Conditioning of Fluorine-Containing Polyimides. 2. Effect of Conditioning Protocol at 8% Volume Dilation on Gas-Transport Properties

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ABSTRACT: The impact of conditioning on the permeability and permselectivity of CO_2 and CH_4 is discussed for two polyimide isomers that have been conditioned with carbon dioxide using several conditioning protocols. Partial depressurization conditioning at pressures that would induce approximately 8% volume dilation; resulted in up to 50% increases in the permeability, diffusivity, and solubility coefficients of the polyimide isomers. The para-connected isomer, 6FDA-6F*p*DA, exhibited a greater conditioning effect following partial depressurization conditioning with CO_2 at 8% volume dilation than did the meta-connected isomer, 6FDA-6F*m*DA. Conditioning of 6FDA-6F*p*DA followed by an exchange with an equimolar mixture of CO_2 and CH_4 resulted in an increase in the methane permeability and a slight decrease in the permselectivity relative to the film prior to conditioning.

Introduction

The ability of highly soluble penetrants (i.e., carbon dioxide and ethane) to induce long-lived hysteretic changes in the properties of glassy polymers is a well-established phenomena.[1−4] Exposure of glassy polymers to high concentrations of CO_2 followed by partial depressurization has been shown to result in new apparent steady-state gas-transport properties and volume dilation that are greater than the values prior to conditioning.[5−8] As long as the polymer is not exposed to an intervening vacuum, this penetrant-induced hysteresis will apparently be maintained indefinitely in the presence of nonconditioning gases. Inclusion of highly soluble penentrants in a mixed gas feed can also result in large increases in permeability with corresponding decreases in permselectivity in a processes known as plasticization.[9,10] A thorough understanding of the conditioning and plasticization response of polymers is necessary to extend the application of polymer-based permselective layers to separations in aggressive environments (i.e., recovery of carbon dioxide from methane).

Fluorine-containing polyimides are interesting polymers for application as membranes for gas separations because of their excellent thermal, mechanical, and gas-transport properties.[11−13] Although the effect of backbone structure on the permeation properties of numerous polyimides has been well characterized, less is known about the impact of exposure to highly soluble penetrants on the properties of this family of polymers. The effect of conditioning with CO_2 at 60 atm on the pure gas-transport properties of several polyimides containing hexafluoroisopropylidene as the central linkage of the diamine residue was discussed in an earlier paper.[14] Conditioning of polyimides with CO_2 at 60 atm resulted in 7−10-fold increases in pure gas permeabilities, whereas conditioning of bisphenol A polycarbonate at the same pressure resulted in a 70% increase in permeability. The large differences in the conditioning responses of the polyimides and polycarbonate are due to differences in volume dilation resulting from the much larger solubility of CO_2 in the polyimides at equivalent pressures. Although polycarbonate exhibited a volume dilation of 8% following exposure to CO_2 at 60 atm, there was an estimated 20% volume dilation of the polyimides at similar pressures. The two fluorine-containing polyimide isomers shown in Figure 1 were conditioned with CO_2 at pressures which would induce an estimated 8% volume dilation, to allow a comparison of the effect of structure on conditioning of polymers. The hysteretic response of the transport properties of the polyimides was investigated using the following penetrant exposure protocols:[7,8]

(1) For mixed gas plasticization studies, the effect of a highly soluble penetrant (i.e., CO_2) in a gas mixture on the permeability and permselectivity of a penetrant which does not induce plasticization (i.e., CH_4) was determined for unconditioned polyimide films.

(2) For partial depressurization conditioning (PDC), the films were equilibrated with a highly soluble penetrant at a predetermined pressure followed by incremental depressurization of the conditioning penetrant so that steady state was reached at each depressurization step.

(3) For exchange conditioning (EC), the films were equilibrated with a conditioning penetrant at a predetermined pressure, followed by replacement of the conditioning agent with a secondary penetrant. A mixture of CO_2/CH_4 was used as the exchange or secondary penetrant for the EC studies of 6FDA-6F*p*DA.

The partial depressurization conditioning responses of the permeability, diffusivity and solubility of carbon dioxide in 6FDA-6F*p*DA and 6FDA-6F*m*DA were investigated. The effect of carbon dioxide on the permeability and permselectivity of a CO_2/CH_4 gas pair in an unconditioned and exchange-conditioned film of 6FDA-6F*p*DA will also be discussed.

Theory and Background

Gas Transport in Polymers. The permeability, P_A, of a membrane for a given penetrant A, is a pressure-

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and thickness-normalized flux that provides a measure of the ease of transport of the penetrant through the material. The permeation of penetrants in polymers occurs through a solution-diffusion mechanism in which penetrant molecules dissolve into the membrane material at the high-pressure feed face, diffuse through the polymer because of the concentration gradient, and reemerge into the gas at the low-pressure permeate face of the membrane. The permeability can be written as a product of a thermodynamic parameter, S_A, called the solubility coefficient and a kinetic parameter, D_A, called the diffusion coefficient.[15-17]

$$P_A = (S_A)\,(D_A) \tag{1}$$

For cases such as those that will be discussed here, in which the downstream pressure of the membrane is negligibly low, the solubility coefficient equals the slope of the sorption isotherm, i.e., $S_A = C_A/p_A$, the concentration of A in the membrane (C_A) divided by the external partial pressure of A (p_A) in equilibrium with the polymeric material.

The permselectivity, $\alpha_{A/B}$, gives a good measure of the ability of a given polymer to provide a permselective barrier for A relative to B.[15-17] The permselectivity is determined from mixed gas permeation studies and is defined by eq 2:

$$\alpha_{A/B} = (Y_A/Y_B) \times (X_B/X_A) \tag{2}$$

where Y_j is the mole fraction of j in the permeate and X_j is the mole fraction of j in the feed. For gases which do not plasticize the polymer, the ideal selectivity, $\alpha^*_{A/B}$, provides a good approximation of the permselectivity. The ideal selectivity can be expressed as the ratio of the pure gas permeabilities of the two penetrants in the membrane.

$$\alpha^*_{A/B} = P_A/P_B = (D_A/D_B)\,(S_A/S_B) \tag{3}$$

By substituting eq 1 into eq 3 for the two components, the selectivity can be factored into a solubility selectivity term, S_A/S_B, and diffusivity or mobility selectivity term, D_A/D_B. Ideal selectivities will be reported for the pure gas measurements and permselectivities will be reported for gas mixtures.

The solubility is thermodynamic in nature and is determined by (i) the inherent condensability of the penetrant, (ii) the polymer−penetrant interactions, and (iii) the amount and distribution of excess free volume in the glassy polymer. The solubility of gases can be discussed in terms of the idealized “dual mode” model, which states that there are two environments available in glassy polymers into which the penetrants can sorb.[15,16] Penetrants sorbed in the first environment (C_D) are viewed as residing in the amorphous densely packed region of the polymer, which is similar to sorption in liquids or rubbery polymers and is modeled using Henry’s Law at low and intermediate pressures. Penetrants sorbed in the second environment (C_H) are held in penetrant-scale packing defects or microvoids, which are formed as the polymer is cooled through the glass-transition temperature. Sorption in these microvoids can be modeled using Langmuir-type sorption in which the solubility increases with pressure and asymptotes as the microvoids become saturated. The dual mode model is written as[15,16]

$$C = k_d\, p + \frac{bC'_H p}{1 + bp} \tag{4}$$

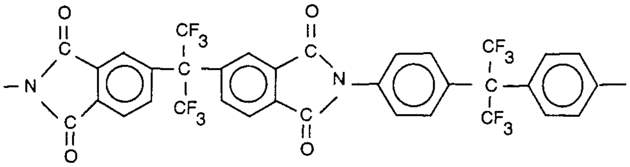
The Henry’s law constant, k_d [(cc(STP)]/[cc(polymer) atm] is a measure of the dissolved gas population, whereas, b (atm^{-1}) is the hole affinity constant and C'_H [cc(STP)/cc(polymer)] is the Langmuir sorption capacity. The relative distribution of free volume in the polymer matrix between these two regions can have a significant impact on both the diffusivity and the solubility coefficient of the penetrant. There is an increase in the solubility coefficient in glassy polymers following conditioning that has been attributed to an increase in the dissolved gas population caused by packing disruptions combined with an increase in the Langmuir sorption capacity caused by the introduction of long-lived packing defects in the polymer matrix.

Diffusive jumps occur within the polymer matrix when thermally activated motions of chain segments generate transient gaps between the polymer chains that are larger than the diffusing penetrant. There is a continuous size distribution of these transient gaps within the polymer matrix that is determined by the overall polymer free volume, distribution of free volume, and polymer segmental mobility. Modifications in the polymer morphology that either inhibit the polymer chain packing or increase chain segmental mobility will tend to shift the distribution of transient gaps to larger sizes and result in an increase in diffusivity. The size distribution of these transient gaps can also be modified to retard diffusion of penetrant B relative to penetrant A, thereby increasing the diffusivity selectivity. For example, modifications in the polymer matrix which result in an increase in the resistance to chain segmental mobility would be expected to narrow this size distribution, thereby increasing the diffusivity selectivity. As will be discussed later, both plasticization and conditioning will result in modifications to the polymer morphology (i.e., free volume and chain mobility), which will tend to result in an increase in the diffusivity and a decrease in the diffusivity selectivity.

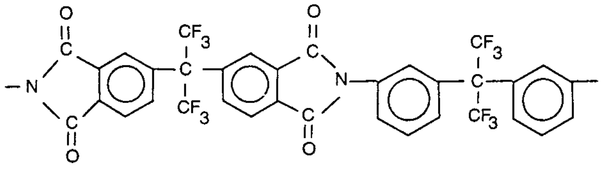
For systems which obey the dual mode sorption model, the effective local diffusion coefficient can be interpreted using the following equation:[18,19]

$$D_{\text{eff}} = D_D \frac{[1 + FK/(1 + C_D b/k_d)^2]}{[1 + K/(1 + C_D b/k_d)^2]} \tag{5}$$

where $F = D_H/D_D$ and $K = C'_H b/k_d$. The D_D and D_H represent the average local measure of mobility of a penetrant in the normally dissolved (D) and Langmuir (H) environments, respectively. Penetrants residing in the lower energy packing defects have much lower diffusivities than the dissolved molecules ($F < 0.1$). There is typically an increase in the effective penetrant diffusivity at high pressures following conditioning which can usefully be visualized as an increase in the diffusivity of the dissolved component (D_D) caused by the “loosening” of the swollen polymer matrix. Because penetrants residing in packing defects have low diffusivities compared to those in the normally dissolved region of the polymer ($D_D \gg D_H$), the increase in the contribution of packing defects to the overall solubility at low pressures has been shown to result in significant decreases in the effective diffusivity (D_{eff}).



6FDA-6FpDA



6FDA-6FmDA

Figure 1. Chemical backbone structure of 6FDA-based polyimides used in this study.

Table 1. Physical Property Data for Polyimide Isomers Used in this Study

polymer	T_g (C)	density (g/cc)	FFV	k_d[a] (carbon dioxide)	conditioning pressure (atm)
6FDA-6F*m*DA	254	1.466	0.175	1.24	25
6FDA-6F*p*DA	320	1.493	0.190	1.94	20

[a] Units of k_d are [cc(STP)]/[cc(polymer) atm].

Experimental Section

Film Formation and Physical Property Measurements. The hysteretic response of polyimides following exposure to carbon dioxide was investigated using the polyimide isomers with hexafluoroisopropylidine as the central linkage of the diamine and dianhydride residues as shown in Figure 1. The Hoechst-Celanese Corporation supplied the polyimides. The physical and pure gas-transport properties of the unconditioned polyimides are listed in Tables 1 and 2. All measurements were made using well-dried films which were cast from solutions of methylene chloride using standard techniques.[9]

The macroscopic densities were measured using a density gradient column with calcium nitrate solutions. The estimated fractional free volume (FFV) has been successfully used to correlate the effect of relative chain packing on the transport properties of permanent gases in glassy polymers.[20] The fractional free volume is the ratio of the estimated specific free volume and the polymer specific volume measured at 35 °C. The specific free volumes were estimated using the method of Lee[21] which uses the group contribution method of Van Krevelen and Hoftyzer[22] for calculation of van der Waals volumes. 6FDA-6F*p*DA has a more open structure than 6FDA-6F*m*DA, as indicated by the larger FFV of 6FDA-6F*p*DA.[9]

The glass-transition temperature (T_g) and the subT_g transition temperature (T_β) will be used to quantify the relative chain rigidity of these polyimides. The glass-transition temperatures were measured using a Perkin-Elmer System 7 differential scanning calorimeter at temperatures up to 400 °C and a scanning rate of 10 °C/min. The subglass-transition temperatures (T_β) were determined using dynamic mechanical spectroscopy, which was performed on films of 6FDA-6F*p*DA ($T_\beta = 151$ °C) and 6FDA-6F*m*DA ($T_\beta = 110$ °C) by the Hoechst-Celanese Corporation at 1 Hz at temperatures up to 400 °C. On the basis of the sub-T_g transition temperatures, there were greater inhibitions to rotational segmental mobility in 6FDA-6F*m*DA than in 6FDA-6F*p*DA. The much lower fractional free volume and more rigid structure of 6FDA-6F*m*DA resulted in significantly lower permeabilities and higher permselectivities for this polymer relative to 6FDA-6F*p*DA, as shown for the CO_2/CH_4 gas pair in Table 2.[9]

Gas-Transport Measurements. The pure and mixed gas permeabilities of CO_2 and CH_4 in the solution cast films were measured at 35 °C using gas permeation cells and a well-established technique.[23] The gas permeation cells can be used to measure mixed and pure gas permeabilities at pressures up to 60 atm. The downstream pressures were measured using a Baratron transducer with a full scale of 10 Torr. The pure gas solubilities were measured using a standard dual volume, dual transducer pressure decay cell at 35 °C and pressures to 60 atm.[24] The pressure decay cell has two chambers of known volume, the reservoir and the polymer chambers. The procedure for measuring solubility of pure gases using the pressure decay cells has been discussed in detail previously.[24] The diffusion coefficients were calculated for the pure gases using the measured values of permeabilities and solubility coefficients.

Penetrant Conditioning Protocols. All penetrant exposure studies were carried out using carbon dioxide as the conditioning agent at pressures that would induce an estimated 8% volume dilation in each of the polyimides. At high penetrant activities, penetrants dissolved in the densely packed region of the polymer result in considerable swelling of the polymer matrix. Penetrants which reside in the packing defects (C_H) do not contribute to volume dilation. Therefore, penetrant-induced volume dilation correlates well with the solubility in the densely packed regions (C_D) and the penetrant volume (V_o) as described in eq 6:[1,8]

$$\frac{\Delta V}{V_o} = \frac{k_d p V_{gas}}{22\,140} \tag{6}$$

where p is the pressure, V_{gas} is the partial specific volume of the gas in the polymer ($\sim$0.8$-$0.9 g/), V_o is the polymer volume at vacuum and ΔV is the volume change.[8] The volume dilation of the polyimide isomers in the presence of carbon dioxide were estimated using eq 6 and the Henry's law constant (k_d) determined from applying the dual mode model to sorption data taken at pressures up to 60 atm. The conditioning pressures were 20 and 25 atm for 6FDA-6F*p*DA and 6FDA-6F*m*DA, respectively. Because the relaxation time of a polymer is much greater than the rate of penetrant removal, rapid depressurization from the conditioning pressure traps much of the excess free volume in the form of packing defects or disruptions or both within the polymer matrix. The effect of exposure to carbon dioxide on the pure and mixed gas-transport properties of the polyimides was investigated using the three penetrant exposure protocols described below:[7,8]

Penetrant-Induced Plasticization of Unconditioned Films. The effect of the presence of a plasticizing agent on the permeabilities and permselectivities of a gas mixture in unconditioned films was determined using an equimolar mixture of CO_2/CH_4 at total pressures up to 40 atm. The permeation measurements were made using the same method as the pure gas measurements combined with a Hewlett-Packard gas chromatograph to determine the composition of the feed and permeate gases at steady state.[22] The feed gas was swept across the feed face of the membrane at a stagecut of 1% to prevent concentration polarization.

Table 2. Gas Transport Properties of the Unconditioned and PDC-Conditioned Polyimides

polymer	$P_{CH_{4,pure}}$[a] (unconditioned 10 atm)	$P_{CO_{2,pure}}$[a] (unconditioned 10 atm)	ideal selectivity (unconditioned 10 atm)	P_R[b] (conditioned 10 atm)	P_R[b] (conditioned 20 atm)
6FDA-6F*m*DA	0.07	4.4	64.0	1.16	1.05
6FDA-6F*p*DA	1.8	66	36.6	1.55	1.43

[a] Units of permeability are Barrers. [b] Reduced permeabilities are dimensionless.

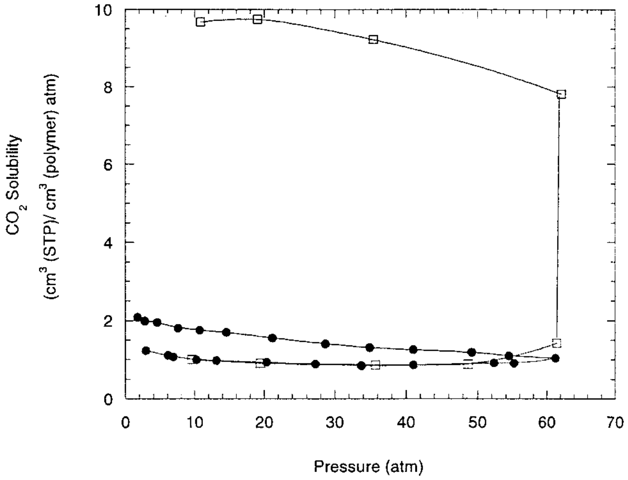


Figure 2. Comparison of partial depressurization conditioning loop of carbon dioxide in bisphenol A polycarbonate (●) and 6FDA-6F*m*DA (□).

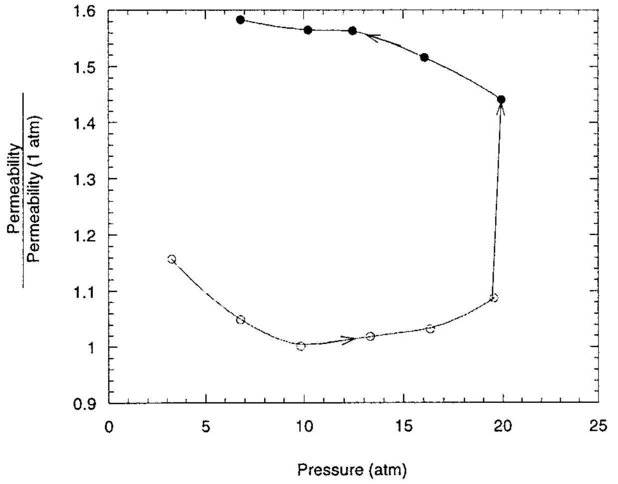


Figure 3. Conditioning loop for the permeability of carbon dioxide in 6FDA-6F*p*DA following partial depressurization conditioning at an estimated 8% volume dilation.

Partial Depressurization Conditioning (PDC). For the PDC procedure, the CO_2 feed pressure was increased incrementally to the conditioning pressure and the permeability was measured at each successive increasing pressure increment.[1,14] The feed was maintained at the conditioning pressure until the carbon dioxide permeability of the film reached steady state. The criteria for steady state was that the permeability changed by less than 0.5% per day over 48 h. Generally, the permeability would increase sharply over the first 2 days following exposure to the conditioning agent followed by a slow creep to the steady-state permeability over 2−3 weeks. After the film reached steady state at the conditioning pressure, the feed pressure was reduced incrementally and the permeabilities at steady state were measured at each successive decreasing pressure increment. The PDC procedure that was used for the permeability measurements was also used for the solubility measurements. The diffusivities in the unconditioned and conditioned samples were estimated using the measured values of the solubility coefficient and permeability combined with eq 1.

Exchange Conditioning (EC). The exchange-conditioning protocol was similar to the PDC protocol in that an unconditioned film was exposed to CO_2 at the conditioning pressure on the feed side until the permeability was at steady state.[5,8] For the EC protocol, the conditioning agent was exchanged for a equimolar mixture of CO_2/CH_4 so that the pressure of CO_2 in the feed remained constant. For example, a 6FDA-6F*p*DA film was conditioned with CO_2 at 20 atm and exchanged with a equimolar mole percent mixture of CO_2/CH_4 at a total feed pressure of 40 atm. The mixed gas-permeability measurements for the EC films were performed using the same methodology as for the mixed gas studies in the unconditioned films. The feed pressure was decreased incrementally after the permeability of each gas at each pressure was at the steady-state value. As with pure gas measurements, the criteria for steady state was that the permeability of each gas changed by less than 0.5% per day over 48 h.

Discussion of Results

Partial Depressurization Conditioning at 8% Volume Dilation. The effect of PDC with carbon dioxide at 60 atm on the sorption and transport properties of several fluorine-containing polyimides was discussed in detail in an earlier paper.[14] Following exposure to carbon dioxide at 60 atm, 6FDA-6F*p*DA and 6FDA-6F*m*DA exhibited conditioning responses which were typical for glassy polymers. The conditioning loops for the pure gas permeability of CO_2 in 6FDA-6F*m*DA and bisphenol A polycarbonate (PC) are shown in Figure 2 in the form of so-called “reduced” permeabilities.[5,14] These reduced permeabilities will be used in this paper to account for differences in permeabilities of the virgin polymers and to allow consistent comparison of the hysteretic response of polymers with a wide range of permeation properties. The reduced permeability is defined as the ratio of the permeability at a specific pressure i (P_i) to the permeability in the unconditioned film at 10 atm ($P_{10,\mathrm{unc}}$) and is shown in eq 7:

$$P_r = P_i/P_{10,\mathrm{unc}} \tag{7}$$

The value at 10 atm was selected because it corresponds roughly to a reasonable carbon dioxide partial pressure found in many practical gas separation systems.

The pure gas permeabilities of CO_2 at 10 atm in the unconditioned polyimide films ($P_{10,\mathrm{unc}}$) are given in Table 2. Conditioning at 60 atm resulted in a 7−10-fold increase in permeability for the polyimides and a 70% increase for the PC (Figure 2). The much larger increases in permeability for the polyimides relative to bisphenol A polycarbonate (polycarbonate) have been attributed to a much greater volume dilation of the polyimides following exposure to CO_2 at equivalent pressures.[14] Although PC exhibited a 8% volume dilation in the presence of carbon dioxide at 60 atm, there was an estimated 20% volume dilation for the polyimides at similar pressures.

The partial depressurization conditioning loop for the permeability of carbon dioxide in 6FDA-6F*m*DA and 6FDA-6F*p*DA following conditioning at 8% volume dilation are shown in Figures3 and 4. The pressures required to induce a 8% volume dilation for the polyimides were estimated using eq 6 and are shown in Table 2. Following conditioning at 8% volume dilation, the polyimides and polycarbonate exhibit similar increases in permeability. 6FDA-6F*p*DA had a larger increase in permeability following conditioning at 8% volume dilation than did 6FDA-6F*m*DA. The permeability of CO_2 at 10 atm in the conditioned polyimides was 15−55% greater than the permeabilities in the unconditioned films. The increase in permeability following PDC was a result of increases in both the diffusivity and solubility coefficient.

The pressure dependence of the permeability of carbon dioxide in the unconditioned 6FDA-6F*p*DA was typical of glassy polymers, as shown in Figure 3. There was a decrease in permeability with increasing pres-

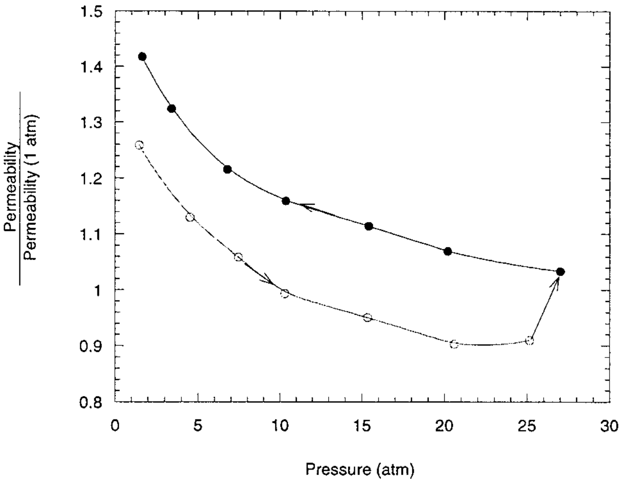


Figure 4. Conditioning loop for the permeability of carbon dioxide in 6FDA-6F*m*DA following partial depressurization conditioning at an estimated 8% volume dilation.

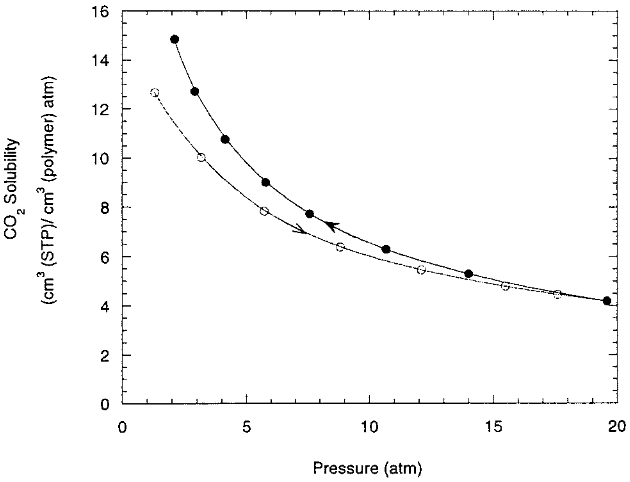


Figure 5. Partial depressurization conditioning loop for the solubility coefficient of CO_2 in 6FDA-6F*p*DA.

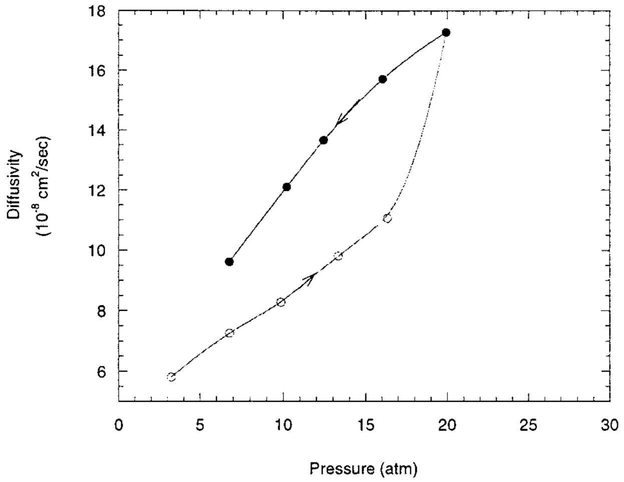


Figure 6. Partial depressurization conditioning loop for the diffusivity of carbon dioxide in 6FDA-6F*p*DA.

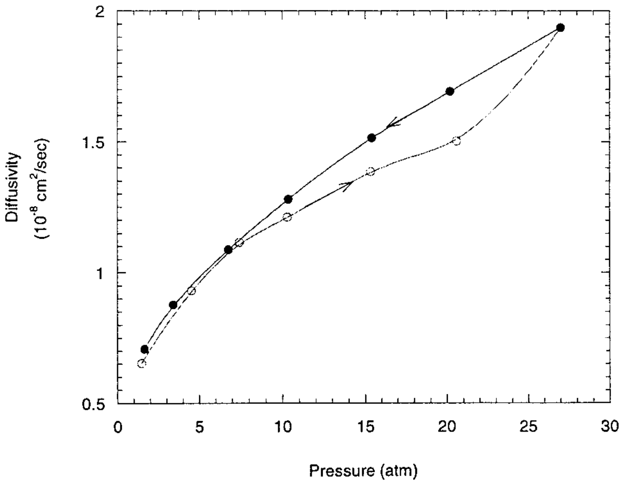


Figure 7. Partial depressurization conditioning loop for the diffusivity of carbon dioxide in 6FDA-6F*m*DA.

sures up to 10 atm for the film prior to conditioning. The initial decrease in permeability with pressure was a result of a decrease in solubility coefficient as the microvoid sorption sites (C'_H) became saturated as shown in Figure 5. There was an upswing in permeability at pressures greater than 10 atm which was a result of a sharp increase in diffusivity at the onset of plasticization. Plasticization occurs when sorption in the densely packed regions of the polymer matrix results in a swelling of the polymer matrix with a corresponding significant reduction in the intersegmental steric resistance to chain motion.[9,25] The increase in chain mobility typically results in a sharp increase in the diffusivity as shown in Figure 6. This increase in the diffusivity offsets the decrease in solubility coefficient with pressure, thereby resulting in an overall increase in permeability with pressure in the plasticized 6FDA-6F*p*DA. Conditioning at 8% volume dilation resulted in up to a 55% increase in permeability relative to the unconditioned film. At 15 atm, the permeability in the conditioned sample was 99 Barrer and was 50% greater than that of the sample prior to conditioning. At pressures near the conditioning pressure, there was a typical increase in permeability at each incremental depressurization step. However, as the feed pressure was decreased below 5 atm, there was an interesting leveling of the permeability with decreasing pressure. Similar pressure-dependent permeabilities were seen for the sample conditioned at 60 atm and was a result of conditioning effect on the diffusivity and solubility coefficient.[14]

The plasticization and conditioning response of the transport properties of 6FDA-6F*m*DA following exposure to CO_2 at 25 atm were similar to those of 6FDA-6F*p*DA. The reduced permeability of CO_2 as a function of pressure for 6FDA-6F*m*DA is shown in Figure 4. There was an initial decrease in permeability with increasing pressure followed by a leveling off of the permeability at pressures greater than 15 atm in the unconditioned film. The onset of plasticization in 6FDA-6F*m*DA occurred at approximately 15 atm as indicated by the sharp increase in diffusivity with pressure in the unconditioned sample at this pressure as shown in Figure 7. 6FDA-6F*m*DA did not exhibit a large increase in permeability at the onset of plasticization because the decrease in solubility coefficient (shown in Figure 8) with pressure balanced the increase diffusivity in the plasticized film. Partial depressurization conditioning at 25 atm resulted in up to a 20% increase in permeability relative to the unconditioned samples. The permeability of 6FDA-6F*m*DA exhibited a pressure dependence on depressurization from the conditioning pressure which was typical of the previously studied polycarbonates but was quite different from that of 6FDA-6F*p*DA.

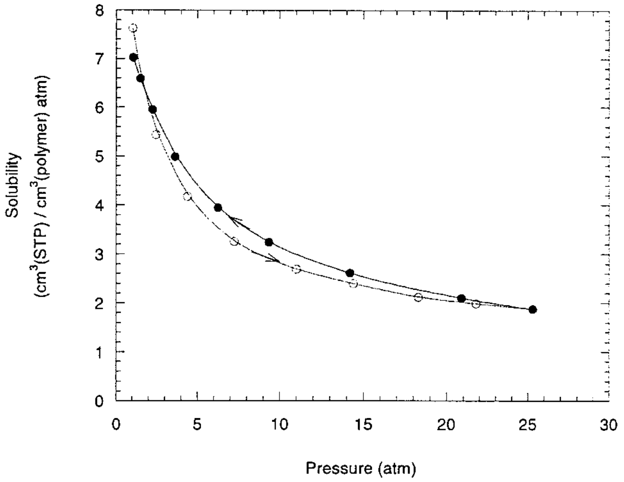


Figure 8. Partial depressurization conditioning loop for the solubility coefficient of CO_2 in 6FDA-6F*m*DA.

Conditioning at 8% volume dilation resulted in a small increase in the solubility coefficient for both 6FDA-6F*p*DA and 6FDA-6F*m*DA. This increase in the solubility coefficient for glassy polymers can be attributed to an increase in the dissolved gas population resulting from the formation of additional packing disruptions of the polymer matrix as well as an increase in the Langmuir sorption capacity resulting from the introduction of long-lived packing defects.[6,8] At pressures near the conditioning pressure, the solubility coefficients in the conditioned polyimides were approximately equal to the solubility in the unconditioned films. For 6FDA-6F*p*DA, the solubility coefficient at low pressures was greater in the conditioned film than in the unconditioned film, which agrees well with previous conditioning studies and is probably due to a residual volume dilation in the polymers following rapid depressurization from the conditioning pressure. For example, the solubility coefficient at 2 and 15 atm in the conditioned sample were 30% and 2% greater than in the unconditioned 6FDA-6F*p*DA. Although a similar response was seen for the solubility in 6FDA-6F*m*DA at pressures greater than 5 atm, the solubility coefficients in the conditioned sample of 6FDA-6F*m*DA were lower than those of the unconditioned film at pressures below 5 atm. There was a larger increase in the solubility coefficient with conditioning for 6FDA-6F*p*DA than for 6FDA-6F*m*DA.

As shown in Figures 6 and 7, conditioning resulted in an increase in the diffusivity of carbon dioxide in both 6FDA-6F*m*DA and 6FDA-6F*p*DA. For both of the polymers, the largest increase in the diffusivity occurred at pressures near the conditioning pressure. At pressures below 5 atm, the diffusivity coefficients in the conditioned 6FDA-6F*m*DA were only slightly greater than those in the unconditioned sample. Similar results were seen for polycarbonates following conditioning with several penetrants. The sharp decrease in effective diffusivity can be discussed in terms of the dual mode model and eq 5. As was discussed for the sorption coefficient, conditioning typically results in a residual volume dilation in the form of both packing defects (C_H) and packing disruptions (C_D).[2] Because penetrants residing in packing defects have much lower diffusivities than those in the normally dissolved region of the polymer ($D_D \gg D_H$), it has been suggested that the increased contribution of packing defects to the solubility at low pressures will result in a significant decrease in the effective diffusivity (D_{eff}).[6]

Conditioning of the polyimide isomers at 8% volume dilation resulted in much smaller increases in the permeability than those of conditioning at 60 atm. In addition, although the permeability increase upon conditioning at 60 atm was slightly greater for the rigid meta-connected 6FDA-6F*m*DA than for the para-connected 6FDA-6F*p*DA, 6FDA-6F*p*DA exhibited a greater permeability increase than did 6FDA-6F*m*DA, following conditioning at 8% volume dilation. The difference in hysteretic response with conditioning pressure may be due to differences in intersegmental resistance to chain motions for these polyimides isomers. There is a suppression of glassy state motion in the meta-connected isomer relative to the para-connected isomer which has been attributed to the following factors: (i) the increase in intersegmental resistance to segmental mobility in the nonsymmetric meta-connected unit relative to the symmetric para-connected unit and (ii) an energetically favorable motion in the symmetric para linkage relative to the meta linkage.[11,14] At high CO_2 pressures, swelling of 6FDA-6F*m*DA (i.e., 20% volume dilation at 60 atm) may supply sufficient free volume to greatly reduce the intersegmental hindrance to segmental mobility of these nonsymmetric groups. This intersegmental hindrance to motion presumably does not affect the diffusivity of 6FDA-6F*p*DA as much as in 6FDA-6F*m*DA. Sufficient swelling of the polymer would be expected to result in a larger plasticization and conditioning effect in the meta-connected polyimide, which is reflected in its larger increase in permeability than that of 6FDA-6F*p*DA. The much smaller penetrant-induced swelling in these polymers at low pressures (~8% volume dilation) suggest that the dilation may not provide a sufficient increase in the free volume to allow for a significant decrease in the intersegmental resistance to chain motions for the meta-connected isomer. This is supported by the smaller increase in diffusivity of CO_2 in 6FDA-6F*m*DA relative to that of 6FDA-6F*p*DA, following conditioning at 8% volume dilation.

Exchange Conditioning of 6FDA-6FpDA. As discussed in the Experimental Section, exchange conditioning involves equilibrating a sample with the conditioning penetrant at a predetermined pressure, followed by replacement of the conditioning agent with a secondary penetrant (i.e., CH_4 or CO_2/CH_4).[7,8] The exchange-conditioning protocol has been used to investigate the impact of conditioning on the permeability and permselectivity of nonplasticizing penetrants for a series of polycarbonates. Preconditioning of a glassy polymer followed by an exchange with a gas mixture has been shown to typically result in an increase in the permeability of each of the penetrants combined with a reduction in the permselectivity relative to the unconditioned film.[7] Penetrants that are not capable of inducing a hysteretic response appear to be able to hold the polymer matrix open and maintain some of the conditioning response following an exchange with the conditioning agent. For this study, an equimolar mixture of CO_2/CH_4 was used as the exchange penetrant for a 6FDA-6F*p*DA film, which was conditioned with carbon dioxide at 20 atm. The permeability and permselectivity in the exchange-conditioned sample will be compared with pure and mixed gas values for the unconditioned film.

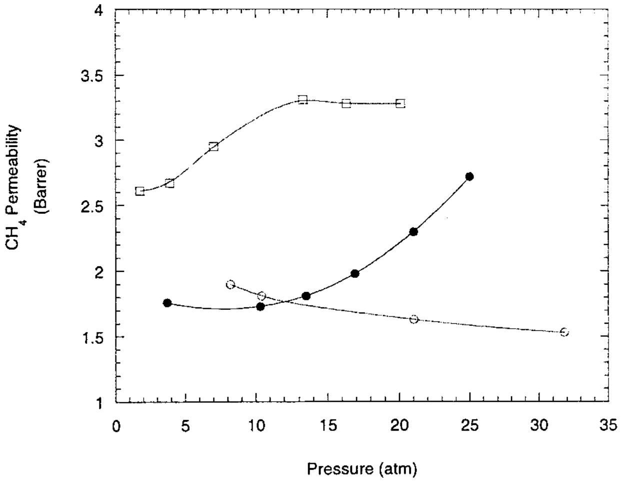


Figure 9. Permeability of pure (○) methane and methane in an equimolar mixture of CO_2/CH_4 in an untreated (●) and exchange-conditioned (□) film of 6FDA-6F*p*DA.

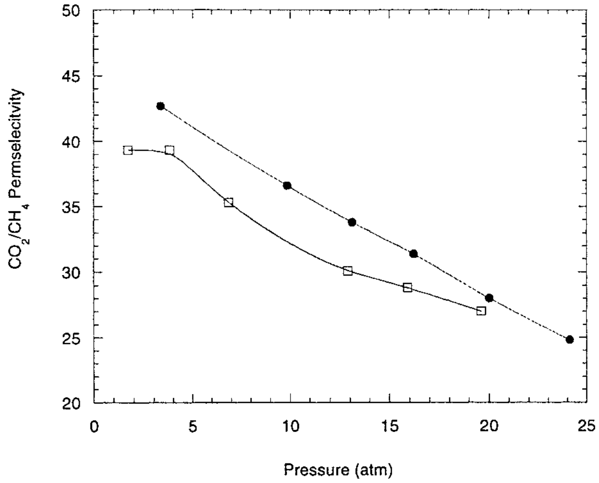


Figure 11. Permeability of an equimolar mixture of CO_2/CH_4 in an untreated (●) and exchange-conditioned (□) film of 6FDA-6F*p*DA.

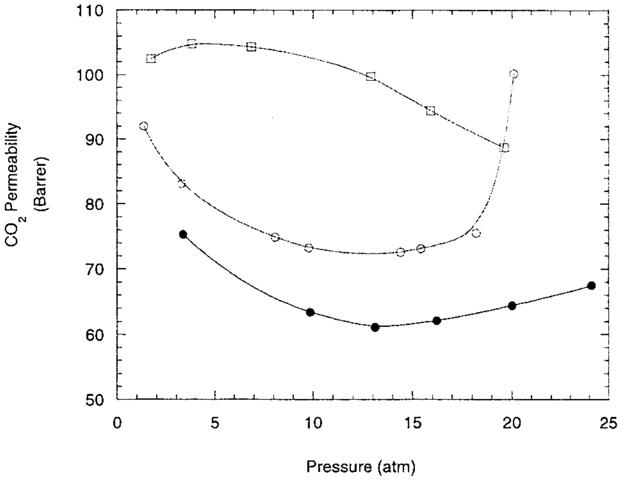


Figure 10. Permeability of pure (○) carbon dioxide and carbon dioxide in an equimolar mixture of CO_2/CH_4 in an untreated (●) and exchange-conditioned (□) film of 6FDA-6F*p*DA.

The permeabilities of CH_4 in an equimolar mixture of CO_2 and CH_4 for an unconditioned sample of 6FDA-6F*p*DA are shown in Figure 9 along with the pure gas permeabilities. At pressures 10 atm of CO_2 partial pressure, the mixed gas permeabilities of methane in the unconditioned film were lower than the pure gas permeabilities. This is due to competition with the CO_2 for Langmuir sorption sites and diffusion pathways in the mixture and agrees well with results from mixed gas studies for a variety of polymers. As was seen for the PDC studies, plasticization of this polyimide occurred at carbon dioxide pressures greater than 10 atm. Following the onset of plasticization, the increase in permeabilities resulting from the increased mobility of the polymer chains segments balanced the competition effect and resulted in mixed gas permeabilities that were greater than the pure gas permeabilities. There was an increase in the mixed gas permeabilities of methane following exchange conditioning of an equimolar CO_2/CH_4 mixture as shown in Figure 10. Therefore, the gas mixture was able to hold open the polymer matrix and maintain the permeability increase following exchange with carbon dioxide at 20 atm. Although the typical trend for glassy polymers is an increase in permeability with decreasing pressure, there was a general decrease in methane permeability with decreasing pressure in the exchange-conditioned film.[7,8]

Figure 10 shows the pure and mix gas permeabilities of CO_2 in the unconditioned film of 6FDA-6F*p*DA. As discussed for the methane permeation at low pressures, there was a reduction in the mixed gas permeabilities of carbon dioxide relative to the pure gas permeabilities because of competition with the methane for sorption sites and diffusion pathways. The increase in permeability resulting from CO_2-induced plasticization of 6FDA-6F*p*DA was greater for the pure gas than for the mixed gas feed. Following the exchange with pure carbon dioxide at the conditioning pressure, there was a decrease in the permeability of CO_2 in the gas mixture. This typical drop in permeability relative to the pure gas value was probably due to competition with the CH_4 in the gas mixture. Although the permeability of CO_2 following exchange conditioning was greater than both the pure and mixed gas permeabilities in the unconditioned film, the carbon dioxide permeabilities for the PDC sample were greater than for the EC sample. The CO_2/CH_4 permselectivities in the unconditioned and exchange-conditioned films of 6FDA-6F*p*DA are shown in Figure 11. At low pressures, the mixed gas permselectivities in the unconditioned film were equivalent to the ideal selectivities, which were estimated using pure gas permeabilities. However, the ideal permselectivity (Table 2) does not accurately estimate the permselectivity in the plasticized samples because it does not account for the effect of CO_2 on the permeability of the nonplasticizing penetrant (CH_4). The permselectivity in the exchange-conditioned sample was lower than the permselectivity in the unconditioned film.

Conclusions

Conditioning of 6FDA-6F*p*DA and 6FDA-6F*m*DA with CO_2 using partial depressurization conditioning at pressures which would induce 8% volume dilation resulted in 20−60% increases in the pure gas permeability. The permeability enhancement was due to an increase in diffusivity following the onset of plasticization, as well as an increase in solubility following depressurization from the conditioning pressure. The fluorine-containing polyimides and polycarbonates exhibit similar increases in permeability (20−70%) following exposure to CO_2 at pressures which induced 8%

volume dilation. Partial depressurization conditioning at 60 atm of the same polymers resulted in an up to 10-fold increase in permeability relative to the unconditioned sample. This difference in conditioning response was due to a much greater solubility level and volume dilation at the higher pressure.

6FDA-6F*m*DA exhibited a greater permeability enhancement than did 6FDA-6F*p*DA following conditioning at 60 atm. However, conditioning at 8% volume dilation resulted in a larger permeability increase for the para-connected isomer than for the meta-connected material. The greater conditioning effect on 6FDA-6F*m*DA at high pressures may be due to a large reduction in the intersegmental hindrance to segmental mobility for the nonsymmetrical meta connected group which would occur at large volume dilations resulting from solubility at higher pressures. Presumably, at 8% volume dilation, the swelling is not sufficient to overcome the greater intersegmental resistance to motion in the meta connected isomer so that a greater permeability enhancement was seen for 6FDA-6F*p*DA.

The effect of conditioning at 20 atm followed by an exchange with an equimolar mixture of CO_2/CH_4 on the permeation properties was investigated for a sample of 6FDA-6F*p*DA. Exchange conditioning resulted in an increase in the permeability of both carbon dioxide and methane relative to mixed gas permeabilities in an unconditioned film. The permeability of CO_2 in the gas mixture was lower than the pure gas permeability in the unconditioned sample. The lower permeabilities of the gas mixtures have been attributed to competition for sorption sites and diffusion pathways for gas mixtures. The permselecitivities in the exchange-conditioned sample were lower than those in the untreated film. Following the onset of plasticization, the mixed gas permselectivities were considerably lower than the ideal permselectivities estimated from pure gas permeabilities.

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