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Physical aging of thin 6FDA-based polyimide membranes containing carboxyl acid groups. Part I. Transport properties

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Abstract

The effect of molecular structure on the kinetics of physical aging of thin films (~350 nm) formed from glassy 6FDA-based polyimides was investigated by tracking the changes in gas permeability (He, O_2 and N_2) at 35 °C for more than 2000 h. The structures studied included homopolymers of 6FDA with 6FpDA and with DAM plus copolymers where a portion of the latter two monomers was replaced with DABA to introduce carboxyl units into the structure for subsequent cross-linking studies. Over this period of aging, the oxygen permeability decreased by a factor of two for the polyimide containing the diamine 6FpDA and by a factor of five for the polyimide containing the diamine DAM. Introduction of DABA units accelerated the aging in the case of 6FpDA and slowed the aging in the case of DAM. Aging rate seems to correlate with the level of free volume of the polymer; the higher the free volume, the faster is the aging. Selectivity for all gas pairs increased upon aging but the rate is not simply explained by free volume alone because the difference in size of the two gas molecules is also reflected in the response to physical aging observed.

Keywords: Physical aging; Thin film; Fluoropolyimide

1. Introduction

Aromatic polyimides are a promising class of materials for gas separation membranes because of their outstanding thermal, physical and transport properties. Many have attractive solvent resistance but the corresponding lack of solubility has limited their usefulness for membrane applications since practical membranes are made by solution processing [1–6]. Recently, fluorine-containing polyimides have been of interest because of their attractive gas separation properties and their solubility in common solvents that enable them to be spun into hollow fibers [7–9]. Monomers containing hexafluoroisopropylidene-bridging moieties appear to be quite effective for achieving a relatively high selectivity in polyimides that can be spun into hollow fibers with an asymmetric structure. These bulky connector groups cause intrachain steric hindrance that disrupts chain order and packing efficiency, which leads to a high free volume and attractive permeability characteristics.

On the other hand, these polyimides are particularly susceptible to plasticization caused by swelling of the polymer matrix by condensable feed components and by high-pressure CO_2 [6,9–11]. Staudt-Bickel and Koros [12] introduced copolyimides that have a diamine monomer with a pendent carboxyl acid group that can be used to cross-link such membranes, which may help reduce the plasticization tendency. They showed that the carboxyl acids units can be reacted with various glycols by several strategies leading to cross-linking and demonstrated that transport properties could be tuned by varying the monomer composition. Wind et al. reported relationships between permeability, selectivity and swelling of cross-linked 2,2-bis(3,4-carboxyphenyl)hexafluoropropane dianhydride (6FDA) based copolyimides [3,6,10] through systematic changes to the polymer structure by chemical modification and thermal treatment. Significant increases in the stability of these materials to the pressure of highly soluble gases (e.g. carbon dioxide) were demonstrated. While the characteristics of these fluorine containing copolyimides are very encouraging, there are complex responses to film molecular weight, chemical structure, thickness and temperature that still need to be better understood.

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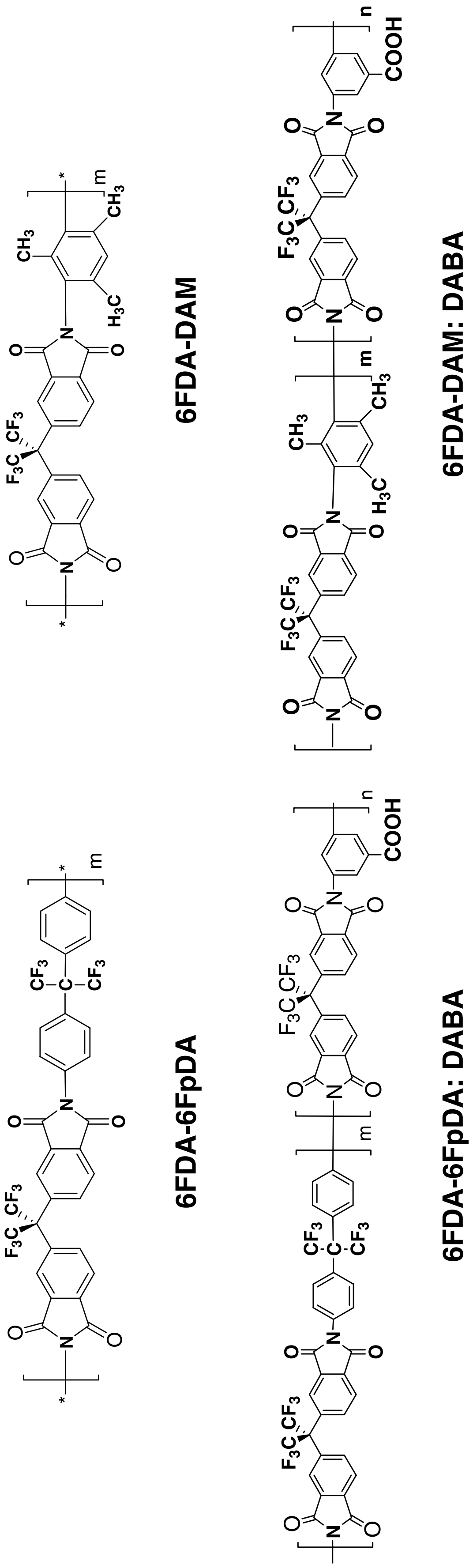

Fig. 1. Structure of the polyimide materials used in this study.

Table 1
Physical properties of 6FDA-based polyimide materials synthesized for this study

Polymer	T_g (°C)	M_w	M_n	Density (g/cm^3)	FFV
6FDA-6FpDA	298	47,000	21,000	1.5044	0.175
6FDA-DAM	372	56,200	28,340	1.3342	0.190
6FDA-6FpDA:DABA 2:1	319	24,400	13,310	1.4823	0.182
6FDA-DAM:DABA 2:1	376	73,030	38,210	1.3936	0.183

Physical aging [13–16] refers to the continual evolution of a glassy polymer towards an equilibrium state with associated changes in physical properties with time at temperatures below T_g. Pfromm et al. [17] reported that the gas permeability of thin films decrease dramatically over relatively short-time scales suggesting greatly accelerated physical aging of these glassy thin films relative to the bulk state. McCaig and Paul [18,19] studied the physical aging of polyarylate films having thicknesses ranging from sub-micron to several tens of microns. By tracking the reduction in gas permeability with aging time, it was found that the aging rate has a strong dependence on thickness and they developed a mathematical model for aging in terms of a dual mechanism [13] involving loss of free volume by 'lattice contraction' and diffusion to the free surface of the film. Recently, Huang and Paul [15,16,20] refined the techniques for studying physical aging of thin films by using ellipsometry to measure thickness and determine refractive index of films as they age. They reported thickness-dependent aging for three glassy polymers of interest as gas separation membranes and showed how aging rate depends on aging temperature over a limited range. These studies show a strong effect of the chemical structure of the polymer on the aging response in thin film form.

This is the first in a series of papers that extend these studies to thin 6FDA-based copolyimide films with and without 3,5-diaminobenzoic acid (DABA) units in the chain. The effect of physical aging on the gas permeation properties of polyimides

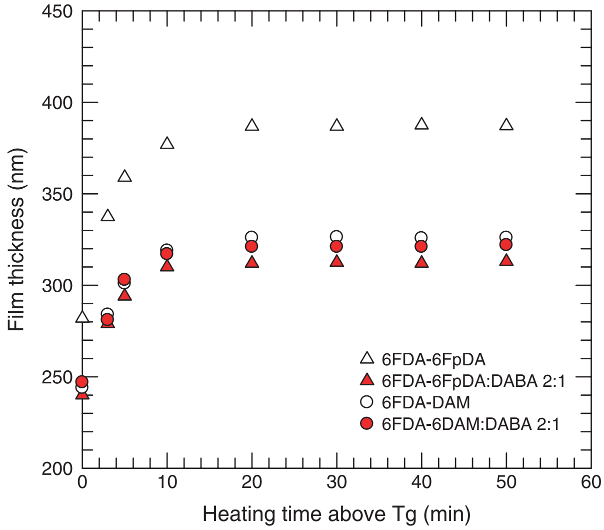

Fig. 2. Change in film thickness for 6FDA-based polyimide films as a function of heating time above T_g.

Table 2
Gas permeation properties of 6FDA-based polyimide films at 35 °C and 2 atm

Polymer	Bulk film					Thin film	
	P_{He}	P_{N_2}	P_{O_2}	P_{O_2}/P_{N_2}	P_{He}/P_{N_2}	P_{O_2} 1 h	P_{O_2} 2000 h
6FDA-6FpDA	147	3.22	18	4.6	45.6	24	13
6FDA-DAM	301	17	55	3.3	18	95	20
6FDA-6FpDA:-DABA 2:1	142	2.17	11.5	5.3	65	23	8
6FDA-DAM:-DABA 2:1	132	4.36	18	4.1	30	34	10

Gas permeability coefficients are given in the units of barrer; 1 barrer = 10^{-10} cm^3 (STP) cm/cm^2 s cmHg.

with and without DABA units in the chain is examined in detail to explore how the polymer structure and its free volume affect physical aging. These 6FDA-based polyimides will be compared with other commercial polymers to better understand how structure affects aging. The second paper in this series will quantify the response in terms of density and fractional free volume by using ellipsometry to monitor refractive index during aging. Future papers in this series will systematically investigate CO_2 induced changes and the effect of cross-linking on aging for 6FDA-based polyimides.

2. Experimental

2.1. Polymer synthesis

6FDA-based copolyimides were prepared by two-step polycondensation of an equimolar mixture of this dianhydride and a diamine followed by a cyclodehydration reaction [21,22]. The diamines used to form homopolyimides were (4,4′-hexafluoroisopropylidene)diamine, 6FpDA, and diaminomesitylene, DAM. The 6FDA monomer was obtained from Lancaster while all of the diamine monomers were from Aldrich. The suppliers claimed higher than 99.7% purity; however, each monomer was further purified by sublimation. Copolymers were formed by replacing a portion of either of these diamines with DABA. In the first step, the polycondensation reaction was carried out for 24 h at room temperature to form a poly(amic acid) solution in *N*-methyl-2-pyrrolidone (NMP). The monomer concentration in the reaction solution was kept at ~25% by volume to produce high molecular weight polymer [21,22]. After the poly(amic acid) solution became sufficiently viscous, dry NMP was added to reduce the polymer concentration to ~12%. Thermal imidization for 24 h at 200 °C with continuous removal of water by dichlorobenzene (DCB) azeotropy was used to form the polyimide. The resultant solution was cooled to room temperature and precipitated in methanol. The precipitated polymer was then filtered, blended and washed with methanol to remove any residual solvent. The polymer was dried at 70 °C for 12 h under vacuum and for 24 h at 150 °C under vacuum. The chemical structures and physical properties of the 6FDA-based polyimides synthesized are shown in Fig. 1 and Table 1, respectively. The glass transition temperature (T_g) of each polyimide was measured at a heating rate of 20 °C/min with a Perkin–Elmer DSC-7. The T_g was defined as the onset of the change in the heat capacity during the second heating from room temperature to 400 °C. Note that there are small T_g differences between polyimide samples whether synthesized

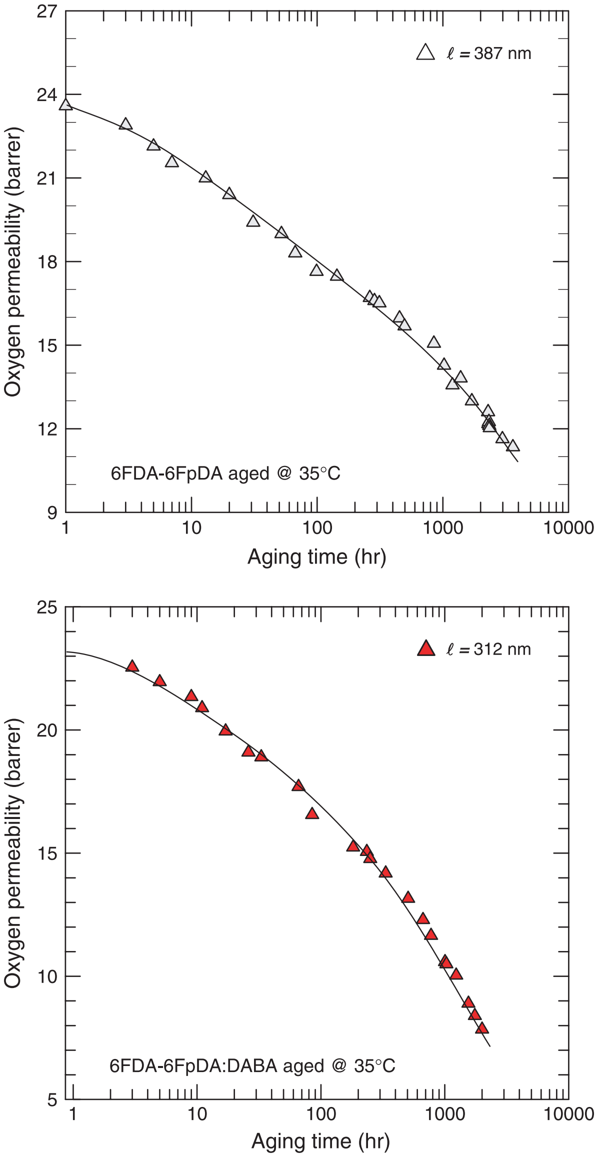

Fig. 3. Oxygen permeability of 6FDA-6FpDA and 6FDA-6FpDA:DABA 2:1 polyimide films as a function of aging time.

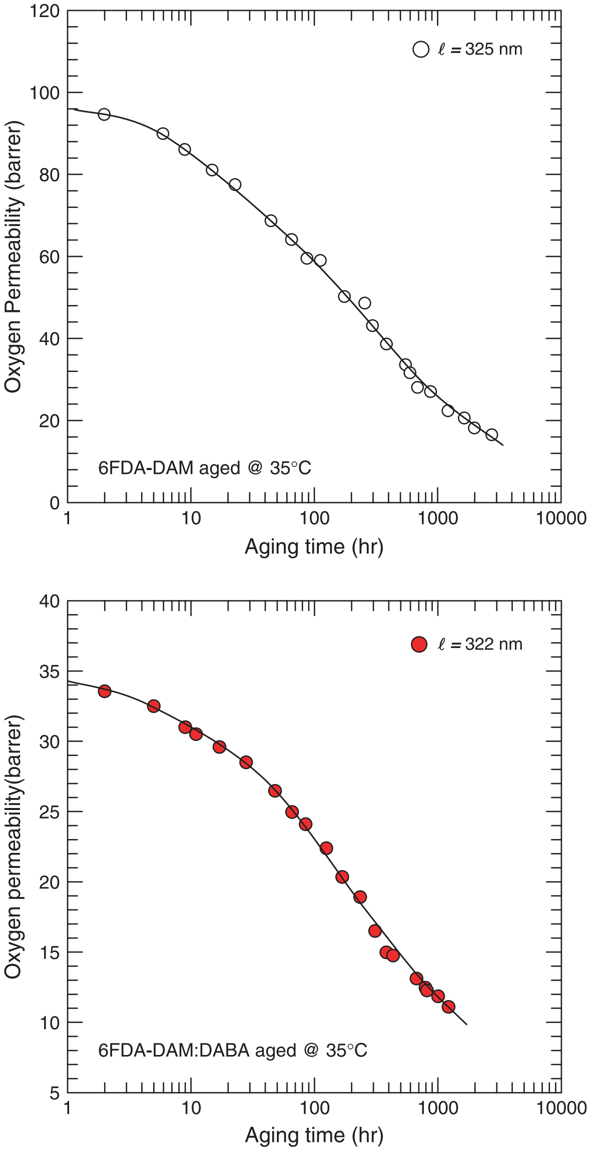

Fig. 4. Oxygen permeability of 6FDA-DAM and 6FDA-DAM:DABA 2:1 polyimide films as a function of aging time.

chemical imidization versus thermal imidization and differences due to molecular weight [3,6,10]. The molecular weights of the synthesized 6FDA-based polyimides were determined by GPC using polystyrene standards. The density was measured by a density gradient column [23,24] while the fractional free volume, FFV, in the bulk state was calculated from

$$\mathrm{FFV} = \frac{V - V_\mathrm{o}}{V} \tag{1}$$

where V = the measured specific volume (inverse of density) and V_o is the 'occupied' volume computed as suggested by Bondi [25], i.e. $V_\mathrm{o} = 1.3\ V_\mathrm{w}$, where V_w in the van der Waals volume of the polymer per unit mass. The latter was calculated using group contribution methods described by Van Krevelen [26]. Note that the density values for polyimides synthesized in this study are somewhat different from those reported in other works [27].

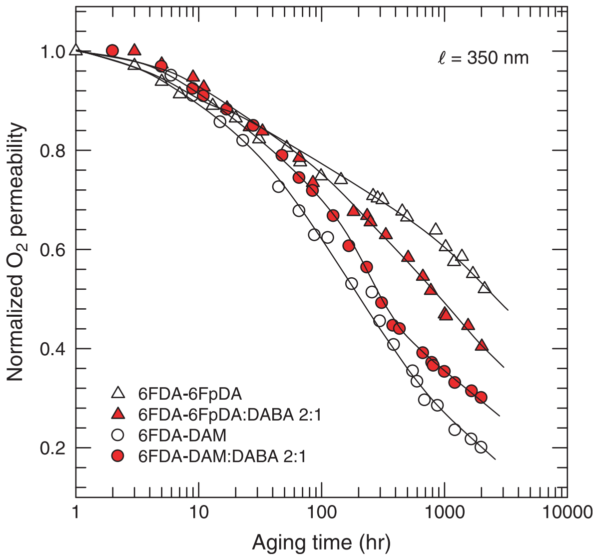

Fig. 5. Normalized oxygen permeability coefficient of 6FDA-based polyimide films as a function of aging time.

2.2. Film formation

All of the techniques briefly summarized below have been described more extensively in prior papers by Huang and Paul [15,16]. Thin polyimide films were spin coated from 2-methyl-4-pentanone (Aldrich, 99+%) solutions of 6FDA-6FpDA based copolyimides and cyclohexanone (Aldrich, 99+%) solutions for 6FDA-DAM based copolyimides at 2500 rpm for about 40 s onto clean silicon wafers by using a photoresist spinner (Headway Research, Inc.). The thickness was controlled by the concentration of the solution, which was filtered using a 0.1–0.45 μm Teflon filter (Whatman Co.). A variable angle spectroscopic ellipsometer (J. A. Woollam Co., Inc.) was used to characterize the thickness of the thin polymer films and to measure refractive index as a function of aging time. The film samples were scanned in the depolarization mode at an incident angle of 70° over the spectral range of wavelengths of the incident light, i.e. from 400 to 800 nm. The accuracy of measurement is within 1 Å for thickness; more details about these measurement, film casting, handling and stress relaxation following are given elsewhere [15,16].

Prior thermal history and molecular orientation will affect the physical aging process [16–18]. To remove such effects and to give a precise beginning to the aging process, each sample was heated while in a N_2 purge for 50 min at a temperature about 15 °C above the T_g. Fig. 2 shows the thickness, measured at 15 °C above T_g, of four different copolyimide films with or without carboxyl acid groups, plotted versus heating time. The increase in thickness is initially rapid and is visually indicated by the color changes of the film but appears to approach a limit after about 15 min. This thickness change on heating above T_g is believed to be driven by relaxation of molecular chain

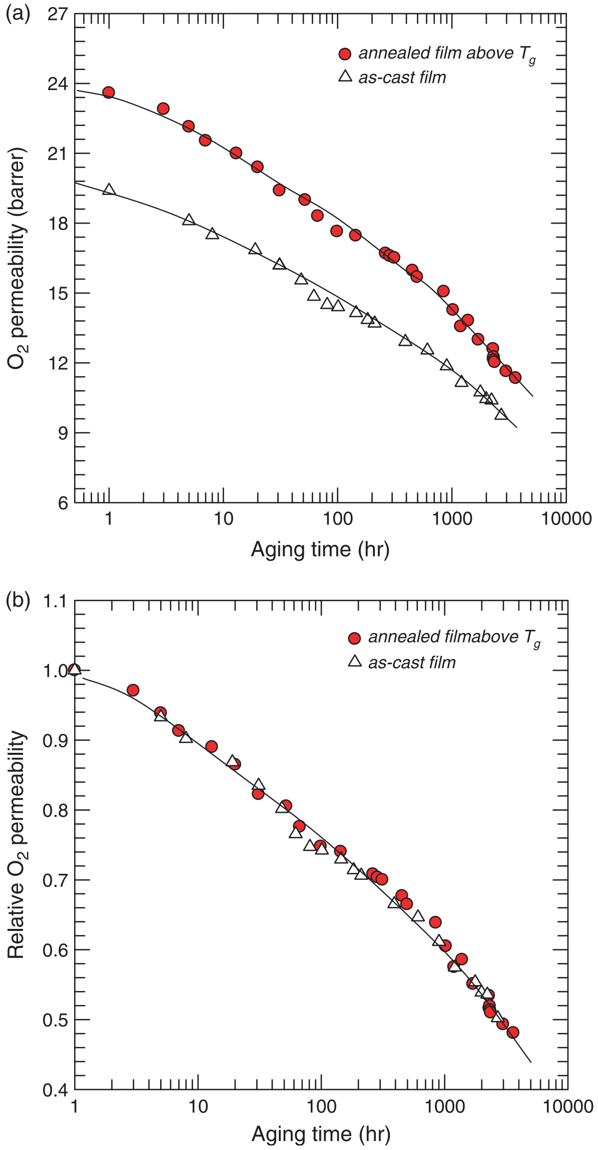

Fig. 6. Comparison of aging response for 6FDA-6FpDA polyimide films as-cast and after quenching from above T_g in terms of (a) absolute oxygen permeability (b) relative oxygen permeability.

orientation imparted during spin coating with possible contributions of surface tension [15,16].

Table 2 shows pure gas permeability coefficients for thick films (thickness ~300 μm) measured at 35 °C and 2 atm for He, N_2, and O_2 using the standard permeation techniques employed in this laboratory [10,15,28]. Addition of DABA units to either system decreases the permeability to all gases and increases the permselectivity. There is, broadly speaking, a trade-off between permeability and selectivity among these materials [29]. The permeability changes for thin films made from each of these polyimides with aging time were obtained using two samples; one was used to measure the permeability of low solubility gases in the sequence N_2, O_2, He, without CO_2 while the other was used to track these same gases but including CO_2. Note that data for films exposed to CO_2 are not included in this paper, because CO_2 has a relatively high solubility in glassy polymers and can alter their physical state including their permeability response. We wanted to avoid the complications of this conditioning effect on the gas permeability changes with aging time in this preliminary study. The effects of CO_2 will be considered in more detail in a subsequent paper.

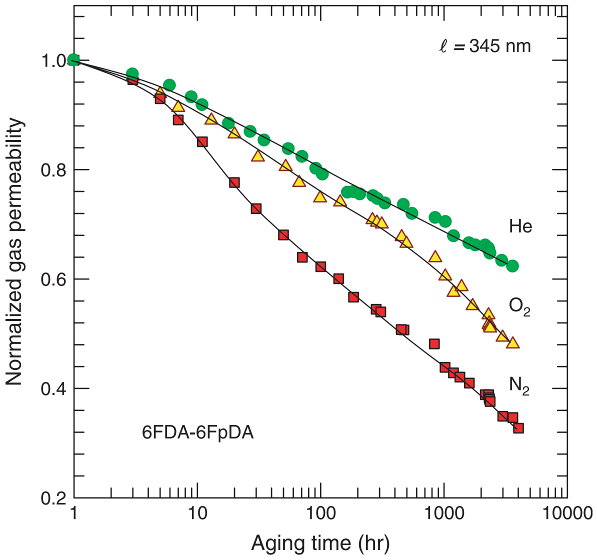

Fig. 7. Normalized gas permeability coefficients for He, O_2 and N_2 of a 6FDA-6FpDA polyimide film (l = 345 nm) as a function of aging time.

3. Results

3.1. Time dependent permeation reduction

The gas permeability and selectivity of polyimides depend on numerous factors such as the molecular structure, temperature, molecular weight, etc. [2,9,16,30,31]. As nearly as possible, all of these factors except polymer structure were held constant in this study in order to focus just on the effect of chemical structure on the gas permeability performance versus aging time.

Figs. 3 and 4 show the evolution of the oxygen permeability coefficients for thin polyimide films based on 6FDA-6FpDA and 6FDA-DAM with and without the DABA component versus aging time, on a logarithmic scale, respectively. Each film has a thickness of approximately 350 nm. In every case, the oxygen, nitrogen and helium permeability coefficients continuously decrease with aging time as reported previously for other glassy polymers in thin films form [15–17]. At the beginning of the aging process, the gas permeability coefficients of the thin films are higher than the so-called bulk values, but after a few 100 h of aging the thin film values fall below the bulk values shown in Table 2. Similar observations were reported for other glassy polymer types by Huang and Paul [15,16]. It appears that quenching these thin films from above T_g leads to a higher free volume state than typically seen in bulk. However, this excess free volume is quickly lost during aging. It is interesting to note that 6FDA-DAM polyimides seem to show a slight inflection in the

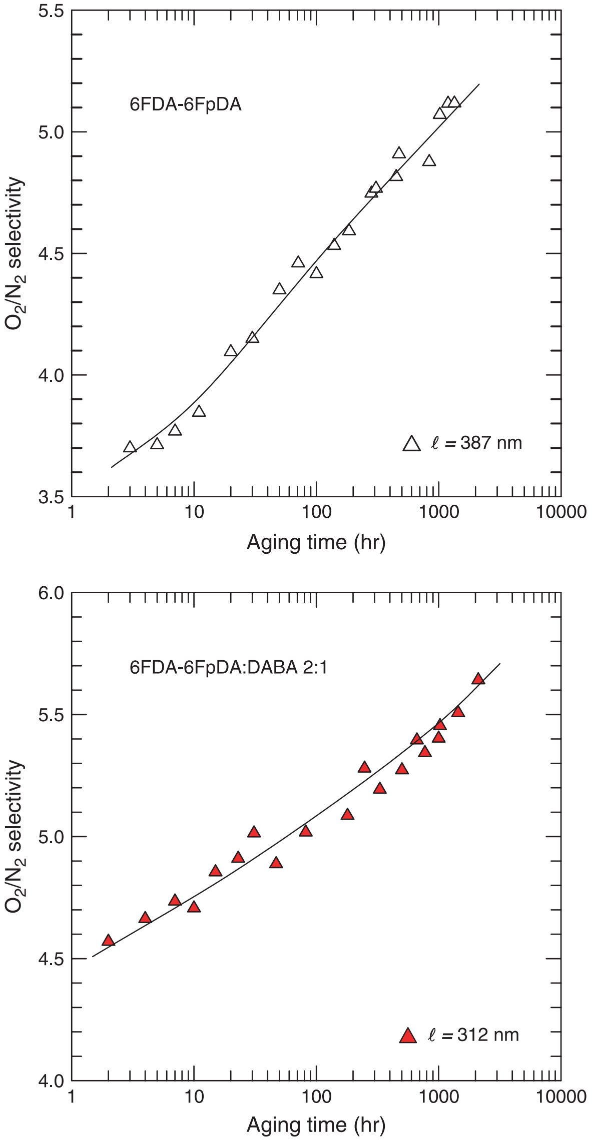

Fig. 8. O_2/N_2 selectivity of 6FDA-6FpDA and 6FDA-6FpDA:DABA 2:1 polyimide films as a function of aging time.

permeability versus log time plot as reported by McCaig and Paul for a different glassy polymer [18,19]; whereas, Huang and Paul [15,16] did not see such inflections in their studies. It is beyond the scope of this paper to explore any potential significance of such inflections in these plots.

Since, the absolute permeability coefficients vary considerably for different polymer structures and gas types, it is useful to have a rational way for comparing rates of aging. We will use a normalized permeability coefficient as proposed by Huang and Paul for this purpose [16]. This relative permeability is computed by dividing the absolute permeability at any aging time by the value at about 1 h of aging. This approach is used to examine the effect of the addition of the DABA moiety to the 6FDA-6FpdA and 6FDA-DAM polyimides. Fig. 5 show the data from Figs. 3 and 4 plotted in this way. On this basis, it is clear that 6FDA-DAM ages more rapidly, i.e. a larger relative oxygen permeability reduction at a given aging time, than 6FDA-6FpDA at a nominal thickness of ∼350 nm. Interestingly, addition of DABA has opposite effects on the agings rates for these two types of polyimides. As seen in Fig. 5, the presence of DABA seems to retard the aging rate of 6FDA-DAM while accelerating the aging rate for 6FDA-6FpDA.

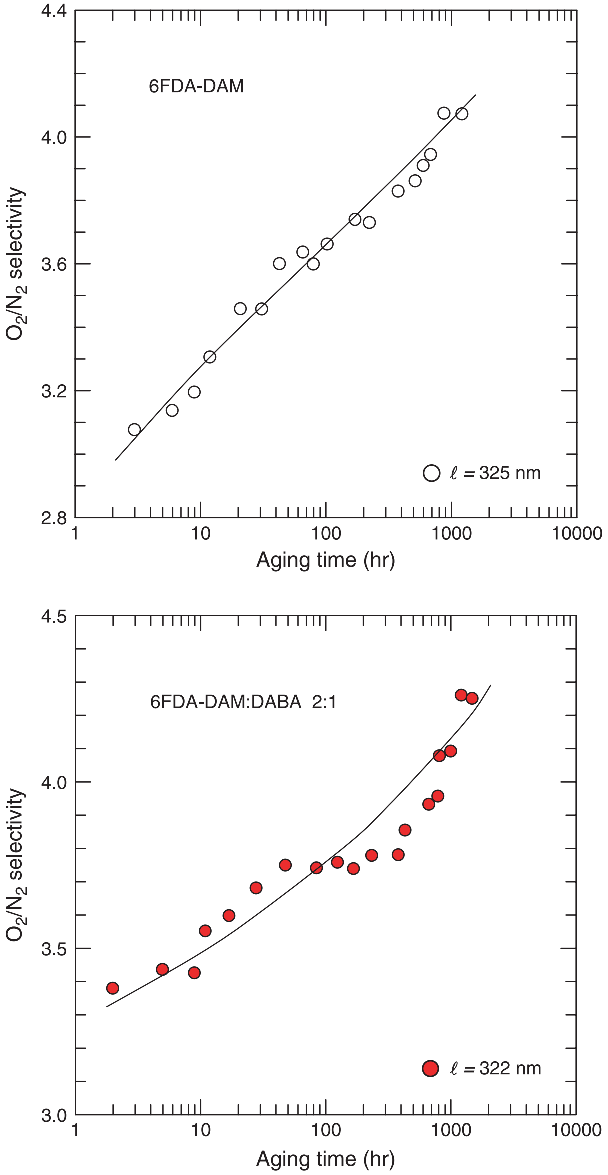

Fig. 9. O_2/N_2 selectivity of 6FDA-DAM and 6FDA-DAM:DABA 2:1 polyimide films as a function of aging time.

In the above, we have used films that were heated above T_g to give each film a common thermal history and to have a well-defined starting time for aging. Clearly, one expects the absolute permeability will depend on this prior history at least to some extent. Since practical membranes have a complex history, it is useful to know if initial history has a strong effect on the rate of aging. An in-depth analysis of prior history is the beyond the scope of this work; however, we do report here one experiment to illustrate this issue. Fig. 6(a) compares the oxygen permeability versus aging time for a film directly cast from solution without subsequent heating above T_g with a

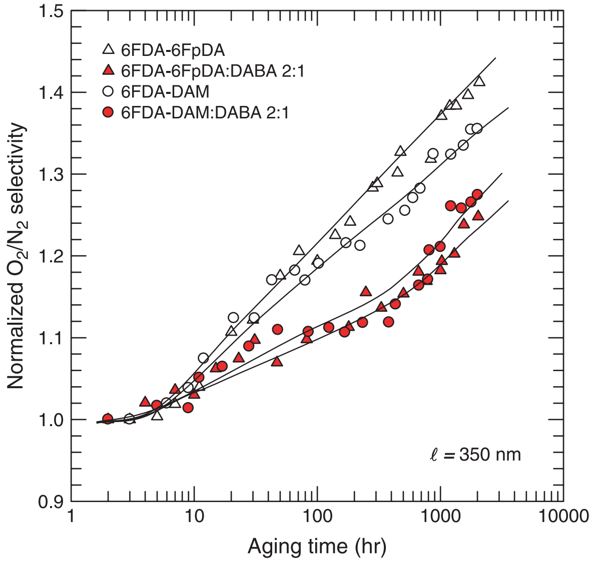

Fig. 10. Normalized O_2/N_2 selectivity of 6FDA-based polyimide films as a function of aging time.

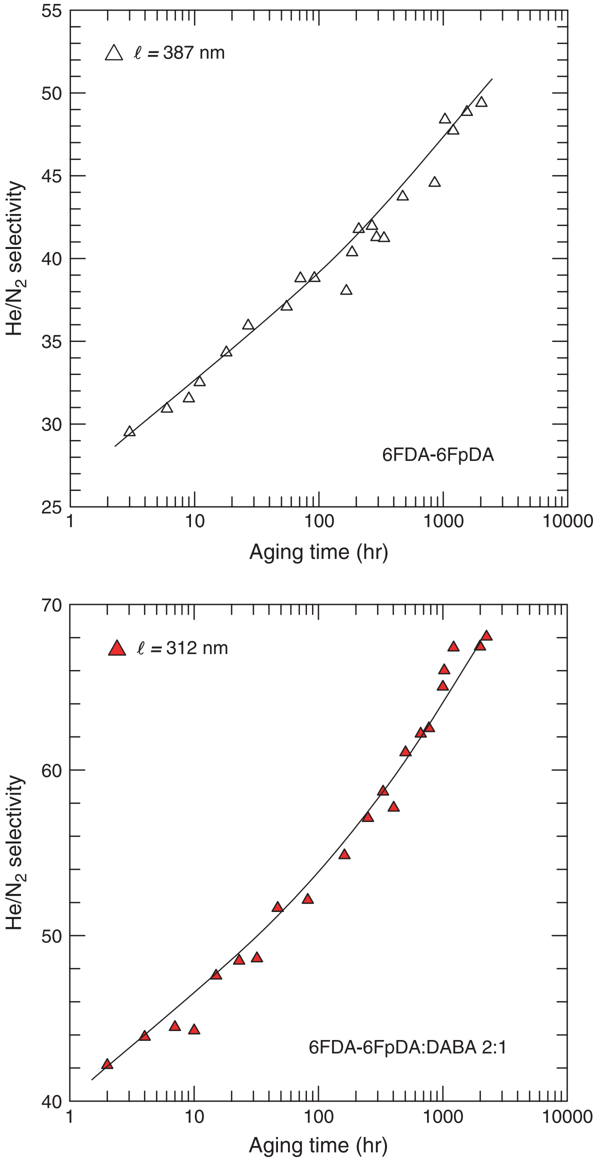

Fig. 11. He/N_2 selectivity of 6FDA-6FpDA and 6FDA-6FpDA:DABA 2:1 polyimide films as a function of aging time.

comparable film that was heated above T_g. The quenched film consistently has a greater permeability than the as-cast film. Fig. 6(b) shows that in terms of the relative oxygen permeability coefficient, i.e. normalized by the permeability at 1 h, the two films exhibit a remarkably similar aging pattern up to 2000 h, which suggests that the aging process is similar regardless of how the film is prepared. More detailed studies along these lines will be reported in the future.

Fig. 7 presents normalized permeability coefficients for He, O_2, and N_2 as a function of aging time for a 6FDA-6FpDA polyimide film. The effective molecular diameter of the diffusing gas molecule has a strong effect on its diffusion coefficient in the polymer, and it is not surprising to see the aging response to depend on penetrant size as well [32,33]. The largest gas molecule in this series (N_2) shows the largest permeability coefficient decrease with aging while the smallest gas molecule (He) shows the least decline in relative permeability. The relative aging response is $N_2 > O_2 > He$, i.e. the same order as the gas molecule size. Huang and Paul reported a similar ranking for polysulfone thin films [16].

3.2. Effect of aging on selectivity

Since, the rate of permeability reduction for a given film is gas specific, the selectivity of permeation of one gas relative to another also changes with aging time. The O_2/N_2 selectivities of the four polyimides are shown as a function of aging time in Figs. 8 and 9. The selectivities start from values lower than observed in bulk (Table 2) but eventually surpass the bulk values for each polyimide type as aging progresses. In each case, the selectivity continues to show a steady increase without any evidence of stabilizing similar to the reports by Huang and Paul [16]. The 6FDA-DAM:DABA polyimide film (Fig. 9) seems to show a slight inflection in the selectivity versus aging time but this may be within the range of the experimental error. Fig. 10 shows the selectivities for the four polyimides normalized by the selectivity observed at about an hour of aging so that the relative changes can be compared. At an aging time of 2000 h, both the 6FDA-6FpDA and 6FDA-DAM base polyimide films show 35–40% higher selectivity than their initial values while the corresponding materials containing DABA exhibit smaller increases. Interestingly, the O_2/N_2 selectivity for thin films of 6FDA-6FpDA with and without DABA eventually exceeded 5.0, which is competitive with commercially available gas separation membranes [29].

Figs. 11 and 12 show the He/N_2 selectivity for the four 6FDA-based polyimides as a function of aging time. As shown for O_2/N_2, the He/N_2 selectivity of each polyimide film continually increases with no significant sign of stabilization observed. Fig. 13 shows the He/N_2 selectivity change normalized by the value at about 1 h of aging for each of the four 6FDA-based polyimide films. The selectivity increase is

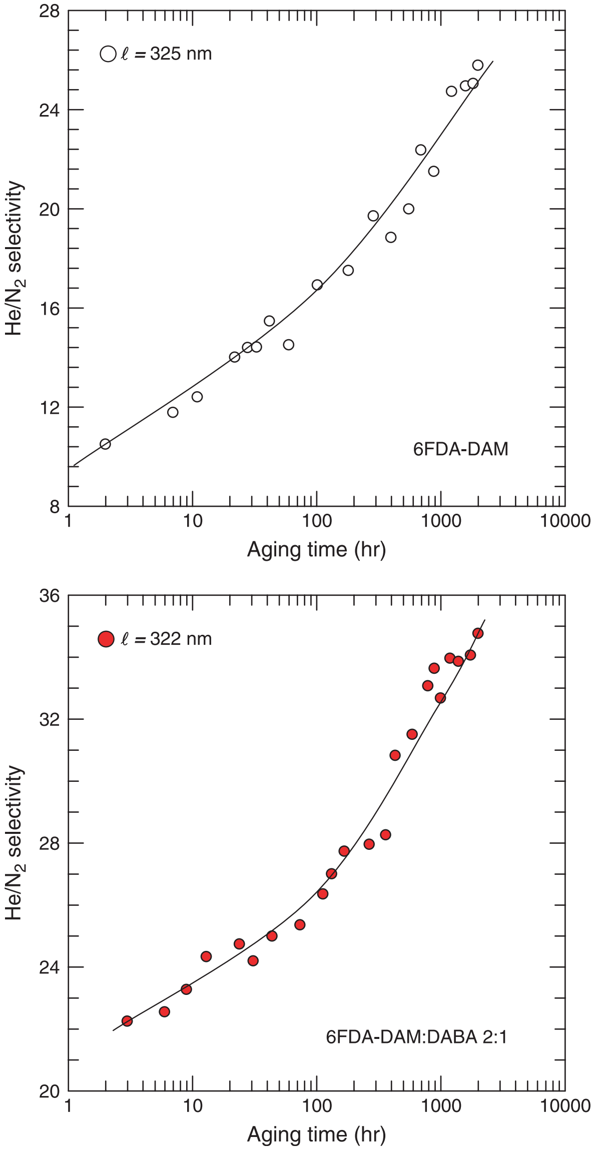

Fig. 12. He/N$_2$ selectivity of 6FDA-DAM and 6FDA-DAM:DABA 2:1 polyimide films as a function of aging time.

even more significant for this gas pair than for the O$_2$/N$_2$ pair due to the larger difference in molecular size. Interestingly, the 6FDA-DAM material shows a much larger change in He/N$_2$ selectivity than any of the other materials; this is contrary to the O$_2$/N$_2$ result. Addition of DABA reduces the change in He/N$_2$ selectivity with aging for both types of polyimides.

Fig. 14 shows a trade-off plot of selectivity versus permeability for the O$_2$/N$_2$ pair including data points for the 6FDA materials in the bulk state and for their thin films after aging for 2000 h along with corresponding data for three other materials, viz. polysulfone (PSF), the commercial polyimide Matrimid, and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). The Robeson upper bound line is shown for Ref. [29]. Clearly, there is a trade-off between permeability and selectivity among these materials. Each of the non-aged bulk films has comparatively lower O$_2$/N$_2$ selectivity and higher oxygen permeability than aged thin films; physical aging shifts the points more and less parallel to the upper bound curve.

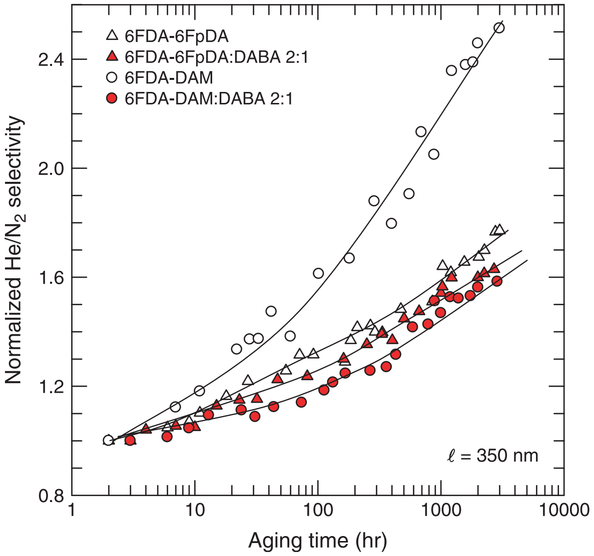

Fig. 13. Normalized He/N$_2$ selectivity coefficient of 6FDA-based polyimide films as a function of aging time.

4. Discussion

Several factors, no doubt, contribute to the physical aging response of thin films as revealed by permeability and selectivity change. However, as a first approximation we propose that fractional free volume, FFV, is the main factor affecting the aging response. We will attempt to interpret the facts described above in terms of this point of view. However, any analysis of this hypothesis is clearly compromised first by

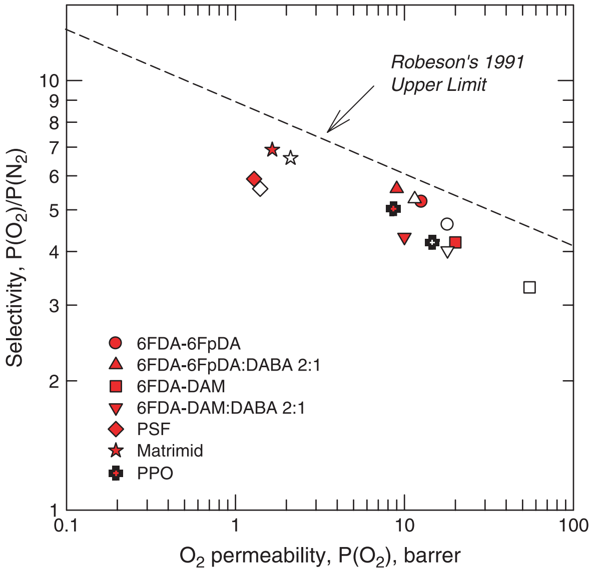

Fig. 14. Trade-off relationship between O$_2$/N$_2$ selectivity and O$_2$ permeability for the materials in this study with other materials in the literature. The open symbols represent bulk thick films and solid symbols represent thin films ($l \approx 350$ nm) after aging for 2000 h at 35 °C.

defining what one means by free volume as there are numerous ways of doing so and second by the approximations inherent in the estimations used for any given definition. For the present purpose, we will restrict the discussion to FFV in the bulk state where the occupied volume in Eq. (1) is calculated from a group contribution method that involves some level of approximations associated with how the groups are defined and constructed. The value of FFV given in Table 1 will be used for this purpose realizing that these values may not uniquely capture the full picture for these structures. Indeed, one can see that the bulk permeability data in Table 2 do not uniquely correlate with the FFV values in Table 1 in the ideal way one might expect, i.e.

$$P = A\mathrm{e}^{-B/\mathrm{FFV}} \tag{2}$$

where A and B are expected to be constants for a given gas.

The polyimide 6FDA-DAM has a higher FFV and gas permeability than does 6FDA-6FpDA. As seen in Fig. 5, the relative aging rate of 6FDA-DAM is faster than that for 6FDA-6FpDA in accord with our hypothesis. Addition of DABA units to 6FDA-DAM reduces its FFV while the opposite is true for 6FDA-6FpDA. Indeed, the relative aging rate of 6FDA-DAM is slowed by addition of DABA while the effect of adding DABA is the opposite for 6FDA-6FpDA. Thus, the data in Fig. 5 are all consistent with our hypothesis that higher FFV leads to faster aging rate, at least quantitatively, since the order of relative aging rates in the same as the order of the FFV values in Table 1. The relative rate of change in selectivity shown in Figs. 10 and 13 cannot be so simply explained. However, it should be recalled that selectivity changes involve the difference in responses of two different gases in a given polymer and, as a result, such correlations may be too simplistic to explain the observations.

A pivotal question, of course, is why thin films physically age at rates orders of magnitude more rapidly than the same glassy polymers would be expected to show, at similar temperatures, in bulk. A plausible explanation is that free volume can diffuse from the interior to the surface where it can escape much as vacancies and defects are known to do in crystals. On this basis thin films would age more rapidly than thick ones. This idea has been discussed more extensively in prior papers and even mathematically modeled [15–19]; however, firm proof of this mechanism has not been established. Experimental approaches to deal with this key issue are being explored.

5. Conclusion

The changes in the gas permeability of He, N_2, and O_2 through thin films (~350 nm) of 6FDA-based polyimides with and without DABA units in the chain were monitored as a function of aging time at 35 °C. For each polymer structure, physical aging leads to a decrease in the permeability of these thin films accompanied by a significant increase in selectivity. This aging response is attributed to the rapid densification of the thin films, relative to the bulk polymer, as will be shown by refractive index changes in Part 2 of this series; this loss of fractional free volume is much more rapid than thick films perhaps due to diffusion of free volume to the film surface as proposed earlier. Incorporation of carboxyl acid groups into the polyimide structure via DABA units accelerated the relative aging rate for the 6FDA-6FpDA polyimide while reducing the rate for the 6FDA-DAM polyimide. An increase in O_2/N_2 and He/N_2 selectivities was observed with aging for each type of polyimide in thin film form. The decrease in permeability and the increase in selectivity showed no sign of stabilization over the 2000 h of these observations. The relative decline in permeability with physical aging time is greater the larger the gas molecule diameter. Therefore, the increase in selectivity with time is greater when the gas pair has a larger difference in molecular size. It appears that the level of fractional free volume, or FFV, as defined here is a primary factor in determining the relative aging rate. This hypothesis will be further tested as we examine more polymer structures in future work.

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