Macromolecules **2002,** *35,* 905−911

Polyimide Membranes Derived from Poly(amic acid) Salt Precursor Polymers. 1. Synthesis and Characterization

Yong Ding,* Benjamin Bikson, and Joyce K. Nelson

Innovative Membrane Systems, Inc., 189 Dean Street, Norwood, Massachusetts 02062

Received September 10, 2001; Revised Manuscript Received November 1, 2001

ABSTRACT: A series of new poly(amic acid) salt polymers were synthesized and characterized. It has been found that these poly(amic acid) salt polymers are highly soluble in alcohol-based solvents, a feature that is useful for membrane preparation. It was also found that poly(amic acid) tertiary amine salts can be quantitatively imidized at 150 °C, a temperature that is lower than the imidization temperature of poly(amic acid) or of poly(amic acid) quaternary amine salts of identical backbone structure. This makes poly(amic acid) tertiary amine salt polymer a preferred precursor for preparation of polyimide gas separation membranes. Gas permeation characteristics of dense polyimide films prepared from poly(amic acid) tertiary amine precursors were further measured and compared to chemically identical polyimide films obtained by conventional methodologies.

Introduction

Numerous studies have indicated that stiffening the polymeric backbone while simultaneously inhibiting chain packing can lead to improved gas permeability combined with an increase in gas selectivity for certain gas mixtures.[1−7] However, polymeric materials with very rigid backbone structures are often extremely difficult to process, including fabrication of membranes. Aromatic polyimides are high-performance materials that frequently combine high gas permeability with high gas selectivity due to their rigid backbone structure. Although a number of polyimides exhibit superior intrinsic gas separation properties as compared to materials currently in use,[2,5,8−11] only a few have found utility in commercial membrane preparation. The three polyimides that have found commercial use in gas separation membrane fabrication are poly(ether imide) marketed under the trade name of Ultem, the phenylindane-containing polyimide marketed under the trade name of Matrimid, and the polyimide derived from biphenyl dianhydride (BPA) and oxy-4,4′-dianiline (ODA).[12−15]

Our goal was to develop a polyimide membrane preparation methodology that can be easily adopted for commercial gas separation use or more specifically a composite polyimide membrane preparation methodology. This in turn required development of soluble membrane forming materials that could be processed into membranes with ultrathin separation layers from mild solvent systems at a relatively low processing temperature. This goal was accomplished by utilizing poly(amic acid) salts as polyimide membrane forming precursors.[16] Herein, we describe synthesis and characterization of three novel poly(amic acid) salt polymers that are used to form polyimides tailored toward gas separation applications. A low-temperature imidization profile for PAAS polymer conversion to polyimide was established and used to form polyimide films.

Experimental Section

Instruments. ATR FT-IR spectra were recorded on a Nicolet Avatar 360 FT-IR instrument equipped with an Omni-ATR attachment. ^{1}H NMR spectra were obtained on an INOVA-400 NMR instrument using DMSO-d_6 as the solvent. Differential scanning calorimetry (DSC) data were recorded with a Seiko DSC 6200 instrument under nitrogen atmosphere. The heating rates were 1 °C/min, except as otherwise stated. Inherent viscosities were measured at 25.0 ± 0.1 °C with an Ubbelohde viscometer.

Materials. 2,2-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) was purchased from Clariant Corp and used as received. 3,3′,4,4′-Benzophenonetetracarboxylic dianhydride (BTDA), 4,4′-hexafluoroisopropylidene dianiline (6FDAn), and 4,4′-oxydianiline were purchased from Chriskev Co., Inc. BTDA was dried at 120 °C overnight prior to use. Triethylamine and tetramethylammonium hydroxide (25 wt % aqueous solution) were purchased from Aldrich Chemicals.

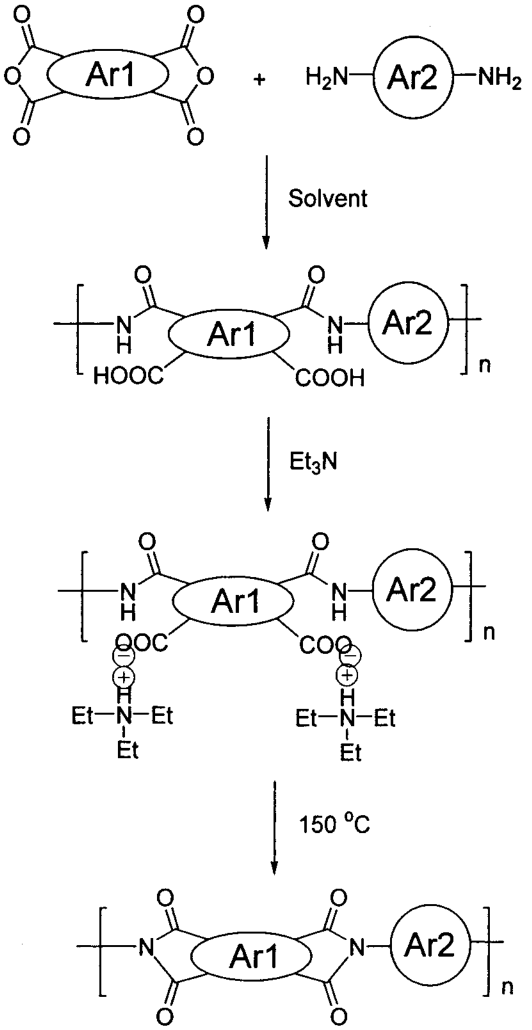
General Procedure for the Synthesis of the Poly(amic acid) Amine Salt Polymers. The synthesis of poly(amic acid) tertiary amine salt polymers and polyimides formed therefrom is depicted in Scheme 1. The structures of poly(amic acid) salts and polyimides synthesized following this procedure are shown in Scheme 2. The synthesis of PAAS polymer **I** provides a representative example of preparation methodology. A 500 mL three-neck, round-bottom flask equipped with a nitrogen inlet and a mechanical stirrer was charged with 10.01 g of ODA and 100 mL of NMP. Once the dianiline was fully dissolved, 22.21 g of 6FDA powder was added and washed down with 50 mL of additional NMP. Within 1 h, the reaction mixture became very viscous, and 50 mL of NMP was added to dilute the solution. The reaction mixture was stirred at room temperature for an additional 2 h, and 16.8 mL of triethylamine in 30 mL of NMP was added slowly to the reaction mixture, which was stirred for an additional 3 h at room temperature. The solid polymer was recovered by precipitation into a large amount of methyl ethyl ketone (MEK) and dried at 50 °C under vacuum for 2 days. The inherent viscosity of the PAAS polymer measured in the methoxyethanol solution (at concentration of 0.4 g/dL) was 0.93 dL/g.

The 6FDA-ODA tetramethylammonium salt (6FDA-ODA/Et_4N) was prepared by adding excess (10% mol) of tetramethylammonium hydroxide aqueous solution to the poly(amic acid) solution. The mixture was stirred at room temperature for 2 h prior to isolation. The polymer was isolated by precipitation into acetone, washed with excess of acetone, and dried at 50 °C under vacuum for 2 days.

Synthesis of Polyimides. The polyimide polymers **IV** and **V** were prepared by thermal imidization of respective PAAS precursors in a two-step process. The PAAS polymer was first treated at 80 °C for 8 h followed by thermal treatment at 150 °C for 24 h. For comparison purposes, polyimide polymers **IV** and **V** were also synthesized by the conventional solution

10.1021/ma0116102 CCC: $22.00

Scheme 1. Synthesis of Poly(amic acid) Salts and Polyimides Formed Therefrom



imidization procedure. The synthesis of polyimide **IV** provides a representative example of preparation methodology. A 500 mL three-neck, round-bottom flask equipped with a nitrogen inlet and a mechanical stirrer was charged with 10.01 g of ODA and 100 mL of NMP. Once the dianiline was fully dissolved, 22.21 g of 6FDA powder was added and washed down with 50 mL of additional NMP. Within 1 h, the reaction mixture became very viscous, and 50 mL of NMP was added to dilute the solution. The reaction mixture was stirred at room temperature for an additional 2 h. At this point, 5.0 mL of triethylamine and 10 mL of acetic anhydride were added to the reaction mixture which was stirred for an additional 24 h at room temperature. The solid polymer was recovered by precipitation into a large amount of methanol and dried at 50 °C under vacuum for 2 days. The inherent viscosity of the 6FDA-ODA polyimide measured in the methylene chloride solution (at concentration of 0.4 g/dL) was 1.12 dL/g.

Synthesis of Poly(amic acid). 6FDA-ODA poly(amic acid) solution was prepared following the 6FDA-ODA polyimide preparation protocol described above, except that the triethylamine and the acetic anhydride were not added to the reaction mixture to effect imidization. The white poly(amic acid) polymer was isolated by precipitating the poly(amic acid) solution into a large amount of methylene chloride. The poly(amic acid) polymer was extensively washed with a fresh methylene chloride, filtered, and dried under vacuum for 24 h at 50 °C.

Preparation of Polyimide Films. Flat sheet polyimide films were prepared by three different routes, as shown in Scheme 3. The polyimide films of type **A** were obtained by thermal imidization of their respective poly(amic acid) tertiary amine salt precursor films at 80 °C for 8 h and then at 150 °C for 24 h under vacuum. The PAAS precursor films were obtained by casting the PAAS polymer solution in methanol (ca. 10% solid) onto a glass plate followed by solvent evaporation in a closed glovebag at room temperature.[17] The films were then removed from the glass plate and dried in a vacuum oven at 50 °C overnight. The polyimide film of type **B** was obtained from the poly(amic acid) precursor film, which was cast from the poly(amic acid) solution in NMP (ca. 15% solid) in an oven set at 70 °C. The imidization procedure included heat treatment at 150 °C for 4 h, at 280 °C for 2 h, and then at 300 °C for 1 h to convert the poly(amic acid) precursor into the polyimide. The polyimide film **1C** was obtained by solution casting the fully imidized 6FDA-ODA polyimide (ca. 10% solids in chloroform) onto a glass plate, followed by drying in a vacuum oven at 150 °C for 24 h. Polyimide film **2C** was cast from a DMF solution (ca. 10% solid) and dried at 150 °C for 24 h. The thickness of the dense flat sheet films studied was about 30 μm.

Gas Permeation Measurements. The permeation testing apparatus and procedures that were utilized to measure the gas permeability of flat sheet films were the same as described by Koros et al.[18] All measurements were made using an upstream pressure of 1−2 atm while the downstream pressure was effectively zero. The pressure in the receiver was monitored with a MKS Baratron pressure transducer.

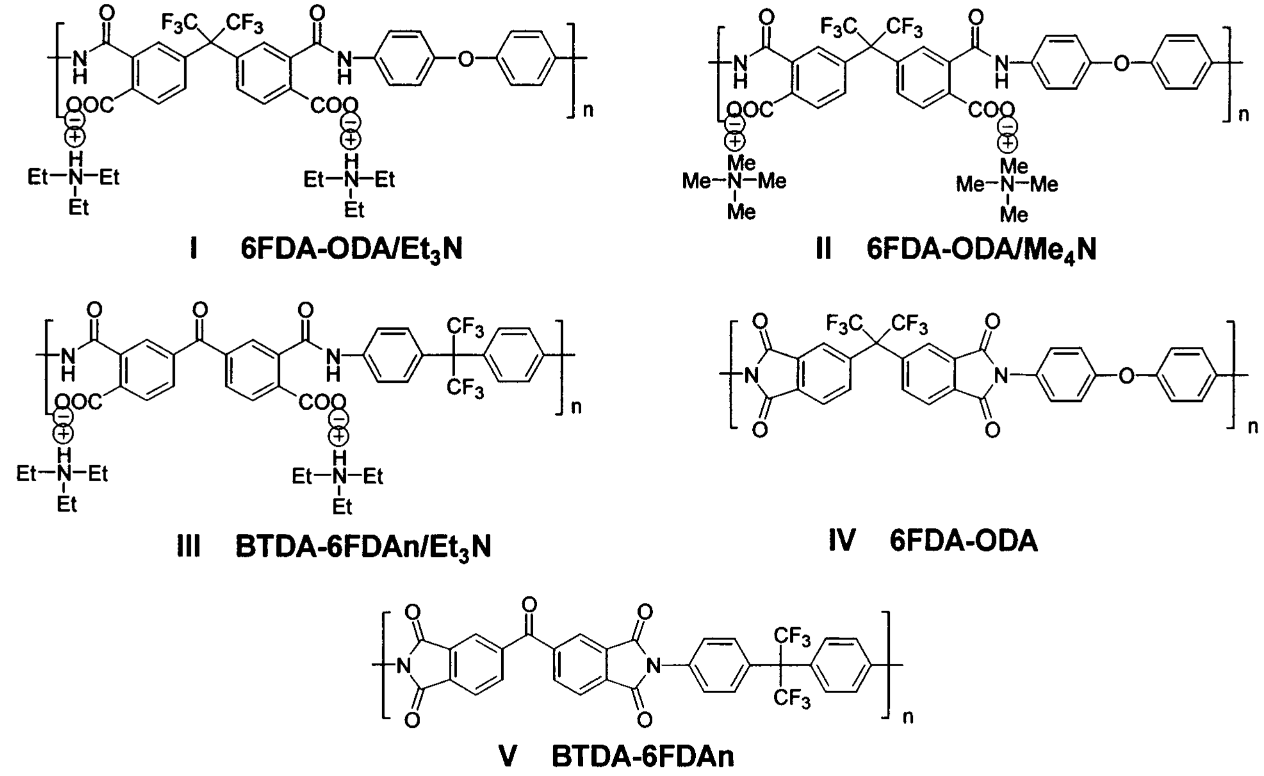
Results and Discussion

Preparation of Poly(amic acid) Tertiary Amine Salt. Three new poly(amic acid) salt polymers were synthesized, and their chemical structures are shown in Scheme 2. poly(amic acid) tertiary amine salt polymers **I** and **III** were derived from their respective poly(amic acid)s by neutralization with triethylamine, while the poly(amic acid) quaternary amine salt polymer **II** was prepared by neutralizing the poly(amic acid) with the tetramethylammonium hydroxide. The 6FDA-ODA and BTDA-6FDAn polyimides were selected in this study because of their attractive intrinsic gas separation characteristics.[9,19−22] The PAAS polymers were isolated from synthetic solutions prior to use. It was found that relatively nonpolar solvents, with solubility parameter δ below 21×10^3 $(J/m^3)^{1/2}$, such as acetone, methyl ethyl ketone, and the mixture of acetone and cyclohexane, are nonsolvents for PAAS polymers, and fibrous PAAS polymers were obtained by precipitation into these nonsolvents.

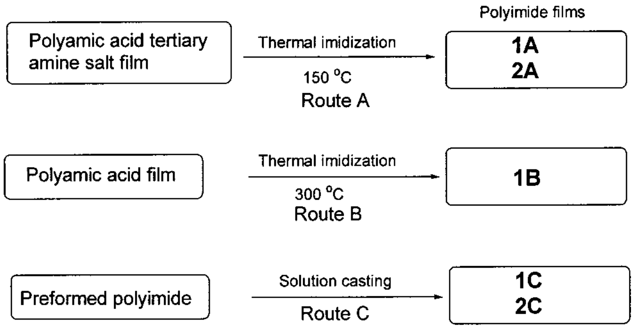
The formation of triethylamine salts was confirmed by ^{1}H NMR spectroscopy. Specifically, ^{1}H NMR spectra of PAAS polymers **I** and **III** displayed chemical shifts of ethyl protons [1.1 ppm (t,) and 2.9 ppm (q)] that were identical to chemical shifts of ethyl protons in a typical triethylamine salt reported in the literature.[23] The ATR FT-IR spectra of 6FDA-ODA/Et_3N and 6FDA-ODA/Me_4N polymers are shown in Figure 1. The spectra of both PAAS polymers exhibit a peak at 1653 cm^{-1} that is assigned to amide linkages in the PAAS polymer backbone.

The solubility characteristics of PAAS polymers in a representative number of solvents are listed in Table 1. It can be seen that PAAS polymers are readily soluble in a broad range of organic solvents, including methanol, ethanol, and DMF, as well as other aprotic solvents such as NMP. The solubility behavior of PAAS polymers is characteristic of polyelectrolytes. The fact that PAAS polymers can be dissolved in alcohol-based solvent systems is very useful for the fabrication of composite membranes, since most of commercially available porous polymeric substrates are inert to alcohol-based solvents. Thus, a thin layer of PAAS polymer can be readily

Scheme 2. Chemical Structures of Poly(amic acid) Salt Polymers and Polyimides



Scheme 3. Preparation of Polyimide Films: Route A, Polyimide Film Prepared from the PAAS Polymer Film; Route B, Polyimide Film Prepared from the Poly(amic acid) Film; Route C, Polyimide Film Prepared from the Solution Imidized Polyimide; 1, Polyimide of Structure IV; 2, Polyimide of Structure V



deposited onto most porous polymeric substrates from an alcohol-based solution.

PAAS polymers show good film-forming characteristics. Transparent and tough PAAS polymer films were readily obtained from all solvents including alcohols.

Poly(amic acid) amine salts are significantly more stable toward hydrolysis as compared to respective poly(amic acid)s.[23-26] Consequently, the shelf life of the PAAS polymer is longer and the handling is easier. Inherent viscosities of polymers **I**–**III** remained unchanged after more than 2 years of storage at room temperature (stored as solid powders).

Thermal Imidization Characteristics of Poly(amic acid) Salt Polymers. The thermal imidization reaction is endothermic. Therefore, the DSC technique can be used to study the thermal imidization behavior of poly(amic acid) salts. Figure 2 shows the DSC scanning charts of polymers **I**, **II**, and **III**. For comparison, the DSC scan of 6FDA-ODA poly(amic acid) polymer is also shown in Figure 2. All polymers exhibited an apparent endothermic peak corresponding to the imidization reaction. The maximum peak temperature for 6FDA-ODA/Et$_3$N was 138 °C, and for BTDA-6FDAn/Et$_3$N it was 144 °C. The maximum peak temperature of the endotherm for 6FDA-ODA poly(amic acid) was 186 °C, and for 6FDA-ODA/Me$_4$N it was 217 °C. These results indicate that the thermal imidization temperature of poly(amic acid) tertiary amine salt polymers is the lowest among three different types of precursors studied. The main chain chemical structure of the polymer had only a minor influence on the thermal imidization characteristics of poly(amic acid) tertiary amine salts. (The maximum peak temperatures of endotherm of **I** and **III** are very close.) The thermal imidization temperature of poly(amic acid) quaternary amine salt was the highest among all precursors studied. The 6FDA-ODA poly(amic acid) polymer attained complete imidization at 225 °C under the DSC running conditions (heating rate of 1 °C/min), indicated by the offset temperature of the endotherm peak. This result corroborates the observation by Foutz that poly(amic acid) polymers can be quantitatively imidized between 170 and 225 °C.[27]

The ability to form polyimides by thermal treatment at a low temperature is preferred in commercial applications. Since the maximum peak temperature of the endotherm for poly(amic acid) tertiary amine salt polymers is ca. 140 °C, it was expected that a complete imidization could be achieved at 150 °C by a prolonged heat treatment. To confirm this, a 6FDA-ODA/Et$_3$N sample was ramped at the rate of 1 °C/min to the 150 °C temperature in the DSC instrument and held at this temperature for 24 h. The sample was then cooled and subjected to a DSC heating scan (heating rate of 20 °C/min, Figure 3). The scan did not show any endothermic peaks up to 350 °C (first scan, Figure 3). This suggested that the sample was completely imidized by the 150 °C

Table 1. Solubility Characteristics of PAAS Polymers[a]

PAAS polymer	methanol	ethanol	IPA	DMF	NMP	acetone	THF	cyclohexane
I	+	+	+ −	+	+	−	−	−
II	+	+ −	−	+	+	−	−	−
III	+	+	+ −	+	+	−	−	−

[a] Solubility: +, soluble at room temperature; −, insoluble at room temperature; + −, slightly soluble.

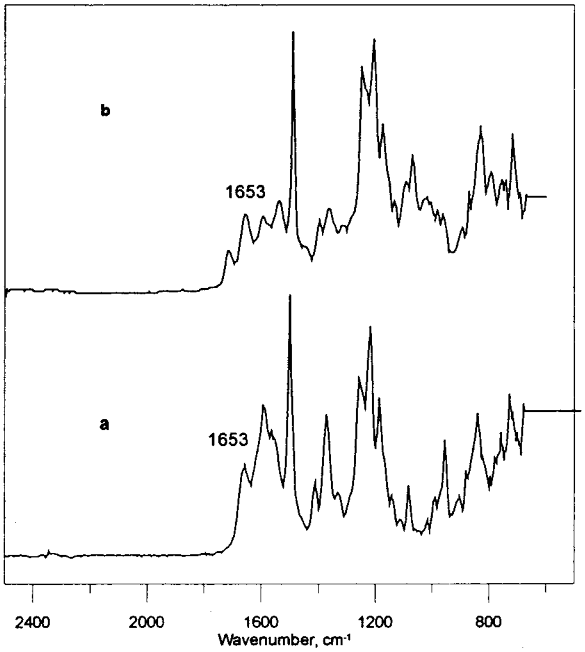


Figure 1. ATR FT-IR spectra of poly(amic acid) salt polymers: (a) 6FDA-ODA/Et_3N; (b) 6FDA-ODA/Et_4N.

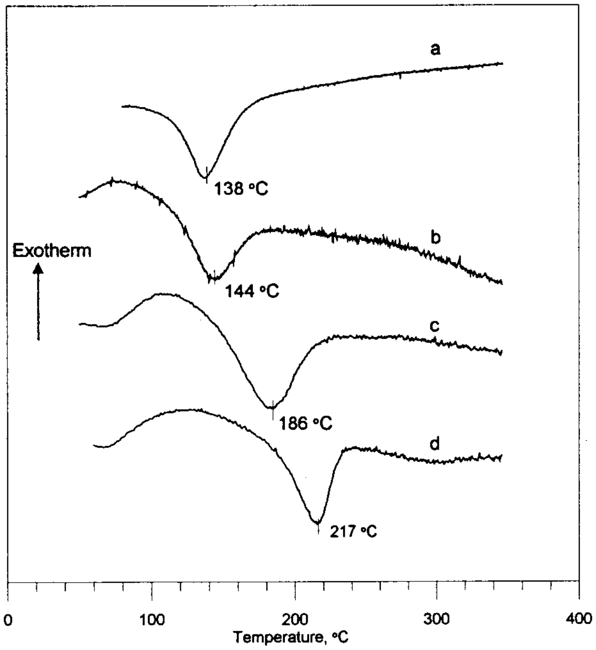


Figure 2. DSC scans of PAAS polymers: (a) polymer **I**, (b) polymer **III**, (c) 6FDA-ODA poly(amic acid), and (d) polymer **II**.

heat treatment. An additional DSC scan of the sample (second scan, heating rate of 20 °C/min, Figure 3) showed a glass transition temperature at 304 °C that is consistent with T_g value reported in the literature for 6FDA-ODA polyimide.[28] This experiment showed that although the glass transition temperature of the polyimide is much higher than the treatment temperature of 150 °C, the complete imidization of the PAAS polymer was achieved. The fact that the first DSC heating scan of the sample heat treated at 150 °C did not show any apparent glass transition temperature is attributed by us to a nonequilibrium polymer morphology. Namely, the low-temperature imidization process generated an excess free volume. Heat treating the sample above the glass transition temperature of the polyimide polymer that was formed during the first heating scan resulted in a morphological change. (The excess free volume has been removed.) Thus, a clear glass transition was observed during the second DSC scan. The high gas permeability of polyimides obtained from the PAAS precursors as compared to that of polyimides formed by conventional procedures may be also attributed to the excess free volume generated during the low-temperature imidization, as further discussed below.

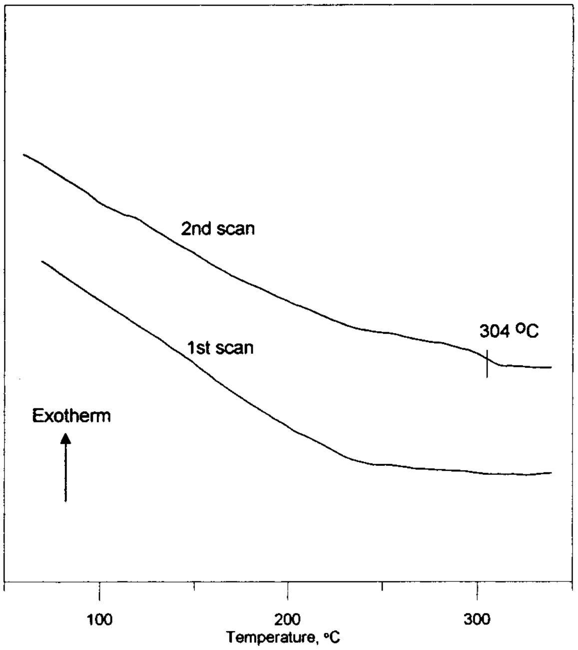


Figure 3. DSC scans of polymer **IV** obtained from **I** by heat treatment at 150 °C for 24 h (heating rate of 20 °C/min under N_2).

The imidization of PAAS polymers by the 150 °C heat treatment was confirmed to be quantitative by FT-IR and ^{1}H NMR spectroscopy. Figure 4 shows the ATR FT-IR spectra of 6FDA-ODA polyimide obtained by two different routes: from the PAAS prepolymer and from the solution imidized polyimide. It can be seen that the 6FDA-ODA polyimide **IV** obtained by thermal imidization of polymer **I** exhibited a FT-IR spectrum identical to that of the 6FDA-ODA polyimide prepared by standard solution chemical imidization. The spectrum shows that after the heat treatment the peak at 1653 cm^{-1} corresponding to amide linkages in polymer **I** had disappeared, and a strong peak at 1724 cm^{-1} corresponding to the imide linkages has appeared. This confirms the formation of cyclic imide linkages from the

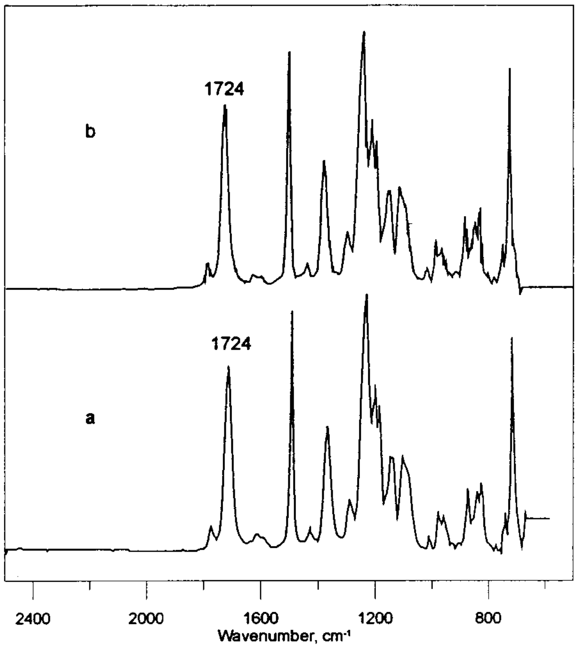


Figure 4. Comparison of ATR FT-IR spectra of 6FDA-ODA polyimide obtained by different routes: (a) from 6FDA-ODA/Et_3N by heat treatment at 150 °C; (b) by solution chemical imidization.

linear polyamide structure. Samples utilized in the IR study were further analyzed by ^1H NMR spectroscopy. The ^1H NMR spectrum of 6FDA-ODA polyimide obtained from 6FDA-ODA/Et_3N by heat treatment at 150 °C is shown in Figure 5. The ethyl protons of triethylamine counterions associated with PAAS polymer were not detected in the NMR spectrum. This indicates that a complete cure was achieved at 150 °C, and Et_3N was quantitatively removed from the sample during the heat treatment. Proton signals in the aromatic region, whose assignments are shown in Figure 5, match exactly the 6FDA-ODA polyimide structure.

Our work demonstrates for the first time that poly(amic acid) tertiary amine salt polymers can be quantitatively imidized at a much lower temperature than poly(amic acid) polymers. It has been reported in the literature that poly(amic acid) tertiary amine salt polymers exhibit faster imidization rates as compared to their respective poly(amic acid) polymers.[24,26] The low imidization temperature is advantageous for the fabrication of composite polyimide membranes since the curing temperature of the polyimide must be lower than the glass transition temperature of the porous polymeric substrate. These advantageous features of PAAS polymers allowed us to prepare composite membranes utilizing conventional, commercially available porous polysulfone substrates by depositing an ultrathin PAAS precursor layer from an alcohol-based solvent system on top of a porous hollow fiber substrate followed by a mild heat treatment.[16] The Udel polysulfone exhibits T_g of 185 °C, and a porous substrate made from polysulfone will be destroyed by the high-temperature heat treatment required to effect the complete imidization of poly(amic acid)s.

Table 2. Gas Transport Characteristics of a PAAS Film and Polyimide Films Obtained by Different Routes

film[a,b]	$P(O_2)$	$P(N_2)$	$P(CO_2)$	$P(CH_4)$	$P(O_2)/P(N_2)$	$P(CO_2)/P(CH_4)$
I	0.9	0.16	4.4	0.18	5.3	24
1A	4.5	0.90	24.2	0.58	5.0	42
1A(ann)[c]	3.5	0.58	14	0.25	6.1	55
1B	1.4	0.22	5.6	0.12	6.3	48
1C	2.3	0.41	10.7	0.23	5.8	47
2A	2.7	0.52	12.8	0.31	5.2	42
2C	2.0	0.33	8.4	0.17	6.1	49

[a] The film designations are shown in Scheme 2. [b] Permeability coefficient (*P*) in barrer (1 barrer = 1 cm^3 (STP) cm cm^{-2} s^{-1} $cmHg^{-1} \times 10^{-10}$), measured at 30 °C. [c] Film **1A(ann)** was obtained from film **1A** by heat treatment at 280 °C for 2 h under nitrogen atmosphere.

Gas Transport Characteristics of Polyimide Films Obtained from the PAAS Precursor. Table 2 lists the measured gas transport characteristics of polyimide films obtained by three different routes as shown in Scheme 3. The table also lists gas permeation coefficients of the PAAS polymer 6FDA-ODA/Et_3N (film **I**). The polyimide film **1A** is a fully imidized 6FDA-ODA polyimide film obtained by heat treatment of the corresponding PAAS film at 150 °C. The 6FDA-ODA polyimide film **1B** was obtained by treating a 6FDA-ODA poly(amic acid) film at 300 °C. The 6FDA-ODA polyimide film **1C** was cast from a fully imidized 6FDA-ODA polyimide solution in chloroform. The BTDA-6FDAn polyimide films **2A** and **2C** were prepared analogously from the BTDA-6FDAn/Et_3N PAAS precursor film and a fully imidized BTDA-6FDAn polyimide cast from the DMF solution, respectively. The details of the film preparation are given in the Experimental Section.

The 6FDA-ODA/Et_3N film exhibited inferior gas transport characteristics in terms of both permeability coefficients and gas separation factors. The permeation coefficients for O_2 and CO_2 were 0.9 and 4.4 barrer, respectively. The CO_2/CH_4 separation factor, $\alpha(CO_2/CH_4)$, of the PAAS film was only 24. The fully imidized polyimide film **1A,** which was obtained from the 6FDA-ODA/Et_3N film, exhibited far superior gas transport characteristics; the permeability coefficients for O_2 and CO_2 were 4.5 and 24.2 barrer, respectively. The CO_2/CH_4 separation factor, $\alpha(CO_2/CH_4)$, of film **1A** was 42, which was almost twice as large as that of the PAAS polymer.

As can be seen from the data in Table 2, polyimide films obtained from the PAAS polymers exhibit equal or superior gas permeation characteristics as compared to polyimides obtained by conventional routes. For example, polyimide films **1A** and **2A**, obtained from poly(amic acid) tertiary amine salt precursors, exhibit higher gas permeation coefficients combined with slightly lower gas separation factors as compared to those of polyimide films obtained from poly(amic acid) or films cast from fully imidized polyimides. The influence of preparation conditions on the gas permeation properties of 6FDA-ODA polyimide has been studied by Matsumoto and Xu,[20] and the gas transport characteristics of the polyimide film **1B** measured by us are in good agreement with their reported value ($P(CO_2) = 6.0$ barrer and $\alpha(CO_2/CH_4) = 42$). Yeom et al. have compiled a list of permeation data for 6FDA-ODA polyimide reported in the literature.[29] The differences in the gas transport properties for the polyimide films of the same chemical structure obtained by different routes are most likely due to differences in the chain packing density. Since the polyimide films **1A** and **2A** were formed at a relatively low 150 °C temperature, which is substantially lower than the glass transition temperature of these polyimides, it is reasonable to assume that the polymer film chain packing is low due to an excess free

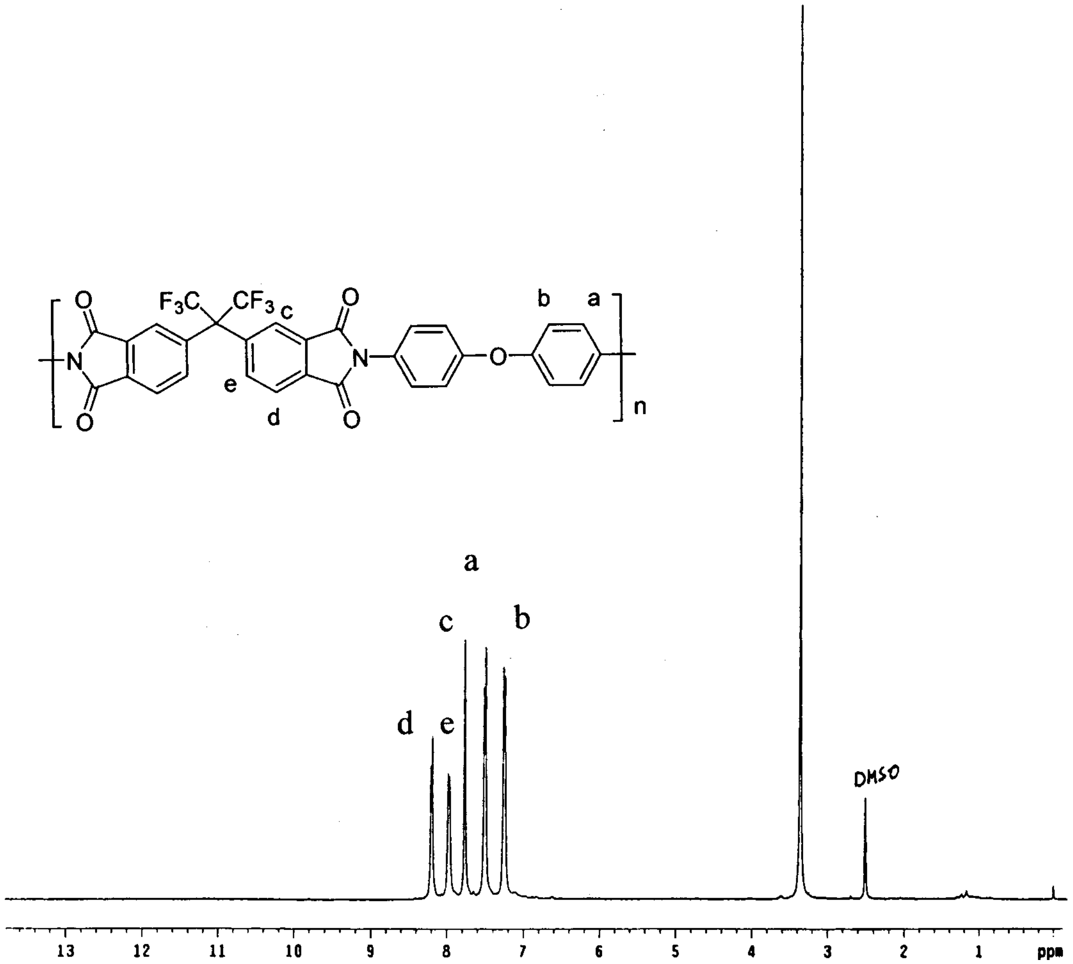


Figure 5. ^{1}H NMR spectrum of polyimide **IV** prepared from 6FDA-ODA/Et_3N PAAS polymer by heat treatment at 150 °C.

volume generated during the imidization process as a result of the release of small molecules (triethylamine and water). Apparently, a larger free volume is built into the polyimide polymer structure obtained from PAAS polymer by low-temperature imidization. The nonequilibrium morphology of polyimides obtained from PAAS precursors by low-temperature heat treatment can also account for the lack of discernible glass transition temperature in the first DSC scan of this polymer sample as discussed above. However, once the film **1A** was annealed by heat treatment at 280 °C for 2 h, the annealed film **1A(ann)** exhibited a decrease in gas permeability coefficients and an increase in gas separation factors, in particular for carbon dioxide, $P(CO_2) = 14.0$ barrer and $\alpha(CO_2/CH_4) = 55$. The high-temperature annealing apparently reduced some of the excess free volume generated by the release of tertiary amine and water molecules. It is noteworthy that a short annealing step at a temperature substantially below the glass transition temperature of the polyimide resulted in a substantial relaxation as manifested by the large decrease in gas permeability coefficients.

Conclusions

Several new poly(amic acid) salt polymers were synthesized, and polyimide films were prepared therefrom. The poly(amic acid) salt polymers, with tertiary amine or quaternary amine counterions, are found to be highly soluble in alcohol-based solvent systems. The peak temperatures of the imidization endotherm for poly(amic acid) tertiary amine salt polymers were found to be ca. 140 °C. The peak temperature of the imidization endotherm for the poly(amic acid) quaternary amine salt polymer (**III**) and for the poly(amic acid) polymers was found to be significantly higher. Polyimides obtained from PAAS precursors exhibited good combination of gas permeation coefficients and gas separation factors. These properties make poly(amic acid) tertiary amine salt polymers very useful for the fabrication of composite polyimide gas separation membranes as well as for other coating applications.

Acknowledgment. We thank the U.S. Department of Energy for financial support (Contract DE-FC26-99FT40497) and Praxair Inc. for allowing us to publish this research work.

References and Notes

(1) Hoehn, H. U.S. Patent 3,822,202, 1974.
(2) Koros, W. J.; Fleming, C. K. *J. Membr. Sci.* **1993**, *83*, 1.
(3) Freeman, B. D. *Macromolecules* **1999**, *32*, 375.
(4) Robeson, L. M. *J. Membr. Sci.* **1991**, *62*, 165.
(5) Robeson, L. M.; Burgoyne, W. F.; Langsam, M.; Savoca, A. C.; Tien, C. F. *Polymer* **1994**, *35*, 4970.
(6) Maier, G. *Angew. Chem., Int. Ed.* **1998**, *37*, 2960.
(7) Alentiev, A. Y.; Yampolskii, Y. P. *J. Membr. Sci.* **2000**, *165*, 201.
(8) Stern, S. A. *J. Membr. Sci.* **1994**, *94*, 1.
(9) Ohya, H.; Kudryavtsev, V. V.; Semenova, S. I. *Polyimide Membranes: Applications, Fabrications, and Properties*; Kodansha: Tokyo, 1996.
(10) Al-Masri, M.; Fritsch, D.; Kricheldorf, H. R. *Macromolecules* **2000**, *33*, 7127.

(11) Al-Masri, M.; Kricheldorf, H. R.; Fritsch, D. *Macromolecules* **1999**, *32*, 7853.
(12) Koros, W. J.; Woods, D. G. *J. Membr. Sci.* **2001**, *181*, 157.
(13) Ekiner, O. M. U.S. Patent, 5,922,791, 1999.
(14) Makino, H.; Kusuki, Y.; Harada, T.; Shimazaki, H.; Isida, T. U.S. Patent 4,440,643, 1984.
(15) Makino, H.; Kusuki, Y.; harada, T.; Shimazaki, H.; Ishida, T. U.S. Patent 4,485,056, 1984.
(16) Ding, Y.; Bikson, B.; Nelson, J. K. EPA Patent 1,086,737, 2001.
(17) Mikawa, M.; Nagaoka, S.; Kawakami, H. *J. Membr. Sci.* **1999**, *163*, 167.
(18) Koros, W. J.; Paul, D. R.; Rocha, A. A. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 687.
(19) Kim, T. H.; Koros, W. J.; Husk, G. R.; O'Brien, K. C. *J. Membr. Sci.* **1988**, *37*, 45.
(20) Matsumoto, K.; Xu, P. *J. Appl. Polym. Sci.* **1993**, *47*, 1961.
(21) Matsumoto, K.; Ping, X. U.S. Patent 5,391,219, 1995.
(22) Matsumoto, K.; Ping, X. EP Patent 0,509,260 B1, 1999.
(23) Echigo, Y.; Miki, N.; Tomioka, I. *J. Polym. Sci., Polym. Chem. Ed.* **1997**, *35*, 2493.
(24) Kreuz, J. A.; Endrey, A. L.; Gay, F. P.; Sroog, C. E. *J. Polym. Sci., Part A-1* **1966**, *4*, 2607.
(25) Reynolds, R. J. W.; Seddon, J. D. *J. Polym. Sci., Part C* **1968**, *23*, 45.
(26) Facinelli, J. V.; Gardner, S. L.; Dong, L.; Sensenich, C. L.; Davis, R. M.; Riffle, J. S. *Macromolecules* **1996**, *29*, 7342.
(27) Foutz, E. L. U.S. Patent 4,643,910, 1987.
(28) Coleman, M. R.; Koros, W. J. *J. Membr. Sci.* **1990**, *50*, 285.
(29) Yeom, C. K.; Lee, J. M.; Hong, Y. T.; Choi, K. Y.; Kim, S. C. *J. Membr. Sci.* **2000**, *166*, 71.

MA0116102