Formation and Analysis of a Polyimide Layer in Composite Membranes

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ABSTRACT: Composite membranes containing a thin-film layer of aromatic polyimides (PI) ensure an advantageous combination of selectivity and permeability in gas separation. A series of rigid-chain PI with different chemical structures were studied as a thin active layer. Composite membranes were prepared by coating a solution of poly(amic acid) (PAA) and an imidization catalyst on a poly(phenylene oxide) (PPO) support with pores filled by decane. The subsequent stage of solid-state catalytic transformation of the PAA/PPO membrane into the PI/PPO membrane determines the specific structure of the PI layer and the transport properties of the PI/PPO composite membranes. The structure of composite membranes was determined by scanning electron microscopy and analyzed in the terms of the resistance model of gas transport in composite membranes. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 1026–1032, 2000

Key words: polyimides; composite membrane; thin-layer formation; catalytic imidization; gas separation

INTRODUCTION

Thin-film composite membranes make it possible to use polymers with high selectivity but low permeability in thin active layers, ensuring their effective productivity in gas separation. These polymers include aromatic polyimides (PI).[1] Owing to their unique gas separation properties, chemical resistance, thermal stability, and mechanical strength, PI can be used for the purification and recovery of hydrogen in the petrochemical industry, for concentration and separation of helium from natural gas and air-containing mixtures, for carbon dioxide removal in gas and petroleum industries, for oxygen and nitrogen separation from air, as well as for water and hydrocarbon vapor separation from air.[2]

Several procedures for obtaining composite membranes with PI active layers have been described in the patent literature. One of these methods[3] was used in our work for the formation of composite membranes consisting of a PI thin layer on a poly(phenylene oxide) (PPO) support.

Membrane structure and properties depend on the PI type and the procedure of top-layer preparation. As a result of synthesis, most polyimides are obtained in the soluble state because the diamine and dianhydride fragments contain swivel bridges and bulky groups.[4] These PI layers are prepared by coating the PI solution on the PPO support with pores protected by decane from the PI solution flow during top-layer formation.[5,6] In the case of rigid-chain PI without swivels, the coating process is possible only from the prepolymer—poly(amic acid) (PAA), because after dehydration, PAA is transformed into insoluble PI[7]:

PAA   PI
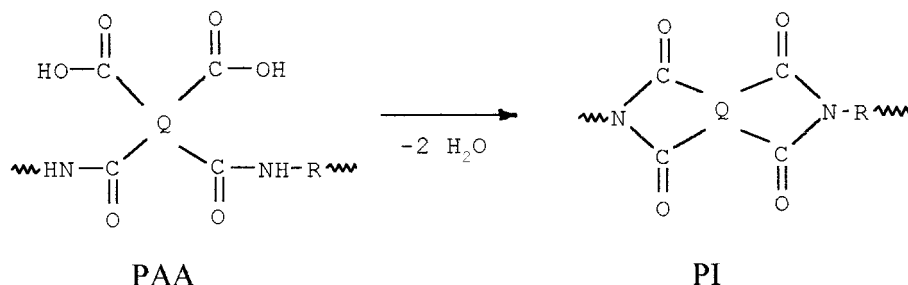
where Q and R are aromatics.

The transformation of PAA into PI by a thermal technique requires gradual heating to 300–400°C. This method is not suitable for PI/PPO composite membrane formation because the glass transition temperature of PPO is about 220°C. There are low-temperature methods in which catalysts and dehydrating agents are used for imidization. We have found an effective catalytic method of low-temperature solid-state transformation of the PAA/PPO membrane into PI/PPO.[8]

In the present work, a series of rigid-chain PI with different chemical structures was studied as a thin active layer in PI/PPO composite membranes. The aim of this work was to study the catalytic formation and structure of the PI top layer.

EXPERIMENTAL

Materials

PAA was synthesized by low-temperature polycondensation in solution. Dry dianhydride was added to the solution of the corresponding diamine in N,N'-dimethylacetamide (DMA).[9] The monomers used for PAA synthesis were purified by vacuum-distillation. DMA was dried over calcium hydride and distilled.

Imidization catalysts, benzimidazole (BI) and imidazole (I), were used after preliminary recrystallization. Their occupied volume ($\sum_i \Delta V_i$) was calculated by a group contribution method.[10] It was found equal to 112.5 Å^3 (BI) and 66.9 Å^3 (I).

Membranes

The PI/PPO composite membranes were obtained in a two-stage process. In the first stage, the PAA/PPO membranes were formed by casting a 2–5% polymer solution in DMA (containing 2 mol of catalyst per mole of PAA) on the surface of a microporous PPO support. Its pores had previously been filled with decane for protection against the penetration of the polymer solution. In the second stage, the PAA/PPO membrane was transformed into the PI/PPO membrane during solid-state catalytic imidization by heating to 150°C for 20 h. The presence of the catalyst in the PI layer was controlled by mass-spectrometric thermal analysis.[11]

Methods of Investigation

The density ρ (g/cm^3) was determined by the flotation method in a mixture of carbon tetrachloride and toluene at 20°C. The free volume v_f (cm^3/g) was calculated from the equation $v_f = v_{sp} - 1.2\ v_w$, where $v_{sp} = 1/\rho$ is the specific volume and v_w is the van der Waals volume calculated by Bondy's method. The molecular packing coefficient

$$k = \frac{N \sum_i \Delta V_i}{M}\, \rho,$$

where N is Avogadro's number and M is a molecular weight of polymer unit, determines the fraction of the occupied volume.[10]

Gas-transport properties were measured on a chromatography installation with a diffusion-type cell for membranes by air transmission at 30°C and a partial pressure of 1 bar. Eight to 10 membrane samples of each polymer were measured for determining the gas permeability of the polymer. There were three or more measurements per a membrane sample.

The apparent gas permeability coefficient P (cm^3 cm/cm^2 s cmHg) for each PI type was calculated using data on the PI/PPO membrane gas permeability P/l (cm^3/cm^2 s cmHg) and the PI

Table I   Gas-transport Properties of PI/PPO Composite Membranes

| No. PI	PI	(Cat)	l_{PI} (μm)	$P/l_{O2} \times 10^7$ (cm^3/cm^2 s cmHg)	$P_{O2} \times 10^{11}$ (cm^3 cm/cm^2 s cmHg)	α O$_2$/N$_2$
1	PMDA–ODA	(BI)	3.0	2.83 ± 0.37	8.49 ± 1.39	6.0
		(I)	5.0	1.68 ± 0.28	8.40 ± 1.57	5.4
2	BPDA–ODA	(BI)	2.1	1.21 ± 0.15	2.56 ± 0.44	7.2
		(I)	4.0	0.66 ± 0.09	2.62 ± 0.42	7.0
3	BPDA–OTOL	(BI)	—	—	—	—
		(I)	3.0	0.77 ± 0.11	2.31 ± 0.41	5.5
4	BPDA–PRM	(BI)	1.8	0.39 ± 0.05	0.70 ± 0.13	5.2
		(I)	3.2	0.22 ± 0.02	0.70 ± 0.09	5.4
5	BPDA–PPD	(BI)	2.8	0.18 ± 0.02	0.51 ± 0.08	4.8
		(I)	—	—	—	—

layer thickness l (cm). The PI layer thickness (for PI/PPO membranes with studied gas-transport properties) was measured with a micrometer after the PPO support had been dissolved in chloroform.

The selectivity or factor of the O$_2$—N$_2$ separation was calculated from the equation $\alpha = P/l$ (O$_2$) : P/l (N$_2$)

A JSM-35 (Jeol) scanning electron microscope was used for the membrane structure investigation.

RESULTS AND DISCUSSION

The scheme shows the chemical structure of PI used for forming the top layer of the PI/PPO composite membranes:

where Q is

PMDA   BPDA

R is

ODA   PRM

PPD   OTOL
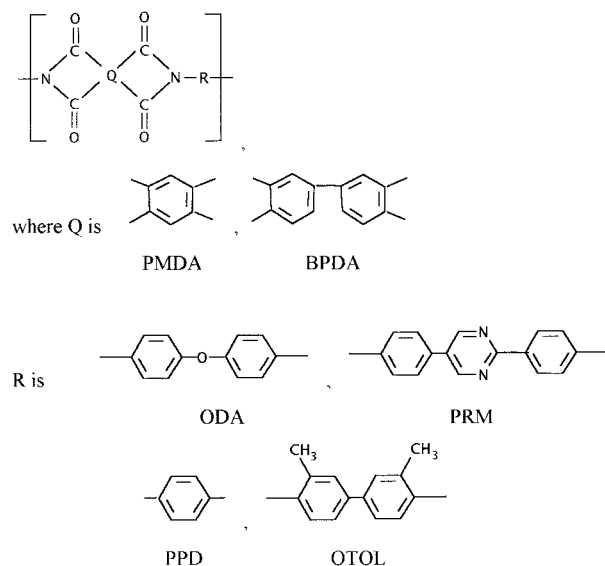
High selectivity of aromatic polyimides in the separation of air, natural gas, synthesis gas, etc., is retained when PI is used in thin layers of composite membranes if these layers have no defects. Their defects were determined by testing the selective separation of O$_2$ and N$_2$ when air was passed through a cell with the PI/PPO membrane. Defectless PI layers have α(O$_2$/N$_2$) > 3.

Table I lists the transport properties of PI/PPO membranes with top layers from PI (2–5) based on the dianhydride of 3,3′,4,4′-biphenyltetracarboxylic acid (BPDA). A polypyromellitimide (PI-1) based on pyromellitic dianhydride (PMDA) and oxydianiline (ODA) was used for comparison. High selectivity α(O$_2$/N$_2$) of PI/PPO membranes indicates that the active layers have no defects. The PMDA–ODA and BPDA–ODA produce the most permeable membranes because they contain the ODA fragment with an oxygen bridge which determines the intramolecular mobility caused by rotational vibrations. The top layer from PMDA–ODA and BPDA–ODA can be obtained by the catalysis with both benzimidazole and imidazole. Thicker PI layers are obtained when imidazole is used, under other equal conditions. The reason is the smaller weight and smaller occupied volume of imidazole molecules. This is significant in the removal of catalyst molecules from PAA solid layers of the same thickness during PAA transformation into PI. However, apparent permeability coefficients (P_{O2}) coincide for both cases of catalysis because these parameters depend considerably on the polymer nature.

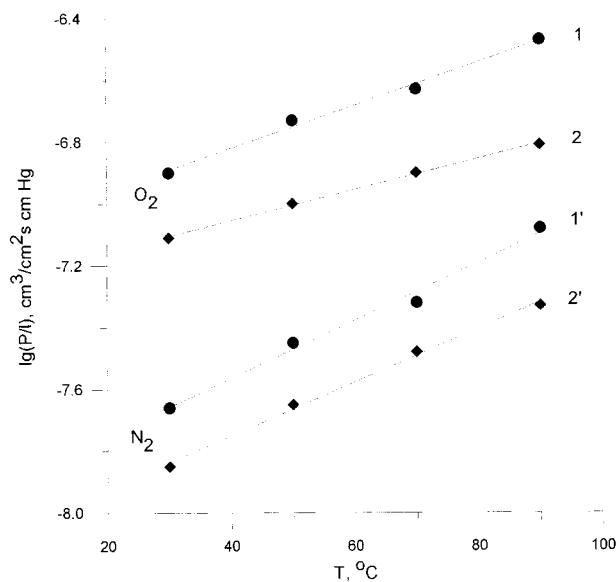PI (3–5) have a rigid-chain structure with limited intramolecular mobility and, therefore, the

Figure 1 Temperature dependence of O_2 and N_2 permeability for PI/PPO composite membranes with the following active layers: (1,1′) BPDA–ODA; (2,2′) BPDA–OTOL.

gas permeability of the composite membranes is lower. In the case of BPDA–OTOL, the use of bulky benzimidazole molecules (112.5 Å^3) leads to microdefects in the active layer. These defects are formed when benzimidazole is removed because of low polymer elasticity (for BPDA–OTOL, elongation at break is 5–10%). When imidazole molecules (66.9 Å^3) are used, a selective membrane is formed and its gas-separation ability is retained during temperature tests. The O_2—N_2 selectivity ranges from 5.5 at 30°C to 3.2 at 90°C. As shown in Figure 1, the temperature dependence of O_2 and N_2 permeability for the BPDA–OTOL/PPO membrane is similar to that for the BPDA–ODA/PPO membrane obtained easily in the presence of both catalysts.

BPDA–PPD had the lowest permeability in the series of PI under study. Gas permeability of the BPDA–PPD/PPO membranes obtained by using imidazole was undetectable by the instrument and is absent in Table I.

Table II gives some physical parameters of PI: density ρ, specific volume v_{sp}, van der Waals volume v_w, and macromolecular packing coefficient k. In Table II, polyimides are listed in the order of decreasing gas permeability which does not correspond to the order of change in ρ or v_w but has the same tendency as the change in v_f. Increase in the packing density of the macromolecules decreases gas permeability because membrane resistance to gas flow increases.

To explain the structure of composite membranes, a model of resistance to gas flow will be used.[12] By definition, membrane resistance R (s cm Hg/cm^3) is inversely proportional to gas flux Q (cm^3/s) through a composite membrane:

$$R = \Delta p/Q \qquad (1)$$

where Δp (cm Hg) is the pressure difference between the two sides of the membrane.

The specific resistance r (cm^2 s cm Hg/cm^3 cm) of a layer with thickness l (cm) and surface area A (cm^2) is given by

$$r = A \; dR/dl \qquad (2)$$

The inverse proportion relationship of specific resistance to the gas permeability coefficient P (cm^3 cm/cm^2 s cm Hg), expressed by

$$r = 1/P \qquad (3)$$

contributes to a deeper understanding of the specific resistance physical meaning.

Table II Physical Parameters of Polyimides

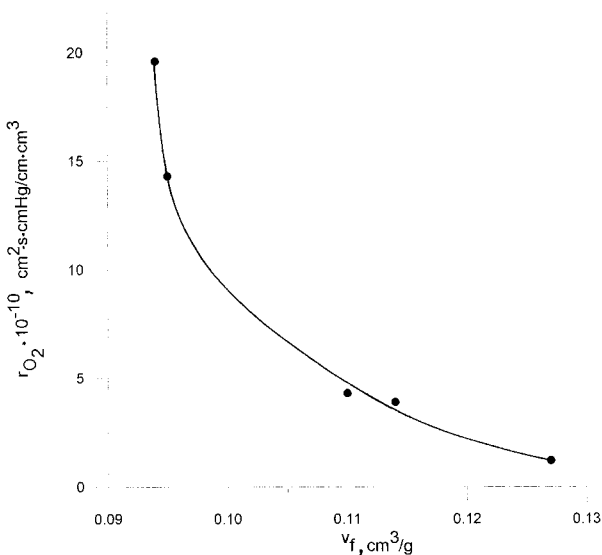| No. PI	PI	ρ (g/cm^3)	v_{sp} (cm^3/g)	v_w (cm^3/g)	v_f (cm^3/g)	k
1	PMDA–ODA	1.408	0.710	0.486	0.127	0.684
2	BPDA–ODA	1.390	0.719	0.504	0.114	0.700
3	BPDA–OTOL	1.354	0.738	0.523	0.110	0.708
4	BPDA–PRM	1.412	0.708	0.511	0.095	0.721
5	BPDA–PPD	1.461	0.684	0.492	0.094	0.719

Figure 2 Specific resistance to O_2 flow versus free volume of PI with different chemical structures.

The dependence of specific resistance to gas flow on the free volume of PI (1–5) was plotted in Figure 2. Specific resistance decreases considerably with increasing free volume in passing from rigid-chain PI to PMDA–ODA in the following series:

BPDA–PPD > BPDA–PRM

> BPDA–OTOL > BPDA–ODA > PMDA–ODA

The dependence of composite membrane resistance on top-layer thickness is very informative (Fig. 3). The plot $R(l)$ was constructed for the most permeable PMDA–ODA/PPO membrane with the top-layer thickness range ($1\ \mu$m $< l < 6\ \mu$m) being of practical importance. Separate points show the level on which the analogous $R(l)$ dependence can be plotted for other PI (2–5) with a higher resistance to O_2 flow. It can be seen from Figure 3 that the resistance of the PMDA–ODA/PPO membrane is virtually constant and, according to calculation, equal to the resistance of an ideal PMDA–ODA film with $P(O_2) = 0.25$ cm^3 cm/cm^2 s cmHg[13] and a thickness of 0.5 μm.

It has been established[8] that the unusual shape of $R(l)$ dependence for the PI/PPO composite membrane is connected with the specific structure of the top layer (Fig. 4). The PI layer has a porous structure in depth and a dense skin on the top. The skin thickness is about 0.5 μm. The PI
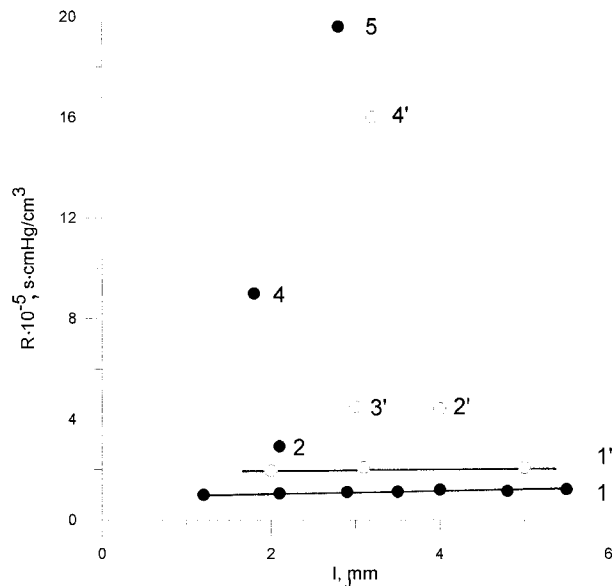

Figure 3 Resistance to O_2 flow versus PI layer thickness in PI/PPO composite membranes obtained with a benzimidazole catalyst: (1) PMDA–ODA, (2) BPDA–ODA, (4) BPDA–PRM, and (5) BPDA–PPD, and with an imidazole catalyst: (1′) PMDA–ODA, (2′) BPDA–ODA, (3′) BPDA–OTOL, and (4′) BPDA–PRM.

layer structure reflects the complex processes occurring in the solid-state transformation of PAA into PI, which is accompanied by the elimination of water and catalyst molecules. This leads to polymer film shrinkage.

These results were confirmed in the present work by a microscopic study of the PI/PPO membrane structure. Figure 5 demonstrates electron micrographs of the BPDA–ODA/PPO composite membranes. Figure 5(a) shows a membrane obtained by using the benzimidazole catalyst: it has the above-described porous-skin structure of the BPDA–ODA active layer. Figure 5(b) shows a membrane prepared with the same sequence of operations but without the catalyst: it is charac-
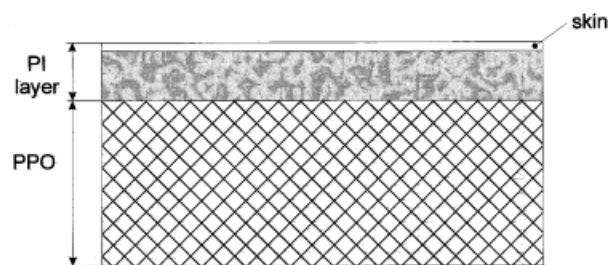

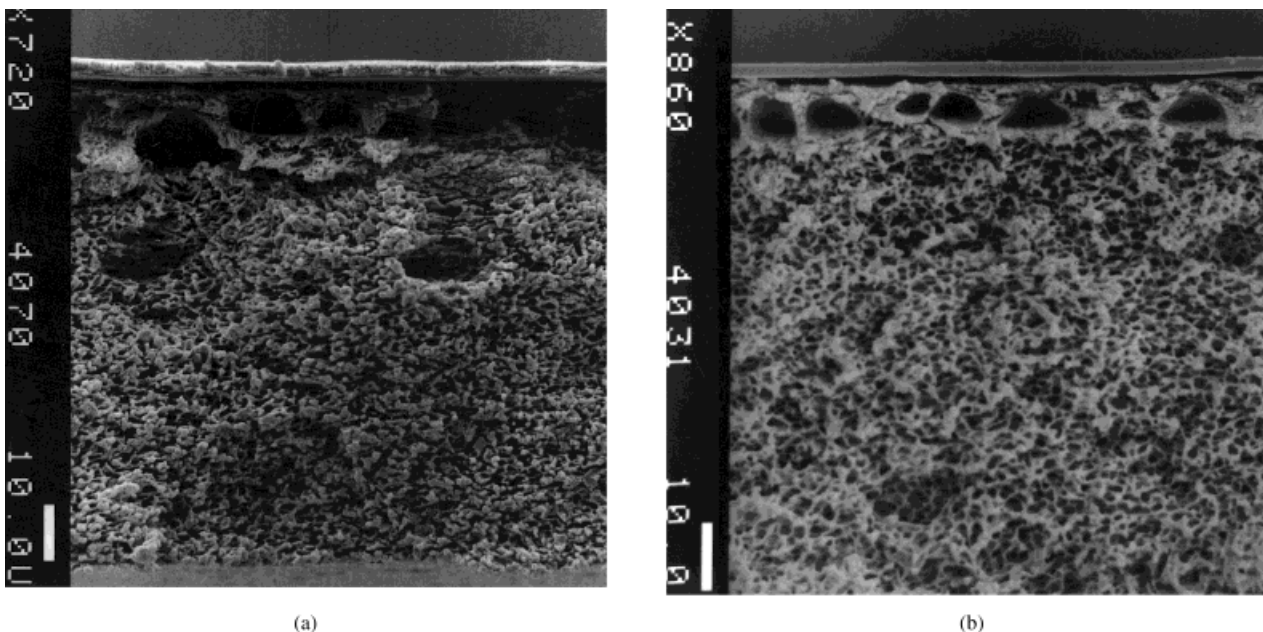**Figure 4** Structure of PI/PPO composite membranes.

Figure 5 SEM micrographs of cross section of the BPDA–ODA/PPO composite membrane prepared (a) in the presence of benzimidazole and (b) without a catalyst.

terized by the dense uniform structure of the top layer.

Let us analyze the PI/PPO composite membranes in terms of the resistance model.[10] According to the law of successive resistance, the overall resistance of the composite membranes is composed of

$$R = R_o + R_{or} + R_{tr} + R_f \qquad (4)$$

where R_o is the resistance of the modified support; R_{or}, the resistance of the top layer polymer oriented on the support surface; R_{tr}, the resistance of the transition zone in the top layer; and R_f, the resistance of the top polymer film (so-called skin).[14]

The unusual shape of the $R(l)$ dependence (Fig. 3) shows that the PI/PPO membranes are not a typical composite membranes for the following reasons: The PPO support remains unmodified because its pores are protected by decane from the PAA solution flow during the top-layer formation; therefore, we have $R_o \approx 0$. The zone of oriented polymer formed during the adsorption of PAA molecules on the surface of the PPO support is destroyed after the PAA layer is transformed into PI, that is, $R_{or} \approx 0$. There is no transition zone, so $R_{tr} = 0$. Consequently, the resistance to gas flow through the PI/PPO membrane is determined principally by the zone of the PI skin, and we have $R \approx R_f$.

Hence, the specific structure of the active layer in PI/PPO composite membranes is a result of the process of top-layer formation. This fact was established by electron microscopy and confirmed by the analysis of the data on PI/PPO membrane gas permeability in terms of the resistance model.

CONCLUSIONS

Catalytic solid-state low-temperature imidization is effective in forming a thin active layer of rigid-chain PI in composite membranes. Imidization catalysts are heterocyclic amines: benzimidazole and imidazole, which promote imidization and decrease the process temperature.

The PI active layer determines the gas-separation properties of the PI/PPO composite membranes. Gas permeability increases in the following series of rigid-chain PI:

BPDA–PPD < BPDA–PRM

< BPDA–OTOL < BPDA–ODA < PMDA–ODA

The analysis of the PI/PPO composite membrane structure in terms of the resistance model in combination with electron micrographs shows that the PI layer has a porous structure in depth and a dense skin on the top. The PI layer structure reflects complex processes occurring in the solid-state transformation of PAA into PI.

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