

Chemical Modification of Poly(2,6-Dimethyl-1,4-Phenylene Oxide) by Friedel-Crafts Reactions

SIMONA PERCEC, *Standard Oil Research and Development,
4440 Warrensville Center Road, Cleveland, Ohio 44128*

Synopsis

The chemical modification of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) by electrophilic sulfonylation and acylation of the aromatic structural units has been investigated. A maximum monosubstitution degree of 79.4 has been reached. Higher substitution levels were difficult to achieve because of both a decrease in the remaining position nucleophilicity and steric hindrances. Minor changes in thermal stability and a broadening of the solubility range of substituted PPO compared with the parent PPO have been recorded. Very good permeation properties to gases, better than for PPO, have been detected for the modified structures.

INTRODUCTION

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) belongs to the class of thermally stable engineering plastics characterized by a high glass transition temperature ($T_g = 212^\circ\text{C}$) and good thermal stability under nonoxidizing conditions.¹⁻⁴ Special properties achieved by modification reactions on PPO have been reported in the literature. The benzylic substitution of PPO with pendant phosphate groups and the properties associated with the incorporation of phosphorus on its backbone were described by Cabasso et al.⁵ The attachment of cyclopentadiene ligands to PPO, followed by their conversion to η^5 -cyclopentadiene with cobalt, rhodium, and titanium, and the catalytic reactions of these polymer-supported complexes were studied by Verdet and Stille.⁶ High molecular weight comblike PPO was prepared⁷ from PPO-styrene macromonomer via radical homopolymerization and copolymerization. The carboxylation of PPO using a lithiation method⁸ followed by treatment with CO_2 as well as further modification to form various carboxylate derivatives such as esters, salts, amides, anhydrides, etc. and their miscibility behavior in different blends was also reported.⁹

One of the most interesting properties of PPO is its rather unique gas permeation characteristics. Among the many aromatic polymers which possess high T_g , PPO shows the highest permeability to gases. Sorption and permeation results for various gases in PPO described by the dual sorption and transport model indicated that the significant factor in its high permeability to gases stems from large diffusion coefficients of gases in PPO compared to other glassy polymers with rigid chain backbone.¹⁰ Although permeation properties to certain gases are superior to other glassy polymers such as polysulfone which is currently used in gas separations, PPO has not yet played an important role in this kind of application. There are at least two important disadvantages associated with PPO when we compare some of its properties with those of polysulfone. The first one is its lower selectivity to

gases. The second one is of the fact that PPO is not soluble in dipolar aprotic solvents, and these are the most conventional solvents used in the membrane fabrication process. The first goal of this paper is to present our results on the chemical modification of the PPO backbone by a variety of electrophilic substitution reactions. The second goal is to correlate the structure of the modified PPO with its influence on both polymer solubility in different organic solvents and the gas polymer permeability properties.

EXPERIMENTAL

PPO was synthesized according to a literature procedure¹¹: $\bar{M}_n = 17,000$, $\bar{M}_w = 51,000$, $\bar{M}_w/\bar{M}_n = 3.0$ (determined by gel permeation chromatography with polystyrene standard). The sulfonyl chlorides and acid chlorides (Aldrich) as well as all the other reagents and solvents (Aldrich) were used as received. AlCl_3 (Aldrich) was sublimed in a Pyrex glass tube before use.

Electrophilic Substitution of the PPO Backbone

The electrophilic substitution reactions were carried out in nitrobenzene solution in the presence of AlCl_3 , under nitrogen in a temperature range of 40–80°C. Sulfonyl chlorides ($\text{R}_1\text{SO}_2\text{Cl}$) and carboxylic acid chlorides [$\text{R}_2\text{C}(\text{O})\text{Cl}$], respectively, were used as sulfonylating and acylating agents. After the required reaction time, the reaction mixture was washed with water until the pH was neutral. The separated polymer solution was dried over anhydrous MgSO_4 , filtered and precipitated in methanol. A final purification was carried out by precipitation of the product from chloroform solution with methanol. The polymer was then vacuum dried to constant weight.

Techniques

200 MHz $^1\text{H-NMR}$ spectra were recorded from CDCl_3 solutions on a Nicolet NT 200 spectrometer. TMS was used as an internal standard. FT-IR spectra were recorded from KBr pellets on a Nicolet 60SX spectrophotometer.

The thermal behavior of the polymers was analyzed on a DuPont differential scanning calorimeter (Model 1090) under N_2 atmosphere with indium used as a calibration standard. The heating and cooling rates were 10°C/min.

The polymer films were prepared by dissolving the polymer in a suitable solvent (chloroform) to form 7 wt % solutions. The solution was then poured over a clean glass plate and spread out evenly to a uniform thickness with the aid of a doctor blade. The films were air-dried, removed from the glass plate, and further vacuum-dried at 60°C for 72 h.


A modified Gilbert cell¹² was used to determine the gas permeation properties of polymer films. The testing area of the film was 45.8 cm². The film thickness was in a range of 1.27×10^{-2} – 2.81×10^{-2} mm. The test side was exposed to a carbon dioxide:methane:nitrogen mixture in a mole ratio 3.11:33.6:63.29. The permeant was picked up by a carrier gas, helium, and injected intermittently through a sample valve into a gas chromatograph for analysis. The partial pressure of the test gas was 29.7 psi (0.21 MPa) while the partial pressure of the product gas on the permeant side was held at an insignificant level by purging with 29.77 psi (0.21 MPa) helium at a flow rate much in excess of the permeation rate.

RESULTS AND DISCUSSION

The tetrasubstituted aromatic units of the PPO backbone are very nucleophilic and therefore are expected to undergo electrophilic substitution under mild reaction conditions. The substitution of the first available position from the aromatic ring occurs easily in one single step by the treatment of the PPO with sulfonyl chloride or acid chlorides in the presence of a Friedel–Crafts catalyst. The last remaining aromatic hydrogen could not be removed by a second abstraction reaction and, consequently, a maximum degree of mono-substitution of only 79.4 mol % was achieved.

The reaction in the presence of AlCl_3 requires a molar equivalent of aluminum chloride for each sulfonyl or acyl group present in the sulfonylating or acylating agent. This is believed to be because aluminum chloride is capable of forming rather stable complexes with the sulfonyl or acyl group. Complex formation thus requires an equivalent quantity of metal halides, and a slight excess over molar equivalent is required in order to ensure that the free agent may be present to act as a catalyst.

TABLE I
Sulfonylation of PPO Under Friedel–Crafts Conditions
(PPO 5% Solution in Nitrobenzene)

No.	$\text{R}_1\text{SO}_2\text{Cl}$	Reaction conditions			Substitution degree ^a (mol %)
		PPO : $\text{R}_1\text{SO}_2\text{Cl}$: AlCl_3 (mol : mol : mol)	Time (h)	Temp (°C)	
1	$\text{N}(\text{CH}_3)_2\text{SO}_2\text{Cl}$	1.0 : 1.5 : 0.55	5.0	70	32.3
2	$\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$	1.0 : 1.0 : 1.10	7.0	80	60.7
3	$\text{BrC}_6\text{H}_4\text{SO}_2\text{Cl}$	1.0 : 1.0 : 1.10	9.5	80	59.0
4	$\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$	1.0 : 1.0 : 1.10	7.5	80	66.6
5	$(\text{CH}_3)_3\text{C}_6\text{H}_2\text{SO}_2\text{Cl}$	1.0 : 1.0 : 1.10	7.0	60	46.3
6		1.0 : 1.0 : 1.10	8.5	80	63.5

^a Determined by NMR.

TABLE II
Acylation of PPO by Friedel–Crafts Reaction
(PPO 5% Weight Solution in Nitrobenzene)

No.	R_2COCl	Reaction conditions			Substitution degree ^a (mol %)
		PPO : R_2COCl : AlCl_3 (mol : mol : mol)	Time (h)	Temp (°C)	
1	$\text{C}_2\text{H}_5\text{COCl}$	1.0 : 1.0 : 1.10	4.0	50	42.7
2	$\text{CH}_3(\text{CH}_2)_2\text{COCl}$	1.0 : 1.0 : 1.10	3.0	50	58.6
3	$\text{CH}_3(\text{CH}_2)_{10}\text{COCl}$	1.0 : 1.0 : 1.10	6.0	50	59.0
4	$\text{CH}_3(\text{CH}_2)_{12}\text{COCl}$	1.0 : 0.5 : 0.55	3.0	50	17.5
5	$\text{CH}_3(\text{CH}_2)_{12}\text{COCl}$	1.0 : 1.0 : 1.10	6.0	50	55.0
6	$\text{CH}_3(\text{CH}_2)_{14}\text{COCl}$	1.0 : 1.0 : 1.10	6.5	50	50.0
7	$\text{C}_6\text{H}_5\text{CH}_2\text{COCl}$	1.0 : 0.5 : 0.55	6.0	50	29.2
8	$\text{CH}_3\text{C}_6\text{H}_4\text{COCl}$	1.0 : 1.0 : 1.10	8.0	60	79.4

^a Determined by NMR.

Table I presents the experimental reaction conditions used in the sulfonylation of the PPO backbone and the degree of substitution obtained, while Table II summarizes the same data for the acylation reactions.

The monosubstitution degree determined by $^1\text{H-NMR}$ spectroscopy was between 17.5 and 79.4%, depending on the reaction conditions and sulfonylating or acylating agent. A complete substitution of the PPO aromatic rings was not obtained under these experimental conditions. The presence of one carbonyl or sulfonyl group attached to a PPO phenyl ring decreases drastically the nucleophilicity of the remaining unsubstituted position and, therefore, no disubstitution of the phenylenic units was realized. This is because of the strong electron withdrawing character of the carbonyl and sulfonyl groups. At the same time, when bulky substituents are attached to the PPO backbone, steric hindrance decreases the accessibility of nearby unsubstituted positions.¹³ Consequently, electronic factors make the second electrophilic substitution on the same PPO phenyl ring not possible. At the same time, steric factors limit the degree of monosubstitution to about 80%.

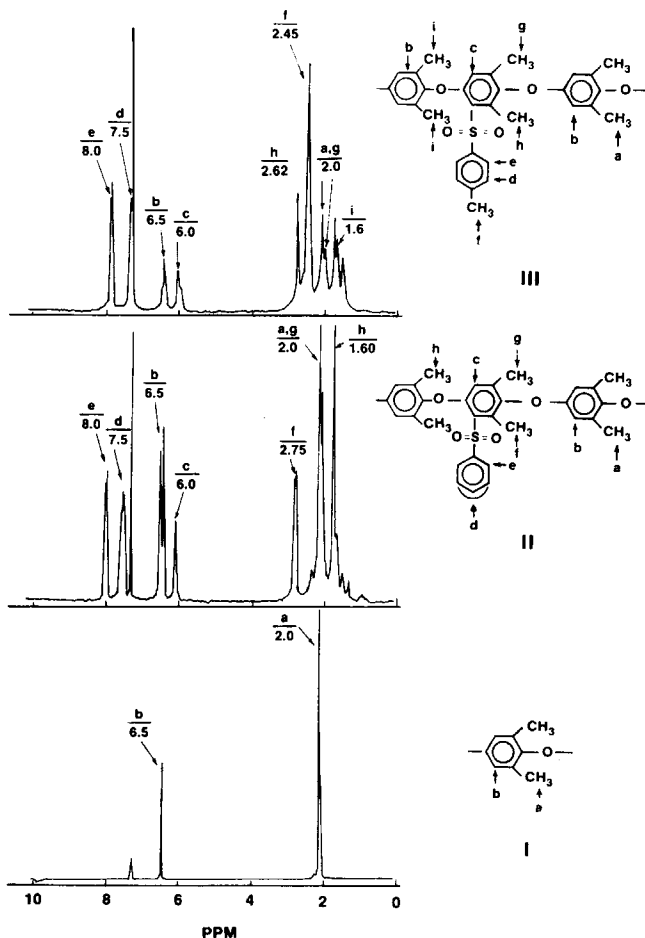


Fig. 1. $^1\text{H-NMR}$ spectra of PPO (I), PPO modified with benzenesulfonyl chloride (sample no. 2, Table I) (II), and PPO modified with *p*-toluenesulfonyl chloride (sample no. 4, Table I) (III).

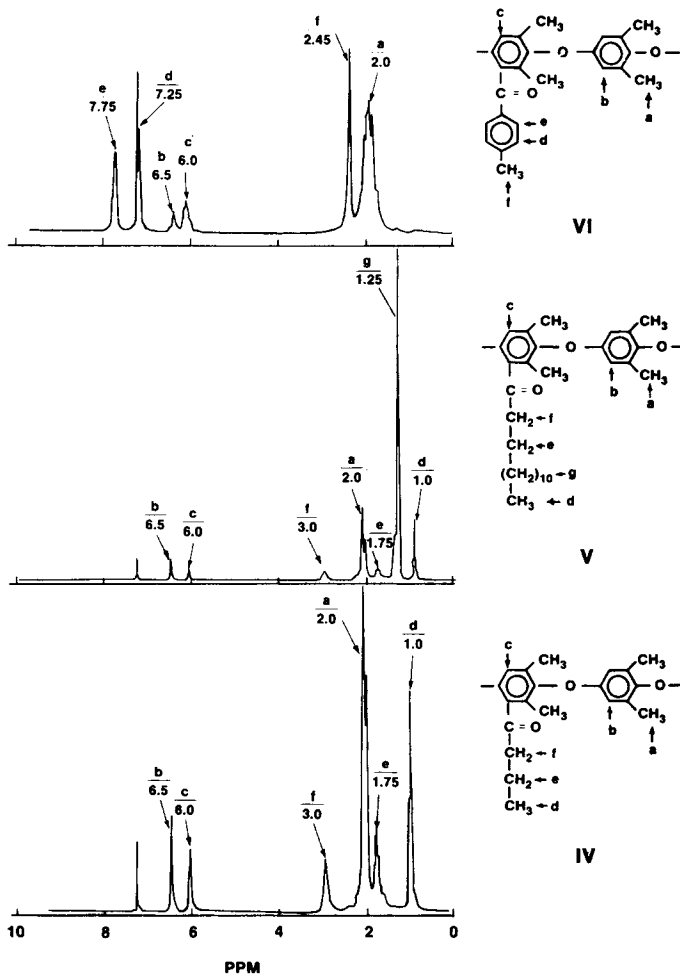
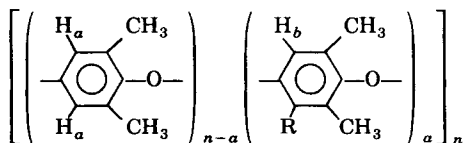


Fig. 2. ¹H-NMR spectra of PPO acylated with propionyl chloride (sample no. 2, Table II) (IV), PPO acylated with myristoyl chloride (sample no. 5, Table II) (V), and PPO acylated with *p*-toluoyl chloride (sample no. 8, Table II) (VI).

Typical ¹H-NMR spectra of the sulfonated PPO and acylated PPO are presented in Figures 1 and 2 together with the assignment of their protonic resonances. Multiple resonances from the aliphatic region in Figure 1 should be due to the sequence distribution of the structural units and it is difficult to provide an exact assignment at this time. The percent of substitution of the PPO aromatic units was determined from the ratio of the integrals of proton resonances due to unsubstituted 2,6-dimethyl-1,4-phenylene units (signal H_a at δ = 6.5 ppm) and substituted units (signal H_b at δ = 6.0 ppm).



The following relationship has been used to calculate the substitution degrees:

$$\% \text{ substitution} = \frac{A_{6.0}}{A_{6.5}/2 + A_{6.0}} \times 100$$

where $A_{6.0}$ and $A_{6.5}$ represent the integrals of the protons at $\delta = 6.0$ ppm and $\delta = 6.5$ ppm, respectively. In all cases monosubstitution was demonstrated by measuring the ratio between the integrals of the unsubstituted aromatic proton of the substituted phenylenic units and some representative protons from the newly attached pendant groups. For example, the ratio between the signals *c* and *e* from spectra II and III (Fig. 1), the ratio between the signals *c* and *f* from the spectra IV and VI (Fig. 2), and *c* and *e* from the spectra VI (Fig. 2) were used to demonstrate monosubstitution.

The FT-IR spectra support the NMR results by demonstrating the presence¹⁴ of the $-\text{SO}_2-$ absorptions at 1176 cm^{-1} in the sulfonylated PPO and the $-\text{CO}-$ absorption at 1700 cm^{-1} . Figure 3 represents some typical IR spectra of PPO (I), sulfonylated PPO (III), and acylated PPO (V). (The numbers I, III, V correspond to those of NMR spectra in Figs. 1 and 2.)

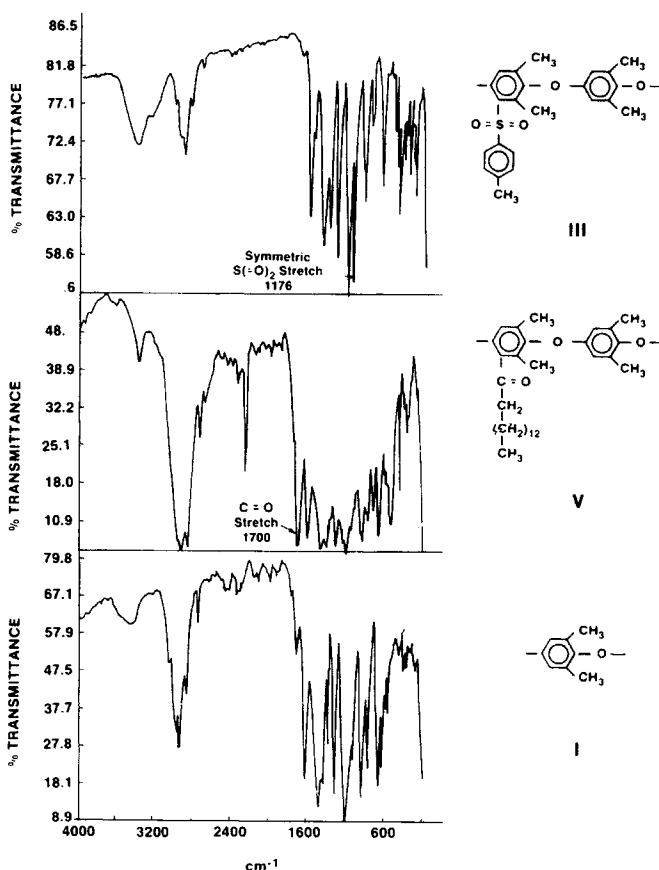


Fig. 3. FT-IR spectra of PPO (I), PPO sulfonylated with *p*-toluenesulfonyl chloride (III), and PPO acylated with myristoyl chloride (V).

Thermal Characterization of the Modified PPO

Both thermogravimetric analysis and differential scanning calorimetric studies have been obtained on modified and unmodified PPO samples. Table III presents the weight losses and the glass transition temperatures of the most representative polymers.

As expected, the substitution of PPO with rigid and bulky side groups decreases the flexibility of the polymer chain and the glass transition temperatures of modified polymers increases. This effect can be exemplified by the PPO modified with *p*-toluenesulfonyl chloride whose T_g is 265°C. An increase in the value of the T_g is also observed when PPO is modified with polar substituents such as dimethylsulfamoyl chloride. In this case the T_g value is 245°C.

The increase in the length of the side chain results normally in an internal plasticization effect caused by a lower polarity of the main chain and an increase in the configurational entropy which results in a lower activation energy of segmental motion and consequently a lower glass transition temperature. The modification of PPO with myristoyl chloride offers the best example. Introducing flexible side groups results in an increase of intermolecular distances and the T_g value is lowered.

No side chain crystallization was detected by DSC for these widely spaced comblike polymers.

Solubility Properties of Modified PPO

The sulfonylated PPO presents some solubility characteristics which are completely different from those of the parent PPO. Table IV presents the solubility of the sulfonylated polymers compared to those of the unmodified PPO. It is very important to note that, after sulfonylation, most of the polymers become soluble in dipolar aprotic solvents like dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMA), etc. This is an important result, since dipolar aprotic solvents are conventional solvents for the preparation of asymmetric membranes. At the same time it is interesting to mention that, while PPO crystallizes from methylene chloride solution, all the sulfonylated polymers do not crystallize and form indefinitely stable solutions in methylene chloride.

Table V presents the solubility of the acylated polymers. While the sulfonylated polymers are all soluble in DMSO, DMF, and DMA, only some of the acetylated polymers become soluble in DMF and DMA, and none are soluble in DMSO. The polymers acetylated with propionyl and butyryl chloride are also soluble in acetone.

The broadening of the range of solvents available for the modified PPO enhances the possibility of casting films as polymer membranes from a large number of solvents.

Permeation Properties of the Modified PPO

The permeation properties of substituted PPO to a carbon dioxide, methane, nitrogen mixture were studied for several systems. The results are presented in Table VI.

TABLE III
Thermal Characterization of Some Modified PPO

Polymer	Number corresponding to Tables I or II	Zone I		Zone II		Zone III		T_g (°C)
		Temp range (°C)	Weight loss (%)	Temp range (°C)	Weight loss (%)	Temp range (°C)	Weight loss (%)	
PPO		75-175	0.3	175-300	0.6	300-400	0.2	212
PPO sulfonylated with <i>p</i> -toluene- sulfonyl chloride	4 (Table I)	100-200	0.4	200-300	0.2	300-400	3.5	225
PPO sulfonylated with dimethyl- sulfamoyl chloride	1 (Table I)	0-250	0.0	250-325	1.9	325-400	11.7	245
PPO acylated with myristoyl chloride	4 (Table II)	0-150	0.0	150-300	0.7	300-400	2.5	116
PPO acylated with myristoyl chloride	5 (Table II)	0-200	0.0	200-300	0.1	300-400	3.0	165

TABLE IV
Solubility of Sulfonylated PPO Derivatives^a

No.	Polymer	Solvent							
		Nitrobenzene	Chloroform	Methylene chloride	DMF	DMSO	DMA	THF	Acetone
1	PPO	+	+	±	-	-	-	-	-
2	PPO modified with benzene sulfonyl chloride	+	+	+	+	±	+	+	-
3	PPO modified with <i>p</i> -toluene sulfonyl chloride	+	+	+	+	±	+	+	-
4	PPO modified with bromo benzene sulfonyl chloride	+	+	+	+	+	+	+	-
5	PPO modified with 2-mesitylenesulfonyl chloride	+	+	+	+	+	+	+	-
6	PPO modified with 2-naphthalene sulfonyl chloride	+	+	+	+	+	+	+	-
7	PPO modified with dimethyl sulfonyl chloride	+	+	+	+	+	+	+	-

^a + = soluble; - = insoluble; ± = tendency of crystallization from solution.

TABLE V
Solubility of Acetylated PPO Derivatives^a

No.	Substituted PPO	Solvent							
		Nitrobenzene	Chloroform	Methylene chloride	DMF	DMSO	DMA	THF	Acetone
1	PPO	+	+	±	-	-	-	-	-
2	PPO modified with <i>p</i> -toluoyl chloride	+	+	+	+	-	+	+	-
3	PPO modified with propionyl chloride	+	+	+	+	-	+	+	+
4	PPO modified with butyryl chloride	+	+	+	+	-	+	+	+
5	PPO modified with lauroyl chloride	+	+	+	-	-	-	+	-
6	PPO modified with myristoyl chloride	+	+	+	-	-	-	+	-
7	PPO modified with palmitoyl chloride	+	+	+	-	-	-	+	-
8	PPO modified with phenyl acetyl chloride	+	+	+	+	-	+	+	-

^a + = soluble; - = insoluble; ± = tendency to crystallize from solution.

TABLE VI
The Permeability to Gases of Some Modified PPO^a

No.	Polymer	P_{CH_4} ^b (barrer)	P_{CO_2} ^b (barrer)	P_{N_2} ^b (barrer)	$\alpha_{\text{CO}_2/\text{CH}_4}$ ^c	$\alpha_{\text{CH}_4/\text{N}_2}$ ^c	$\alpha_{\text{CO}_2/\text{N}_2}$ ^c
1	PPO	3.90	64.00	3.30	16.40	1.18	19.39
2	PPO modified with toluenesulfonyl chloride	3.20	75.00	1.55	23.40	2.06	48.38
3	PPO modified with dimethyl sulfamoyl chloride	3.31	80.99	2.45	24.47	1.35	33.05
4	PPO modified with myristoyl chloride (polymer 5, Table II)	20.26	58.09	11.84	2.87	1.71	4.90

^a Testing temperature = 25°C.

^b 1 barrer = 10^{-10} (cm³(STP) cm)/(cm² s cm Hg)

^c α = separation factor.

The permeation of a gas through a polymer film can be described in terms of the gas or vapor dissolving at one surface of the film, diffusing through the film under a concentration gradient and evaporating from the other surface at the low concentration, i.e., low pressure side.¹⁵

If a constant pressure difference is maintained across the film, the gas will diffuse through the film at a constant rate. Under steady-state conditions the permeability is described by Fick's first law:

$$J = -D \frac{\partial c}{\partial x} \quad (1)$$

where J is the flux or the amount of gas diffusing through unit area of the film in unit time, expressed by STP (standard temperature and pressure) composite unit system as

$$J = \frac{(\text{amount of gas})}{(\text{membrane area}) (\text{time})}$$

where D is the diffusion coefficient and $\partial c/\partial x$ is the concentration gradient across a thickness x . After integration of eq. (1) across the total thickness of the film (I) the amount of gas diffusing through the polymer film (J) is given by

$$J = \frac{D(C_1 - C_2)}{I} \quad (2)$$

where C_1 and C_2 are the concentration of gas in the two surfaces and I is the thickness of the polymer film. Gas concentrations are normally measured in terms of the pressure (p) of the gas which is at equilibrium with the film. According to Henry's law,

$$C = Sp \quad (3)$$

where C is the gas concentration. The permeability constant (P) is defined as

the product $D \times S$ and is given by

$$P = DS = \frac{JI}{p_1 - p_2} \quad (4)$$

where S is solubility coefficient of the gas in the polymer film.

The steady-state separation factor for two species, the ratio of the individual permeabilities, is the product of the diffusion coefficient and solubility coefficient ratios:

$$a = (D_1/D_2)(S_1/S_2)$$

An increase in permeability together with an increase in selectivity for CO_2/CH_4 is clearly demonstrated for PPO substituted with *p*-toluenesulfonyl chloride and for PPO substituted with dimethylsulfamoyl chloride (Table VI).

An interesting case is that of PPO substituted with myristoyl chloride. It can be noticed from Table VI that permeability for methane increases 5.19 times whereas the permeability for carbon dioxide remains approximately in the same range (slightly decreases from 64 to 58.08). Since the differences in gas permeability between PPO and substituted PPO consists only in CH_4 permeability, this might indicate that the gas permeation characteristic of the polymeric membrane is altered mainly in the solubility term. It can also be supposed that certain differences in permeability of PPO vs. substituted PPO among different hydrocarbon gases must occur with an increase in the length of hydrocarbon side chains. This is a very interesting aspect which may prove useful for hydrocarbon/hydrocarbon separations.

CONCLUSIONS

Chemical modification of PPO has been realized by electrophilic sulfonylation and acylation of the aromatic structural units. One additional substituent can be easily introduced on the 2,6-dimethyl-1,4-phenylene structural units. More than 50% substitution is difficult to accomplish due to both a decrease in the remaining position nucleophilicity and steric hindrances.

The thermal stability of the modified polymers does not change much when compared to that of the parent PPO. The change in the glass transition temperature by chemical modification follows the expected trend. An unusually broad range of solubilities was observed for the modified PPO. At the same time, in some cases, an increase in both permeability and selectivity to gases was obtained.

References

1. C. Arnold, *Macromol. Rev.*, **14**, 265 (1969).
2. J. Jachowicz, M. Kryszewski, and A. Sobol, *Polymer*, **20**, 995 (1979).
3. A. S. Hay, in *Encyclopedia of Polymer Science and Technology*, H. Mark, N. G. Gaylord, and N. Bikales, Eds., Wiley, New York, 1969, Vol. 10, p. 92.
4. A. S. Hay, *Adv. Polym. Sci.*, **4**, 496 (1967).
5. I. Cabasso, J. J. Grodzinski, and D. Vofsi, *J. Appl. Polym. Sci.*, **18**, 1969 (1974).
6. L. Verdet and J. K. Stille, *Organometallics*, **1**, 380 (1982).
7. V. Percec and B. C. Auman, *Polym. Bull.*, (Berlin) **10**, 385 (1983).
8. A. J. Chalk and A. S. Hay, *J. Polym. Sci., Part A-1*, **7**, 691 (1968).

9. S. Xie, W. J. MacKnight, and F. E. Karasz, *J. Appl. Polym. Sci.*, **29**, 1678 (1984).
10. K. Toi, G. Morel and D. R. Paul, *J. Appl. Polym. Sci.*, **27**, 2997 (1982).
11. A. S. Hay, in *Macromolecular Synthesis*, Collective Volume I, J. A. Moore, Ed., Wiley, 1977, p. 81.
12. R. A. Pasternak, J. F. Schimscheimer, and J. Heller, *J. Polym. Sci., Part A-2*, **8**, 467 (1970).
13. G. A. Olaf, S. Kobayashi, and J. Nishimura, *J. Am. Chem. Soc.*, **95**, 564 (1973).
14. R. M. Silverstein, G. C. Bassler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds*, Wiley, New York, 1976, p. 97.
15. J. F. Rabek, *Experimental Methods in Polymer Chemistry*, Wiley, 1980, p. 611.

Received March 20, 1986

Accepted May 22, 1986