

# Effects of Polymer Molecular Weight and Chemical Modification on the Gas Transport Properties of Poly(2,6-dimethyl-1,4-phenylene oxide)

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Received 10 March 1999; accepted 17 December 1999

**ABSTRACT:** Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) of different intrinsic viscosities has been studied to understand the effect of polymer molecular weight on the permeability and permeability ratio of CO<sub>2</sub>/CH<sub>4</sub> and O<sub>2</sub>/N<sub>2</sub> gas pairs. The increase in permeability of dense films prepared from higher molecular weight PPO was explained in terms of increased free volume. Gas permeability for the high molecular weight was further improved by attaching bulky bromine groups to the phenyl ring of the PPO backbone. Permeability ratio of PPO was greatly improved by attaching polar groups such as —COOH or —SO<sub>3</sub>H. The loss in permeability because of the presence of the polar groups was compensated by using PPO that was brominated and sulfonated. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1137–1143, 2000

**Key words:** polyphenylene oxide (PPO); gas separation; sulfonated–brominated PPO

## INTRODUCTION

The selection of a polymer for use as a gas separation membrane is essentially based on a number of intrinsic properties that control the performance characteristics of the separation system. These properties are gas permeation properties, permselectivity, mechanical behavior, and cost. A polymer is considered to be ideal if it can be easily converted into high productivity, selectivity, and durable membranes at minimum cost. Unfortunately, most polymers that are highly permeable are usually not very selective. On the other hand, highly selective polymers are not very permeable. This typical trade-off has been well demonstrated

by Robeson<sup>1</sup> who has analyzed in great detail the existing permeability data for many polymers. It has been noted by a few authors<sup>2</sup> that polymer molecular structure can be manipulated to achieve the most favorable balance of transport properties. Kesting and Fritzsche<sup>3</sup> have made note of the importance of the effect of molecular weight of polymers on the performance of gas separation membranes. According to these authors, when dense membranes are prepared from equal viscosity sols, porosity and free volume ( $V_f$ ) will increase with polymer molecular weight. They have also pointed out the extremely favorable mechanical properties, along with high permeability characteristics of membranes from higher molecular weight polymers. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is an example of a fairly permeable polymer having alternating aromatic cycles and C—O linkage in the main chain. Among the many aromatic polymers that

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Contract grant sponsor: British Gas.

*Journal of Applied Polymer Science*, Vol. 77, 1137–1143 (2000)  
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possess high glass transition temperature ( $T_g$ ), PPO shows the highest permeability to gases. It is not evident why this polymer is much more permeable than polysulphone or bisphenol A polycarbonate having similar structures of repeat units. A possible reason could be the absence of polar groups attached to the main chain. Whatever the reason for its properties, PPO drew attention as a permeable and, rather permselective material.<sup>4-6</sup> Thus, separation factors have been reported as follows:

$$(\text{CO}_2/\text{CH}_4) = 12 - 13,$$

$$(\text{O}_2/\text{N}_2) = 4.6, \quad \text{and} \quad (\text{H}_2/\text{CH}_4) = 10^{6-9}$$

Meanwhile, a substantial scatter of the permeability coefficients ( $P$ ) observed by different authors can be noted.<sup>6</sup> This could be due to the fact that PPO can crystallize under some conditions and the variation of the crystallinity can cause the changes of the  $P$  values.<sup>6</sup> The Langmuir capacity parameters reported for this polymer are relatively high,<sup>6</sup> which agrees with the assumption of large free volume in PPO and is in accordance with its high permeability. Free volume in polymers can be further increased by increasing the stiffness of the chains. Stiffness of the chain will reduce the packing density, thus causing an increase in the polymer free volume which in turn may lead to higher permeability. Because  $T_g$  increases with increase in molecular weight, chain stiffness would increase with an increase in molecular weight of polymer, resulting in an increase in free volume. Therefore, molecular weight parameter may be one of the most important characteristics of polymers that determine the transport properties of polymeric membranes. It may be noted that further increase in permeability can be achieved by the introduction of bulky substituents. This effect is greater the stiffer the main chain is.

A possible mode of improving permselective property is by introduction of polar groups inducing stronger interchain interactions. In a sense, permselectivity is a more important property than permeability because the deficiency of the latter can be overcome by manufacturing very thin defect-free layers of membranes or by making use of thin film composite membranes.

Smid and others<sup>10</sup> have shown that oxygen permeability increased with increasing intrinsic viscosity of polyphenylene oxide used to prepare integrally skinned hollow fiber membranes. Auer-

bach et al.<sup>11</sup> have also found that in the permeation of octadecane through Hevea rubber, diffusivity increases with increasing molecular weight. Takada et al.<sup>12</sup> showed that in the case of polyacetylene, both selectivity and permeability increased with an increase in molecular weight and gradually leveled off. Effect of PPO molecular weight parameters on gas transport properties of membranes has also been reported by Polotskaya et al.<sup>13</sup> It has also been shown<sup>14</sup> that although homogeneous and asymmetric membranes could be prepared from PPO of low molecular weight with an intrinsic viscosity,  $[\eta]$ , 0.46 dL/g in chloroform at 25°C, they would rupture in most cases under the testing conditions. It was therefore important to use PPO which would give a mechanically stronger membrane possessing good permeability properties.

Regarding the use of bulky substituents, Percec and Li<sup>7</sup> increased  $\text{CO}_2$  permeability of PPO from 64 to 158 Barrer by bromination. Interestingly, the permeability ratio of  $\text{CO}_2/\text{CH}_4$  also increased from 16.4 to 23.7.

Regarding the introduction of polar groups, Fu et al.<sup>15</sup> reported that the permeability ratio of  $\text{O}_2/\text{N}_2$  increased while  $\text{O}_2$  permeability decreased significantly by sulfonation of PPO. Kruczek and Matsuura<sup>16</sup> found that  $\text{CO}_2/\text{CH}_4$  permeability ratio of 43 could be achieved but the  $\text{CO}_2$  permeability went down to 11 Barrer by sulfonating PPO.

In this work, the effect of molecular weight on the permeability and permeability ratio is studied systematically using PPO of different molecular weights. Then, bromination of PPO of high molecular weight is attempted to prepare PPOBr with different degrees of substitution.

PPOBr is further sulfonated to prepare SPPOBr with different degrees of bromination and sulfonation.

Dense films are prepared from PPO, PPOBr, and SPPOBr and permeability data are obtained for  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{O}_2$ , and  $\text{N}_2$  gases. Permeability ratios are further calculated for  $\text{CO}_2/\text{CH}_4$  and  $\text{O}_2/\text{N}_2$  gas pairs to investigate the permselectivity of polymers.

Thus the objective of this work is to study the following: 1. the effect of the molecular weight; 2. the effect of the degree of bromination; and 3. the effect of simultaneous bromination and sulfonation on the permeability and permselectivity of PPO.

## EXPERIMENTAL

### Materials

A sample of PPO of  $[\eta]$  equal to 1.0 dL/g in chloroform at 25°C was kindly supplied by B. Ward of General Electric Company, Schenectady, NY. A sample of PPO of  $[\eta]$  equal to 1.73 dL/g was kindly supplied by General Electric Company, Selkirk, NY. PPO of  $[\eta]$  equal to 2.2 dL/g was synthesized by us in our laboratory following the method of Hay.<sup>17</sup> The polymers were dried in vacuum oven for several hours before preparing the solutions. All organic chemicals used in the preparation of the casting solution were of reagent grade purity and used as received.

### Gel Permeation Chromatography (GPC)

GPC study of PPO and brominated PPO was done on a PL-Gel column of particle size 5  $\mu\text{m}$  using chloroform as the eluting solvent. Calibration of the column was done using polystyrene as the standard. The chromatograph used a UV detector reading at  $\lambda = 254 \text{ nm}$ .

### Modification of PPO

The modification of PPO by bromination and subsequent sulfonation was performed only for PPO of  $[\eta]$  equal to 1.73 dL/g in chloroform at 25°C. Carboxylation of PPO was also conducted on PPO of the same intrinsic viscosity.

### Bromination of High Molecular Weight PPO

The bromination of the aromatic ring of PPO was achieved at room temperature following a general procedure described by White.<sup>18</sup> Details of the procedure are given below.

### Preparation of PPOBr20 (20% Brominated PPO)

Ten grams of PPO was dissolved in approximately 300–350 mL of chloroform. The reaction kettle was covered with aluminium foil to prevent direct light. One milliliter of bromine in 20 mL of chloroform was added from a separating funnel to the PPO solution in 1–2 min under nitrogen atmosphere. Stirring of the solution was performed continuously during addition of the bromine solution and was continued for another one and a half hours after addition of bromine. The solution was then precipitated in excess of methanol with vigorous stirring. The precipitate was washed 2–3 times in methanol, soaked in methanol overnight,

filtered, and then dried at first under ambient conditions and then in a vacuum oven until ready to use. The degree of bromination was determined by <sup>1</sup>H-NMR and was calculated to be in the range of 20–22% for different reaction batches.

### PPOBr40 (40% Brominated PPO)

Ten grams of PPO was dissolved in approximately 350 mL of chloroform. Two milliliters of bromine in approximately 50 mL of chloroform was added in 2 min. The rest of the reaction procedure was similar to that mentioned above for making of PPOBr20. The degree of substitution according to NMR analysis was 39–41%.

### PPOBr60 (60% Brominated PPO)

Twenty grams of PPO was dissolved in approximately 500 mL of chloroform. Bromine, 2.5 mL, in 50 mL of chloroform was added to the solution in 20 min. The rest of the procedure was similar to that mentioned above. The degree of substitution was 60%.

It may be noted that in all cases, only ring bromination took place. <sup>1</sup>H-NMR analysis did not show any methyl bromination.

Gel permeation chromatography of PPOBr indicated that there was no decrease in molecular weight of PPO during bromination of the polymer.

### Sulfonation of PPOBr

The general procedure for the sulfonation of PPOBr was similar to that described by Plummer et al.<sup>19</sup> for the sulfonation of low molecular weight PPO. However, slight changes had to be made to adjust to the increased viscosity of the solution in chloroform. A 2 wt % solution was reacted with stoichiometric amount of chlorosulfonic acid instead of 10 wt % solution as was used for sulfonating PPO of low molecular weight. The amount of chlorosulfonic acid required for the reaction was based on the amount of unreacted repeat units in the PPOBr molecules. For example, 5 g of PPOBr20 will have 4 g of nonbrominated groups. Therefore, the amount of the acid required for the reaction was calculated based on 4 g of the polymer.

The ion exchange capacity (IEC) was determined by the titration method. For all three different types of PPOBr it was attempted to achieve an IEC of 2.0 meq/g of dry polymer. However, the IEC values were different for the polymers with different degrees of bromination. The values ob-

tained are as follows: PPOBr before sulfonation—SPPOBr20, SPPOBr40, SPPOBr60; SPPOBr after sulfonation—SPPOBr20-1.78, SPPOBr40-1.47, SPPOBr60-1.01; and IEC, meq/g of dry polymer—1.78, 1.47, 1.01.

### Carboxylation of PPO (CPPO)

CPPO was performed following the method described by Chalk and Hay.<sup>20</sup> A solution of 5 g of PPO in 400 mL of tetrahydrofuran was prepared and reacted with 17 mL of 2.5M butyllithium in hexane. This is approximately 2.7 g of pure butyllithium. This amount was calculated so that for each structural unit of the polymer, one atom of lithium would be attached. The reaction was performed for 50 min with continuous stirring after which the mixture was poured into a slurry obtained from 500 mL of ether and 1 kg of dry ice. The slurry was left overnight to warm up to room temperature. The precipitate was filtered and treated with excess of 1M hydrochloric acid to convert the Li form of CPPO to the hydrogen form. The polymer was then dissolved in methanol and ultracentrifuged. It was filtered and put in a dialysis bag for washing. The polymer was then dried. Presence of the carboxyl group in the polymer chain was confirmed by FTIR analysis. The IEC of CPPO was determined by the acid-base titration method and was of 2.8 meq/g of dry polymer.

### Preparation of Dense Films from PPO

Dense films were prepared from 3 wt % solutions of PPO of different intrinsic viscosities in trichloroethene. Polymer solutions were filtered using 0.45  $\mu\text{m}$  pore size Teflon filters. Approximately 2.5 mL of the polymer solution was poured into a metal ring of 9.6-cm inner diameter placed on a glass plate. Small pieces of scotch tape were used to hold the ring in place and to prevent leakage of the solution from underneath the ring. The ring with the solution in it was covered on top with a 15-cm diameter Wattman filter paper to enable slow evaporation of the solvent. The solution was left in the casting box for 24 h at room temperature. Care was taken to check that the glass plate was leveled to avoid differences in thickness due to solution moving to one side. After 24 h of evaporation, the glass plate was immersed in distilled water, and the film surfaces carefully wiped with a low lint wiper. The film was then vacuum dried at room temperature for a minimum of 3 days.

### Preparation of Dense Films from Modified PPO

#### *Preparation of Dense Films from PPOBr*

All the films from PPOBr were prepared from 3 wt % solutions. Films from PPOBr20 and 40 were prepared from their solutions in trichloroethene (TCE) whereas films from PPOBr60 were prepared from chloroform solution. It was difficult to dissolve PPOBr60 in TCE, so no attempt was made to make films from a TCE solution of PPOBr60. The film-making procedure is similar to that described for preparation of dense films from PPO. After pouring 2–3 mL of the solution into the metal ring placed on a clean glass plate, the ring was covered with a filter paper and the solvent allowed to evaporate for 1 day. The films were then dried at ambient temperature for 24 h, and dried in vacuum oven for a period varying between 1 to 4 weeks at room temperature.

#### *Preparation of Dense Films from SPPOBr*

The SPPOBr dense films were made from 3 wt % solutions. Depending on the degree of sulfonation, the casting solutions were made from different solvent mixtures. A 3 wt % solution of SPPOBr60 was made from a 30 : 70 wt ratio mixture of methanol and chloroform. Solutions of SPPOBr40 and SPPOBr20 were made from a 45 : 55 wt ratio mixture of methanol and chloroform. The rest of the procedure was similar to that used for preparation of films from PPO.

#### *Preparation of Dense films from CPPO*

A 3 wt % solution of the polymer was dissolved in a 80 : 20 wt mixture of chloroform and methanol. The foggy solution thus obtained was centrifuged for 20 min and filtered. Dense films were then made from this solution using the procedure mentioned above for preparing films from PPO. They were then dried in vacuum oven for 4 weeks before tested for gas permeation.

### Permeation and Separation Experiments

For the dense films, the permeation rates of single gases were measured using the constant volume system described elsewhere.<sup>21</sup> Films were placed between the two chambers of the testing cells having a permeation area of 10.2 cm<sup>2</sup>. Two rings of silicone rubber membrane (1–2 mil thickness and 1.2 cm wide) were placed on both sides of the film surrounding the permeating area, at the edges where the two chambers of the test cell sit



**Table I Permeability and Permeability Ratios of Dense Films Prepared from PPO of Different Molecular Weights for Gas Pairs O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub>**

[ $\eta$ ], dL/g	Mol Wt	Intrinsic Permeability, Barrer <sup>a</sup>				Permeability Ratio	
		O <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	O <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>
1.10	176 000	14.34	2.99	70.50	3.43	4.80	20.55
1.73	370 000	16.71	3.52	80.81	4.59	4.76	17.61
2.20	520 000	18.47	3.87	89.70	4.51	4.77	19.89

<sup>a</sup> 10<sup>10</sup> Barrer = 1 cm<sup>3</sup> (STP) cm/cm<sup>2</sup> s cmHg.

on each other. The use of the silicone rubber rings served two purposes: the rings prevented damage to the films when the cell was sealed, and the presence of the silicone rubber rings decreased the leak rates of the cell to almost negligible amounts. Single gas permeation tests were performed at an upstream pressure of 5000 Torr, whereas the downstream pressure varied from 0.01 to 10 Torr. Permeation tests were performed over several cycles until the average permeation rate reached a constant value over several consecutive cycles. Gas permeation tests were performed at room temperature (22–24°C). Permeability data were expressed in Barrer where:

$$10^{10} \text{ Barrer} = 1 \text{ cm}^3 \text{ (STP) cm/cm}^2 \text{ s cmHg}$$

In addition to the single gas permeation tests, separation experiments for CO<sub>2</sub>/CH<sub>4</sub> gas mixture were also performed under similar conditions. Before conducting the tests, analysis was done to determine the actual feed composition using mass spectroscopy (MS) method. According to MS, the feed was 19.3% of CO<sub>2</sub> in CH<sub>4</sub>. The permeate samples were also analyzed by MS.<sup>21</sup> The separation factor,  $\alpha$ , was calculated as follows:

$$\alpha = \frac{[(\text{CO}_2 \text{ mol fraction}) \div (\text{CH}_4 \text{ mol fraction})]_{\text{permeate}}}{[(\text{CO}_2 \text{ mol fraction}) \div (\text{CH}_4 \text{ mol fraction})]_{\text{feed}}}$$

## RESULTS AND DISCUSSION

The intrinsic permeabilities and permeability ratios of O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> of dense films prepared from PPO of different intrinsic viscosities are shown in Table I. It should be noted that 3 wt % solutions were used to prepare films from PPO of

different molecular weights. The films from PPO of [ $\eta$ ] equal to 0.46 dL/g were not mechanically strong and therefore could not be tested. As seen from Table I, the permeability ratio of O<sub>2</sub>/N<sub>2</sub> does not change very much and lies in the range of 4.76–4.80. The permeability ratio of CO<sub>2</sub>/CH<sub>4</sub>, on the other hand, lies within the range 17.6–20.6.

Intrinsic permeability data, however, indicate an increasing trend with an increase in molecular weight of PPO for all gases studied. These are in agreement with Kesting's hypothesis<sup>3</sup> that free volume of dense films increases with an increase in the molecular weight of the polymer. An increase in molecular weight causes an increase in chain entanglement, which may in turn result in an increase in chain stiffness leading to a decrease in packing density. It may be noted that the intrinsic permeabilities studied by other authors<sup>22</sup> using PPO of lower intrinsic viscosity (weight average molecular weight equal to 31,200) of 42–50 Barrer which is much less than the value obtained for the higher molecular weight PPO studied in this work.

Test results on dense films made from PPOBr (Table II) indicate that the permeabilities of these films are significantly higher than dense films prepared from PPO. The permeability ratios for PPOBr for the gas pair CO<sub>2</sub>/CH<sub>4</sub> showed increasing tendency with an increase in the degree of bromination. It may be noted that CO<sub>2</sub> permeability increased by 72% when PPO was brominated to 60%. The increase in CH<sub>4</sub> permeability was only 24% for a similar degree of bromination. This resulted in an increase in permeability ratio with an increase in the degree of bromination. However, the tendency was not clearly observed for the O<sub>2</sub>/N<sub>2</sub> gas pair. Similar trends for the gas pair CO<sub>2</sub>/CH<sub>4</sub> was observed by Chern et al.<sup>23</sup> Polymer packing and chain rigidity led to membrane materials of improved permeability properties.

**Table II Permeability and Permeability Ratio for Gas Pairs O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> of Dense Films Prepared from PPOBr**

Polymer	Permeability, Barrer <sup>a</sup>				Permeability Ratio	
	O <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	O <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>
PPO	16.71	3.52	80.81	4.59	4.76	17.61
PPOBr20	18.24	3.62	88.69	3.98	5.04	22.28
PPOBr40	23.13	5.03	118.42	5.53	4.60	22.20
PPOBr60	24.57	4.88	139.30	5.70	5.03	24.40

<sup>a</sup> 10<sup>10</sup> Barrer = 1 cm<sup>3</sup> (STP) cm/cm<sup>2</sup> s cmHg.

The permeability and permeability ratio of dense films made from SPPOBr of varied degrees of sulfonation and bromination are shown in Table III. Performances of CPPO dense films are also presented. Table III also includes data of permeability and permeability ratio for SPPO, details of which were presented earlier.<sup>24</sup>

Comparing the data of SPPO and CPPO with those of the parent polymer (PPO of intrinsic viscosity equal to 1.73 dL/g) in Table I, one can see that both sulfonation and carboxylation brought about a significant decrease in permeability associated with an increase in permeability ratio. This confirms the fact that addition of polar groups induced interchain interaction, the effect being stronger in case of the more polar SPPO. The same conclusion may be drawn when the data on SPPOBr in Table III are compared with those of parent PPOBr polymers with corresponding degree of bromination in Table II.

Dense films from SPPOBr, however, showed improved permeability and permeability ratio compared with both SPPO and CPPO. Permeability ratio for the gas pair CO<sub>2</sub>/CH<sub>4</sub> was 51.39 for SPPOBr40-1.47, which was close to 50.60

achieved for SPPO. However, the permeability for CO<sub>2</sub> was twice as high for the SPPOBr films. Permeability ratio as high as 59.40 for CO<sub>2</sub>/CH<sub>4</sub> with CO<sub>2</sub> permeability of 39.80 Barrer was obtained for dense films from SPPOBr20-1.78. It may be noted that both permeability ratio and CO<sub>2</sub> permeability for films from SPPOBr20-1.78 were higher than those obtained for SPPO of similar IEC. One possible reason could be that the total degree of substitution in the case of SPPOBr is higher than that of the corresponding SPPO. The bulky groups could be filling up the V<sub>f</sub> more in the case of SPPOBr than in the case of SPPO.

Table IV shows the results of separation experiments of a CO<sub>2</sub>/CH<sub>4</sub> gas mixture containing 19.3% of CO<sub>2</sub>. The separation factor is given for each SPPOBr. The data for CPPO is also included for comparison. Since permeate pressure is nearly equal to zero Torr, the separation factor should be equal to the permeability ratio. In fact, the separation factor was lower than the permeability ratio, suggesting some plasticization effect of CO<sub>2</sub>.

**Table III Permeability and Permeability Ratios of Dense Films Prepared from SPPOBr, SPPO, and CPPO for Gas Pairs O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub>**

Polymer	Permeability, Barrer <sup>a</sup>				Permeability Ratio	
	O <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	O <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>
SPPOBr20-1.78	9.09	1.53	39.80	0.67	5.94	59.40
SPPOBr40-1.47	5.17	0.76	27.22	0.53	7.22	51.39
SPPOBr60-1.01	15.96	2.92	112.50	3.83	5.47	29.37
SPPO	2.38	0.41	14.10	0.28	5.83	50.60
CPPO	6.48	1.12	32.63	0.98	5.78	33.30

<sup>a</sup> 10<sup>10</sup> Barrer = 1 cm<sup>3</sup> (STP) cm/cm<sup>2</sup> s cmHg.

IEC value of SPPO = 1.8 meq/g of dry polymer; IEC value of CPPO = 2.8 meq/g of dry polymer.

**Table IV Results of Separation Experiments for a CO<sub>2</sub>/CH<sub>4</sub> Mixture<sup>a</sup> by Dense Films Prepared from SPPOBr and CPPO**

Polymer	Separation Factor (CO <sub>2</sub> /CH <sub>4</sub> )
SPPOBr20-1.78	36
SPPOBr40-1.47	36
SPPOBr60-1.01	22
CPPO	30

<sup>a</sup> CO<sub>2</sub> content of gas mixture, 19.3%.

## CONCLUSIONS

From the present work it may be concluded that for PPO, the molecular weight of the polymer is an important parameter governing the permeability and permeability ratio of PPO dense films for CO<sub>2</sub>/CH<sub>4</sub> and O<sub>2</sub>/N<sub>2</sub> gas pairs. Bromination of PPO of  $[\eta]$  equal to 2.2 dL/g at the aromatic ring position increased gas permeability of the polymer which is attributed to the main chain rigidity and hence the packing density. Slight increase in the permeability ratio for CO<sub>2</sub>/CH<sub>4</sub> gas pair was observed for the brominated samples. This is the result of a larger increase in CO<sub>2</sub> permeability as compared with CH<sub>4</sub> permeability when the degree of bromination is increased from 0 to 60%.

Introduction of polar groups such as —COOH and —SO<sub>3</sub>H to the aromatic ring of PPO is an effective means to increase the permeability ratio of PPO, the effect being stronger for SPPO than for CPPO. The loss in permeability due to the polar group substitution can be compensated by using SPPOBr.

The authors greatly acknowledge the financial support from British Gas.

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