# Polyimide Membranes Derived from Poly(amic acid) Salt Precursor Polymers. 2. Composite Membrane Preparation

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ABSTRACT: A novel two-step process for fabrication of composite polyimide hollow fiber membranes using poly(amic acid) tertiary amine salts, PAAS, is described. In the first step, a precursor membrane is formed by depositing a thin PAAS polymer layer from an alcohol-based solution onto a porous hollow fiber substrate. In the second step, the final composite polyimide membrane is obtained upon thermal treatment of the precursor composite PAAS membrane at 150 °C. The novel process was demonstrated by preparing a composite polyimide membrane on a polysulfone hollow fiber substrate from the PAAS polymer (6FDA-ODA/$Et_3N$) derived from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA), 4,4′-oxydianiline (ODA), and triethylamine. The surface layer and cross section of the precursor composite PAAS membrane and the final polyimide membrane were studied by SEM. The quantitative transformation of PAAS prepolymer into the respective polyimide by heat treatment at 150 °C was confirmed by ATR FT-IR analyses. Gas permeation characteristics of composite PAAS and polyimide membranes were measured and are reported.

## Introduction

Polymeric gas separation membranes can be divided into two configurations, asymmetric and composite.[1,2] The composite membrane consists of a dense thin polymer layer that provides desired gas separation characteristics, deposited on top of a porous support material. Asymmetric membrane is formed from a single membrane forming material and consists of a substantially dense separation layer supported by a graduate density porous structure. Composite membranes offer several advantages over the more widely used asymmetric membranes.[3] The composite configuration offers the ability to decouple the gas separation and permeation characteristics of the separation layer from the membrane forming characteristics and mechanical strength requirements of the porous support.[4,5] It is economically feasible to use unconventional and frequently expensive polymers in the preparation of the separation layer due to the small amount of the material required. Furthermore, it is feasible to utilize an inexpensive commercial polymer, such as polysulfone, as the porous support material in composite membrane preparation.

A major challenge in the preparation of composite membranes is to find a solvent system for the deposition of the selective polymer layer that is compatible with the porous support. Frequently, a solvent for the coating material swells or dissolves the substrate. Even though numerous polymeric materials have been discovered with good combination of gas separation and permeation properties that are attractive for industrial applications, they have found little use in real world membrane manufacturing due to the solvent compatibility issue.

A number of attempts have been made to fabricate composite polyimide membranes from poly(amic acid), PAA, precursors.[6−8] Poly(amic acid) polymers are frequently processed into the target article utilizing aggressive aprotic solvents, such as DMF. This makes it difficult to form composite membranes from PAA precursors. Poly(amic acid)s are also known to be hydrolytically unstable. The storage time of the precursor polymer is limited. This makes it difficult to obtain composite membranes with reproducible gas separation characteristics. To convert the poly(amic acid) prepolymer into the final polyimide by thermal treatment, high temperature, as high as 300 °C, is often utilized. A porous polymeric substrate that possesses a glass temperature in excess of 300 °C will thus be required to form a composite polyimide membrane from the polyamic acid precursor by thermal imidization in order to maintain the substrate porosity. For this and other reasons, fabrication of composite polyimide membranes from the poly(amic acid) precursors has achieved limited success. Most recently, Polotskaya et al. reported fabrication of composite polyimide membranes from poly(amic acid) solutions containing large amounts of imidazole or benzimidazole.[8,9] They found that the use of these specific membrane casting compositions significantly lowered the imidization temperature. However, the authors used a high-temperature boiling solvent, DMF, and a nonvolatile catalyst in composite membrane preparation that presented severe drawbacks. The final composite membrane thus exhibited inferior gas permeation characteristics.

Herein, we describe the fabrication and characterization of composite polyimide hollow fiber membranes by using poly(amic acid) salt precursors.[10] In an accompanying paper, we described the synthesis and characterization of poly(amic acid) tertiary amine salt polymers tailored toward composite gas separation membrane preparation needs. The methodology is broadly applicable to preparation of a wide variety of composite polyimide membranes, and the novel approach is demonstrated here with a polyimide derived from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride and 4,4′-oxydianiline. The 6FDA-ODA polyimide was chosen for initial experiments because numerous studies have shown that this polyimide exhibits good combination of gas separation factors and permeability coefficients for $CO_2/CH_4$ separation application.[11−14] Despite the fact that the 6FDA-ODA polyimide is one of the most organo-

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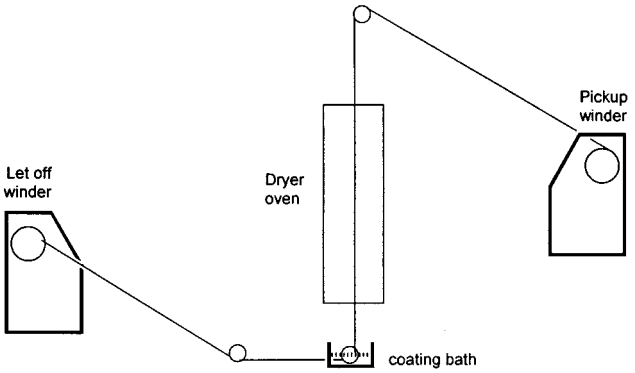



**Figure 1.** Schematic process for the preparation of composite membranes.

soluble polyimides, its solubility characteristics still make it impossible to fabricate composite membranes utilizing a conventional polymeric substrate, such as polysulfone.[14,18,19] To the best of our knowledge, we report here the first example of preparation of a composite polyimide hollow fiber membrane that is based on a polysulfone substrate.

## Experimental Section

**Instruments.** ATR FT-IR spectra were recorded on a Nicolet Avatar 360 FT-IR instrument equipped with an Omni-ATR attachment. Scanning electron micrographs were obtained on an ISI DS 130 SEM instrument by Analytic Answers, Inc. The hollow fiber cross sections were prepared by freeze fracture in liquid nitrogen.

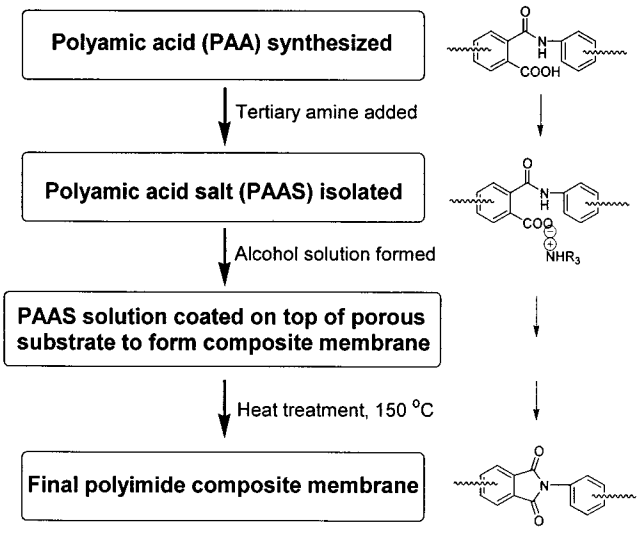
**Materials.** 2,2-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride and 4,4′-oxydianiline were purchased from Clariant Corp. and Chriskev Co., Inc., respectively, and used as received. Triethylamine was purchased from Aldrich Chemicals. The synthesis of poly(amic acid) triethylamine salt polymer 6FDA-ODA/$Et_3N$ is reported in an accompanying paper. Porous polysulfone hollow fibers with o.d./i.d. of 0.40 mm/0.20 mm were prepared in this company by a dry-wet spinning process according to procedures described elsewhere.[15] The polysulfone material was Udel3500 polysulfone from Amoco. Other solvents and materials were all acquired from commercial sources and used as received.

**Preparation of Composite Polyimide Hollow Fiber Membranes.** The precursor composite PAAS hollow fiber membranes were obtained by coating predried porous polysulfone hollow fibers with a dilute solution of PAAS polymer in methanol. The hollow fibers were drawn through the coating solution at a speed of 10 m/min, and the solvent was evaporated in a dryer oven at temperatures ranging from 50 °C at the entrance to 125 °C in the final stage. The coating process was similar to the one described in the literature and is shown schematically in Figure 1.[16,17] The coating solution contained 0.25 g of PAAS polymer per 100 mL of methanol. The precursor composite PAAS membrane was converted into a composite polyimide hollow fiber membrane by a heat treatment in a convection oven at 150 °C for 24 h.

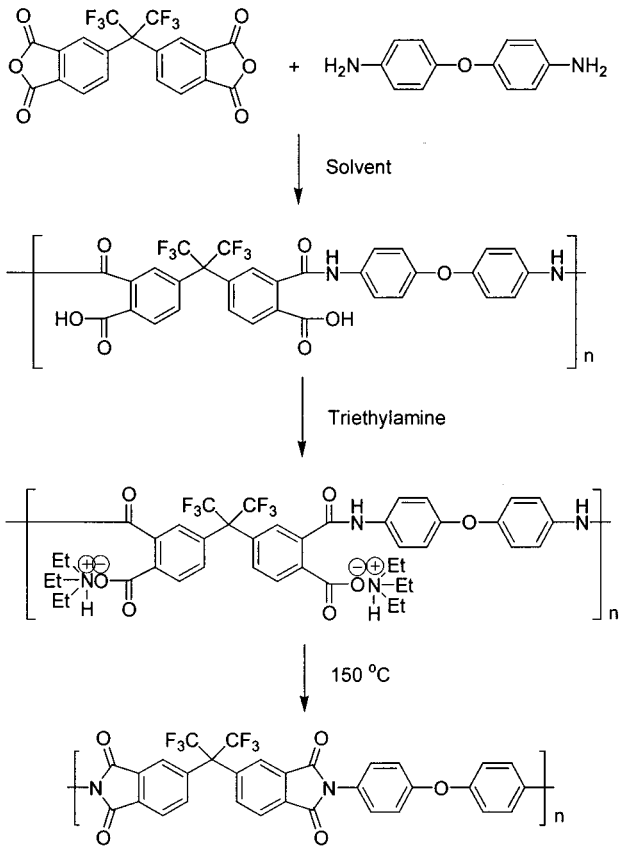
The hollow fiber membrane samples used for gas permeation measurements were over coated with poly(dimethylsiloxane) by immersing the composite hollow fibers into 1% solution of Sylgard 184, Dow Corning, in hexane followed by drying, essentially as described elsewhere.[4] The application of poly(dimethylsiloxane) overcoating was necessary to repair residual defects in the composite polyimide membrane.

**Gas Permeation Measurements.** The gas transport characteristics of composite membranes were measured using a gas mixture containing 10% $CO_2$ and 90% $CH_4$. The feed gas pressure was $1.38 \times 10^6$ Pa, and the temperature was 50 °C. The measurements were carried out at a less than 1% stage cut, and the permeate gas concentration was measured with a Shimadzu gas chromatograph equipped with a thermal conducting detector, as described elsewhere.[3] The reported gas permeances represent average values obtained with three samples.

**Scheme 1. Strategy for the Preparation of Composite Polyimide Membranes**

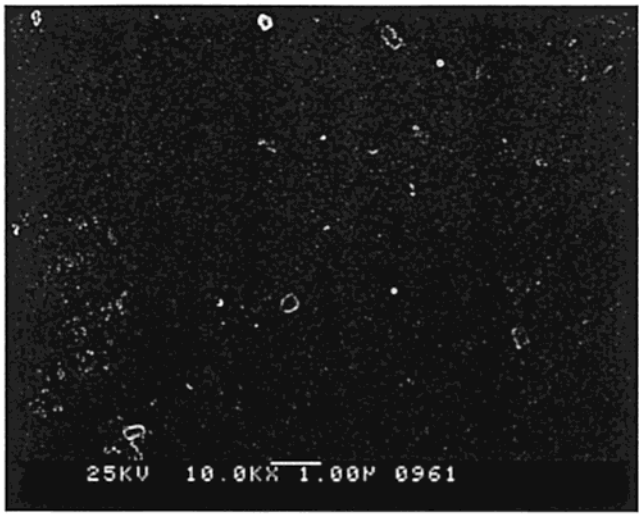



**Scheme 2. Synthesis of 6FDA-ODA Polyimide from the PAAS Precursor**

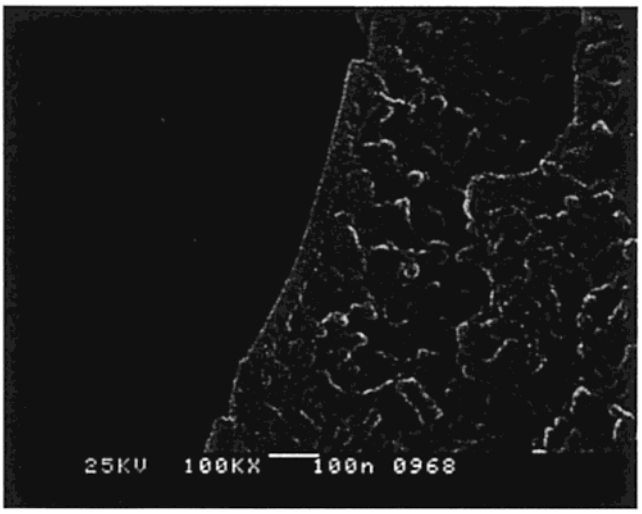



## Results and Discussion

**Fabrication of Composite Polyimide Hollow Fiber Membranes.** The strategy for composite polyimide membrane preparation is shown in Scheme 1. A two-step process was developed for preparation of composite polyimide membranes. First, the precursor composite membrane is obtained by depositing a thin dense layer of the PAAS prepolymer from an alcohol-based solution on top of a porous substrate. Second, the




(a)




(b)

**Figure 2.** SEM micrographs of composite 6FDA-ODA/$Et_3N$ membrane based on polysulfone substrate: (a) outside surface section; (b) cross section.

final composite polyimide membrane is obtained upon thermal treatment of the precursor composite membrane. The membrane preparation strategy is based on the finding that polyamic acid triethylamine salt polymers are highly soluble in alcohol-based solvents and can be completely imidized at 150 °C, as described in the accompanying paper. The precursor PAAS composite membrane can be converted into the final polyimide composite membrane by thermal or chemical imidization method. In this work, the thermal imidization method was used exclusively since it is environmentally benign.

The PAAS polymer characteristics are critical prerequisites for preparation of composite polyimide membranes, because a mild coating solvent and a relatively low processing temperature are needed to preserve the porosity of the porous support. In particular, the heat treatment temperature that effects imidization should be lower than the glass transition temperature of the substrate-forming material. Polysulfone is widely used as a substrate in composite membrane preparation. The glass transition temperature of the Udel polysulfone substrate utilized in the current study is 185 °C.

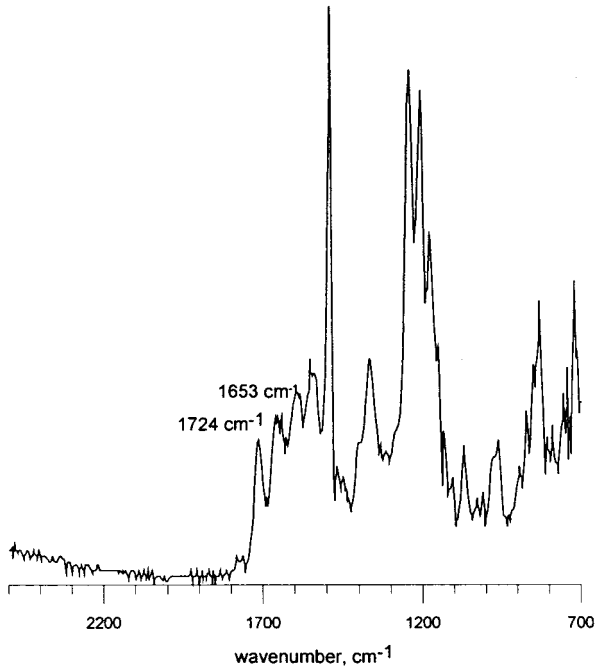
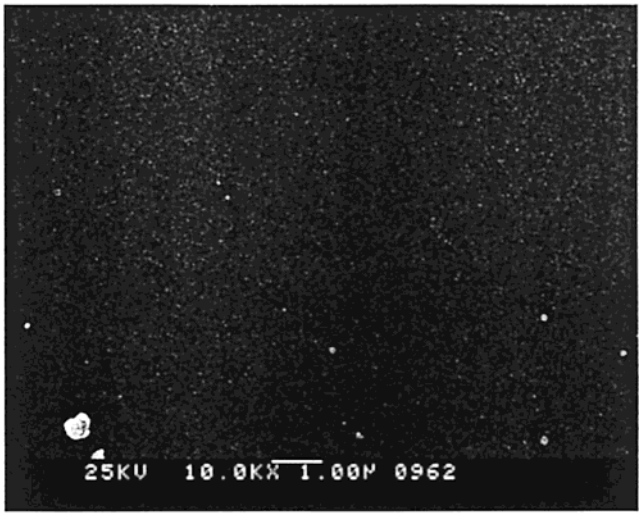



**Figure 3.** ATR FT-IR spectra of 6FDA-ODA/$Et_3N$ PAAS coating layer of the precursor composite membranes (obtained by subtraction of IR spectrum of the polysulfone substrate).

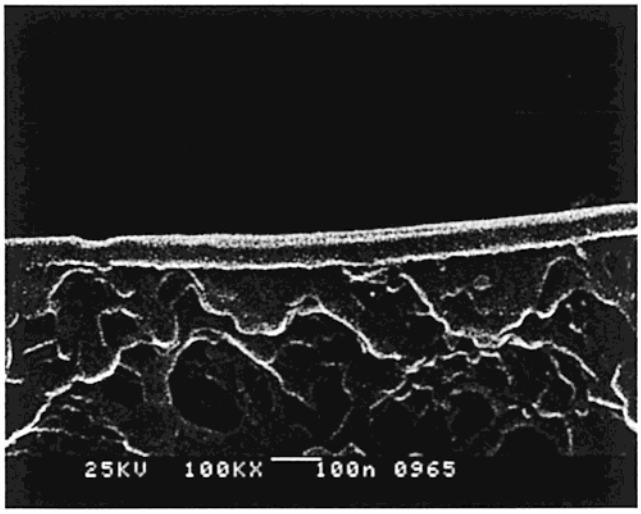
Composite membranes can be prepared in the form of flat sheet films or hollow fibers. In this work, hollow fiber membranes were used exclusively. The preparation of composite polyimide membranes is demonstrated by forming a 6FDA-ODA polyimide membrane on top of a porous polysulfone hollow fiber. The 6FDA-ODA PAAS polymer is synthesized and converted into the polyimide as shown in Scheme 2. Precursor composite PAAS membranes were prepared by depositing a thin dense layer of 6FDA-ODA/$Et_3N$ polymer onto the outer surface of the porous polysulfone hollow fiber by a dip-coating process. SEM pictures of the outside surface, i.e., the surface of the PAAS coating layer, and the cross section of the precursor composite hollow fiber membrane close to the outside coated edge are shown in parts a and b of Figure 2, respectively. It can be seen that the surface of the precursor composite membrane is substantially defect-free. The PAAS polymer layer, which is approximately 500 Å thick, can be clearly discerned in the SEM picture of the hollow fiber cross section.

The chemistry of the coating layer was studied by ATR FT-IR. The ATR FT-IR spectrum of the PAAS coating layer was obtained by subtracting the IR spectrum of the polysulfone substrate from the spectrum of the composite PAAS membranes (Figure 3). The spectrum is essentially identical to the FT-IR spectrum of the pure 6FDA-ODA/$Et_3N$ polymer except for the peak at 1724 $cm^{-1}$ which is attributed to the imide linkage. The presence of the imide peak in the spectra of the coating layer is most probably due to the partial imidization of PAAS polymer that occurred during the coating process. A temperature of 125 °C was utilized in the final drying stage during hollow fiber coating process, which is above the minimum temperature to effect initial imidization.

**Thermal Imidization of Precursor PAAS Composite Membrane.** To obtain the final composite polyimide hollow fiber membrane, the composite PAAS membrane was treated at 150 °C under vacuum for 24 h. SEM pictures of the outside surface area of the final




(a)




(b)

**Figure 4.** SEM micrographs of composite 6FDA-ODA polyimide membrane prepared from the composite 6FDA-ODA/$Et_3N$ membrane by heat treatment at 150 °C: (a) outside surface section; (b) cross section.

polyimide coating layer and the cross section of the composite polyimide hollow fiber membrane close to the outside coated surface are shown in parts a and b of Figure 4, respectively. The SEM picture (Figure 4a) shows that after the heat treatment the surface of the composite membrane did not develop significant defects or cracks. The coating layer can still be clearly discerned from the SEM picture of the cross section. The thickness of the coating layer is still in the range of 500 Å. The SEM picture of the hollow fiber cross section also demonstrates that the porosity of the polysulfone substrate layer remained intact after the 150 °C thermal treatment (Figure 4b).

To confirm that the imidization of the coating layer was quantitative, ATR FT-IR spectra of the final heat treated hollow fiber were recorded. The FT-IR spectra of the coating layer was obtained by subtracting the polysulfone FT-IR spectrum from the FT-IR spectra of the composite membrane. The ATR FT-IR spectrum of the coating layer of the final composite polyimide membrane is shown in Figure 5. The spectrum is identical to the FT-IR spectrum of the 6FDA-ODA

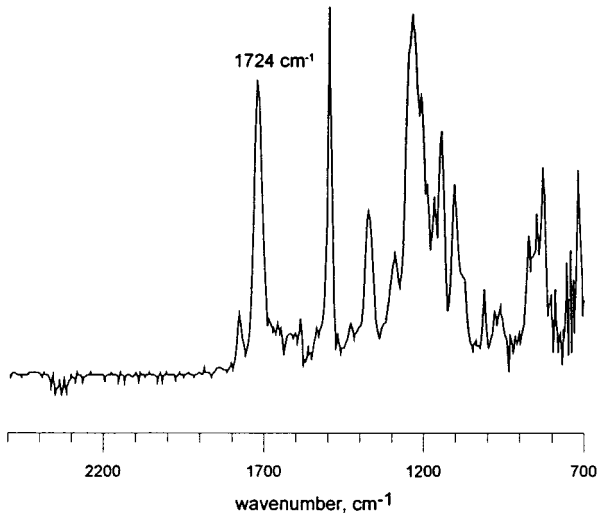



**Figure 5.** ATR FT-IR spectra of 6FDA-ODA polyimide coating layer of the composite polyimide membrane after heat treatment at 150 °C (obtained by subtraction of IR spectrum of the polysulfone substrate).

**Table 1. Gas Transport Characteristics of Composite Membranes**

| no. | heat treatment temp (°C)[a] | $P/T$ $(CO_2)$[b] | $P(CO)_2)/P(CH_4)$[b] |
|---|---|---|---|
| 1[c] | | 1.1 | 24.0 |
| 2 | 100 | 2.5 | 26.6 |
| 3 | 120 | 3.5 | 29.3 |
| 4 | 150 | 5.7 | 30.1 |

[a] Heat-treated for 24 h. [b] Measured at 50 °C; unit of $P/T$ is $cm^3/(cm^2 \cdot cmHg \cdot s) \times 10^5$. [c] Precursor composite 6FDA-ODA/$Et_3N$ membrane prior to heat treatment.

polyimide prepared by a conventional solution imidization process. The presence of the strong peak at 1720 $cm^{-1}$ corresponding to the imide linkage and the disappearance of the peak at 1653 $cm^{-1}$ corresponding to the amide linkage in the PAAS prepolymer confirmed that the coating layer of the final composite membrane was quantitatively converted into polyimide.

**Gas Separation Characteristics of the Composite Polyimide Membrane.** Gas separation characteristics of the novel composite membrane was measured with a mixed gas $CO_2/CH_4$ stream, and the data are listed in Table 1. The precursor composite 6FDA-ODA/$Et_3N$ hollow fiber membrane exhibited inferior gas separation characteristics, wherein the $CO_2$ permeance was $1.1 \times 10^{-5}$ $cm^3$ (STP)/($cm^2$ cmHg s) and the $CO_2/CH_4$ separation factor was only 24.0. The precursor composite membrane was then subjected to sequence of heat treatments of a progressively higher temperature. The gas permeation/separation characteristics progressively improved with increase in temperature and duration of the treatment. The precursor membrane heat treated at 100 °C for 24 h exhibited $CO_2$ permeance of $2.5 \times 10^{-5}$ $cm^3$ (STP)/($cm^2$ cmHg s) and a $CO_2/CH_4$ separation factor of 26.6. The properties further improved after a 120 °C thermal treatment. The fully imidized composite polyimide membrane heat-treated at 150 °C for 24 h exhibited the best gas transport characteristics. Namely, the $CO_2/CH_4$ separation factor was 30.1, and $CO_2$ permeance was $5.7 \times 10^{-5}$ $cm^3$ (STP)/($cm^2$ cmHg s). These results indicate that the temperature of 150 °C is needed for attainment of optimal gas separation characteristics, which is consistent with the prior observation that the 150 °C treatment is needed

to effect the complete imidization of the 6FDA-ODA/$Et_3N$ coating layer. Heat treatment below 150 °C resulted in only partial imidization, and membranes formed under these conditions exhibited inferior gas separation characteristics. The gas transport behavior of composite PAAS and polyimide membranes is consistent with transport behavior of PAAS and polyimide films. In the accompanying paper, we observed that the gas transport characteristics of PAAS films improved after the thermal imidization and conversion into the polyimide.

For both the composite PAAS membrane and the composite 6FDA-ODA polyimide membrane the coating layer largely controls the gas permeation and separation characteristics across the membrane, while the porous polysulfone substrate provides the mechanical support. An asymmetric polysulfone hollow fiber membrane exhibits a $CO_2/CH_4$ separation factor of only about 13 when tested under identical test conditions. The composite 6FDA-ODA/$Et_3N$ membrane exhibits a $CO_2/CH_4$ separation factor of 24, which is significantly higher than that of the asymmetric polysulfone membrane. Therefore, even in the precursor composite 6FDA-OAD/$Et_3N$ membranes, the coating layer controls the gas transport characteristics. The $CO_2/CH_4$ separation factor increased to 30.1 for the composite polyimide 6FDA-ODA hollow fiber membrane, which is more than twice as high as that of polysulfone.

## Conclusions

We have developed a novel method for the fabrication of composite polyimide membranes from poly(amic acid) tertiary amine salt precursor polymers. In the first step, a thin dense layer of PAAS polymer is deposited onto a porous polysulfone hollow fiber surface. The final composite polyimide membrane is obtained upon thermal treatment of the PAAS composite membrane at ca. 150 °C. We expect that this methodology can be extended to prepare a broad range of composite polyimide membranes based on commercial substrates by utilizing PAAS polymers with different chemical structures.

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