the absence of EDA. This implies that aryl substitution has an equivalent role as EDA from the membrane's stability point of view, though the mechanism is not completely same. For the practical preparation, we can have a balance choice between them and manufacture a series of membranes to meet different industrial demands.

4. Conclusion

Based on the fundamental studies of a new route for preparing an anion exchange membrane as reported in the previous paper, the effect of simultaneous amination-crosslinking process is investigated on the membrane IEC and dimensional stability.

The membrane IECs increase with amination time and attain a plateau value after some time. This time is dependent on temperature, e.g. 56 h at 10 °C, 32 h at 25 °C, 10 h at 35 °C and 4 h at 45 °C. To consider both the dimensional stability and the amination rate, it is recommended that the amination be conducted at 35 °C for 10 h in most cases.

The IECs of the final membranes increases with content of TMA but the membrane dimensional stability decreases with this content. Addition of some EDA in the amination agent is favorable to the membrane stability because it can react with the brominated polymers and form crosslinking structure in the membrane bone. However, IECs of the membranes will decrease to a little extent due to the formations of both weak basic group and crosslinkage. In practical preparation, it is recommended that addition of a 10% saturated EDA solution to the amination agent is necessary for the membrane stability with only a slight decrease in IEC.

The IECs and stability of a membrane is also related to the kind of the base membranes. Just as described in the previous paper [1], IECs increase with benzyl substitutions and keep approximately unchanged with aryl substitutions. But the membrane dimensional stability can be improved by aryl substitutions. Even in the absence of crosslinking agent, the membranes with some bromine content in the aryl position remain extraordinarily stable in all kinds of amination mediums. Therefore, there are alternative ways to increase the membrane stability or mechanical strength, e.g. to increase the content of ethylenediamine (crosslinking

agent) and aryl bromine, and to decrease the amination time, temperature and content of TMA, etc. By properly balancing them, a new series of anion exchange membranes can be obtained to comply with different industrial requirements, such as diffusional dialysis, electrodialysis and water splitting processes.

Acknowledgements

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