

Fundamental Studies of Homogeneous Cation Exchange Membranes from Poly(2,6-dimethyl-1,4-phenylene oxide): Membranes Prepared by Simultaneous Aryl-Sulfonation and Aryl-Bromination

He Yu, Tongwen Xu

Laboratory of Functional Membrane, School of Chemistry and Material Science, University of Science and Technology of China, Hefei 230026, People's Republic of China

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ABSTRACT: Strong acid homogenous cation exchange membranes were obtained by simultaneously introducing sulfonic and bromine groups into poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). The ion-exchange capacity (IEC), water content, transport number, diffusion coefficient, contact angle, and tensile strength of the obtained membranes were studied. The results show that the membrane intrinsic properties are largely dependent on the substitution of bromine: the IEC and water content decrease with bromine content, while the area resistance and permselectivity of the membranes increase with this trend. Therefore, by properly

balancing them, a series of homogenous cation exchange membranes having good electrical properties and physical stability can be obtained to comply with different industrial electromembrane processes, such as diffusion dialysis, electrodialysis, electrodeionization, etc. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2238–2243, 2006

Key words: poly(phenylene oxide); homogenous membrane; cation permeable membranes; sulfonation; bromination

INTRODUCTION

The development of synthetic ion exchange membrane reported by Juda and Retardant¹ in 1949 and Juda and McRae² in 1950 stimulated both commercial and academic interest in such membranes and the related processes. There are two main classes of ion exchange membranes: one for cation permeability, called as cation exchange membranes; and another for anion permeability, called as anion exchange membranes. Nowadays, cation permeable membranes seem to receive more attention than the anion ones, because of their various electrochemical applications, such as in fuel cells, proton conductors, and chlor-alkali production, in addition to the traditional elect-

rodialysis and diffusion dialysis.^{3–8} Following the general route of ion exchange membranes, cation exchange membranes can be prepared by various approaches that can be classified into three categories on the basis of the starting materials.^{9,10}

1. Starting with a monomer containing a moiety that either is or can be made cationic exchange group, which can be copolymerized with non-functionalized monomer to eventually form a cation exchange membrane.
2. Starting with a polymer film, which can be modified by introducing cationic characters either directly (by grafting of a functional monomer) or indirectly (by grafting nonfunctional monomer), followed by functionalization reaction.
3. Starting with a polymer or polymer blends, by introducing cationic moieties, followed by the dissolving of polymer and casting it into a film.

Among these methods, sulfonation of available aromatic polymers (method 3) provides the most convenient route for preparation of a cation exchange membrane.^{11–13} Poly(phenylene oxide) (PPO) is one of the commonly used polymers for such membranes because of its good chemical stability, high glass-transition temperature, and low cost.^{14–16} Unfortunately, sulfonated PPO (SPPO), which is also a strong hy-

Correspondence to: T. Xu (twxu@ustc.edu.cn).

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drophilous material, will swell strongly in the water. For example, the degree of swelling will be 200%, if the ion-exchange capacity (IEC) of the membranes reaches 2.5 mmol/g dry membrane; and the membrane will dissolve in water almost, if the IEC reaches 4.0 mmol/g dry membrane. Thus, this often limits its application as an ion exchange membrane.

It can be theoretically expected that the mechanical properties and the permselectivity of SPPO membranes can be improved, if PPO is simultaneously modified by introducing the hydrophobic bromine groups in the polymer backbone. Though the analogous modifications have been reported for a few times, all are focused on the gas-separation applications.^{17,18} The preparation and characterization of homogeneous cation exchange membranes by simultaneous sulfonation and bromination of PPO is not available to date.

For these reasons, in this article, attempts are made to develop a new kind of cation exchange membrane based on PPO, by simultaneously attaching bulky bromine groups and sulfonic groups to the phenyl ring of the polymer backbone. The bromination and sulfonation processes as well as their effect on membrane dimensional stability and properties such as IEC, water content, membrane area resistance, transport number, diffusion coefficient, etc. will be investigated; a new type of membrane for electromembrane process will be obtained with both excellent mechanical stability and good conductivity, i.e., low resistance.

EXPERIMENTAL

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 supplied by Institute of Chemical Engineering of Beijing (China). Chlorosulfonic acid, chloroform, *N*-methyl-2-pyrrolidone (NMP), and other chemicals used in the preparation of the casting solution were obtained commercially and used without further purification. All chemicals used in the experiments were of analytical grade.

Bromination of PPO

The bromination of the aromatic ring of PPO was achieved at room temperature, by following a general procedure described previously.^{19,20} Dried PPO powder was dissolved in chloroform to form a 10 wt % solution and this solution was subjected to bromination, by adding chloroform-diluted bromine. The extent of bromination was controlled by the amount of bromine being added. Stirring of the solution was performed continuously during addition of the bromine solution and was continued for another 3 h after

addition of bromine at 30°C. The final solution was precipitated in excess of methanol, with vigorous stirring, then filtered, washed several times, and finally dried at 80°C for at least 20 h to obtain the aryl-brominated polymers. The degree of bromination was determined by ¹H-NMR (Unity plus 400) and was calculated to be 15, 25, 40, 50, and 60% for five different reaction batches. The brominated polymers were thus designated as PPOBr15, PPOBr25, PPOBr40, PPOBr50, and PPOBr60, respectively. For example, PPOBr15 represents that the degree of bromination of PPO is 15%.

It may be noted that, in all cases, only aryl substitution took place. ¹H-NMR analysis did not show any benzyl substitution.

Sulfonation of PPOBr

The general procedure for the sulfonation of PPOBr was similar to that described by Plummer et al.²¹ Sulfonation of PPOBr was carried out in a chloroform solvent, using chlorosulfonic acid as the sulfonating agent. To minimize the effect of moisture in atmosphere on the reaction, the dissolution of PPOBr in chloroform and sulfonation were carried out under a continuous purge of the reactor with N₂. All five different types of PPOBr batches were respectively dissolved in chloroform to form a 10 wt % solution. Chlorosulfonic acid in chloroform (8% solution) was slowly added to the polymer solution with stirring at 30°C. The amount of chlorosulfonic acid required for the reaction was based on the amount of unreacted repeat units in the PPOBr molecules. For example, in the case of PPOBr40, 5 g of the polymer was assumed to contain 3 g of nonbrominated groups and the amount of the acid required for the reaction was calculated accordingly. The precipitated sulfonated product was removed by filtration, left to stand in an excess of distilled water overnight, filtered off, washed thoroughly with distilled water, and dried. The sulfonated polymers were designated as SPPOBr15, SPPOBr25, SPPOBr40, SPPOBr50, and SPPOBr60, respectively. Such reaction was shown in Figure 1.

Membrane preparation

Membranes synthesized for the study were prepared by solution casting and solvent evaporation technique. The SPPOBr batches were dissolved in NMP to form a casting solution of ~10–15 wt %. The casting solutions were prepared, filtered, and spread on a clean glass plate, to obtain dense membranes of 0.10–0.15 mm dried thickness. The cast films were evaporated to dryness in open air at 60°C and were later vacuum dried for a period of 12 h at ambient temperature to expel traces of solvent. The SPPO membranes were also prepared from respective nonbrominated poly-

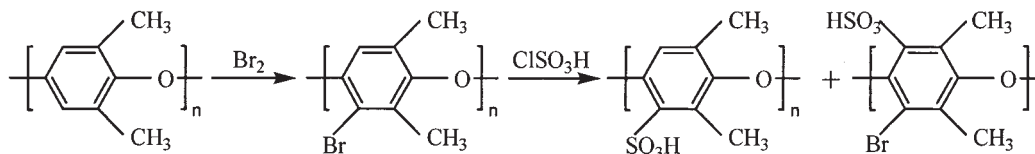


Figure 1 Reaction schemes of SPPOBr preparation.

mers, using a similar procedure, for comparison of various characteristics.

Membrane measurements

The characteristic properties of the membranes investigated include the IEC, water content (W_R), wet thickness (d), area resistance (R_m), diffusion coefficient (D), and the membrane potential (E). The methods were completely the same as those described in our previous studies.^{13,20,22,23} Then, fixed group concentration (C_R), which is expressed as the ratio of IEC to water content, and the transport number (t_+) can be calculated from them.

In addition, to elucidate the change in hydrophobicity and mechanical properties, contact angles and the tensile strength were also determined for SPPO membranes and SPPOBr membranes, with different aryl-substitutions. Direct measurements of contact angle of distilled water on the air-side surface of membranes were conducted at room temperature, using a contact angle meter (Model JY-82 SERIES, ChengDe Instrument Plant, China). The procedure used to carry out the contact angle measurements in this study was described in detail elsewhere.^{24,25}

The mechanical properties of the dry and wet SPPO/SPPOBr membranes were studied by a tensile testing machine (Model XL-50A, GuangZhou Instrument Plant, China) equipped with a 10 kg f load cell, at a crosshead speed of 12.5 mm/min. The tensile strength was calculated from the kg f load divided by the cross section area.

All these properties were evaluated with the independent measurements at room temperature.

RESULTS AND DISCUSSION

IEC, water content, and fixed group concentration

As mentioned earlier, different brominated polymers (SPPOBr) can be obtained by controlling the amount of bromine added, allowing the manufacture of a series of membranes with different properties. Figure 2 illustrates the effect of the bromination degree of SPPOBr on these three properties. As can be seen, the IEC of the membrane slightly decreases with the degree of bromination of SPPOBr. This is mainly due to a decrease in aryl-substitution points of PPO when

aryl-bromination degree increases, i.e., the existence of bromine in aryl position will prevent the following sulfonation of PPOBr from taking place at aryl position of polymers. However, it was also reported that the sulfonation agents could also react with the bromic groups if its substitution is low²⁶ and this will make contribution to the active points at the same time. This can explain why IEC decrease to more great extent when aryl-bromination degree is higher (after 40%).

As far as water content is concerned, it decreases remarkably with an increase in the degree of bromination of SPPOBr. The reason may be that, like most charged membranes, the water content increases in the order of IEC because of the strong hydration effect of the functional groups. In addition, the bromine group is the strong hydrophobic group; existence of aryl-bromine group will increase the rigidity of the polymer and thus, increase the hydrophobicity. Thus, W_R of the prepared membranes dramatically decreases with the degree of bromination compared with the nonbrominated SPPO, and the swelling and dimensional stability of the cation-exchange membranes improved greatly after introducing bromic groups.

Furthermore, the relative hydrophobicity of the membrane surfaces was studied by measuring contact angles of water. The results are summarized in Table I. Obviously, compared with SPPO membrane, the

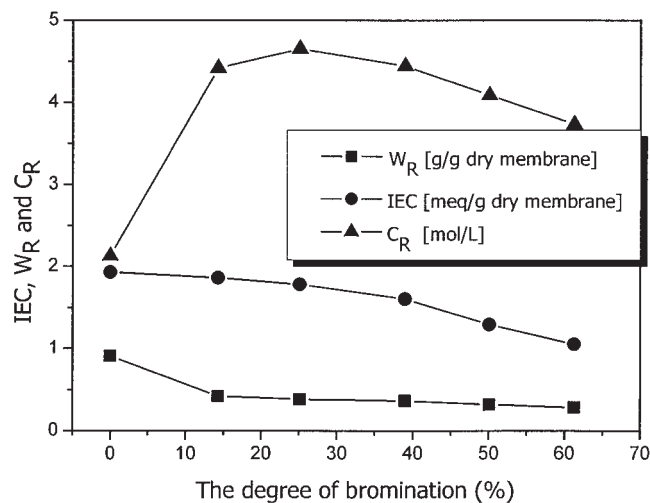


Figure 2 Effect of the bromination degree of SPPOBr on IEC, W_R , and C_R .

TABLE I
Water Contact Angle of SPPO and SPPOBr Membranes

| Membranes | Water contact angle, θ ($^\circ$) |
|-----------|--|
| SPPO | 38.5 ± 2.5 |
| SPPOBr15 | 62.0 ± 1.2 |
| SPPOBr25 | 68.6 ± 2.0 |
| SPPOBr40 | 73.8 ± 1.8 |
| SPPOBr50 | 75.5 ± 1.2 |
| SPPOBr60 | 80.1 ± 2.8 |

contact angle of SPPOBr had a remarkable increase, indicating that the membrane become hydrophobic after introducing bromine group into aryl-position of PPO. When the SPPOBr membranes with different substitution was compared, it was shown that the contact angle increases (or membrane hydrophilicity decreases) with the aryl-bromination content. This result is consistent with the trend of IEC and W_R .

Nevertheless, fixed group concentration (C_R), which is expressed as the ratio of IEC to water content, increased remarkably at first and then decreased slightly, when the degree of bromination was higher because of the decrease in both IEC and water content. The prepared cation-exchange membranes at each preparation condition possessed a wide range in properties. This provides a convenience to control both the water content and IEC by adjusting the degree of bromination and sulfonation. Then, a series of membranes with both desired IEC and water content can be reasonably acquired to satisfy with different industrial demands.

Area resistance

Besides sufficient IEC and proper water content, the membrane should have good electrical resistance. Figure 3 illustrates the relationship between the resistance and the bromine substitution of SPPOBr. It is observed that the area membrane resistance increases at first compared with the nonbrominated SPPO, and then remain approximately unchanged at a value about $2.4 \Omega \text{ cm}^2$ when the degree of bromination of SPPOBr is $<40\%$. This trend is related with ionic conductivity mechanism in a charged membrane and follows the analogous explanation in our previous studies.²⁷ Ionic conduction in a charged membrane depends mainly on two factors: water content and active point (IEC). A cation exchange membrane has been considered from the viewpoint of a three-phase membrane model,^{27,28} in which the membrane consists of hydrophobic polymer, an active exchange zone, and an interstitial zone. 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 because of the min-

imal repulsive force caused by ion exchange sites. Thus, both the interstitial region and the 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. The more active point exists, the more clusters are formed and the more conductive is the membrane.

Thus, the area resistance will increase with the degree of bromination of SPPOBr owing to a decrease in water content and small decrease in active zone. However, compared with the nonbrominated SPPO, the area resistance of the SPPOBr membrane whose bromine substitution ratio is within 40% has a certain extent increase, but all the same remain a relatively perfect value ($R_m = 2.4 \Omega \text{ cm}^2$). It will have a favorable commercial value and satisfy different industrial demands.

Static transport number

To characterize the permselectivity of the membranes prepared at different bromine substitution of SPPOBr, the concentration membrane potential between 0.2/0.1M KCl solutions were measured. The transport numbers of cations (potassium ions) were calculated on the basis of these potentials and are demonstrated in Figure 4. It can be observed that the transport number increases significantly after introducing bromic groups into polymers, and then remain slightly shifted (keep approximately unchanged within an error) with an increase in the degree of bromination. It elucidates that the transport selectivity for counterions (potassium ions) is affected by the bromine substitution, to significantly large extent. Theoretical explanation to this change trend brings us back to the change of both water content and fixed group concentration, with the degree of bromination. As discussed earlier, both IEC and W_R decrease with the degree of bromi-

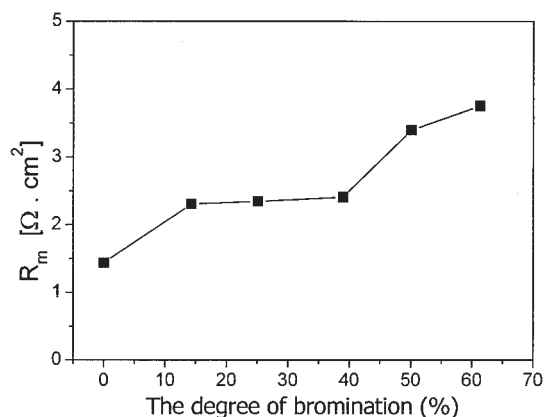


Figure 3 Effect of bromine substitution of SPPOBr on the area resistance.

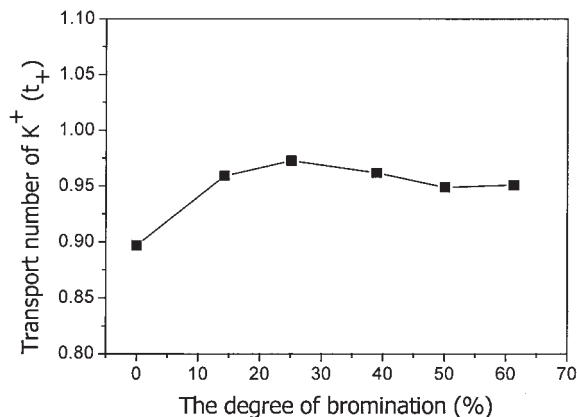


Figure 4 Effect of bromine substitution of SPPOBr on transport number.

nation, and C_R increased remarkably at first and then decreased slightly. Theoretically, transport number or selectivity tends to increase with the same trend as a fixed group concentration, that is, an increase with the degree of bromination and then decrease slightly.

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.²⁹ In other words, if the water content in the 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, and vice versa. Therefore, for the SPPOBr membrane series, the selectivity keeps approximately unchanged within the range of 95%, with the cooperation of water content and fixed group concentration. For an excellent ion exchange membrane, the water content should be decreased from the view of selectivity and the IEC should be maintained in proper range from the view of permeability. This aim can be easily realized as mentioned earlier, for these SPPOBr membrane series.

Diffusion coefficient

The diffusion coefficient (D) of the membranes prepared from different bromination degree of SPPOBr was shown in Figure 5. As can be seen, diffusion coefficient decreases with the degree of bromination. Theoretically, electrolytes transport in an ion exchange membrane is related to two important reasons; one is the active point, which can attract counterions of electrolyte and thus speed the diffusion, and the other is the homogeneity of active points distribution, which provides a channel for ionic transport. Therefore, for the homogeneous cation exchange membranes of SPPOBr, the active point is the direct factor that leads to the decrease in diffusion coefficient of the membranes. That is, the decrease in diffusion coefficient with the

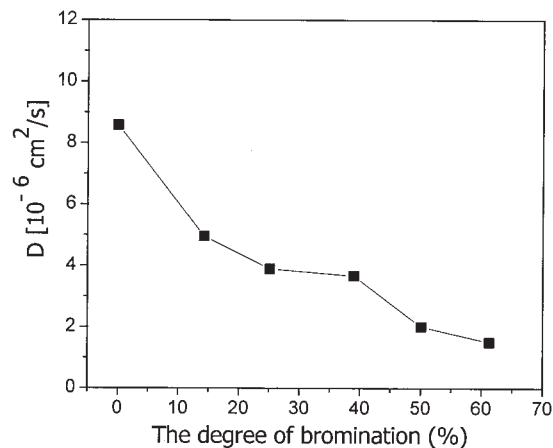


Figure 5 Effect of bromine substitution of SPPOBr on diffusion coefficient.

degree of bromination comply with the change trend of intrinsic parameters of the membranes, such as IEC and water content, which have been discussed in detail as the aforementioned one.

Mechanical properties

To compare the mechanical properties of the membranes with various degree of aryl-bromination, tensile strength at break of both the dry and wet SPPOBr membranes were tested and the results were shown in Figure 6. It can be observed that, for the dry membranes, there is a slight decrease in the tensile strength with an increase in aryl-bromination content. The possible explanation may be that an increase in aryl substitution makes the SPPOBr harder and brittle because of the rigorosity of bromine groups.^{30,31}

As far as the wet membranes are concerned, the tensile strength increases first with aryl-substitution

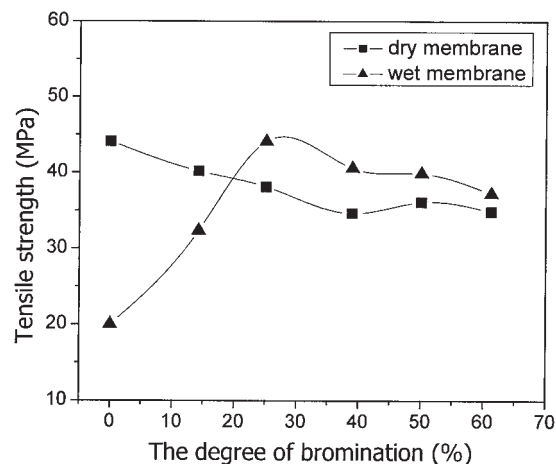


Figure 6 Effect of bromine substitution of SPPOBr on tensile strength.

and then decreases a little. At about 25% aryl-substitution, the tensile strength attains a plateau. This may be a combined effect of both membrane swelling properties and the rigorousness of bromine groups. As described earlier, water content of the membranes decreases with aryl-substitution, and this factor tends to increase the membrane mechanical strength. However, as indicated by the results of dry membrane, an increase in aryl-bromination will decrease the membranes mechanical strength because of the rigorousness of bromine groups. The two factors counteract with each other to give the available trend shown in Figure 6. In addition, it can be also shown that at high aryl-substitutions (after aryl-bromine content is 20%), the tensile strength of wet membranes is greater than that of dry ones. This is because that proper water content in the membranes permits an increase in the free volume, thereby increasing the chain movements, which makes the polymer material softer and flexible.³² However, exorbitant water content causes the membrane swelled up strongly and breakable; therefore, the tensile strength of wet membranes was less than the dry ones, when the aryl-bromine content is low.

CONCLUSIONS

In this study, a series of homogeneous cation exchange membranes were prepared directly from PPO by conducting the processes of sulfonation and bromination. As expected, the membrane fundamental properties such as IEC, water content, electrical resistance, transport number, diffusion coefficient of electrolytes, mechanical properties, etc., are largely dependent on the degree of bromination.

In general, the IEC of the SPPOBr membrane was little less than that of the SPPO membrane. Thus, the area resistance increased to a certain extent (it could be improved by increasing the degree of sulfonation). However, the dimensional stability, mechanical strength, and permselectivity ameliorated remarkably because of the reduction in water content. It is revealed that the relative perfect degree of bromination is within the range of 15–40%, and the homogeneous cation exchange membranes prepared in these conditions have the balanceable membrane properties and are satisfied with different industrial requirements, such as electro dialysis and diffusion dialysis.

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