

Development and Characterization of Homopolymers and Copolymers from the Family of Polyphenylene Oxides

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ABSTRACT: Poly(2,6-dimethyl-1,4-phenylene oxide), PDMPO, poly(2,6-diphenyl-1,4-phenylene oxide), PDPPPO, as well as their copolymers of different compositions, having both random and block structures, have been synthesized and characterized by Fourier transform infrared spectroscopy, proton nuclear magnetic resonance, and gel permeation chromatography. Solution-cast films were prepared from all synthesized polymers using chloroform as a solvent. The thermal properties of the resulting films were characterized by differential thermal analysis and differential scanning calorimetry, whereas their morphology was investigated using X-ray diffraction. Ultimately, the potential of the synthesized polymers for gas separation was studied by examining gas permeation properties of the respective thin films in single gas permeation tests involving N₂, O₂, CH₄, and CO₂. In general, the O₂ and CO₂ perme-

ability coefficients decrease with the PDPPPO content. However, the largest drop in the permeability coefficients occurs between PDMPO and a copolymer having the lowest PDPPPO content, and the permeability coefficients PDPPPO are comparable or even lower than the permeability coefficients of the copolymers having the largest PDPPPO content. On the basis of combination of the permeability coefficients and their ratios for CO₂/CH₄ and O₂/N₂, random copolymers appear to be a better candidate for gas separation membranes than their block counterparts. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2140–2148, 2007

Key words: polyphenylene oxide-based random and block copolymers; polymer films and their characterization; gas permeability

INTRODUCTION

Glassy polymers, in spite of a recent shift toward hybrid materials that incorporate dispersions of carbon molecular sieves, zeolites, or other nanoparticles in polymer matrices, remain to be very important class of materials for commercial gas separation membranes. In general, gas transport in glassy polymers is associated with a trade-off between permeability and selectivity;¹ nevertheless by tailoring the chemical structure of polymers it is possible to improve permeability and selectivity simultaneously.² It is generally easier to increase the selectivity than the permeability of the polymer; therefore, the search of polymers having a positive deviation from the trade-off between permeability and selectivity often starts from a highly permeable base polymer.³

Poly(2,6-dimethyl-1,4-phenylene oxide), PDMPO, which is the best known representative of the family of polyphenylene oxides, was first synthesized in late 1950s.⁴ It shows one of the highest permeability to

gases among glassy polymers, which is attributed to the absence of polar groups in the polymer backbone.^{5–8} At the same time, PDMPO can be easily modified by various electrophilic and nonelectrophilic substitutions including bromination,^{9–11} carboxylation and methyl esterified carboxylation,¹¹ sulfonylation and acylation,¹² benzylation,¹³ sulfonation,^{14–16} and silylation.^{17,18} There are literature examples of the modified PDMPOs having the combination of permeability and selectivity placing them above the so-called upper bound line.³

One of the problems associated with PDMPO, and in particular with some modified PDMPOs, is their insufficient chemical and thermal resistance. While some of electrophilic substituents are not thermally stable, a more fundamental problem arises from the methyl groups, which do not have a good thermal and oxidative stability.⁶ The chemical and thermal resistance can be improved by replacing the methyl groups by more stable phenyl groups. This can be accomplished by using 2,6-diphenylphenol, DPP, rather than 2,6-dimethylphenol, DMP, as a monomer. The resulting polymer, poly(2,6-diphenyl-1,4-phenylene oxide), PDPPPO, was synthesized in late 1960s;^{19,20} however, its potential as a membrane material for gas separation was considered only in 1990s. Gas permeation of He, O₂, N₂, CH₄, and CO₂ in PDPPPO were characterized by Aguilar-Vega and Paul,⁶ while the

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potential of this polymer for the separation of hydrocarbons was considered by Ilinich et al.²¹ In general, PDPPPO is more selective and less permeable than PDMPO. It is important to note, however, that gas permeation properties in PDPPPO, and in particular PDMPO, vary considerably, which is attributed to variation in the content of crystalline phase in the polymer.²²

Another group of polymers with interesting potential for gas separation, which however has not been thoroughly explored, is copolymers of PDMPO and PDPPPO. Synthesis of block and random copolymers of PDMPO and PDPPPO was reported in early 1970s,^{23,24} however, the information on gas permeation in these polymers is very limited. Permeability coefficients of CH₄, C₂H₆, and C₃H₈ in two random copolymers with the PDPPPO content of 2.5 and 25% were reported by Ilinich et al.,²¹ while Alentiev et al.²² investigated physical properties and gas permeation of O₂, N₂, CO, and CO₂ in these two copolymers.

In this article we report the synthesis and characterization of random and block copolymers of PDMPO and PDPPPO of different compositions, as well as of the respective homopolymers. The molecular weight, polydispersity index, and the degree of polymerization of the synthesized polymers are determined. The polymers are characterized by considering their thermal properties and X-ray diffraction spectra. Gas permeation in the experiments with single gases such as O₂, N₂, CH₄, and CO₂ are determined, and the ideal selectivities for O₂/N₂ and CO₂/CH₄ are evaluated.

EXPERIMENTAL

Synthesis of polymers

The PDPPPO and PDMPO were synthesized via oxidative polycondensation of DPP and DMP, respectively, following a well-known procedure of Hay.²⁵ The monomers were purchased from Sigma-Aldrich (St. Louis, MO). The catalyst for both reactions was prepared by dissolving cuprous bromide (Acros Organics, FairLawn, NJ) and of N,N,N',N'-tetramethyl-1,3-

butanediamine (Fluka Chemicals, Milwaukee, WI) in benzene (BDH, Toronto, Canada); anhydrous magnesium sulfate (Mallinck, Point Claire, Canada) was also added to remove water formed during the reaction. The temperature of the solution was maintained at 60°C for the synthesis of PDPPPO and at 25°C for the synthesis of PDMPO. The polymerization of homopolymers was carried out for 4 h under continuous mechanical stirring. During the reaction the solution changed its color from yellowish to reddish. The reaction mixture was then filtered and methanol (BDH) was added to precipitate the polymer from the filtrate. To remove the catalyst, the polymer was dissolved in chloroform (BDH) and reprecipitated in methanol.

Block copolymers containing PDPPPO and PDMPO were synthesized following the procedure suggested by Bennett and Cooper.²⁴ Accordingly, first the polymerization of DPP was carried out for 3 h, after which DMP was added to the growing PDPPPO chains and the reaction was continued for another 2 h. The random copolymers, on the other hand, were synthesized by simultaneous oxidation of both monomers for 5 h. Both syntheses were carried out at 25°C under a continuous purging of the reactor with oxygen in the presence of a copper-amine catalyst as in the case of the synthesis of homopolymers.

Table I summarizes the amounts of chemicals used in the synthesis of homopolymers, and block and random copolymers. The amounts of monomers used in a given reaction determine the targeted composition of the polymer, which is given in Table I as a mole fraction of DPP relative to all monomers used in the reaction.

Basic characterization of polymers

The Fourier transform infrared (FTIR) spectra of synthesized polymers in form of thin films were obtained using Nicolet Magna 860 infrared spectrometer equipped with a DTGS detector. Proton Nuclear Magnetic Resonance (¹HNMR) spectra of the synthesized polymers were obtained using a Bruker AMX 500 NMR spectrometer. Gel permeation chromatography (GPC) of the synthesized polymers in dilute solutions (0.02 wt % in tetrahydrofuran) was performed using a

TABLE I
Quantities of Chemicals Used in Synthesis of PDMPO, PDPPPO, and their Block and Random Copolymers

| DPP (g) | DMP (g) | Polymer type | Target DPPPO (mol %) | CuBr (g) | TMEDA (g) | MgSO ₄ (g) |
|---------|---------|--------------|----------------------|----------|-----------|-----------------------|
| 0 | 3.06 | Homo | 0 | 0.141 | 0.0865 | 1.51 |
| 1.53 | 3.07 | Bloc | 18.7 | 0.340 | 0.1700 | 3.06 |
| 3.00 | 1.50 | Bloc | 48.0 | 0.138 | 0.0852 | 1.57 |
| 3.31 | 0.41 | Bloc | 78.8 | 0.105 | 0.0852 | 1.52 |
| 2.00 | 3.00 | Random | 23.5 | 0.092 | 0.0568 | 1.51 |
| 3.00 | 1.50 | Random | 48.0 | 0.170 | 0.0852 | 1.51 |
| 3.00 | 0.50 | Random | 73.6 | 0.095 | 0.0866 | 1.51 |
| 3.06 | 0 | Homo | 100 | 0.141 | 0.0865 | 1.51 |

Gel Permeation Chromatograph (from Waters) equipped with a 410 Refractive Index Detector.

Formation and characterization of polymer films

Solubility tests with different solvents revealed that chloroform, benzene, and trichloroethylene could dissolve all polymers synthesized in this study. Out of these solvents, chloroform was chosen for the preparation of casting solutions.

A fixed amount of dry polymer was dissolved in a fixed volume of Omnisolv chloroform (BDH) to form a 4 wt % casting solution, which was then filtered through a 3- μm Teflon filter, and degassed for 24 h before further processing. A sample of approximately 2.0 cm^3 of casting solution at ambient temperature was poured inside a 9-cm-diameter aluminum ring, which was placed on a leveled glass plate in a fume hood. The cast solution was then covered by a filter paper and the solvent was allowed to evaporate for at least one day. The plate with a dry film was then immersed into the water bath to facilitate the removal of the film from the plate. Such prepared films, also referred here as membranes, were dried in a vacuum oven for at least two days before any analysis.

Two types of thermal analyses were performed, differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The DTA spectra were obtained using Seiko's Simultaneous Thermal Analyzer TG/DTA 320, while the DSC spectra were obtained using a Seiko 2920 Modulated DSC.

The X-ray diffraction spectra of polymer films were obtained using a Philips Diffractometer PW370 BASED in a continuous scan with a scan step of $2\theta = 0.020^\circ$ and a scan speed of $0.020^\circ/\text{s}$ between 2θ equal to 5° and 40° . The values of 2θ are correlated with d -spacing (d) through the Bragg equation:

$$d = \frac{\lambda_X}{2 \sin \theta} \quad (1)$$

where λ_X is a wavelength of X-rays. A copper cathode generated a monochromatic beam of $\lambda_X = 1.54 \text{ \AA}$.

Permeation rates of N_2 , O_2 , CH_4 , and CO_2 through the films formed from the synthesized polymers were determined using a constant pressure technique. The utilized testing system consisted of six cells, so that six films could be tested simultaneously. The permeation area in each cell was approximately 10 cm^2 . The permeation rate was measured manually using a soap bubble flow meter attached to the permeate side of each cell via a flexible tube.

The films were initially tested with N_2 to check their integrity. The successful films were then tested in the following order: CO_2 , N_2 , O_2 , and CH_4 . The test with CO_2 was carried out for at least six days to condition the membranes, while the other gases were tested for

at least two days or until the permeation rate attained a constant value, which was considered as steady state permeation rate.

Assuming that films had a homogeneous structure, the steady state permeation rate of gas i (Q_i) was used to evaluate the permeability coefficient (P_i) in polymer:

$$P_i = \frac{Q_i l}{A \Delta p} \quad (2)$$

where l is the membrane thickness, A is the permeation area of the membrane, and Δp is the partial pressure gradient across the membrane. The permeability coefficient is traditionally expressed in barrers, where $1 \text{ barrer} = 10^{-10} \times \text{cm}^3 (\text{STP}) \times \text{cm}^{-1} \times \text{s}^{-1} \times \text{cm Hg}^{-1}$. The membrane thickness required for the evaluation of P_i was determined by calculating the average from at least 10 readings taken by a Mitutoyo micrometer from the entire permeation area the tested membrane.

Permeability coefficients obtained in single gas permeation tests were used for the evaluation of the selective properties of membranes. The ideal selectivity (α_{ij}) for the separation of a mixture containing gases i and j is defined as

$$\alpha_{ij} = \frac{P_i}{P_j} \quad (3)$$

In particular, two pairs of gases were of interest in this project, O_2/N_2 and CO_2/CH_4 .

RESULTS AND DISCUSSION

Basic characterization of polymers

Apart from the desired polymers, oxidation of 2,6-disubstituted phenols could lead to the formation of diphenoquinone,²⁵ which is an undesirable byproduct. To verify whether diphenoquinone was formed, the synthesized polymers in form of thin films were analyzed using FTIR spectroscopy. The FTIR spectra did not reveal any peaks in the $1725\text{--}1705 \text{ cm}^{-1}$ frequency range, which would indicate the presence $>\text{C}=\text{O}$ groups.²⁶ These groups are present in diphenoquinone but not in PDMPO, PDPPPO, and their copolymers. Therefore, the absence of peaks in the $1725\text{--}1705 \text{ cm}^{-1}$ frequency range confirmed that the synthesized polymers were free from diphenoquinone.

The actual %PDPPPO was determined by ^1H NMR spectroscopy using the following equation:²⁴

$$\% \text{PDPPPO} = \frac{\frac{I_1 + I_2 + I_3}{10}}{\frac{I_1 + I_2 + I_3}{10} + \frac{I_4}{6}} 100\% \quad (4)$$

where I_1 , I_2 , and I_3 are the intensities arising from the 10 protons attached to the phenyl side groups of the

TABLE II
Comparison of the Targeted and the Actual %DPPO in Synthesized Copolymers

| Target %DPPO block copolymers | Actual %DPPO block copolymers | Target %DPPO random copolymers | Actual %DPPO random copolymers |
|----------------------------------|----------------------------------|-----------------------------------|-----------------------------------|
| 18.7 | 16.8 | 23.5 | 28.0 |
| 48.0 | 51.4 | 48.0 | 53.6 |
| 78.8 | 75.7 | 73.6 | 75.6 |

PDPPO segments, and I_4 is the intensity arising from the 6 protons attached to the methyl side groups of the PDMPO segments. Table II compares the targeted %PDPPO with the values calculated using eq. (4). From this point on, the synthesized copolymers will be abbreviated using the following scheme: copolymer type (B or R)/the actual %PDPPO determined by eq. (4). For example, B/16.8 indicates block copolymers with 16.8% of PDPPO.

The number average (M_n) and weight average (M_w) molecular weights of homopolymers and copolymers were determined by the GPC technique. The ratio of M_w and M_n was used to calculate the polydispersity index (PDI) of the analyzed polymers. As already mentioned, the samples for the GPC analysis were prepared using THF as a solvent. However, PDMPO and B/16.8 were only partly soluble in this solvent. As a result, the reported values of M_n , M_w , and PDI for PDMPO and B/16.8 could be associated with an error.

Since the molecular weight of PDMPO segments of 120 is significantly lower than the molecular weight of PDPPO segments of 244, the experimentally determined molecular weights are not proportional to the degree of polymerization of copolymers. To determine the average degree of polymerization (ADP) of copolymers, the following set of equations was solved:

$$120n_1 + 244n_2 = M_n \quad (5)$$

$$\frac{n_2}{n_1 + n_2} \times 100\% = \%PDPPO \quad (6)$$

where, n_1 and n_2 represent the number of segments of PDMPO and PDPPO, respectively. The ADP is

TABLE III
Summary of Determination of M_n , M_w , PDI, and ADP for PDMPO, PDPPO, and their Block and Random and Copolymers

| Actual % of DPPO | Polymer type | M_n | M_w | PDI | ADP |
|---------------------|-----------------|--------|---------|------|-----|
| 0 | Homo | 10,054 | 13,357 | 1.38 | 84 |
| 16.8 | Block | 18,663 | 43,862 | 2.35 | 131 |
| 28.0 | Random | 25,470 | 52,505 | 1.49 | 161 |
| 51.4 | Block | 12,674 | 50,072 | 3.95 | 67 |
| 53.6 | Random | 22,558 | 44,544 | 1.98 | 126 |
| 75.6 | Random | 18,663 | 43,862 | 2.35 | 91 |
| 75.7 | Block | 65,856 | 104,685 | 1.59 | 317 |
| 100 | Homo | 45,883 | 68,468 | 1.49 | 188 |

simply equal to $n_1 + n_2$. Table III provides the summary of M_n , M_w , PDI, and ADP for all polymers synthesized in this project.

The synthesis of PDPPO is more difficult than the synthesis of PDMPO because of bulkiness of the phenyl groups.²⁵ Therefore, one could anticipate a decrease in the molecular weight of polymer with an increase in the targeted %PDPPO. This anticipated effect is clearly evident in case of random copolymers, in particular when the ADP is considered. It is important to emphasize that the larger ADP of PDPPO than that of R/75.6 is probably because the former was synthesized at 40°C while the latter at 25°C. According to Hay, the yield of PDPPO and its molecular weight increase with the temperature at which the oxidation of the monomer takes place.²⁵ Considering block copolymers, there is no clear trend between the molecular weight and the %PDPPO.

Thermal properties

Thermogravimetry and DSC were utilized to determine the decomposition temperature (T_d) and the glass transition temperature (T_g) of the synthesized polymers, respectively, and Table IV summarizes the results of these thermal analyses. If polymer decomposes in a single stage, its decomposition temperature is provided as T_{d1} . As seen in Table IV homopolymers

TABLE IV
Summary of Determination of the Decomposition and Glass Transition Temperatures for PDMPO, PDPPO, and their Block and Random and Copolymers

| Actual %DPPO | Polymer Type | T_{d1}^a [°C] | T_{d2}^b [°C] | T_g [°C] |
|-----------------|-----------------|-----------------|-----------------|------------|
| 0 | Homo | 464 | – | 218.7 |
| 16.8 | Block | 467 | 577 | 214.1 |
| 28.0 | Random | 484 | – | 215.0 |
| 51.4 | Block | 467 | 586 | 219.4 |
| 53.6 | Random | 506 | – | 218.4 |
| 75.6 | Random | 538 | – | 213.6 |
| 75.7 | Block | 467 | 582 | 215.3 |
| 100 | Homo | 571 | – | 217.1 |

^a T_{d1} is the decomposition temperature of homopolymers and random copolymers, or the first decomposition temperature of block copolymers.

^b T_{d2} is the second decomposition temperature of block copolymers.

and random copolymers decompose in a single stage. The T_d of PDPPPO of 569°C is significantly greater than the T_d of PDMPO of 464°C, which is an indication of an improved thermal stability of PDPPPO in comparison with PDMPO. The decomposition temperature of random copolymers increases with an increase in the %PDPPPO, which is a direct consequence of a higher T_d of PDPPPO compared to the T_d of PDMPO. Unlike homopolymers and random copolymers, block copolymers decompose in two stages, which are denoted as T_{d1} and T_{d2} in Table IV. It can be noticed that for block copolymers, regardless of the %PDPPPO, T_{d1} is comparable with the decomposition temperature of PDMPO, while T_{d2} is comparable with the decomposition temperature of PDPPPO. The existence of two decomposition temperatures in block copolymers proves that block copolymerization DMP and DPP monomers was indeed successful.

In general, for a given polymer an increase in the molecular weight is associated with an increase in T_g .²⁷ For PDMPO of a typical molecular weight ranging from 40,000 and 50,000 the literature values of T_g vary from 205 to 210°C.²⁸ However, for the PDMPO with the molecular weight of 550,000, $T_g = 224^\circ\text{C}$ has been reported.²⁹ Consequently, the T_g of 218.7°C for the PDMPO synthesized in this project is high considering its low M_w . On the other hand, the T_g of PDPPPO of 217.1°C is rather low in comparison with the literature values of 220°C³⁰ and 230°C.¹⁹ In general, T_g should increase with the DPPPO content because bulkiness of the phenyl groups prevent the rotations around the ether linkages.²⁷ This effect, however, is not evident considering the T_g values summarized in Table IV.

Film morphology

PDMPO is a crystallizable polymer, which, however, is difficult to crystallize from the melt and behaves essentially as an amorphous polymer.²⁸ On the other hand, PDMPO may crystallize from the solutions, in particular those involving good solvents,³¹ such as chloroform, and the solution-cast PDMPO films may have semicrystalline structure. The degree of crystallinity of the solution-cast PDMPO films, however, may vary even when the same solvent is used. For example, on the basis of the experimental density the PDMPO films prepared by Aguilar-Vega and Paul contained only 3% of the crystalline phase.⁶ On the other hand, Alentiev et al. reported 37% of the crystalline phase in the chloroform-cast PDMPO films.²² The former films were cast at 50°C while the latter at ambient temperature. In general, rapid evaporation of solvent suppresses the formation of the crystalline phase.²²

Figure 1 presents the X-ray diffraction spectra of PDMPO and random copolymers [Fig. 1(a)], and

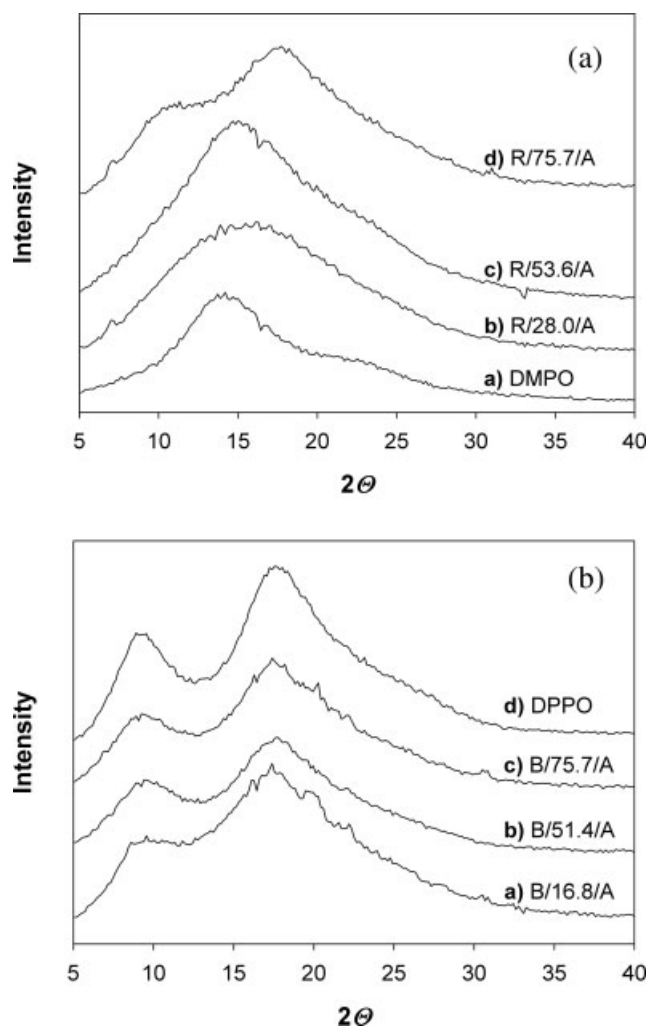


Figure 1 Effect of the PDPPPO content on X-ray diffraction spectra of polyphenylene oxides; (a) PDMPO and random copolymers; (b) PDPPPO and block copolymers.

block copolymers and DPPO [Fig. 1(b)]. In both figures the spectra are shown in the order of increasing the PDPPPO content. The major feature of the PDMPO spectrum in Figure 1(a) is a broad amorphous peak with a maximum at 2θ of 14.2° , which corresponds, according to eq. (1), to d -spacing of 6.2 [Å]. The right shoulder of the PDMPO peak is higher in its intensity than the left one, which indicates the presence of a lower intensity peak at around 2θ of $22\text{--}23^\circ$. Although the PDMPO films in the current study were cast at ambient temperature, its spectrum is similar to the spectrum of almost completely amorphous PDMPO⁶ rather than to the spectrum of a semicrystalline PDMPO,²² which in addition to the main peak at around 2θ of 14° contained a series of smaller peaks over amorphous halo for 2θ lying in the $5\text{--}25^\circ$ range. This apparent inconsistency can be explained as follows. The thickness of PDMPO films prepared by Alentiev et al. varied from 50 to 150 μm ,²² while the thickness of the films in the current investigation

varied from 15 to 25 μm . An increase in the dry thickness of film might be achieved by using a more concentrated casting solution and/or a greater volume of the casting solution inside the ring. In either case, the formation of the film would be slower, enhancing crystalline formation.

As the PDPPO content increases to 28.0% and 53.6% the peak becomes more symmetric; also the maximum is shifted to 2θ of 15.4 and 15.0°, respectively. The spectrum of R/75.7 is different from the spectra of the other two random copolymers. The maximum of the main peak is shifted to 2θ of 17.7° and similarly to PDMPO, the spectrum is not symmetrical. However, unlike PDMPO, the left shoulder of the R/75.7 peak is higher in its intensity than the right one, which indicates the presence of a lower intensity peak at around 2θ of 10°. Despite some differences arising from different PDPPO content, the spectra of all random copolymers in Figure 1(a) are typical for completely amorphous materials.²²

The spectrum of R/75.7 resembles more the spectra of block copolymers and PDPPO shown in Figure 1(b), than the spectra of other random copolymers. In general, the spectra of all block copolymers presented in Figure 1(b) reveal two peaks, the smaller one at around 2θ of 10° and the larger one at around 2θ of 18°, which correspond to d -spacing of 8.8 [Å] and 4.9 [Å], respectively. Unlike the random copolymers, the peaks in block copolymers do not shift noticeably with the %PDPPO. On the other hand, as the %PDPPO increases, the peaks become sharper, which indicates a more ordered structure. The spectrum of PDPPO in Figure 1(b) is similar to those reported for this polymer in the literature.^{6,22,30} Using the analogy with polystyrene,³² Aguilar-Vega and Paul suggested that the peak at 8.8 [Å] d -spacing may be attributed to stacking of phenyl groups from several neighboring PDPPO chains, while the peak at 4.9 [Å] d -spacing is due to intraphenyl interactions between interchain and interchain phenyl groups.⁶

Gas permeation properties

Initially, for each polymer six films were prepared for the tests with gases. If out of these six films at least four survived the complete experimental run, no additional membranes were prepared, and the gas permeation properties for a given polymer were determined based on performance of the successful films. If, however, less than four from the original six membranes survived the complete experimental run, additional films were prepared to have at least four successful membranes. In case of some polymers, the fulfillment of this condition required preparation up to five additional films. Depending on the polymer, the percentage of successful membranes, varied from 45.5 to 83%. The lowest percentage of the successful

membranes of 45.5% was observed in case of both homopolymers.

Regardless of the polymer, the experimentally determined permeability coefficients increase in the following order $\text{CH}_4 \cong \text{N}_2 < \text{O}_2 < \text{CO}_2$. This order of permeability coefficients arises from the properties of the utilized gases and is consistent with the solution diffusion mechanism of gas transport in polymers.

Figure 2 presents the effect of the PDPPO content on the permeability coefficients of CO_2 [Fig. 2(a)] and O_2 [Fig. 2(b)] in the synthesized polymers. The error bars in Figure 2 represent the standard deviation from the permeation data of at least four identical membranes. In general, the literature permeability coefficients of CO_2 and O_2 in PDMPO vary from 27 to 76 barrers,^{6,9–11,13,17,22,33–36} and from 12.0 to 16.1 barrers,^{6,13,17,22,33,35,36} respectively. In comparison with these values the permeability coefficients CO_2 and O_2 in PDMPO observed in this study of 71.7 ± 6.0 and

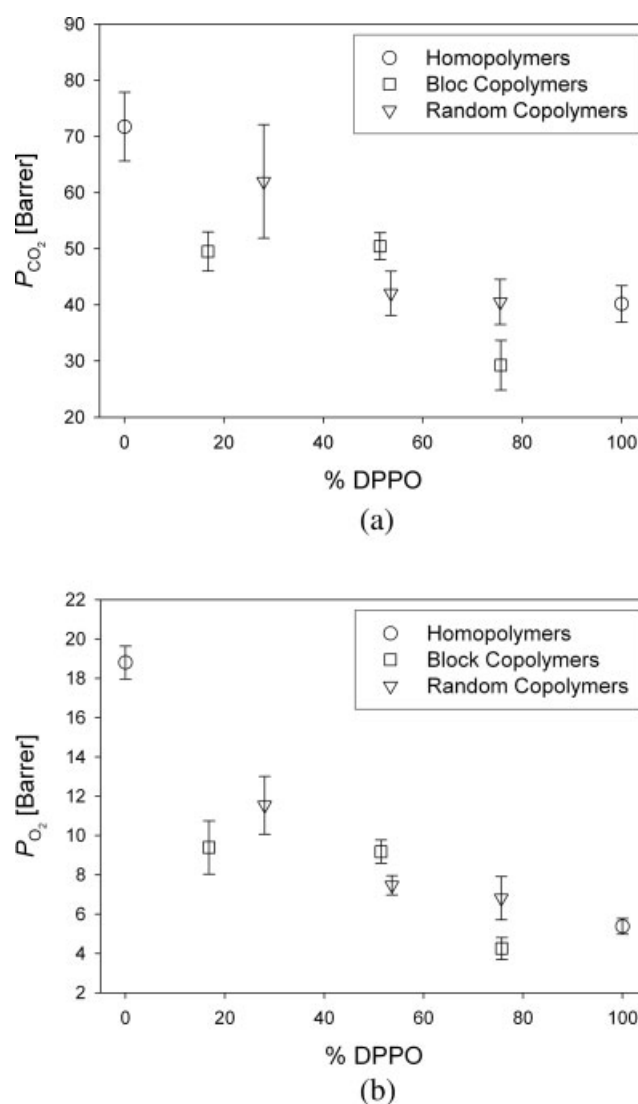


Figure 2 Effect of the PDPPO content on the permeability coefficients of CO_2 (a) and O_2 (b) in polyphenylene oxides.

18.9 ± 0.9 barrers, respectively, are quite high, in particular in case of O₂. This is even more so considering a relatively low molecular weight of the synthesized homopolymers, because according to Poloptskaya et al.,³⁷ the permeability of PDMPO improves with the molecular weight. For example, as the molecular weight of PDMPO increases from 176,000 to 520,000, the permeability coefficients of CO₂ and O₂ increase from 70.5 and 14.3 barrers to 89.7 and 18.5 barrers, respectively.³⁸ In case of PDPPO, the observed permeability coefficients of CO₂ and O₂ of 39.8 ± 3.0 barrers and 6.1 ± 0.3 barrers are comparable or slightly greater than the values reported in the literature.^{6,22}

The relatively high permeability coefficients of CO₂ and O₂ in the synthesized homopolymers might be due to the fact that the structure of the resulting films was not truly homogeneous. Using an atomic force microscope Khulbe et al.³⁹ reported different structures of the top and bottom surfaces of the solution-cast PDMPO membranes. Although both surfaces had uniform nodular structures, the size of nodules at the bottom surface (polymer solution–glass plate interface) was twice the size at the top surface, suggesting a decreasing density from the top to the bottom surface of presumably “homogeneous” membranes. If there is a density gradient from the top surface to the bottom surface, the “effective” thickness of a membrane would be less than the measured value, and thus the permeability coefficient evaluated from eq. (2) would be overestimated. If correct, the above argumentation would be applicable not only to membranes made from homopolymers but also to those made from copolymers.

A general decrease in the permeability coefficients with increase in the PDPPO content is consistent with the results reported by Ilinich et al.⁴⁰ Using ¹²⁹Xe NMR spectroscopy they observed that the effective pore size decreases from 0.56 nm for PDMPO to 0.50 nm for PDPPO. A decrease in the effective pore size must be associated with a decrease in the diffusion coefficient. It is also important to note that also the observed decrease in the permeability coefficient correlates well with the X-ray diffraction spectra presented in Figure 1. On the one hand, as the PDPPO content of random copolymers increases the main peak is shifted toward greater 2θ, which indicates a decrease in *d*-spacing. On the other hand, as the PDPPO content of block copolymers increases the peaks became sharper, which may indicate an increased occurrence of less permeable crystalline regions.

Considering block and random structures of comparable PDPPO content, two random copolymers are more permeable and one is less permeable than their block counterparts. Therefore, it is difficult to draw any definite conclusion. At the same time, it should be noted that R/28.0 is more permeable than B/16.8 despite its greater PDPPO content.

Figure 3 presents the effect of the %PDPPO on the permeability ratios of CO₂/CH₄ [Fig. 3(a)] and O₂/N₂ [Fig. 3(b)] in the synthesized polymers. It can be noticed that the size of the error bars in Figure 3 is significantly greater than in Figure 2. This is because of uncertainty associated with the permeability coefficient of the slower gases. Generally, the ratios shown in Figure 3 are greater than those reported in the literature for the PDMPO,^{6,9–11,13,17,22,33–36} PDPPO,^{6,22} and random copolymers with low PDPPO content.²² As already mentioned, all gas permeation experiments in this study were performed in a constant pressure system, in which the permeate side of membrane was open to atmosphere. As a result the effects of back diffusion of air components, which are not present in the forward permeating gas (e.g., O₂ in tests with N₂, and O₂ + N₂ in tests with CH₄), could be significant, leading to underestimation of the permeability coefficient

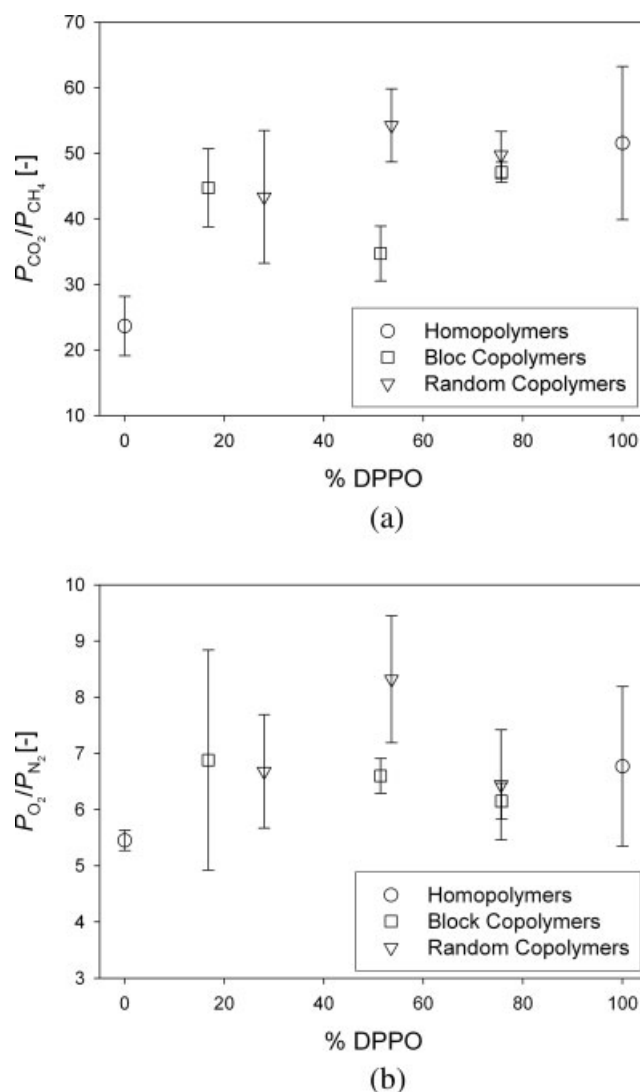


Figure 3 Effect of the PDPPO content on the ratio of permeability coefficients of CO₂/CH₄ (a) and O₂/N₂ (b) in polyphenylene oxides.

of the slower gases such as N_2 and CH_4 .⁴¹ Thus, the permeability ratios shown in Figure 3 might be overestimated. Nevertheless, qualitative comparisons between the permeability ratios of different polymers in Figure 3 are still appropriate.

It can be noticed that the CO_2/CH_4 and O_2/N_2 permeability ratios increase drastically between PDMPO and B/16.8. As the PDPPPO content increases beyond 16.8% its influence on the permeability ratios appears to be rather weak. A decrease in the permeability coefficient with %PDPPPO shown in Figure 2 was attributed to a decrease in the diffusion coefficient resulting from the reduction in pore size. Normally, a decrease in the diffusion coefficient is associated with an increase in the diffusion selectivity.² Since the diffusion effects dominate the solubility effects in glassy polymers, it appears that after the initial jump in the diffusion selectivity resulting from introduction of a small fraction of side phenyl groups, this parameter is not affected by further introduction of these groups. The fact that in case of CO_2/CH_4 the permeability ratio slightly increases with the PDPPPO content beyond B/16.8 is probably due to the solubility effects, arising from strong interactions between CO_2 and the pendent phenyl groups. Interestingly, the O_2/N_2 permeability ratios of block and random copolymers containing 75% of DPPO are lower than those other copolymers, and there is no immediate explanation of this fact.

Considering block and random structures of comparable PDPPPO content it is important to note that R/75.6 is both more permeable and more selective than B/75.7, which represent a positive deviation from a general trade-off between permeability and selectivity.¹ In case of the other two pairs of copolymers, the trade-off between permeability and selectivity is observed. However, while R/28.0 is clearly more permeable than B/16.8, it is just little bit less selective than its block counterpart. Considering R/53.6 and B/51.4, the former is just little bit less permeable but significantly more selective than the latter. Therefore, it appears that random copolymers of PDMPO and PDPPPO offer a better combination permeability and selectivity than their block counterparts.

CONCLUSIONS

Block and random copolymers of PDMPO and PDPPPO of different compositions, as well as the respective homopolymers, have been synthesized, and their potential for gas separation has been investigated using chloroform-cast films in single gas permeation experiments with CO_2 , N_2 , O_2 , and CH_4 . In addition, the thermal properties of the films by DTA and DSC, and their morphology by X-ray diffraction have been characterized.

The ADP of random copolymers decreases, as expected, with increasing the PDPPPO content. In case of block copolymers, there is no clear trend between the PDPPPO content and the ADP. As the PDPPPO content increases, the resulting films have more ordered structure as shown by X-ray diffraction spectra. This effect is more evident in block than in random copolymers. The permeability coefficients of O_2 and CO_2 decrease with increasing PDPPPO content; however, this decrease is not linear. The largest drop in the permeability coefficient occurs between PDMPO and a copolymer having the lowest PDPPPO content. At the same time, the permeability coefficients of PDPPPO are comparable or even slightly higher than the permeability coefficients of the copolymers having the largest PDPPPO content. On the basis of combination of the permeability coefficients and their ratios for CO_2/CH_4 and O_2/N_2 , random copolymers appear to be a better candidate for gas separation membranes than their block counterparts.

References

- Robeson, L. M. *J Membr Sci* 1991, 62, 165.
- Koros, W. J.; Fleming, J. K. *J Membr Sci* 1993, 83, 1.
- Kruczek, B.; Matsuura, T. *J Membr Sci* 2000, 167, 203.
- Hay, A. S.; Blanchard, H. S.; Enders, G. F.; Eustance, J. W. *J Am Chem Soc* 1959, 81, 6335.
- Toi, K.; Morel, G.; Paul, D. R. *J Appl Polym Sci* 1982, 27, 2997.
- Aguilar-Vega, M.; Paul, D. R. *J Polym Sci [B]* 1993, 31, 1577.
- Plate, N. A.; Yampolskii, Y. In *Polymer Gas Separation Membranes*; Paul, D. R., Yampolskii, Y., Eds.; CRC Press: London, 1994; p 154.
- Mahajan, S. S. *Polym Plast Tech Eng* 1991, 30, 27.
- Chern, R. T.; Sheu, F. R.; Jia, L.; Stannet, V. T.; Hopfenberg, H. B. *J Membr Sci* 1987, 35, 103.
- Percec, S. *J Appl Polym Sci* 1987, 33, 191.
- Story, B. J.; Koros, W. J. *J Membr Sci* 1992, 67, 191.
- Percec, S.; Li, G. *ACS Symposium Series* 364, Chapter 4.
- Bhole, Y. S.; Kharul, U. K.; Somani, S. P.; Kumbharkar, S. C. *Eur Pol J* 2005, 41, 2461.
- Huang, R. Y. M.; Kim, J. J. *J Appl Polym Sci* 1984, 29, 4029.
- Fu, H.; Jia, L.; Xu, J. J. *J Appl Polym Sci* 1994, 51, 1399.
- Kruczek, B.; Matsuura, T. *J Membr Sci* 1998, 146, 249.
- Assogna, A.; Perego, G.; Roggero, A.; Sisto, R.; Valentini, C. *J Membr Sci* 1992, 71, 97.
- Pedretti, U.; Gandini, A.; Roggero, A.; Sisto, C.; Valentini, C.; Assogna, A.; Stopponi, A. U.S. Pat. 5,169,416 (1992).
- Hay, A. *Macromolecules* 1969, 2, 107.
- White, D. M.; Klopfer, H. J. *J Polym Sci [A]* 1970, 8, 1427.
- Ilinich, O. M.; Semin, G. L.; Chertova, M. V.; Zamarev, K. I. *J Membr Sci* 1992, 66, 1.
- Alentiev, A.; Drioli, E.; Gokzhaev, M.; Golemme, G.; Ilinich, O.; Lapkin, A.; Volkov, V.; Yampolskii, Y. *J Membr Sci* 1998, 138, 99.
- Bennett, J. G.; Cooper, G. D. *Macromolecules* 1970, 3, 101.
- Bennett, J. G.; Cooper, G. D. *J Org Chem* 1972, 37, 441.
- Hay, A. S. *J Polym Sci* 1998, 36, 505.
- Rao, C. N. R. *Chem Applications of Infrared Spectroscopy*; Academic Press, New York, 1963; p 617.
- Kesting, R. E.; Fritzsche, A. K. *Polymeric Gas Separation Membranes*; Wiley, New York, 1993.

28. Karasz, F. E.; O'Reilly, J. M. *J Polym Sci Polym Lett Ed* 1965, 3, 561.
29. Chowdhury, G. In *Polyphenylene Oxide and Modified Polyphenylene Oxide Membranes, Gas, Vapour and Liquid Separations*; Chowdhury, G.; Kruczek, B.; Matsuura, T., Eds.; Kluwer Academic: Norwell, MA, 2001; p. 109.
30. Wrasidlo, W. *Macromolecules* 1971, 4, 642.
31. Berghmans, S.; Mewis, J.; Berghmans, H.; Meijer, H. *Polymer* 1996, 36, 3085.
32. Mitchell, G. R.; Windle, A. H. *Polymer* 1984, 25, 906.
33. Yasuda, H.; Rosengren, K. *J Appl Polym Sci* 1970, 14, 2839.
34. Story, B. J.; Koros, W. *J Polym Sci: Polym Phys Ed* 1927, 1989, 27.
35. Ghosal, K.; Chern, R. T. *J Membr Sci* 1992, 72, 91.
36. LeRoux, J. D.; Paul, D. R.; Kampa, J.; Lagow, R. J. *J Membr Sci* 1994, 90, 21.
37. Polotskaya, G. A.; Agranova, S. A.; Gazdina, N. V.; Kuznetsov, Yu. P.; Nesterov, V. V. *J Appl Polym Sci* 1996, 62, 2215.
38. Chowdhury, G.; Vujosevic, R.; Matsuura, T.; Lavery, B. *J Appl Polym Sci* 2000, 77, 1137.
39. Khulbe, K. C.; Kruczek, B.; Chowdhury, G.; Gagne, S.; Matsuura, T. *J Appl Polym Sci* 1996, 59, 1151.
40. Ilinich, O. M.; Fenelonov, V. B.; Lapkin, A. A.; Okkel, L. G.; Terskikh, V. V.; Zamarev, K. I. *Micropor Mesopor Mater* 1999, 31, 97.
41. Tran, A. MSc Thesis, University of Ottawa 2003.