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Polymer 47 (2006) 3104–3111

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

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Received 22 December 2005; received in revised form 20 February 2006; accepted 21 February 2006
Available online 23 March 2006

Abstract

The change in refractive index with time for thin films (∼350 nm) formed from glassy 6FDA-based polyimides was monitored by ellipsometry to quantitatively track the physical aging process. The refractive index increased linearly, attributed to the densification of the glassy polyimide, with respect to aging time, on a logarithmic scale; this result is consistent with the decrease in gas permeability during physical aging reported in part I of this series. An excellent correlation was formed between the volumetric aging rate r, computed from the refractive index change by the Lorentz–Lorenz equation, and the permeability reduction rate, $-(\partial \log P/\partial \log t)$; this relationship depends on the type of gas but appears to be the same for all polymer structures examined. The change in fractional free volume was examined from the refractive index data using parameters determined by group contribution methods. The free volume versus aging time results are well-described by the self-retarding relaxation model of Struik; however, this model does not explain the strong effect of thickness on aging rate. The change in free volume correlates well with the change in gas permeability of these thin films.

Keywords: Physical aging; Refractive index; Volumetric relaxation

1. Introduction

The first paper in this series showed that the gas permeability of thin, glassy 6FDA-based polyimide membranes (see part I in this series [1] for the chemical structure) decreases significantly with aging time while selectivity increases moderately; these changes in permeation behavior are strongly influenced by the molecular structure of the polyimide. This reduction in gas permeability with time is due to physical aging or volume relaxation of the glassy polymer film; the rate of aging for the thin films studied ($\ell \sim 350$ nm) is orders of magnitude faster than expected for bulk glassy polymers as demonstrated in previous studies [1–7]. Such changes in performance with time have considerable relevance for membrane separation systems and needs to be better understood. This paper complements the prior paper by tracking the changes in optical properties with aging as means of quantifying the densification of these polyimides.

Various relationships have been proposed to relate the refractive index of materials, $\bar{n}$, to their physical and chemical structure. One very useful relationship for current purposes is the Lorentz–Lorenz equation [6,8,9]

$$L = \frac{\bar{n}^2 - 1}{\bar{n}^2 + 2} = \frac{\rho N_{\mathrm{av}} \sum n_i \bar{\alpha}_i}{3 M_0 \varepsilon_0} = \rho C \tag{1}$$

where N_{av} is Avogadro's number, M_0 is the molecular weight of the polymer repeat unit, ε_0 is the permittivity of free space constant, $\bar{\alpha}_i$ is the average polarizability of the ith type chemical bond and n_i is the number of such bonds per repeat unit. These parameters can be lumped into one material constant C that relates the Lorentz–Lorenz parameter L to the polymer density ρ. The refractive index depends on the wavelength via the polarizability; however, the electronic polarizability can be assumed independent of temperature and density due to its sole dependency on the distribution of the electronic cloud [8,10]. Therefore, for a given polymer structure, there is a unique relation between refractive index and density; thus, tracking refractive index during physical aging effectively provides information on the densification or loss of free volume by the polymer film.

Recently, Huang and Paul [3,4,6,11] reported that ellipsometry can be used to monitor the refractive index change

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doi:10.1016/j.polymer.2006.02.079

during the physical aging of thin films, $\ell < 1$ μm, using a single sample over long periods of time with high sensitivity but without any damage to the film. They showed that the refractive indices of thin glassy films increased more or less linearly with logarithmic time during the densification process due to physical aging. The reduction in gas permeability due to the physical aging is related to the change in refractive index via free volume relationships.

Pfromm and co-workers [2,12,13] suggested that glassy polymers with high free volume undergo a rapid permeability reduction with time due to physical aging. Indeed, it was found in the first paper in this series that the relative rate of physical aging, as judged by permeability decline with time, among the 6FDA-based polyimides studied, seems to correlate with estimates of fractional free volume as suggested. McCaig and Paul suggested that the volume relaxation associated with physical aging of polymer glasses proceeds by two simultaneous mechanisms [5,9]. One mechanism involves the progressive reduction of the distance between chain segments, or the so-called 'lattice contraction' process, whose rate can be argued to be independent of thickness. The lattice contraction process can be modeled using self-retarding relaxation kinetic expressions such as those given by Kovacs et al. [14–17] and by Struik [18]. The other proposed mechanism involves diffusion of free volume to the membrane surface where it escapes. It is the latter process that gives rise to the thickness dependence of aging rate, and it can be modeled by the Fickian formalism used for describing diffusion of molecular species in a polymer matrix [19,20]. While the concept of diffusion of free volume is appealing since it gives a rational way to explain the extremely rapid aging of thin glassy films compared to the rate expected for a bulk sample, this idea must be regarded as a hypothesis since at this time there is no direct evidence for a spatial distribution of density as would be expected if free volume were escaping to the surface driven by a gradient in free volume.

In this paper, ellipsometry is used to track the changes in refractive index for four thin 6FDA-based polyimide films described in the first paper [1] as a function of aging time. The densification of these thin films is quantified using the Lorentz–Lorenz equation. The Struik lattice contraction model of physical aging is used to correlate fractional free volume with aging time for thin films having different chemical structures but the same thickness; this model does not address the thickness dependence. These volumetric changes for polyimides with and without DABA units in the chain are used to gain insight about the corresponding changes in gas permeability during aging via fractional free volume relationships and the dependence on chemical structure. The calculation of density from refractive index and free volume from density for these materials requires the use of group contribution methods for estimating various properties.

2. Experimental methods

2.1. Materials

The same four glassy 6FDA-based polyimides described in the previous paper were used in this work [1]. Each is based on 2,2-bis(3,4-carboxyphenyl) hexafluoropropane dianhydride, which is reacted with either (4,4′-hexafluoroisopropylidene) diamine to form 6FDA-6FpDA or diaminomesitylene to form 6FDA-DAM polyimides with and without 3,5-diaminobenzoic acid (DABA) units; where present, the DABA units are in a 2:1 ratio with the other diamine. The detailed procedure of synthesis and several physical properties have been described previously. Table 1 lists bulk values for their density, ρ, measured for thick films (∼20 μm) using a density gradient column. The refractive index values, $\bar{n}$, listed for 'bulk' 6FDA-based polyimides was estimated by the group contribution of molar refraction described by Van Krevelen [21] because there are no data in the literature for these materials as far as we know. The material constant C was computed from Eq. (1) using the ρ and $\bar{n}$ values in Table 1. The bulk fractional free volume was estimated from the bulk density. The van der Waals volume, V_w, was computed by van Krevelen's group contribution method as described in the previous paper [1]. The occupied volume, V_0, was computed from $V_0 = 1.3V_w$ as proposed by Bondi. The bulk fractional free volume, FFV, was computed from $\text{FFV} = (V - V_0)/V$ where V is the reciprocal of the measured ρ. The equilibrium specific volume, V_e, at 35 °C was estimated from the relationship $V_e = 1.466V_w$ developed by Huang and Paul [22] using volumetric data extrapolated from above T_g for various polymers with aromatic backbones since volume versus temperature data are not available for the current polymers as far as we know. The values of V_i are estimates of the initial specific volumes right after quenching from above T_g that were obtained by fitting the experimental observations to the Struik model as described later [6,22].

2.2. Film preparation and ellipsometry measurement

The thin films were prepared by spin coating and their thicknesses were determined using ellipsometry [23–26]. The thin films were removed from the silicon wafer surface using de-ionized water and installed on a sample holder that allows

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

Polymer	ρ (g/cm^3)	Refractive index	V_w (cm^3/g)	V_0 (cm^3/g)	V_i (cm^3/g)	V_e (cm^3/g)	FFV	C
6FDA-6FpDA	1.504	1.538	0.422	0.548	0.671	0.618	0.175	0.208
6FDA-6FpDA:DABA 2:1	1.482	1.549	0.424	0.551	0.682	0.621	0.182	0.215
6FDA-DAM	1.334	1.544	0.467	0.602	0.804	0.678	0.190	0.237
6FDA-DAM:DABA 2:1	1.394	1.553	0.451	0.586	0.716	0.661	0.183	0.230

the film to be in a free standing state while being heated for 50 min at a temperature about 15 °C above the T_g in a nitrogen purged furnace to remove the prior thermal history according to the protocol reported previously [1,23]. The sample was then gently placed onto the silicon wafer avoiding any scratches or trapped bubbles under the film to reduce the errors in measuring the refractive index. Finally, the sample on the silicon wafer was placed in a vacuum storage chamber at 35 °C for aging and was periodically removed for measurement of refractive index by ellipsometry at 25 °C.

The ellipsometric technique for measuring the refractive index change of thin glassy polymer films described by Huang and Paul [6,23] was used here for the thin 6FDA-based polyimide films. The technique employs a variable angle spectroscope ellipsometer (Woollam Co.) with an accuracy of 10^{-4} for refractive index measurement. To minimize measurement errors, the sample was placed in exactly the same position for every measurement. The measurement was conducted in the spectral range from 400 to 800 nm while the refractive index is determined at the sodium *D* wave length ($\lambda = 589.3$ nm) at room temperature for each polyimide films; more details are given elsewhere [23].

3. Result and discussion

3.1. Ellipsometric observations

Each sample was prepared for ellipsometry characterization in exactly the same way as for the gas permeability measurements described in the previous paper [1]. However, the thin films for ellipsometry were left on the silicon wafer during aging rather than remaining in a free standing state since repeated removal from and re-application to the wafer increases the probability of damage. It should be noted that these films were not firmly bonded to the wafer as they could be easily removed. Any effect of the wafer substrate on the aging of the response of the polymer film is believed to be rather minimal as discussed previously [23]. The films used for ellipsometry and for permeation differed slightly in thickness because it is not easy to make multiple films of exactly the same thickness; however, the effect of these differences is relatively small and does not materially effect the conclusions reached when comparing aging responses from permeation and ellipsometry.

Figs. 1 and 2 show the evolution of the refractive index 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; this is consistent with the thickness of the samples used for gas permeability measurements [1]. In every case, the refractive indices continuously increase with aging time as reported recently for other glassy polymers in thin film form [23]. In each case, the refractive index seems to be a linear function of aging time when plotted using a logarithmic scale. The quenched thin film shows values of refractive index that are initially lower than the bulk values, but the steady increase with aging time eventually leads to refractive index values larger than the estimated bulk values shown in Table 1.

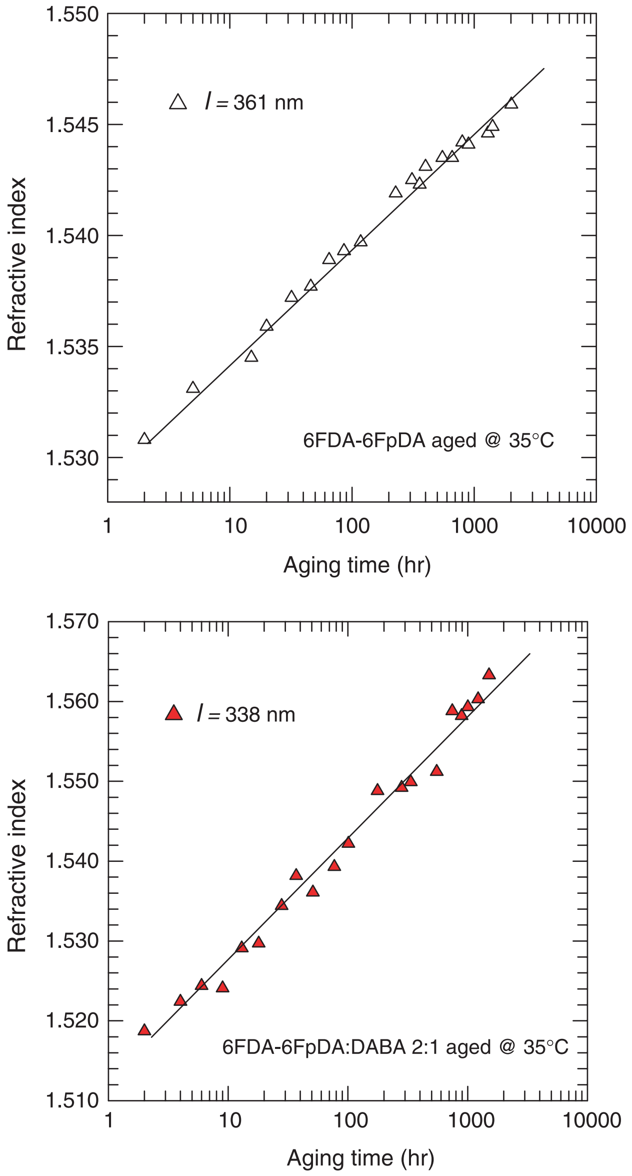

Fig. 1. Refractive index changes for 6FDA-6FpDA-based polyimide films as a function of aging time.

The increase in refractive index provides a direct measure of the densification, as may be seen via Eq. (1), that occurs during aging and mirrors the trends in gas permeability since densification corresponds to a loss of free volume. Fig. 3 shows the normalized density changes of 6FDA-based polyimide films as a function of aging time computed from the refractive index as suggested by Eq. (1)

$$\frac{L(t)}{L(1\ \mathrm{h})} = \frac{\rho(t)}{\rho(1\ \mathrm{h})} \tag{2}$$

where the numerator represents values at any aging time *t* while the denominator corresponds to values at about 1 h of aging. Note that this representation does not require knowledge of the

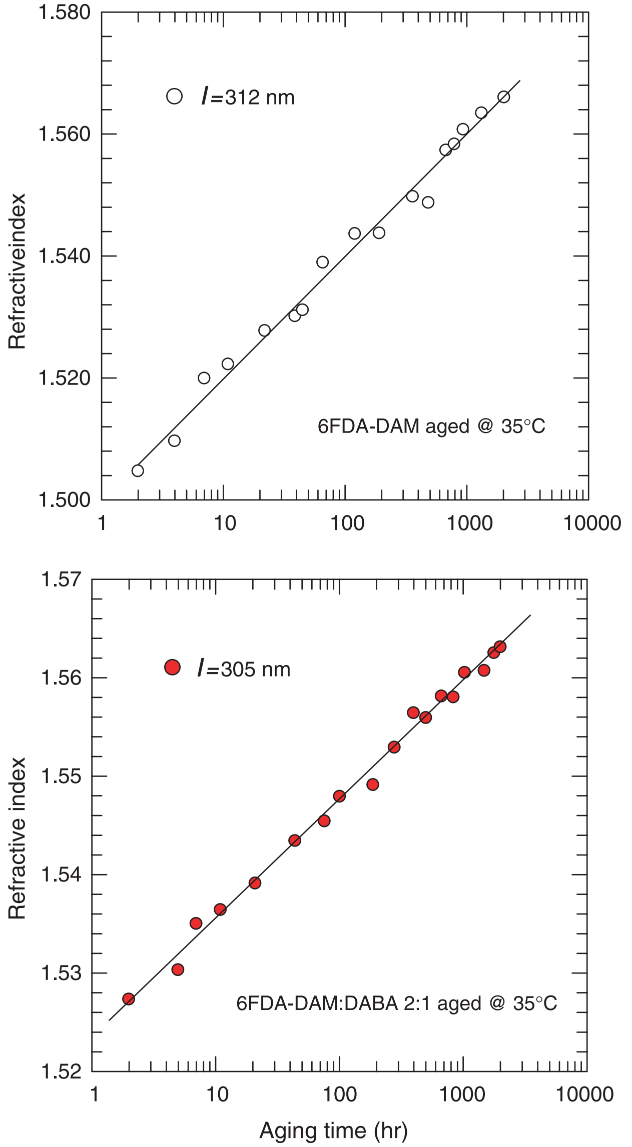

Fig. 2. Refractive index changes for 6FDA-DAM-based polyimide films as a function of aging time.

parameter *C*. Clearly, the rate of increase in density for 6FDA-DAM is the greatest while 6FDA-6FpDA is the least. The addition of DABA has the opposite effect on the rate of change in density for these two types of polyimides; the rate of increase in density for the 6FDA-DAM:DABA is retarded while that for the 6FDA-6FpDA:DABA is accelerated. These results are consistent with the changes in normalized gas permeability coefficients during aging reported in the previous paper [1] except that the order of increasing rate in density for 6FDA-6FpDA:DABA and that for 6FDA-DAM:DABA are reversed when compared with the order of decreasing gas permeability during aging. The difference in the aging rates, by either method, for the two DABA containing materials is quite small and may lie within the range of experimental errors.

To obtain an indication of the long term aging behavior of 6FDA-based polyimide membranes, we characterized the aging rate in terms of the slope of plots of log *P* vs. log *t* as typically done in the membrane industry [22,23,27]. Generally such plots yield a nearly linear relationship at long aging times. In Fig. 4, it is clear that the approximate linear relationship develops after aging times of 100 h regardless of the polymer structure.

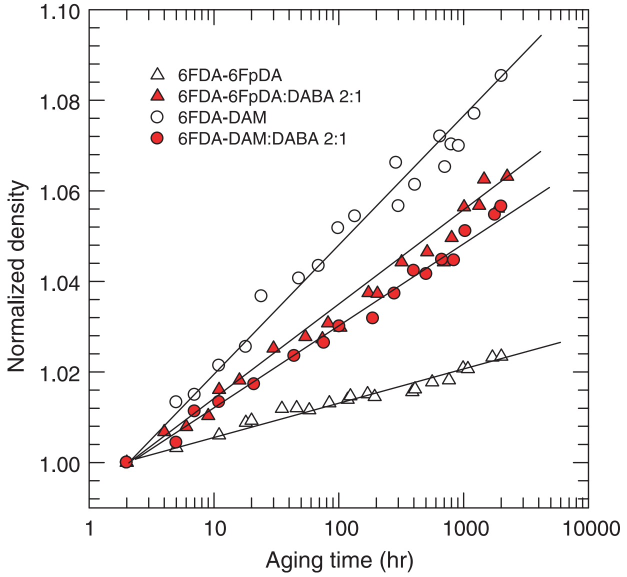

Fig. 3. Normalized density changes of 6FDA-based polyimide films as a function of aging time.

The refractive index data can be used to define a volumetric aging rate, *r*, using the Lorentz–Lorenz equation, as follows [6,23]

$$r = -\frac{1}{V}\left[\frac{\partial V}{\partial \ln t}\right]_{PT} = \left[\frac{\partial \ln \rho}{\partial \ln t}\right]_{PT} = \left[\frac{\partial \log L}{\partial \log t}\right]_{PT} \tag{3}$$

Plots of log *L* vs. log *t* are quite linear over the time range of aging employed here. It is of interest to know if there is a

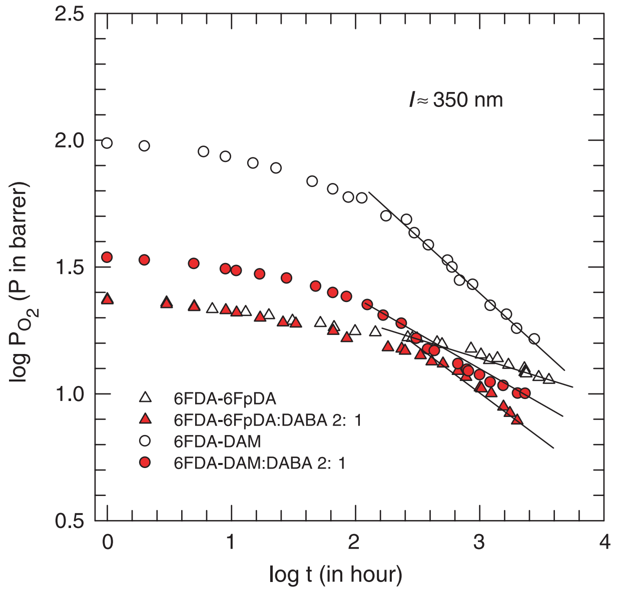

Fig. 4. Log–log plots of oxygen permeability coefficient versus aging time for 6FDA-based polyimides.

correlation between the volumetric aging rate deduced from the ellipsometry data and the aging rate from gas permeability $-(\partial \log P_{O_s}/\partial \log t)$ calculated from Fig. 4, since both techniques reflect changes in free volume. Fig. 5 compares the oxygen, nitrogen and methane permeability reduction rates vs. the corresponding volumetric relaxation rate for the 6FDA-based polyimides thin films aged at 35 °C with other thin glassy polymer films, viz., polysulfone (PSF), the commercial polyimide Matrimid, and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). Clearly, there is a strong correlation between the two measures of aging rate that is consistent among all these polymers. Note that the multiple points for the latter three polymers from the literature correspond to films of different thickness. Interestingly, the 6FDA-based polyimide thin films show much larger aging rates than the other materials which is consistent with the higher free volume of these polyimides.

3.2. Free volume interpretation

From the refractive index measurements, absolute densities of the 6FDA thin films can be computed provided the parameter *C* in Eq. (1) is known. We have estimated values of *C* for each material from the density measured for thick films, i.e. 'bulk' values, and the bulk refractive indices obtained by a group contribution method. Of course, any error in *C* will translate into a proportional error in ρ; with the latter caveat, the computed values of thin film density versus aging time are shown in Fig. 6. In each case, the density starts from values lower than observed in bulk (Table 1) but eventually goes beyond the bulk value for each polyimide type as aging progresses; this is also consistent with the previous results for refractive index and for gas permeability for the 6FDA-based polyimide films [1] and for other materials [23].

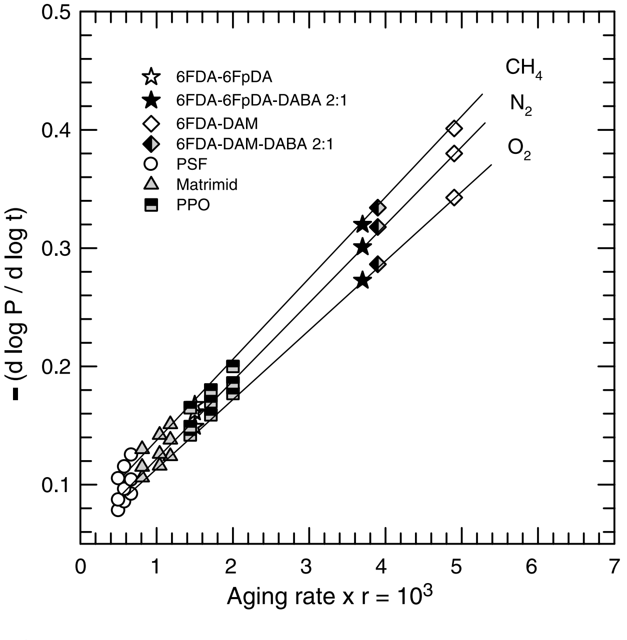

Fig. 5. Correlation between O_2, N_2, and CH_4 permeability reduction rates and their volumetric relaxation rates for 6FDA-based polyimide thin films with thickness less than ~400 nm.

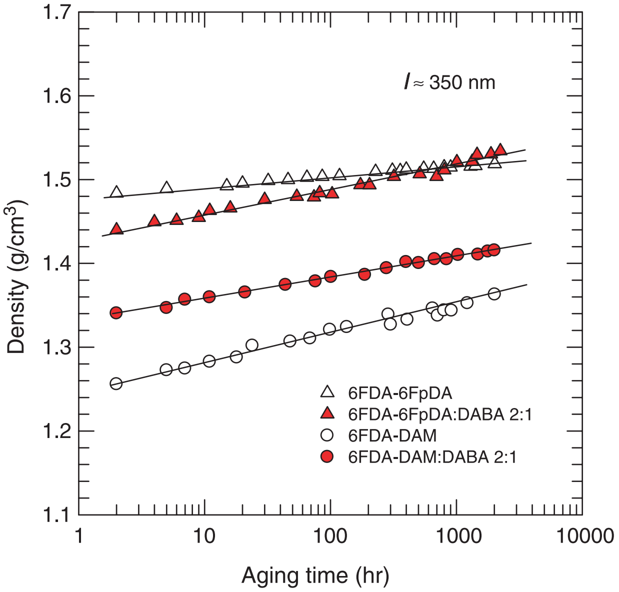

Fig. 6. Estimated density changes of 6FDA-based polyimide films as a function of aging time.

For the interpretation of the aging responses, it is useful to have a rational way for determining the fractional free volume as a function of aging time. The definition of the fractional free volume can be combined with Eq. (1) to obtain the following

$$f = \frac{V - V_0}{V} = 1 - \rho V_0 = 1 - \frac{L}{C} V_0 \tag{4}$$

where *V* is the specific volume at any aging time and V_0 is the occupied volume which can be estimated by Bondi's method as explained earlier. Thus, the fractional free volume can be determined at each aging time for these thin films using the observed refractive index or *L* value. Of course, any errors in either *C* or V_0 will be reflected in the values of *f* so obtained and the errors may be amplified, more than proportionally unlike the case of density, owing to how *f* is defined. It is important not to overlook the level of approximations involved in calculating the free volume; however, at this time there is no simple way to remove this limitation.

Several theories have been proposed for describing the physical aging of bulk samples of polymer glasses in terms of loss of free volume by the 'lattice contraction' model. Struik proposed a simple self-retarding model for free volume change consistent with, but in a simpler form than Kovacs's first order isothermal volume relaxation concepts [14,16,18]. Of course, this model does not explain the effect of sample thickness, or size, on the aging rate. Recently, Huang and Paul proposed using the Struik model as a convenient way to represent the free volume change in thin films where the parameters in the model are understood to be thickness dependent, i.e. these values should be regarded as nothing more than fitting parameters [22]. The well-known Struik model can be written as follows [18]

$$\frac{d\Delta f}{dt} = -\frac{\Delta f}{\tau_\infty \exp(-\gamma \Delta f)} \tag{5}$$

The solution to this differential equation can be expressed in terms of the integral exponential function

$$Ei(-x) = -\int_{x}^{\infty} \frac{e^{-u}}{u} \mathrm{d}u \tag{6}$$

as follows

$$Ei(-\gamma\Delta f|_t) - Ei(-\gamma\Delta f|_{t=0}) = \frac{t}{\tau_\infty} \tag{7}$$

The arguments of the integral exponential functions in Eq. (7) are defined as follows

$$\Delta f|_t = f_t - f_e \tag{8}$$

$$\Delta f|_{t=0} = f_i - f_e \tag{9}$$

where f_t is the free volume at time t, f_i is the value at $t=0$ (i.e. immediately after quenching from above T_g), f_e is the equilibrium value that will be reached at $t=\infty$. The latter would correspond to the appropriate extrapolation of equilibrium specific volume data from the melt state to the aging temperature to get V_e where

$$f_e = \frac{V_e - V_0}{V_e} \tag{10}$$

Since no melt state specific volume data seem to be available for these polyimides, we must resort to a correlation scheme to estimate V_e. Huang and Paul used extrapolated melt state data for eleven glassy polymers with aromatic backbones to establish the following correlation, $V_e = 1.466V_w$ with an $R^2 = 0.999$ [22]. Since our estimate of V_0 is also expressed in a similar form, i.e. $V_0 = 1.3V_w$, it turns out that the value of f_e is 0.113 for all polymers when these approximation schemes are used. The term γ in Eq. (4) is a constant while τ_∞ should correspond to the relaxation time at equilibrium at the designated aging temperature. Values for γ, τ_∞ and f_i were obtained by non-linear fitting of the f vs. t data for each 6FDA-based polyimide film. The results are given in Table 2; a more detailed description of this procedure is given elsewhere [22,23]. The points in Fig. 7 show the value of f calculated at each aging time from the refractive index measurement using Eq. (4). The lines shown were computed from Eq. (6) using the parameters in Table 2; as can be seen, the lines represent the data points quite well. The principal value of the model is to give an analytical expression for f as a function of time and an estimate of f_i.

Table 2
Parameters for the Struik model for 6FDA-based polyimide films

Polymer	f_i	f_e	τ_∞ (h)	γ
6FDA-6FpDA	0.191	0.113	3.21×10^{11}	372
6FDA-6FpDA:DABA 2:1	0.220	0.113	2.73×10^{7}	139
6FDA-DAM	0.251	0.113	2.23×10^{7}	114
6FDA-DAM:DABA 2:1	0.226	0.113	1.19×10^{5}	131

Note that τ_∞, γ and f_i were obtained by the curve fitting shown in Fig. 7. The values of τ_∞ and γ will be different for films of different thicknesses than those used and perhaps the same is true for f_i.

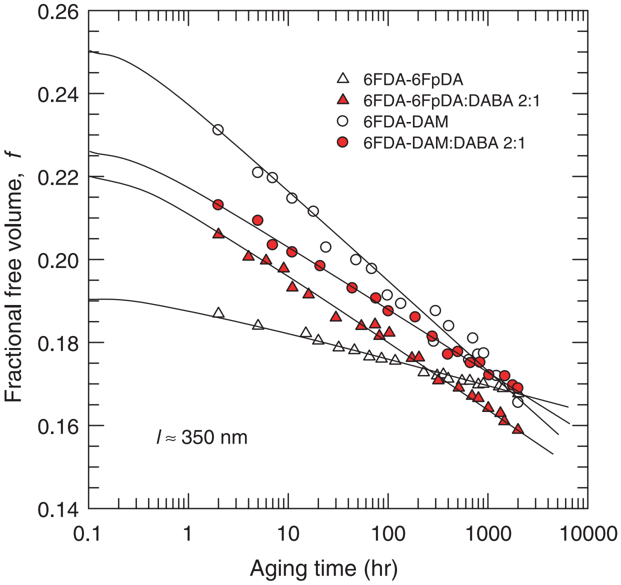

Fig. 7. Fractional free volume of 6FDA-based polyimide films as a function of aging time. The solid lines represent the best fit of the Struik model to experimental values (points) calculated from refractive index.

The fractional free volume decreases continuously for each polymer with the highest rate of decline for 6FDA-DAM and the lowest rate for 6FDA-6FpDA, as expected. The shape of the curves should reflect an asymptotic approach to $f_t \rightarrow f_e = 0.113$ at very long times; however, this is not seen over the time scale of these observations. In broad terms, the decrease in fractional free volume for each polyimide films is quantitatively

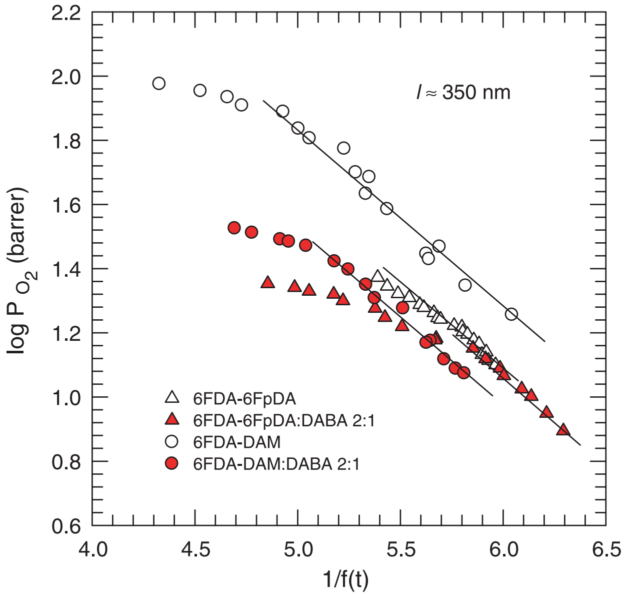

Fig. 8. Correlation of oxygen permeability coefficients with fractional free volume for 6FDA-based polyimide thin films (thickness ∼350 nm) aged at 35 °C.

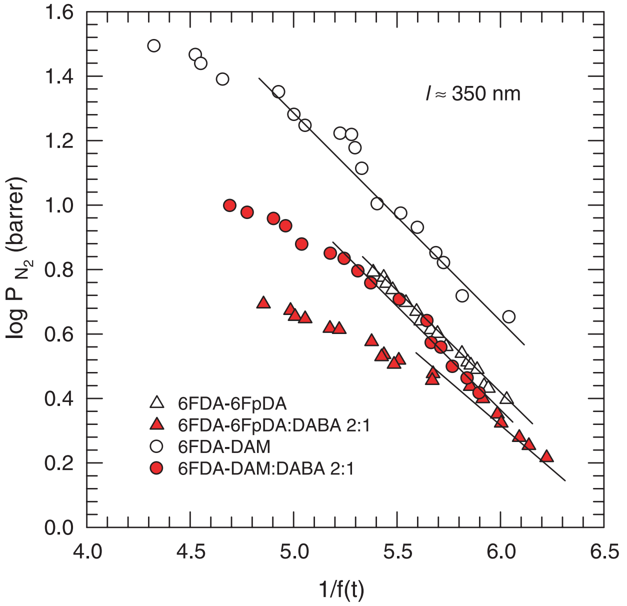

Fig. 9. Correlation of nitrogen permeability coefficients with fractional free volume for 6FDA-based polyimide thin films (thickness 350 nm) aged at 35 °C.

consistent with the gas permeability reduction behavior. Penetrant diffusion and solubility both depend on polymer free volume. It is generally believed that gas permeability and fractional free volume can be fairly well described by the equation

$$P = Ae^{(-B/f)} \tag{11}$$

where A and B are constants for a particular gas. However, to some degree, the values of A and B may also depend on the polymer type. Eq. (11) suggests cross plotting the permeability data from the first paper with the free volume results shown in Fig. 7 in the form of log $P(t)$ vs. $1/f(t)$. Fig. 8 shows plots in this form using the oxygen, nitrogen, and helium permeability coefficient data for each of four different 6FDA-based polyimide thin films with thicknesses around 350 nm aged at 35 °C. In each case, there is generally a good linear form of the plots except in the earliest stages of the aging process. However, the data for the different polymers do not collapse into a single line. It is not yet clear if this is a failure of the basic premises of Eq. (11) or the errors in evaluating $f(t)$; recall the previous discussions about the approximations used to obtain the values of C and V_0 needed for calculating fractional free volume via Eq. (3). At the present time, there is no simple way to resolve this. The parameters A and B obtained from the best fit of the plots in Figs. 8–10 taken at the latter stages of aging (see the lines drawn) are given in Table 3. For a given gas, the parameter B is apparently more or less the same regardless of the polymer type while A seems to depend on the polymer structure; Huang and Paul observed similar results for other glassy polymers [22].

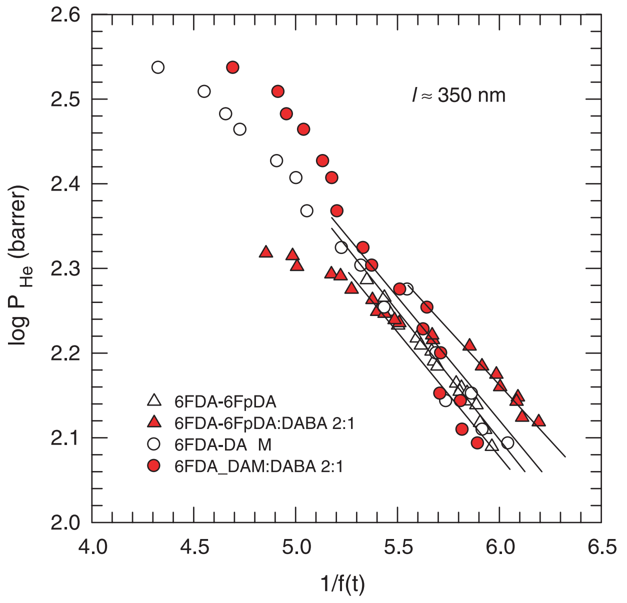

Fig. 10. Correlation of helium permeability coefficients with fractional free volume for 6FDA-based polyimide thin films (thickness ∼350 nm) aged at 35 °C.

Table 3
Values of A and B in Eq. (10) obtained from Figs. 8–10

Polymer	A (barrer)			B		
	O_2	N_2	He	O_2	N_2	He
6FDA-6FpDA	563	592	744	0.581	0.620	0.279
6FDA-6FpDA:DABA 2:1	390	142	807	0.580	0.622	0.278
6FDA-DAM	1063	374	952	0.581	0.621	0.281
6FDA-DAM:DABA 2:1	467	101	855	0.582	0.624	0.279

4. Conclusion

The change in the refractive index for thin films formed from 6FDA-based polyimides was measured by using ellipsometry to track the time-dependent physical aging response. For each polymer, the refractive index increased with aging time due to the film densification caused by physical aging; this result is consistent with aging behavior following by gas permeability measurement reported in the previous paper [1]. The volumetric aging rate was determined from the ellipsometry data by using the Lorentz–Lorenz equation and correlated with the permeability reduction rate. The aging rates determined for these polyimides seem to correlate well with other glassy polymers recently studied [3,4,6,22,23]. Values of the density and fractional free volume were computed as a function of aging time using parameters estimated by group contribution methods. The fractional free volume results for a given film thickness are well described by the self-retarding kinetic model proposed by Struik; however, this model does not explain the thickness dependence of aging rate. The permeability as a function of aging time generally fits the expected form $P = Ae^{(-B/f)}$; however, the data for the different polymers do not exactly collapse into one relationship; we cannot rule out the possibility that errors coming from the various approximations used may be responsible for this.

Acknowledgements

This research was sponsored by the US Department of Energy. The authors express their appreciation to Y. Huang and A. M. Kratochvil for helpful discussions and technical assistance.

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