Available online at www.sciencedirect.com
SCIENCE DIRECT®
Polymer 44 (2003) 4533–4540
polymer
www.elsevier.com/locate/polymer

Improvement in polyetherimide gas separation membranes through the incorporation of nanostructured metal complexes

J. Kurdi, A.Y. Tremblay*

Department of Chemical Engineering, University of Ottawa, P.O. Box 450 Stn. A, 161 Louis Pasteur, Ottawa, Ont., Canada K1N 6N5

Received 7 March 2002; received in revised form 5 May 2003; accepted 7 May 2003

Abstract

Polyetherimide (PEI) gas separation membranes were tailored, at the molecular scale, by the incorporation of nanostructured metallic complexes into the PEI network. The influence of these additives on the micropore size distributions of the membranes produced and on their performance for oxygen/nitrogen separation was investigated. Changing the metal within the same ligand had a significant influence on the microporosity and gas separation performance of these membranes. Magnesium (II) phathalocyanine (MgPc) in PEI membranes was found to be an excellent additive to increase membrane performance for air separation. The performance of these membranes increases with increasing additive concentrations. Membranes with this additive also exhibit an improved stability as determined through the annealing process. Annealing these membranes caused a slight decrease in their gas permeance and total micropore volume but a significant increase in their gas selectivity. The results show that the properties of the nanophase additive and nanophase-polymer interactions play a pivotal role in stabilizing and determining membrane performance for air separation.

Keywords: Polymer engineering; Microporosity; Gas separation membranes

1. Introduction

Molecular engineering and molecular architecturing of novel materials having superior characteristics and properties are rapidly growing technologies that will be pervasive in all fields of science and engineering such as machines at molecular levels [1], electronic and optical devices [2,3], chemistry [4], supramolecular polymers [5,6], polymer nanocomposites [7], thin film and coatings [8], metal-containing polymers [9,10], high surface area materials including molecular sieves and catalysts [11–14]. The development of tailor-made materials is based on a common physico-chemical fundamental that recognizes how materials are assembled starting from the atomic scale, to the nanoscale and ending at the bulk scale [1]. Common fabrication processes to produce these nanomaterials were reviewed in the literature [11,12,15,16]. One of these processes involves the incorporation of a second organic or inorganic nanophase into polymeric materials. This technique was found to be successful in the production of novel superior plastics [17]. For example, it is estimated that using polymer nanocomposites by US vehicle manufacturers would save 1.5 billion liters of gasoline over one year reducing the emission of carbon dioxide by more than 4.5 billion kilograms [17]. In another application such as gas separations, the incorporation of transition metal complexes such as Schiff base oxygen carriers [18–20] into polymeric membranes gave a significant improvement in performance. For example, the permeability and selectivity of oxygen over nitrogen were increased by increasing the Co(II) content in poly(vinyl alcohol)/poly(*N*-salicylidene allyl amine) blend membranes [21] or in Cobalt (II)–neutralized sulfonated Ethylene–Propene–Diene terpolymer (EPDM) ionomer membranes [22,23]. In other studies, a trade off between permeability and selectivity was observed. Increasing the content of the oxygen carrier (Cosalen) in polycarbonate films leads to a decrease in the permeability of oxygen and nitrogen gases but an increase in the selectivity of oxygen over nitrogen. These results were also obtained with the addition of Cosalen to polyurethane [24]. It was also reported that the conditions of the permeation test such as upstream pressure and temperature affect membrane performance [22,23,25,26]. The above results

* Corresponding author. Tel.: +1-613-562-5920; fax: +1-613-562-5172.
E-mail address: tremblay@uottawa.ca (A.Y. Tremblay).

0032-3861/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0032-3861(03)00405-1

show different membrane performance for different systems. There is no general rule for the results obtained from the incorporation of transition metal complexes into polymers. However, many studies attribute these results to a structural diffusion factor using X-ray diffraction measurements [27] or diffusion models [25]. The correlation between the micropore size distribution and the performance of gas separation membranes was not investigated. For this reason and due to the importance of this correlation [7], we have selected five different metal complex additives classified into two groups. The first group includes metal (II) phthalocyanines of three different metals: Cobalt (CoPc), Iron (FePc) and Magnesium (MgPc) and the second group includes 1,1′-bis (di-I-propylphosphino) ferrocene (1,5-cyclooctadiene) Rhodium (I) tetrafluoroborate, (Rh-DiPFc) and Cobalt (II) 2,3-naphthalocyanine (CoNPc). These additives were incorporated into polyetherimide/*N*-methylpyrrolidinone solutions to prepare asymmetric flat membranes. For the purpose of comparison, the additives CoPc and CoNPc have been selected from our previous work as membranes produced using this additive shown the best air separation performance among other Cobalt complexes [28]. The micropore size distributions of these membranes were determined using nitrogen adsorption and the Horvath–Kawazoe slit model. The membrane performance for separation of oxygen from air was also tested. The correlation between the performance of gas separation membrane and its micropore size distribution for each of the above five additives was discussed. The stability and durability of membrane performance for air separation were examined for membranes containing CoPc and MgPc additives through an annealing process and performance test.

2. Experimental

2.1. Materials

Polyetherimide (PEI, Ultem® 1000) was obtained from General Electric Plastics, USA, in pellet form and was dried in a vacuum oven (725 mm Hg vacuum) at 140 °C for 24 h. Methyl alcohol (BDH, Microscopic grade), hexanes (BDH, reagent grade), and isopropyl alcohol (OmniSolv®, EM Science, water 0.05% max) were supplied by VWR CANLAB (QC, Canada). Anhydrous 1-methyl-2-pyrrolidinone (Aldrich, 99.5%, reagent grade, water $<0.005\%$) was supplied from Sigma-Aldrich Canada LTD, ON., Canada. Five different metal complexes shown in Table 1 were supplied from Sigma-Aldrich Canada LTD, ON., Canada except Rh-DiPFc was supplied from Strem Chemicals, INC., MA, USA. These metal complexes and anhydrous *N*-methylpyrrolidinone were used as supplied but under dried nitrogen atmosphere. All other solvents were used without purification. Medical air (PRAXAIR, Ottawa, ON., CA) was used to test the membrane for oxygen separation. Ultra high purity gases, nitrogen and helium (PRAXAIR, Ottawa, ON., CA) were used in the nitrogen adsorption measurements. All gases were used as supplied without any further purification.

2.2. Membrane preparation

Casting solutions were prepared using polyetherimide (PEI), anhydrous *N*-methyl-2-pyrrolidinone (NMP) and one of the additives shown in Table 1. The preparation was under a nitrogen atmosphere using a glove bag placed in a fume hood. We kept the ratio of PEI to the total weight of solution at 23 percent by weight. The ratio of additive to PEI was 1, 3, 10 and 15% (weight additive/weight PEI). One PEI membrane was prepared without additive served as a base case.

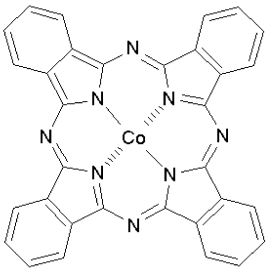
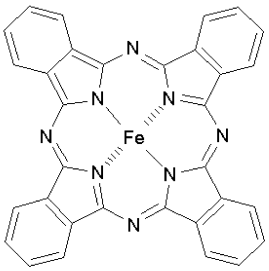
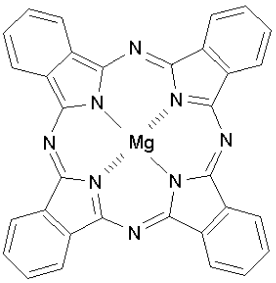
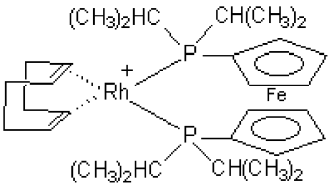
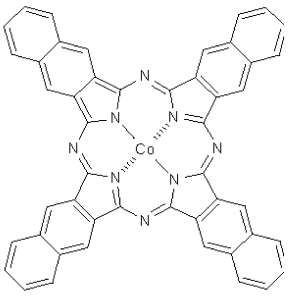
The same preparation procedures were followed for all samples. All mixing and casting were carried out under a nitrogen atmosphere in order to not expose materials to the atmospheric air. A particular additive was first dissolved in NMP using a Nalgene polypropylene jar having a screw cap. Dissolving was done by rolling the sealed jar at room temperature for many days until a clear solution was obtained. The polymer was then added to the dissolved additive/NPM solution under nitrogen atmosphere, sealed and rolled again for many days until a clear homogenous casting solution was obtained.

The solution was cast onto a clean glass plate at room temperature using a knife gap of 250 μm. The film was quickly immersed for 5 min in a coagulation bath containing isopropyl alcohol. The coagulated film was moved to a methanol bath where it was kept for 16 h. Finally the film was immersed in a bath of hexanes for two days. The membrane was dried in air for three days. We cut three circular coupons of 65 mm diameter from each membrane film. These coupons were used in the permeation tests and the rest of the film was cut into small strips in order to be used in the nitrogen adsorption measurements.

2.3. Determination of the micropore size distribution

A standard procedure was used to determine the micropore size distribution. An automated volumetric porosity analyzer ASAP 2000M produced by Micromeritics (GA, USA) was used to measure the nitrogen adsorption isotherm. Approximately 1 g of small strips of each membrane sample were weighed to $+/-0.0005$ g. The small strips were placed inside a sample tube and degassed at 0.002 ± 0.0005 mm Hg and temperature at 40 °C for 12 h. Nitrogen adsorption was performed at 77 K using a liquid nitrogen bath. Ultra high purity gases, nitrogen and helium were used for adsorption and purging the sample. The Horvath–Kawazoe slit model was used to calculate the micorpore size distribution from the measured isotherm data. The method and the determination of the parameters used in Horvath–Kawazoe model for nitrogen and PEI were explained elsewhere [29].

Table 1
Metal complexes used in this study

Group	Abbreviations	Chelate complex name	Chemical structure
1	CoPc	Catalog No. 30,769-6, Cobalt (II) phthalocyanine	
	FePc	Catalog No. 37,954-9, Iron (II) phthalocyanine	
	MgPc	Catalog No. 40,273-7, Magnesium (II) phthalocyanine	
2	Rh-DiPFc	Catalog No. 45-0205, 1,1′-Bis(di-I-propylphosphino) ferrocene (1, 5-cyclooctadiene)	
	Co(2,3NPc), CoNPc	Catalog No. 38,192-6, Cobalt (II) 2,3-naphthalocyanine	

All additives in Table 1 were supplied from Aldrich, Sigma-Aldrich Canada LTD, Ont., Canada, except the additive Rh-DiPFc was supplied from Strem Chemicals, Inc., MA, USA.

2.4. Permeation test

The same permeation test was used for all samples. A test cell having an effective cross-flow section of 20 cm^2 was used. The upstream side of the cell was pressurized with medical grade air at 12.8 bar gauge and the retentate flow was set at 400 ml (STP)/min. The permeate was discharged to the atmosphere. A soap bubble flowmeter was used to measure the volumetric permeate gas flow. An automatic gas sampling valve having a sample volume of 0.5 cm^3 was connected in line with the permeate. The valve was connected to a Gas Chromatograph to measure the oxygen concentration in the permeate gas stream. The oxygen concentration was corrected for the difference in the thermal

conductivity between oxygen and nitrogen using the following equation [30]:

$$y_{\text{corr}} = \frac{\left(\frac{y}{40}\right) \times 100}{\left(\frac{y}{40}\right) + \left(\frac{100 - y}{42}\right)} \quad (1)$$

where y is the percentage of oxygen concentration in the permeate stream as calculated by gas chromatography and y_{corr} is the corrected value. The oxygen permeance and nitrogen permeance were determined as explained elsewhere [31]. The total gas permeance is the sum of permeances of oxygen and nitrogen. The true selectivity was considered to be the ratio of oxygen permeance to nitrogen permeance.

3. Results and discussion

3.1. Influence of additives on the microporosity of PEI membranes

The micropore size distributions of the membranes prepared using the additives shown in Table 1 and one membrane without additive were shown in Fig. 1 for group 1 additives and Fig. 2 for group 2 additives. It is clear that all additives increased the total differential micropore volume of the polymer. This can be attributed to an increase in the connectivity and accessibility among the micropores of the polymeric network of PEI and the possible creation of new micropores at the interface between the dispersed nanoparticles and the polymer network.

In the first group, Fig. 1, changing the metal (II) in the phthalocyanine complexes leads to a change in the micropore size distribution within the membranes. This

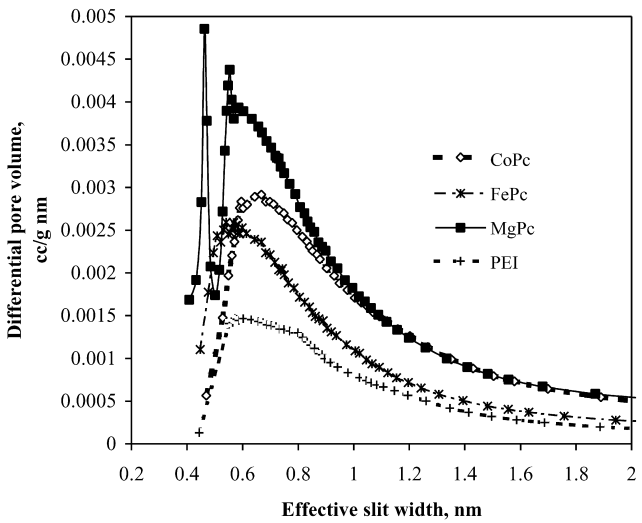


Fig. 1. Micropore size distribution for PEI membranes cast from solutions containing group 1 additives shown in Table 1 and one without additive. Differential pore volume (cm^3/g nm) vs. effective slit width in nm. Casting solutions contain 3% additive/PEI by weight.

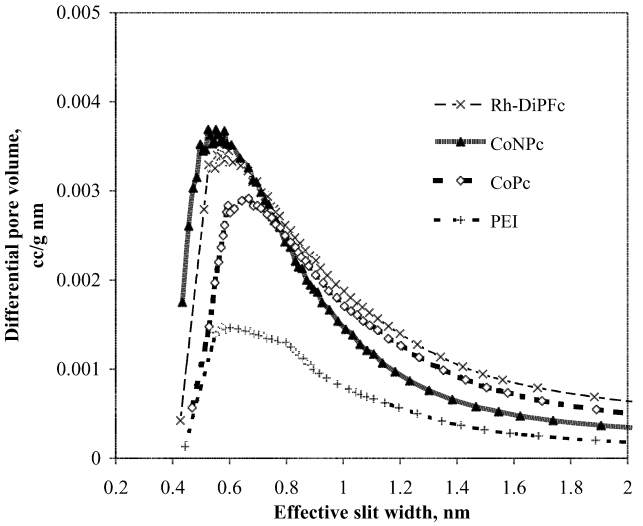


Fig. 2. Micropore size distribution for PEI membranes cast from solutions containing group 2 additives shown in Table 1 and one without additive. Differential pore volume (cm^3/g nm) vs. effective slit width in nm. CoPc additive was included for comparison purpose. Casting solutions contain 3% additive/PEI by weight.

was attributed to different properties and characteristics of the dispersed nanoparticles and the affinity between each of these complexes and PEI chains. The smallest mode in the distribution and the greatest micropore volume was for the membrane containing the MgPc additive. This indicates that the complex has a higher affinity to PEI and enhances pore connectivity. MgPc is not a planar molecule but the magnesium atom is placed outside the plane over the center of the macrocyclic moiety. It has a shuttlecock shape as explained by McKeown [32]. This leads to an enhancement in the $\pi-\pi$ intermolecular interactions operating through the Mg atom [33] forming a nanocrystallic structure [33,34]. The alkaline property of Mg in phthalocyanines was reported to form complexes having an improved solubility in aromatic polar solvents [32]. Therefore, a better dispersion and the smaller nanophases of MgPc expected in NMP lead to a greater micropore volume compared to that obtained using other additives in group 1.

Magnesium (II) is a hard Lewis acid while Co(II) and Fe(II) are at the borderline between soft and hard Lewis acids [35]. Therefore, MgPc is a harder base than CoPc and FePc that leads to a higher affinity of this complex to a hard base solvent such as methanol. For this reason, the presence of the double peak in the micropore size distribution of the membrane containing MgPc was attributed to the presence of methanol in its structure. This was confirmed in our lab as the double peak changed to a single peak upon further drying. The double peak was not observed when methanol was not used in membrane preparation.

According to the hard–soft acid–base principle [35] hard acids prefer to coordinate to hard bases, and soft acids prefer to coordinate to soft bases. The affinity of the hard base, MgPc to PEI is greater than for CoPc and FePc because the imide group is a hard base [36]. This higher

affinity leads to a smaller mode in the micropore size distribution for membranes containing MgPc.

Membranes containing FePc have a smaller mode in their micropore size distribution compared to membranes containing CoPc because of the higher affinity of the former to the imide groups in PEI. This can be explained through the lower electron affinity of FePc than CoPc. Fe has a greater positive charge than Co [37] and as a result is more attracted by the imide group in PEI.

In the second group, Fig. 2, replacing the phthalocyanine in Cobalt (II) complex by naphthalocyanine i.e. adding four aromatic rings leads to an increase in the micropore volume and a decrease in the mode and skewness of the micropore size distribution. This can be attributed to an increase in the aromatic (nucleophillic) environment that increases the $\pi-\pi$ stacking interactions leading to microporous nanoscale structures [38]. This also tends to increase the affinity of the CoNPc to PEI chains as well as to the NMP solvent. The cationic Rhodium (1) bearing the air stable and crystalline diphosphine 1,1′-bis-(diisopropylphosphino) Ferrocene (Rh-DiPFc) has the same micropore volume as a membrane with CoNPc but a very small shift to a larger size especially for larger micropore sizes. The micropore size distribution of a membrane containing CoPc was added to Fig. 2 for the purpose of comparison.

3.1.1. Effects of MgPc concentration

For most incorporated metallic complexes such as CoPc into PEI, increasing the additive concentration leads to an increase in the total micropore volume but no change in the shape of the micropore distribution as previously discussed by Kurdi and Tremblay [28]. However, this is not the case with the incorporation of MgPc. The micropore size distributions of membranes containing different concentrations of this additive were plotted as shown in Fig. 3. The possibility of forming a double peak due to the presence of methanol is higher for lower concentrations as found for membranes containing 1 and 3% additive. This means that the higher concentrations of 10 and 15% additive formed different nanoparticles that hosted less methanol. With an increase in the concentration of the additive, the mode in the micropore size distribution remained constant while the volume of the micropore of pore size between 0.6 and 2 nm decreased. In this pore size range, membranes containing 10% additives had the lowest micropore volume. This was even lower than the PEI micropore volume in the range of 0.9–2 nm. This indicates that incorporating MgPc into PEI has a great benefit in reducing the number of larger micropores that are responsible for decreasing the selectivity of gas separation membranes. The greater affinity of MgPc is responsible for the tighter structure and narrow pore size distribution for membranes containing higher concentration of 10 and 15% of magnesium phthalocyanine.

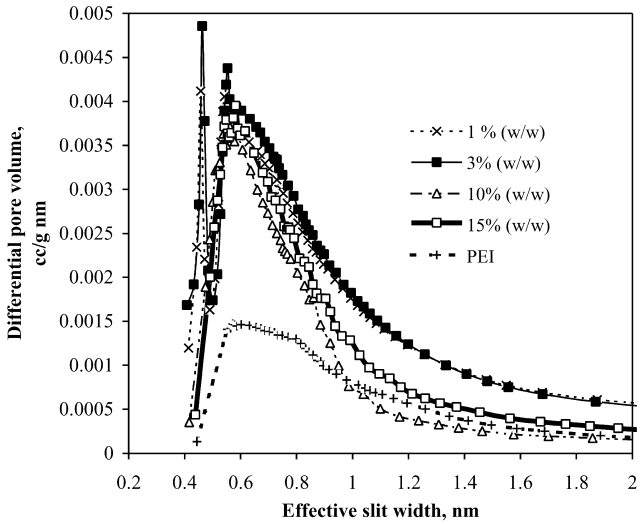


Fig. 3. Micropore size distribution for PEI membranes cast from solutions containing MgPc additive at concentrations 1, 3, 10 and 15% (w/w), and one without additives. Differential pore volume (cm^3/g nm) vs. effective slit width in nm.

3.1.2. Effects of drying and annealing of membranes containing MgPc or CoNPc

PEI membranes containing 3% of MgPc or CoNPc were dried and annealed in a vacuum oven under 725 mm Hg vacuum pressure and temperature of 90 °C for 48 h. The micropore size distributions of these membranes before and after drying were shown in Fig. 4 for MgPc and in Fig. 5 for CoNPc additive. It is clear that drying and annealing lead to decrease in the membrane micropore volume for both additives. The first peak in the micropore size distribution of the membrane containing MgPc disappeared due to the removal of the residual methanol as previously discussed in

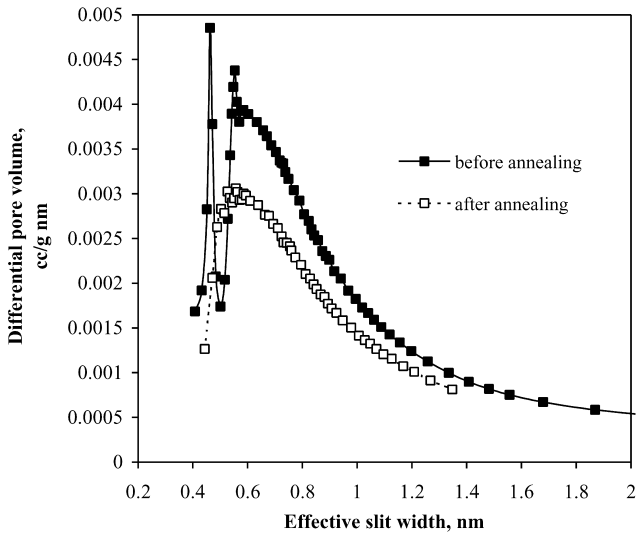


Fig. 4. Micropore size distribution for PEI membranes cast from solutions containing MgPc additive at concentration 3% (w/w), before and after annealing process in oven under 725 mm Hg vacuum pressure and temperature of 90 °C for 48 h. Differential pore volume (cm^3/g nm) vs. effective slit width in nm.

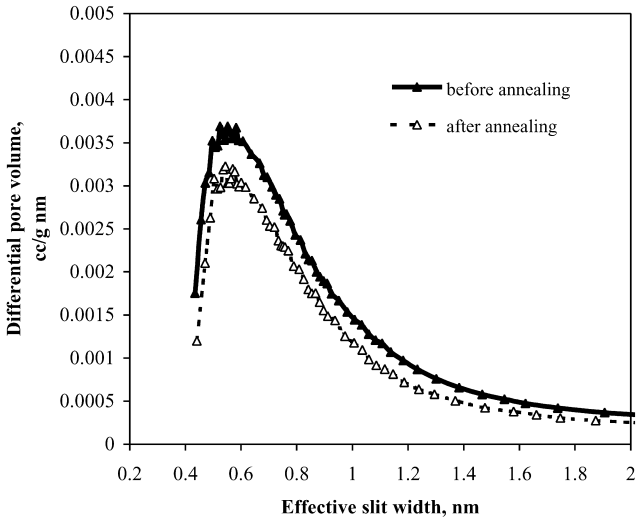


Fig. 5. Micropore size distribution for PEI membranes cast from solutions containing CoNPc additive at concentration 3% (w/w), before and after annealing process in oven under 725 mm Hg vacuum pressure and temperature of 90 °C for 48 h. Differential pore volume (cm^3/g nm) vs. effective slit width in nm.

this work. The decrease in the micropore volume after drying and annealing is attributed to the shrinkage of the composite membranes as well as removal of solvents.

3.2. Influence of additives on the O_2/N_2 separation of PEI membranes

The gas permeances of membranes containing additives shown in Table 1, group 1 were plotted versus the additive weight ratio as shown in Fig. 6. The membranes containing the additives CoPc and MgPc were first tested for permeation. They were then dried and annealed in a vacuum oven under 725 mm Hg vacuum pressure and temperature of 90 °C for 48 h and retested. The results of both annealed membranes were shown in Fig. 6. It is clear that the permeance of the non-annealed membranes containing CoPc and FePc additives increased with increasing additive concentration. The permeance of non-annealed MgPc membranes decreased slightly with increasing additive concentration. These results are consistent with the relatively constant microporosity shown in Fig. 3. The slight decrease in permeance was attributed to a small decrease in the micropore volume between 0.6 and 2 nm. Comparing membranes containing MgPc before and after annealing, the decrease in the permeance is lower at higher additive concentrations in the range 0.9–2 nm. This indicates that the increase in the concentration of the additive leads to an increase in the stability of the PEI membrane. It was reported that the MgPc is the most effective additive among other metal phthalocyanines to inhibit the thermal degradation and increase the stability of polymers such as polyesters, polyamide and aromatic heterocyclic polymers [39]. The results of our work are consistent with previous studies found in the literature. Membranes containing CoPc exhibit a larger decrease in the permeance especially at higher concentration that may be attributed to different shrinkage between PEI and the CoPc nanoparticles. Larger variations in the data and the higher permeance for membranes containing FePc are attributed to the disorder and impurities that influence the structure of FePc nanoparticles [40].

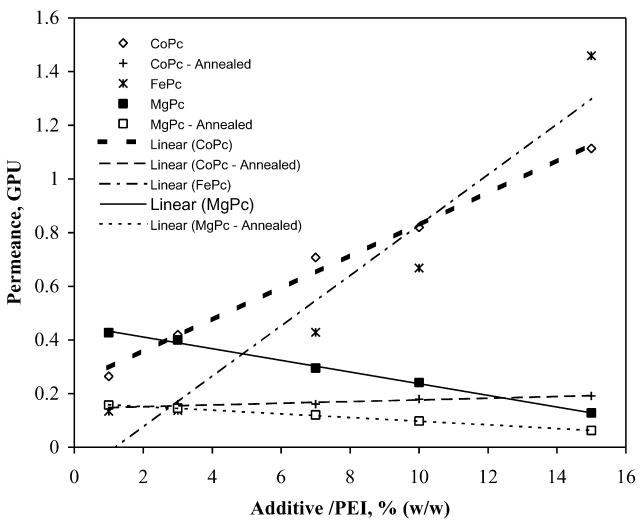


Fig. 6. Plot of the total permeance, GPU vs. the percentage of the (additive/PEI) ratio in the casting solution for air separation by membranes containing group 1 additives shown in Table 1. Permeation test was included membranes containing CoPc and MgPc which were annealed in an oven under 725 mm Hg vacuum pressure and temperature of 90 °C for 48 h.

The permeances of membranes containing group 2 additives versus the concentration of these additives were shown in Fig. 7. Although the membrane containing the additive Rh-DiPFc has a similar micropore size distribution to membranes containing CoNPc. It has a higher permeance that can be attributed to the bulky structure of this additive compared to the planar structure of the CoNPc. The

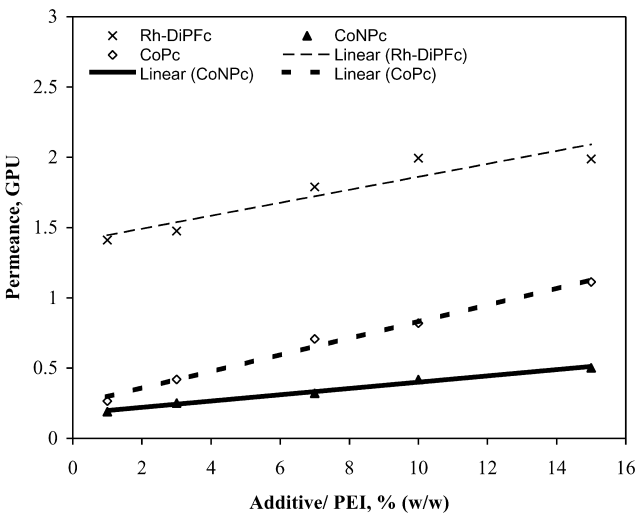


Fig. 7. Plot of the total permeance, GPU vs. the percentage of the (additive/PEI) ratio in the casting solution for air separation by membranes containing group 2 additives shown in Table 1.

electrophillic property known from the reducing activity of Rh-DiPFc for aldehydes and ketones [41] leads to a lower affinity to imide groups in PEI. The bulky structure inhibits aggregating the Rh-DiPFc and enhances its solubility. Therefore, smaller nanophases and less affinity to PEI lead to an increase in micropore volume at different sizes as shown in Fig. 2.

The selectivity of membranes containing group 1 additives was also plotted versus additive concentration as shown in Fig. 8. The selectivity of annealed membranes containing CoPc and MgPc were also included. The selecitivity trade off with permeance is clear for all membranes except the ones containing the MgPc additive. The selectivity of membranes containing MgPc increased with increasing additive concentration. An increase in the MgPc concentration from 1 to 15% (w/w) leads to an increase in selectivity from 2.28 to 5.39 before annealing and from 2.67 to 5.46 after annealing. A slight increase in the selectivity upon membrane annealing is observed. However, the annealing of membranes containing CoPc leads to a decrease in the selectivity especially at low additive concentrations.

The selectivity of membranes containing group 2 additives decreases with increasing additive concentrations following the trade off behavior as shown in Fig. 9. Membranes containing Rh-DiPFc had macroporous defects in their skin layer indicated by their inability to separate oxygen from air. The presence of nonselective pores larger than 0.8 nm can be observed in Fig. 2.

To study the performance of the above membranes for oxygen/nitrogen separation, the selectivity versus the air permeance was plotted for membranes containing group 1 and 2 additives as shown in Fig. 10. Membranes containing Rh-DiPFc were excluded because they were not selective to oxygen. It is clear from Fig. 10 that the highest performance before annealing is obtained for the membrane containing (CoPc) when the permeance is greater than 0.36 GPU but at lower than this permeance the membrane containing CoNPc had the best performance.

Comparing the annealed membranes containing MgPc with the annealed ones containing CoPc as shown in Fig. 10, it is clear that membranes containing MgPc maintained a high performance for oxygen separation from air especially at higher additive concentrations. The performance is highly improved with an increase in the content of MgPc. The MgPc additive was the only one to provide an increase in selectivity when its concentration was increased. All other

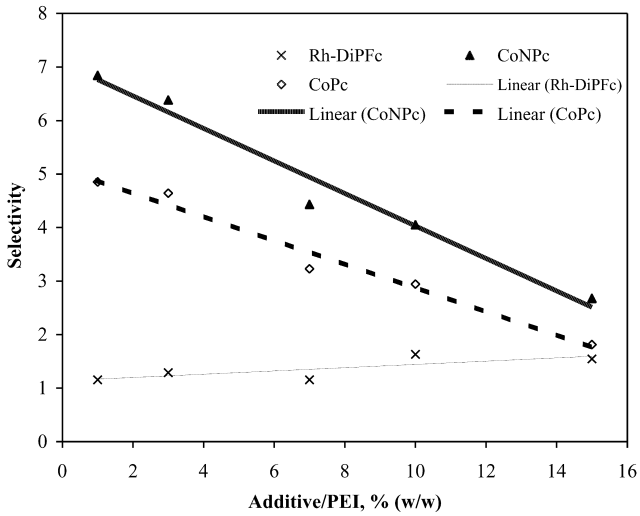


Fig. 9. Plot of O_2/N_2 selectivity vs. the percentage of the (additive/PEI) ratio in the casting solution for air separation by membranes containing group 2 additives shown in Table 1. Additive CoPc was included for comparison purpose.

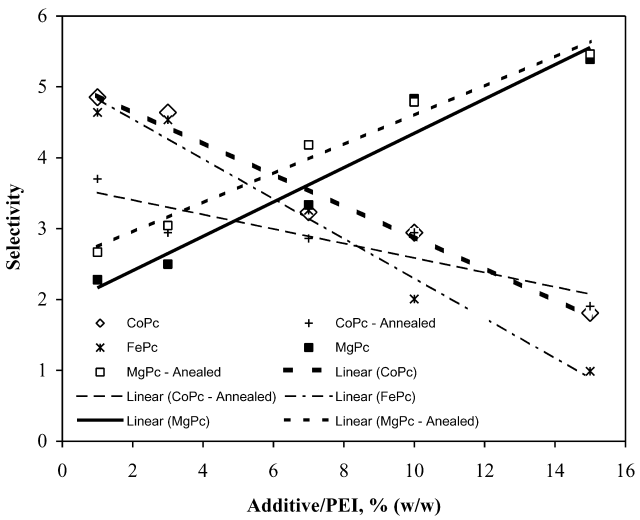


Fig. 8. Plot of O_2/N_2 selectivity vs. the percentage of the (additive/PEI) ratio in the casting solution for air separation by membranes containing group 1 additives shown in Table 1. Permeation test was included membranes containing CoPc and MgPc which were annealed in an oven under 725 mm Hg vacuum pressure and temperature of 90 °C for 48 h.

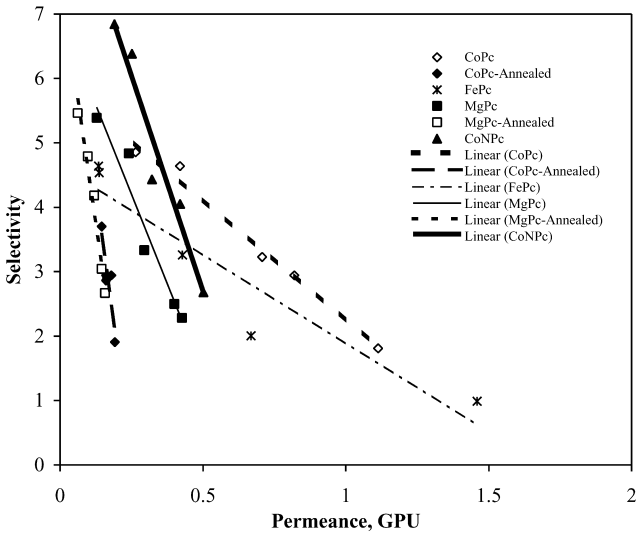


Fig. 10. Performance plot of O_2/N_2 selectivity vs. the total permeance, GPU for air separation by membranes containing additives shown in Table 1. Membranes containing Rh-DiPFc was excluded as it is not selective to O_2/N_2 separation.

additives showed a decrease in selectivity with an increase in additive concentration as shown in Fig. 8 and our previous work [28].

At higher MgPc concentrations, annealing had the least effect on permeance and selectivity compared to CoPc. The MgPc additive tends to increase the stability of the membrane as the permeance was maintained after the annealing process as shown in Fig. 6. This result agrees well with the reported ability of MgPc to inhibit the thermal degradation and increase the thermal stability of polymers [39].

4. Conclusions

Incorporating of metallic complexes as additives into PEI was found to be a useful method to structure this polymeric material at the molecular scale. The micropore volume increased significantly on the inclusion of planar additives. It was found that PEI membranes containing a bulky additive such as (Rh-DiPFc) could not separate oxygen from air due to the presence of macroporous defects in the skin layer of the membrane. CoPc forms high performance gas separation membranes. However, its performance was reduced with the annealing process. On the other hand, MgPc was found to be the best additive as it forms a membrane with a narrow micropore size distribution that improved by increasing the additive concentration. The stability of the composite material was also significantly improved as the annealing process tends to increase membrane selectivity without a decrease in the micropore volume and with only a slight decrease in membrane permeance. This result was attributed to the high affinity of MgPc to PEI as well as for the solvent used. This explains why increasing the content of MgPc leads to a finer membrane structure and a significant improvement in membrane performance. It was concluded that MgPc is a promising additive that can be used to improve the stability and the performance of PEI gas separation membranes.

Acknowledgements

The authors wish to thank the Natural Science and Engineering Research Council of Canada, Ontario Graduate Scholarship and the University of Ottawa excellence scholarship programs for their financial support.

References

[1] Balzani V, Credi A, Raymo FM, Stoddart JF. Angew Chem Int Ed 2000;39:3348–91.
[2] Pease AR, Jeppesen JO, Stoddart JF, Luo Y, Collier CP, Heath JR. Acc Chem Res 2001;34:433–44.
[3] Timp G, editor. Nanotechnology. New York: Springer; 1999.
[4] Klabunde KJ, editor. Nanoscale materials in chemistry. New York: Wiley; 2001.
[5] Ciferri A, editor. Supramolecular polymers. New York: Marcel Dekker; 2000.
[6] Schubert US, Eschbaumer C. Angew Chem Int Ed 2002;41: 2892–926.
[7] Krishnamoorti R, Vaia RA, editors. Polymer nanocomposites: synthesis, characterization and modeling. Washington: American Chemical Society; 2002.
[8] Chow G-M, Ovid'ko IA, Tsakalakos T, editors. Nanostructured films and coatings. Dordrecht: Kluwer Academic Publishers; 2000.
[9] Chen L, Xu H, Yang C-Z. Polym Adv Technol 1996;8:335–8.
[10] Sheats JE, Carraher Jr CE, Pittman Jr CU. Metal-containing polymeric systems. New York: Plenum Press; 1985.
[11] Ying JY, editor. Nanostructured materials. San Diego: Academic Press; 2001.
[12] Pinnavaia TJ, Thorpe MF, editors. Access in nanoporous materials. New York: Plenum Press; 1995.
[13] Tanev PT, Chibwe M, Pinnavaia TJ. Titanium-containing mesoporous molecular sieves for catalytic oxidation of aromatic compounds. Nature 1994;368:321–3.
[14] Davis ME. Nature 1993;364:391–3.
[15] Hu EL, Shaw DT. Synthesis and assembly, Chapter 2. In: WTEC Panel Report on: Nanostructure Science and Technology, R & D status and trends in nanoparticles, nanostructured materials, and nanodevices, Loyola College Baltimore, MD 21210, USA; September 1999.
[16] Edelstein AS, Cammarata RC, editors. Nanomaterials: synthesis, properties and applications. Bristol: Institute of Physics Publishing; 1998.
[17] Vaia RA. AMPTIAC Newslett 2002;6(1):17–24.
[18] Li GQ, Govind R. Ind Engng Chem Res 1994;33:755–83.
[19] Martell AE, Sawyer DT. Oxygen complexes and oxygen activation by transition metals. New York: Plenum Press; 1988.
[20] Niederhoffer EC, Timmons JH, Martell AE. Chem Rev 1984;84: 137–203.
[21] Choi MJ, Park CK, Lee YM. J Appl Polym Sci 1995;58:2373–9.
[22] Zhang Z, Lin S. J Appl Polym Sci 1999;74:1071–7.
[23] Zhang Z, Lin S. Macromol Rapid Commun 1995;16:927–33.
[24] Chen SH, Yu KC, Houng SL, Lai JY. J Membr Sci 2000;173(1): 99–106.
[25] Nishide H, Suzuki T, Nakagawa R, Itakura K, Tsuchida E. J Phys Chem 1995;99:12312–7.
[26] Nishide H, Suzuki T, Nakagawa R, Tsuchida E. J Am Chem Soc 1994; 116:4503–4.
[27] Chen SH, Lai JY. J Appl Polym Sci 1996;59:1129–35.
[28] Kurdi J, Tremblay AY. The influence of cobalt complexes on the microporosity and performance of polyetherimide gas separation membranes. Submitted for publication.
[29] Kurdi J, Tremblay AY. Desalination 2002;148:341–6.
[30] Academy of China, Physics Institute of Dalian, Gas Chromatography, China: Science Press Inc. of China; 1972.
[31] Kurdi J, Tremblay AY. J Appl Polym Sci 1999;73(8):1471–82.
[32] McKeown NB. Phthalocyanine materials: synthesis, structure and function. Cambridge: Cambridge University Press; 1998.
[33] Mizuguchi J. J Phys Chem 2001;A105:10719–22.
[34] Breeze A, Salomon A, Ginley D, Gregg B. Photovoltaic cells based on conducting polymers and perylene diimides, NCPV Program Review Meeting, Lakewood, CO; 14–17 October 2001.
[35] Pearson RG. Chemical hardness. Weinheim: Wiley-VCH; 1997.
[36] Benrabah D, Arnaud R, Sanchez J-Y. Electrochim Acta 1995;40(13–14):2437–43.
[37] Liao M-S, Scheinder S. J Comput Chem 2002;23:1391–403.
[38] Inabe T. J Porphyrins Phthalocyanines 2001;5:3–12.
[39] Moser FH, Thomas AL, The phthaolcyanines, vol. 1. Boca Raton: CRC Press; 1983.
[40] Evangelisti M, Bartolomé J, de Jongh LJ, Filoti G. Phys Rev 2002; B66:144410–20.