

Membranes Based on Poly(styrene-*N*-phenylmaleimide)/Poly(2,6-dimethyl-1,4-phenylene oxide) Blends

J. LOKAJ,* A. SIKORA, Z. PIENKA, and M. BLEHA

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic,
162 06 Prague 6, Czech Republic

SYNOPSIS

Blend membranes were prepared by casting chloroform solutions of mixtures of styrene-*N*-phenylmaleimide copolymer containing ca. 10 mol % imide units with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), and their phase behavior was evaluated. At a content of 20% PPO, the membranes were homogeneous; those having 40 or more % PPO exhibited phase separation. Membranes made of the parent polymers and their blends were tested in the pervaporation of aqueous ethanol solutions; permeabilities to oxygen, nitrogen, and carbon dioxide were also determined. The pervaporation characteristics and gas transport properties are discussed considering the interactions of polymer chains and the phase structure of the membranes. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The polymer blending is an important means of obtaining useful new materials for various applications, including membrane operations.¹⁻⁶ Compared to the original, compatible polymers, mixtures of these polymers often have better physical properties, which can be affected by the content and composition of the polymer components.

This study deals with binary mixtures of the styrene (S) copolymer with *N*-phenylmaleimide (PMI) blended with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). The copolymer contained approx. 10 mol % PMI units. It could be expected that, when the copolymer has a high content of styrene units, interaction will occur between the polystyrene segments and PPO, facilitating the miscibility of the components.^{7,8} Both polymers are used as membrane materials with preferential permeability to water in the pervaporation separation of aqueous ethanol solutions.^{9,10} In addition, PPO is characterized by excellent film-forming ability, mechanical and chemical resistance, and thermostability, and has also been found useful for the separation of gases.¹¹ This

work was carried out in order to evaluate the phase behavior and membrane properties of material consisting of these polymer components. Blend membranes were prepared by casting chloroform solutions of a mixture of the two polymers; the pervaporation characteristics of these membranes were determined in the separation of various concentrations of aqueous alcohol. We also studied the transport of oxygen, nitrogen, and carbon dioxide through these membranes.

EXPERIMENTAL

Materials

N-Phenylmaleimide (PMI) (m.p. 89°C) was obtained by cyclodehydration of *N*-phenylmaleamic acid (m.p. 201°C) prepared by the addition of aniline to maleic anhydride.¹² Styrene (b.p. 36°C/1.56 kPa) and 2,2'-azobis(isobutyronitrile) (AIBN) (m.p. 105°C) were purified by the procedure described in an earlier work.¹³ The copolymer of styrene with *N*-phenylmaleimide [poly(S-PMI)] was synthesized by radical polymerization at 50°C initiated by AIBN.¹⁴ The content of PMI units was determined by elemental analysis. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was a commercial product (Spolana, Neratovice, Czech Republic). The number-average molecular weights \bar{M}_n , determined by

* To whom correspondence should be addressed.

the GPC method in toluene using polystyrene standards, were 169, 460, and 37,800 for the copolymer and PPO, respectively. Aqueous ethanol solutions were prepared from EtOH for UV spectroscopy and redistilled water.

Membrane Preparation

Membranes were obtained by pouring a chloroform solution (0.1 g cm^{-3}) of poly(S-PMI), PPO, or mixtures thereof onto a glass plate to form a layer 0.35 mm thick. After evaporation of the solvent at room temperature, a membrane with a thickness of about $30 \mu\text{m}$ was released by immersion in water.

Measurements

Sorption

The dry membrane (about 0.3 g) was weighed and left in an EtOH-H₂O mixture at room temperature for 24 h; then the liquid was removed from the surface of the swollen membrane using filter paper and the membrane was again weighed. The degree of swelling (DS; %) was found from eq. (1):

$$\text{DS} = (\text{weight of swollen membrane} / \text{weight of dry membrane} - 1) \times 100 \quad (1)$$

Membrane Densities

The membrane densities were measured using Mohr-Westfal scales (by the floating method). The dry membrane (about 40 mg) was weighed first in the air and then in dodecane at 23°C. The weight difference in the two measurements divided by the density of dodecane (0.745 g cm^{-3}) gives the sample volume. The membrane density was calculated from its weight in the air and the determined volume.

Pervaporation

The pervaporation process was studied by the procedure described previously.¹⁴ Prior to testing, the membranes were left for 15 h in the EtOH solution to be separated. They were characterized by their permeation fluxes (in $\text{g m}^{-2} \text{ h}^{-1}$) and separation factors $\alpha_{\text{H}_2\text{O}}$, defined by eq. (2):

$$\alpha_{\text{H}_2\text{O}} = (w^{\text{P}}/w^{\text{F}})_{\text{H}_2\text{O}} / (w^{\text{P}}/w^{\text{F}})_{\text{EtOH}} \quad (2)$$

where w is the weight fraction of H₂O and EtOH in the permeate (P) and in the feed (F). The permeate flux of various membranes was related to a thickness of $30 \mu\text{m}$ on the basis of the assumption of propor-

tionality between the flux and the reciprocal value of the membrane thickness.

Gas Transport

The transport properties of the membranes were studied using a laboratory instrument fitted with a katharometer (hot wire detector).¹⁵ The permeabilities P were determined from the determined amounts of O₂, N₂, or CO₂ after passage of the individual gases through a membrane placed in the measuring cell at 100 kPa and 25°C. Average experimental permeability values were tabulated on the basis of repeated measurements. Selectivities $\alpha_{\text{O}_2/\text{N}_2}$ and $\alpha_{\text{CO}_2/\text{N}_2}$ were expressed in terms of the ratio of the corresponding permeabilities $P_{\text{O}_2}/P_{\text{N}_2}$ and $P_{\text{CO}_2}/P_{\text{N}_2}$ respectively.

Thermal Analysis

Differential scanning calorimetry (DSC) of the membrane materials was carried out on a Perkin-Elmer DSC-2 calorimeter. The temperature and output scales of the calorimeter were calibrated using indium and sapphire as standards. The measurement was carried out in two scans in nitrogen atmosphere in the temperature interval 230–250 K at a heating rate of 10 K/min. The sample weight was about 5 mg. In the first scan to 550 K, the initial relaxed sample was used, which was then cooled at the same rate to the initial temperature of 230 K; this was then followed by the second scan. The glass transition temperature (T_g) and relaxation maximum (T_r) were determined from the thermogram obtained.

RESULTS AND DISCUSSION

Poly(styrene-N-phenylmaleimide)/PPO Membranes

Table I gives some of the characteristics of the membranes. The membranes of the individual polymer components were transparent, and those of the polymer mixtures were almost transparent. All the blended membranes were characterized by excellent mechanical resistance during handling. The membrane swelling in variously concentrated aqueous EtOH solutions was low and did not exceed 5%.

The density of poly(S-PMI) and of the blends was greater than that of PPO (Table I), whose chains are apparently more loosely ordered, i.e., the free volume is greater in PPO. Blend 1 was found

Table I Poly(S-PMI)/PPO Membranes

Membrane	PPO Content (wt %)	1st Scan			2nd Scan			Density (g cm ⁻³)
		T_{g1}	T_{g2}	T_r	T_{g1}	T_{g2}	T_r	
Poly(S-PMI) ^a	0	370.7	—	—	375.0	—	—	1.082
1	20	403.8	—	—	404.3	—	—	1.091
2	40	413.9	—	510.4	422.6	—	—	1.085
3	60	423.0	471.9	510.9	414.6	—	—	1.083
4	80	414.9	485.1	512.7	420.2	450.8	—	1.083
PPO ^b	100	505.2	—	519.5	483.6	—	489.5	1.069

^a $\bar{M}_n = 169,460$; 10.0 mol % incorporated PMI units.

^b $\bar{M}_n = 37,800$.

T_g and T_r are the glass transition temperature and the temperature of the relaxation maximum, respectively.

to have the greatest density, indicating the most compact structure.

The phase behavior of the blends was evaluated on the basis of data obtained in DSC measurements, carried out in two scans (Table I and Fig. 1). The first scan for PPO alone yielded a very large relaxation maximum and higher glass transition temperature T_{g1} than that given in the literature.¹⁶ A relaxation maximum and a second weak glass transition temperature T_{g2} were observed in the first scan for mixtures containing 40% or more PPO at temperatures of about 510 K and 480 K, respectively. The S-PMI copolymer and blend 1 exhibited only one glass transition. The second scan was characterized by a marked decrease in the relaxation maximum for PPO alone and its glass transition temperature was identical with the literature value. No relaxation maximum was observed in the second scan for the other samples and two glass transitions were found only for blend 4 containing 80% PPO.

The presence of the relaxation maxima and of two glass transitions in the binary polymer mixture indicates separation of the components of the mixture.^{17,18} It is thus clear from Table I that the S-PMI copolymer mixtures with 20% PPO are homogeneous, while those with more than 40% PPO have limited miscibility. While interactions between the phenyl groups of the PPO chains and the polystyrene segments of the S-PMI copolymer predominate in membrane 1, leading to compatibility of the two polymers,⁷ at higher PPO contents the repulsion between PPO molecules and the maleimide groups becomes important and prevents miscibility of the polymer components.⁸ The better solubility of PPO in the copolymer than that of the copolymer in PPO (cf. blends 1 and 4) is due to the different molecular weights of both components.

The behavior of the mixtures containing 40, 60, and 80% PPO also reflects their phase structures. The practically constant T_{g1} values of these mixtures in the second scan indicates that one phase contains about 40% PPO. The presence of the relaxation maxima and, where present, the weak T_{g2} found in the first scan for samples containing 40 and 60% PPO indicates separation of a minority phase with high PPO content. This minority phase is finely dispersed in a majority phase, rich in poly(S-PMI), which is reflected in the disappearance both of the relaxation maxima of both samples in the second

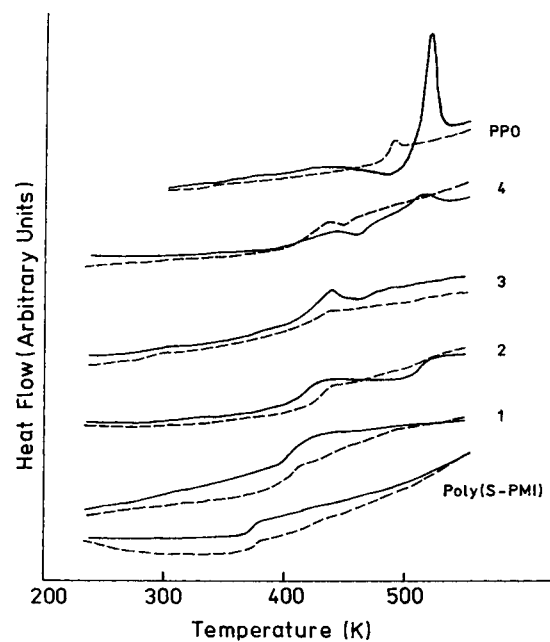


Figure 1 DSC thermograms of poly(S-PMI), PPO, and their blends 1, 2, 3, and 4 from the first (—) and second (---) scan.

scans and also of the glass transition temperature T_{g2} in samples with 60% PPO. The mixture containing 80% PPO also exhibited two glass transition temperatures in the second scan; its two-phase structure is apparently far better developed than in the mixtures with 40 and 60% PPO.

Pervaporation

The results of pervaporation of aqueous ethanol solutions through poly(S-PMI)/PPO membranes are given in Table II. The solutions to be separated contained 38.7–87.6 wt % EtOH. The pervaporation process has the following characteristics: (1) in the pervaporation through the individual membranes, the permeate flux decreased with decreasing EtOH content in the feed. The greatest flux decrease was observed when using poly(S-PMI) membranes (63.6 $\text{g m}^{-2} \text{h}^{-1}$ on dilution by 35.7 wt %) and PPO membranes (47 $\text{g m}^{-2} \text{h}^{-1}$ on dilution by 34.3 wt % EtOH), i.e., membranes of the individual polymer components. (2) In blended membranes 3 and 4, the decrease in the EtOH concentration in the feed by about 40% produced a flux decrease of about 26 $\text{g m}^{-2} \text{h}^{-1}$, while this value equalled only 4.8 $\text{g m}^{-2} \text{h}^{-1}$ for membrane 2. (3) Poly(S-PMI) and PPO membranes exhibited much higher permeate flux and, thus, lower selectivity than the blended mem-

branes in the separation of solutions containing 84.5–87.6 wt % EtOH. Membrane 4 was an exception, with a separation factor higher than that for poly(S-PMI) membranes and somewhat lower than that for PPO membranes. (4) The highest separation factors for membranes 1 and 2 were found for the separation of the most concentrated ethanol solutions, while the separation factors for the other membranes under these conditions were always lower than for the separation of more dilute mixtures.

Similar to the determined membrane densities, the data obtained for the permeate flux and selectivity indicate that, compared to poly(S-PMI) and PPO, membranes 1 and 2 have more compact structures as a consequence of interactions between the polymer chains. This fact is apparent especially in the separation of a solution containing 87.6 wt % EtOH using membrane 2. The value of its separation factor corresponds to more than three times the value of the separation factor of the poly(S-PMI) membrane and more than twice that of the PPO membrane, determined for the pervaporation of 84.5–86.3 wt % ethanol solutions. The permeate flux through the membranes of the individual polymers is more than three times that through membrane 2. Because of their closer chain packing, membranes 1 and 2 are apparently more resistant to swelling by

Table II Pervaporation of EtOH-H₂O Mixtures through Poly(S-PMI)/PPO Membranes at 35°C

Membrane	EtOH Content (wt %)		Flux ($\text{g m}^{-2} \text{h}^{-1}$)	Separation Factor $\alpha_{\text{H}_2\text{O}}$
	Feed	Permeate		
1	85.9	28.3	27.2	15.4
	48.0	7.0	27.0	12.3
	38.7	4.9	10.2	12.1
2	87.6	27.3	21.8	18.9
	56.3	7.8	21.1	15.3
	48.0	5.7	17.0	15.4
3	86.3	34.9	49.0	11.7
	63.6	10.5	25.9	14.9
	46.5	5.6	23.8	14.7
4	85.7	45.6	53.1	7.1
	59.2	15.5	44.7	7.9
	46.6	8.9	27.2	9.0
Poly(S-PMI)	84.5	49.5	76.5	5.6
	68.3	15.0	25.5	12.2
	48.8	7.4	12.9	12.0
PPO	86.3	42.3	70.1	8.6
	63.6	16.3	39.1	9.0
	52.0	9.7	23.1	10.1

ethanol than poly(S-PMI) and PPO membranes. Membrane 3 behaves similarly to membranes 1 and 2 in the pervaporation process. However, the determined lower separation factor and higher permeation flux of the solutions to be separated containing 86.3% EtOH indicate lower cohesion of the chains in this membrane. The observed pervaporation properties of membrane 4 are probably associated with its highly heterogeneous structure, formed during the evaporation of the solution of the mixture of polymer components.

Gas Transport

Table III lists data on the transport of oxygen, nitrogen, and carbon dioxide through poly(S-PMI)/PPO membranes. The poly(S-PMI) membrane exhibited the lowest permeability to gases, while the PPO membrane had the highest permeability, which was more than 8 times, 10 times, and 5 times as great to oxygen, nitrogen, and carbon dioxide, respectively, than the corresponding permeability values for the poly(S-PMI) membranes. This is in agreement with the finding that the density of the PPO membranes was the lowest of all the determined membrane densities, i.e., its free volume and diffusivity are highest. The greater diffusivity in PPO than in poly(S-PMI) and blends produces the greater permeability of PPO membranes. In blend membranes, the permeability increased with increasing amount of PPO; however, membrane 4 with a nonhomogeneous phase composition had permeability to CO₂ comparable to that of the poly(S-PMI) membrane. As mentioned above in connection with the evaluation of the pervaporation results, the transport characteristics of membrane 4 are probably affected by its degree of heterogeneity.

The calculated ratio of the permeability to oxygen or CO₂ to that to nitrogen, i.e., selectivities α_{O_2/N_2}

and α_{CO_2/N_2} , were greater for membranes 1 and 2. Similarly, as in pervaporation, the behavior of these membranes is apparently the result of interaction of polymer chains accompanied by the formation of a compact structure. Their α_{O_2/N_2} values greatly exceed the selectivities of common homopolymers and copolymers of N-substituted maleimides^{19,20} and are even somewhat higher than the selectivities of blended membranes of PPO and homopolymers of N-arylmaleimides, described in our earlier works.^{21,22} In addition, the α_{CO_2/N_2} values of membranes 1 and 2 were higher than the corresponding selectivities of common polymers, including PPO.

High values of the ratio of the permeability to oxygen or carbon dioxide to that to nitrogen were also found for membranes of the copolymer of styrene with N-phenylmaleimide. However, in contrast, membranes 1 and 2 were characterized by higher mechanical resistance and exhibited greater permeability to gases.

The results obtained demonstrate that, similar to the pervaporation process, gas transport can also be affected by the choice of suitable poly(S-PMI)/PPO membranes. In particular, poly(S-PMI)/PPO blends containing $\leq 40\%$ PPO seem to be promising membrane materials for gas separation because of their high selectivities to oxygen or carbon dioxide and the excellent mechanical resistance of transparent films of these materials.

CONCLUSIONS

The copolymer of styrene with N-phenylmaleimide (10 mol % PMI) and PPO produces film-forming blends that are homogeneous at a PPO content of 20%, and consist of very fine dispersions of the minority phase enriched in PPO in a majority phase with predominant poly(S-PMI) content at PPO

Table III Gas Separation through Poly(S-PMI)/PPO Membranes at 25°C

Membrane	Permeability (Barrer ^a)			Selectivity	
	P _{N₂}	P _{O₂}	P _{CO₂}	α_{O_2/N_2}	α_{CO_2/N_2}
1	0.38	3.00	16.7	7.7	43.0
2	0.50	3.50	19.7	7.0	39.0
3	1.02	5.20	26.1	5.1	25.6
4	1.74	8.73	12.5	5.0	12.5
Poly(S-PMI)	0.36	2.30	12.0	6.4	33.0
PPO	4.70	18.90	65.0	4.2	13.8

^a 10⁻¹⁰ cm³ (STP) cm/cm² s cmHg.

contents of 40 and 60%; blends containing 80% PPO clearly exhibit phase separation. Membranes prepared from poly(S-PMI)/PPO blends exhibited preferential permeability to water in the pervaporation of aqueous ethanol solutions. The greatest separation factors were exhibited by membranes of blends containing 20 and 40% PPO in the separation of solutions with the highest EtOH concentrations. These blends were also found to be useful as membrane materials with high permeability ratios of oxygen or carbon dioxide to nitrogen in the transport of these gases. The transport characteristics of poly(S-PMI)/PPO blend membranes are determined by their structure, which is a consequence of the interactions between the poly(S-PMI) and PPO chains.

The study was supported by Grants No. 203/93/1059 and No. 450102 of Grant Agency of the Czech Republic.

REFERENCES

1. I. Cabasso, J. Jagur-Grodzinski, and D. Vofsi, *J. Appl. Polym. Sci.*, **18**, 2137 (1974).
2. Q. T. Nguyen, in *Synthetic Polymeric Membranes*, B. Sedláček and J. Kahovec, Eds., Walter de Gruyter, Berlin, 1987, p. 479.
3. E. Ruckenstein and J. S. Park, *J. Appl. Polym. Sci.*, **40**, 213 (1990).
4. W. H. Jo, Y. S. Kang, and H. J. Kim, *J. Membrane Sci.*, **85**, 81 (1993).
5. H. C. Park, R. M. Meertens, M. H. V. Mulder, and C. A. Smolders, *J. Membrane Sci.*, **90**, 265 (1994).
6. F. Sun and E. Ruckenstein, *J. Membrane Sci.*, **90**, 275 (1994).
7. G. R. Mitchell and A. A. Windle, *J. Polym. Sci., Polym. Phys. Ed.*, **23**, 1967 (1985).
8. A. Gottschalk, K. Mühlbach, F. Seitz, R. Stadler, and C. Ansehra, *Macromol. Symp.*, **83**, 127 (1994).
9. M. Yoshikawa, H. Yokoi, K. Sanui, and N. Ogata, *Polym. J.*, **17**, 363 (1985).
10. J. Schauer and M. Bleha, *J. Appl. Polym. Sci.*, **46**, 1807 (1992).
11. I. Cabasso, in *Encyclopedia of Polymer Science and Engineering*, Vol. 9, J. Wiley & Sons, Inc., New York, 1987, p. 511.
12. M. P. Cava, A. A. Deana, K. Muth, and M. J. Mitchell, *Org. Synth., Coll. V*, 944 (1973).
13. J. Lokaj and F. Hrabák, *Angew. Makromol. Chem.*, **67**, 1 (1978).
14. J. Lokaj and J. Bílá, *J. Appl. Polym. Sci.*, **46**, 2039 (1992).
15. M. Bleha and E. Votavová, in *Theorie und Praxis der Membrantrennprozesse*, K. Gramlich, Ed., Ingenieurhochschule Köthen, Köthen, 1988, p. 298.
16. D. W. van Krevelen, in *Properties of Polymers*, Elsevier, Amsterdam, 1990, p. 790.
17. G. ten Brinke and R. Grooten, *Colloid Polym. Sci.*, **267**, 992 (1989).
18. L. A. Utracki, in *Polymer Alloys and Blends*, Hanser Publishers, Munich, 1989, p. 93.
19. A. Matsumoto, Y. Oki, and T. Otsu, *Polym. J.*, **23**, 201 (1991).
20. D. Fritsch, *Polym. Mater. Sci. Eng.*, **61**, 502 (1989).
21. J. Lokaj, Z. Pientka, J. Kovářová, and M. Bleha, *J. Appl. Polym. Sci.*, **46**, 1507 (1992).
22. J. Lokaj, M. Bleha, Z. Pientka, and F. Lednický, *Collect. Czech. Chem. Commun.*, **59**, 2552 (1993).

Received February 10, 1995

Accepted May 28, 1995