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Ultra-thin polyimide film as a gas-separation layer for composite membranes

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Composite membranes with an ultra-thin polyimide separation layer have been prepared by the deposition of dimethylalkylammonium salt of polyamic acid on a poly(phenylene oxide) porous support layer by the Langmuir–Blodgett technique and subsequent thermal cyclization of the polyimide precursor. In spite of a relatively mild thermal treatment, complete cyclization was achieved as observed by Fourier transform infra-red spectroscopy. The composite membrane with polyimide ultra-thin separation layer exhibited a considerably high permeation rate, maintaining a good selectivity. Copyright © 1996 Elsevier Science Ltd.

(Keywords: Langmuir–Blodgett films; polyimides; gas separation)

Introduction

Aromatic polyimides (API) are frequently used in the microelectronics[1–3] and aerospace industries[3] owing to their excellent thermal stability, good mechanical properties and durability. Recently, they have also attracted attention as materials applicable in separation techniques[4–8]. In addition to their use in pervaporation and pressure-driven separations[8] (microfiltration, ultrafiltration and reverse osmosis), polyimides are studied mainly for the separation of gases[4–6]. In spite of the high selectivity, their application as homogeneous membranes is limited by relatively low permeability[4–6,9,10]. According to Fick's first law, the gas flux is proportional to the reciprocal value of the membrane thickness[11]. Therefore, ultra-thin films prepared by the Langmuir–Blodgett (LB) technique, the thickness of which can be adjusted in molecular dimensions by the successive deposition of monomolecular layers, represent a promising way of increasing the permeation rate.

Several attempts to use LB films as gas-separation layers for composite membranes have been published, but a satisfactory permselectivity has rarely been achieved[12–16]. The reasons for the low permselectivity of many studied systems seem to be both the use of low-molecular-weight compounds resulting in poor mechanical properties of the LB films (leading to cracks) and use of macroporous support membranes, which are difficult to cover by ultra-thin films. This work describes the preparation and permeation properties of the composite membrane containing an LB ultra-thin API separation layer and a poly(phenylene oxide) (PPO) porous asymmetric support membrane with the largest pore diameter of 18 nm in its skin[17]. Advantages of the application of API for the ultra-thin layer consist in their highly selective permeability and good mechanical strength. Moreover, ultra-thin API films consisting of an eligible number of monomolecular layers, each 4–6 Å thick, can be prepared by the LB technique with a low number of defects[18–21].

Experimental

Synthesis of precursors of polyimides. Polyamic acid (PAA) was synthesized by reaction of dianhydride of 3,3′,4,4′-benzophenonetetracarboxylic acid and bis-(4-aminophenoxy) ether in *N*,*N*-dimethylformamide (DMF)[22]. Dimethyldodecylammonium salt of PAA (PAA-12) and dimethylhexadecylammonium salt of PAA (PAA-16) were prepared by neutralization of PAA with dimethyldodecylamine and dimethylhexadecycl-amine, respectively[18].

Preparation of ultra-thin polyimide films. Monomolecular films of PAA-12 and PAA-16 were spread on water ($\rho = 18\,\mathrm{M\Omega\,cm}$) from DMF/hexane solutions. LB films consisting of 30 molecular layers of PAA-12 or PAA-16 were deposited on the skin of the PPO support by horizontal touching of the monomolecular films compressed on the air–water interface at $10\,\mathrm{mN\,m^{-1}}$.

The cyclization reaction described in *Scheme 1* was carried out by heating the composite membrane under 0.5 mmHg pressure at 80°C for 60 min, at 150°C for 60 min, at 165°C for 30 min and at 190°C for 10 min, successively.

Spectroscopic characterization. Chemical structure of the ultra-thin layers was determined by Fourier transform infra-red spectroscopy (*FT* i.r.) using a Bruker IFS 55 spectrometer and a Ge 45° reflection element.

Permeation experiments. The permeation rates of O_2, N_2 and CO_2 through composite membranes were

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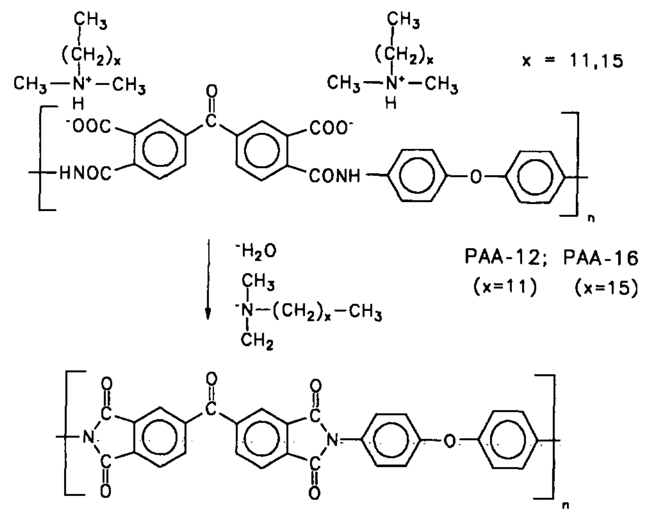

Scheme 1

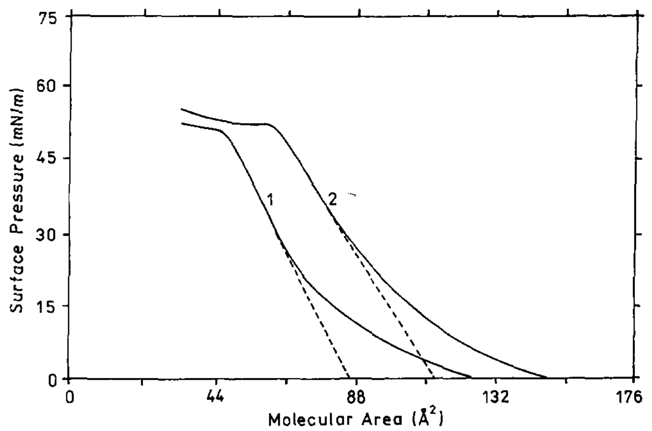

Figure 1 Surface pressure–area isotherms of Langmuir films of polyamic acid salts on water at 11°C: curve 1, PAA-12; curve 2, PAA-16

measured by the differential permeation method using apparatus with a thermal conductivity detector, as described elsewhere[23]. The given permeation rates represent average values obtained with two samples.

Results and discussion

The PAA-12 and PAA-16 polyimide precursors were deposited by the LB technique on PPO asymmetric porous membranes. Preparation and characterization of the support has been described elsewhere[17]. The pressure–area (π–A) isotherms of the films at 11°C are shown in *Figure 1*. The slow non-linear increase of the surface pressure with decreasing area indicated a structural reorganization of the polymer film on water, particularly at the beginning of the compression. Repeating units with shorter aliphatic chains occupied smaller areas. Limiting molecular areas of 0.86 nm^2 and 1.13 nm^2 were estimated by extrapolation of the linear parts of π–A curves for a repeating unit of the dimethyldodecylammonium salt and the dimethylhexadecylammonium salt, respectively.

Temperatures above 300°C were reported as a necessary condition for the complete cyclization of PAA[24]. However, the temperature range applicable to

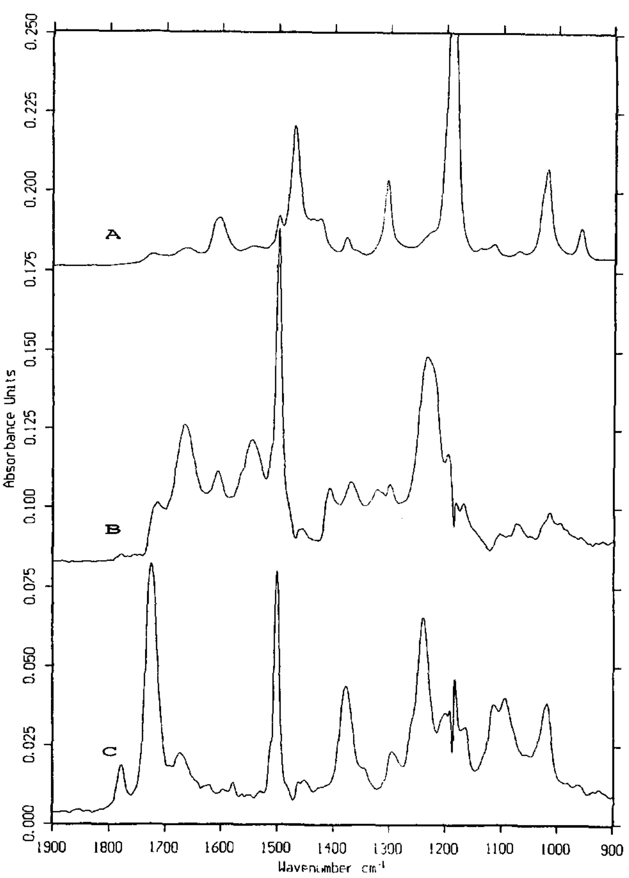

Figure 2 *FT* i.r. multiple internal reflection spectra of LB films (20 layers): (A) PAA-16 on PPO support, ordinate compressed 10 times; (B) PAA-16 on PPO support, PPO spectral bands subtracted; (C) thermally treated PAA-16 (PI) on PPO support, PPO spectral bands subtracted

the composite membranes was limited by the glass transition temperature of the PPO support[25], T_g = 224°C. *FT* i.r. was used for the determination of the extent of cyclization achieved by thermal treatment. Surface-enhanced spectra scanned in a reflection mode show spectral bands of the PPO support with only the most intense bands of the LB film apparent (*Figure 2A*). Using a digital subtraction procedure the spectrum of PPO was eliminated and the spectra of ultra-thin films, both before and after the thermal treatment, were developed. The spectrum of the PAA-16 precursor in *Figure 2B* shows characteristic bands of amide group at 1666 and 1546 cm^{-1} and the band of ionized carboxyl group at 1606 cm^{-1}. After the thermal treatment (*Figure 2C*) all the mentioned bands completely disappeared (the residual absorption at 1670 cm^{-1} corresponds to the benzophenone carbonyl group previously overlapped by the band of the amide group)[26,27]. Simultaneously, a typical doublet of carbonyl group corresponding to imide moiety appeared at 1779 and 1726 cm^{-1} together with the imide C–N band at 1370 cm^{-1}. The spectral changes correspond to the changes found when the precursor was heated in bulk at 300°C. The spectra suggest that the PAA salt in the LB film was completely cyclized even if the applied temperature did not exceed 190°C.

Permeation properties of the composite membranes with the LB ultra-thin separation layers of precursors PAA-12 and PAA-16, and polyimides PI-12 and PI-16

Table 1 Permeation rates *R* through composite membranes with ultra-thin separation layer of PAA-12, PAA-16 and polyimide (PI). *R* ($\times 10^{10}\,\mathrm{mol\,s^{-1}\,m^{-2}\,Pa^{-1}}$) for various gases and therefrom calculated selectivities, α

Ultra-thin layer	R_{O_2}	R_{N_2}	R_{CO_2}	α_{O_2/N_2}	α_{CO_2/N_2}
PAA-12	5.80	2.54	20.51	2.28	8.08
PAA-16	27.30	12.70	76.81	2.15	6.04
PI-12	19.44	8.68	70.13	2.24	8.08
PI-16	12.52	1.60	41.10	7.71	25.73
PI[a]	0.085	0.011	0.277	8.10	26.38
PDA[b]	25.00	50.0	–	2.0	–

[a] Ref. 10

[b] Ref. 13

prepared from PAA-12 and PAA-16, respectively, are summarized in *Table 1*. Permeation rates of N_2, O_2 and CO_2 through the PPO support without an LB film were above the upper limit measurable with the apparatus used. With the separation layer, the permeation decreased to measurable values and the apparent selectivity suggested that pores in the PPO suppport were efficiently overcoated with LB films. All the composite membranes showed permeation rates that were two to three orders of magnitude higher than those of homogeneous films tens of micrometres thick, of other API[9,28]. Homogeneous films, a few micrometres thick, having identical chemical structure to the polyimides used in this work (PI) show permeation rates approximately two orders of magnitude lower than those of the composite membranes with PI-12 and PI-16 LB separation layers[10]. The composite membranes with PAA-12 and PAA-16 ultra-thin films showed only a slightly higher ratio of permeation rates of O_2 over N_2 than composite membranes with a poly(dodecylacrylamide) (PDA) separation layer[13]. The cyclization of PAA-16 LB film decreased the permeation rate particularly for nitrogen, forming a defect-free ultra-thin polyimide separation layer with a high selectivity similar with that of the thick homogeneous polyimide membrane (*Table 1*)[10]. The increase in selectivity of the membrane after cyclization probably reflects considerable differences in the chemical structure of the polyimides and their long-alkyl-chain containing precursors. These differences in chemical structure may be responsible for changes of many polymer properties affecting the gas permeation (charge-transfer complexes, hydrogen bonding, flexibility, ordering, free volume distribution, interchain spacing, etc.)[5,11,29–31] during cyclization, which in consequence can lead to diffusivity selectivity especially favouring the smallest molecules.

As can be seen from *Table 1*, the cyclization of PAA-12 LB film did not lead to a selectivity increase. Aromatic rings of polyamic acid cannot lie flat on the water surface if the long alkyl chain of the amine is shorter than the hexadecyl group[21]. This effect impairs the quality of an LB film because the resulting folds and other structural inhomogeneities are vulnerable to the formation of defects[32] (pinholes), especially during the thermal cyclization (when a film shrinks[33]), with a negative impact on the selectivity.

It may be concluded that a composite membrane with a high permeation rate and good selectivity for gases can be prepared by coating a porous asymmetric thick film of poly(phenylene oxide) with the ultra-thin LB polyimide separation layer.

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