Gas Transport Properties of Soluble Aromatic Polyimides with Sulfone Diamine Moieties

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SYNOPSIS

Aromatic polyimides derived from 2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and 3,3'- or 4,4'-diaminodiphenylsulfone (m-DDS or p-DDS) have been synthesized with a chemical imidization. The disappearance of amic acid groups and the appearance of imide groups are determined by IR and ^{1}H-NMR spectroscopies. The obtained polyimides are amorphous and soluble in organic solvents. The gas transport properties of the polyimide membranes to CO_2, O_2, N_2, and CH_4 have been determined at 35°C and at a pressure up to 10 atm. The (PCO_2/PCH_4) and (PO_2/PN_2) selectivities of the membranes are augmented due to their large gas diffusivity selectivities. This is considered to be due primarily to the high packing density of polymer chain. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

For more than a decade, the commercial polymers such as cellulose acetate, polycarbonate, and polysulfone have been widely used to form hollow-fiber or spiral-wound membranes for gas separations. Membrane-based gas separation technology has been applied to CO_2 and H_2O separation from natural gas or O_2 or N_2 enrichment from air.[1,2] An important objective in gas separation membrane materials is the development of the new polymer membranes with combining high gas permeability and high gas permselectivity. The polymer membranes are also required to have the excellent thermal and antioxidative properties over a wide temperature range in the presence of the feed gas components and the mechanical stability over a high gas pressure.

Aromatic polyimides are one of the most important classes of high-performance polymers.[3-5] Due to their excellent thermal and mechanical properties, the various polyimides have been employed in many applications such as semiconductor devices, high-temperature adhesive, and high-performance composite materials. Recently, the polyimides have been

especially received as gas separation materials because of their surprisingly high permselectivities to (PH_2/PN_2), (PO_2/PN_2), and (PCO_2/PCH_4).[6-10] There have been many active studies on the novel polyimides structurally modified to enhance gas permselecitivty. However, most of the aromatic polyimides prepared by thermal imidization process in a solid state show insolubility and infusibility due to some branches or crosslinks formed during high-temperature "curing" processes. Thus, the membrane formations such as an asymmetric membrane with a ultrathin skin layer or ultrathin composite membrane are limited by their polymer chain rigidity as well as their poor solubility.

We have synthesized organic solvents soluble aromatic polyimides to overcome these problems, and the aromatic polyimides with improved solubility and flexibility have been synthesized with a chemical imidization. The main focus of our research is to increase fundamental understanding of the effects of gas transport parameters (diffusivity and solubility) and structure of polyimides on the gas permeability. A better understanding of the relationship between the structure of polyimides and the gas transport properties is one of the very important factors for gas separation membranes.

This article gives an evaluation of gas transport properties of aromatic polyimides with sulfone di-
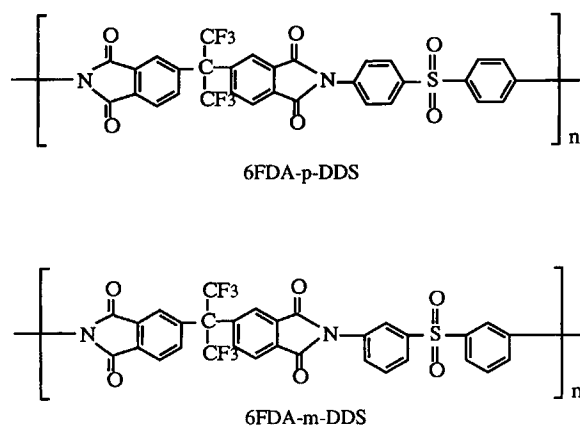

Figure 1   Structure of polyimides.

amine moieties. We have synthesized soluble and amorphous aromatic polyimides derived from 2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and 3,3'- or 4,4'-diaminodiphenylsulfones (m-DDS or p-DDS). The permeabilities of the polyimide membranes to CO_2, O_2, N_2, and CH_4 have been determined at 35°C and at a pressure up to 10 atm.

EXPERIMENTAL

Materials

The dianhydride monomer used for the synthesis of polyimides was 2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA). The diamine monomers were 3,3'-diaminodiphenylsulfones (m-DDS) and 4,4'-diaminodiphenylsulfones (p-DDS). 6FDA was purified by sublimation prior to use. The monomers, m-DDS and p-DDS, were recrystallized in ethanol solution prior to use, respectively.

Synthesis of Soluble Aromatic Polyimides

The soluble aromatic polyimides were synthesized with the chemical imidization of the poly(amic acid) precursors. The poly(amic acid)s derived from

6FDA dianhydride and p-DDS or m-DDS diamine were prepared by solution condensation at 70°C and at concentration of 20 wt % solid in N,N'-dimethylacetamide (DMAc) solution under nitrogen atmosphere. After being stirred at 70°C for 5 h, the poly(amic acid) precursors were converted into the corresponding polyimides at 70°C under nitrogen atmosphere by the chemical imidization with seven-equimolar of acetic anhydride and triethylamine. After a reaction of 24 h, 6FDA-p-DDS and 6FDA-m-DDS were precipitated by methanol, recovered, and filtered. Subsequently, 6FDA-p-DDS and 6FDA-m-DDS were washed with methanol several times and dried in vacuum oven at 150°C for 24 h. The structures of polyimides synthesized are presented in Figure 1 and are determined by IR and ^{1}H-NMR, as given in detail later. The polyimides could be dissolved in common organic solvents, as shown in Table I.

Preparation of Polyimide Membranes

Polyimide membranes used in this study were prepared with a solvent-casting method as follows. First, the tetrahydrofuran solutions of the polyimides were carefully cast on the glass plate. Then, the plates were placed in vacuum oven at 45°C for 8 h to slowly remove most of solvent. After cooling, the membranes were stripped from the plates by submersion in hot water. The membranes were finally dried in vacuum oven at 200°C for 15 h to remove the residual solvent. The transparent and flexible polyimide membranes with thickness of ca. 30–40 μm were obtained.

Physical Properties

The physical properties of soluble aromatic polyimides synthesized were presented in Table II. The molecular weights (M_w and M_n) of the polyimides were estimated by gel-permeation chromatography (column: Shodex KF-805L and detector: Jasco 830-RI monitor) with tetrahydrofuran as the solvent and polystyrene as the standard. Thermal behaviors of

Table I   Solubility of 6FDA-p-DDS and 6FDA-m-DDS in Various Solvents

Polyimide	Acetone	THF	MC	NMP	DMAc	DMSO
6FDA-p-DDS	VS	VS	VS	S	S	VS
6FDA-m-DDS	VS	VS	VS	S	S	VS

VS: very soluble; S: soluble; THF: tetrahydrofuran; MC: methylene chloride; NMP: N-methylpyrrolidone; DMAc: dimethylacetamide; DMSO: dimethylsulfoxide.

Table II   Physical Properties of 6FDA-*p*-DDS and 6FDA-*m*-DDS

Polyimide	M_w	M_w/M_n	ρ (g/cm^3)	T_g	T_5^a	V_F	d-spacing
6FDA-*p*-DDS	46000	1.4	1.483	325	528	0.149	5.24
6FDA-*m*-DDS	69000	1.4	1.487	254	528	0.146	5.02

[a] 5% weight loss temperature by TGA.

polyimides under nitrogen atmosphere were evaluated as a 5% weight loss temperature (T_5) by thermogravimetric analysis (TGA: Seiko TG/DTA300, SSC/5200H) with a heating rate of 20°C/min. The glass transition temperature (T_g) was determined by differential scanning calorimetry (DSC: Seiko DSC200, SSC/5200H). The samples enclosed in an aluminum pan with a cover were heated at 10°C/min. The density of polyimide membranes was measured by means of a density gradient column at 25°C. The mean intersegmental distance was taken to be represented by the "d-spacing" obtained from wide angle X-ray diffraction spectra (MAC SCIENCE MXP).[18]

The fractional free volume (V_F) was estimated from the following equation,

$$V_F = (V - V_0)/V \qquad (1)$$

where V is the specific volume and V_0 is the specific van der Walls volume of sample calculated from the group contribution method reported by Bondi at 0 K.

Permeability Measurements

Carbon dioxide, methane, oxygen, and nitrogen used in this study were represented to be at least 99.9 mol % pure and were used without further purification.

Gas permeability coefficients for pressure up to 10 atm were determined with a low-vacuum permeation apparatus (Rika Seiki Inc. K-315-H). The pressure on the upstream and the downstream sides were detected by using a Baratron absolute pressure gauge.

Permeation parameters were calculated from diffusion time lags, θ, using

$$D = l^2/6\theta \qquad (2)$$

where D is the diffusion coefficient, l is the membrane thickness, and θ is time lag. The solubility coefficient, S, was calculated from the permeability coefficient, $P(=DS)$.

RESULTS AND DISCUSSION

Characterization of Soluble Aromatic Polyimides

The soluble polyimides with sulfone diamine moieties were synthesized by chemical imidization according to treatment with a mixture of acetic anhydride and triethylamine. The content of residual amide groups of poly(amic acid) was followed by monitoring the IR spectroscopy. The IR bands in 6FDA-*p*-DDS membrane were located at 1768 cm^{-1}, 1728 cm^{-1}, 1369 cm^{-1}, and 722 cm^{-1}. The bands in 6FDA-*m*-DDS membrane appeared at 1786 cm^{-1}, 1728 cm^{-1}, 1363 cm^{-1}, and 721 cm^{-1}. The bands near 1780 cm^{-1} and 1720 cm^{-1} are attributed to the symmetric and asymmetric stretches of carbonylgroups, respectively.[3,11,12] The absorbances near 1370 cm^{-1} and 720 cm^{-1} are attributed to the C—N stretch and to deformation of the imide ring or to the imide carbonyl groups, respectively.[3,11,12] The band near 1720 cm^{-1} is not generally used to determine the degree of imidization because it is strongly affected by carbonyl groups from acid moieties. Recently, Pryde has reported that the bands near 1780 cm^{-1} and 720 cm^{-1} are also affected by anhydride absorptions.[12] Therefore, the degree of imidization in 6FDA-*p*-DDS and 6FDA-*m*-DDS membranes was calculated from imide absorbance at 1369 cm^{-1} and 1363 cm^{-1}, because these imide bands did not appear to suffer direct interference by any other peak. The conversion to imide determined by IR spectroscopy showed more than 99.5%.

The degree of solution imidization of polyimides was also measured by ^{1}H-NMR spectroscopy. ^{1}H-NMR spectra of poly(amic acid)s showed two peaks that were located at 13 ppm due to the carboxylic acid and at 10.4 ppm due to the amide groups. However, these peaks measured by ^{1}H-NMR completely disappeared after the imidization was completed. The result of ^{1}H-NMR spectroscopy also supported that the aromatic polyimides synthesized with a chemical imidization were completely imidized.

As shown in Table I, 6FDA-*p*-DDS and 6FDA-*m*-DDS were soluble in various organic solvents. Most of the aromatic polyimide membranes are prepared by casting solutions of poly(amic acid) pre-
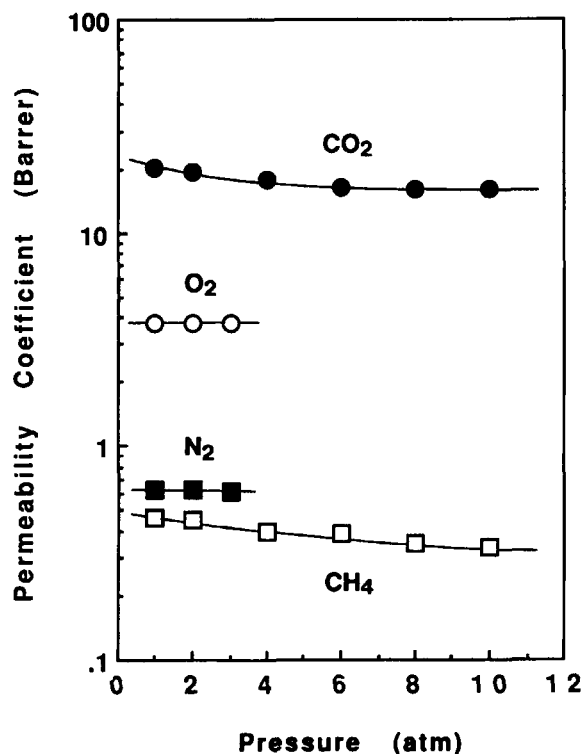
Figure 2 Pressure dependence of permeability coefficients for four gases in the 6FDA-p-DDS membrane at 35°C. Barrer = 10^{-10} [cm³(STP)cm/cm² s cmHg].

cursors onto a substrate and then converting them into the polyimide membranes. Because this conversion is thermally accomplished by heating to temperature in over 300°C, the aromatic polyimides synthesized with a thermal imidization show insolubility and infusibility due to some branches or crosslinks formed during this high-temperature process. It is extremely difficult for the insoluble aromatic polyimides to produce perfect gas separation membranes composed of an ultrathin and defect-free layer. Soluble aromatic polyimides, however, offer an advantage as applications of gas separation materials such as asymmetric membranes with ultrathin skin and detect-free layers or ultrathin composite membranes. The polyimide membranes obtained in this study were almost colorless and flexible.

The results of physical properties for 6FDA-p-DDS and 6FDA-m-DDS are listed in Table II. These polyimides had high molecular weights, which were constant during chemical imidization. This may be due to the fact that the molecular weight decrease observed in thermal imidization does not occur, because the reverse propagation reaction does not occur during chemical imidization.[13,14] 6FDA-p-DDS

with para-isomeric diamine moiety exhibited higher T_g compared to 6FDA-m-DDS with meta-isomeric diamine moiety. The reason for the lower T_g of 6FDA-m-DDS is considered to be a higher configurational entropy due to a larger degree of conformational freedom of the main chains than that of 6FDA-p-DDS.[15] The intersegmental distance (d-spacing) and fractional free volume of 6FDA-p-DDS increased slightly as compared to those of 6FDA-m-DDS.

Permeability and Permselectivity of 6FDA-p-DDS and 6FDA-m-DDS Membranes

The permeabilities of 6FDA-p-DDS and 6FDA-m-DDS to CO_2, O_2, N_2, and CH_4 at 35°C are reported in Figures 2 and 3 in the form of semilogarithmic plots of the permeability coefficient, P, vs. the upstream pressure, p_2. The apparent diffusivity and solubility parameters, which were calculated from the diffusion time lag, for 6FDA-p-DDS and 6FDA-m-DDS at 10 atm for CO_2 and CH_4 and at 3 atm for O_2 and N_2 are summarized in Tables III and IV. PCO_2 and PCH_4 decrease slightly with the increasing p_2 in the range from 1 to 10 atm, while PO_2 and
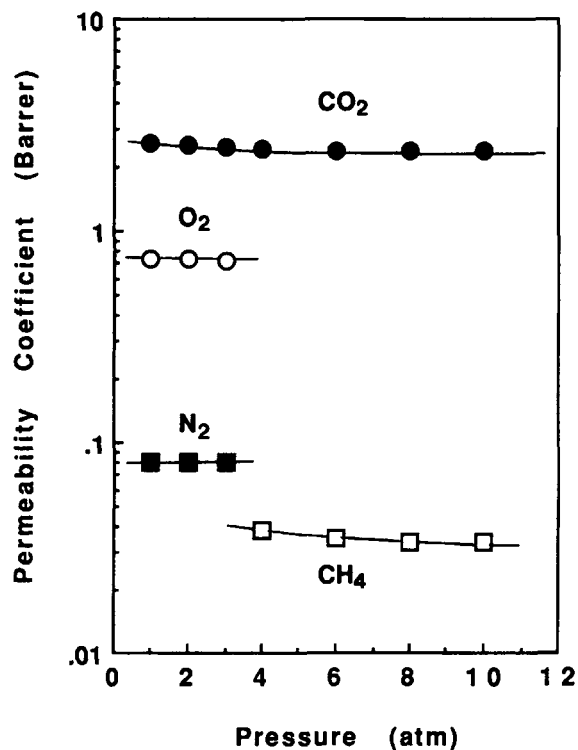

Figure 3 Pressure dependence of permeability coefficients for four gases in the 6FDA-m-DDS membrane at 35°C. Barrer = 10^{-10} [cm³ (STP)cm/cm² s cmHg].

Table III   Apparent Diffusivity and Solubility of 6FDA-*p*-DDS and 6FDA-*m*-DDS Membranes to CO_2 and CH_4 at 35°C

Polymer	$PCO_2 \times 10^{10}$	PCO_2/PCH_4	$DCO_2 \times 10^8$	$SCO_2 \times 10^2$	DCO_2/DCH_4	SCO_2/SCH_4
6FDA-*p*-DDS	16	47	2.1	7.3	12	3.8
6FDA-*m*-DDS	2.3	74	0.41	5.6	18	3.8
PSF[16]	5.6	22	2.0	2.7	5.9	3.7
PC[17]	6.8	19	3.2	2.1	4.7	4.0

P: [cm^3(STP)cm/cm^2 s cmHg]; D: [cm^2/s]; S: [cm^3(STP)/cm^3 cmHg].

PN_2 were independent of p_2 in the range from 1 to 3 atm. The permeability coefficients for the 6FDA-*p*-DDS membrane were markedly higher than those for 6FDA-*m*-DDS, as shown in Figures 2 and 3. It is evident from data represented in Table III and IV that the diffusivity coefficients of each gas in the 6FDA-*p*-DDS membrane are remarkably larger than those in 6FDA-*m*-DDS, while the solubility coefficients in these polymers are not so different. 6FDA-*p*-DDS, with para-isomeric diamine moiety, had a larger intersegmental distance and fractional free volume than 6FDA-*m*-DDS with meta-isomeric diamine moiety. One factor that contributes to gas diffusivity is the intersegmental distance and fractional free volume.

Figure 4 gives the polyimide structures investigated using molecular simulations that were performed by molecular dynamic calculation (Mopac 7.1). The two polyimides showed a helix configuration due to the bending and twisting of the polymer chain at —C(CF_3)— group in the 6FDA repeat unit, and this configuration in 6FDA-*m*-DDS formed more packed structure than 6FDA-*p*-DDS due to the bending and twisting of the polymer chain at the *m*-DDS repeat unit composed of the meta-isomeric diamine moiety. The conformation of 6FDA-*p*-DDS forms more open structure than that of 6FDA-*m*-DDS, which appear to be reflected in the fact that the intersegmental distance and fractional free volume of 6FDA-*p*-DDS are larger than those of 6FDA-*m*-DDS.

Referring to Figures 2 and 3, it is seen that the values for permeability coefficients for four kind of gases in 6FDA-*p*-DDS and 6FDA-*m*-DDS membranes decrease in the order: $PCO_2 > PO_2 > PCH_4 > PN_2$; this is the order of increasing kinetic molecular diameter of penetrate molecules.[7]

The permselectivities, PCO_2/PCH_4 and PO_2/PN_2, for these polyimides were large compared with those obtained with other glassy polymer membranes such as polysulfone (PSF) and polycarbonate (PC), as shown in Tables III and IV and, in particular, the 6FDA-*m*-DDS membrane exhibited high PCO_2/PCH_4 selectivity. For 6FDA-*p*-DDS and 6FDA-*m*-DDS, the diffusivity selectivities were significantly higher than those in PSF and PC, while the solubility selectivities were similar to those in PSF and PC. That is, the large diffusivity selectivities are the principal factors that dominate in the determination of permselectivities of PCO_2/PCH_4 and PO_2/PN_2. The greater diffusivity selectivity of 6FDA-*p*-DDS and 6FDA-*m*-DDS relative to PSF and PC may be due to the high packing density of polymer chain; ρ(6FDA-*p*-DDS) = 1.483, ρ(6FFDA-*m*-DDS) = 1.487, ρ(PSF) = 1.240, and ρ(PC) = 1.200.

Because the aromatic polyimides contain an alternating sequence of electron-rich donor and electron-deficient acceptor subunits, it has been suggested that their physical properties are dependent on the existence of charge–transfer complexes formed between their polymer chains. The recent

Table IV   Apparent Diffusivity and Solubility of 6FDA-*p*-DDS and 6FDA-*m*-DDS Membranes to O_2 and N_2 at 35°C

Polymer	$PO_2 \times 10^{10}$	PO_2/PN_2	$DO_2 \times 10^8$	$SO_2 \times 10^3$	DO_2/DN_2	SO_2/SN_2
6FDA-*p*-DDS	3.7	6.1	5.5	6.8	4.9	1.2
6FDA-*m*-DDS	0.73	9.1	1.1	6.7	6.7	1.3
PSF[16]	1.4	5.6	4.4	3.1	3.6	1.6
PC[17]	1.6	4.8	5.8	2.7	3.2	1.5

P: [cm^3(STP)cm/cm^2 s cmHg]; D: [cm^2/s]; S: [cm^3(STP)/cm^3cmHg].
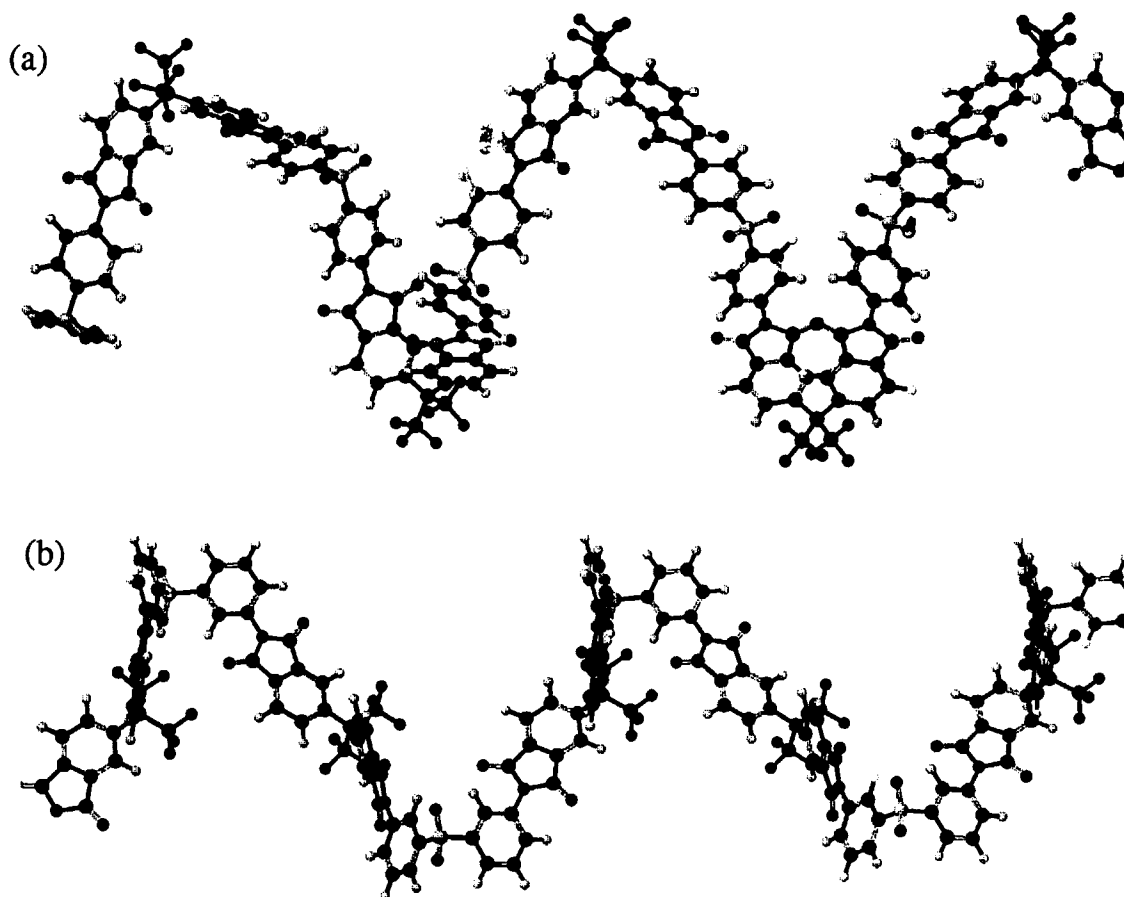
Figure 4   Structures of 6FDA-*p*-DDS (a) and 6FDA-*m*-DDS (b) simulated by using molecular dynamic calculation.

studies of spectroscopy and X-ray diffraction provide strong support for the existence of a charge–transfer complex formation of polyimides.[18,19] Figure 5 gives the results of emission spectra in 6FDA-*p*-DDS and 6FDA-*m*-DDS membranes measured using fluorescence spectrophotometer. The polyimide membrane with thickness of 50 μm were annealed at 150°C for 3 h or at 200°C for 3 h prior to measure. 6FDA-*p*-DDS and 6FDA-*m*-DDS membranes had an emission spectra bands at 472 nm and 469 nm, respectively, when excited at 350 nm. This finding supports that the charge–transfer complex in 6FDA-*p*-DDS and 6FDA-*m*-DDS membranes is undoubtedly formed.[20] Formation of this complex in polyimides appears to increase the packing density of polymer chain to facilitate the inter- and intramolecular interactions and to suppress the mobility of main chains. Even though this work provides firm evidence for a charge–transfer complex of aromatic polyimides from measurement using fluorescence spectrophotometer, it is clear that further work is necessary to evaluate a correlation between the charge–transfer complex and the mobility of the polymer chain.

CONCLUSIONS

The above studies show the synthesis, the characterizations, and the gas transport properties of soluble aromatic polyimides. 6FDA-*p*-DDS and 6FDA-*m*-DDS, synthesized by a chemical imidization, exhibit a higher gas permselectivity than presently available polymers. An important factor is the packing density of the polymer chain. The mobility of the polymer chain controls the diffusivity of gas molecules in aromatic polyimides. Due to the high packing density of the polymer chain, the diffusivity selectivities in the polyimides used in this study increase significantly compared with those obtained with other glassy polymers.

The difference in the gas permeability between 6FDA-*p*-DDS and 6FDA-*m*-DDS membranes is explained by the difference in the gas diffusivity be-
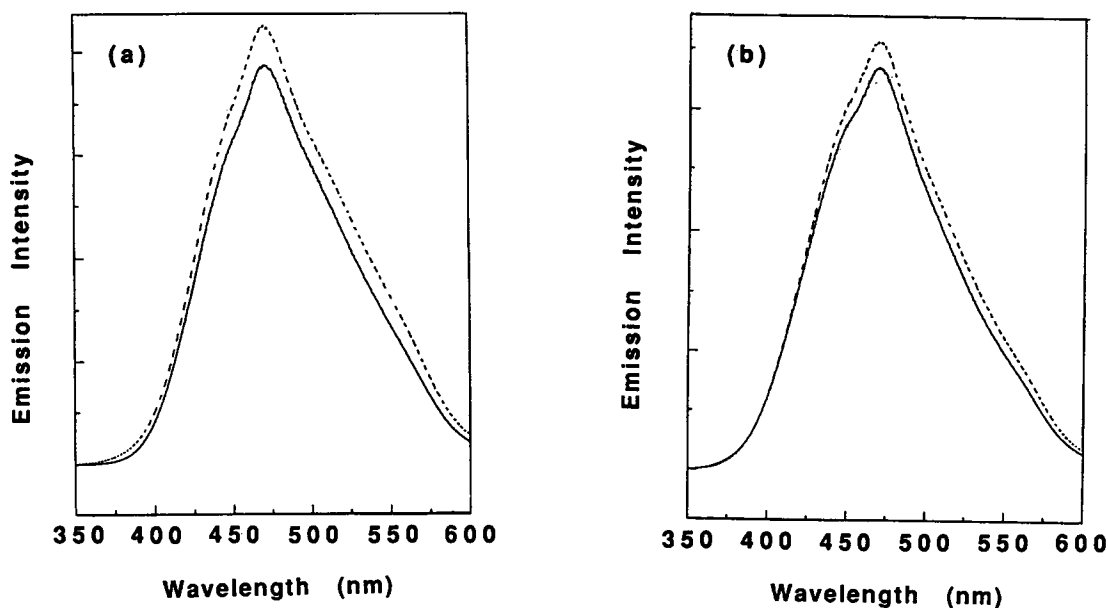
Figure 5   Emission spectra excited at 350 nm for 6FDA-*p*-DDS (a) and 6FDA-*m*-DDS (b) membranes. (—): 150°C, (---): 200°C.

tween the two polymers. This may be due to the fact that the helix configuration of 6FDA-*m*-DDS with meta-isomeric diamine moiety forms more packed structure than that of 6FDA-*p*-DDS with para-isomeric diamine moiety due to the bending and twisting of the polymer chain at the *m*-DDS repeat unit. We have demonstrated here that these physicochemical factors play an important role in permeability and permselectivity of aromatic polyimides.

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