Conditioning of Fluorine Containing Polyimides. 1. Effect of Exposure to High Pressure Carbon Dioxide on Permeability

M. R. Coleman[†] **and W. J. Koros***

University of Texas at Austin, Department of Chemical Engineering,
Austin, Texas 78712-1062

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ABSTRACT: This paper discusses the effect of penetrant-induced conditioning on the gas transport properties of four fluorine- containing polyimide isomers. The effects of substitution of bulky groups within the dianhydride residue of the polyimide and isomerism of the diamine residue on the penetrant-induced hysteresis of CO_2 permeability were investigated. The CO_2 permeability in the polyimide films that had been conditioned with carbon dioxide at 60 atm are compared to those in the untreated films. Exposure of the polyimides to CO_2 at 60 atm resulted in *4.5- to 10-fold* increases in the permeability of CO_2 relative to unconditioned films. The permeability enhancement was a result of increases in both the solubility and diffusivity following conditioning. There was also a surprising maximum in the permeability at intermediate pressures in conditioned samples of two of the polyimides. The permeability of CO_2 in the conditioned polymers initially increased with decreasing pressure, exhibited a maximum value at approximately 30 atm, and decreased in permeability at low pressures.

Introduction

Membrane-based gas separations are increasingly being applied commercially because of their energy efficiency, low capital investment, and compact size.[1] Advances in the development of glassy polymers specifically for application as membranes for gas separations have led to a number of structural characteristics that result in improved transport properties.[2,3] These improvements in material properties have increased the commercial viability of polymeric membrane-based gas separation systems. Properties of glassy polymers are dependent upon process history, including thermal cycling and exposure to swelling agents such as CO_2 and CH_4.[4−6] This issue needs to be better understood.

Conditioning is defined here to be the hysteretic change in properties of glassy polymers following exposure to penetrants at high activity.[4] Specifically, conditioning results in large increases in the permeability of gases and excess free volume of the polymer. The presence of highly sorbing penetrants in mixed gas feeds can also plasticize the polymer, resulting in a large increase in permeability with a corresponding loss in permselectivity. An important step in the further development of membrane materials is the identification of structural characteristics which improve resistance to penetrant-induced plasticization and conditioning. Such materials would extend the potential applications of polymer-based membranes to include streams containing highly soluble components, such as the removal of carbon dioxide from natural gas.

Polyimides have been identified as unusually good polymers for use as permselective layers in membranes.[2,7,8] Polyimides containing hexafluoroisopropylidene as the central linkage of the dianhydride and/or diamine residues have been found to have both high permeabilities and permselectivities.[7,8] The relationship between transport properties of permanent gases and the backbone structures of several polyimide isomers with hexafluoroisopropylidene central linkages has been discussed in an earlier paper.[7] This paper focuses on the effects of conditioning and plasticization on the pure gas transport properties of four polyimides which were exposed to CO_2 at approximately 60 atm.

Theory and Background

Gas Transport in Polymers. The permeability, P_A, of a membrane for a given penetrant is a pressure and thickness normalized flux that provides a measure of the ease of transport of a penetrant through a material. The transport of penetrants in polymers occurs through a solution-diffusion mechanism. Penetrant molecules dissolve into the membrane material at the high pressure feed face, diffuse through the material because of the concentration gradient, and reemerge into the gas at the low-pressure permeate face of the film. 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.[9−11]

$$P_A = S_A D_A \tag{1}$$

For cases such as those that will be discussed here, where 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 ideal selectivity, $\alpha^*_{A/B}$, can be expressed as the ratio of the pure gas permeabilities of the two penetrants in the membrane.[9−11]

$$\alpha^*_{A/B} = P_A/P_B = (D_A/D_B)(S_A/S_B) \tag{2}$$

The ideal selectivity gives a good measure of the ability of a given polymer to provide a permselective barrier for A relative to B. By substituting eq 1 into eq 2 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.

The solubility is thermodynamic in nature and is determined by (i) the inherent condensibility of the penetrant, (ii) the polymer−penetrant interactions, and

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* To whom correspondence should be addressed.

[†] Current address: 3202 Bell Engineering Center, University of Arkansas, Fayetteville, AR 72701.

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(iii) the amount and distribution of excess free volume in the glassy polymer. The solubility of gases in glassy polymers will 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.[9,10] Penetrants sorbed in the first environment (C_D) are ideally viewed to be in the amorphous densely packed region, 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 believed to be formed as the polymer is quenched through the glass transition temperature. Solubility in these microvoids can be modeled using Langmuir type sorption in which the solubility increases with pressure and asymptotes as the microvoids are saturated. The "dual mode" model is written as[9,10]

$$C = k_d p + \frac{bC'_H p}{1 + bp} \tag{3}$$

The Henry's law constant, k_d ((cm^3 (STP))/cm^3 (polymer) atm), is a measure of the dissolved gas population, whereas, b (atm^{-1}) is the hole affinity constant and C_H' (cm^3 (STP)/cm^3 (polymer)) is the Langmuir sorption capacity. The effect of penetrant-induced hysteresis on the solubility of penetrants will be discussed in simple terms of the solubility in these two environments.

Diffusive jumps of penetrants within the polymer matrix occur 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 transient gaps in the polymer matrix. Chemical modifications can also be used to change the size distribution of transient gaps to retard diffusion of one penetrant relative to another. The effective local diffusion coefficient can also be interpreted using the following equation for systems which obeys the "dual mode" sorption model:[12,13]

$$D_{\text{eff}} = D_D \frac{[1 + FK/(1 + C_D b/k_D)^2]}{[1 + K/(1 + C_D b/k_D)^2]} \tag{4}$$

Here $F = D_H/D_D$ and $K = C_H'b/k_D$. 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 ($F \leq 0.1$).[14,15] The effect of conditioning and plasticization on the diffusivity in glassy polymers will be discussed in terms of the "Dual Mode" model in the form of eq 4, the polymer chain packing, and the resistance to chain segmental mobility.

Penetrant-Induced Hysteresis in Glassy Polymers. The effect of penetrant-induced hysteresis (conditioning) on the gas transport properties in glassy polymers has been the focus of numerous studies.[4-6,14-16] A typical conditioning response is shown in Figure 1 for the pressure-dependent permeability of CO_2 in Bisphenol A polycarbonate.[4] At low pressures in the untreated sample, the permeability decreases with increasing pressure due to a decrease in the solubility coefficient, S_A in eq 1, as the packing defects (C_H') become saturated. This decrease in solubility with increasing pressure is illustrated in Figure 2 for CO_2 dissolved in 6FDA–6FpDA. As the pressure is further increased, there is an increase in permeability at the onset of plasticization. Plasticization is the increase in diffusivity of a penetrant due to the presence of other penetrants in the surrounding neighborhood.[17] Swelling of the polymer by penetrants dissolved in the well-packed region (C_D) of the polymer matrix will lead to a decrease in the intersegmental steric resistance to motion with a corresponding increase in the generation of transient gaps as well as an increase in penetrant diffusivity.[4,17] There is typically a decrease in diffusivity selectivity following the onset of plasticization, because smaller penetrants do not require this increased size and frequency of transient gaps for diffusion. Therefore, differences in plasticization responses of glassy polymers are a function of the following factors: (i) *solubility level in the Henry's law mode,* (ii) polymer chain packing, (iii) intersegmental resistance to chain motions, and (iv) intrasegmental resistance to chain motions.[5]

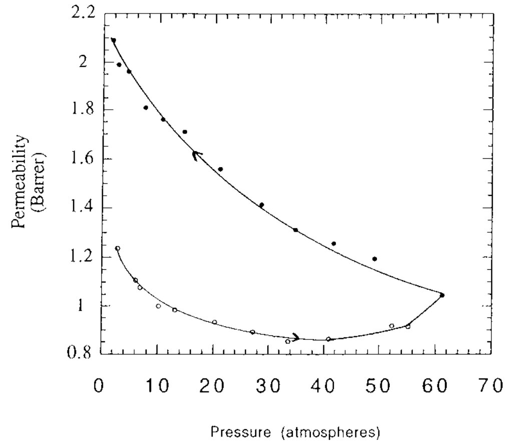

Figure 1. Reduced permeability for CO_2 in conditioned Bisphenol A polycarbonate (**4**).

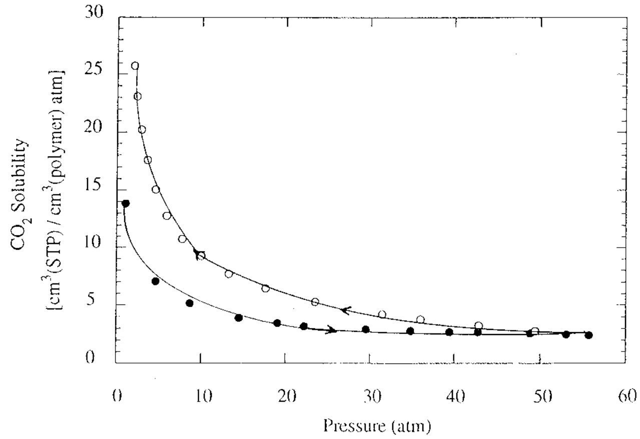

Figure 2. Solubility of CO_2 in conditioned 6FDA–6FpDA at 35 °C.

In partial depressurization conditioning (PDC), the feed side of the film is equilibrated with a highly sorbing penetrant at the conditioning pressure followed by incremental depressurization of the feed. Depressurization of the conditioned sample results in a large increase in the permeability relative to the untreated sample because of an increase in both the diffusivity and solubility.[4,14] At high penetrant activities, the polymer matrix is highly swollen and contains considerable excess free volume.[5] For a series of polycarbonates, the volume dilation was found to correlate with the solubility in the densely packed regions and penetrant volume as described in eq 5, where p is the pressure, V_{gas} is the

$$\frac{\Delta V}{V_o} = \frac{k_d p V_{gas}}{22140} \tag{5}$$

partial specific volume of the gas in the polymer (~0.8–0.9 gm/cm^3)[6], V_o is the polymer volume under vacuum, and ΔV is the volume change.

Rapid depressurization from the conditioning pressure traps much of this excess free volume within the polymer matrix in the form of packing defects or disruptions because the relaxation time of the polymers is much greater than the rate of penetrant removal.[15] A large increase in solubility following conditioning has been attributed to an increase in the dissolved gas population caused by additional disruptions in the packing of the polymer matrix as well as an increase in the Langmuir sorption capacity caused by the introduction of long-lived packing defects.[15] There is also an increase in the effective diffusivity at high pressures following conditioning. This effect can be usefully visualized as an increase in the diffusivity of the dissolved component (D_D) caused by the "loosening" of the polymer matrix. Since penetrants residing in packing defects have low diffusivities compared to those in the normally dissolved region of the polymer ($D_D >> D_H$), the increased contribution of packing defects to the solubility at low pressures can result in a significant *decrease* in the effective diffusivity (D_{eff}). Therefore, for rigid materials at low pressure the effective diffusivity in the conditioned polymer can be either higher or lower than in the untreated film.[4,15]

Experimental Section

Polymers and Physical Property Measurements. The structure and properties of the four polyimides used in this study are shown in Figure 3 and Table 1. These polyimides were kindly supplied by the Hoechst-Celanese Corp. The effect of substitution of bulky groups within the dianhydride residue on the CO_2-induced hysteresis was investigated using three polyimides with the para-connected diamine residue containing hexafluoroisopropylidine as the central group (6FpDA). The effect of isomerism of the diamine residue on the hysteresis of the polyimides was investigated using two polyimides containing the hexafluoroisopropylidine as the central group of the dianhydride residue (6FDA). All measurements were taken using well-dried films cast from solutions of dimethylacetimide or methylene chloride using standard techniques.[7]

The macroscopic densities were measured using a density gradient column with $CaNO_3$ solutions. The specific free volumes were estimated using the method of Lee[18] which uses the group contribution method of Van Krevelen[19] for calculation of van der Waals volumes. The estimated fractional free volume (FFV) correlates well with the diffusivity for structurally related polymers in the absence of significant differences in intrasegmental rotational mobility.[9] The fractional free volume (FFV) has been used successfully to correlate the effect of relative chain packing on the transport properties of permanent gases in glassy polymers.[7,20] The fractional free volume is the ratio of the estimated specific free volume and the polymer specific volume measured at 35 °C. For the polyimides containing the 6FpDA diamine residue shown in Figure 3, the fractional free volume increases in the following order BTDA< BPDA << 6FDA as shown in Table 1. For the isomers with the 6FDA dianhydride residue, the fractional free volume of the para-connected polyimide (6FDA−6FpDA) was greater than that of the meta-connected isomer (6FDA−6FmDA).

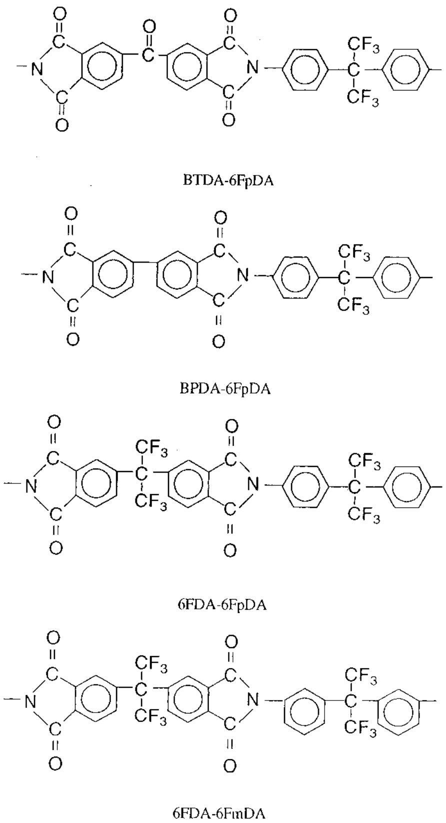
BTDA-6FpDA
BPDA-6FpDA
6FDA-6FpDA
6FDA-6FmDA

Figure 3. Structures of polyimides used in this study.

The effect of inhibitions to rotational mobility within a family of materials will be quantified using the glass transition temperature (T_g) and the sub-T_g transition temperature (T_β). The glass transition temperatures were measured using a Perkin-Elmer System 7 differential scanning calorimeter at temperatures up to 400 °C. The sub glass transition temperatures (T_β) were determined using dynamic mechanical spectroscopy. Dynamic mechanical spectroscopy was performed on films of 6FDA−6FpDA (T_β = 151 °C) and 6FDA−6FmDA (T_β = 110 °C) by the Hoechst-Celanese Corp. at 1 Hz at temperatures up to 400 °C. On the basis of the sub-T_g transition, the 6FDA−6FmDA has greater inhibitions to rotational segmental mobility in the glassy state than does the 6FDA−6FpDA.

Partial Depressurization Conditioning. Gas permeation cells were used to measure the permeabilities in the solution cast films using a well-established technique.[21] All permeability measurements were made with ultrahigh purity carbon dioxide at 35 °C and pressures up to 60 atm. The effect of conditioning on the permeability of pure CO_2 in the polyimides was investigated using the partial depressurization conditioning (PDC) technique. For the PDC technique, the feed pressure of CO_2 in the untreated film was increased incrementally and the permeability measured at each successive pressure increment. The feed was maintained at the conditioning pressure until the film was at a steady state. The criteria for steady state was that the permeability changed by less than 0.5%/day over a 48 h period. Generally, the permeability would increase significantly over the first 2 days following exposure to the conditioning agent followed by a slow creep to the steady state permeability over a 2−3 week period. After the film reached steady state at the conditioning pres-

Table 1. Properties of Fluorine Containing Polyimides

polymers	T_g (°C)	FFV	k_D (carbon dioxide)	P_{CO_2} (unconditioned, 10 atm)	P_R (conditioned, 10 atm)	P_R (conditioned, 30 atm)	P_R (conditioned, 60 atm)
BTDA−6FpDA	310	0.156	1.11	7.30	5.3	6.3	4.2
BPDA−6FpDA	360	0.161	1.97	27.4	4.4	6.5	5.9
6FDA−6FpDA	320	0.190	1.94	63.9	NA	8.7	6.7
6FDA−6FmDA	254	0.175	1.24	5.60	9.8	9.3	7.9

sure, the feed pressure was reduced incrementally and the steady state permeabilities were measured at each successive decreasing pressure increment.

The CO_2 solubilities were measured using a standard dual volume, dual transducer pressure decay cell at pressures up to 1000 psia using the method described previously.[22] This technique for determining solubility depends upon the principle of maintaining an absolute material balance of the sorbing gas entering the system. The pressure decay cell consists of two calibrated chambers, the reservoir and polymer chamber, which were fitted with pressure transducers. Approximately 1.8−2 cm^3 of polymer sample were placed in the polymer chamber, and the system was evacuated overnight. The polymer chamber was isolated by shutting the interconnecting valve, and the gas reservoir was charged with a measured pressure of gas. The valve between the chambers was opened, and the gas was expanded into the polymer chamber. The pressure transducer monitored the decrease in pressure in the polymer chamber as gas was sorbed into the polymer. The equilibrium sorption value was determined from a mass balance using the initial and equilibrium pressures in each of the chambers.

Results

Conditioning of Fluorine-Containing Polyimides. The effect of partial depressurization conditioning on the CO_2 permeability in the polyimides was determined for films conditioned with CO_2 at approximately 60 atm. The permeability of CO_2 at 10 atm in unconditioned samples of these polymers ranged in value from 5.8 to 64 Barrers as shown in Table 1. The effect of pressure on the CO_2 permeability in these polymers will be compared for convenience in terms of the reduced permeability, P_r, as described in eq 6. The reduced

$$P_r = P_i/P_{10,unc} \qquad (6)$$

permeability, which is defined as the ratio of the permeability at a specific pressure i (P_i) to the permeability in the unconditioned film at 10 atmospheres ($P_{10,unc}$), will allow a consistent comparison of the effect of conditioning and plasticization in materials with a wide range of permeabilities.

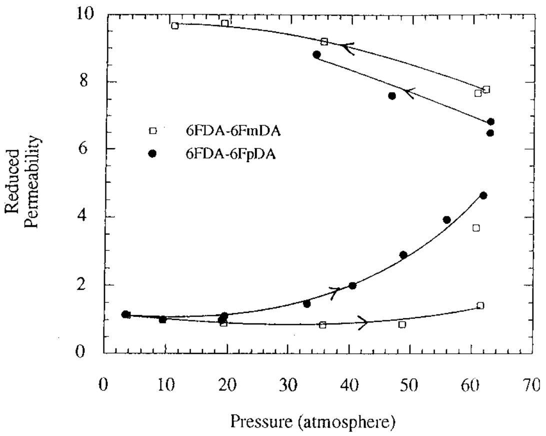

Figure 4. Conditioning of 6FDA−6FmDA and 6FDA−6FpDA. Reduced permeability of CO_2.

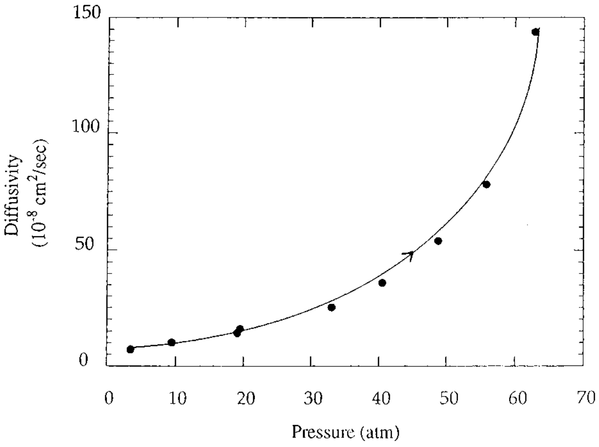

Figure 5. Diffusivity of CO_2 in 6FDA−6FpDA at 35 °C.

The reduced permeability of CO_2 as a function of pressure in 6FDA−6FpDA is shown in Figure 4. The decrease in permeability of CO_2 in the untreated film with increasing pressure up to 10 atm is typical of the "Dual Mode" behavior in glassy polymers, as noted earlier. This decrease in permeability with increasing pressure at low pressures is due to a reduction in the solubility coefficient (S) as the microvoid sorption sites become saturated as shown in Figure 2. At pressures greater than 10 atm, there is a sharp increase in permeability resulting from an increase in CO_2 diffusivity in the plasticized film as shown in Figure 5.[17] The increase in diffusivity with pressure in the plasticized films offsets the decrease in the solubility resulting in an overall increase in permeability at pressures greater than 10 atm. As shown in Table 1, the steady state permeability of CO_2 at 60 atm is nearly 7 times greater than at 10 atm in the unconditioned films.

The CO_2 conditioning of 6FDA−6FpDA is reflected in a 7−9-fold increase in the permeability following depressurization from the conditioning pressure of 60 atm. For example, the permeability of CO_2 at 50 atm in the conditioned sample of 6FDA−6FpDA was nearly 500 Barrers and was more than 3-fold greater than in the film prior to exposure to CO_2. This increase in permeability was the result of a large increase in both the solubility and diffusivity following conditioning as shown in Figures 2 and 5.

The reduced permeability of CO_2 in BPDA−6FpDA is shown in Figure 6. Carbon dioxide plasticized the BPDA−6FpDA at feed pressures greater than 15 atm as indicated by the upturn in permeability with pressure in the untreated film. Following conditioning at 60 atm, the maximum increase in permeability of the conditioned sample occurred at 30 atm where the permeability was 5.6 times greater than in the unconditioned sample; however, the permeability in the conditioned sample had a maximum value at 30 atm. There was a 20% decrease in permeability following depressurization

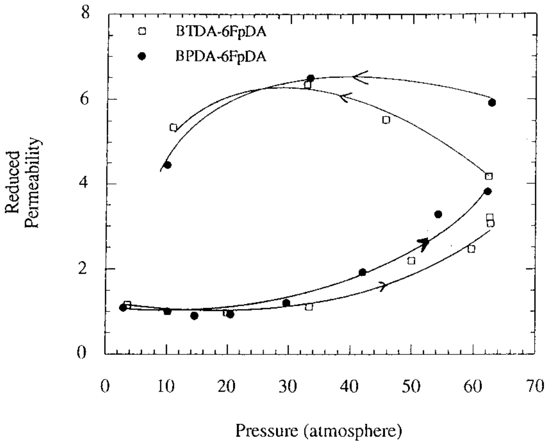

Figure 6. Conditioning of BPDA−6FpDA and BTDA−6FpDA. Reduced permeability of CO_2.

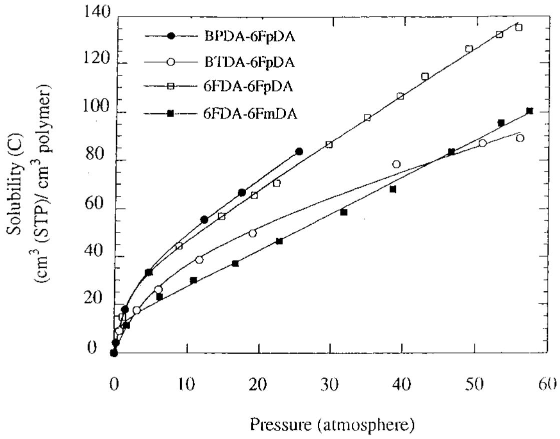

Figure 7. Solubility of CO_2 in the fluorine-containing polyimides at 35 °C.

from 30 to 10 atm in the conditioned sample. As shown in Figure 1, samples of polycarbonate conditioned with CO_2 exhibited no such local maximum in permeability.[4]

The reduced permeability of CO_2 in the BTDA−6FpDA is also shown in Figure 6. As was seen for the other 6FpDA-based polyimides, the unconditioned film of BTDA−6FpDA exhibited an upswing in permeability at about 10 atm as well as a considerable increase in permeability following conditioning. As was seen for BPDA−6FpDA, the permeability of CO_2 in the conditioned sample initially increased with decreasing pressure, exhibited a maximum value at approximately 30 atm, and decreased in permeability at low pressures.

The reduced permeability of CO_2 as a function of pressure in 6FDA−6FmDA is shown in Figure 4. The plasticization and conditioning responses in 6FDA−6FmDA followed a trend similar to the para-connected polyimides. There was considerable plasticization in the unconditioned 6FDA−6FmDA, resulting in a large increase in permeability at feed pressures greater than 10 atm. Conditioning also resulted in a substantial increase in permeability relative to the unconditioned sample of 6FDA−6FmDA. For example, at 35 atm the permeability in the conditioned sample was 9 times greater than in the unconditioned sample. Unlike the previously discussed BPDA−6FpDA and BTDA−6FpDA, the permeability of CO_2 in the conditioned sample of 6FDA−6FmDA did not decrease significantly at lower pressures.

Discussion

The large increase in permeability at the onset of plasticization in these polyimides results from an increase in diffusivity, presumably caused by the reduction in the intersegmental resistance to chain motions in the swollen polymer matrix as demonstrated for 6FDA−6FpDA in Figure 5. The permeability enhancement upon plasticization and conditioning was considerably higher for the polyimides than for the Bisphenol A polycarbonate shown in Figure 1. This difference is probably due to the much higher solubility level of CO_2 in the polyimides at the conditioning pressure. While there was a significant increase in permeability for all of the polyimides, the effect of plasticization on the CO_2 permeation varied considerably. The reduced permeability at 60 atm shown in Table 1 ranged from 4.2 to 7.9 in the unconditioned samples of these polyimide isomers and increased in the following order: BTDA−6FpDA < BPDA−6FpDA < 6FDA−6FpDA < 6FDA−6FmDA.

The solubility of CO_2 in 6FDA−6FpDA and BPDA−6FpDA at 60 atm was much higher than in BTDA−6FpDA as shown in Figure 7. As seen for a series of related polycarbonates, the greater plasticization effect in these two polyimides relative to BTDA-6FpDA is likely to be due to the greater penetrant induced swelling at higher solubilities.[4,5] Since the solubility of CO_2 in the densely packed region of the BPDA−6FpDA and 6FDA−6FpDA are approximately equal, the volume dilation at 60 atm of the BPDA−6FpDA and 6FDA−6FpDA estimated using eq 5 would be similar. Therefore, small differences in plasticization and conditioning in these two polymers can be attributed to differences in chain packing as well as resistance to chain motions. Swelling of the polymer increases the average spacing between the polymer chains and reduces the intersegmental resistance to chain mobility. The more dense packing of the BPDA−6FpDA (FFV = 0.161) with the long flat biphenyl linkage should result in a greater contribution from the intersegmental resistance than for the 6FDA−6FpDA (FFV = 0.191) with the bulky hexafluoroisopropylidene linkage in the dianhydride residue. At 60 atm, the large volume dilation of the polymer matrix may be sufficient to overcome the intersegmental resistances in the more open 6FDA−6FpDA but be insufficient to overcome the resistance in the BPDA−6FpDA. This reduction in intersegemental resistance would be expected to result in a greater plasticization effect in the 6FDA−6FpDA.

The permeability increase upon plasticization was slightly greater for the rigid 6FDA−6FmDA than for its para connected counterpart, 6FDA−6FpDA. Dynamic mechanical thermal analysis indicated that there is suppression of glassy state motion in the meta connected 6FDA−6FmDA relative to the 6FDA−6FpDA. This suppression of motion has been attributed to two factors: (i) the increased intersegmental steric resistance 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 nonsymmetric meta linkage.[7] At high CO_2 pressures or solubilities, swelling of the 6FDA−6FmDA would supply sufficient free volume to greatly reduce the intersegmental hindrances to segmental mobility from the nonsymmetric groups. This hindrance presumably does not affect the diffusivity in the 6FDA−6FpDA as much as in the 6FDA−6FmDA. Therefore, sufficient swelling of the polymer would be expected to result in a larger plasticizing and conditioning effect in the meta-connected 6FDA−6FmDA which is reflected in the larger permeability increase than for 6FDA−6FpDA.

As noted above, the permeabilities of CO_2 in BTDA−6FpDA and BPDA−6FpDA have a maximum which occurs at 30 atm following conditioning. This atypical decrease in permeability at lower pressures in the conditioned sample can be discussed in terms of the effect of conditioning on both the solubility and diffusivity. Typically, CO_2 solubility coefficients decrease with increasing pressure in both untreated and conditioned samples of glassy polymers because of saturation of the packing defects as was shown for the conditioned sample of 6FDA−6FpDA in Figure 2.[14,15] The decrease in permeability in the conditioned films of BPDA−6FpDA and BTDA−6FpDA at low pressures is, therefore, probably due to a large drop in diffusivity. This counterbalance of an increase in solubility and significant decrease in diffusivity at low pressures can result in an overall decrease in permeability relative to those at high pressures.

The effective diffusivity is determined by contributions from penetrants residing in packing defects and those within the densely packed region as shown in eq 4. Penetrants sorbed in the packing defects will have much lower diffusivities than those in the densely packed region. Packing defects and disruptions are trapped in the polymer matrix following depressurization because of the long relaxation time of the polymer chain segments relative to the penetrant removal rate in a process analogous to thermal quenching.[15] Therefore, conditioning tends to increase the relative fraction of penetrants in the low-diffusivity packing defects (“H”) compared to those in the high-diffusivity dissolved gas population (“D”).[5] This increased relative contribution to diffusivity from penetrants in packing defects at low pressures would tend to result in an overall decrease in the effective diffusivity.[5,15]

The decrease in permeability for the conditioned BPDA−6FpDA at low pressures was greater than that for BTDA−6FpDA. We speculate that the higher segmental mobility of the BTDA (carbonyl) relative to the BPDA (biphenyl) reduces the formation of packing defects in this material during rapid depressurization. The reduced contribution to the diffusivity from penetrants residing in the packing defects would minimize the loss in diffusivity and permeability in the conditioned samples of BTDA−6FpDA at low pressures. The conditioned sample of the meta-connected 6FDA−6FmDA did not show the large decrease in permeability with decreasing pressure that was seen for the BTDA−6FpDA and BPDA−6FpDA. Low-pressure permeability measurements are not available for the conditioned sample of 6FDA−6FpDA to determine whether this material follows a similar trend.

Conclusions

Exposure of four polyimides with hexafluoroisopropylidene as the central linkage of the dianhydride and/or diamine residue to CO_2 at 60 atm resulted in up to 10-fold increases in permeability relative to untreated samples. This permeability enhancement was due to considerable increases in diffusivity with the onset of plasticization and conditioning at CO_2 pressures greater than 10 atm, as well as large increases in solubility following conditioning at 60 atm. The plasticizing and conditioning effect of CO_2 on these rigid polyimides was much greater than that in Bisphenol A polycarbonate because of the much higher solubility of CO_2 in the polyimides.

The permeability measured after conditioning of these four polyimides was from 4.5 to 10 times greater than in untreated samples. The maximum permeability enhancement was seen for the meta-connected 6FDA−6FmDA and the minimum increase was seen for BTDA−6FpDA. The differences in plasticizing and conditioning effects were due to differences in (i) CO_2 solubility, (ii) initial packing density, (iii) intersegmental resistance to chain motions, and (iv) intrasegmental resistance to chain motions. The lower solubility in the BTDA−6FpDA presumably results in less swelling of the polymer matrix, which translates into a lower diffusivity and solubility enhancement following conditioning at a specific pressure. For polyimides with equivalent volume dilation, such as BPDA−6FpDA and 6FDA−6FpDA, the more densely packed polymer (BPDA−6FpDA) exhibited a smaller increase in permeability. To further clarify the effect of plasticization on the transport properties in these polyimides, additional data (i.e. volume dilation, solubility, and diffusivity) are needed.

Both the BTDA−6FpDA and BPDA−6FpDA had a maxima in permeability following conditioning at 60 atm. Conditioning at high pressures tends to trap excess free volume within the polymer matrix in the form of packing defects or disruptions. This maximum is probably a result of a significant decrease in effective diffusivity at low pressure resulting from the large contribution to diffusivity from low-mobility penetrants residing in the packing defects. The decrease in diffusivity would counteract the increase in solubility, resulting in an overall drop in the permeability in the conditioned sample at low pressures.

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