Effect of Thermal Hysteresis on the Gas Permeation Properties of 6FDA-Based Polyimides

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ABSTRACT: The effect of thermal hysteresis on the polymer chain packing and permeation properties of two 6FDA-based polyimide isomers was investigated. Thermal quenching resulted in a small increase in the fractional free volume of the polyimides with respect to the samples that had been annealed. Quenching from above the glass-transition temperature also resulted in larger increases in the permeabilities for both 6FDA–6FmDA and 6FDA–6FpDA with respect to annealed samples. Meta-connected 6FDA–6FmDA exhibited a larger increase in the permeability after quenching than the para-connected isomer, 6FDA–6FpDA. This larger increase in the permeability for 6FDA–6FmDA may have been due to differences in the effects of the increases in the free volume on the intersegmental resistance to chain motions. Although physical aging over a 3-month period resulted in a reduction in the permeability of quenched samples of 6FDA–6FpDA, the quenched samples maintained higher permeabilities than the annealed samples. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1174–1182, 2004

Key words: polyimides; annealing; ageing; membranes

INTRODUCTION

Polyimides have been the focus of a number of structure–property studies because of their excellent thermal, mechanical, and gas-transport properties.[1–7] Specifically, these polymers are interesting as permselective materials for applications as membranes for gas separation, protective coatings in sensors, and barrier packaging. Although the relationship between the backbone structure and transport properties of polyimides has been thoroughly studied, the impact of processing and operating conditions on the transport properties of these glassy polymers requires further investigation. For example, the exposure of glassy polymers to highly soluble penetrants, followed by rapid depressurization, can result in dramatic increases in the residual fractional free volume (FFV) with corresponding increases in the permeabilities.[8–11] The hysteretic effect of exposure to CO_2 on the gas-transport properties of the polyimide isomers used in this study was reported in two earlier articles.[10,11] The conditioning of polyimides with CO_2 at 60 atm resulted in up to 10-fold increases in the pure gas permeabilities. These large increases in the permeability were attributed to a residual volume dilation of the polymer matrix after rapid depressurization from the conditioning pressure.[10] These results demonstrate the importance of the process history in determining the transport properties of these rigid polymers. Thermal cycling can also result in significant modifications to the packing structure and transport properties of glassy polymers. The effect of thermal hysteresis and physical aging on the permeation properties of several pure gas pairs in 6FDA-based polyimide isomers is the focus of this article.

The results are discussed in terms of a general structure–property analysis and a dual-mode transport model.[12–14] Penetrant transport within a polymer matrix occurs through a solution–diffusion mechanism in which the penetrant dissolves into the polymer at the high-pressure feed side, diffuses through the polymer because of the concentration gradient, and desorbs into the low-pressure permeate side. 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. The ideal selectivity, $\alpha^*_{A/B}$, of the membrane for component A with respect to component B is the ratio of the pure gas permeabilities. The ideal selectivity can be factored into the product of the solubility selectivity, S_A/S_B, and diffusivity selectivity, D_A/D_B.

The solubility of gases in glassy polymers can be discussed in terms of the dual-mode sorption model, which states that there are two environments in the polymer matrix into which a penetrant can sorb.[12,13] The first sorption environment is penetrant-scale

packing defects or microvoids that are formed as the polymer is cooled through the glass-transition temperature (T_g). The solubility in these microvoids can be modeled with Langmuir-type sorption, in which the solubility sharply increases with the pressure and reaches an asymptote as the microvoids become saturated. The second sorption environment is the densely packed amorphous region, which is similar to the sorption environment in liquids or rubbery polymers and is modeled on Henry's law at low or moderate pressures. Sorption in these microvoids can be modeled with Langmuir-type sorption, in which the solubility increases with pressure and asymptotes as the microvoids become saturated. The dual-mode model is written as follows:[12,13]

$$C = k_d p + \frac{b C_H' p}{1 + bp} \qquad (1)$$

The Henry's law constant [k_d; cc (STP)/cc (polymer) atm] is a measure of the dissolved gas population; b (atm^{-1}) is the hole affinity constant, and C_H' [cc (STP)/cc (polymer)] is the Langmuir sorption capacity. The relative distribution of the free volume in the polymer matrix between these two regions can have a significant impact on both the diffusivity and solubility coefficient of the penetrant. There is an increase in the solubility coefficient in glassy polymers after conditioning, and it has been attributed to an increase in the dissolved gas population caused by packing disruptions combined with an increase in C_H' caused by the introduction of long-lived packing defects in the polymer matrix. The solubility of a penetrant in a polymer matrix is, therefore, controlled by (1) the inherent condensability of the penetrant, (2) the polymer–penetrant interactions, and (3) the amount and distribution of the free volume in the polymer matrix.

A penetrant molecule can be visualized as residing in the polymer in a sorbed cage surrounded by polymer chains. For a penetrant to make a diffusive jump within the polymer matrix, a transient gap between the polymer chains greater than the sieving diameter of the penetrant must be generated. Thermally activated motions of the polymer chain segments generate these transient gaps, through which diffusive jumps of the penetrant occur. Modifications of the polymer structure that inhibit chain packing or increase chain segmental mobility can be used to shift the distribution of transient gaps in the matrix to larger sizes to increase the diffusivity of each of the penetrants. If these modifications simultaneously narrow the size distribution of the transient gaps to retard the diffusion of one penetrant with respect to another, the diffusivity selectivity will be increased. The average size and size distribution of transient gaps required for diffusion to occur are determined by the chain packing and chain segmental mobility of the polymer, as well as the size and shape of the penetrant molecules.

The results of extensive structure–property studies of glassy polymers for membrane applications suggest that it is desirable to modify the backbone structure within a family of polymers so that the intersegmental packing and chain segmental mobility are simultaneously inhibited.[1–7,12–14] Inhibitions to intersegmental packing are reflected by an increase in the FFV of the polymer matrix not occupied by the electron cloud comprising the filled space. The inhibition of chain segmental mobility is reflected by increases in T_g and the sub-T_g transition temperature (T_β). In particular, the sub-T_g transition is important because it reflects the scale of motion necessary for diffusion to occur within the polymer matrix. Finally, one can image a situation in which the total FFV may be identical but the distribution of the free volume may differ.[7] In such a case, a different gas-separation performance can result if the free volume is distributed in large microvoids versus small microvoids.

The dependence of the packing density and thermal–mechanical properties (i.e., T_g) of glassy polymers on the thermal history is very well documented.[15–22] Rapid quenching through T_g typically traps excess free volume within the polymer matrix, and this results in a decrease in the density and an increase in the FFV. This departure from equilibrium packing after thermal quenching results in an increase in the permeability through increases in both the diffusivity and solubility.[16–18] The increase in the solubility coefficient in glassy polymers after thermal quenching has been attributed primarily to an increase in the solubility of the penetrants in the packing defect regions combined with small increases in the solubility in the densely packed region.[16–18] Specifically, Paul et al.[17] found that annealing of polycarbonate at temperatures below T_g resulted in sharp drops in C_H' with little effect on k_d. The increase in the diffusivity that is typically seen after thermal quenching can be attributed to the increase in the free volume with respect to the annealed samples. These results imply that there is both an increase in and a redistribution of the polymer free volume after thermal quenching. Glassy polymers that are maintained at a temperature below T_g will relax toward a meta-stable packing density in a process known as annealing or aging.[19–22] This densification of the polymer matrices has been shown to result in a decrease in the permeability combined with increases in the permselectivity.

The effect of thermal cycling on the packing density and permeation properties of the 6FDA-based polyimide isomers shown in Figure 1 was investigated with several thermal treatment protocols. Polyimide isomers with hexafluoroisopropylidene groups as the central linkages of the diamine and dianhydride residues were chosen for this study because of their excellent potential for applications as membrane materials. Both 6FDA–6FpDA and 6FDA–6FmDA exhibit

6FDA-6FpDA
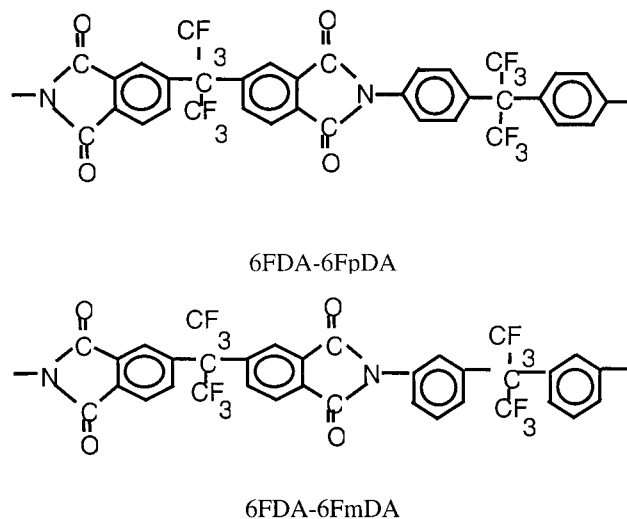
6FDA-6FmDA

Figure 1 Structures of 6FDA–6FpDA and 6FDA–6FmDA.

gas-transport properties that lie on or above the upper bound on the permeability–permselectivity tradeoff curve for typical membrane polymers. Several thermal treatment protocols were used, including thermal quenching, slow cooling, and annealing at temperatures below T_g. The permeabilities and permselectivities of a series of gases of various molecular sizes (i.e., 2.6 Å for He to 3.8 Å for CH_4) at 35°C were used to probe the effect of the thermal history on the microstructure environment of 6FDA–6FpDA and 6FDA–6FmDA. The impact of thermal cycling and physical aging at room temperature on the permeation properties of the polyimides is reported in this article.

EXPERIMENTAL

The polyimides used in this study were supplied by Hoechst–Celanese Corp. The physical and inert gas-transport properties of the bulk polymers were reported in an earlier article and are given in Table I. The bulk polymer results were reported for films that were used after drying and that were not heated above T_g.[1] Therefore, any hysteresis from the film casting and drying procedure was not eliminated for the bulk films. Before the thermal treatment study, films were cast from methylene chloride with standard techniques and dried in a vacuum oven for several days at temperatures up to 150°C for the removal of any residual solvent.[1] The films used in this study were between 1.5 and 2.5 mils thick.

The thermal treatment protocols and designations for the films used in this study are summarized in Table II. For each protocol, well-dried films were heated above T_g in an oven for at least 1 h to allow the films to reach thermal equilibrium. During the heating process, the oven was purged with argon to prevent polymer degradation. Attenuated total reflectance

Fourier transform infrared spectroscopy of quenched and annealed samples indicated that there was no degradation of the chemical structure of either of the polyimides after thermal treatment. For the thermal quenching protocol, the equilibrated films were submerged in an ice bath to cool the samples rapidly through T_g. To provide slowly cooled samples for the annealing process, films were heated above T_g, the oven was turned off, and the samples were cooled slowly to room temperature. For the annealing protocol, slowly cooled films were heated in an oven at 150°C under an argon atmosphere for 7 days. After annealing, the oven was turned off, and the films were allowed to cool to room temperature. The permeabilities in the films were determined immediately after the thermal treatment to minimize the effect of physical aging on the permeation properties. Films that were used for the physical aging studies were kept in air at atmospheric pressure and 35°C.

In the absence of significant differences in the intrasegmental rotational mobility, FFV has been used successfully to correlate the effect of the relative chain packing on the transport properties of glassy polymers.[23] The FFV is the ratio of the specific free volume to the polymer specific volume measured at 35°C. The specific free volumes were estimated with the method of Lee,[24] which uses the group-contribution method of Van Krevelen and Hoftyzer[25] for the calculation of the van der Waals volumes. The FFV, a purely volumetric quantity, is not distorted by the various molecular masses of the substituent atoms as the density and specific free volume are. The FFV and density are used to probe the impact of thermal hysteresis on the relative chain packing of the polyimides. The density and FFV were determined for several quenched and annealed samples of each polyimide. The macroscopic densities were measured in a density gradient column at 35°C with $CaNO_3$ solutions. 6FDA–6FpDA has a more open structure than 6FDA–6FmDA, as indicated by the larger FFV of 6FDA–6FpDA shown in Table I.[1]

T_g and T_β have been used to quantify the relative chain rigidity of the bulk polyimides. Although para-connected 6FDA–6FpDA has a higher T_g than meta-connected 6FDA–6FmDA, 6FDA–6FpDA has a lower T_β. Work with polycarbonates and polyesters indicates that differences in the sub-T_g transitions are more indicative of the chain motions that are necessary for diffusion

TABLE I
Physical Property Data for the Bulk Polyimide
Isomers Used in This Study[1,27]

Polymer	T_g (°C)	T_β (°C)	Density (g/cc)	FFV	d-spacing (Å)
6FDA–6FmDA	254	151	1.493	0.175	5.7
6FDA–6FpDA	320	110	1.466	0.190	5.9

TABLE II
Thermal Treatment Protocol and Physical Properties of 6FDA–6FpDA and 6FDA–6FmDA

Sample designation	Polymer	Thermal treatment	Density (g/cm³)[a]	FFV
M-bulk	6FDA–6FmDA	Bulk Film No heat treatment	1.493	0.175
MA-150	6FDA–6FmDA	Heat: T_g + 15°C Cooled: Slow Cool Anneal at 150°C	$1.502 \pm 1 \times 10^{-4}$	0.171
MQ-15	6FDA–6FmDA	Heat: Tg + 15°C Cooled: Quench into ice bath	$1.494 \pm 9 \times 10^{-4}$	0.175
P-bulk	6FDA–6FpDA	No heat treatment	1.466	0.190
PA-150	6FDA–6FpDA	Heat: T_g + 15°C Cooled: Slow Cool Anneal at 150°C	$1.469 \pm 4 \times 10^{-4}$	0.189
PQ-15	6FDA–6FpDA	Heat: T_g + 15°C Cooled: Quench into ice bath	$1.464 \pm 1.1 \times 10^{-3}$	0.191
PQ-50	6FDA–6FpDA	Heat: T_g + 50°C Cooled: Quench into ice bath	NA	NA

NA = not applicable.
[a] Data for samples with no thermal treatment from ref. 1.

to occur in glassy polymers than T_g. On the basis of T_β, there are greater inhibitions to rotational segmental mobility in 6FDA–6FmDA than in 6FDA–6FpDA. The much lower FFV and more rigid structure of 6FDA–6FmDA result in significantly lower permeabilities and higher permselectivities for this polymer with respect to 6FDA–6FpDA.[1] These differences in chain segmental mobility and packing were shown to significantly affect the responses of these polyimides to CO_2-induced plasticization and conditioning.[10,11]

The pure gas permeabilities were measured at 35°C with standard gas permeations cells at pressures of up to 10 atm.[26] The equipment and procedure for the permeation measurements have been described in detail elsewhere. The permeabilities in each of the films were measured in the following order—N_2, O_2, CH_4, CO_2, He, and N_2—to minimize differences in measurements due to aging effects on the permeation properties of films after different thermal treatment protocols. For each of the films tested, there were negligible differences between the N_2 permeabilities measured immediately after thermal treatment and those measured at the end of the test cycle. After the permeation measurements for each gas, the films were evacuated overnight on both sides for the removal of any dissolved gas in the films. All of the permeation measurements were made at pressures below 10 atm to prevent any potential plasticization or conditioning effects.

RESULTS AND DISCUSSION

Effect of the thermal history on the polyimide isomers

The densities and FFVs of thermally treated 6FDA–6FmDA and 6FDA–6FpDA films are compared with the bulk polymer properties in Table II. The values reported for the quenched and annealed films are based on an average of three samples. The densities reported for the quenched protocol are for films equilibrated at 15°C above T_g. For both of the polymers, the density and FFV of the films after thermal treatment were very similar to the values for the bulk polymers reported in the literature.[1] Thermal cycling resulted in only subtle changes in the average chain packing of the polymer matrix, as reflected by the small increase in the FFV and by the decrease in the density (<2%) for the thermally quenched films with respect to the annealed films. Although the FFV and density showed average chain spacing, no information was provided about the relative distribution of the free volume. The distribution of the free volume can have a significant impact on the gas-transport properties of glassy polymers.[7] For example, fluorine-containing polyimide and polycarbonate analogues had very similar FFVs but very different permeabilities and permselectivities. These differences were attributed to variations in the distribution of the free volume from large packets to areas of low free volume.

The permeabilities of a series of gases of various molecular sizes (i.e., 2.6 Å for He to 3.8 Å for CH_4) were used to further probe the effects of the thermal history on the microstructures of the polyimides. Although there were only small differences in the FFV, the thermal history had a significant effect on the permeation properties. The permeabilities are reported in Table III for samples of 6FDA–6FpDA with the following thermal treatment histories: (1) quenching from 50°C above T_g into an ice bath (PQ-50), (2) quenching from 15°C above T_g into an ice bath (PQ-15), and (3) annealing of a slowly cooled film at 150°C

TABLE III
Pure Gas Permeabilities of Thermally Treated Samples of 6FDA–6FpDA

Thermal history	PO_2^a (a)	PCO_2^b (b)	PHe^b (b)	$PO_2\ PN_2$	PCO_2PCH_4	$PHe\ PCH_4$
PA-150	19.3	75	159	4.78	38.5	81.5
PQ-15*	21.5 ± 0.5	89.0 ± 2.3	175 ± 2.1	4.64 ± 0.067	39.5 ± 3.5	78.0 ± 0.33
PQ-500	25.7	106	211	4.56	38.5	76.7
Bulk film, no treatment	18	68	147	4.62	36.8	79.5

Data for bulk films is from ref. 1.
Permeabilities were averaged over three quenched films.
[a] Permeability for O_2 was measured at 35°C and 2 atm and was reported in barrer.
[b] Permeabilities for CO_2, N_2, He and CH_4 were measured at 35°C and 10 atm and were reported in barrer.

for 1 week (PA-150). Note that the 6FDA–6FpDA films were annealed approximately 175°C below T_g and 40°C above T_β. Therefore, there was considerable polymer segmental mobility at the annealing temperature that would enable the polymer to densify.[19–22] The permeabilities of three films quenched independently with the PQ-15 protocol were compared to determine the variations in the properties for films with similar thermal histories. As shown in Figure 2, the three PQ-15 films exhibited similar CO_2 permeabilities that were intermediate between those of the PQ-50 and PA-150 films. Because all of these samples were heated above T_g before the thermal treatment, any variation in the permeation properties could be attributed to differences in the polymer microstructure resulting from the thermal treatment. Note that there was little variation in the properties of the PQ-15 samples with a similar thermal history.

The permeabilities in the thermally quenched films were consistently greater than those for the annealed or bulk polymer films (Table III). Although annealed films generally exhibited higher permselectivities than the quenched films, the variations in the permselectivities were much smaller than for the permeabilities. For example, the average permeability of O_2 in the PQ-15 films was 11% greater in the PA-150 film, and there was a 2% decrease in the O_2/N_2 permselectivity. Increasing the quench temperature resulted in simultaneous increases in the permeability, with slight decreases in the selectivity, for each gas pair studied. Because there is an increase in the specific volume of polymers with increasing temperature, a greater excess free volume will be trapped within the polymer matrix after rapid cooling through T_g. This increase in the free volume should translate into a larger permeability for each of the gases in the PQ-50 film. The
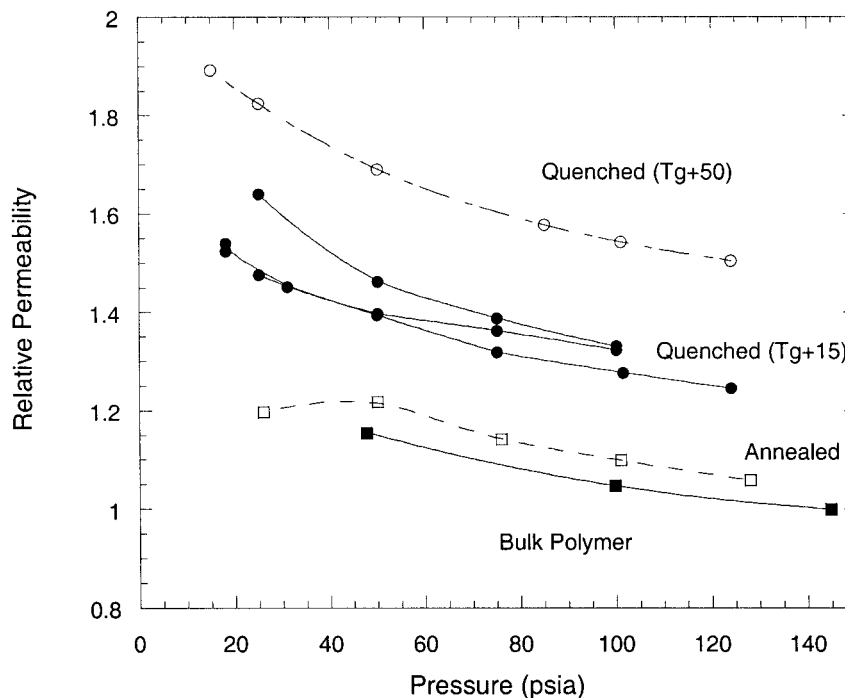

Figure 2 Relative permeability of CO_2 in thermally treated samples of 6FDA–6FpDA.

TABLE IV
Pure Gas Permeabilities of Thermally Treated Samples of 6FDA–6FmDA

Sample designation	PO_2^a	PCO_2^b	PHe^b	$PO_2\ PN_2$	$PCO_2\ PCH_4$	$PHe\ PCH_4$
MA-150	1.80	5.9	46.0	7.1	69.8	540
MQ-15	3.30	10.8	73.1	6.7	68.4	460
Bulk Film No treatment	1.80	5.6	47.0	6.9	65.9	550

Data for bulk films is from ref. 1.
Permeabilities were averaged over three quenched films.
[a] Permeability for O_2 was measured at 35°C and 2 atm and was reported in barrer.
[b] Permeabilities for CO_2, N_2, He and CH_4 were measured at 35°C and 10 atm and were reported in barrer.

permeability of oxygen in PQ-50 was 19% higher than the average for PQ-15. Finally, although the annealed films of 6FDA–6FpDA exhibited slightly lower FFVs than the bulk polymer, the permeabilities in the annealed films were slightly larger than the values for the bulk polymer. Interestingly, the permselectivities in the annealed sample were also greater than those reported for the bulk polymer. The films used for the bulk polymer measurements were used after drying below T_g without heating above T_g. Therefore, the history imparted upon the bulk film during the casting and drying process was not erased and could potentially impart a different free volume distribution that might account for the small differences in permeabilities for these films.

The permeabilities and permselectivities of several gas pairs at 35°C in thermally treated samples of 6FDA–6FmDA are compared with the bulk polymer properties in Table IV. The pressure-dependent permeability of CO_2 in the thermally treated samples of 6FDA–6FmDA is shown in Figure 3. The permeabilities are reported for samples of 6FDA–6FmDA with the following thermal histories: (1) quenching from 15°C above T_g into an ice bath (MQ-15) and (2) annealing a slowly cooled film at 150°C for 1 week (MA-150). As was seen for 6FDA–6FpDA, films that were rapidly cooled through T_g exhibited the largest permeabilities, followed by annealed samples and the bulk polymer. Note that the 6FDA–6FmDA films were annealed at T_β, approximately 100°C below T_g. The permeabilities in the thermally quenched films were considerably larger than the permeabilities in the annealed sample and bulk polymer. There was a corresponding small decrease in the permselectivities for the MQ-15 films. For example, the permeability of O_2 in MQ-15
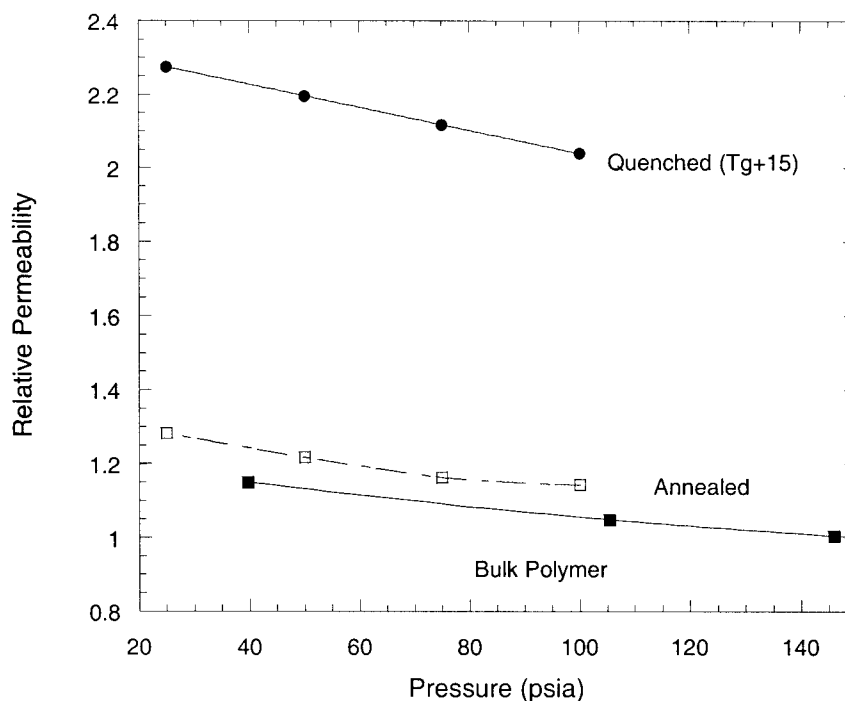

Figure 3 Permeability of CO_2 in thermally treated samples of 6FDA–6FmDA.

was 83% greater than that in MA-150, and the O_2/N_2 permselectivity was 6% lower in the quenched film than in the annealed film. Similar results were seen for the CO_2/CH_4 and He/CH_4 systems, as reported in Table IV.

The pressure-dependent permeability can be used as an indicator of the relative distribution of the free volume between densely packed regions and packing defects. For a glassy polymer, there is a decrease in the solubility coefficient at low pressures followed by a leveling off at higher pressures as the packing defects become saturated. The diffusivity coefficient exhibits slight increases in value with increasing pressure. In general, the overall result will be a decrease in the permeability with increasing pressure, particularly at low pressures. Polymers with high free volumes in the form of packing defects (Langmuir-type sites) will exhibit larger decreases in the solubility coefficient with increasing pressure that will translate into larger drop-offs in the permeability isotherm. Because carbon dioxide is the most soluble gas studied, the permeability isotherms for this gas are used to represent the system.

Bulk films of both 6FDA–6FmDA and 6FDA–6FpDA have fairly large Langmuir solubilities. For example, C_H' of CO_2 is 31.1 $cm^3(STP)/cm^3$(polymer)atm in 6FDA–6FpDA and 19.5 $cm^3(STP)/cm^3$(polymer)atm in 6FDA–6FmDA.[26] This results in the fairly sharp decrease in the CO_2 permeabilities of the bulk polyimide films with increasing pressure, as shown in Figures 2 and 3. The results are reported in terms of a relative permeability to facilitate a comparison between the polyimide isomers with very different bulk-transport properties. The relative permeability is defined as the ratio of the permeability at each pressure to the permeability in the bulk polymer at 10 atm: 5.1 barrer for 6FDA–6FmDA and 65.6 barrer for 6FDA–6FpDA. A small pressure range was used for the CO_2 studies to avoid any plasticization of the films at pressures greater than 10 atm. For all thermal histories, there was a decrease in the permeability at low pressures followed by a general leveling off at higher pressures. The quenched samples exhibited slightly larger decreases in permeability with pressure than the annealed and bulk samples. These results are consistent with previous studies indicating that annealing results in a reduction in C_H'.[16–18] Although 6FDA–6FmDA had slightly larger increases in permeability after quenching, there was a larger pressure effect on permeability for the more inherently highly open 6FDA–6FpDA.

Thermal quenching, which resulted in only small variations in the FFV and density, had a greater impact on the permeabilities of each of the gases with respect to the bulk polymer or annealed films. Both the FFV and density are measures of the average packing density of the polymer matrix and do not account for subtle differences in the distribution of the free volume. Similar results were seen for polycarbonate samples after annealing at temperatures near T_g.[17,18] Thermal quenching typically traps excess free volume within the polymer matrix, as shown by the slight increase in the FFV for both polymers, and may result in a subtle reorganization in the distribution of the free volume. A comparison of polyimides and polycarbonates with similar structures and overall free volumes indicated that the distribution of the free volume could have a significant effect on gas-transport properties.[7] For example, the permeabilities in the polyimides were up to 5 times greater than in structurally analogous polycarbonates, whereas the permselectivities were quite similar. The higher combined permeability and selectivity in the polyimides were a result of a combination of increases in the diffusivity selectivity and solubility with respect to the polycarbonates. These variations in the transport properties without significant changes in the overall FFV have been attributed to the formation of large areas of high local free volume interconnected with regions of low free volume in the polyimides.[7] The increase in the diffusivity selectivity, coexisting with the solubility increase, may reflect an improved ability to control jumping through lower FFV regions in the polyimides between local areas of high FFV, which can easily accommodate sorbing penetrants. Thermal quenching may result in a similar subtle rearrangement in the distribution of the free volume that is evidenced by the small changes in the density and larger differences in the permeability, which is sensitive to the distribution of the free volume.

Additionally, there was a larger increase in the permeability for 6FDA–6FmDA after thermal quenching than for 6FDA–6FpDA. This difference in the hysteretic response may be due to large differences in the steric resistance to chain motions for these polyimides isomers.[1] There is a suppression of glassy-state motion in the meta-connected isomer with respect to the para-connected isomer that is reflected in the higher T_β's for 6FDA–6FmDA. The suppression of glassy-state motion in the meta-connected isomer has been attributed to an increase in the resistance to segmental mobility due to the larger volume required for motion of the nonsymmetric meta-connected unit with respect to the symmetric para-connected unit. The increase in the FFV after thermal quenching of the 6FDA–6FmDA may supply sufficient free volume to allow motion for these nonsymmetric groups. This intersegmental hindrance to motion presumably does not affect the diffusivity of 6FDA–6FpDA as much as that of 6FDA–6FmDA. The effect of thermal cycling on the diffusivity and solubility must be determined to fully understand the effect of the microstructure on the transport properties.

TABLE V
Effect of Physical Aging at Room Temperature on the Permeation Properties of 6FDA–6FpDA, Which Was Thermally Quenched from 15°C above the T_g

Days after quench	PO_2^a	PCO_2^b	PHe^b	$\dfrac{PO_2}{PN_2}$	$\dfrac{PCO_2}{PCH_4}$	$\dfrac{PHe}{PCH_4}$
Annealed sample	18	68	147	4.62	36.8	79.5
Initial	21.6	86.5	177	4.76	38.8	79.4
21	21.4	84.8	177	4.73	38.6	80.5
29	20.3	82.8	177	4.56	39.4	84.3
60	20.0	84.5	177	4.76	41.8	87.6

 ᵃ Permeability for O_2 was measured at 35°C and 2 atm and were reported in barrer.

ᵇ Permeabilities for CO_2, N_2, He, and CH_4 were measured at 35°C and 10 atm and were reported in barrer.

Aging of the permeation properties of 6FDA–6FpDA

Physical aging occurs when a polymer is maintained at a temperature at which local motions can occur in the glassy state, and this results in a densification of the polymer matrix.[15] For this study, the permeation properties were measured to probe the physical aging of thermally quenched (T_g + 15) and untreated films of 6FDA–6FpDA (Table V). Both films were aged at 35°C, which is well below T_g of 6FDA–6FpDA (T_g = 320°C). As discussed in the previous section, the thermally quenched samples exhibited much larger permeabilities and slightly greater FFVs than the annealed and bulk polymer films. The permeability and permselectivity of the O_2/N_2 gas pair as a function of the aging time in the thermally quenched film are compared to those of the untreated sample in Figure 4. Although the time-dependent permeabilities of an annealed sample were not measured, the permeability of O_2 in PA-150 immediately after the thermal treatment is represented in Figure 4 by a dashed line. For both the bulk polymer and the PQ-15 film, there is a reduction in the permeability combined with little change in the permselectivity with the aging time. There was a 7% decrease in the O_2 permeability in PQ-15, and there was a 8.3% decrease for the untreated sample, after aging at 35°C for 100 days. For both the quenched and bulk polymer, the largest decreases in the permeability were seen initially, and they were followed by a leveling off in the permeability with time.

CO_2/CH_4 and He/CH_4 exhibited similar aging behavior in the quenched sample, showing increases in the permselectivity and decreases in the permeability with the aging time. In each case, the magnitude of the increase in the permselectivity was small in comparison with the decrease in the permeability.[16–19] Because the permeabilities of all the components of the gas mixture followed a similar trend with the aging time as the polymer matrix was densified, physical aging had a much smaller impact on the permselectivity. Although there was a 5% decrease in the CO_2 permeability, there was no change in the permeability of He with the aging time. Small molecules, such as He, have fairly low solubilities and high diffusivities and require small pathways to diffuse. Therefore, He showed little change in the permeability with the ag-
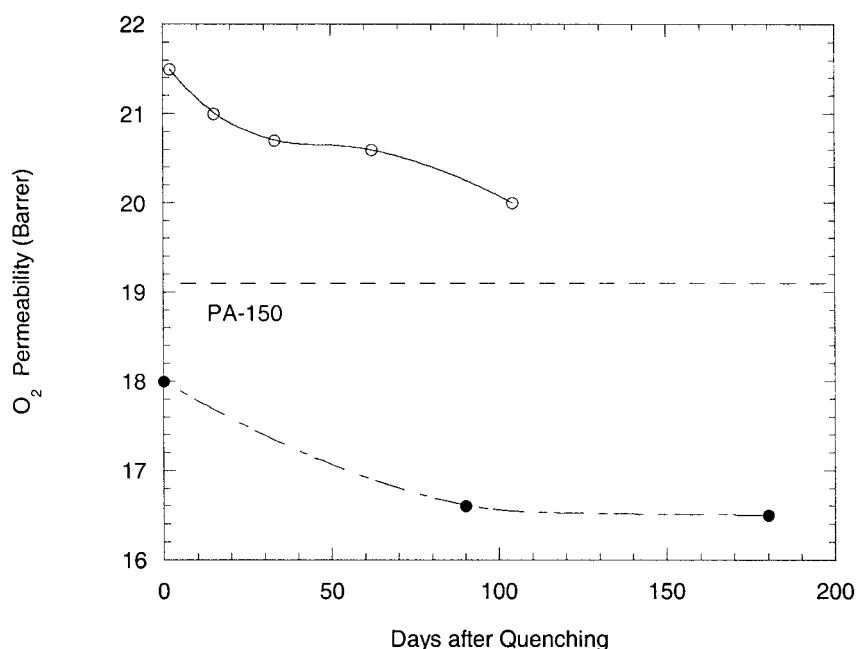
Figure 4 Impact of physical aging on the permeability of O_2 in (○) thermally quenched and (●) bulk films of 6FDA–6FpDA. The data for the untreated samples are taken from ref. 27.

ing time and polymer densification. In contrast, CO_2 has a very high solubility and an intermediate diffusivity more strongly affected by a decrease in the free volume with aging.

These results are consistent with results reported for the physical and transport properties of other classes of glassy polymers.[20–22] As discussed previously, glassy polymers are in out-of-equilibrium packing conformations, which incorporate excess free volume within the polymer matrix in the form of packing defects as well as slight increases in the average chain spacing. As the polymer film is maintained at temperatures below T_g, the polymer matrix will densify, and this is typically reflected in increases in the density and decreases in the FFV. The decrease in the FFV is expected to result in decreases in both the solubility and diffusivity of penetrants within the polymer matrix.

CONCLUSIONS

As shown for penetrant-induced hysteresis, thermal cycling had a significant impact on the permeability and permselectivity of 6FDA–6FpDA and 6FDA–6FmDA. Thermal quenching resulted in small decreases in the packing density for both polymers with respect to the annealed and bulk polymer. However, thermal hysteresis had a much larger impact on the permeation properties of these polyimide isomers. As expected, thermal quenching resulted in up to a 90% increase in the permeabilities of 6FDA–6FmDA with respect to the annealed samples. Similar results were seen for 6FDA–6FpDA after thermal cycling. Increasing the heating temperature before thermal quenching resulted in a higher free volume of the sample and led to larger increases in the permeability, with little change in the permselectivity. Pressure-dependent permeation studies indicated the increased formation of Langmuir-type sorption sites after thermal quenching, which resulted in somewhat sharper decreases in the permeability with pressure for the quenched films. These results were consistent with earlier studies on polycarbonates.[17,19] The effect of physical aging at 35°C on the permeability in a thermally quenched and a bulk film of 6FDA–6FpDA was studied. In both cases, aging resulted in a decrease in the permeability

with slight increases in the permselectivity. However, over the 100-day period of the aging studies, the thermally quenched sample did not approach the value of the annealed or bulk polymer.

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