# Gas Transport and Structural Features of Sulfonated Poly(phenylene oxide)

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**ABSTRACT:** The effect of ionomer structure on gas transport properties of membranes was investigated. For this purpose physical and transport properties of poly(phenylene oxide)(PPO) and its sulfonated derivative (SPPO) were compared. SPPO has a more rigid structure and a lower free volume, which determines low gas permeability and high permselectivity. Gas transport properties of two types of SPPO–PPO composite membranes with top layers prepared from solutions in methanol or $N,N$-dimethylacetamide (DMA) were investigated. The use of SPPO solution in DMA leads to the formation of membranes with higher gas permeability. It was shown that DMA is a morphologically active solvent for SPPO. Strong complexes of SPPO with DMA are formed in solution and retained upon transition into the condensed state. The plasticizing effect of DMA on SPPO determines the high gas permeability of the membranes and is in agreement with their mechanical properties. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66**: 1439–1443, 1997

**Key words:** gas transport; composite membrane; ionomer; sulfonated poly(phenylene oxide); polymer–solvent interaction

## INTRODUCTION

Ionomers are widely used in such ion-exchange processes of membrane separation as electrodialysis. Hence, their employment for gas separating membranes has been investigated fairly recently.[1–3] Diffusive gas separation is based on different permeabilities of polymer membranes for individual gases. Permeability is governed by the structural order in the membrane-forming polymer. The present work investigates sulfonated poly(phenylene oxide)(SPPO), which is an ionic derivative of a widely known gas separating material, poly(2,6-dimethyl-1,4-phenylene oxide) (PPO).[4,5] The PPO molecule is a random coil with limited chain mobility.[6] It readily undergoes sulfonation by the action of chlorosulfonic acid to form SPPO. The presence of charged substituents ensures a rigid structure of the SPPO chain.

The aim of this work was to study the effect of the SPPO structure and molecular parameters on the properties of gas separating membranes. For this purpose gas transport properties of SPPO and PPO were compared, and the properties of composite membranes with an SPPO top layer prepared by using two solvent types were investigated. Solvent nature is one of the most important factors that determines the structure of polymer membranes in their preparation stage. Chain conformation, size, and asymmetry of the polymer coil are profoundly affected by the solvent. This dependence in turn influences the conditions of the contact between the macromolecule and the surface on which the top layer of the composite membrane is formed, the possibility of macromolecule orientation, and the membrane structure.

## EXPERIMENTAL

### Materials

Commercial PPO with a molecular weight (MW) of 172,000 (Brno, Czech Republic) was used. SPPO was obtained by reacting PPO with a stoichiometric amount of chlorosulfonic acid in chloroform at low temperature.[7] The degree of polymer sulfonation was 65%. SPPO obtained in the $H^+$ form was transformed into a more stable $Na^+$ form by treating the polymer with a NaOH solution. The polymer was precipitated from a methanol solution into diethyl ether.

$N,N$-Dimethylacetamide (DMA) and methanol were used as SPPO solvents after preliminary drying and distillation.

### Membranes

Composite membranes were prepared by casting a 1–10% SPPO solution in methanol or DMA on the surface of a PPO support by the procedure similar to that in the literature.[8] Excess solution was poured off, and the membrane was dried in the vertical position to constant weight.

The amount of SPPO in the top layer of the composite membrane was determined by weighing the membranes before and after the SPPO layer had been removed from the surface of the PPO support as a result of its dissolution in methanol.

### Methods of Investigation

The intrinsic viscosity $[\eta]$ of SPPO was determined with an Ubbelohde viscometer in methanol or DMA at 25°C. Ionic SPPO polymer exhibits polyelectrolyte properties in methanol and DMA. Therefore, in measuring the $[\eta]$ value, salts (NaCl or LiCl) were added to suppress polyelectrolytic swell (Fig. 1).

SPPO density was established from the weight to size ratio of film samples. The free volume was calculated by a known procedure, $V_f = V_{sp} - 1.3 \times V_w$, where $V_{sp} = 1/\rho$ is the specific volume and $V_w$ is the van der Waals volume calculated by Bondy's method.

Gas transport properties were measured on a chromatography installation with a diffusion type cell for membranes by He, air ($O_2$ and $N_2$ mixture), and $CO_2$ transmission at 30–100°C and a partial pressure of 1 bar.

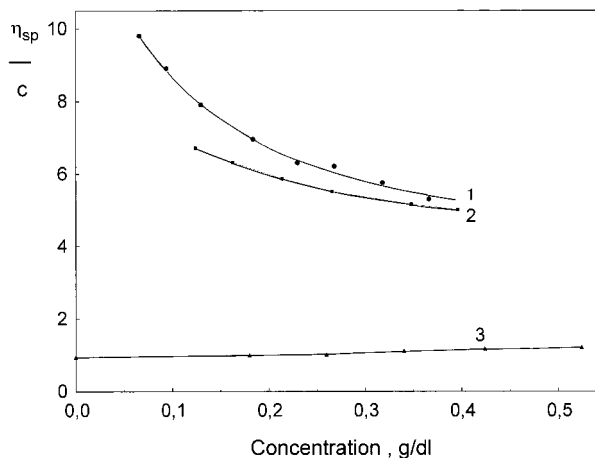An M-40 UV spectrophotometer was used to



**Figure 1** Concentration dependence of SPPO reduced viscosity in a solution of (1) DMA, (2) methanol, and (3) methanol with the addition of 0.1$N$ LiCl.

investigate SPPO complexes with solvents. Mass-spectrometric thermal analysis (MTA) was carried out with an MX-1320 instrument.

The mechanical properties of tensile strength ($\sigma$), elastic modulus ($E$), and elongation at break ($\varepsilon$) were determined with an R-5 machine (Russia).

## RESULTS AND DISCUSSION

### Comparison of Physical Properties of SPPO and PPO

Table I lists the physical and transport properties of SPPO in comparison with those of PPO, which were studied in detail in our previous work.[9]

The inclusion of ionogenic sulfonate groups into PPO leads to a more rigid chain structure and profoundly affects the polymer properties. Sulfonation of PPO is not accompanied by the degradation of the polymer molecule. Therefore, a slight decrease in the $[\eta]$ value for SPPO can be due to its more compact structure because of the salt additives' effect on the polyelectrolyte molecules during $[\eta]$ measurements. It was shown that SPPO is characterized by a much greater density and a lower free volume than PPO. The lower value of free volume determines low permeability coefficients of $O_2$, $N_2$, He, and $CO_2$ and high selectivity of their separation on SPPO homogeneous membranes (Table I).

**Table I Physical and Transport Properties of Polymers Investigated**

| Polymer | $[\eta]$ (dL/g) | $\rho$ (g/cm$^3$) | $V_f$ (cm$^3$/g) | Permeability Coeff. (barrer) | | | | Selectivity | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $O_2$ | $N_2$ | He | $CO_2$ | $O_2/N_2$ | $He/N_2$ | $CO_2/N_2$ |
| PPO | 0.96 | 1.06 | 0.348 | 20.60 | 6.06 | 152.0 | 91.0 | 3.4 | 25 | 15 |
| SPPO | 0.92 | 1.34 | 0.217 | 0.98 | 0.16 | 15.0 | 13.8 | 6.1 | 94 | 86 |

1 barrer $= 1 \times 10^{-10}$ cm$^3$ cm/cm$^2$ s cmHg.

## SPPO–PPO Composite Membrane

Gas transport properties of SPPO were investigated in greater detail by using composite membranes in which SPPO is a thin top layer with controlled thickness and, hence, with controlled permeability. Microporous PPO membrane was applied as a support in composite membranes because PPO is a relatively inert material with respect to the two solvents used for SPPO top layer formation (methanol and DMA). According to the Henis–Tripodi resistance model,[10] support of the composite membrane provides a certain contribution to the transport of gas molecules. However, this contribution is constant for the cases considered here and is not discussed.

In the Flory–Huggins solution theory, the interaction between the polymer and the solvent is characterized by the interaction parameter ($\chi$).[11] Table II gives the interaction parameter of methanol and DMA with SPPO, the polymer of the top layer, and with PPO, the support polymer. These solvents have the same thermodynamic quality for SPPO ($\chi$ values are approximately equal); moreover, this quality is much better than that for PPO.

Transport properties for two types of composite membranes with top layers prepared from SPPO solutions in methanol or DMA were investigated by He, $N_2$, $O_2$, and $CO_2$ transmission (Fig. 2). High separation factors of composite membranes
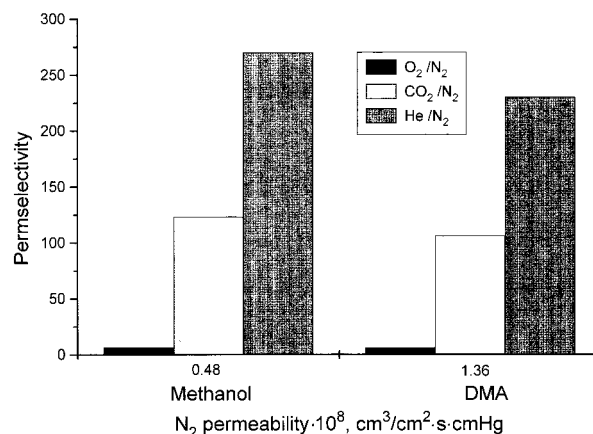
exceeding those of polymer components must be pointed out. Thus, permselectivity of an $O_2$–$N_2$ mixture is 6–8 and that of a $CO_2$–$N_2$ mixture is about 100. The permselectivity of the $CO_2$–$N_2$ mixture is much higher than that for cellulose acetate membranes used in industry [$\alpha(CO_2/N_2) \cong 20$].[12] The ionic character of SPPO evidently ensures facilitated transport of the polar $CO_2$ molecule because $CO_2$ dissolves in an ionic polymer better than $N_2$.

Moreover, it was established that gas permeability of composite membranes depends on the thermodynamic quality of solvents used for SPPO top layer formation. Figure 3 shows the dependence of $O_2$ permeability through composite membranes on the SPPO concentration of casting solution when methanol (curve 1) or DMA (curve 2) are used as solvents. Gas permeability is higher in the case of top layer formation from the DMA solution.

The different permeabilities of membranes prepared from the SPPO solution in methanol or DMA are caused by several factors. The first is

**Table II Parameters of Polymer–Solvent Interaction**

| No. | Solvent | Interaction Parameter, $\chi$ | |
|---|---|---|---|
| | | SPPO | PPO |
| 1 | Methanol | 0.53 | 1.71 |
| 2 | DMA | 0.59 | 1.23 |



**Figure 2** Permselectivity versus $N_2$ permeability through SPPO–PPO composite membranes prepared by using SPPO solutions in methanol or DMA.
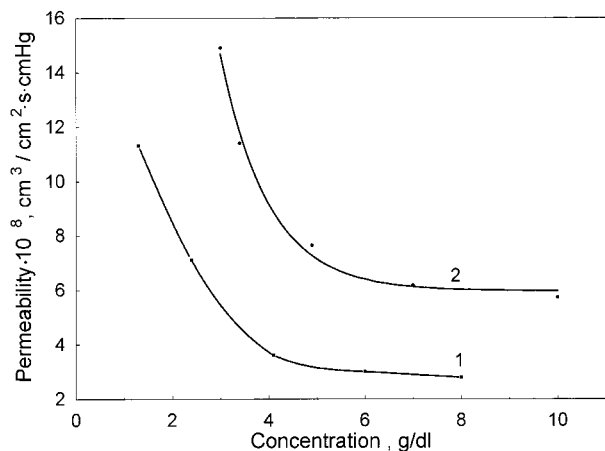
**Figure 3**  O$_2$ permeability through SPPO/PPO composite membranes versus SPPO concentration in (1) methanol and (2) DMA solutions.



**Figure 5**  MTA curves of (1, 2) sulfur dioxide ($m/e$ = 64) yield and (3) DMA ($m/e$ = 87) yield for SPPO films prepared from solutions in (a) methanol and (b) DMA.

the thickness of the SPPO top layer determined by the amount of the polymer adsorbed on the support. Figure 4 shows the dependence of the SPPO top layer weight on SPPO concentration in methanol (curve 1) and DMA (curve 2). When solutions of the same concentration are used, a smaller amount of SPPO molecules is adsorbed from the DMA solution. According to data in Table II, the affinity of DMA for PPO is much higher than that of methanol. This indicates that DMA molecules can be adsorbed on the support surface, which hinders the adsorption of SPPO molecules. It should also be taken into account that methanol vapor is more volatile. Therefore, a greater amount of SPPO is retained on the surface of the
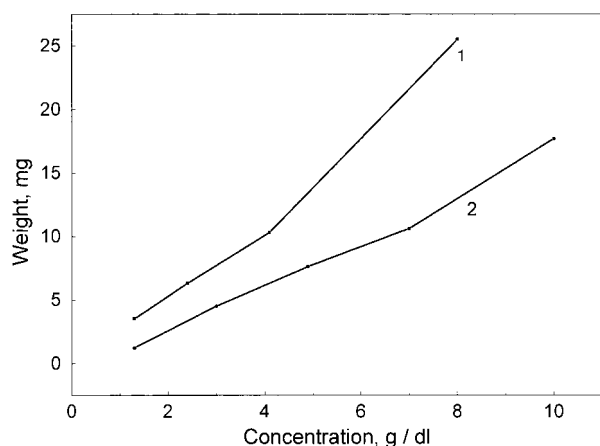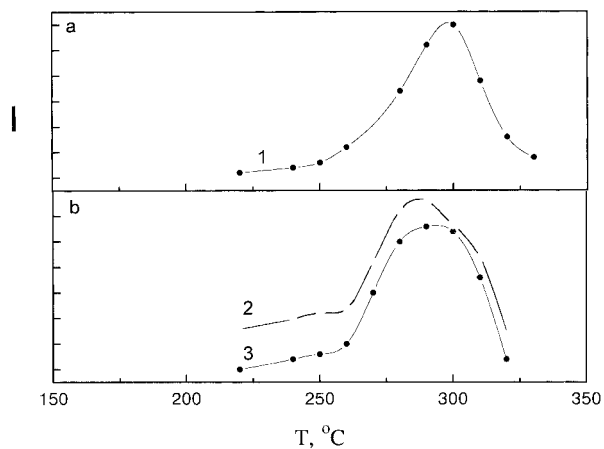
PPO support when the membrane is dried in the vertical position.

Another reason for the high permeability of membranes prepared from SPPO solution in DMA is the higher dipole moment of DMA ($\mu$ = 3.79) and its tendency toward complexation. UV spectroscopy showed that DMA forms strong complexes with ionogenic groups of SPPO molecules in solution. These complexes are so strong that they are retained upon passing into the condensed state. According to MTA data (Fig. 5), the SPPO film cast from the DMA solution contains DMA that is isolated not at 165°C ($T_{\text{boil DMA}}$), but in the 240–320°C temperature range ($T_{\text{max}}$ = 300°C) during thermal destruction of the sulfonate group and, hence, that of the SPPO–DMA complex. This destruction is accompanied by the isolation of sulfur dioxide molecules from the samples of both films. It should be noted that the presence of solvent in the film cast from methanol was not established by the MTA method.

The high permeability of membranes prepared by using DMA can also be related to the plasticizing activity of this solvent. Note that the increase in permeability after the inclusion of plasticizing additives has already been described.[13,14]

The plasticizing effect of DMA is also revealed by the investigation of the mechanical properties of SPPO films. According to data in Table III, the film cast from DMA solution is characterized by lower strength ($\sigma_b$), lower rigidity ($E$), but higher elongation ($\varepsilon$) than that from methanol.

These data indicate that DMA is a morphologi-



**Figure 4**  Weight of SPPO top layer versus SPPO concentration in (1) methanol and (2) DMA solutions.

**Table III  Mechanical Properties of SPPO Films**

| No. | Solvent | $\sigma_b$ (MPa) | $E$ (MPa) | $\varepsilon$ (%) |
|-----|---------|--------|--------|--------|
| 1 | DMA | 48 | 1010 | 6.7 |
| 2 | Methanol | 92 | 1780 | 4.0 |

cally active solvent for SPPO that determines the film structure owing to the formation of SPPO–DMA complexes in solution, which also exist in the condensed state.

## CONCLUSIONS

The inclusion of the ionogenic sulfonate groups into PPO renders the chains' structure more rigid and greatly decreases the free volume that determines low gas permeability and high selectivity of membranes based on SPPO.

Gas transport through SPPO–PPO composite membranes depends on the nature of the solvent for the SPPO top layer. The use of DMA leads to the formation of membranes with higher permeability than those from methanol because in this case a smaller amount of the polymer is adsorbed on the support because of lower vapor volatility and higher affinity of DMA for the support polymer.

It is very important that SPPO forms strong SPPO–DMA complexes that are retained upon transition from solution to the condensed state. DMA is a morphologically active solvent.

The plasticizing effect of DMA on SPPO determines the high gas permeability of the membranes and is in agreement with mechanical properties.

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