

Fundamental Studies of a New Series of Anion Exchange Membranes: Membranes Prepared from Bromomethylated Poly(2,6-dimethyl-1,4-phenylene oxide) and 4-Vinylpyridine

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ABSTRACT: A series of anion exchange membranes with pyridinium groups were prepared by aminating 100% bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) with 4-vinylpyridine. These membranes exhibited higher ion exchange capacity, lower water uptake, lower area resistance, and better thermal stabilities than the membranes prepared from pyridine. Trimethylamine was used for further amination, but it did not enhance the membrane's permselectivity for fluoride, chloride, bro-

midate, iodide, hydroxyl, nitrate, nitrite, or thiocyanate anions. Accordingly, 4-vinylpyridine was the better aminating agent to enhance the permselectivity of membranes for some monovalent anions. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3016–3025, 2009

Key words: anion exchange membrane; poly(2,6-dimethyl-1,4-phenylene oxide); 4-vinylpyridine; permselectivity

INTRODUCTION

Ion exchange membranes have found many applications ever since they were invented in the last century. For example, they can be used for electrodia-lytic concentration of seawater to produce sodium chloride, demineralization of saline water, desalina-tion of cheese whey solutions, and demineralization of sugarcane juice.^{1–6} Among these, the separation of specific salts from aqueous electrolyte solutions using electrodialysis is one of the most important applications. Nonetheless, there is still a big chal-lenge in exploring high-permselectivity membranes to separate ions of a sign and/or charge.⁷ As reported,⁸ one promising strategy can be taken to achieve an effective separation between anions of a sign and/or charge: adjusting the hydrophobicity of membranes. Sata et al.^{8–12} prepared a copolymer via reaction of chloromethylstyrene and divinylbenzene with different amines, such as trimethylamine (TMA) and 4-vinylpyridine. Because of the differ-ence in hydrophilic–lipophilic balance (HLB) of

amines, the obtained membranes correspondingly showed different hydrophobicities¹² and thus differ-ent permselectivities for anions. However, these membranes have a high manufacture cost since an expensive chemical is used for preparation: chloro-methylstyrene. Furthermore, the preparation process is relatively complicated since it involves several steps, such as mixing of monomers, casting, and polymerization at a relatively high temperature.

This work reports two strategies to obtain a highly-permselective anion-exchange membrane with a lower manufacture cost and in a simple pre-paration process without using chloromethylating reagents. One is to employ bromomethylation, instead of chloromethylation, to treat poly(2,6-di-methyl-1,4-phenylene oxide) (PPO).^{13,14} Naturally, the use of carcinogenic chemical—chloromethyl methyl ether—can be avoided. The other strategy is to choose 4-vinylpyridine as the aminating agent for membrane preparation. 4-vinylpyridine is expected to improve the stability of membranes since pyridine was identified to degrade bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) base membranes.¹⁴ Subsequent characterizations include ion exchange capacity (IEC), water uptake (W_R), membrane area resistance (R_m), energy dispersive X-ray analysis (EDXA), and thermogravimetric anal-ysis (TGA). Since 4-vinylpyridine has lower HLB value than TMA or pyridine, the membranes pre-pared with 4-vinylpyridine should possess different

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properties from those reacted with pyridine or TMA. The permselectivity¹⁵ for different ions will be compared between the membranes prepared with 4-vinylpyridine and other membranes.

EXPERIMENTAL

Materials

The base membrane, 100% BPPO with poly(vinyl chloride) substrate, was kindly supplied by Tianwei Membrane Corporation Ltd. of Shandong (China). Preparation procedures for the base membranes were described in our previous article.¹⁶ 4-Vinylpyridine (96%, stabilized with 100 ppm hydroquinone) was used without distillation. TMA was purchased as a saturated aqueous solution and diluted to 1 mol/dm³ when used for amination. Methanol, pyridine, and *n*-butanol were of analytical grade. Deionized water was used throughout.

Membrane preparation

As shown in Scheme 1, the preparation process comprises several steps. First, different samples of the base membranes of BPPO (4.0 cm × 4.0 cm) were immersed into the reaction bath of 4-vinylpyridine (30 wt %) methanol solution at room temperature (25°C), and the solutions were stirred for 4, 14, 24, and 48 h, respectively. The membranes were taken out of the reaction bath and washed with methanol and then deionized water. The prepared membranes were denoted as D1, D2, D3, and D4, respectively. In another group of experiments, the samples of base membranes were reacted with 4-vinylpyridine by following the same procedure as that for D series of membranes and subsequently immersed into a TMA aqueous solution (1 mol/dm³) at room temperature for 24 h to aminate the remaining bromomethyl groups with TMA. Such membranes were denoted as E1, E2, E3, and E4, respectively. For comparison, some membranes were prepared using pyridine¹⁴ and characterized correspondingly. All the synthesized anion exchange membranes were equilibrated with a NaCl aqueous solution (1 mol/dm³) to ensure the chloride form.

Membrane characterizations

The chemical structure of both the base membrane and the final membranes (D and E series of membranes) was investigated using FTIR with a Bruker Equinox-55 FTIR spectrometer.

The surface morphologies of the membranes reacted with pyridine and those with 4-vinylpyridine were observed by a scanning electron microscope (XT30 ESEM-TMP PHILIP). The morphology

of the fracture surface of the final membranes was observed by the same instrument, and the distributions of the chlorine and bromine atoms in the thickness direction were analyzed through EDXA.

Thermal behaviors of the membranes prepared from 4-vinylpyridine or pyridine was determined by TGA on a Shimadzu DTG-60H analyzer in 50 mL/min nitrogen gas atmosphere with a heating rate of 10°C/min.

The base and final membranes were characterized by ion-exchange capacity (IEC, mmol/g dry membrane), water uptake (W_R , g H₂O/g dry membrane), and area resistance (R_m , Ω cm²).

The ion-exchange capacity was determined using the Mohr method,¹⁶ in which membranes in the chloride form were transformed into the sulfate form by immersing in a Na₂SO₄ aqueous solution (0.5 mol/dm³) for 8 h. The chloride ions released from the membranes were titrated with a AgNO₃ aqueous solution ($C_{\text{AgNO}_3} = 0.100$ mol/dm³), and the consumed volume (V_{AgNO_3}) was recorded. The ion-exchange capacity (IEC, mmol/g dry membrane) of membrane (in chloride form) was calculated according to the following equation:

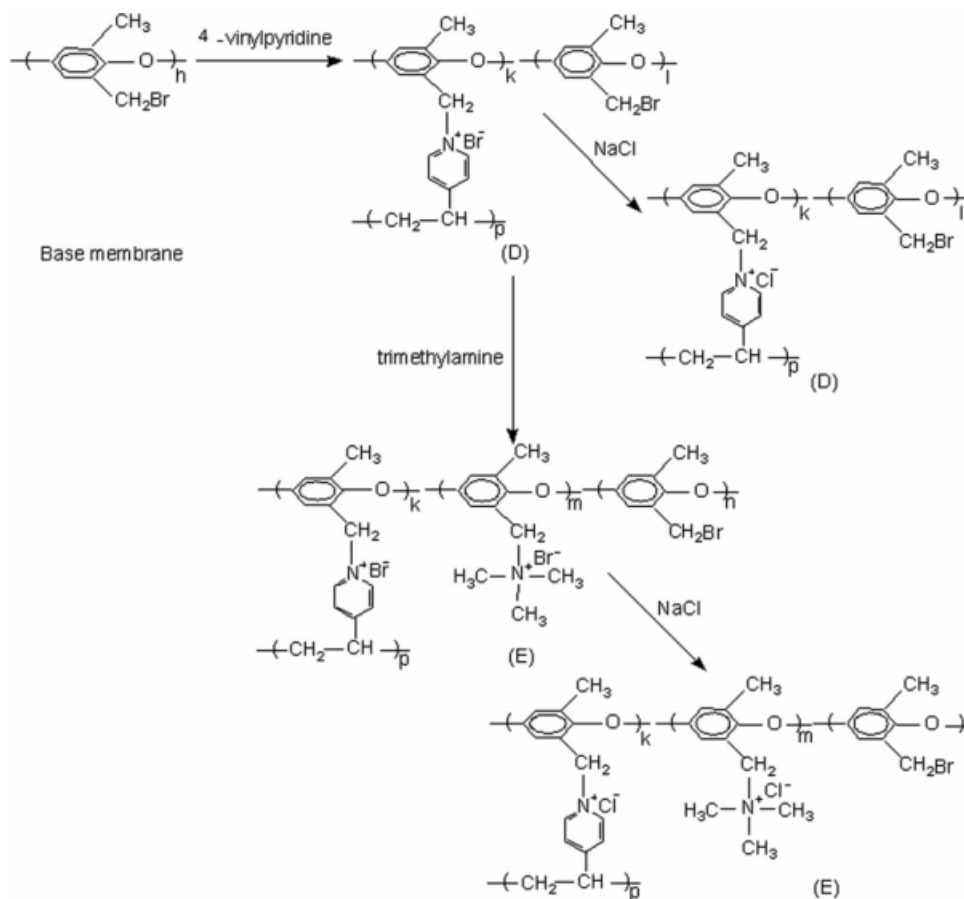
$$\text{IEC} = \frac{C_{\text{AgNO}_3} \times V_{\text{AgNO}_3}}{W_D} \times 1000 \quad (1)$$

where W_D is the weight of dry membrane.

The water uptake (W_R) was determined by equilibrating membrane samples (in the chloride form) with deionized water at room temperature for more than 8 h. The membrane samples were taken out of water and weighed immediately after removing surface water (W_1 , wet weight). The anion exchange membranes were then dried under dynamic vacuum at 40°C until constant weight, and then the dry weight (W_2) was recorded. The W_R was calculated by subtracting the dry weight (W_2) from the wet weight (W_1) of the membrane in the unit of g H₂O/g dry membrane (in the chloride form) and the equation is as follows¹³:

$$W_R = \frac{W_1 - W_2}{W_2} \times 100\% \quad (2)$$

The membrane area resistances (R_m) were determined using a clip cell and a LCR meter (TH2816, Changzhou Tonghui Electronics Co. Ltd, China) with a frequency of 100 kHz. The membrane samples were equilibrated in 0.5 mol/dm³ NaCl aqueous solution at 25°C for more than 24 h before measurement. The magnitude of impedance ($|Z|$) and the phase angle of impedance (θ) of the



Scheme 1 Preparation process of D and E series of membranes.

membranes were measured and used for calculating R_m ($\Omega \text{ cm}^2$) according to the following equation¹⁷:

$$R_m = \frac{\left(|Z|_{\text{sample}} \cdot \cos \theta_{\text{sample}} - |Z|_{\text{blank}} \cdot \cos \theta_{\text{blank}} \right)}{\times \text{area}} \quad (3)$$

Determination of permselectivity for monovalent anions

The permselectivity was calculated from the relation between bi-ionic potential and the concentration ratio of two ionic species. The theory has been validated in our previous article.¹⁵ A brief introduction of determination procedures is presented below.

As shown in Figure 1, the bi-ionic membrane potential is determined by a setup composed of two sections (made of poly(methyl methacrylate) resin) and is equipped with a glass stirrer and a calomel electrode for each section. The membrane has an effective area of $5.07 \times 10^{-4} \text{ m}^2$ and is installed between the compartments with silicon rubber gaskets as seals. The membranes should be conditioned for 2 days in 1 mol/dm^3 referenced electrolyte (NaCl) before determination. As a starting step for

permselectivity determination, both half-cells are filled with 100 mL of 0.01 mol/dm^3 NaCl solution, and the equilibrium is accelerated by stirring. Then a given volume (0.2 mL for each time) of 1 mol/dm^3 NaX ($X = \text{Cl}^-, \text{F}^-, \text{Br}^-, \text{I}^-, \text{SCN}^-, \text{NO}_3^-, \text{NO}_2^-, \text{OH}^-$) solution is added at the left compartment. Meanwhile, an equal volume of water is added in the right side to keep the concentration of NaCl equal on two sides. After stirring, the stable potential value is attained and recorded with a digital meter (DT9205, Zhangzhou Meter Electronics Co. Ltd., China). A series of membrane potential ($\Delta\phi$)-concentration ratios ($C_{\text{NaX}}/C_{\text{NaCl}}$) in the left compartment can be obtained, and these data are used to calculate the permselectivity referenced to Cl^- (T_{Cl}^X) by linearly regressing the equation¹⁵:

$$\exp\left(\frac{z_X F(-\Delta\phi)}{RT}\right) - 1 = T_{\text{Cl}}^X \frac{C_{\text{NaX}}}{C_{\text{NaCl}}} \quad (4)$$

z_X is the absolute valences of X ions, F the Faraday constant, R the gas constant, and T the absolute temperature. It should be pointed out that, before adding NaX in the left cell, the potential is not equal to zero due to the asymmetry of two electrodes. And

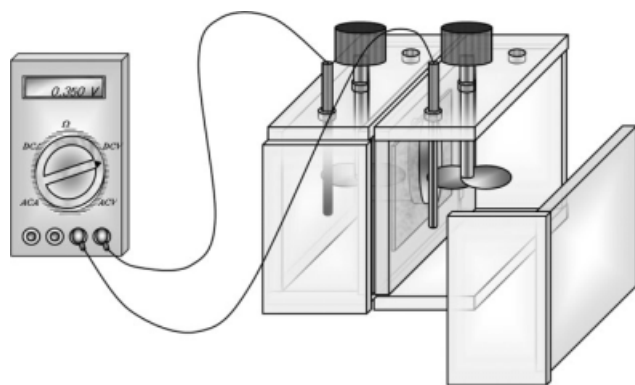


Figure 1 Schematic of the experimental setup for determination of permselectivity.

this systematic error should be subtracted from every potential reading.

RESULTS AND DISCUSSION

FTIR confirmation of the reaction of BPPO with 4-vinylpyridine

As mentioned in Section 2, D series of membranes were directly prepared by aminating BPPO base membrane with 4-vinylpyridine, and E series of membranes were subsequently aminated with TMA after synthesis in an identical manner to D series of membranes. Scheme 1 shows the reaction schemes for the preparation of the two series of membranes. To confirm these reactions, FTIR was employed and the resulting spectra are shown in Figure 2. A new characteristic peak appears at 1637 cm^{-1} in Figure 2 (D4) and (E4), which is the stretching vibration of C=C and C=N bonds in pyridine ring. This can be attributed to the quaternized 4-vinylpyridinium groups and thus indicates successful amination.¹¹ The pendant vinyl groups in 4-vinylpyridine, however, cannot find evidence in FTIR because vinyl groups disappear after polymerization. Besides, the characteristic peak of quaternary ammonium salts in E series of membranes (in Scheme 1), though expected at 960 cm^{-1} , is also submerged in the BPPO bands. To sum up, the results of FTIR indicate

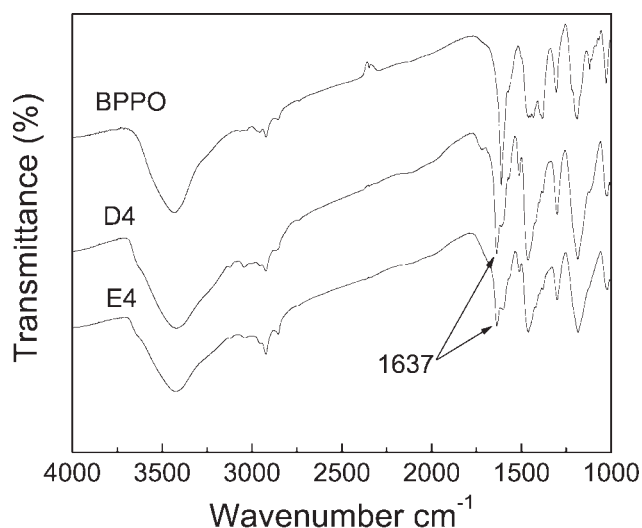


Figure 2 FTIR spectra of base and final membranes: D4, membrane aminated by 4-vinylpyridine for 48 h; E4, membrane aminated by 4-vinylpyridine for 48 h and then reacted with trimethylamine for 24 h.

a successful amination of the bromomethyl groups of the BPPO membrane with 4-vinylpyridine and polymerization of vinyl groups in membrane matrix.

Surface morphologies of the anion exchange membranes prepared from pyridine and 4-vinylpyridine

Figure 3(a,b) shows the surface morphologies of the membranes reacted with pyridine and those with 4-vinylpyridine for the same time (4 h). As described in our previous article, BPPO membranes were degraded by pyridine, resulting in the ruggedness of membrane surfaces.¹⁴ In comparison, the membrane prepared from 4-vinylpyridine is apparently smoother than that of the membrane prepared from pyridine. Furthermore, the mechanical and chemical properties of the final membranes can be maintained since 4-vinylpyridine does not degrade the membrane.

Energy dispersive X-ray analysis

Figure 4(a–e) shows the SEM images of the fracture surfaces of final membranes and the EDXA images

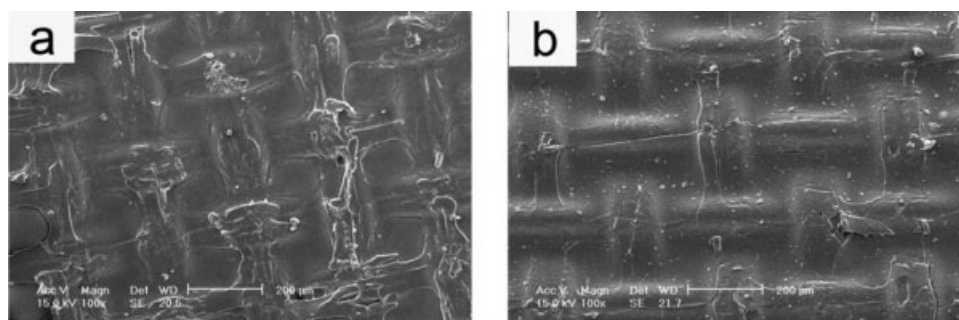


Figure 3 SEM images of final membranes. (a) aminated by pyridine for 4 h (b) aminated by 4-vinylpyridine for 4 h.

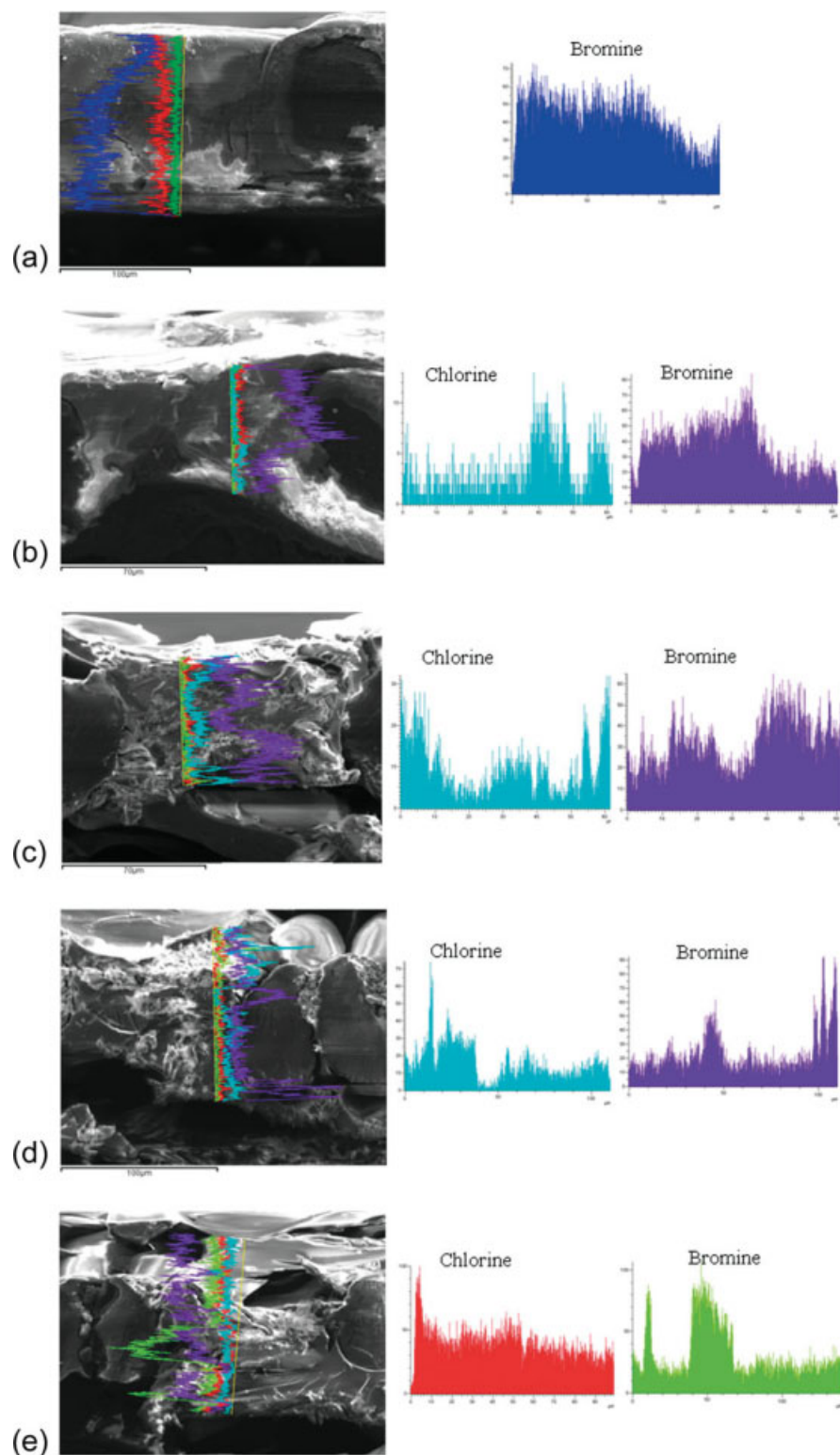


Figure 4 SEM-EDXA images of fracture surfaces of the membranes: (a) BPPO; (b) D1; (c) D3; (d) D4; (e) E4. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of chloride and bromide ions. The samples shown in the figures are the BPPO base membrane and the aminated ones, i.e., D1, D3, D4, and E4 (in the chloride form), respectively. In the EDXA images, the thickness of the membranes is estimated to be

150 μm . Comparing the results of BPPO base membrane and the final membranes with different amination time [Fig. 4(a–d)], there is an increase in chloride ions and decrease in bromide ions as the reaction time elapses, but there is no chloride ion in

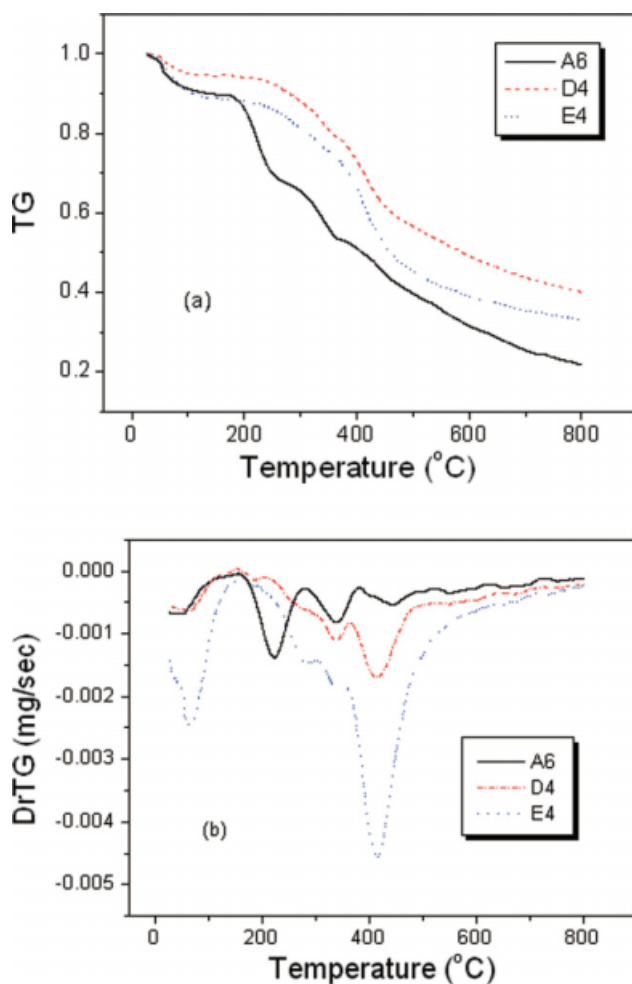


Figure 5 TGA (a) and DrTGA (b) of the prepared membranes (A6, D4, and E4). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

BPPO base membrane. Besides, D4 and E4 were taken for the investigation of the subsequent amination with TMA [Fig. 4(d,e)]. It can be found that the content of chloride ions and bromide ions in D4 are identical with those in E4 in the main. Besides, the content of quaternary ammonium groups and bromomethyl groups in the final membranes can be reflected by the content of the chloride ions linked to quaternary ammonium groups and the bromide ions linked to benzyl groups, respectively. Accordingly, the subsequent amination of TMA is not noticeable. This is probably due to the compact texture of the membrane after cross-linking of the vinyl groups in 4-vinylpyridine and the degradation of the available pyridinium groups in a TMA aqueous solution.

Thermal stability

To examine the thermal stability of the final membranes, the following samples were chosen for com-

parisons: the membrane reacted with pyridine for 48 h (A6),¹⁴ the membrane reacted with 4-vinylpyridine for 48 h (D4), and the membrane aminated by TMA for 24 h after reacted with 4-vinylpyridine for 48 h (E4). The results of TGA and its first-derivative curves DrTGA are shown in Figure 5, respectively. For all the three samples, the weight loss is divided into four stages and the first stage is at the range of 30–150°C, which can be ascribed to the residual moisture in the membranes. The third stage begins at 270°C, which is due to the breakup of the bromine at the pendant of BPPO. The fourth stage begins at 370°C and can be attributed to the thermal degradation of the polymer backbones.¹⁸ The second stage of weight loss, due to the degradation of quaternary ammonium groups,¹⁹ begins at different temperature for different samples: 150°C for A6 and 195°C for both D4 and E4 (Fig. 5). The corresponding weight loss peaks appear at 220°C for A6 and at 280°C for D4 and E4 (c.f. Fig. 5). Obviously, D4 and E4 exhibit the higher thermal stability than A6, and this is due to the cross-linking of the vinyl groups in D4 and E4.

Intrinsic properties of the final membranes

Figure 6 shows the relations between IEC and the reaction time of 4-vinylpyridine. Whether or not the membranes were subsequently aminated by TMA, IEC increases with the reaction time of 4-vinylpyridine. This can be explained by the increase in the amount of ion exchange groups (pyridinium groups) linked to the BPPO chains. Additionally, the IECs of two series of membranes follow the order D > E though the reaction time is the same. Theoretically, the IECs of E series should be higher than those of D series after subsequent amination with TMA.

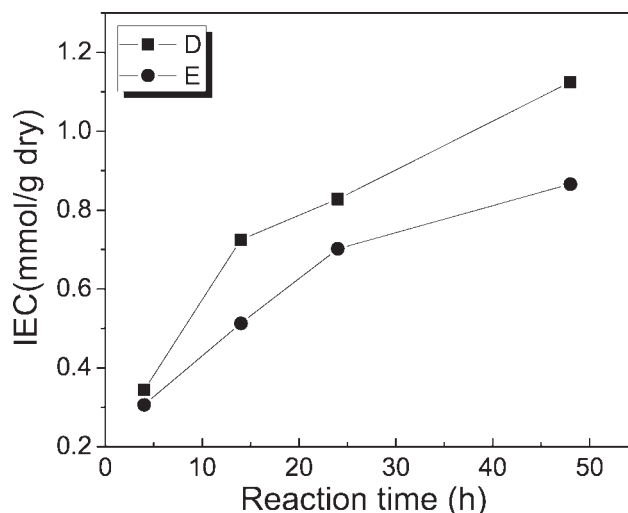


Figure 6 Effect of amination time on membrane IEC (30 wt % 4-vinylpyridine methanol solution was used).

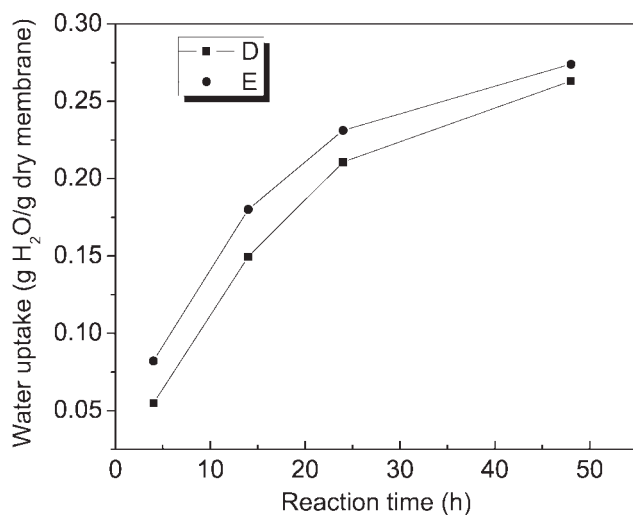


Figure 7 Effect of amination time on water uptake of the membranes (30 wt % 4-vinylpyridine methanol solution was used).

Possible reasons are as follows. First, polymerization of the vinyl groups in 4-vinylpyridine makes the membranes compact and the steric hindrance will suppress the reaction of TMA with the remaining bromomethyl groups. This assumption is in accord with the results of EDXA. Second, a compact texture after subsequent amination with TMA makes it difficult for sulfate ions to migrate into the inner part of cross-linked membranes and then to replace the chloride ions. So in the measurement of ion exchange capacity, the amount of the chloride ions decreases and thus the IEC decreases. Last, the pyridinium groups on the membranes may partially decompose in the TMA aqueous solution, resulting in a decrease in IEC.

Comparing with the membranes aminated by pyridine for the same reaction time (0.140, 0.453, 0.814, and 1.150 mmol/g dry for 4, 14, 24, and 48 h, respectively¹⁴), the membranes aminated by 4-vinylpyridine have higher IECs. As reported in our previous article,¹⁴ pyridine degraded membranes seriously and there was a large loss of bromomethylated polymers. Accordingly, the formed membrane had a low IEC. As for 4-vinylpyridine, there is no apparent membrane degradation, and, thus, the IEC value is relatively higher.

As shown in Figure 7, water uptakes of both series of membranes (D series and E series) increase with the reaction time of 4-vinylpyridine. This is consistent with the general principle in membrane preparation: W_R increases with IEC due to the hydration effect of the functional ion-exchange groups. In addition, the W_R values of two series of membranes follow the order $E > D$. Because E series of membranes has more hydrophilic functional groups (trimethylbenzylammonium groups), they are more hydro-

philic than D series and thus exhibit higher water uptakes.⁹ But the increment in W_R of E series is slight, and this is because only a small amount of TMA can aminate the remaining bromomethyl groups due to the steric hindrance. Note that the W_R values were reported to be 0.042, 0.276, 0.487, and 1.249 g H₂O/g dry membrane for the membranes aminated by pyridine for 4, 14, 24, and 48 h, respectively.¹⁴ In comparison, the W_R values of the membranes aminated by 4-vinylpyridine are lower. This phenomenon can be explained as follows: (i) the HLB (hydrophilic lipophilic balance) values of two amines (4-vinylpyridine and pyridine) are 13.08 and 14.03, respectively ($HLB = \sum(\text{hydrophilic group numbers}) - \sum(\text{hydrophobic group numbers}) + 7$),¹⁰ and, thus, the membranes aminated by 4-vinylpyridine are more hydrophobic; (ii) polymerization of vinyl groups in membrane matrix makes membranes more compact, resulting in a lower water uptake. Meanwhile, pyridine degrades membranes and gives the membranes a loose structure,¹⁴ leading to a higher water uptake. In conclusion, the final membranes aminated by 4-vinylpyridine are more hydrophobic than those aminated by pyridine. Therefore, they are expected to show better selectivities for the anions with different Gibbs free energies of hydration.

Apart from a sufficient IEC and optimal W_R value, good ion-exchange membranes should have low electrical resistance. The area resistance (R_m) values of the two series of membranes are presented in Figure 8. It can be found that the area resistance of the membranes aminated with 4-vinylpyridine (D series) decrease rapidly at the very beginning and after 14 h it decreases very slightly. The sample aminated for 4 h (D1) has a R_m value about 32.7 $\Omega \text{ cm}^2$. After further

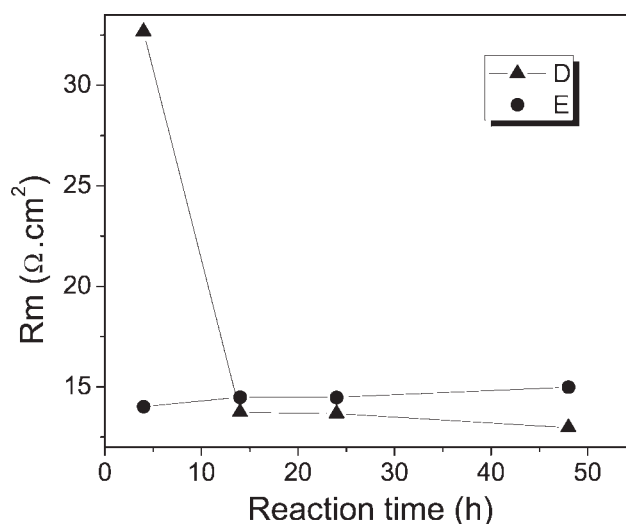


Figure 8 Effect of amination time on area resistance of the membranes (30 wt % 4-vinylpyridine methanol solution was used).

TABLE I
Permselectivity for Various Monovalent Anions Referenced to Chloride Ion in D and E series of Membranes

Membrane	D1	D2	D3	D4	E1	E2	E3	E4
P_{Cl}^F	0.171	0.100	0.080	0.089	0.138	0.104	0.090	0.099
P_{Cl}^{Cl}	1	1	1	1	1	1	1	1
P_{Cl}^{Br}	1.49	2.15	1.59	2.16	1.83	2.10	2.33	2.03
P_{Cl}^I	1.62	4.11	5.46	3.88	3.02	3.72	4.70	3.36
P_{Cl}^{SCN}	2.17	7.65	11.8	11.3	4.87	6.97	9.09	11.5
$P_{Cl}^{NO_3}$	1.67	2.60	4.13	3.80	2.32	2.68	2.67	3.74
$P_{Cl}^{NO_2}$	1.36	1.70	1.98	1.95	1.46	1.71	1.66	1.97
P_{Cl}^{OH}	0.671	0.348	0.219	0.144	0.418	0.302	0.213	0.150

animation with a 1 mol/dm³ TMA aqueous solution at room temperature for 24 h, the membranes (E series) have approximately equal R_m values but a little higher than the corresponding D series membranes (except D1). The results can be explained by the mechanism of ionic conduction in charged membranes, which primarily depends on two factors: IEC and W_R .²⁰ On one hand, the highest R_m value of D1 is corresponding to the lowest ion exchange capacity, which results from the shortest time of reaction with 4-vinylpyridine. Since the base membranes were reacted with 4-vinylpyridine for a longer time, the number of active ion-exchange sites in the two series of final membranes also increases. Hence, the rest membrane samples have lower R_m values than D1. After further amination with TMA, E series of membranes possess a relatively high water uptake, which favors the increment in conductivity. Nonetheless, the increase in water uptake can not compensate the decrease in IEC despite the decisive role of the active zones in ionic conductivity. Consequently, E series exhibit higher resistances than D series.

In our previous article, the R_m values were reported to be 57.3, 18.8, 15.1, and 8.0 Ω cm² for the membranes aminated by pyridine for 4, 14, 24, and 48 h, respectively.¹⁴ Obviously, the membranes aminated with 4-vinylpyridine have lower R_m values. For one thing, D series of membranes have higher IECs. For another, 4-vinylpyridine does not degrade base membranes, and, thus, the membrane structure and active zones can be preserved. From the viewpoint of a three-phase membrane model, an ion-exchange membrane consists of a hydrophobic polymer zone, an active exchange zone, and an interstitial zone.^{21,22} Counterions transport mainly through the active zone on the basis of the hopping mechanism, whereas co-ions transport mainly through the interstitial zone due to the minimal repulsive force caused by the ion exchange zones. Both transports contribute to ion conduction. The transition from an insulator to a conductor requires at least one infinite cluster comprising

these two zones. The more active zones contained in charged membranes, the more clusters are formed and the more conductive the membrane will be. In this case, the membrane aminated by 4-vinylpyridine has more active exchange zones and thus a lower R_m value than the membrane aminated by pyridine.

To compare with D and E series, the IEC, water uptake, and R_m values of base membrane (BPPO) were also determined. They are 0.058 mmol/g dry membrane, 2.43%, and $2.34 \times 10^4 \Omega$ cm², respectively. Theoretically, there is no ion exchange group, so the IEC and water uptake of the base membrane should approach to zero, and R_m values should be infinite. However, the sorption of base membrane results in a very low IEC and water uptake as well as a certain R_m . After comparison, the sorption does not bring much error to the IEC, water uptake, or R_m value in the cases of D and E series of membranes.

Permselectivity of membranes for monovalent anions

The permselectivities of D and E series of membranes for some anions are shown in Table I. For hydrophobic anions (such as SCN⁻, I⁻, Br⁻, NO₃⁻, and NO₂⁻), the permselectivity increases with the reaction time of 4-vinylpyridine in each series of membranes, whereas for hydrophilic anions (such as OH⁻ and F⁻) the permselectivity decreases. Since pyridinium groups adds to the hydrophobicity of these membranes, the permselectivity for hydrophobic anions increase in these membranes, whereas it is

TABLE II
Stokes Radii¹⁶ and Gibbs Free Energies of Hydration of Various Anions in Water²⁵

Anion	F ⁻	Cl ⁻	Br ⁻	I ⁻	OH ⁻	NO ₂ ⁻	NO ₃ ⁻	SCN ⁻
r_{stj} (Å)	1.64	1.19	1.17	1.18	0.46	1.27	1.28	1.38
$-\Delta G_{hydr}^0$ (kJ mol ⁻¹)	472	347	321	283	439	339	306	287

opposite for hydrophilic anions^{16,23,24} (the Gibbs free energies of hydration are shown in Table II). The permselectivity of both series of membranes have the following order: $\text{SCN}^- > \text{I}^- > \text{NO}_3^- > \text{Br}^- > \text{NO}_2^- > \text{Cl}^- > \text{OH}^- > \text{F}^-$. The sequence is consistent with most of the reports on permselectivity for anions^{8,26,27} as well as our previous article.¹⁶ This is determined by both the Stokes radii of ions (shown in Table II) and the affinity of ions to the membrane surface (reflected by Gibbs free energies of hydration).¹² To explain their effect on the permselectivity of anions, a conventional permeation process was introduced for ions which has five main steps in the case of a batch cell^{16,23,24}: (1) ion transport through left liquid film to membrane surface; (2) adsorption at the membrane surface; (3) transport through the membrane matrix by concentration gradient that is affected by electro-attraction (counter ions) or repulsion (co-ions); (4) desorption at the another side of the membrane surface; (5) transport from this side to liquid film of another side. The diffusion in membrane matrix and adsorption on the surface were the key steps. As well known, the former is mostly dependent on the size of hydrated ion (Stokes radii) and the latter is dependent on the affinity of ions to the membrane surface, which is affected by both the hydration ability of ions and the hydrophobicity of membranes. So the permeation progress will be finally attributed to Stokes radii and the hydration ability of ions, as well as the hydrophobicity of membranes, whereas the hydration ability of ions (hydrophilicity of ions) can be expressed by the standard molar Gibbs free energies of ions.

To compare the permselectivity of the membranes with similar IECs, we selected three pieces of membranes as samples: A5 (reacted with pyridine for 24 h),¹⁴ D3, and E4 (with an IEC about 0.8 mmol/g dry). The results are shown in Figure 9. In comparison, the permselectivity of D3 for SCN^- , I^- , Br^- , NO_3^- , and NO_2^- are the highest, and those for F^- and OH^- are the lowest, indicating the highest permselectivity of D3. However, it is opposite for A5. The results can be explained by the lowest water uptake of D3 (0.211 g H_2O /g dry membrane) and the highest water uptake of A5 (0.487 g H_2O /g dry membrane).^{14,28} So we can draw the conclusion that with the similar IECs, the membranes with the lowest water uptake exhibit the highest permselectivity for some anions with relatively low Gibbs free energies of hydration.

Sata et al. reported the selectivities of monovalent anions (such as Br^- , F^- , and NO_3^- ; referenced to Cl^-) through two strongly basic anion exchange membranes. The membranes were prepared via alkylation of a poly(4-vinylpyridine-co-divinylbenzene) membrane (crosslinkage: 5%) with *n*-propyl bromide (water uptake 0.46 g H_2O /g dry mem-

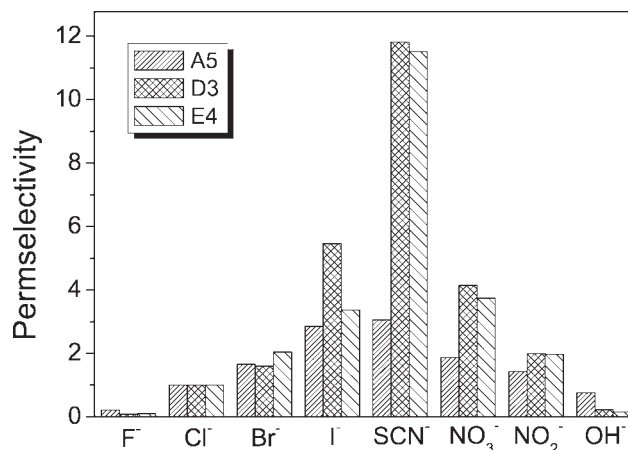


Figure 9 Comparison of permselectivity of some anions relative to Cl^- among the three pieces of anion exchange membranes with close ion exchange capacity (A5, D3, and E4).

brane) or 1,3-dibromopropane (water uptake 0.34 g H_2O /g dry membrane). The permeabilities for Br^- , F^- , and NO_3^- were 1.3, 0.25, and 1.35 for the former membrane and 1.4, 0.30, and 1.52 for the latter membrane.^{9,28} According to our previous investigations,^{16,29} the modification with pyridine (hydrophobic) can improve the permselectivities of the BPPO-based membranes. For instance, the permselectivities for I^- , OH^- , and NO_3^- are respectively 3.61, 0.25, and 2.32 in the membrane denoted as M00, which was prepared by aminating the base membrane of BPPO with a TMA aqueous solutions for 8 h and thus has trimethylbenzylammonium as fixed groups. The permselectivities for I^- , OH^- , and NO_3^- are 3.46, 0.62, and 1.74, respectively in the membrane denoted as C3, which was prepared by pre-cross-linking with ammonia for 1 h before amination with pyridine and finally reacting with TMA.²⁹ In comparison, most of the membranes in this study can separate these anions more effectively than the membranes reported.

CONCLUSIONS

A facile route is used for preparation of anion exchange membranes containing pyridinium groups without using the carcinogenic chloromethylating agent. Moreover, the aminating agent—4-vinylpyridine—does not degrade the membranes, so the mechanical and chemical properties of the base membranes can be preserved. And the polymerization of vinyl groups of 4-vinylpyridine also improves the thermal stability of the final membranes.

The anion exchange membranes were characterized by IEC, water uptake (W_R), and area resistance (R_m). The results show that IEC and W_R increase with the reaction time of 4-vinylpyridine in the case

of the two series of membranes. Although the membrane aminated by 4-vinylpyridine for 4 h (D1) had the highest R_m value, the rest membranes had lower values. The E series of membranes exhibit lower IEC values, higher W_R and R_m values than D series. Subsequent amination with TMA does not improve the intrinsic properties of the final membranes for practical applications.

The permselectivity sequence of some monovalent anions in the final membranes prepared here is in accordance with most of the reports. Still, the subsequent amination with TMA does not improve the permselectivity of the final membranes. The membranes prepared by aminating BPPO with 4-vinylpyridine show better permselectivity and thus have more practical applications.

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