

Gas-Separation Applications of Miscible Blends of Isomeric Polyimides

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SYNOPSIS

Blends of polyimide isomers containing hexafluoroisopropylidene in the central moiety of the diamine residue have been studied. The isomers differed by having either a *meta* or a *para* linkage between the diamine and dianhydride residues. The miscibility of these materials was investigated by studying the glass transition temperature behavior using differential scanning calorimetry. Mixtures of isomer pairs, such as 6FDA–6FmDA and 6FDA–6FpDA, exhibited one glass transition temperature, T_g , and were therefore miscible. Mixtures of nonisomer pairs exhibited two T_g 's and were immiscible. The gas sorption and transport properties of the blends of the 6FDA–6FmDA and 6FDA–6FpDA isomers were characterized for a variety of gases at 35°C for pressures up to 60 atm. The permeabilities and permselectivities in the miscible blends fell between those of the pure components and were approximately logarithmic averages of the pure component properties. The miscibility of the polyimide isomers enables one to tailor the composition of the material to optimize the gas separation and mechanical properties. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Several methods can be used for developing new materials for commercial applications; among these are the synthesis of new polymers, copolymerization, and blending of miscible polymers.¹ In principle, the most economical method is the blending of miscible materials, resulting in a product with properties that lie between those of the pure components. Unfortunately, it is difficult to find polymers that are miscible, due to thermodynamic constraints arising primarily from the low combinatorial entropy of mixing of polymers.^{1–4}

Recent work within families of polymers has shown that structural variations, leading to systematic changes in chain mobility and packing, can be

used to achieve increases in permeability and permselectivity.^{5–7} Other studies of polyimides in which the location of the bond linking the diamine and dianhydride residues has been changed indicate that the *para*-connected polymer has much higher permeabilities with tolerably lower permselectivities than those of the *meta*-connected material.^{8–10}

The present work considers the miscibility of the isomers of several polyimides with a hexafluoroisopropylidene moiety in the diamine residue and a *meta* (6FmDA) or *para* (6FpDA) linkage between the diamine residue and dianhydride residue. Also, the gas-separation properties of a range of concentrations of the blends of the polyimides with hexafluoroisopropylidene moiety in the dianhydride (6FDA) are investigated. The large differences in the properties of these polyimide isomers make them ideal candidates for blending for property optimization.

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BACKGROUND

The permeability of a membrane, P , can be written in terms of a product of an average diffusion coef-

cient, D , and an average solubility coefficient, S (Refs. 5 and 6):

$$P = D \cdot S \quad (1)$$

For conditions such as those used here, in which a vacuum is maintained downstream, S is equal to the secant slope of the sorption isotherm evaluated at the upstream conditions, designated by subscript "2", e.g., $S = C_2/p_2$. Also, under these conditions, the diffusion coefficient, D , averaged across the membrane between the upstream and downstream conditions may be a function of the upstream pressure.

Increasing the diffusivity or solubility of a desired gas by polymer structural variations allows one to raise the gas permeability. Similarly, to improve the permselectivity of a desired gas over an undesired one, the diffusivity selectivity or solubility selectivity can be increased. It has been demonstrated that increases in diffusivity and diffusivity selectivities can result from simultaneously inhibiting intersegmental chain packing and intrasegmental chain mobility.⁵⁻⁹ The findings of these earlier studies can be generalized as two principles for membrane material selection:

1. Structural alterations within a family of materials that inhibit chain packing with a secondary inhibition to rotational mobility about flexible linkages on the polymer backbone will tend to increase permeability while maintaining permselectivity.
2. Structural alterations within a family of materials that significantly suppress the segmental mobility while causing only small changes in chain packing will tend to decrease permeability with desirable increases in permselectivity.

When miscible blends of amorphous polymers form glasses, a single composition-dependent glass transition temperature, T_g , is exhibited. Immiscible blends of amorphous polymers exhibit separate glass transition temperatures associated with each phase.^{1,2} The transport properties of amorphous miscible blends or random copolymers can be estimated based on those of the pure components, using the following mixing rule developed from a simple free-volume model^{3,4}:

$$\ln Y_{12} = \phi_1 \ln Y_1 + \phi_2 \ln Y_2 \quad (2)$$

where ϕ_i is the volume percent; Y_i , the transport property of component i ; and Y_{12} , the property of the blend.

EXPERIMENTAL

Materials

The polyimide isomers used in this study are experimental polymers supplied by Hoechst-Celanese and are listed in Table I. The 6FDA-6FmDA, 6FDA-6FpDA, BTDA-6FmDA, and BPDA-6FpDA were cast from methylene chloride (CH_2Cl_2) as described in an earlier paper.⁸ The BTDA-6FpDA and BPDA-6FmDA, which were insoluble in methylene chloride, were cast from dimethylacetamide (DMAC). The polymers were cast from DMAC under vacuum at 25°C on a glass plate and allowed to dry for 12-18 h, after which the temperature was raised gradually to 200°C to remove residual solvent. None of the polyimides exhibited crystallinity as sensed by X-ray and DSC or orientation as sensed by birefringence.

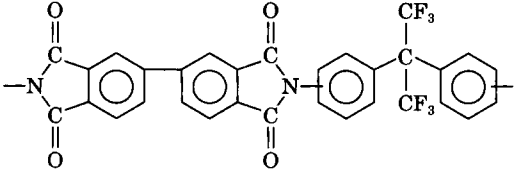
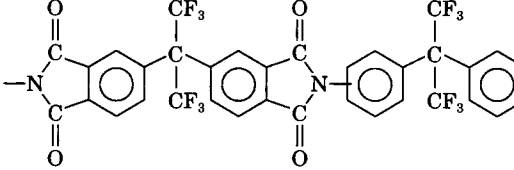
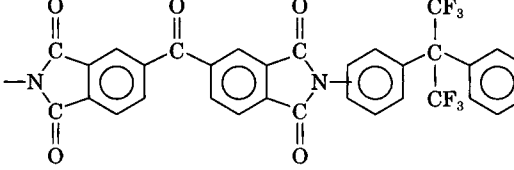
The polymer blends were made by mixing powders of the *meta* and *para* isomers of each of the polyimides and dissolving the resulting mixture in either DMAC or CH_2Cl_2 . The dissolved mixtures were cast from solution in the same manner used for preparing films of the pure components. The criterion for miscibility for the resulting film was the observation of a single glass transition temperature as measured by differential scanning calorimetry (DSC).

Permeation and Sorption

The permeabilities of He, N_2 , O_2 , CH_4 , and CO_2 were measured in films of 6FDA-6FmDA, 6FDA-6FpDA, and their miscible blends. The data were taken using the standard permeation techniques employed in our labs.¹¹ The gases used in the study were Linde UHP and Big 3 Industries chromatographic grades with purities of 99.97% and higher. The permeation measurements were made at 35°C at pressures up to 60 atm. Only pure gas permeabilities were measured; however, previous studies suggest that mixed-gas results will be comparable until plasticization occurs.^{11,12} The downstream pressure was always 10 Torr or less.

Pure gas-sorption measurements on the 6FDA-6FmDA, 6FDA-6FpDA, and the 50%/50% (by weight percent) mixture of the 6FDA isomers were

Table I Glass Transition Temperatures of Blends of Polyimide Isomers

Polymer Structure	Polymer	T_g °C
	BPDA-6FmDA	266
	50/50%	297
	BPDA-6FpDA	361
	6FDA-6FmDA	254
	50/50%	270
	6FDA-6FpDA	320
	BTDA-6FmDA	247
	50/50%	263
	BTDA-6FpDA	310

carried out with He, O₂, N₂, CH₄, and CO₂. The measurements were made with a pressure decay sorption cell as described previously.^{11,12}

RESULTS

Miscibility of Polyimide Isomers

The glass transition temperatures of the pure components and the 50%/50% (weight percent) mixture of each polyimide isomer pair are listed in Table I. The blends of these isomer pairs, such as BPDA-6FpDA and BPDA-6FmDA, have a single glass transition temperature as measured by differential scanning calorimetry (DSC). As mentioned earlier, the DSC curve of a miscible blend will have a single, concentration-dependent glass transition temperature.²⁻⁴

The glass transition temperature of mixtures of 6FDA-6FmDA and 6FDA-6FpDA isomers were also measured using DSC and were found to be miscible over a wide range of compositions. Mixtures of *non-isomer* pairs of these polyimides, such as 6FDA-6FpDA and BTDA-6FmDA, exhibited two T_g 's and were found to be *immiscible*. The miscibility of these fluorine-containing polyimides, therefore, is apparently limited to isomer pairs.

Gas-separation Properties of 6FDA-6FmDA/6FDA-6FpDA Blends

In an earlier paper, we showed that the *meta*-connected isomers of the fluorine-containing polyimides had much lower permeabilities with correspondingly higher selectivities than did their *para*-connected

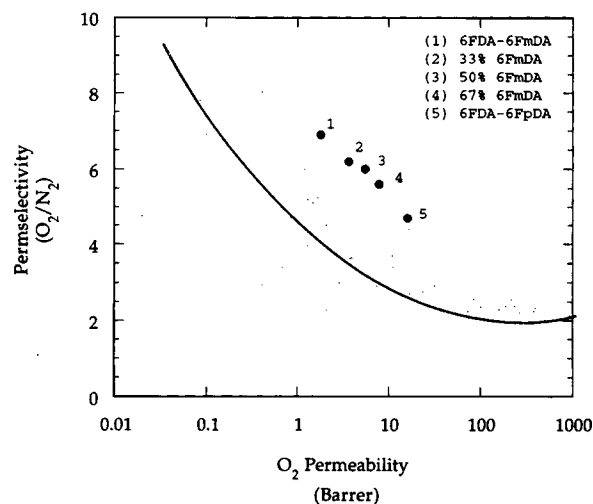


Figure 1 Tradeoff between permeability and permselectivity in blends of the 6FDA polyimides at 2 atmospheres and 35°C.

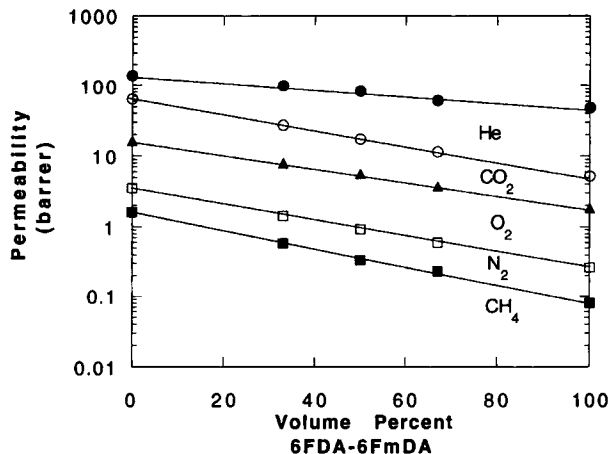


Figure 2 Permeability of *meta/para* isomeric blends of polyimides.

counterparts.^{8,9} Since the *meta/para* isomers of these polyimides have widely variant properties, their miscible blends may have an advantageous tradeoff between permeability and permselectivity.

The advantage of blending can be seen by plotting the O_2/N_2 selectivity vs. the O_2 permeability as shown in Figure 1 for the 6FDA polyimides. The permeability of the 6FDA polyimides are well above the typical tradeoff of lowered selectivity with increased permeability that is seen for many engineering polymers. The miscibility of the blends of the 6FDA polyimides results in materials that have an advantageous tradeoff of permeability and selectivity that falls between those of the pure components.

The permeability of several gases for miscible blends of the 6FDA-6FmDA and 6FDA-6FpDA isomers are shown in Figure 2. The permeabilities of the miscible blends agree well with eq. (2), which predicts that the properties of the miscible blends will be a volume logarithmic average of those of the pure components. The permselectivities of the 6FDA-6FmDA and 6FDA-6FpDA blends also fall between those of the pure components and agree with selectivities estimated using eq. (2).

The permeability and permselectivities for the blends containing the 6FDA-based isomers are listed

Table II Permeabilities and Permselectivities in Blends of 6FDA-6FpDA and 6FDA-6FmDA

Weight Percent 6FDA-6FmDA	P_{He}^a	$P_{O_2}^a$	$P_{CO_2}^a$	$\frac{P_{He}}{P_{CH_4}}$	$\frac{P_{CO_2}}{P_{CH_4}}$	$\frac{P_{O_2}}{P_{N_2}}$
0	137.0	16.30	63.9	85.6	39.9	4.7
33	99.0	7.89	27.4	170.0	47.1	5.6
50	83.1	5.54	17.2	252.0	52.1	6.0
67	61.0	3.67	11.4	265.0	49.6	6.2
100	48.0	1.80	5.1	600.0	63.7	6.9

^a Barrers.

Table III Comparisons of O_2 Permeabilities, Diffusivities, and Their Selectivities over N_2 in Blends of 6FDA-6FpDA and 6FDA-6FmDA

Polymer	$P_{O_2}^a$	$\frac{P_{O_2}}{P_{N_2}}$	$S_{O_2}^b$	$\frac{S_{O_2}}{S_{N_2}}$	$D_{O_2}^c$	$\frac{D_{O_2}}{D_{N_2}}$
6FDA-6FpDA	16.30	4.7	0.990	1.48	12.50	3.15
50% 6FpDA/50% 6FmDA	5.54	6.0	0.790	1.61	5.53	3.68
6FDA-6FmDA	1.80	6.9	0.612	1.73	2.23	3.92

^a Barrers.

^b [cc(STP)]/[cc polymer atm].

^c 10^8 (cm²/s).

in Table II. There is a tradeoff of increased permeability and decreased permselectivity for the miscible blends of the 6FDA polyimide isomers. For example, the permeability of O_2 in the 50%/50% blend is 3.1 times higher than in the pure 6FDA-6FmDA, while the selectivity of O_2/N_2 in the blend is only 13% less than in the pure material.

The permeability of O_2 and N_2 in the 6FDA-6FmDA, 6FDA-6FpDA, and their 50%/50% blend can be factored into the diffusion coefficient (**D**) and solubility coefficient (**S**) (see Table III). The solubility coefficient of O_2 and the solubility selectivity of O_2/N_2 for these materials are shown in Figure 3. The solubility coefficient of the O_2 in the 50%/50% blend is 20% less than that in 6FDA-6FpDA and the solubility selectivity of O_2/N_2 is 9% greater in the 50%/50% blend than in the pure component.

The diffusion coefficients of O_2 for the blends 6FDA polyimide isomers are shown in Figure 4. The diffusion coefficient of O_2 in the 50%/50% blend is 57% less than that in the 6FDA-6FpDA and the diffusivity selectivity of O_2/N_2 is 17% greater in the blend than in the pure component. The solubility and diffusion coefficients of the 50%/50% blend also fall between those of the pure components and agree well with those predicted using Eq. (2).

The relationship between volume percent and permeability or permselectivity may enable one to tailor the composition of miscible materials to obtain a membrane with the optimal physical and gas-separation properties. Similar results are anticipated for the miscible blends of the polyimide isomers with the BTDA and BPDA dianhydrides.

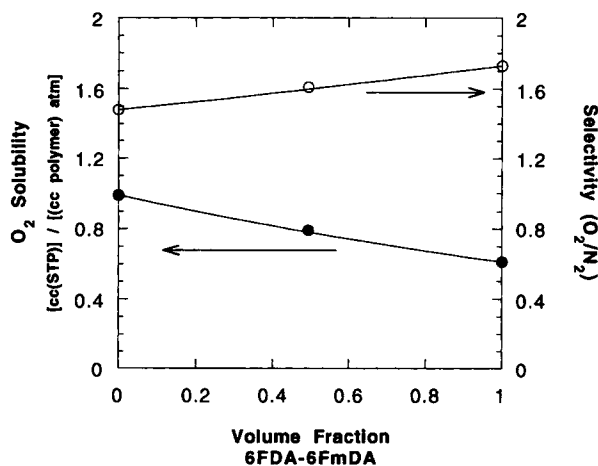


Figure 3 Solubility of O_2 and solubility selectivity of O_2/N_2 in blends of 6FDA-6FmDA and 6FDA-6FpDA.

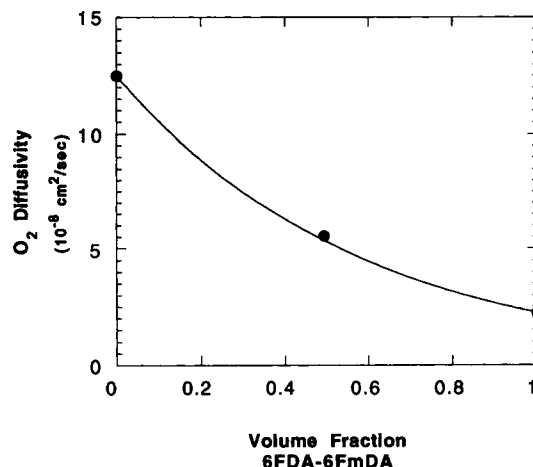


Figure 4 Diffusivity of O_2 in blends of 6FDA-6FmDA and 6FDA-6FpDA.

CONCLUSIONS

The *meta* and *para* isomers of polyimides containing hexafluoroisopropylidene in the central moiety of the diamine residue form miscible blends at 50 wt % of each of the pure components. The miscible blends have a single glass transition temperature measured using differential scanning calorimetry. The polyimide isomers with the hexafluoroisopropylidene in the central moiety of the dianhydride are miscible over a wide range of concentrations. The polyimides did not form miscible blends for nonisomer pairs such as 6FDA-6FpDA and BTDA-6FmDA.

The permeabilities and permselectivities of several gases were measured for the blends of 6FDA-6FmDA and 6FDA-6FpDA. The permeabilities and permselectivities of the miscible blends fell between those of the pure components and were approximately logarithmic averages of the properties of the pure components. Similar results were seen for the diffusivities and solubility coefficients for the 50%/50% blend of the 6FDA isomers. The miscibility of the polyimide isomers enables one to tailor the composition of the material to optimize the gas-separation properties.

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