Fundamental studies of a new series of anion exchange membranes: membrane preparation and characterization

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Abstract

Chemical cross-linking anion exchange series membranes were prepared from linear engineering plastics poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) by conducting the processes of bromination and amination at both benzyl and aryl positions. Compared with the traditional technologies, the membrane route described in this paper has cancelled the chloromethylation process and thus, given up the use of chloromethyl methyl ether, which has been considered as a potential harmful toxicity material. The ion exchange capacity, water content, membrane potential and transport number of membranes were studied. The results show that the membrane properties are significantly affected by the bromination processes: benzyl-substitution will enhance the ion exchange capacity and water content, while the aryl-substitution will decrease the water content with approximately unchanged ion exchange capacity. By properly balancing them, a series of membranes can be obtained to comply with different industrial requirements, such as diffusional dialysis, electrodialysis, and water splitting processes. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The development of synthetic ion exchange membrane reported by Juda [1] in 1949 and Juda and McRae [2] in 1950 stimulated both commercial and academic interest in such membranes and the related processes. Nowadays, synthetic ion exchange membranes have been improved by various methods and have many practical uses [3,4]. For the preparation of a traditional hydrocarbon type ion exchange membrane for industrial uses, the most commonly utilized neutral starting material is styrene-divinylbenzene copolymer, from which a strongly basic anion

exchange membrane is usually prepared by two steps [5], chloromethylation and quaternary amination. In the chloromethylation, the used chloromethyl methyl ether is a carcinogen and is potentially harmful to human health [6]. In addition, to improve the mechanical stability, the membranes will suffer to cross-linking, and thus, this will result in limitation of molding of the membrane with intricate shape. To avoid the use of chloromethyl methyl ether, a class of such membranes were directly prepared from chloromethylated polymers [6–8]. But the resultant membranes have decreased mechanical stability due to their high hydrophilicity if a proper ion exchange capacity (IEC) is desired and thus, limit the uses in industries. Furthermore, the expensive chloromethylated polymers will bring about high membrane cost

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in the manufacturing. For these reasons, we attempt to develop a new series of anion exchange membranes directly from engineering polymer and examined the influence of membrane preparation conditions on the membrane properties including water content, IEC, membrane area resistance, transport number, etc.

2. Experimental

2.1. Materials

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) of intrinsic viscosity equal to 0.57 dl/g in chloroform at 25°C was obtained from Institute of Chemical Engineering of Beijing (China); trimethylamine and ethylenediamine are saturated aqueous solution and chlorobenzene, methanol, dimethyl formide (DMF) and bromine are of analytical grade. All of them are used as received.

2.2. Bromination

PPO was dissolved in chlorobenzene to form an 8% solution and this solution was subjected to bromination by adding cholorobenze-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. The final solution was precipitated with methanol, washed and dried at 80°C for at least 20 h to get the brominated polymers. These polymers were conducted to ^{1}H NMR (Unity plus 400) measurements for the precise determination of bromine contents in aryl and benzyl position, respectively [9,10].

2.3. Membrane preparation

The brominated polymers were dissolved in DMF to form a casting solution of about 15 wt.% and cast onto a polyvinyl chloride substrate to form a base membrane of 0.1–0.2 ml dried thickness. This base membrane was functionalized and crosslinked simultaneously by amination–crosslinking reaction at about 35 ± 1°C for at least 10 h with a properly proportional aqueous solution of trimethylamine, ethylenediamine (water:trimethylamine:ethylenediamine = 7:2:1, v/v),

and then washed and equilibrated with 1 M NaCl solution to be transformed into chloride form [9,10].

2.4. Membrane measurements

2.4.1. Water content

The water content (W_R) of the final membrane was determined after equilibrating a sample of membrane in chloride ion form with deionized water at room temperature. The membrane samples were removed from the water and weighed immediately after blotting the free surface water. Then, they were dried for over 4 h at 100 ± 5°C. The water content was deduced from the difference in weight between the wet (W_1) and the dry (W_2) membrane in unit gram H_2O/g dry membrane (in Cl^- form) based on the following formula.

$$W_R = \frac{(W_1 - W_2)}{W_2} \tag{1}$$

2.4.2. Ion exchange capacity (IEC) and fixed group concentration (C_R)

Membrane samples in the chloride form and in equilibrium with deionized water were converted to the sulfate form by leaching with a 0.5 M Na_2SO_4 solution. The chloride ions released from the membranes were determined by a titration of 0.1 M $AgNO_3$ solution with K_2CrO_4 as an indicator (Mohr method), and are given as meq/g dry membrane (in Cl^- form). The fixed group concentration (C_R) was determined directly from the ratio of IEC to W_R and was expressed in M (mol/l).

2.4.3. Membrane area resistance (R_m)

The apparatus for this determination is illustrated in Fig. 1. The membrane samples pretreated with 0.1 M NaCl were cut into 4 cm × 4 cm and then placed between two special designed Ag–AgCl electrodes with a nylon fiber on both sides (effective area 9.07 cm^2) so as that proper amount of electrolyte solution attains in the surfaces due to surface tension. Alternating current is supplied through a conductive meter (Model DDS-11A, Shanghai Leici instrument plant, China) and the potential between electrodes AB is read through a digital multimeter (model: GDM-8145, Good will instrument Co. Ltd., Taiwan). Prior to membrane measurements, a standard resistance box is connected between A and B extremes. By altering the
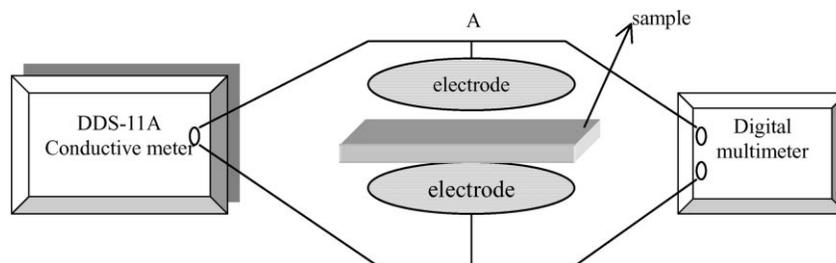
Fig. 1. Apparatus for area resistance determination.

value of resistance, a standard curve on *V–R* (voltage drop–resistance) can be obtained. Then the resistance box was replaced by the mentioned electrodes and the potentials were recorded in the same way with and without a membrane sample, respectively. From the difference of the potentials, the resistance of a membrane sample can be obtained from the standard *V–R* curve and thus, the membrane area resistance is obtained by multiplying effective area of the electrodes. In practical measurements, slope of *V–R* cure and effective area are multiplied and considered to be an instrument constant which is equal to 0.5962 in our experiments. The area resistance is directly obtained from potential difference (with and without a membrane sample) times this instrument constant.

This procedure for area resistance determination is very fast and convenient. Its validity has been confirmed by Mo and Liu [11].

2.4.4. Membrane potential (E_m) and the transport number t

A membrane sample was interposed between two halves of acrylate resin cells, fitted with double junction special-designed Ag–AgCl electrodes [12]. As shown in Fig. 2, the unit was designed to permit continuous flow of 0.1 M KCl and 0.2 M KCl on the membrane surfaces of each side. The potential between the electrodes (E) was determined through a digital multimeter (model:GDM-8145, Good will instrument Co. Ltd., Taiwan). As the potential of Ag–AgCl electrode is related with concentration in solution, the membrane potential is obtained from the difference of E and the standard solution potential E_0 [12]:

$$E_m = E - E_0 \text{ with } E_0 = -\frac{RT}{F}\ln\frac{C_2}{C_1} \qquad (2)$$
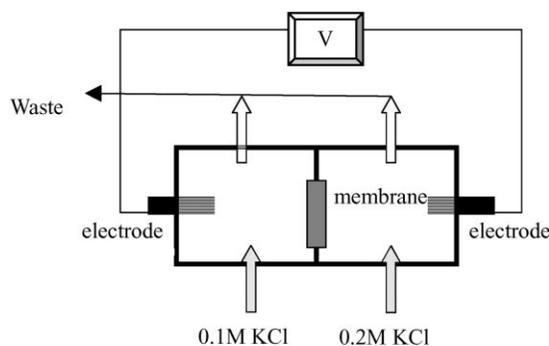

Fig. 2. Cell apparatus for measuring membrane potential.

where R is gas constant, T is absolute temperature, F is faraday constant, C_1 and C_2 are the concentration of aqueous solution in the two sides. The static transport number t of the anion in the membrane is given by [12]

$$t_- = \frac{0.5E}{E_0} \qquad (3)$$

Compared with most methods used in literatures [4,6,7,14], this method has discarded Calomel reference electrodes and the corresponding salt bridges and thus, the results will not be affected by any of liquid-junction potentials or asymmetric potentials of reference electrodes.

3. Results and discussion

3.1. The effect of temperature on the bromination processes

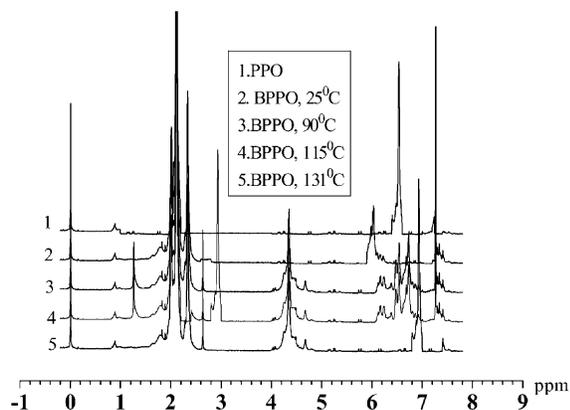The ^{1}H NMR spectra for both PPO and the brominated polymers were shown in Fig. 3. As can be

Fig. 3. PPO and its brominated series polymers (BPPOs).

These precise determinations further reveal the importance of temperature control on the bromination reaction. Obviously, below 60°C, bromination is completely conducted in aryl position (the spectrum at 60°C was not shown in the figure for clarity). When temperature increase to some point, such as 90°C, this bromination can be proceeded in both aryl and benzyl positions. With an increase in temperature, aryl bromine content (ABC) decreases while benzyl bromine content (BBC) increases until almost benzyl-substituted polymers were obtained at the boiling state (131°C). The sum of total bromine substitution listed in Table 1 exceeded 95%, indicating that the bromination of these polymers was almost complete.

3.2. Ion-exchange capacity, water content and fixed group concentration

As mentioned above, different brominated polymers can be obtained by controlling reaction temperature allowing a manufacture of series membranes with different properties. Figs. 4 and 5 illustrate the effect of the position and content of bromine substitution on these three properties. As can be seen, both the IEC and W_R increase with the BBC if the ABC remains unchanged. Nevertheless, fixed group concentration (C_R), which are expressed as the ratio of IEC to water content, decreased at first and remain approximately unchanged due to the increase in water content. If BBC remain unchanged, it is observed that IEC slightly
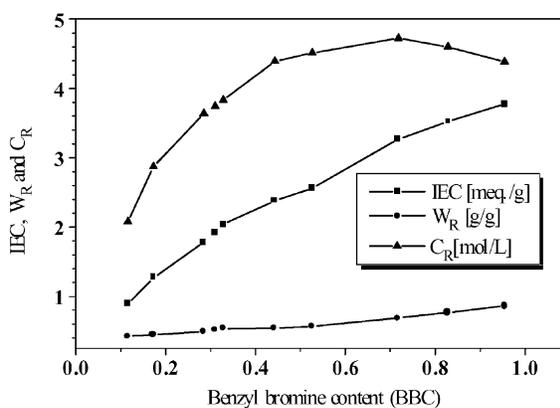
seen, temperature has a significant large effect on the bromination processes. If the bromination was conducted at low temperature, such as at 25°C, no new peaks is observed except that the peaks at 6.5 ppm (aryl H) move toward an up-field at 6.0 ppm (curve 2). It is indicative that the bromination is conducted at aryl position of PPO and no any benzyl-H has been substituted. When temperature reaches about 90°C, a new peak different from that of original PPO is observed at about 4.4 ppm and show the existence of –CH$_2$Br (curve 3). Due to both the benzyl and aryl bromine substitutions at this case, the peaks at original methyl and aryl positions have divided into several small peaks at 1.5–2.5 and 6–7 ppm, respectively (curve 3). If the temperature was raised to 115°C, no great change is observed (c.f. curve 4) except that relative magnitude of integrating peak intensity at the three positions was changed. However, when bromination was conducted at boiling state (131 ± 2°C), the peak at aryl H position was recovered from its original state (curve 5). The precise determination of bromine content and position can be calculated from the relative magnitude of integrating peak intensity of ^{1}H NMR spectra and the results are shown in Table 1.

Table 1
Effect of temperature on bromination processes[a]

Temperature (°C)	25	60	90	115	131
Aryl-substitution (%)	96	99	58	88	3
Benzyl-substitution (%)	0	0	38	10	97

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

Fig. 4. Effect of BBC on membrane, IEC, W_R and C_R with ABC = 0.11.
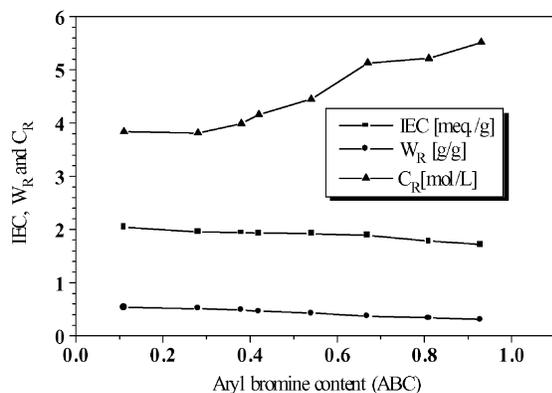
Fig. 5. Effect of BBC on membrane, IEC, W_R and C_R with BBC = 0.33.

Fig. 6. Effect of bromine substitution on area resistance.

decreases (keep approximately unchanged within an error) while the fixed concentration increases with aryl-substitutions due to a decrease in water content entrapped in the membrane with an increase in ABC. Theoretical explanation to this change trend brings us back to the bromination and amination processes. As we know, the amination agents can only react with a benzyl-substitution group, giving rise to quarter-amine groups functioned as active point, which will increase the hydophilicity of the polymer. So both the IEC and water content will increase with BBC and the ratio of them, i.e. fixed group concentration will correspondingly increase at first and then decrease. On the other hand, aryl-substitution groups can't react with any of bromination agents and thus, make no contribution to the active points and therefore the IEC will remain approximately unchanged from theoretical point of view. A slight decrease is caused by the weight gain of the base membrane when ABC increases. In addition, existence of aryl-bromine group will increase the rigidity of the polymer and thus, increase the hydrophobicity. Therefore, W_R decreases and fixed group concentration increases with ABC.

The prepared anion membranes at each preparation condition possessed a wide range in properties. It should be noted that unlike most charged membranes [2,4,6–8,13], water content does not definitely increase with IEC, because we can increase ABC to decrease the water content with IEC remaining approximately unchanged. And thus, from this point of view, by adjusting the portions of benzyl and
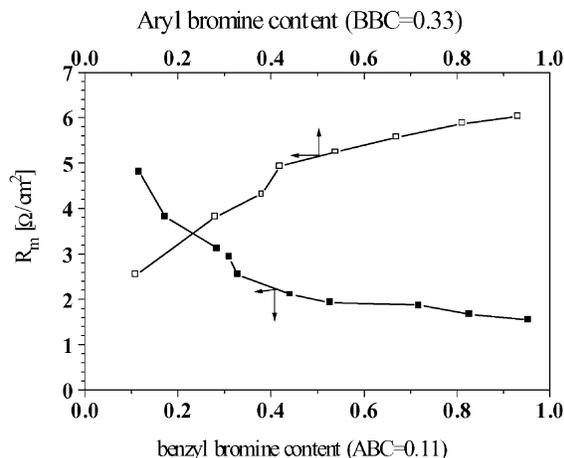
aryl-substitutions, a series of membranes with both desired IEC and water content can be reasonably acquired to satisfy with different industrial demands.

3.3. Area resistance

Fig. 6 illustrates the relationship between the resistance and the brominations. It is observed the resistance decreases with benzyl-substitution until a constant value about 1.6 is attained and increase with ABC. This trend is related with ionic conductivity mechanism in a charged membrane. Ionic conduction in a charged membrane depends mainly on two factors: water content and active point (IEC). An anion exchange membrane has been considered from the viewpoint of a three-phase membrane model where the membrane consists of hydrophobic polymer, an active exchange zone and an interstitial zone [15,16]. A counter ion transport occurs mainly through the active region where it moves by a hopping mechanism and a co-ion transport occurs mainly through interstitial region due to the minimal repulsive force caused by ion exchange sites. Thus, both the interstitial region and active exchange zone make contribution to the conductance. The necessity for an insulator transition to a conductor requires at least one infinite cluster composed of these two regions [17–19]. The more cluster are formed, the more conductive is the membrane. And thus, the area resistance will increase with ABC due to a decrease in water content and decrease

with IEC due to increase in active zone. However, as mentioned above, the membrane contains a substrate made from inert porous polyvinyl chloride fiber. So it can not be decreased to a value which is below the resistance resulted from the substrate.

3.4. Static transport number

In order to characterize the permselectivity of the membrane series prepared at each condition, the concentration membrane potential between 0.2/0.1 M KCl solutions were measured. The transport numbers of chloride ions were calculated based on these potentials and demonstrated in Fig. 7. Obviously, transport number decreases with benzyl-substitution and increase with aryl-substitution. It elucidates that the transport selectivity for counterions (chloride ions) is affected by the bromine substitution to significant large extent. Benzyl-substitution gives rise to a decrease in selectivity while aryl-substitution results in an increase in selectivity. This observation can be explained by both fixed group concentration and water content. Theoretically, transport number or selectivity tends to increase with fixed group concentration, so selectivity increases with aryl-substitution for the aryl-substitution membrane series. However, It is followed from the three-phase model that hydrated ions will require a certain volume of water within the membrane to permit migration through the membrane [14–16]. In other words, if the water content in membrane increases, it

will provide more channels for co-ionic transport (adsorb more electrolyte ions due to Donnan equilibrium) and thus, the selectivity of a counterion is decreased. Therefore, for benzyl-substitution membrane series, even fixed group concentration increases with BBC at first, the selectivities decrease with BBC because of the increase in membrane hydrophilicity. Obviously, water content makes a decisive role in selectivity. For an excellent ion exchange membrane, the water content should be decreased from the selectivity of view and the ion exchange capacity should be maintained in proper range from permeability of view. This aim can be easily realized by adjusting the BBC and ABC as mentioned above. A diffusion–dialysis membrane has been developed based on this theme, which has behaved both high acid diffusional ability and high selectivity of acids over the existing salts [9,20].

3.5. Comparison with the commercial membranes

A typical membrane based on this job is prepared with ABC = 0.11 and BBC = 0.33 (denoted as DF1133). The main characteristics of this membrane is compared with some commercial homogeneous and heterogeneous anion membranes, such as AFN, AMX, ACS, ACM from Tokuyama Soda (Japan), MA-40 from Moscow and S203, PE 3362 from China. The data on AFN, AMX, ACS, ACM, MA-40 are compiled and checked by Elattar el al. [21] and the S203 and PE3362 from the suppliers and checked at our experimental conditions. These membranes are for different industrial purposes, such as AFN is an organic fouling-resistant membrane, AMX, ACS, MA-40, PE3362 are used for electrodialysis, S203 for diffusional dialysis and ACM for low proton transport. As shown in Table 2, the area resistance of DF 1133 is a little higher than that of AFN. But this resistance is very close to those of the conventional electrodialysis membranes, such as AMX and ACS. It should be noted that the resistance of the membranes, such as AFN, AMX and ACS were checked in 0.5 M NaCl while DF1133 determined in 0.1 M NaCl, so the resistance of DF1133 is well compared with those of AMX, ACS. Obviously, the area resistance of DF1133 is superior to the low proton transport membrane ACM and the heterogeneous anion exchange membranes, such as PE3362, MA-40 as well as homogeneous membrane
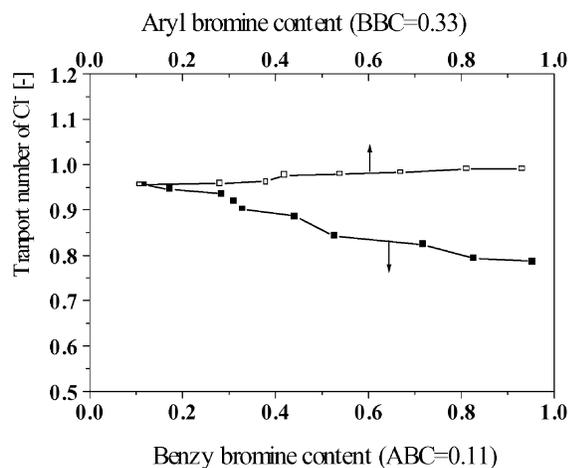

Fig. 7. Effect of bromine substitution on transport number.

Table 2
Main characteristics of a typical membrane in this paper and some commercial anion exchange membranes[a]

Name	Thickness (mm)	IEC (meg/g dry)	Water content (%)	R_m ($\Omega\,cm^{-2}$)	t_- (Cl$^-$)
AFN	0.15–0.20	2.0–3.5	40–55	0.4–1.5	0.92
AMX	0.23	2.0	37	2.1	0.91
ACS	0.10–0.14	2.0–2.3	15–16	2.0–3.5	0.96
ACM	0.30	1.1–1.3	30–40	5–10	0.93
MA-40	0.15	0.6	17	5.0	0.98
PE3362	0.45	1.8–2.0	30–45	13.1	0.89
DF1133	0.20	2.0–2.5	40–55	2.0–3.0	0.95
S203	0.22–0.28	1.0–1.3	23–30	5.0–8.0	0.90

[a] AFN, AMX, ACS, ACM from Tokuyama Soda and S203 from Linbo Chemical Plant of China are homogeneous and contain quarter ammonium group. MA-40 from the institute of Plastic Material of Moscow and PE 3362 from Shanghai Chemical Plant of China are heterogeneous and prepared from the mixture of ion-exchanges and polyethylene. The data on AFN, AMX, ACS, ACM MA-40 are from Tables 1 and 3 in Ref. [21] and the data of S203 and PE3362 from the products specifications.

S203. As far as the transport number is concerned, DF1133 has a value above 0.95. This value is higher than those of most commercial membranes. However, the transport number data in Table 2 for AFN, AMX, ACS, ACM is determined by Elattar et al. from Hittorf method and current–voltage curves (CVC) [21]. The data from the suppliers for these membranes are greater than 0.98. DF1133 is only a little less than this magnitude. It is emphasized that S203, which is prepared from chloromrthylated polysolfone, has a lower transport number than DF1133 due to the lack of chemical crosslinking. The others characteristics, such as thickness, IEC, water content, are also within the reasonable limits for the membrane in this paper and the commercial membranes even though they are less important to consider than the area resistance and transport number in practical applications. To sum, DF1133 has an equivalent conventional properties as those of the international commercial membranes and can be used in a manner analogous to AMX and ACX for the operation of electrodialysis.

4. Conclusion

A new route for preparing an anion exchange membrane is initiated in this paper. The membranes were prepared directly from polymers which contain benzyl group, such as poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) investigated here, by conducting the processes of bromination and amination. This process has eliminated the use of chloromethyl methyl ether, which has been considered as a potential harmful toxicity material and thus, the new technology is promising from environmental point of view.

PPO can be experiencing both aryl and benzyl-substitution. The substituted position mainly depends on temperature. Below 60°C, bromination is completely conducted in aryl position; thereafter, bromination takes place at both aryl and benzyl positions and BBC increase with temperature, ABC decreases while BBC increases until almost benzyl-substituted polymers were obtained at the boiling state

The membrane properties is significantly affected by the bromination processes: benzyl-substitution will bring about an increase in ion exchange capacity, water content and decrease in area resistance and transport number; while the aryl-substitution has the opposite effect on these properties except that ion exchange capacity keeps approximately unchanged. Therefore, by properly balancing them, a series of membranes can be obtained for different industrial requirements. For example, in the diffusion dialysis, the area resistance is not significant, we can improve the selectivity by increasing aryl-substitution [20], allowing a increase in area resistance; if the membrane acts as a anion layer of a bipolar membrane, water content and area resistance seem to be more important than transport number, we may have a choice to increase the benzyl-substitution or decrease the aryl-substitution; while by optimizing the portions of benzyl and aryl-substitutions, a desirable membrane can reasonably achieved with both the proper area resistance and the transport number for conventional electrodialysis.

Acknowledgements

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