The Effect of Molecular Structure on the Gas Transmission Rates of Aromatic Polyimides

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Synopsis

A series of high-molecular weight condensation polyimides was evaluated to determine the effect of polymer molecular structure on the transmission rate of oxygen, carbon dioxide, and water vapor. The polyimide films were prepared from either 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) or pyromellitic dianhydride (PMDA) with various diamines. The study shows that molecular structure had a strong influence on gas transmission rates with results for some films varying three orders of magnitude from that of other polyimide films. In general, the BTDA series of polyimides had overall lower gas transmission rates than the PMDA-derived series. Polymers prepared with *meta*-oriented diamines characteristically displayed lower gas transmission than those prepared with *para*-oriented diamines.

INTRODUCTION

The transmission rates of gases and vapors through a polymer depend to a large degree upon polymer molecular structure. For those polymers that have widespread commercial use, the relationship of molecular structure and gas transmission rate is well characterized.[1-3] For aromatic polymers, such as polyimides which are currently being considered for electronic, composite, and adhesive applications, little transmission data is available. Water vapor transmission rate studies[4] have been performed on a widely used commercial polyimide film and the data indicate that this polymer has relatively low gas transmission rates. Because of the lack of information and the current interest in polyimides as a class, a study was undertaken to evaluate the transmission rates of these materials and to determine the effect of molecular structure upon gas transmission rates. The study was performed on solution cast films from polymers that had systematic dianhydride and diamine changes as well as isomeric variations. Transmission rates for water vapor, oxygen, and carbon dioxide are reported.

EXPERIMENTAL

Materials and Polymer Solutions

All of the monomers used in this investigation are listed in Table I. Dianhydride and diamine monomers were acquired from commercial sources or prepared and purified as previously reported.[5-8] The dimethylacetamide (DMAc) used as a solvent for polymerization was vacuum distilled at 102°C from calcium hydride.

Polyamic acid precursors were prepared by solution condensation of an aromatic dianhydride with an aromatic diamine in dimethylacetamide. The general reaction route for preparation of a polyamic acid and thermal conversion to the fully cured polyimide is shown below.
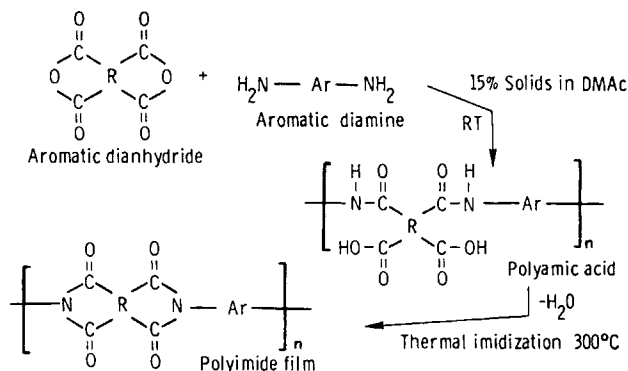
The dianhydride was added over a 30-minute-period to the stirred diamine solution under an air atmosphere. Stoichiometry for all reactions was held at a 1:1 ratio of dianhydride to diamine except in cases where a viscosity buildup was not noted after 24 hr stirring. When this occurred, the stoichiometry was upset by the addition of 1.0% excess dianhydride to build the molecular weight. Viscosity buildup was evident for most of the polyimides after stirring for 3 hr at ambient temperature. The inherent viscosity of each solution, as used for film casting, was determined at 35°C and is given in Tables II and III. Solutions were generally prepared at a 15% solids (w/s) concentration. In several cases (BTDA + pp'-DAS, PMDA + DAF and PMDA + benzidine), dilution of the solutions to 8–10% solids was necessary to provide adequate mixing.

In preparation for film casting, the amic acid solutions were either centrifuged for 15 min or filtered. When filtered, a metal chamber containing a 10 μm glass matt filter was used and a nitrogen head pressure of 5–20 psi was used to push the viscous solution through the filter.

PREPARATION OF FILMS

Films were cast from solution on soda-lime glass plates in a controlled dust-free environment. The glass plates were precleaned with an abrasive type soap cleaner, washed thoroughly with water, and then cleaned with ethanol before use. The film casting bench consisted of an enclosed flat table on which the precleaned glass plates (30 × 60 cm) were pulled under a stationary knife edge. Solutions were poured across the glass plate in front of the knife edge, and the plate was pulled under the knife edge at about 4–5 cm/min. The freshly cast film was then heated from beneath to about 50–60°C to speed drying. The relative humidity, in air, during casting and drying was maintained between 5 and 15%. Films normally dried tack free in about 2–3 hr.

Each film was thermally imidized on the glass plate in a forced air oven by heating one hour each at 100°, 200°, and 300°C. Although some polymers had glass transition temperature (T_g's) higher than the final cure temperature, 300°C was chosen to provide a basis for comparison and to eliminate any competition with thermal degradation that might occur with higher cure temperatures. After cooling to below 60°C, the polyimide film was removed from the glass plate by stripping in a water bath. The resultant polyimide films generally were about 0.0025 cm in thickness. Glass transition temperatures (T_g) of the cured polyimide films were obtained using a DuPont Model 981 thermomechanical analyzer (TMA) in static air at 5°C/min and are reported in Tables II and III. The T_g data given in these tables agrees well with values determined in previous studies[2-4] of these polymers.

EQUIPMENT

Oxygen transmission rate (OTR) was the primary means of evaluating the gas transmission characteristics of the polyimide films. A Modern Controls Inc. Oxtran 100 analyzer conforming to ASTM D-3985-81 was used for this analysis and a schematic of the flow system for this instrument is shown in Figure 1(a). Tests were performed at atmospheric pressure on films having a diameter of 10 cm. Each film was clamped in the film holder and purged with the carrier gas (nitrogen) for 12 hr to remove all traces of oxygen from the flow lines, test chamber, and film. Following the 12-hr purge, the carrier gas flow was diverted so that it crossed only the lower side of the test film before passing to the detector. The flow across the top half of the test chamber was changed at the same time to moisture-free oxygen. The oxygen which passed through the test film was carried by the nitrogen carrier stream to a coulometric detector with output calibrated directly in units of flow per unit area-time. The transmission rate for each film was determined at preselected temperatures between ambient and 70°C.

Transmission rates for carbon dioxide were obtained by using the time lag method[9] and the apparatus schematically shown in Figure 1(b). This set-up used a standard 90 mm diameter filter holder as the test cell and a capacitative-type pressure sensor, made by Datametrics Division of CGS,
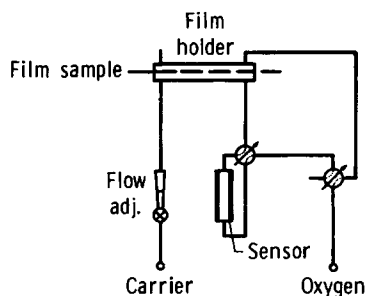

Fig. 1(a). Schematic of apparatus used for determining oxygen transmission rates of polyimide films.

TABLE I
Monomers Used in Preparation of Polyimide Films

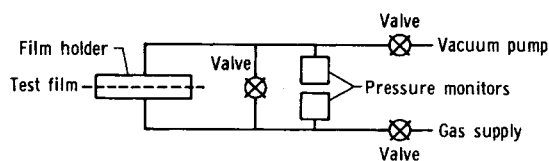| Monomer	Molecular structure	Melting point, °C
BTDA		224^a
PMDA		285^a
p,p'-DAS		231^a
DAFO		286 (ref. 5)
DAF		163 (ref. 5)
Benzidine		127^a
p-PDA		138^a
DADPyS		178–180 (ref. 6)
m,m'-DABP		151–152 (ref. 7)
m,m'-MDA		82–83 (ref. 7)
m-PDA		59^a
p,p'-DABP		241–242 (ref. 7)
m,p'-DABP		126 (ref. 7)
m,p'-MDA		86–87 (ref. 7)
m,m'-DADPC		123 (ref. 8)
p,p'-ODA		$74–75^a$
DADPS		106^a
p,p'-MDA		93^a

^{a} Commercial source

Fig. 1(b). Schematic of apparatus used for determining carbon dioxide transmission rates in polyimide films.

to follow pressure increases in the low pressure side of the system. This pressure detector was sensitive to 1.3×10^{-3} N/m^2 changes in pressure. The test sequence involved evacuation of the system by pumping on both sides of the film for 24 hr before testing. After the pump down period, the cross-over valve and the vacuum valve were closed and carbon dioxide was admitted to the lower side of the film. The input pressure was set at 3.44×10^4 N/m^2. The pressure on the upper side of the film was monitored as a function of time and used to calculate the transmission rate. All tests were performed at room temperature.

Water vapor transmission rates (WVTR) for each polyimide film were determined with a Modern Controls Inc. Model IRD-2 infrared water vapor diffusometer, conforming to ASTM F 372-78. A schematic of the test cell for this instrument is shown in Figure 2. The test cell consists of a single dry chamber and two wet chambers which are separated by the test film. The dry chamber is a machined Teflon block with two windows (test area) which have a total area of 107 cm^2. The concentration of water in the dry chamber was determined using an infrared detector system operating at 2.6 μm and 2.5 μm. In the first region, water molecules absorb infrared radiation while the second wavelength region is unaffected by water vapor. The con-

TABLE II
Solution and Film Properties of BTDA-Derived Polymers

Polymer	Polyamic acid η_{inh}[a]	TMA T_g, °C
BTDA + p,p'-DAS	1.58	303
BTDA + DAFO	1.29	331
BTDA + DAF	1.17	333
BTDA + Benzidene	1.40	344
BTDA + p-PDA	1.31	333
BTDA + DADPyS	0.77	246
BTDA + m,m'-DABP	0.70	259
BTDA + m,m'-MDA	0.73	265
BTDA + m-PDA	0.86	300
BTDA + p,p'-DABP	0.79	288
BTDA + m,p'-DABP	0.64	277
BTDA + m,p'-MDA	0.99	281
BTDA + m,m'-DADPC	0.85	317
BTDA + p,p'-ODA	1.08	279
BTDA + DADPS	1.04	276
BTDA + p,p'-MDA	0.83	296

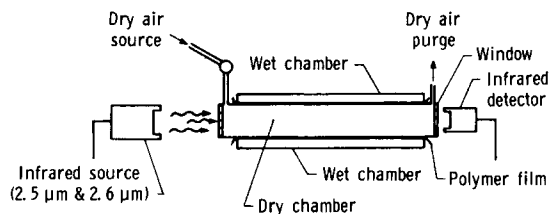[a] η_{inh} determined at 35°C.

Fig. 2. Schematic of water vapor transmission rate apparatus.

centration of water vapor present in the chamber was determined from the ratio of the absorption band intensities of the two wavelengths. This detector system has a sensitivity of one part per million. The rate of transmission was obtained by determining the length of time necessary for the concentration to build to a predetermined value. Water vapor transmission rates were obtained at 37.8°C and 100% relative humidity.

RESULTS AND DISCUSSION

Effect of Solution Viscosity and Film-Casting Techniques on OTR

Since all transmission rate data in this study was obtained on experimental polymers synthesized and cast in the laboratory, several variables associated with the synthesis and casting steps were examined for their effect upon results. For these experiments, only oxygen transmission rates were determined.

The effect of starting solution viscosity and film-casting techniques upon OTR are shown in Figure 3. The top portion of this figure shows the OTR variation with temperature for two films of PMDA + p,p'-DABP of the same thickness cast from solutions having different viscosities. The slight difference in OTR for the two films shows the range of scatter generally observed for polymers having the same molecular structure but varying viscosities. The viscosity range of the PMDA +p,p'-DABP solutions, from which the

TABLE III
Solution and Film Properties of PMDA-Derived Polymers

Polymer	Polyamic acid $\eta_{inh}{}^b$	TMA T_g, °C
PMDA + DAF	1.92	322
PMDA + Benzidine	2.12	a
PMDA + m,m'-DABP	1.00	318
PMDA + DADPyS	0.81	359
PMDA + p,p'-DABP	0.69	412
PMDA + p,p'-ODA	1.46	399
PMDA + DADPS	1.26	400
PMDA + p,p'-MDA	1.51	338

a Film too brittle for T_g measurement.
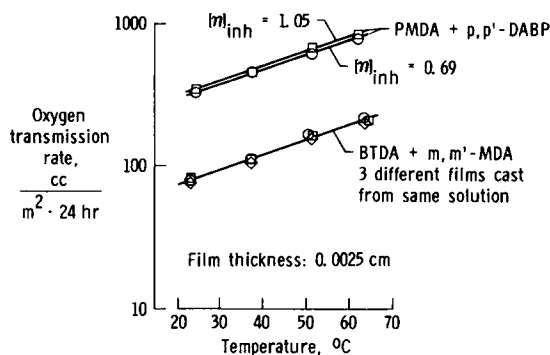b η_{inh} determined at 35°C.

Fig. 3. Solution viscosity and film-casting effects on oxygen transmission rates of two polyimides.

films were made, generally spans the range of solution viscosities of the prepolymer solutions used to make films in this investigation. In the lower portion of Figure 3, data is shown for three different films of BTDA + m,m'-MDA which were cast on different days from a single polymer solution. The data from the two experiments in Figure 3 indicate that the polyamic acid solution properties (viscosities) and film-casting techniques had very little effect upon the observed oxygen transmission rate.

All films evaluated in this study were cast on glass plates as previously described. Since the drying process results in solvent evaporation from one side only, a possible side-to-side effect could develop, resulting in a variation in OTR depending upon the side which the penetrating gas entered. Figure 4 shows the results from one film, BTDA + p,p'-MDA, where the OTR was determined in both directions. That is, the OTR was determined by allowing the penetrating oxygen to enter the film from the side cured against the glass plate and the experiment was repeated with the film reversed. A slight difference was observed but this difference was within the experimental data scatter. Several other polymer films were evaluated for this side-to-side effect, and no differences greater than that shown in Figure 4 were
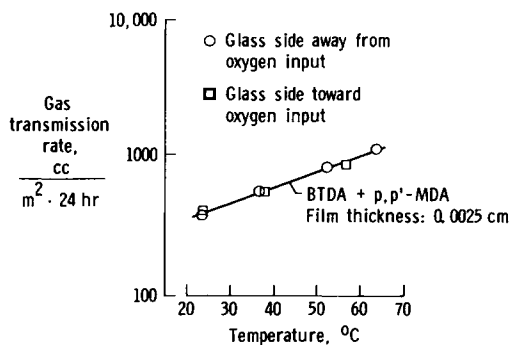

Fig. 4. Effect of film-casting orientation on oxygen transmission rate.

found. From this data it was concluded that the film drying process did not alter the gas transmission characteristics.

EFFECT OF TEMPERATURE ON OTR

All OTR data in this study was obtained at several preselected temperatures between ambient and 70°C. The temperature effect observed was generally a good indication of the presence of holes in the film as shown in Figure 5. The data shown in this figure were obtained from two separate films from BTDA + benzidine. The upper curve shows the temperature response from a defective film (response attributed to an invisible hole) while the lower curve shows that from another film without a defect. For homogeneous, hole-free films, it was found that temperature had a significant effect on OTR while defective films did not exhibit this effect. For each polyimide, several films were evaluated to insure that the data obtained represented homogeneous hole-free films.

EFFECT OF MOLECULAR STRUCTURE ON OXYGEN, CARBON DIOXIDE, AND WATER TRANSMISSION RATES

The overall results of this study are given in Tables IV and V where the transmission rate for oxygen, carbon dioxide, and water vapor are given for the BTDA and PMDA-derived polyimides, respectively. In each table, polymers are listed in order of increasing oxygen transmission rates. Carbon dioxide and water vapor transmission rates were not determined for all films as indicated in this table. The transmission rates given in these tables are expressed in units of $cc/m^2 \cdot 24$ hr for oxygen and carbon dioxide and $g/m^2 \cdot 24$ hr for water vapor. All data given in Tables IV and V are normalized to 0.00254 cm film thickness. The chemical structure variations for polyimides derived from BTDA and several diamines resulted in three orders of magnitude variation in oxygen and carbon dioxide transmission rates. For films with the lowest transmission rates, the absolute value of transmission compares favorably with the best commercial barrier materials.[1] Water vapor transmission rates are high compared to other polymers but
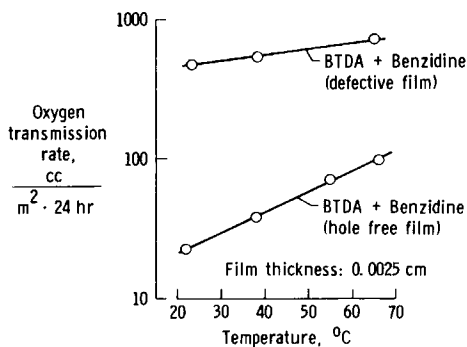

Fig. 5. Effect of film imperfections on oxygen transmission rate.

TABLE IV
Oxygen, Carbon Dioxide, and Water Vapor Transmission Rates for BTDA Polyimide Films

	Transmission rate		
Polymer	Oxygen[a]	Carbon dioxide[a]	Water vapor[b]
BTDA-p,p'-DAS	7.4	23.9	—
BTDA-DAFO	8.0	—	12.2
BTDA-DAF	12.8	39.9	22.4
BTDA-Benzidine	23.1	81.0	17.1
BTDA-p-PDA	35.6	—	41.8
BTDA-DADPyS	68.6	217.6	82.2
BTDA-m,m'-DABP	75.6	278.8	77.5
BTDA-m,m'-MDA	81.3	117.5	52.7
BTDA-m-PDA	106.4	304.7	145.7
BTDA-m,p'-DABP	155.7	306.5	94.5
BTDA-p,p'-DABP	156.0	455.1	108.5
BTDA-m,p'-MDA	199.9	—	103.8
BTDA-m,m'-DADPC	250.6	—	—
BTDA-p,p'-ODA	320.2	1232.4	130.2
BTDA-DADPS	342.9	1060.1	142.6
BTDA-p,p'-MDA	485.5	1121.0	178.3

[a] cc/m^2 · 24 hr for a 0.0025 cm film at ambient temperature.
[b] g/m^2 · 24 hr for a 0.0025 cm film at 37.7°C and 100% RH.

generally follow the ranking established for oxygen and carbon dioxide transmission rates (Table IV). Films formed with diamines which have relatively "rigid" molecular structures, such as DAF, DAFO, and benzidine, have the lowest transmission rates for both gases and water vapor while those with more flexible linkages, such as —C—, —CH$_2$—, and —O— (DABP, MDA and ODA, respectively) have higher transmission rates. The polyimide film found with the lowest oxygen and CO$_2$ transmission rates was BTDA + pp'-DAS. The low transmission rate found for this polymer may indicate that other chemical structure factors such as cross-link density

TABLE V
Oxygen, Carbon Dioxide, and Water Vapor Transmission Rates for PMDA Films

	Transmission rate		
Polymer	Oxygen[a]	Carbon dioxide[a]	Water vapor[b]
PMDA-DAF	12.9	29.3	17.8
PMDA-Benzidine	15.6	27.3	23.8
PMDA-m,m'-DABP	89.9	—	131.7
PMDA-DADPyS	104.3	378.4	99.2
PMDA-p,p'-DABP	380.8	467.4	182.9
PMDA-p,p'-ODA	834.7	4694.0	341.0
PMDA-DADPS	1162.0	—	341.0
PMDA-p,p'-MDA	1272.0	4576.0	286.7

[a] cc/m^2 · 24 hr for a 0.0025 cm film at ambient temperature.
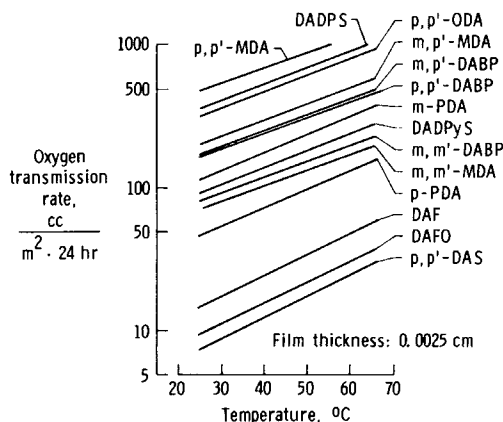[b] g/m^2 · 24 hr for a 0.0025 cm film at 37.7°C and 100% RH.

Fig. 6.   Effect of temperature on oxygen transmission rate of BTDA-derived polyimide films.

may have a significant effect upon transmission rate since this polymer may be the most susceptible of those evaluated to thermal crosslinking.

Temperature affected all of the polyimides in a similar manner as indicated in Figure 6 where the OTR for the polyimide series is given. For each film, 4 data points were obtained to establish the slope of the transmission rate/temperature curve. In general, for each 10°C increase from RT to 70°C (temperature range studied) the rate of oxygen transmission increased by about 50%. For the BTDA-derived polymers, meta isomers generally had lower oxygen, CO_2, and water vapor transmission rates than the corresponding para-oriented isomers. The OTR for a typical isomer series (BTDA + MDA) is shown in Figure 7 and this data shows that each isomer has about the same OTR temperature response.

The oxygen, CO_2, and water vapor transmission rates for PMDA-based polyimides generally paralleled those observed for BTDA polymers. As shown in Table V, a complete parallel series to the BTDA polymer was not available for evaluation. Of those materials tested, however, the PMDA + DAF film was found to have the lowest gas transmission rates for oxygen and water vapor and the second lowest for CO_2. Although comparison of BTDA and
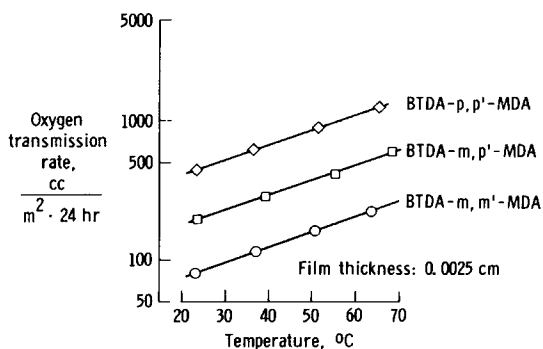

Fig. 7.   Effect of diamine isomer on oxygen transmission rate of BTDA-MDA polyimides.

PMDA polyimide films in this study indicates that BTDA-based films generally had lower rates of transmission for all three gases, additional studies would be required to determine the effect of dianhydride structure on gas transmission rates for these polymers.

CONCLUSIONS

A study was conducted on two series of high molecular weight, condensation polyimides to determine the effect of polymer molecular structure on gas transmission rate. A total of 24 polymer films were prepared by reacting either 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) or pyromellitic dianhydride (PMDA) with various aromatic diamines. Polyamic acid solution viscosities and various film-casting techniques including orientation of the film on the glass curing plate were found to have little or no effect on the oxygen transmission rate through resulting polyimide films. An increase in the test temperature of the polymer films was found to produce a directly proportional increase in the logarithm of oxygen transmission rate. The molecular structure of the polyimide films had a strong influence on oxygen, carbon dioxide, and water vapor transmission rates with results for some films varying three orders of magnitude from that of other polyimide films. In general, the BTDA series of polymers had overall lower gas transmission rates than the PMDA-derived series. Polymers prepared with meta-oriented diamines characteristically displayed lower gas transmissioon than those prepared with para-oriented diamines.

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