

Membranes Based on Poly[*N*-(3-dimethylaminophenyl) maleimide]–Poly(2,6-dimethyl-1,4-phenylene oxide) Blends for Gas Separation

INTRODUCTION

Homopolymers and copolymers of *N*-substituted maleimides rank among promising membrane materials for the separation of gases and for the pervaporation of liquid mixtures.^{1–4} The presence of maleimide structural units in the polymeric membranes can lead to increased selectivity and permeability of these membranes in separation processes. However, information is lacking in the literature on membranes based on polymeric mixtures (blends) containing maleimide groups, although, recently, blend technology has drawn increasing interest as an economically advantageous means of obtaining materials with various applications.

Our study was devoted to membranes prepared from a mixture of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and the homopolymer of *N*-(3-dimethylaminophenyl)maleimide (I). PPO was selected for its film-forming ability and the mechanical resistance of the films; the structure units of the *N*-substituted maleimide were introduced into the membrane through poly(I), which does not form films by itself. We wanted to evaluate the effect of the combination of these polymers in the membrane material on the membrane properties. Chloroform solutions of the poly(I)/PPO mixtures with various content of poly(I) were prepared and used in the casting of membranes. The latter were characterized by the permeabilities for oxygen and nitrogen and by the separation factors.

EXPERIMENTAL

Monomeric *N*-(3-dimethylaminophenyl)maleimide (I) was synthesized by the reaction of 3-dimethylaminoaniline with maleic anhydride and subsequent cyclodehydration of the maleamic acid obtained.⁵ Poly(I) was prepared by heating an acetone solution of maleimide I (1.15 mol/L) and 2,2'-azobisisobutyronitrile (0.015 mol/L) in an inert atmosphere in a sealed glass ampule at 60°C for 48 h; the homopolymer was precipitated from solution by a sixfold excess of ethanol. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was the commercial product (Spolana Neratovice, Czechoslovakia). The number-average molecular weight \bar{M}_n of poly(I) was measured on a VP Perkin-Elmer osmometer, whereas the \bar{M}_n value for PPO was determined by GPC in toluene; polystyrene standards were used for calibration.

The glass transition temperatures T_g of the poly(I)/PPO membrane materials were determined by DSC on the Perkin-Elmer DSC 7 apparatus at a heating rate of 20°C/min in a nitrogen atmosphere. Their thermal stability was measured by thermogravimetric analysis.

The membranes were obtained by casting a 10 wt % chloroform solution of PPO or poly(I)/PPO mixture on a glass plate to form a 0.35 mm layer. After evaporation of the solvent at room temperature, membranes with a thickness of approximately 30 μm were released by immersing in water.

The transport properties of the membranes were studied using a laboratory-made apparatus⁶ with a thermal conductivity detector. The permeability values, P , were determined from the found amounts of O₂ and N₂ that passed through a membrane placed in the cell. The selectivity was expressed by the separation factor $\alpha_{\text{O}_2/\text{N}_2} = P_{\text{O}_2}/P_{\text{N}_2}$.

RESULTS AND DISCUSSION

Table I lists information on the composition of the membrane materials. Commercial PPO had a number-average molecular weight by one order higher than the synthesized poly(I); as determined in an earlier publication,⁷ the radical homopolymerization of maleimide I involves considerable transfer to monomer, leading to the formation of short chains of poly(I). The difference in the molecular weights of PPO and poly(I) is reflected in the calculated amounts of polymer chains per 1 g of polymer or poly(I)/PPO mixture. Mixtures 1, 2, 3, and 4 contained, respectively, approximately 1.4, 3.2, 5.3, and 8.3 times more chains of poly(I) than of PPO.

The various amounts of the chains of the two polymer components are also reflected in the properties of the membranes prepared. All the membranes were characterized by excellent mechanical resistance during manipulation, but they had different appearances and separation characteristics. Whereas the PPO membranes were transparent, as the poly(I) content increased in the polymer mixture, the membranes gradually became more opaque; membranes containing 40 wt % poly(I) were distinctly inhomogeneous. Compared with the PPO membranes, the blend membranes showed a pronounced decrease in the permeabilities for O₂ and N₂ (Table II). The permeabilities of membranes prepared from mixture 1 for O₂ and N₂ decreased by 25.4 and 44.7%, respectively. This decrease continued almost linearly with increasing content of poly(I) in the membranes; it was slower for N₂ than for O₂.

The poly(I)/PPO membranes exhibited high selectivity in the separation process. Their separation factors α_{O_2/N_2} were much greater than those of known homopolymers and copolymers of *N*-substituted maleimides.^{1,2} The determined selectivities are comparable with the high selectivities of polymer membranes based on polypyrrolone⁸ or on the aromatic polyimides synthesized by Husk et al.⁹

Apparently, the combination of short rigid chains of poly(I) with the PPO chains facilitates preferential transport of O₂ through the membrane. The separation efficiency of blend membranes was up to 65% greater than that for membranes of PPO alone.

The miscibility of PPO and poly(I) was evaluated on the basis of the T_g values for the membrane materials (Table I). Identical thermal history of the samples was ensured by their heating up to 260°C (first run) and subsequent gradual cooling to room temperature at a rate of 20°C/min. T_g values were determined from the second run at the same heating rate. Only one sharp T_g transition was found for each of mixtures 1, 2, and 3, indicating the existence of a homogeneous, single-phase system. The two values found for mixture 4, one of which corresponds to poly(I) and the second to PPO, could be a consequence of the poor miscibility of the polymer components or phase separation of the components during film preparation. The single T_g value for 4 resulted from the third run.

The difference in the molecular weight of the two components apparently plays a substantial role in the mixing process; the combinatorial contribution to the miscibility is apparently important for the lower molecular component poly(I) and is reflected in the easier distribution of the polymaleimide throughout the high molecular weight PPO. This process is somewhat similar to plastification, as mixing poly(I) with PPO leads to a decrease in the T_g value compared with that for PPO alone.

The TGA measurements demonstrated the high thermal stability of the membranes, which can be heated up to approximately 300°C without a mass loss.

Table I Poly(I)/PPO Membranes

Polymer Blend	Poly(I) ^a		PPO ^b (10 ⁵ mol/g)	T_g^c (°C)
	Wt %	(10 ⁵ mol/g)		
1	10	3.3	2.4	205
2	20	6.7	2.1	211
3	30	10.0	1.9	211
4	40	13.3	1.6	209, 226 207 ^d
Poly(I)	100	33.3	—	209
PPO	0	—	2.6	226

^a $\bar{M}_n = 3000$.

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

^c From the second heating curve.

^d From the third heating curve.

Table II Separation Properties of Poly(I)/PPO Membranes at 25°C

Polymer Blend	Permeability (barrer ^a)		Selectivity α_{O_2/N_2}
	P_{O_2}	P_{N_2}	
1	14.1	2.6	5.4
2	12.0	1.9	6.5
3	9.5	1.4	6.6
4	7.7	1.2	6.5
PPO	18.9	4.7	4.0

^a 10⁻¹⁰ cm³ (STP) cm/cm² s cmHg.

CONCLUSIONS

Membranes prepared from a mixture of poly(2,6-dimethyl-1,4-phenylene oxide) and poly[*N*-(3-dimethylaminophenyl)maleimide] are mechanically resistant, thermally stable, and exhibit good permeability and high selectivity in the separation of O₂ and N₂. Their separation factors α_{O_2/N_2} depend on the content of poly(I) and reach the values of 5.4–6.6.

Our study of membranes based on polymer mixtures containing maleimide groups is continuing.

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