

Studies on the Sulfonation of Poly(phenylene oxide) (PPO) and Permeation Behavior of Gases and Water Vapor Through Sulfonated PPO Membranes. II. Permeation Behavior of Gases and Water Vapor Through Sulfonated PPO Membranes

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SYNOPSIS

The permeation behaviors of water vapor and gases were studied for both PPO and SPPO of different sulfonation degree. It was found that the permeability of water vapor increased, and those of oxygen and nitrogen decreased; thus the selectivity for water vapor over gases increased remarkably with the increase of sulfonation degree. The possibility of using SPPO as a gas dehumidification membrane material is discussed. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In Part I of this series¹ the sulfonation of PPO and its physical properties, except gas permeation behavior of SPPO, were discussed in detail. In this part the permeation behavior of gases and water vapor through SPPO membranes will be discussed in detail.

Removing water vapor from air or other gases is an important process in a wide range of industries including chemical, electric, and electronic industries; precision machine industries; and food and fiber industries.² It is also useful for the production of moisture-reduced (or controlled) air for air conditioning of buildings, for compressed air for various meters (instruments), or for removal of moisture from natural gas.² The membrane dehumidifying method is advantageous over other conventional methods such as the compression method, the cooling method, and the adsorption method, in that the running cost is low, the construction of the apparatus is simple, and a dry gas can be obtained con-

tinuously without contamination. The key to dehumidification based on the membrane method is to provide a moisture-removing membrane having both high water vapor permeation rate and high separation factor of water vapor over gases. It was found that SPPO was just this kind of membrane material.

Detailed studies of the mechanism of water vapor permeation through polymer membranes have been far fewer than those of gases and organic vapors. This is because the permeation of water vapor through polymer membranes is more complex than other gases. Experiments were conducted to study the sorption kinetics and equilibria of water in polymers over a range of activities (equal to relative vapor pressure) and temperatures. At low activities, sorption of gases and vapors into glassy polymers is usually described by a superposition of Henry's law and a Langmuir isotherm.³⁻⁶ At high activities, sorption of vapors in polymers often involves strong positive deviations from Henry's law. Water sorption isotherms in hydrophobic glassy polymers generally show a dramatic upturn at activities above 0.5 to 0.8,⁷⁻⁹ and the effective diffusion coefficient in such cases often decreases with increasing water concentration.^{9,10} The combined sorption and

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transport observations described above are conveniently interpreted in terms of models that involve "clustering" or nonrandom aggregation of penetrant molecules. Vieth has discussed a dual mode sorption and transport model for describing cases in which formation of relatively immobile clusters is a dominant feature.¹¹

EXPERIMENTAL

Both the preparation and the characterization of SPPO have been described in detail in Part I of this series.¹

The permeabilities of gases were measured on a model K315-N-03 manometric permeation apparatus (Reikaseiki). The two-chamber, steady-state method was used. After evacuation to 10^{-2} torr for several hours, the permeating gas was introduced to the upstream side of the membrane and maintained constant at 1 atm. The flux of gas permeating through the membrane to the downstream side was monitored by the increase in pressure measured by an MKS Baratron.

The permeability of water vapor was measured by the cup method. The membrane to be measured was fixed on a standard cup half-filled with water. Cups were placed into a chamber with circulating air maintained at constant relative humidity of 37%

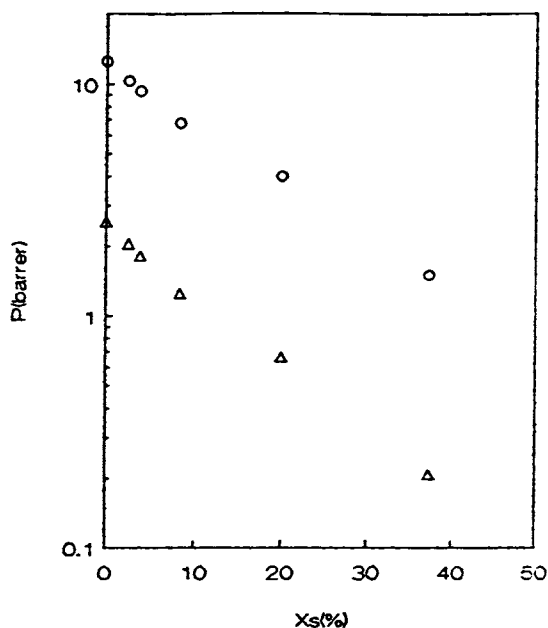


Figure 1 The permeabilities of free-acid form SPPO for oxygen and nitrogen as a function of sulfonation degree. (O): O₂; (Δ): N₂.

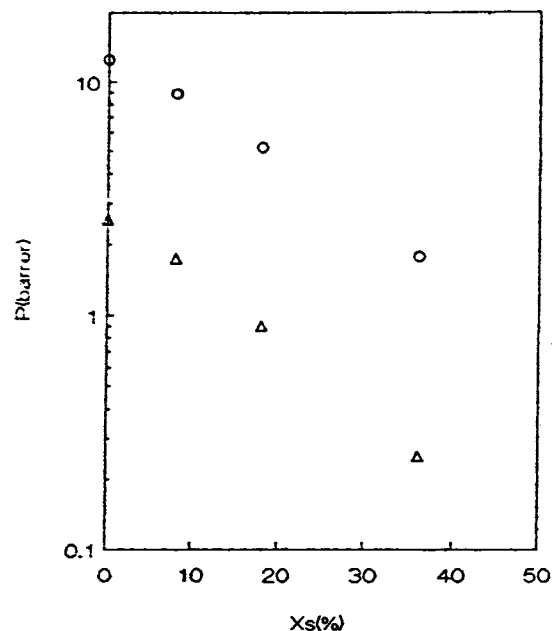


Figure 2 The permeabilities of sodium-salt form SPPO for oxygen and nitrogen as a function of sulfonation degree. (O): O₂; (Δ): N₂.

and at constant temperature of 38°C. The weight of cup with water was quickly measured on an electronic semimicro balance from time to time and the water vapor permeability (P_w) was determined by the following relationship:

$$P_w = q \cdot l / t \cdot A \cdot \Delta p \quad (1)$$

where q/t is the mean value of cup weight loss rate in g/sec; l is the membrane thickness in cm; A is the area of membrane sample in cm², and Δp is the transmembrane water vapor pressure difference in cm Hg, which is equal to $S(R_1 - R_2)$, where S is the saturation pressure of water vapor at the test temperature in cm Hg and R_1 , R_2 are the relative humidity of the upstream and downstream sides of the membrane, respectively.

RESULTS AND DISCUSSION

I. Gas Permeation of SPPO

Results of the permeability measurements of oxygen and nitrogen through SPPO membranes are presented in Figures 1–3. It can be seen that the permeabilities of oxygen and nitrogen through SPPO decreased linearly with the increase of sulfonation degree, whereas the selectivity for oxygen over nitrogen was rapidly increased. Furthermore, the per-

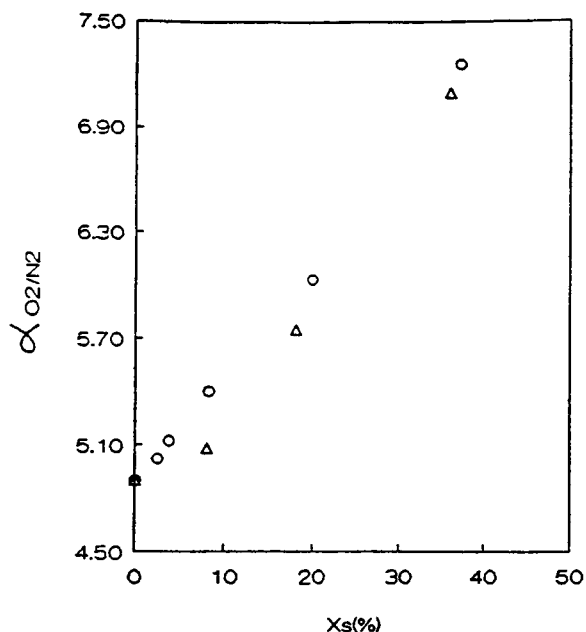


Figure 3 The O_2/N_2 selectivities of SPPO as a function of sulfonation degree. (○): Free-acid form; (△): Sodium-salt form.

meabilities of oxygen and nitrogen through SPPO in sodium-salt form are slightly higher than those in free-acid form, and the selectivity for oxygen over nitrogen is almost the same, especially at higher sulfonation degree (cf. Fig. 3). For SPPO in both free-acid and sodium-salt form, when sulfonation degree reached about 37%, the permeability of oxygen decreased by a factor of 7 or 8 but the selectivity for oxygen over nitrogen increased by 50% as compared with that of unsubstituted PPO. This can be interpreted as follows: The gas permeation through polymer membranes was mainly determined by the packing density and the segmental motion of polymer chains in addition to the inherent nature of gases.¹² The fractional free volume (V_f) and the glass transition temperature (T_g) can represent these two terms, respectively. From the analysis of wide angle X-ray diffraction (WAXD) of SPPO and PPO, it was observed that the intermolecular distance remained constant but the density was increased after sulfonation. This indicated that the packing of polymer chains became denser after sulfonation. In addition, the increasing T_g value after sulfonation¹ indicated that segmental motion of polymer chains decreased as a result of the increase of interaction between polymer chains caused by the introduction of $-SO_3H$ group. These two factors led to the decrease of gas permeabilities. The permeability of nitrogen decreased more rapidly than that of oxygen

because the size of the nitrogen molecule is larger than that of oxygen. Thus, the selectivity for oxygen over nitrogen increased. The relationship between the logarithm of permeabilities of oxygen and nitrogen of SPPO with varying sulfonation degree both in free-acid and sodium-salt form and the reciprocal of absolute temperature are shown in Figures 4–7. It was obvious that a linear relationship exists between $\lg P$ and $1/T$ in each case. In other words, the Arrhenius equation holds:

$$\lg P = \lg P_0 - E_p/(2.303RT) \quad (2)$$

where R is the universal gas constant, T is the absolute temperature (K), and E_p is the apparent activation energy of gas permeation.

Because both the SPPO and PPO were in the glassy state in the experimental temperature range, the apparent activation energy of gas permeation did not change with temperature. It was found from the E_p data shown in Table I that the permeation activation energy of oxygen and nitrogen increased with the increase of sulfonation degree for SPPO both in free-acid and sodium-salt form.

II. Water Vapor Permeation Through SPPO Membranes

The water vapor permeability of SPPO with different sulfonation degree is shown in Figure 8. Water

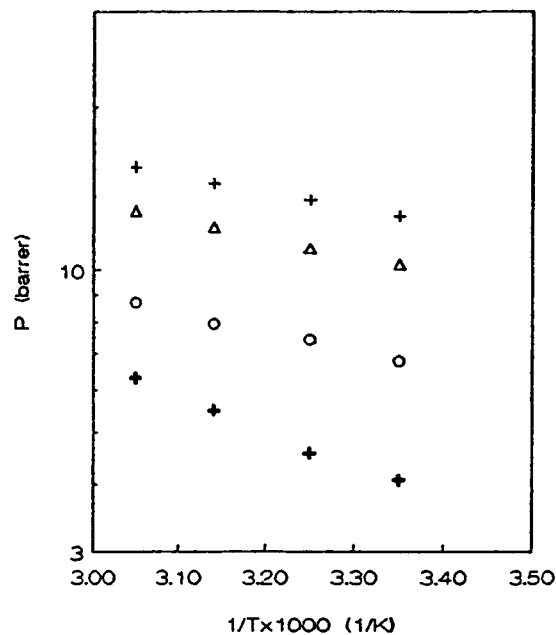


Figure 4 The relationship between $\lg P_{O_2}$ and $1/T$ for free-acid form SPPO. Xs %: (+): 0; (△): 2.5; (○): 8.3; (+): 20.0.

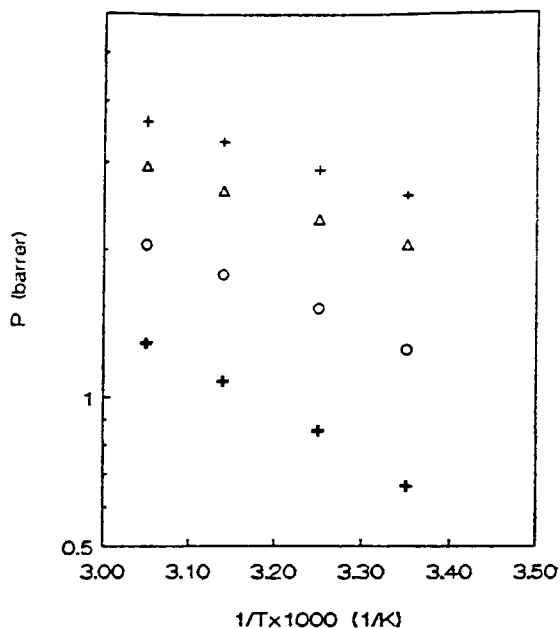


Figure 5 The relationship between $\lg P_{N_2}$ and $1/T$ for free-acid form SPPO. X_s %: (+): 0; (Δ): 2.5; (\circ): 8.3; (\oplus): 20.0.

vapor permeability obviously increases with increasing sulfonation degree. The permeability of water vapor through SPPO in free-acid form, with sulfonation degree of 37.3%, was 10.6 times as large as that of PPO. This was mainly because of the relatively large hydrophilicity of the sulfonic group,

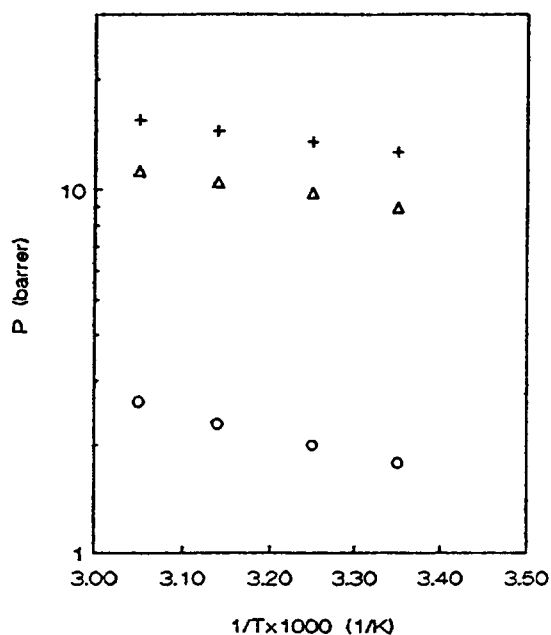


Figure 6 The relationship between $\lg P_{O_2}$ and $1/T$ for sodium-salt form SPPO. X_s %: (+): 0; (Δ): 8.1; (\circ): 36.1.

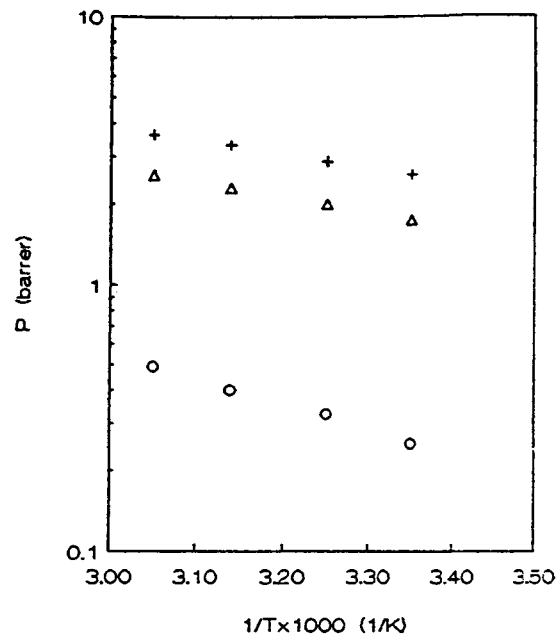


Figure 7 The relationship between $\lg P_{N_2}$ and $1/T$ for sodium-salt form SPPO. X_s %: (+): 0; (Δ): 8.1; (\circ): 36.1.

which resulted in a large solubility coefficient for water vapor, thus the high permeability. It was evident that sulfonation of PPO was an effective method for increasing the water vapor permeability. It was also found that the water vapor permeability of SPPO in free-acid form was larger than that in sodium-salt form at comparable sulfonation degrees. The reason is that H-bonds are easily formed between the sulfonic groups in SPPO(H) and water molecules. This leads to greater hydrophilicity than for SPPO in its sodium-salt form and results in higher permeability of water vapor. It was interesting that sulfonation of PPO not only increased the water vapor permeability but also decreased the permeabilities of other gases, so that the selectivity for water vapor over other gases, such as nitrogen, increased remarkably after sulfonation (see Fig. 9). This is meaningful for a dehumidification mem-

Table I The Apparent Permeation Activation Energy of Oxygen and Nitrogen through SPPO Samples (KJ/mol)

Counter Ion	X _s , %					
	—	H ⁺	H ⁺	H ⁺	Na ⁺	Na ⁺
E_{O_2}	5.68	6.45	6.89	12.30	6.47	10.64
E_{N_2}	9.86	10.14	13.16	18.16	10.66	18.19

brane. For polymer-based separation membranes in general, it is very difficult to combine high permeability with high selectivity. But it is shown in this work that high permeability of water vapor and high selectivity of water vapor over other gases can be combined quite well through sulfonation. Thus, this is a very useful method to obtain gas dehumidification membrane materials with high performance. In fact, both the permeability of water vapor and the selectivity of water vapor to nitrogen in SPPO membranes were much higher than those of the polyimide membranes of Ube Industries.¹³

CONCLUSIONS

Sulfonation of PPO not only increased its permeability to water vapor but also depressed its oxygen and nitrogen permeabilities, so that the selectivity for water vapor over oxygen and nitrogen increased remarkably after sulfonation. SPPO looks promising for use as a dehumidification membrane material. The permselectivity of PPO for oxygen over nitrogen increased 50% after sulfonation. The Arrhenius equation holds for the relationship between the logarithm of permeabilities of oxygen and nitrogen through SPPO with varying sulfonation degree and the reciprocal of absolute temperature.

This work was supported by the National Natural Science Foundation of China (NNSFC).

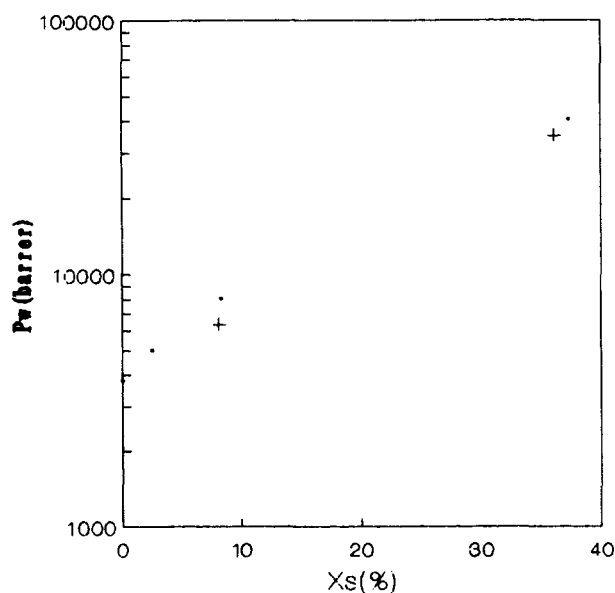


Figure 8 The water vapor permeabilities for SPPO as a function of sulfonation degree. (□): Free-acid form; (+): Sodium-salt form.

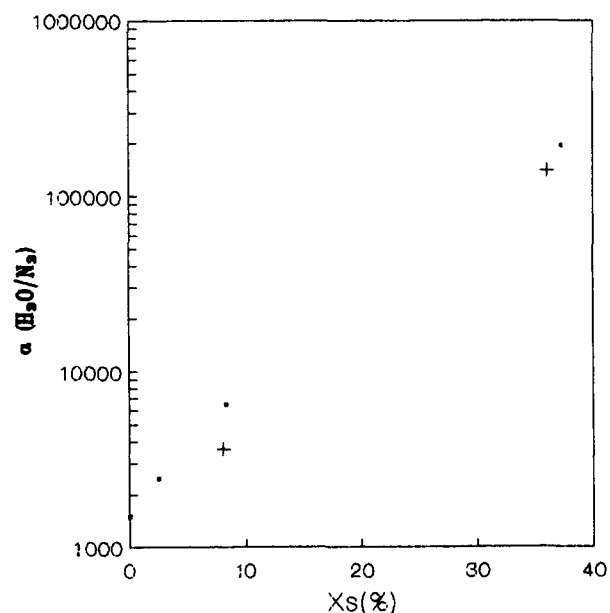


Figure 9 The selectivities of water vapor over nitrogen for SPPO as a function of sulfonation degree. (□): Free-acid form; (+): Sodium-salt form.

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Received March 3, 1993

Accepted May 20, 1993