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

HONGYONG FU, LIANDA JIA,* and JIPING XU

Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

SYNOPSIS

Poly(2,6-dimethylphenylene oxide) (PPO) was sulfonated to varying degrees using different sulfonating agents. Physical properties such as solubility, density, and thermal properties were studied for both PPO and sulfonated PPO (SPPO) with different degrees of sulfonation. Density and T_g value were increased after sulfonation. The solubility in dipolar aprotic solvents was improved and was dependent on the degree of sulfonation, and the thermal stability of PPO was slightly decreased after sulfonation. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

For membrane processes to compete with well-established separation processes, polymers must be designed with specific membrane applications in mind. The molecular engineering approach requires a more complete understanding of the molecular-scale processes that govern the solubility, diffusivity, and permeability of gases or water vapor in polymers. Such an understanding must come from careful, systematic studies of a homologous series of polymers whose structures differ only slightly from one another.

The polymer series chosen for the present structure/property study was derived from poly (phenylene oxide) (PPO), a high T_g amorphous polymer that has already proven to be a highly permeable membrane material with excellent mechanical properties and resistant to a number of chemical agents. But its selectivity for gases is relatively low. Therefore, a series of modifications has been performed by a variety of electrophilic substitution re-actions—bromination, acylation, sulfonylation, and sulfonation[1-4]—to improve its permselectivities.

The major gas chosen for study was water vapor because its humidity control is a widespread problem and the dehydration of water vapor containing gas mixtures, such as natural gas, air, and others, is of importance in many industries, such as the microelectronics, petroleum, and chemical industries.

PPO is ranked among the hydrophobic polymers. The contact angle (a measure of hydrophilicity) of a homogeneous PPO film is 67°, whereas by comparison, the contact angle of a cellulose acetate (CA) film is 32° and that of a polyethylene film is 95°.[5]

In fact, the solubility of water in PPO film is only one-tenth of that in CA film, but the diffusivity of water vapor through PPO film is higher than that for CA film by a factor of at least 6.[6]

The present series of papers is concerned with the chemical modification of PPO for improved water-vapor permeability by adding a sulfonate group to the polymer backbone, which should improve its solubility and, thus, its permeability to water vapor. Part I deals with the sulfonation of PPO and characterization of the products, whereas Part II will deal with the permeation behavior of gases and water vapor through SPPO membranes, and in Part III, water-vapor sorption and desorption behavior in both PPO and SPPO will be discussed in detail.

EXPERIMENTAL

Materials

PPO was purchased from the Beijing Institute of Chemical Industry. The intrinsic viscosity is 0.5 dL/g. The polymer was purified by reprecipitation twice from a chloroform solution into methanol together with active carbon decoloration.

Sulfonation Procedures

Sulfuric Acid as Sulfonating Agent

A definite amount of PPO powder was suspended in 98% H_2SO_4 under stirring at room temperature for a certain period of time. The sulfonated PPO was then filtered, washed with distilled water to neutral pH, and dried in vacuo for 3 days at room temperature.

Chlorosulfonic Acid as Sulfonating Agent

PPO was stirred at room temperature for 0.5–1.0 h with chloroform to form a 4 wt % solution. A proper amount of chlorosulfonic acid was introduced via a dropping funnel over a period of 20 min while the solution was stirred vigorously and allowed to react for an additional 30 min at room temperature. The products were precipitated in methanol, filtered, washed with distilled water, and dried at room temperature in vacuo for 3 days.

Conversion to a stable salt form can generally be accomplished by contacting the solid acid form of SPPO with an aqueous salt, preferably a base solution such as sodium or a potassium hydroxide solution. After equilibrating the polymer with the solution, the solid is rinsed with distilled water to remove excess electrolytes and dried.

Preparation of the Membranes

A 7 wt % solution of SPPO in methanol was cast on a glass plate to ca. a 20 or 40 μm-thick membrane; after 30 min, the membrane was taken off carefully from the plate and dried at 80°C in vacuo for 24 h. The procedure for preparing the PPO membrane is similar to that above except that the solvent is chloroform instead of methanol.

Characterization of the Products

The sulfonation degree was expressed as the average number of $-SO_3H$ (or $-SO_3Na$) groups in 100 repeating units of polymer. It was determined using DIONEX 2120i ion-exchange chromatography. IR spectra were recorded on a DIGILAB FTS-20E IR spectrometer.

T_g was determined on a Perkin-Elmer DSC-2C at a heating rate of 10°C/min in a nitrogen atmosphere. The thermogravimetric analysis spectra were obtained at the same conditions as above. Density was measured by the buoyancy method at 25°C.

RESULTS AND DISCUSSION

Sulfonation of PPO

In the sulfonation process of PPO with sulfuric acid, the reaction rate was slow and a relatively low degree of conversion was reached. For example, the sulfonation degree of the products is only 2.5 and 3.8%, respectively, after 5 and 10 h of reaction. It was reported[5] that the highest sulfonation degree of the products obtained by this method was 9.5%. The low sulfonation degree of the products resulted from the fact that the heterogeneous sulfonation reaction

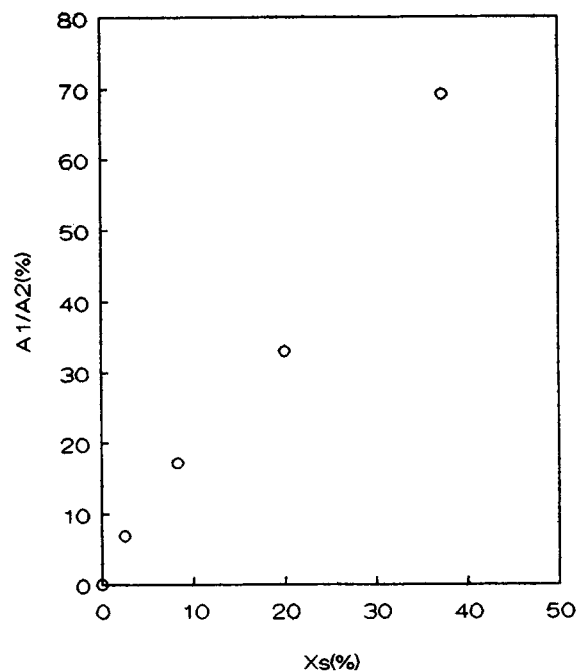**Table I   Reaction Conditions and the Sulfonation Degree of SPPO**

	Sample No.					
	3	4	5	6	7	8
Counter ion	H^+	H^+	H^+	Na^+	Na^+	Na^+
Temperature (°C)	0	25	25	25	25	25
Concentration of PPO solution (%)	4	4	4	4	4	4
Reaction time (h)	2	0.5	0.5	0.5	0.5	0.5
Reactant ratio ($ClSO_3H$/PPO) (mol %)	24.4	20.8	95.0	9.5	18.7	95.0
Sulfonation degree of products (Xs %)	8.3	20.0	37.3	8.1	18.1	36.1
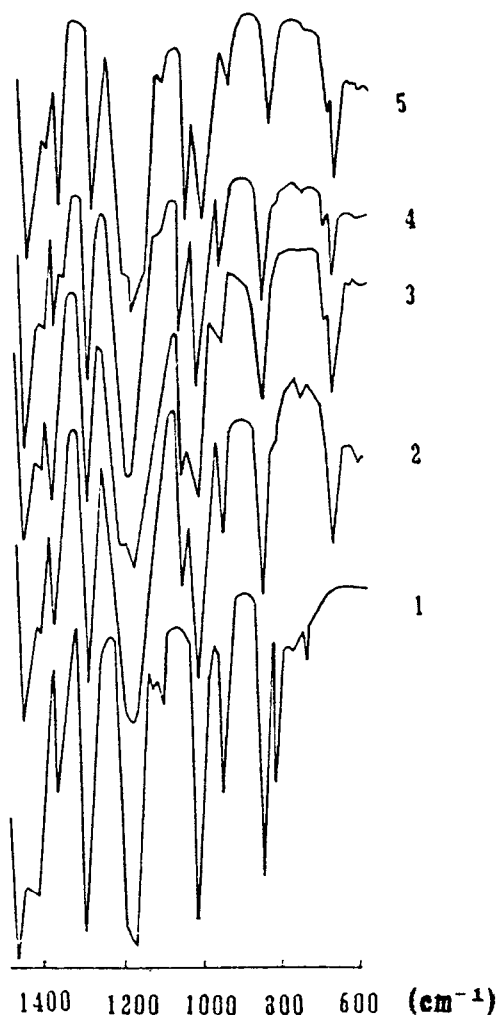
Figure 1 IR spectra of SPPO with different sulfonation degrees: (1) PPO; (2) SPPO 20% (H^+); (3) SPPO 37.3% (H^+); (4) SPPO 18.1% (Na^+); (5) SPPO 36.1% (Na^+).

Figure 2 Relationship between the relative intensity of the characteristic peak on IR spectra and sulfonation degree for SPPO (free acid form).

takes place only at the interface of sulfonation acid and PPO powder. The sulfonated PPOs with a lower sulfonation degree can be obtained by controlling the reaction time.

Products with a relatively high sulfonation degree were obtained when chlorosulfonic acid was the sulfonating agent. The extent of reaction was controlled mainly by the reaction temperature and the reactant ratio (the molar ratio of $ClSO_3H$ to PPO) (see Table I). If the reaction was carried out at 0°C, the sulfonation degree of the products was lower than that at room temperature even at a high reactant ratio and a long reaction time. When the reaction was carried out at room temperature, the higher the reactant ratio, the higher the sulfonation degree of

the products within a certain range. But the sulfonation degree could hardly exceed 40% due to the limited solubility of sulfonated PPO in chloroform.[4]

Infrared Spectra of SPPO

Infrared (IR) spectra were obtained from solution-casted film samples. As shown in Figure 1, IR spectra of the samples of SPPO showed some changes in the molecular structure compared to the original PPO. The peaks at the frequencies of 1064 and 675

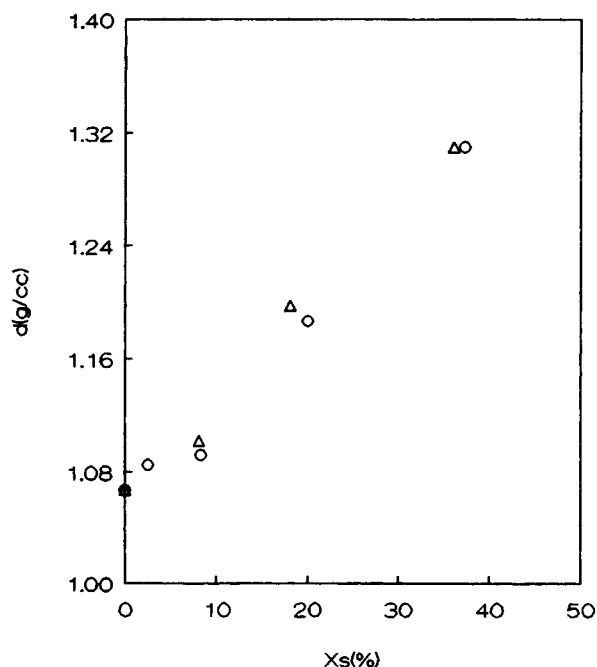**Table II   The Relative Intensity of the Characteristic Peak on IR Spectra for SPPO (Sodium Salt Form)**

	Sample No.		
	6	7	8
Xs (%)	8.1	18.1	36.1
A_1/A_2 (%)	7.53	59.7	108.1

A_1 and A_2 are the intensities of the 1064 and 1300 cm^{-1} peaks, respectively.
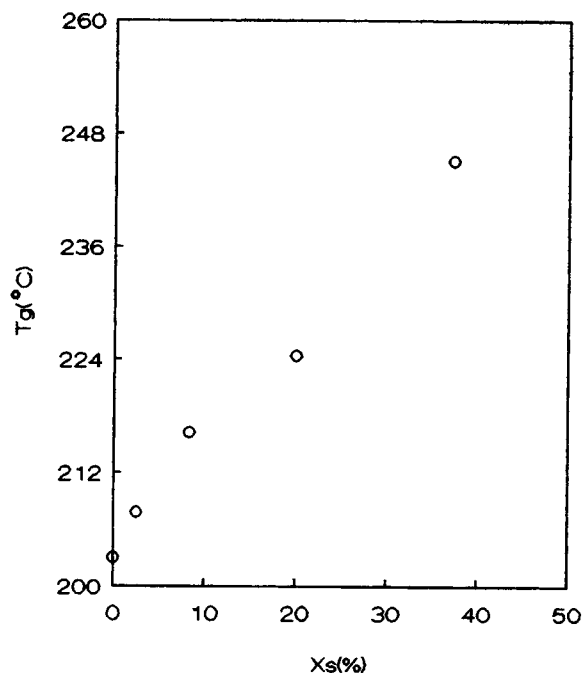
Table III   Solubilities of PPO and SPPO

Solvent	PPO	SPPO
n-Hexane	–	–
Cyclohexane	–	–
Carbon tetrachloride	+	–
Carbon disulfide	+	–
Benzene	+	–
Toluene	+	–
Chlorobenzene	+	–
Dichloromethane	+(Δ)	–
Chloroform	+	–
Ethyl ether	–	–
THF	–	+
Ethyl acetate	–	+
Acetone	–	+
Ethanol	–	+
Methanol	–	+
DMF	–	+
DMAc	–	+
DMSO	–	+
Water	–	–

SPPO: sulfonation degree 37.3%, free acid form; +, soluble; –, insoluble; +(Δ) soluble in hot solvent.

Figure 4   Glass transition temperature of free acid form SPPO as a function of sulfonation degree.

Figure 3   Relationship between the density of SPPO and sulfonation degree: (Δ) sodium salt form; (O) free acid form.

cm^{-1} appeared after sulfonation. These bands are assigned to symmetric stretching of $-SO_3$ and $C-S$ stretching vibrations, respectively. Another $-SO_3$ band at 1200 cm^{-1} was overlapped with the aromatic ether band. IR spectra can be used as a method to assess the level of sulfonation. The ratio of intensity, at 1064 cm^{-1} (the $-SO_3$ stretching) to that of the internal standard (the asymmetric $C-O-C$ stretching of the aryl ether group) increased with increase of the sulfonation degree for both the free acid form (Fig. 2) and the sodium salt form (Table II).

Solubility of SPPO in Organic Solvents

The solubility characteristics of sulfonated PPO were completely different from those of PPO. Table III describes the solubility of SPPO with a sulfonation degree of 37.3% compared to unmodified PPO. It is very important to note that SPPO becomes soluble in dipolar aprotic solvents such as DMSO, DMF, and DMAc in which PPO is insoluble. This is of vital importance since dipolar aprotic solvents are conventional solvents for the casting of asymmetric membranes.
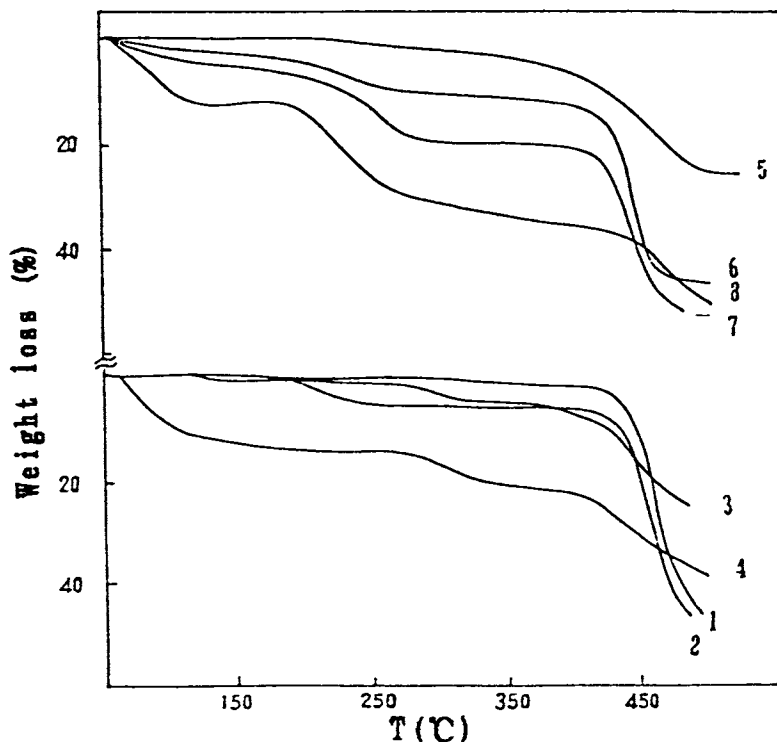
Figure 5 TGA spectra for SPPO of different sulfonation degrees (in nitrogen atmosphere at 10°/min heating rate): (1) PPO; (2) SPPO(Na) 8.1%; (3) SPPO(Na) 18.1%; (4) SPPO(Na) 36.1%; (5) SPPO(H) 2.5%; (6) SPPO(H) 8.3%; (7) SPPO(H) 20.0%; (8) SPPO(H) 37.3%.

The Density of SPPO

It is seen from Figure 3 that the density of the sulfonated PPO increases linearly with the increase of the sulfonation degree and the density of the sodium salt form SPPO is slightly higher than that of the free acid form SPPO.

Thermal Properties of SPPO

Both the differential scanning calorimetric (DSC) and the thermogravimetric analysis (TGA) studies have been made on SPPO and PPO. Figure 4 presents the relationship between the glass transition temperature (T_g) and the sulfonation degree for the free acid form SPPO. The T_g value increases linearly with the increase of sulfonation degree. The reason is that the $-SO_3H$ groups on adjacent chains may easily form H bonds between macromolecular chains, leading to increase in the interaction between macromolecular chains. In addition, the substitution of PPO with a relatively rigid and bulky side group of $-SO_3H$ may directly suppress torsional motions in the polymer by interfering with one another,

leading to increase in the chain stiffness.[3] Both of these two factors lead to increase of the T_g.

PPO is a thermally stable polymer. The initial decomposition temperature is 470°C at a heating rate of 10°C/min, which is the result of the splitting of the main chains. Figure 5 presents the TGA spectra of free acid and the sodium salt form of SPPO and unmodified PPO. Three weight loss stages are observed on the TGA curves of SPPO. The first one at about 100°C is attributed to the loss of moisture absorbed from the air. The second one at 252–263°C for SPPO(H) and around 304°C for SPPO(Na), which has not been observed on the TGA spectra of PPO, can be taken as the splitting of $-SO_3H$ or $-SO_3Na$ side groups, respectively. The third one is close to the decomposition temperature of PPO and related to the splitting of main chains. Table IV presents both the side-group and main-chain splitting temperatures of free acid and the sodium salt form of SPPO with different sulfonation degrees. There is no definite relationship between these temperature values and the sulfonation degrees, but the decomposition temperature of SPPO(Na) is higher than that of SPPO(H), which is because

Table IV   The Side-group and the Main-chain Splitting Temperatures of SPPO

	Sample No.							
	0	1	3	4	5	6	7	8
Xs (%)	0	2.5	8.3	20.0	37.3	8.1	18.1	36.1
T_{side} (°C)	—	—	260	263	252	—	304	304
T_{main} (°C)	470	463	463	456	460	470	462	470

Samples 1–5: free acid form; samples 6–8: sodium salt form.

SPPO(H) is unstable and acid-catalyzed degradation is likely to occur. The initial decomposition temperatures of both forms of SPPO are lower than that of PPO due to the side-group splitting (lower than 310°C). The main-chain splitting temperature is also slightly lower than that of PPO. Therefore, the thermal stability of PPO was decreased after sulfonation.

CONCLUSIONS

Sulfonation using chlorosulfonic acid as the sulfonating agent is an effective modification method and the products with a relatively high sulfonation degree can be obtained at room temperature, whereas a relatively low degree of conversion is reached when sulfuric acid is used as the heterogeneous sulfonation agent. The solubility of PPO in dipolar aprotic solvents is obviously improved after sulfonation. It is also found that the density and T_g value are linearly increased with increase of the sulfonation degree. The thermal stability of SPPO decreases as compared with PPO, and the sodium salt form of SPPO is more stable than is the free acid form.

REFERENCES

1. S. Percec and G. Li, ACS Symp. Ser. 364, American Chemical Society, Washington, DC, 1988, p. 46.
2. L. Jia, F. R. Sheu, R. T. Chern, and H. B. Hopfenberg, *Chin. J. Polym. Sci.,* **7**(4), 306 (1989).
3. S. Percec, *J. Appl. Polym. Sci.,* **33**, 191 (1987).
4. W. J. Ward and R. M. Salemme, U.S. Pat. 3,780,496 (1973).
5. J. Schauer, P. Lopour, and J. Vacik, *J. Membr. Sci.,* **29**, 169, (1986).
6. S. Pauly, *Polymer Handbook,* 3rd ed., in J. Brandrup and E. H. Immergut, Eds., Wiley, New York, 1989, Vol. I., p. 435.