GAS TRANSPORT PROPERTIES AND STRUCTURE OF POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE)/ POLY(*N*-ARYLMALEIMIDE) MEMBRANES

Jan LOKAJ, Miroslav BLEHA, Zbyněk PIENTKA and František LEDNICKÝ
Institute of Macromolecular Chemistry,
Academy of Sciences of the Czech Republic, 162 06 Prague 6, The Czech Republic

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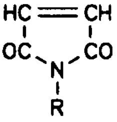
Dedicated to Professor Otto Wichterle on the occasion of his 80th birthday.

Blend membranes containing poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and homopolymers of substituted *N*-phenylmaleimides were prepared by casting from chloroform solutions of mixtures of the polymers. The polyimides were synthesized by the radical polymerization of dimethylamino, chloro, and bromo derivatives of *N*-phenylmaleimide. The membranes were characterized by permeabilities to oxygen and nitrogen; the permeability ratio O_2/N_2 equaled to 5.3 – 6.8. Unlike transparent PPO membranes, the PPO/polyimide membranes were cloudy. The phase structure of the membranes was examined by optical and scanning electron microscopy. The relation between gas transport properties and the structure of the membranes is discussed.

Polymers with built-in *N*-substituted maleimide structural units have been the subject of several studies concerned with the membrane separation of gases and liquid mixtures[1 – 5]. Maleimide structural units in polymer membranes increase their thermal stability and could also improve separation characteristics in membrane processes.

We have recently prepared[3] membranes based on mixtures of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with the homopolymer of *N*-(3-dimethylaminophenyl)maleimide (*I*). The membranes were robust, thermally stable and exhibited good permeability to oxygen and nitrogen. Their selectivities α_{O_2/N_2} depended on the content of the homopolymer of *I* and reached the values from 5.4 to 6.6, while most membranes have this parameter between 2 and 5.

The present work deals with membranes consisting of PPO and homopolymers of halogenated *N*-phenylmaleimides. The study was aimed at evaluating the effect of combination of different polymaleimides with PPO on transport properties of the membrane material prepared. For this purpose, a series of poly(*N*-phenylmaleimides) substituted on the phenyl ring by chlorine or bromine atoms was prepared, and by casting from chloroform solutions of mixtures of these homopolymers with PPO, blend membranes were obtained. These were characterized by permeabilities to oxygen and nitrogen and by selectivities. In addition, the phase structure of the membranes made from PPO and poly(*I*) was also subjected to examination.



I – V

I, R = 3-dimethylaminophenyl
II, R = 2,4,6-tribromophenyl
III, R = 2,3,4,5,6-pentabromophenyl
IV, R = 2,4,6-trichlorophenyl
V, R = 2,3,4,5,6-pentabromophenyl

EXPERIMENTAL

Materials

Substituted *N*-phenylmaleimides were prepared by the reaction of the corresponding aniline with maleic anhydride, followed by cyclodehydration of the maleamic acids obtained[6]. The following maleimides were obtained: *I*, m.p. 98 °C; *II*, m.p. 142 °C; *III*, m.p. 215 °C; *IV*, m.p. 131 °C; *V*, m.p. 150 °C. Acetone solutions of the imides (1.15 mol l^{-1}) and 2,2′-azobis(isobutyronitrile) (0.015 mol l^{-1}) were heated in sealed glass ampoules at 60 °C for 48 h; the polymaleimides were precipitated from solutions by a sixfold excess of ethanol. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was a commercial product (Spolana Neratovice, The Czech Republic).

Preparation of Membranes

The membranes were obtained by casting a chloroform solution (0.1 g ml^{-1}) of PPO or PPO/polyimide mixture on a glass plate to form a 0.35 mm layer. After solvent evaporation at room temperature, the membranes with a thickness of approximately 30 μm were released by immersing in water.

Methods

Number-average molecular weights $\overline{M}_n$ of poly(*N*-arylmaleimides) were measured on a Perkin–Elmer vapour pressure osmometer. The molecular weight of PPO was determined by GPC in toluene. In both cases, polystyrene standards were used for calibration.

Transport properties of the membranes were studied with the use of a laboratory-made apparatus[7] equipped with a thermal conductivity detector. The permeabilities, P, were determined from the amounts of O_2 and N_2 which passed through a membrane placed in the cell. The selectivity was expressed by the permeability ratio $\alpha_{O_2/N_2} = P_{O_2}/P_{N_2}$.

The phase structure of the membranes was examined by scanning electron microscopy (SEM) both from the membrane and the fracture surfaces. The samples were sputter-coated with a gold layer about 10 nm thick, observed and micrographed, using Jeol JSM 35 and JSM 6400 instruments.

RESULTS AND DISCUSSION

Homopolymers of Halogenated N-Phenylmaleimides

Similarly to *N*-(3-dimethylaminophenyl)maleimide[8], the radical homopolymerization of halogenated *N*-phenylmaleimides proceeds with significant chain transfer to monomer. As follows from the determined relative molecular weights (Table I), the resulting products correspond to maleimide tetramers, their polymerization degree being three times smaller compared to that of the poly(*I*). The halogen atoms on the phenyl ring thus make transfer reaction more favourable, when compared to the effect of the dimethylamino group.

The polymaleimides prepared are white powder-like substances, well soluble in chloroform, benzene, acetone, dimethylformamide, and tetrahydrofuran. Because of the low degree of polymerization and their rigid structural units, the polymaleimides do not form films on casting their solutions.

TABLE I
PPO/poly(halogenated *N*-phenylmaleimide) membranes

Membrane	Polymaleimide[a] wt.%	Polymaleimide[a] amount of chains mmol/g	PPO[b] amount of chains mmol/g
PPO/poly(*II*)	10	610	240
	20	1 210	210
	30	1 820	190
PPO/poly(*III*)	10	440	240
	20	880	210
	30	1 320	190
PPO/poly(*IV*)	10	910	240
	20	1 820	210
	30	2 730	190
PPO/poly(*V*)	10	720	240
	20	1 450	210
	30	2 170	190
PPO	–	–	260

[a] $\overline{M}_n$ = 1 650, 2 270, 1 100, and 1 380 for poly(*II*), poly(*III*), poly(*IV*), and poly(*V*), respectively; [b] $\overline{M}_n$ = 37 800.

Membranes from PPO/Poly(N-arylmaleimide) Mixtures

The commercial PPO used to prepare blend membranes had by one order of magnitude greater molecular weight than homopolymers of substituted *N*-phenylmaleimides. It exhibited excellent film-forming properties, transparency and good mechanical resistance of the films during manipulation. The membranes prepared from PPO/poly(halogenated *N*-phenylmaleimide) mixtures became cloudier with increasing content of the polyimide, and also their mechanical resistance was poorer. However, the polyimides in amounts of from 10 to 30 wt.% did not affect much the appearance and mechanical properties of the blend membranes. Due to the great difference in molecular weights of the polymer components, the polyimide chains were always prevailing in the membrane material (Table I). The greatest excess of these chains – in comparison with the amount of PPO chains – was in the PPO/30 wt.% poly(*IV*) mixture (14.4 fold), the smallest in the PPO/10 wt.% poly(*III*) blend (1.8 fold).

Optical microscopy of the blend membranes proved the phase heterogeneity with a broad particle size distribution. The phase structure was evaluated by using SEM (scanning electron microscopy). Figure 1 shows the fracture surface with a part of the surface of the membrane containing 40 wt.% of *N*-(3-dimethylaminophenyl)maleimide homopolymer. The surface of the membrane exposed to the atmosphere is shown in Fig. 2. From these figures it becomes evident that polyimide particles are dispersed in the form of spheres in the membrane and, at the same time, they occur as lense-like aggregates on its surface. The morphology of the fracture surface is in favour of the low interface adhesion of both polymer components of the membrane. The polyimide lenses on the membrane surface can be removed by a careful treatment with dimethylformamide which dissolves poly(*I*) but not PPO. This was proved by microscopic measurements (SEM).

In the previous work[3], we have determined the glass transition temperatures (T_g) for PPO and PPO/poly(*I*) mixtures, using DSC method (differential scanning calorimetry).

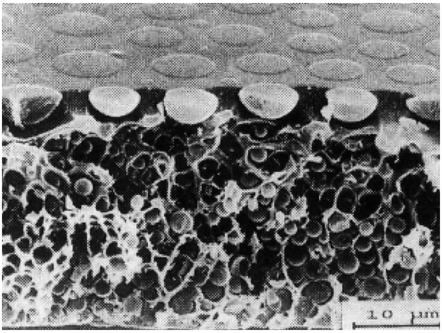


FIG. 1
Fracture surface of the PPO/40 wt.% poly(*I*) membrane

The mixtures with 10, 20, and 30 wt.% content of the poly(*I*) showed only one sharp T_g transition which was close to T_g of poly(*I*) and indicated the presence of a single-phase homogeneous system. With respect to the small difference between T_g's of PPO and poly(*I*) (17 °C), DSC is not likely to be suitable for determining the miscibility of the components of these mixtures.

Transport of Oxygen and Nitrogen through PPO/Poly(N-arylmaleimide) Membranes

In Table II are presented permeabilities to O_2 and N_2, along with the calculated selectivities of the membranes from PPO and PPO/poly(halogenated *N*-phenylmaleimide) mixtures. In contradistinction to the membranes made from the PPO itself, the blend membranes showed distinctly lower permeability to both gases which decreased with increasing content of the polyimide in the mixture. Exception were the membranes from PPO/poly(*III*) containing 10 and 20 wt.% of the polyimide, the reason of this deviation from the above trend being most probably hidden defects. On the other hand, the selectivity to oxygen increased on addition of polyimides to PPO, and for the membrane containing 30 wt.% poly(*II*) was almost by 70% greater compared to the PPO membrane. These data indicate similarity in transport properties of the membranes of PPO/poly(halogenated *N*-phenylmaleimide) and PPO/poly(*I*) (ref.[3]). The calculated selectivities are comparable with the high selectivities of the polymer membranes based on polypyrrolone[9] or on aromatic polyimides[10].

Similar transport characteristics of the membranes from PPO and homopolymers of different maleimide derivatives document a small effect of the chemical composition of polymaleimides on the behaviour of these membranes in oxygen and nitrogen permeation. Their properties are determined rather by morphology, i.e. by mutual arrange-

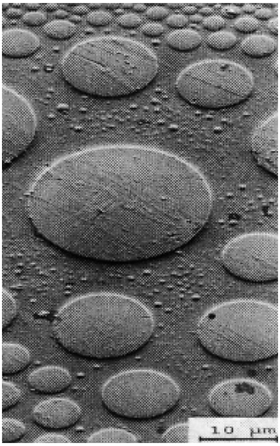


FIG. 2
Surface of the PPO/40 wt.% poly(*I*) membrane

ment of short rigid polymaleimide chains and much longer PPO chains. Testing of the membranes from PPO/40 wt.% poly(*I*) showed that the removal of the surface polyimide layer by dimethylformamide does not result in any significant changes in the permeabilities of the membranes to oxygen and nitrogen. The experiments performed so far document that the transport process during gas permeation depends above all on the internal structure of the membranes based on PPO/poly(*N*-arylmaleimide) mixtures.

CONCLUSIONS

Membranes based on PPO/poly(*N*-arylmaleimide) mixtures show good permeability to oxygen and nitrogen and a high permselectivity to oxygen. Transport of gases is not affected by the type of the substituent on the ring in poly(*N*-phenylmaleimide) but predominantly by the structural arrangement of chains of both polymer components in the membranes.

TABLE II
Separation properties of PPO/poly(halogenated *N*-phenylmaleimide) membranes at 25 °C

Membrane	Polymaleimide wt.%	Permeability[a], mol m^{-1} s^{-1} Pa^{-1}		Selectivity α_{O_2/N_2}
		$P_{O_2} \cdot 10^{15}$	$P_{N_2} \cdot 10^{15}$	
PPO/poly(*II*)	10	4.25	0.67	6.1
	20	3.55	0.60	5.9
	30	2.81	0.40	6.8
PPO/poly(*III*)	10	3.31	0.64	5.3
	20	4.12	0.67	6.3
	30	3.08	0.57	5.4
PPO/poly(*IV*)	10	5.39	0.94	5.7
	20	3.82	0.57	6.7
	30	3.51	0.64	5.4
PPO/poly(*V*)	10	4.45	0.74	6.2
	20	3.48	0.54	6.4
	30	2.24	0.40	5.5
PPO	–	6.33	1.57	4.0

[a] 1 . 10^{-15} mol m^{-1} s^{-1} Pa^{-1} = 2.99 Barrer.

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