Mixed Matrix Membranes Based on 3-Aminopropyltriethoxysilane Endcapped Polyimides and Silicalite-1

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ABSTRACT: To improve membrane permeability and the quality of the polymer-zeolite interface such that the separation factor is maintained or enhanced, we adopted a novel approach to the preparation of mixed matrix membranes (MMMs). Our approach involved endcapping polyamic acid (PAA) with the coupling agent 3-aminopropyltriethoxysilane (APTES) and then bonding the endcapped polyimide (PI) to silicalite-1. The APTES-endcapped polyimide precursors reacted with silanol groups on the silicalite-1 surface and were transformed into the final polyimide (PI) matrices. Five precursors were used to create five series of MMMs; each series contained membranes with a content of silicalite-1 ranging from 0 to 50 wt %. The helium perme-ability coefficient of the membranes was measured and found to be dependent on both the amount of filler and type of PI matrix. In the most permeable series, helium permeability coefficient increased from 16.3×10^{-15} mol m^{-1} s^{-1} Pa^{-1} for unfilled membranes to 69.1×10^{-15} mol m^{-1} s^{-1} Pa^{-1} for membranes containing 30 wt % silicalite-1. The ideal helium/nitrogen separation factor ranged between 22 and 45. Thus, it seems that our novel approach improves the interfacial adhesion of MMMs. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 124: E233–E240, 2012

Key words: membranes; polyimides; zeolites; interfaces; gas permeation

INTRODUCTION

Gas separation by selective permeation through polymer membranes is one of the fastest growing branches of separation technology. Much attention has been devoted to polyimides (PIs) because of their high selectivity in gas separation and their excellent thermal, chemical, and mechanical stability. Nevertheless, PI membranes have traditionally had low gas fluxes. The incorporation of microporous/mesoporous materials, such as zeolites, into PIs may increase their permeability. Consequently, many researchers have prepared zeolite-filled mixed matrix membranes (MMMs).[1–13] Early attempts at designing MMMs focused on using rubbery polymers to serve as the polymer matrix. Some improvements in separation performance associated with adding zeolites to rubber polymers were reported.[1] However, the preparation of MMMs based on glassy polymers, such as PIs, has generally resulted in a decrease in selectivity, primarily due to a poor qual-ity polymer-zeolite interface.[2,3] Several authors have attempted to improve the interface by modifying the filler surface.[4–6] But filler treatment has various risks, including the formation of a multilayer and treatment agent penetration into the filler pores, both of which effects may result in pore blockage.

Therefore, to improve polyimide/silicalite-1 interfacial adhesion, we developed a novel approach to polymer modification. Our modification consisted of endcapping the PI precursor, polyamic acid (PAA), with 3-aminopropyltriethoxysilane (APTES). This endcapped precursor can subsequently react with silanol groups on the silicalite-1 surface and, thus, form chemical bonds between the polymer and the filler surface.[14] We prepared APTES-terminated PIs that differed in chemical composition, containing up to 50 wt % silicalite-1 (with a crystal length of about 20 μm). We measured the helium permeability of the MMMs and determined the ideal helium/nitrogen separation factors for selected series.

EXPERIMENTAL

Materials

Before use, 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), 4,4′-oxydiphthalic anhydride

(ODPA) (both Chriskev) and pyromellitic dianhydride (PMDA) (Aldrich, Czech Republic) were heated under vacuum to 180°C overnight; 4,4′-(1,4-Phenylenediisopropylidene)bisaniline (BIS P) (Mitsui, Japan), 4,4′-oxydianiline (ODA) (Aldrich), and 3-aminopropyltriethoxysilane (APTES) (ABCR, Germany) were used as received. N,N-Dimethylformamide (DMF) (Aldrich) was distilled under vacuum over phosphorus pentoxide and stored in an inert atmosphere. Tetrapropylammonium bromide (Fluka, Czech Republic), sodium bicarbonate (Aldrich) and a 30 wt % aqueous suspension of amorphous silica particles (Tosil) (Tonaso Nestemice, Czech Republic) were used as received.

Preparation of silicalite-1 crystals

The synthesis proceeded according to the protocol by Kornatowski.[15] The silica sol (Tosil) was reacted with the tetrapropylammonium bromide and sodium bicarbonate to form silicalite-1 crystals. The reaction gel was heated without stirring at 180°C in a Teflon-lined stainless steel autoclave at autogenous pressure. Crystal size was controlled by the duration of crystallization, which ranged from 8 to 24 h. After cooling of the autoclave, the crystals were filtered, washed, and dried. The template tetrapropylammonium cations were removed in a single-step calcination process under an air stream of 600 mL min^{-1}. The following heating program was applied to a thin layer of crystals: heated up to 550°C at a rate of 0.5°C min^{-1}; maintained at 550°C for 12 h; cooled down to laboratory temperature at a rate of 2°C min^{-1}. The pore size of silicalite-1 zeolite is in the range 0.51 to 0.56 nm.

Synthesis of polymer precursors

To exclude the effects of air humidity, all glassware was dried in an oven at 120°C for 3 h before use and all syntheses were carried out under an inert atmosphere. Each polyimide precursor (PAA) was prepared in a 250-mL two-necked flask equipped with a magnetic stirrer and a nitrogen inlet/outlet. A typical example of the PAA synthesis carried out (M_n = 10,000 g mol^{-1}) is described as follows for PAA(ODPA-ODA):

- 5.926 g (0.0191 mol) ODPA was dissolved in 30 mL of DMF
- 0.454 g (0.0021 mol) of APTES was added to the reaction mixture (weighing dish and funnel rinsed with 15 mL DMF) and allowed to react with ODPA for 2 h
- 3.658 g (0.0183 mol) ODA was added (15 mL DMF again used for rinsing) and allowed to react at room temperature for 24 h

All PAAs were prepared as 15 wt % solutions, but, to reduce membrane thickness, were subsequently diluted with more DMF to 10 wt % solutions. The diluted PAA solutions were used as the PI precursors.

Membrane preparation

The membranes were prepared either from PAA solution alone (unfilled PI membranes) or from filler-dispersed PAA solution (filled PI membranes). Each dispersion was prepared by adding silicalite-1 crystals to a PAA solution and stirred for at least 1 h. Each solution or dispersion was then cast on a Teflon support and heated at 50°C for 12 h. When most of the solvent had evaporated, the film was thermally imidized stepwise at 100°C/1 h, 150°C/1 h, 200°C/2 h, and 230°C/1 h. The imidized film was removed from the support and characterized. The silicalite-1 content in the resulting MMMs ranged from 0 to 50 wt %.

Characterization techniques and instrumentation

An M80 infrared spectrometer (Carl Zeiss Jena, Germany) was used to analyze the PIs and their precursors (solutions in DMF). A Jeol JSM-5500LV scanning electron microscope was used to observe the separate particles (filling) and areas of membrane fracture. The membranes were cut and covered by a thin layer of platinum to prevent the accumulation of surface charge. A DuPont 951 thermogravimetric analyzer was used to carry out thermogravimetric analyzes as the temperature rose from 25 to 800°C at a rate of 10°C min^{-1} under an air stream of 60 mL min^{-1}.

Permeation measurements and data treatment

A non-stationary permeation apparatus (Fig. 1) was used to measure the permeation of single component gases through the membranes by observation of the pressurized gas release from a reservoir throughout the membrane cell.[16] The downstream membrane side was either evacuated or kept at ambient pressure. All measurements were carried out at 25°C. The fluxes (permeances and permeabilities) are determined from the mass balance of the species in the volume V_{Σ} of the semiopen system of the apparatus which makes possible to estimate simultaneously both flux and its driving force by monitoring the time dependence of the pressure p in the apparatus on time. The volume V_{Σ} is represented optionally either as $V_{\Sigma} = \Sigma V_{ti}$ (calibrated total volume of the tubings—for slow permeation runs) or as V_{Σ}
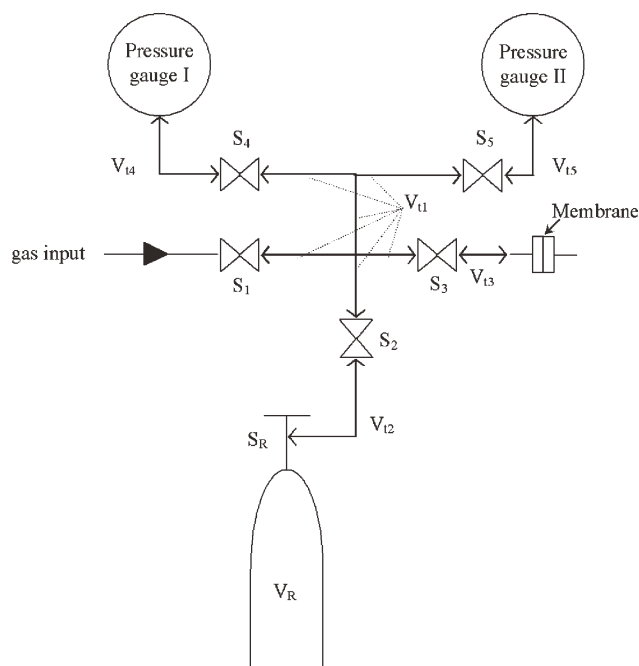
Figure 1 Scheme of the permeation apparatus. $V_{t1}...$ V_{t5} are the volumes of the respective tubing sections; V_R is the cylinder volume; $S_1 ... S_R$ are the on-off valves (stopcoks).

$= \Sigma V_{ti} + V_R$ (for rapid permeation runs). For explanation of the symbols compare Figure 1.

The treatment of the permeation runs is based on eq. (2), which combines the mass balance for permeation apparatus [cf. left equation of eq. set (2) and the constitutive equation for single component (species) transport through the membrane compare eq. (1).

$$j = P\frac{\Delta p}{\delta} = P\frac{p - p_a}{\delta} \qquad (1)$$

$$-\frac{d\Delta p}{dt} = \frac{jQRT}{V_\Sigma} = \frac{PRTQ}{V_\Sigma\,\delta}\Delta p = \alpha\Delta p \qquad (2)$$

In these equations,

- P represents the permeability coefficient of the penetrant [mol m^{-1} s^{-1} Pa^{-1}],
- δ represents the membrane thickness,
- p is the actual pressure in the apparatus,
- p_a is the pressure of the ambient atmosphere,
- j is the flow density [mol m^{-2} s^{-1}] of the penetrant through the membrane, and
- Q denotes the membrane area.

Equation (1) assumes the existence of a quasi-stationary state namely, that a steady-state concentration profile of the penetrant is in the membrane at any given (instance of) time. The existence of a quasi-stationary state in the membrane also validates

relation (3), where K_Σ is the overall Henry's law constant for the penetrant in the membrane.

$$\frac{V_\Sigma}{RT} >> Q\delta K_\Sigma \qquad (3)$$

The solution of differential equation for $\Delta p(t)$ [eq. set (2)] with the initial condition $\Delta p\,(0) = \Delta p_0$ can be rewritten as eq. (4), which is suitable for the evaluation of the parameter α and thus the permeability coefficient P [cf. the right of eq. set (2)].

$$\ln\{\Delta p(t)/\Delta p_0\} = \ln\{\exp(-\alpha t)\} = -\alpha t \qquad (4)$$

The separation efficiency is characterized here by ideal separation factor $S_{\text{He-N2}}$ defined as the ratio of the He permeability coefficient divided by N$_2$ permeability coefficient.

RESULTS AND DISCUSSION

Preparation and characterization of MMM constituents

We prepared calcined silicalite-1 crystals of a length of 20 μm. The iodine indicator method was used to check the accessibility of the silicalite-1 pores (completeness of calcination).[17] The silicon : aluminum ratio of the silicalite-1 crystals was approximately 360 : 1. Due to their low aluminum content, the crystal samples were sufficiently hydrophobic to be exposed to atmospheric humidity under manipulation.

To achieve good polymer-filler adhesion, we prepared PI precursors endcapped with APTES (Scheme 1). The amount of APTES influences the concentration and molecular weight of the final polymer. Because a lower molecular weight means poorer mechanical characteristics, PIs with a theoretical number average molecular weight of 10,000 g mol^{-1} were used to ensure self-standing MMMs.

The APTES-endcapped PAAs were based on the following dianhydride and diamine combinations: PMDA and ODA [PAA(PMDA-ODA)]; ODPA and ODA [PAA(ODPA-ODA)]; PMDA and BIS P [PAA (PMDA-BIS P)]; ODPA and BIS P [PAA(ODPA-BIS P)]; and 6FDA and ODA [PAA(6FDA-ODA)]. All PAAs were prepared as 15 wt % solutions in DMF. Because higher concentrations of PAA resulted in higher viscosity solutions and, thus, thicker final membranes, all PAAs were subsequently diluted to 10 wt % solutions in DMF.
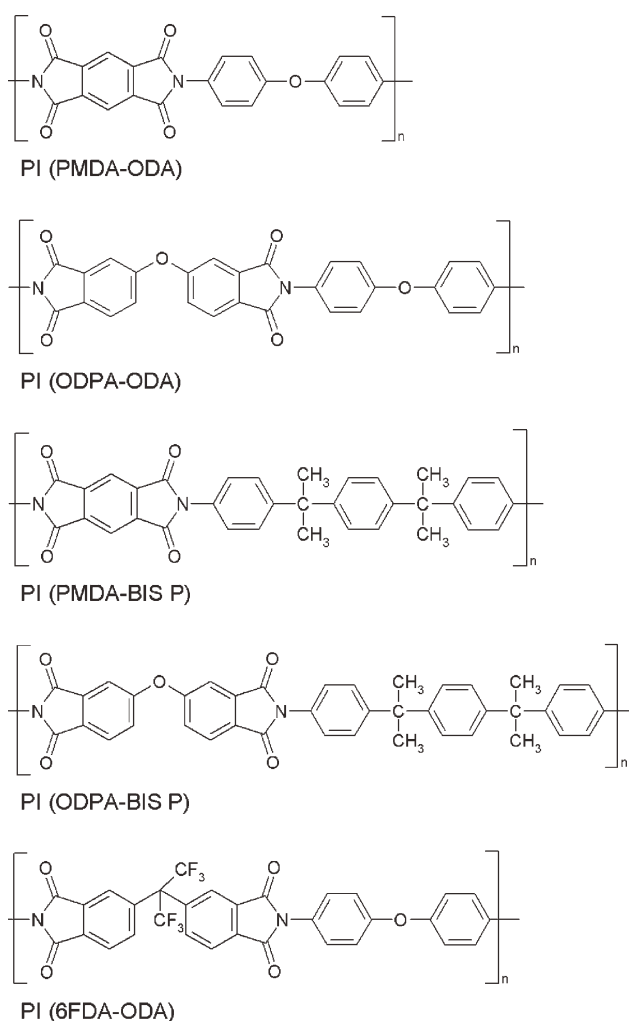
Thermal treatment of these precursors was used to obtain their corresponding endcapped PIs [PI (PMDA-ODA), etc.]; the chemical structures of these PIs are shown (without end groups) in Figure 2. The PI structures were analyzed by IR spectroscopy and the IR records compared with those of their
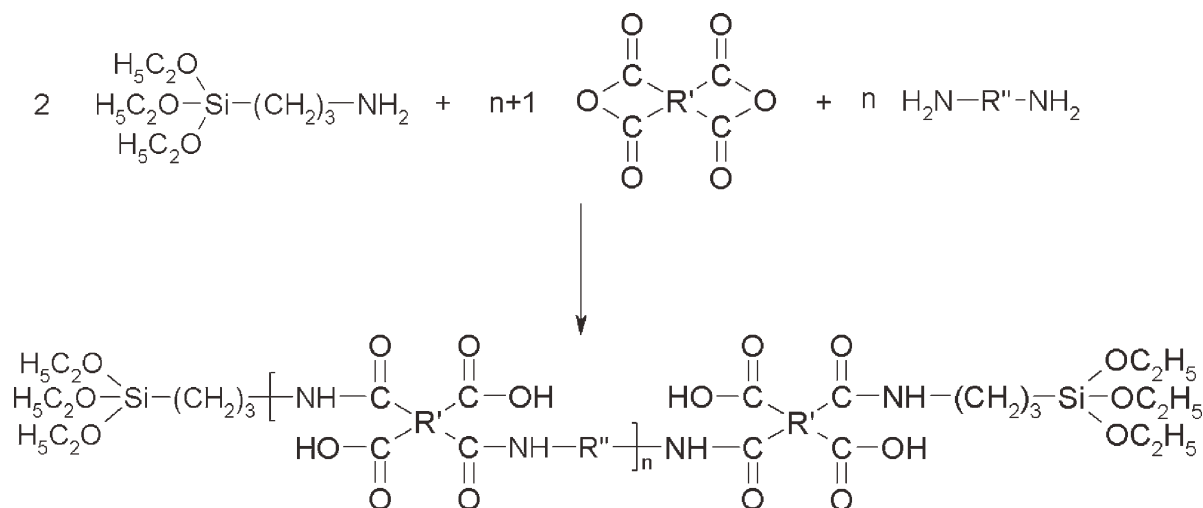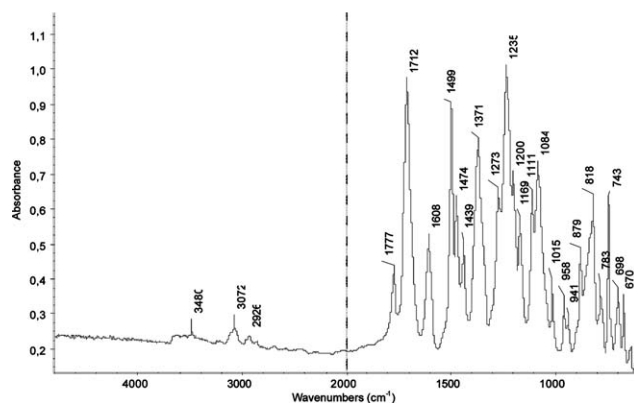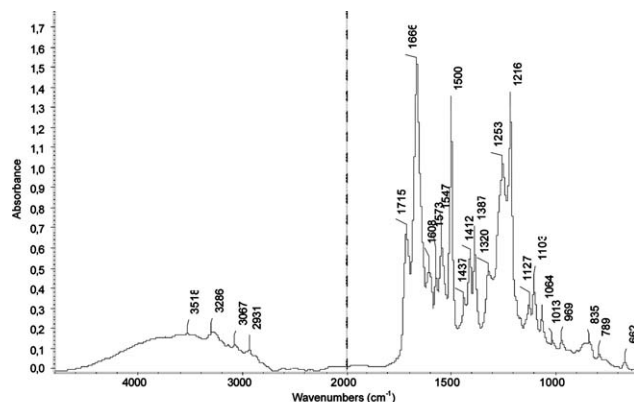
Scheme 1 Preparation of APTES endcapped PI precursors.

precursors. The IR spectra of PAA(ODPA-ODA) and PI(ODPA-ODA) are shown in Figure 3 to illustrate the typical absorption bands of these polymers. The


PI (PMDA-ODA)

PI (ODPA-ODA)

PI (PMDA-BIS P)

PI (ODPA-BIS P)

PI (6FDA-ODA)

Figure 2 Chemical structures (without end groups) of PIs used in this study.

band at about 1670 cm^{-1} in the PAA(ODPA-ODA) spectrum belongs to the —CONH— groups of PAA and its absence from the PI(ODPA-ODA) spectrum suggests a high degree of imidization (PAA transformed to PI). So, too, does the presence in PI(ODPA-ODA) of absorption bands around 720 cm^{-1} (ring deformation), 1370 cm^{-1} (C—N stretching), and 1780 and 1720 cm^{-1} (symmetric and

Figure 3 Infrared spectra of APTES-endcapped PAA (ODPA-ODA) (top) and APTES endcapped PI(ODPA-ODA) (bottom).
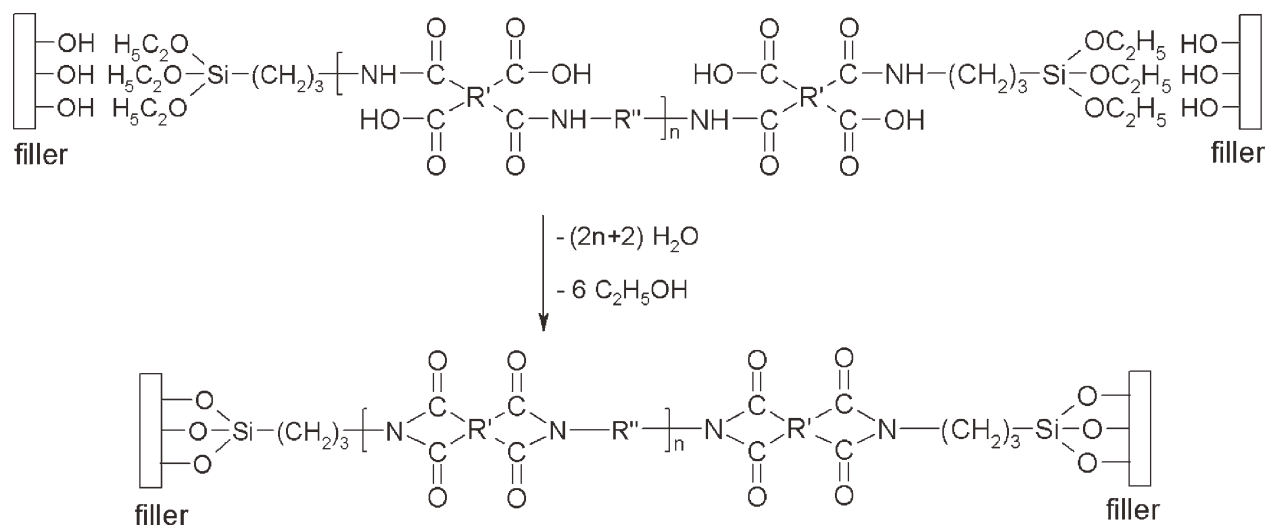
Scheme 2 Reaction between APTES-endcapped PI precursor and silicalite-1.

asymmetric stretching of carbonyl groups), all of which are characteristic of an imide ring structure.[18] The band around 1080 cm^{-1} represents Si—O—Si linkages derived from APTES.

Mixed matrix membranes were prepared by the thermal treatment of the APTES endcapped-PAA containing silicalite-1. During heating, the groups of APTES endcapped-PAA reacted with silanol groups on the silicalite-1 surface, and the PAA was transformed into the final PI matrix shown in Scheme 2. The thickness of the MMMs was around 100 μm, increasing slightly as the amount of filler increased.

Five series of MMMs were prepared; one series for each of the monomer combinations specified above. For each series, membranes were created with a silicalite-1 content of 0, 10, 20, 30, or 50 wt % silicalite-1 [also 40 wt % in the case of PI(ODPA-ODA)]. Each of the APTES-endcapped PIs formed self-standing membranes filled with silicalite-1. When APTES was not used, only PI(6FDA-ODA) formed self-standing membranes.[19]

Figure 4 shows the SEM cross-section of the MMM prepared from PI(6FDA-ODA) and 50 wt % silicalite-1. It indicates satisfactory adhesion between the organic and inorganic phases and a fairly low concentration of micropores under the thin and compact polymer layer.

To establish more clearly the quality of the PI/silicalite-1 interface, we prepared two MMMs containing larger filler crystals (190 μm) and analyzed them by SEM. The first MMM was prepared from PI(6FDA-ODA) without being endcapped by the coupling agent. A cross-section of this MMM (Fig. 5, top) shows the smooth surfaces of two large crystals that are clearly detached from the PI surrounding them. The second MMM was prepared from APTES-endcapped [PI(6FDA-ODA]. A cross-section of this

MMM (Fig. 5, bottom) shows the surface of two large crystals surrounded by PI that, in this case, is strongly attached to the crystals. Pieces of PI are clearly adhered to the front surface of both crystals. This is clear evidence that the use of APTES improves the adhesion between the PI and the surface of silicalite-1.

TGA established the excellent thermo-oxidative stability of the prepared samples. Figure 6 shows the results for APTES-endcapped PI(6FDA-ODA) filled with silicalite-1.

We assumed that thermal stability is dependent on the amount of filler, but this was not confirmed. The degradation of all materials started at about 400°C, with a 5 wt % loss being observed around 500°C. The amount of ash roughly corresponded with the amount of filler in the APTES-endcapped PIs.
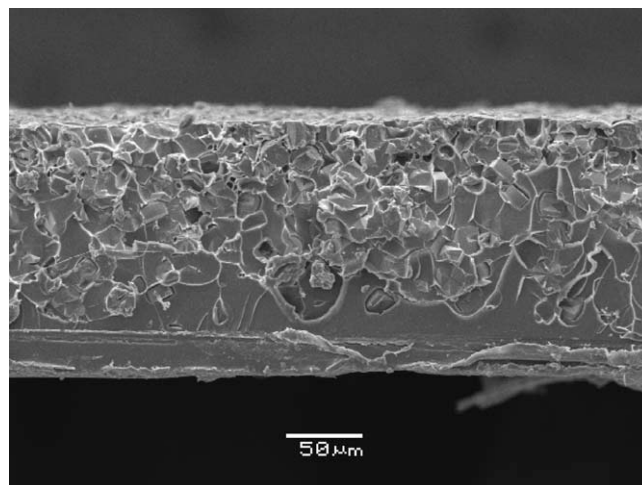
Figure 4 SEM cross-section of MMM prepared from APTES-endcapped PI(6FDA-ODA) and 50 wt % silicalite-1 (size 20 μm).
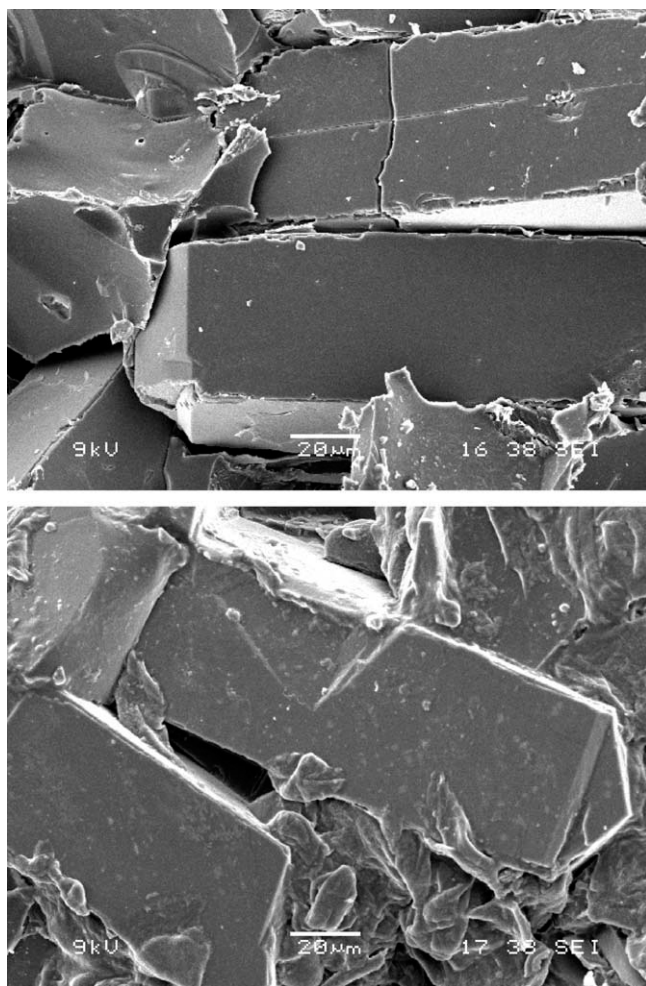
Figure 5 SEM cross-section of MMM prepared from PI(6FDA-ODA) and silicalite-1 (crystal size 90 μm) (top) and of MMM prepared from APTES-endcapped PI(6FDA-ODA) and silicalite-1 (bottom).

Permeation characteristics of MMMs

To study the dependence of membrane permeability on the amount of filler and type of PI matrix, we prepared five series of membranes by combining a given type of PI with different amounts of silicalite-1. However, the MMMs from the series [PI(PMDA-BIS P)] and some of those containing a higher silicalite-1 concentration could not be well attached to the measuring cell because of their brittleness. The results are presented in Table I. The uncertainty for the permeability coefficient values was determined to be better than 10 rel % (for 95% probability level). From this point of view the differences in permeability coefficients are statistically significant with exception of those for PI(PMDA-ODA) and PI(ODPA-ODA) up to 30 and 20 wt.% silicalite-1 content, respectively.

The helium permeability coefficients of the unfilled APTES-endcapped PIs were in good agreement with other values published for unfilled PIs

prepared from the same monomer combinations.[20–22] For the filled PIs, helium permeability was found to be dependent on both the amount of filler and type of PI matrix.

The PI(PMDA-ODA) and PI(ODPA-ODA) series had much lower permeability than the PI(ODPA-BIS P) and PI(6FDA-ODA) series. At each level of filler content, the permeability of the PI(PMDA-ODA) and PI(ODPA-ODA) membranes was practically identical, which means that the substitution of PMDA with ODPA had no effect on helium permeability.
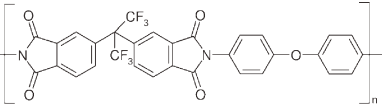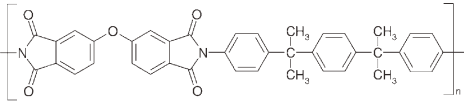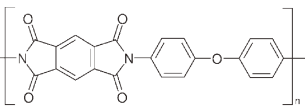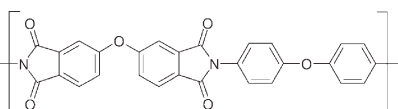
Conversely, the replacement of PMDA with 6FDA increased the permeability coefficient by a factor of about eight: from 2.1×10^{-15} to 16.3×10^{-15} mol m^{-1} s^{-1} Pa^{-1}. This increase was greater for the MMMs with higher filler content; for example, the permeability coefficient of the membrane containing 30 wt % of silicalite-1 increased by more than one order of magnitude from 6.1×10^{-15} mol m^{-1} s^{-1} Pa^{-1} to 69.1×10^{-15} mol m^{-1} s^{-1} Pa^{-1} (see Table I). Therefore, it seems that the replacement of PMDA with 6FDA enlarged the free volume by causing a significant increase in d-spacing, the average intersegmental distance in the polymer structure; the d-spacing for PI(PMDA-ODA) was 0.46 nm, but for PI(6FDA-ODA) was 0.56 nm.[23] Although the chain stiffness of PI(6FDA-ODA) is influenced by the $-C(CF_3)_2-$ linkages [PI(6DA-ODA) with uncontrolled molecular weight shows a glass transition temperature $T_g = 294°C$],[24] it is still lower in comparison with PI(PMDA-ODA) ($T_g > 400°C$, if any). Thus, the increase in the free volume probably namely explains the higher permeability of the PI(6FDA-ODA) series compared with the PI(PMDA-ODA) series.

The ideal helium/nitrogen separation factor S_{He-N2} was evaluated only for the membrane series PI(6FDA-ODA) which exhibited the highest permeability of both penetrants. The permeability
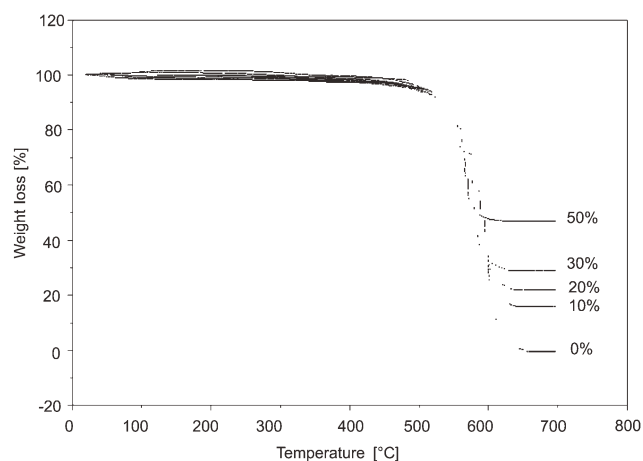
Figure 6 TGA results for APTES-endcapped PI (6FDA-ODA) filled with 0 to 50 wt % of silicalite-1.

TABLE I
Characteristics of Membranes Filled with Silicalite-1 (size 20 μm)

Polymer matrix type	Content of filler (wt %)	Permeability of He (10^{-15} mol m^{-1} s^{-1} Pa^{-1})
6FDA-ODA	0	16.3
	10	27.6
	20	43.2
	30	69.1
ODPA-BIS P	0	6.4
	10	9.3
	20	24.7
	30	35.8
PMDA-ODA	0	2.1
	10	3.7
	20	5.9
	30	6.1
	50	17.2
ODPA-ODA	0	2.2
	10	3.5
	20	5.0
	30	9.7
	40	10.1
	50	12.6

coefficients of N_2 were 0.74×10^{-15}, 0.81×10^{-15}, and 1.54×10^{-15} mol m^{-1} s^{-1} Pa^{-1} for PI(6FDA-ODA), PI(6FDA-ODA) + 10 wt % silicalite-1 and PI(6FDA-ODA) + 30 wt % silicalite-1, respectively. The separation factor of PI(6FDA-ODA) without silicalite-1 was 22 (Xiao et al.[25] presented for PI(6FDA-ODA) with uncontrolled molecular weight $S_{\text{He-N2}}$ 45), but increased, as the amount of filler increased, to between 34 and 45. This is another strong indication of the good interfacial adhesion that can be achieved by endcapping a PI precursor that subsequently reacts with silanol groups on the filler surface. Thus, a preparation approach that leads to the formation of chemical bonds between the polymer matrix and the filler surface seems to be a highly promising way of increasing both MMM permeability and selectivity.

CONCLUSIONS

We successfully used a novel approach for the preparation of MMMs from APTES-endcapped PIs filled with silicalite-1 crystals. APTES acted as a coupling agent, chemically bonding the organic polymer with the inorganic filler.

The helium permeability coefficients of the prepared membranes ranged from 2.1×10^{-15} to 69.1×10^{-15} mol m^{-1} s^{-1} Pa^{-1}. It increased as the amount

of filler increased and was shown to be dependent on both the accessibility of the filler pores and the type of polyimide matrix. Nitrogen permeability was also measured for selected membranes. The ideal helium/nitrogen separation factor increased from 22 (membrane without filler) to 45 (membrane with 30 wt % silicalite-1). These results suggest that our novel approach to the preparation of MMMs is a highly promising way of increasing both the permeability and selectivity of these membranes, and, thereby, of improving interfacial adhesion.

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