Novel Polyamide Composite Membranes for Gas Separation Prepared by Interfacial Polycondensation

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ABSTRACT: Interfacial polycondensed composite membranes are well known for reverse osmosis. This study describes the preparation of interfacial polymerized composite membranes for gas separation obtained from new polyamides. The polymers were synthesized by derivates of terephthaloylchloride and commercially available multifunctional amines. The membrane polymers consist of linear or crosslinked chains. A high flux of carbon dioxide, 0.3 m^3 m^{-2} h^{-1} bar^{-1}, was observed, combined with a carbon dioxide/nitrogen selectivity up to 30. The permeability to hydrocarbons increased with hydrocarbon vapor concentrations. The synthesis of the thin polyamide layer was transmitted to a continuous production. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 1557–1563, 1997

Key words: interfacial polycondensation; polyamide; gas separation; membranes

INTRODUCTION

Polyamides are very well known for reverse osmosis membranes but less for gas separation.[1] Since 1981, interfacial polyamide composite membranes[2,3] have the best performance in desalination properties. Why choose this kind of membranes for gas separation tasks? Polyamides are very heat resistant and stable in a wide range of pH. The interface reaction guarantees the formation of a very thin polymer film. This method allows the preparation of insoluble polyamide films, which cannot prepared by the Loeb–Sourirajan method. Interfacial condensations mean polycondensation between monomers or crosslinking of a precipitated polymer layer. Until now, the polyamide membranes have usually very low fluxes for gases and vapors. New monomers give the chance to rise the gas permeabilities.

The aim of this study was the development of new monomers for polyamides to prepare interfacial condensed polyamide composite membranes on top 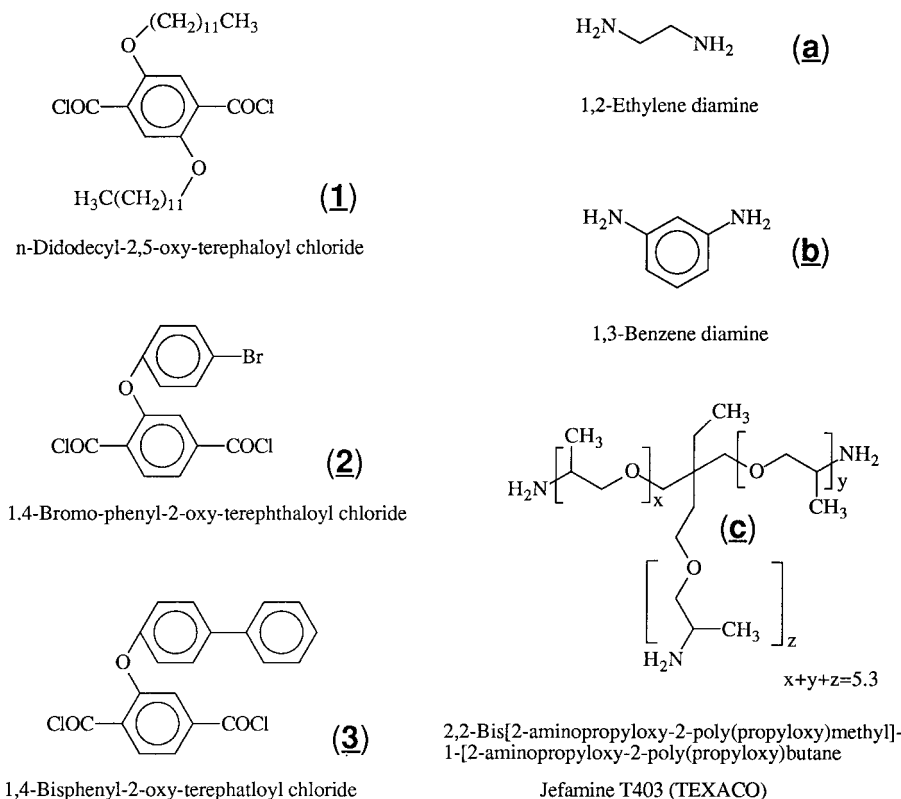of a porous support for gas separation applications. The resulting polyamide films consisted of linear aromatic chains, altering aliphatic/aromatic chains, and crosslinked polymers. A modified and optimized preparation method was developed following the procedure of the preparation of the Cadotte FT-30™ reverse osomsis membrane. The composite gas separation membranes were investigated for gas and vapor fluxes. The polyamide layer was detected by scanning electron microscopy (SEM) analytics. The most promising membrane was prepared in a semiautomatic production. The membrane polymer structure was confirmed by nuclear magnetic resonance (NMR) and elemental analysis.

The interfacial condensation of an amine with a carboxylic acidchloride is a kind of a Schotten Baumann reaction. Figure 1 shows the typical reaction scheme and the types of monomers. The synthesis was carried out between two immiscible solvents like water and hydrocarbons or fluorochlorocarbon.

Membranes of these polymers were not available by casting a polymer solution because they were only soluble in NMP or sulphuric acid. Both attacked the porous polymer support, and a formation of films was not observed.
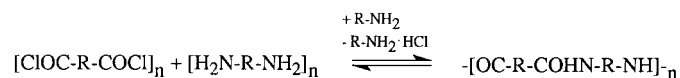

Figure 1   Compounds for interfacial polycondensation.

FUNDAMENTALS

The performance of the composite membrane (polymer film, substrate) is described with the total flux of a gaseous permeant in $m^3\,m^{-2}\,h^{-1}\,bar^{-1}$. The flux for gases were calculated as follows: $m_v = V/(A \cdot t \cdot p)$, where V is the volume of permeated gas, A the membrane area, t the time, and p the pressure driving force across the membrane. A membrane polymer is characterized by its permeability coefficient (P) in cm^3 (STP) cm $cm^{-2}\,s^{-1}$ $cmHg^{-1}$. The permeability coefficient is independent of the the membrane thickness (I): $P = m_v \cdot IIt$ emanates from the product of the Fick's kinetic diffusivity coefficient (D) and the thermodynamic solubility coefficient (S): $P = D \cdot S$. The diffusivity depends on the chain packing and chain flexibility in the polymer matrix. The solubility depends on the condensibility, the free vol-

ume, and the interaction of polymer and permeant. The permeabilities of two gases, A and B, relative towards each other are given by the ideal separation factor $(\alpha)\alpha_{a,b} = P_a/P_b$.

In the case of reverse osmosis, the driving force decreases with the concentration of the minor component because of the increase in osmotic pressure. Therefore, flux is described at given concentrations and pressure. The separation factor is usually given by the rejection $(R\ [\%])$ of the minor component from the feed solution (M_f) to the permeate solution (M_p):

$$R/100 = 1 - M_p/M_f$$

EXPERIMENTAL

Synthesis

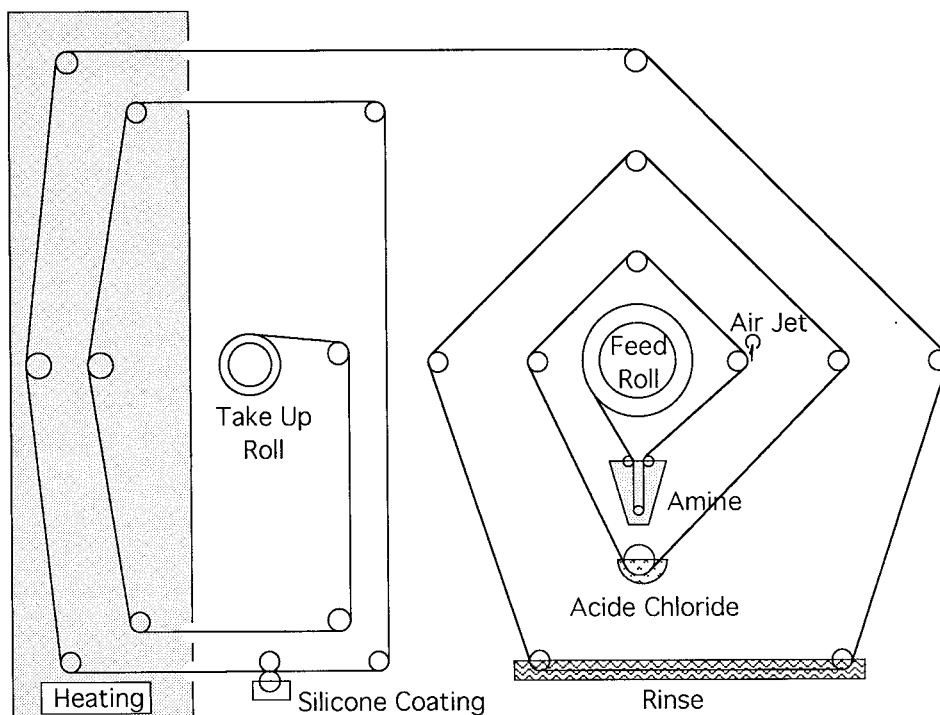During Williamson Ether Synthesis, the 2-nitro-terephthalicacidmethylester or the 2,5-dihydroxy-

Figure 2 Continuous membrane formation apparatus.

terephthalicacidmethylester reacted with the alkane- or aryl-halogenide to get the mono- or dioxy compounds. The product was deesterificated with alcaline. The free acid was converted to the acid chloride. Before each usage for the interface reaction, it was recrystallized from thionylchloride to refresh the acidchloride. The ethylenediamine was distilled under normal pressure, and the *m*-phenylenediamine was distilled under vacuum at about 80°C. The triamine T403 (Texaco) was used as supplied.

Porous Membrane Support

The substrate for the polyamide membrane was a polyetherimide (PEI Ultem™ 1000, General
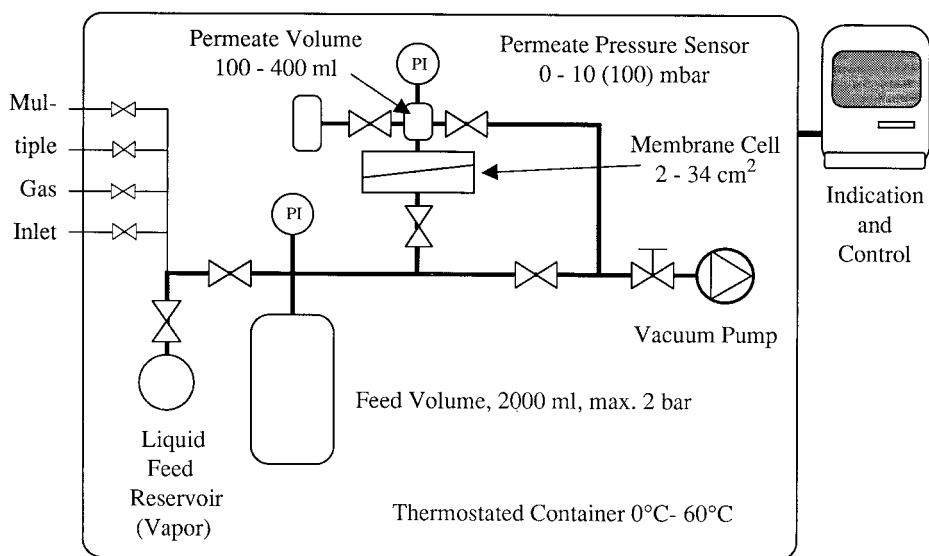

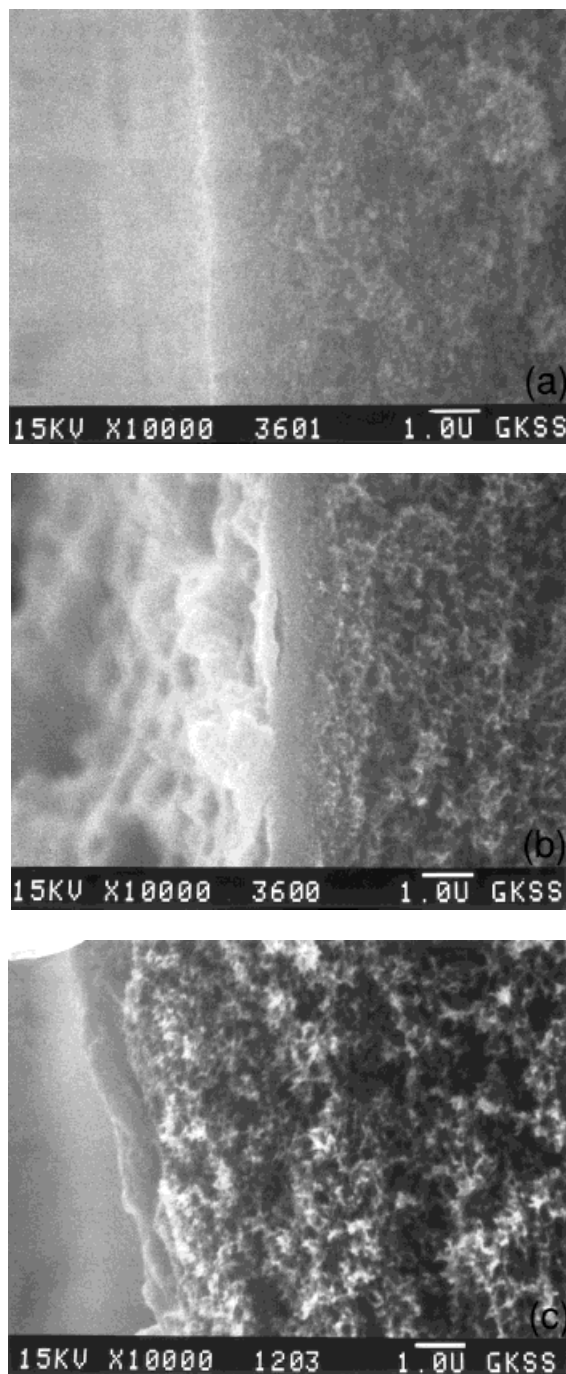**Figure 3** Single gas permeation measurement unit.

Figure 4 Cross section of membranes using different amines: SEM of **1a**, surface layer of about 0.65 μm thickness; SEM of **1b**, surface layer of about 0.5 μm thickness; SEM of **1c**, surface layer of about 0.8 μm thickness.

Electric) ultrafiltration membrane with a cutoff of about 20,000 [kg/mol]. In comparison with polysulfone supports, we found a better adhesion between PEI and the active membrane layer on top of it. In an continuous preparation, a 17.5% solution in dimethylacetamide was continuously cast on top of a fabric nonwoven (Freudenberg 2403) support using a 200 μm knife gap. The polymer was gelled and washed with water. Before the interface reaction took place, the drops of water were removed by a rubber roller from the surface of the wet PEI support.

Interfacial Condensation

The wet drop free support was immersed in a 9.25 millimolar amine water solution for 2 min. After draining the excess solution, it was immersed in a 0.375 millimolar solution of the acidchloride in hexane. The polycondensation was finished after a few seconds. The composite membrane was exposed to air for about 30 min and immersed in methanol to remoisten the pores of the substrate. The composite membrane was washed with water at a temperature of about 60°C for 20 min. After rinsing with water overnight, the membrane was ready to use.

Continuous Membrane Fabrication

This apparatus is shown in Figure 2. The wet PEI support was taken from the feed role and was immersed in the amine solution for about 1 min. Afterwards, the support was freed from an excess of the solution by a strong air stream. The amine-coated support was immersed into a acid chloride solution where the interfacial condensation took place. After finishing the reaction exposure and exposure to air, the residual amine was washed out with water. Finally, a drying procedure with a temperature up to 110°C and an additional coating with silicone closed the composite membrane formation.

Analytical

The synthesis of the acid chlorides was monitored by melting point, NMR, and elemental analysis. Polymers prepared as model substances were examined with with NMR (Bruker AMX-300), differential scanning calorimetry (DSC) (V2, .2A DuPont 9900), and elemental analysis. SEM photographs (JOEL JSM 35C), water flux, and gas permeation experiments were carried out with GKSS equipment. The desalination properties were carried out by a dead end filtration under 10 bar pressure in a 250 mL test cell. The conductivity of the permeate solution was compared with the 0.3% sodium chloride concentration on the feed side.

Table I   Analytical Data of the Polycondensates

Polymer	T_g (°C)	M_p (°C)	Decomposition (°C)	Elemental Analysis (Calculated)	C/H/N Found (Wt %)
1a	—	246.0	359.1	73.1/10.5/5.01	73.0/11.4/5.30
1b	140.7/meso.	274.2	>330.0	75.2/9.63/4.62	74.4/10.2/4.60
1c	no transitions observed	—	—	70.6/10.6/3.53	69.9/10.8/3.57
2a	—	368.3	381.6	73.7/5.06/7.82	72.4/4.91/8.12
2b	172.7	—	337.0	76.8/4.46/6.89	74.5/4.52/6.73
2c	75.7	355.8	367.2	70.2/7.37/4.72	68.2/7.60/4.62
3a	—	346.2	353.8	53.2/3.63/7.76	52.8/3.33/7.92
3b	199.8	—	345.0	58.7/3.20/6.85	57.9/3.31/7.41
3c	60.1	339.8	344.2	57.8/6.49/4.70	57.2/6.75/4.65

Permeation Measurements

Gas flux at high feed pressure was detected using a soap bubble flow meter. The pressure normalized flux m_v was calculated $m_v = V/(A \cdot p \cdot t)\,(\mathrm{m}^3\,\mathrm{m}^{-2}\,\mathrm{h}^{-1}\,\mathrm{bar}^{-1})$. For lower feed pressure up to 2 bar and for the measurement of organic vapor at low partial pressures, an automatic permeation apparature was used, shown in Figure 3. The basis of this method is the detection of a pressure increase in a closed permeate volume. The normalized flux was calculated as $m_v = \{(V \cdot 22.41 \cdot 3600)/(R \cdot T \cdot A \cdot p \cdot t)\} \cdot \ln\{(P_f - P_o)/(P_f - P_t)\}$ with T for temperature, R for gaseous constant, P_f for feed pressure, P_o for permeate pressure at $t = 0$, and P_t for permeate pressure at $t = t$. The apparatus was controlled by computer. Automatic measurements up to ten gases or vapors were possible (Fig. 4).

RESULTS AND DISCUSSION

DSC and Elemental Analysis

Table I shows the glass transition temperatures, melting points, and decomposition temperatures. Polymers **1a** and **1b** have a separate melting points; for all others, decomposition follows directly after melting. Polymer **1b** has an additional transition point at 173.3°C. This transition point and the molecular structure of **1b** suggests the presents of mesophases. Polymer **1c** has a mechanical strength like elastic polymers, but no significant DSC were obtained.

NMR

All polymer compounds were examined by ^{1}H-NMR, 300 MHz, 128 scans, dissolved in sulphuric

Table II   NMR Data of the Polycondensates

Polymer **1a**	Polymer **1b**	Polymer **1c**
$\delta = 7.55$ ppm H_{arom}	$\delta = 7.87$ ppm H_{arom}	$\delta = 7.86$ ppm H_{arom}
$\delta = 4.32$ ppm H_{O-CH}	$\delta = 4.41$ ppm $H_{O-\underline{CH}}$	$\delta = 4.84-3.63$ ppm H_{O-CH} and H_{N-CH}
$\delta = 4.16$ ppm H_{N-CH}	$\delta = 1.91$ ppm $H_{O-CH-\underline{CH}}$	$\delta = 1.96$ ppm $H_{O-CH-CH}$
$\delta = 1.87$ ppm $H_{O-CH-CH}$	$\delta = 1.39$ ppm $H_{O-CH-CH-\underline{CH}}$	$\delta = 1.49$ ppm $H_{O-CH-CH-\underline{CH}}$
$\delta = 1.19$ ppm $_{aliph}$	$\delta = 1.16$ ppm H_{aliph}	$\delta = 1.18$ ppm H_{aliph}
$\delta = 0.78$ ppm H_{CH_3}	$\delta = 0.78$ ppm H_{CH_3}	$\delta = 0.78$ ppm H_{CH_3}
Polymer **2a**	Polymer **2b**	Polymer **2c**
$\delta = 8.02-7.29$ ppm H_{arom}	$\delta = 8.09-7.38$ ppm H_{arom}	insoluble
$\delta = 4.09$ ppm H_{N-CH}		
Polymer **3a**	Polymer **3b**	Polymer **3c**
$\delta = 7.93$ ppm H_{arom}	$\delta = 8.32$ ppm H_{arom}	$\delta = 7.55$ ppm H_{arom}
$\delta = 7.56$ ppm H_{arom}	$\delta = 7.85$ ppm H_{arom}	$\delta = 7.55$ ppm H_{arom}
$\delta = 7.16$ ppm H_{arom}	$\delta = 7.61$ ppm H_{arom}	$\delta = 4.68-3.57$ ppm H_{O-CH} and H_{N-CH}
$\delta = 7.03$ ppm H_{arom}	$\delta = 7.42$ ppm H_{arom}	$\delta = 1.54-1.21$ ppm H_{aliph}
—	$\delta = 7.14$ ppm H_{arom}	$\delta = 0.91$ ppm H_{CH_3}

Table III   Permeation Data of Polycondensates Using Monomer 1

	Nitrogen	Oxygen	Helium	Methane	Carbon Dioxide	Butane (1.5 bar)	Butane (2.0 bar)
Polymer **1a** Flux	29.00	49.62	87.39	55.16	195.37	1,967	4,730
α (Gas/N$_2$)	—	1.71	3.01	1.90	6.74	67.82	163.1
Polymer **1b** Flux	53.84	107.91	241.31	111.65	460.53	3,684	6,870
α (Gas/N$_2$)	—	2.01	4.48	2.07	8.55	68.42	127.6
Polymer **1c** Flux	6.03	23.53	171.56	13.17	144.61	452	1.013
α (Gas/N$_2$)	—	3.90	28.45	2.18	23.99	74.96	168.6
FT-30 like Flux	17.4	16.2	93.6	—	—	—	17.1
α (Gas/N$_2$)	—	0.90	5.38	—	—	—	0.98
α (Knudsen N$_2$)	—	0.93	2.65	1.32	0.80	0.65	0.65

a Flux in 10^{-3} m^3 m^{-2} h^{-1} bar^{-1}.

acid-d_2 exposed to air. The expected polymer structures were confirmed by the chemical shift data (Table II).

Membrane Formation

Interfacial polycondensations carried out in a flask were always successful. A visable thin film was formed at the boundary layer between the immiscible phases of the nonpolar acidchloride solution and the polar amine solution. Stable pressure-resistant polycondensed thin films on top of a porous support were only gotten from polycondensed membranes prepared from terephthaloylchloride derivates (**1a, 1b,** and **1c**) with long aliphatic side chains. Terephthaloylchloride derivates with aromatic side chains were, in general, not able to form a pressure-resistant layer on top of a substrate. Therefore, permeation results could only be obtained from derivates **1a, 1b,** and **1c.**

Reverse Osmosis

The interfacial reaction preparation method was developed and optimized for a polyaramide system well known for reverse osmosis membranes

consisting of 1,3,5-benzene-tricarbonylchloride and m-phenylenediamine. The desalination capabilities of these membranes were compared with the commercially available so-called FT-30™ polyaramide membrane from FilmTec Coorp. With the original FT-30 membrane, we observed a water flux of 19.5 L m^{-2} h^{-1} · 10 bar^{-1} and a rejection of NaCl about 93 (%) using a 0.3% NaCl solution. Our fresh prepared membrane reached a water flux about 24.7 L m^{-2} h^{-1} · 10 bar^{-1} and a rejection of NaCl 94.5 (%). There was no water flux observed across polymers **1a, 1b,** and **1c**.

SEM Pictures

The SEM photographs in Figure 4 show a dense polymer layer of **1a, 1b,** and **1c** on top of the PEI support. All kinds of the layers have different appearances. The surface of **1a,** which has a very poor contrast to the support, is a dense layer of about 0.5 μm. Polymer **1b** has a very rough surface with a thickness of about 0.65 μm. The polyamide layer **1c** with a three-dimensional polymer network has a thickness of about of 0.8 μm and a smooth surface.

Gas Permeation

The permeation values of fluxes of **1a, 1b,** and **1c** were carried out by silicone-coated polyamide

Table IV   Permeation Data of Polycondensate 1c Prepared by Continuous Membrane Formation Method

		Nitrogen	Oxygen	Carbon Dioxide	Methane
Silicone-coated	Flux	12.86	43.53	253.5	29.48
	α (Gas/N$_2$)	—	3.43	19.92	2.32
Non-silicone-coated	Flux	28.14	61.48	301.3	54.65
	α (Gas/N$_2$)	—	2.18	10.70	1.94

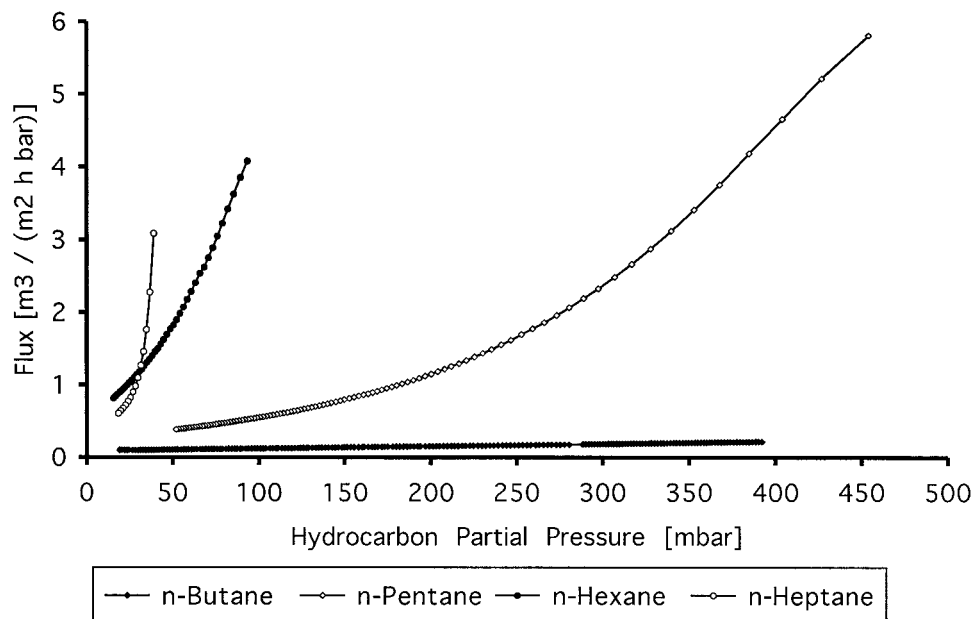Flux in 10^{-3} m^3 m^{-2} h^{-1} bar^{-1}.

Figure 5 Fluxes of organic vapors across the continuous interfacial condensed (1c) composite membrane.

membranes to prevent the influence of small defects of the membrane layer and nonsilicone-coated membranes. All membranes presented in Table III showed a strong affinity to condensable hydrocarbons, which depends on their feed concentration. The linear polymers showed lower N_2/O_2 selectivities of about 2 but higher n-butane fluxes than the crosslinked polymer. The membrane consisting of polymer **1c** had an interesting selectivity for CO_2/N_2 of about 24 and for CO_2/CH_4 of about 11.

The preparation method of **1c** were optimized and transposed to an automatic preparation procedure. Table IV shows the average permeation results of inert gases, and Figure 5 shows the permeation of organic vapors related to the feed concentration. The flux rates shown in table IV are higher than those shown in Table III. The reproducibility of the membranes can be expressed by the standard deviation of their flux. The standard deviation of the average value of the nitrogen flux decreases from ±3.59 for uncoated automatic prepared membranes to 0.43 for silicone coated ones. Compared to the nonautomatic prepared membranes, this interfacial condensed films seems to

be more homogeneous, and the fluxes of each gas increased twice times.

CONCLUSION

It was shown that interfacial condensed polyamide composite membranes for gas separation have sufficient performance in flux and selectivity. The data show high selectivities and high fluxes. Investigated membrane polymers showed a intensive interaction to condensible gases and vapors. Long aliphatic side chains supported a successful membrane formation. The interfacial polycondensation preparation method is a tool to design poly- and copolymers without any limits about solubilities of the membrane polymers.

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