A Governing Equation for Physical Aging of Thick and Thin Fluoropolyimide Films

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ABSTRACT: An equation based on the segmental/chain mobility in free volume theory was derived to correlate the gas permeation coefficient and the aging time. An accelerated physical aging of a fluoropolyimide was observed and employed to validate this equation. A strong thickness-dependent aging process was found by employing pure O_2 and N_2 tests to monitor the change of gas permeation properties as a function of aging time. Experimental results also suggest that chain rigidity and configuration play important roles in physical aging. As a result, the thin 2,2'-bis(3,4'-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) based polyimide films studied here have different permeability versus time relationship from conventional polyarylate in the early stage of aging, and the experimental data seem to fit the proposed equation well. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1758–1764, 2004

Key words: accelerated physical aging; glassy polymer; thin film; fluoropolyimide

INTRODUCTION

Hollow fibers of glassy polymers with an ultrathin selective layer have been extensively employed for large-scale industrial membrane-based gas separation processes because of the high gas permeance and nearly intrinsic gas selectivity. However, the physical aging, characterized in the drastic gas permeance or flux drop, has been commonly observed for polymeric hollow fibers.[1–4] Our works were tailored to examine the aging profile of 2,2'-bis(3,4'-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA)-Durene polyimide dense films with different thicknesses, thus to correlate the aging of hollow fiber containing a thin and dense selective layer with the aging of dense films of comparable thickness. Most importantly, we attempted to add a new understanding on the evolution of glassy polymers toward equilibrium state by putting forward a simplified but novel half-quantitative equation to directly describe the relationship between the gas permeation coefficient and the aging time for film samples from the standpoint of segmental/chain mobility.

Physical aging of glassy polymers originates from the nonequilibrium nature, which is associated with the reduction of free volume frozen in below the glass transition temperature.[5–10] As an example, poly(trimethylsilylpropyne) (PTMSP), known as a glassy polymer with an extremely high excess free volume, was reported to undergo a rapid decrease of free volume and permeability over time.[11–14] In literature, there are arguably two mechanisms to explain such glass state volume relaxation phenomenon, namely, the free volume diffusion and the lattice contraction.[15–21] As first proposed by Alfrey et al.,[17] the free volume in the form of holes or gaps will diffuse to the surface to accommodate the volume contraction, which is sample-size-dependent. Later on, Kauzmann[18] argued that a simple hole-diffusion model might not be able to cover the whole issue and consequently Curro et al. and Hirai and Eyring [15,16] put forward the concept of lattice contraction, where the lattice of an amorphous system containing a distribution of holes (free volume) will contract uniformly, which results in a non-sample-size-dependent process.

Whether the physical aging of glassy polymer is sample-size-dependent has been much debated in literature. Since the pioneering works of Kovacs,[19,21] of which the researcher found no size dependence for powdered and bulk polystyrene, a growing number of researchers discovered evidence for size-dependent physical aging.[1,5,11,22] For example, McCaig and Paul demonstrated size-dependent permeability decay as a

function of testing time (i.e., over the time scale of observation, the permeation coefficients of O_2 were found to decrease drastically for thin and intermediate films while less significant phenomenon was found for thick films). Similar results were observed by Koros et al., Pfromm, and Pinnau.

Although phenomenological observations are available, suitable models to describe the permeability change/physical aging of glassy polymer have lagged behind. Among available models put forth from the perspective of free volume diffusion, lattice contraction, and T_g depression,[15,17,23–24] on the basis of diffusion concept, McCaig and Paul found that the free volume diffuses out in a way whereby the permeability scales to t/l^2 (where t is aging time and l is sample thickness) as t/l^2 progresses, while in the early stage, a nonlinear trend is obvious. Here, we derive the equation on the basis of segmental/chain mobility to rationalize the gas permeation coefficient changing with time.

DERIVATION OF THE PROPOSED EQUATION

Park and Paul[25] proposed the following equation to relate the permeability of a glass polymer with its fraction free volume (FFV)

$$P = A_1 \exp(-B_1/\text{FFV}) \qquad (1)$$

where A_1 and B_1 are constants for a particular gas, and the FFV is defined as

$$\text{FFV} = (V - V_0)/V \qquad (2)$$

Equation (1) can be further expressed as

$$\ln P = \ln A_1 - \frac{B_1}{\text{FFV}} \qquad (3)$$

where V is the volume of polymer and V_o is the occupied volume. For most glassy polymers, aging usually takes place at a temperature between T_g and the first β transition,[26] whereby the chain configuration changes continuously via the movement of segments. In polymers, the segmental/chain mobility, M, can be related to the rate factor for changes in free volume and chain reconfiguration (where $M = 1/\tau$, and τ is the relaxation time),[26] which is exactly the origin of the permeability decay with time. Meanwhile, the relationship between mobility, fractional free volume, and temperature is well accepted to be the following general form extracted from most models in the free volume theory[26–32]

$$\ln M = A_2 - \frac{k(T)}{\text{FFV}^\gamma} + \phi(T) \qquad (4)$$

where A_2 is a constant, $k(T)$ is a nonincreasing function of temperature, γ is a positive exponent, and $\varphi(T)$ is an increasing function of temperature. Equation (4) can be rearranged to yield the fractional free volume as a function of M,

$$\frac{1}{\text{FFV}} = \left[\frac{A_2 + \phi(T) - \ln M^1}{k(T)} \right]^{1/\gamma} \qquad (5)$$

In the self-retarding aging (relaxation) process, M decreases continuously, as suggested by Struik and Kovacs,[26,33] as follows,

$$M \propto \frac{B_2}{t} \qquad (6)$$

where B_2 is a constant and t is the aging time. Substituting eqs. (5) and (6) into eq. (3) yields

$$\ln P = \ln A_1 - B_1 \times \left[\frac{A_2 + \phi(T) - \ln B_2 + \ln t^1}{k(T)} \right]^\gamma \qquad (7)$$

Following the widely referenced models applicable for a large variety of glassy polymers by Doolittle, Turnbull, and Cohen,[27–30] where empirically γ is equal to 1, $k(T)$, and $\varphi(T)$ can be assumed as constants as A_3 and B_3, respectively, eq. (7) can be rewritten as

$$\ln P = \ln A_1 - \frac{B_1 \times [A_2 + A_3 - \ln B_2]}{B_3} - \frac{B_1}{k(T)} \ln t \qquad (8)$$

which can be further expressed as

$$\ln P = A + B(T) \ln t \qquad (9)$$

where $A = \ln A_1 - (B_1 \times [A_2 + A_3 - \ln B_2])/B_3$, and $B(T) = -[B_1/k(T)]$. This equation suggests that permeability and aging time follow a log–log relationship. In fact, plotting the permeability and functioning time on a log–log coordinate system, which is normally linear over a long-term time scale, is not new. A log–log relationship was empirically observed for the long-term performance of asymmetric membranes.[34–35] Note that the drawback of the proposed eq. (9) is that it becomes numerically meaningless if t approaches to 0. However, parameter A is a temperature-dependent constant possibly corresponding to the logarithm of approximate reference starting value of permeability during the aging process, where $t \to 0$, thus $\tau \to \tau_0$ and $M \to M_0$. Therefore, physically the original free volume is finite; thus, the permeability is finite, which can at least clarify the unbounded situation in this logarithmic equation. $B(T)$ is a temperature-dependent parameter bearing the physical meaning of aging rate at a temperature below T_g, which hypothetically accounts for the rate of changes in inter- and intrachain/
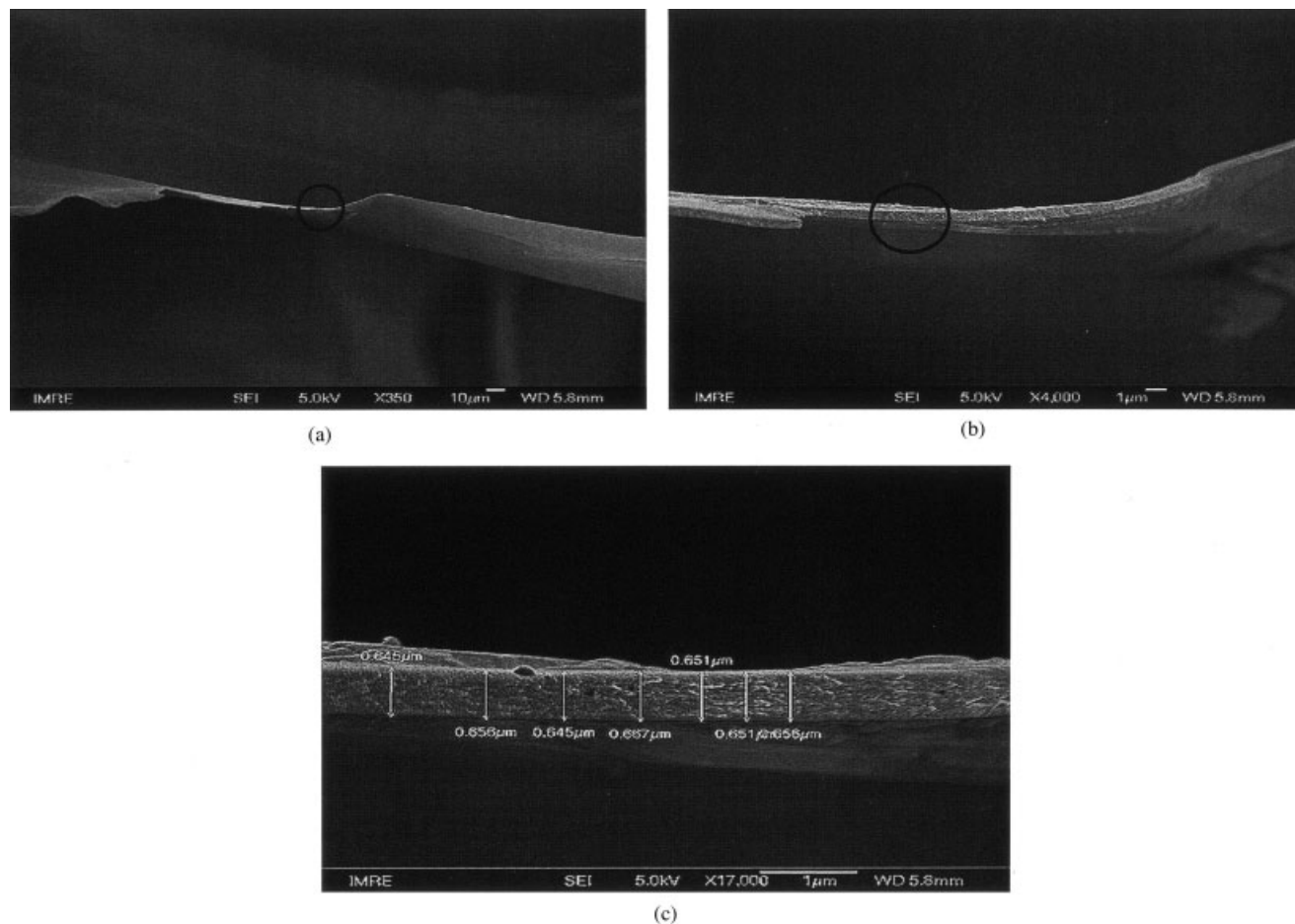
Figure 1 A typical series of SEM photographs of a thin film. Scale bar—(a) 10 microns; (b) 10 micron; (c) 1 μm micron.

segmental packing and configuration during the relaxation and densification for different samples. This hypothesis will be furthered validated as discussed in Results and Discussion.

EXPERIMENTAL

Materials and dense film preparation

The chemical structure of 6FDA-Durene polyimide is shown here.
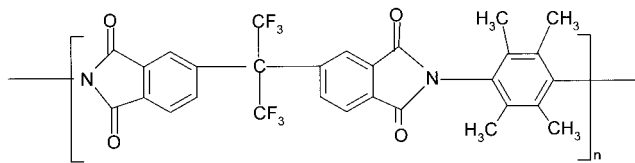
It was synthesized in our lab by using the procedure described elsewhere.[36] All the dense films were obtained by a solution casting method. For thick films (>5 μm), solutions with 2% (w/w) polymer were prepared by dissolving the polyimide in dichloromethane. For thin and intermediate films (0.5–5 μm), solutions with different concentrations ranging from 0.3 to 0.5% (w/w) were used. The polymer solution was then filtered through a Whatman's filter (1 μm for thick films, 0.2 μm for intermediate and thin films) and cast onto a silicon wafer. After solvent evaporation, films were floated off the plate with deionized water and moved onto a highly porous ceramic support base (Whatman Anodisc[TM]) followed by drying the samples. All chemicals were purchased from Aldrich (Milwaukee, WI) and were used as received.

Drying procedure and thermal history

A detailed description of the drying procedure for thick films (>5 μm) can be found in our previous publications.[37] For the intermediate and thin films (0.5–5 μm), a different drying procedure was adopted. Films with a ceramic support were put in the oven to dry at 60°C under vacuum for 24 h. Subsequently, the temperature was increased from 60 to 250°C at a heating rate of 12°C/20 min. After 2-h baking at 250°C, the samples were quenched to room temperature naturally.
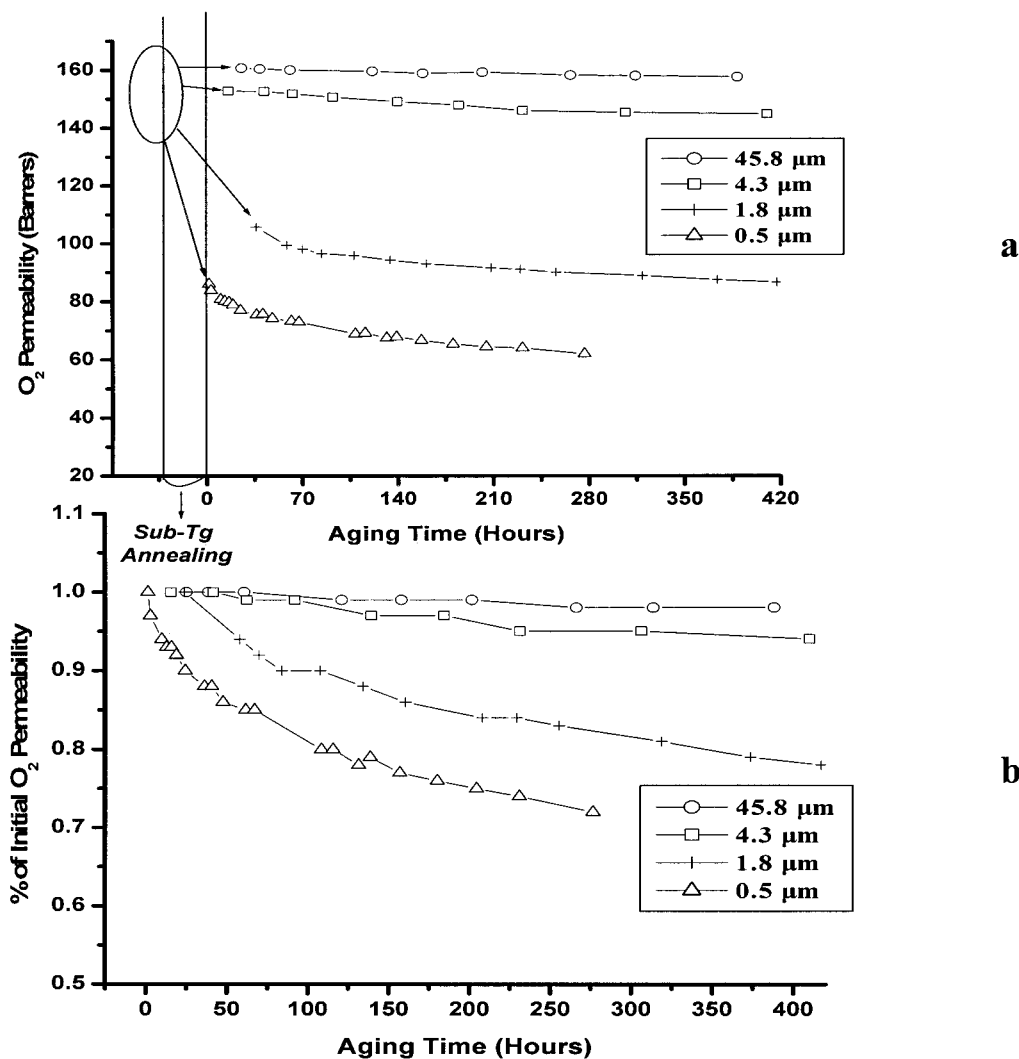
Figure 2 (a) O_2 permeability vs. aging time for films with different thicknesses; (b) percentage change of O_2 permeability vs. aging time.

It is well known that the physical aging of glassy polymers is strongly affected by the heat treatment of the samples.[33] The standardization of thermal history of all the samples has become a must to avoid any ambiguous effects of the heat treatment. For low T_g polymers, this can be achieved by simply heating the samples up to above the glass transition temperature followed by quenching, which can be defined as the starting point of the aging process proposed by other researchers.[5,22] However, not only because of the high glass transition temperature (about 450°C) of 6FDA-Durene, but importantly because of the possibility of thermal crosslinking when our polymer is heated up to above 350°C, we did not heat the samples up to above the glass transition temperature. Nevertheless, the validity of the comparison of aging behaviors of different films discussed below can be reinforced by the fact that the thick films hardly age in this study, and we can compare the aging trend of the thin and

intermediate films with an identical sub-T_g annealing, to the thick film.

Gas permeation experiments

The pure gas permeabilities for O_2 and N_2 were obtained by a constant volume method at 35°C and 2 atm. A detailed description of the apparatus (permeation cell) design and testing conditions can be found elsewhere.[37] The ideal permselectivity is defined as follows: $\alpha_{A/B} = P_A/P_B$. It is noteworthy that the X-ray photoelectron spectroscopy (XPS) results of the original (as-cast) and tested samples show no significant difference.

Thickness acquisition

The actual thickness information of the thin films has always been a serious obstacle because of the small
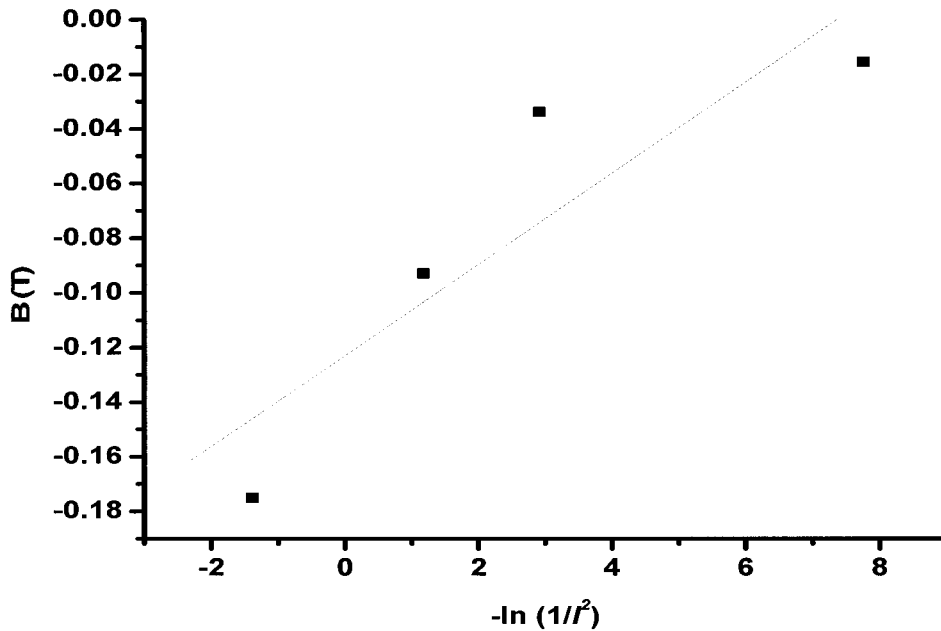
Figure 3 The double logarithmic curve of permeability and aging time for films with different thickness.

amount and fragile nature. We employed an effective method by using SEM to get the real tested film thickness. Following the completion of all the tests, the sample was taken out from the permeation cell and immersed in liquid nitrogen and fractured along the radial direction of two small cuts, which were set prior to the SEM sample preparation, to obtain the cross section of the film. The ceramic support was readily lifted away from the films. A typical series of SEM pictures of the cross section of the films is presented in

Figure 1. A uniform and nonintruded cross section of the thin film sample is clearly shown. For samples thicker than 3.5 μm, the thickness was measured by using a micrometer with a good level of accuracy.

RESULTS AND DISCUSSION

Figure 2(A) presents the time dependence of O_2 permeability for films with different thickness, demonstrating the effect of film thickness on physical aging
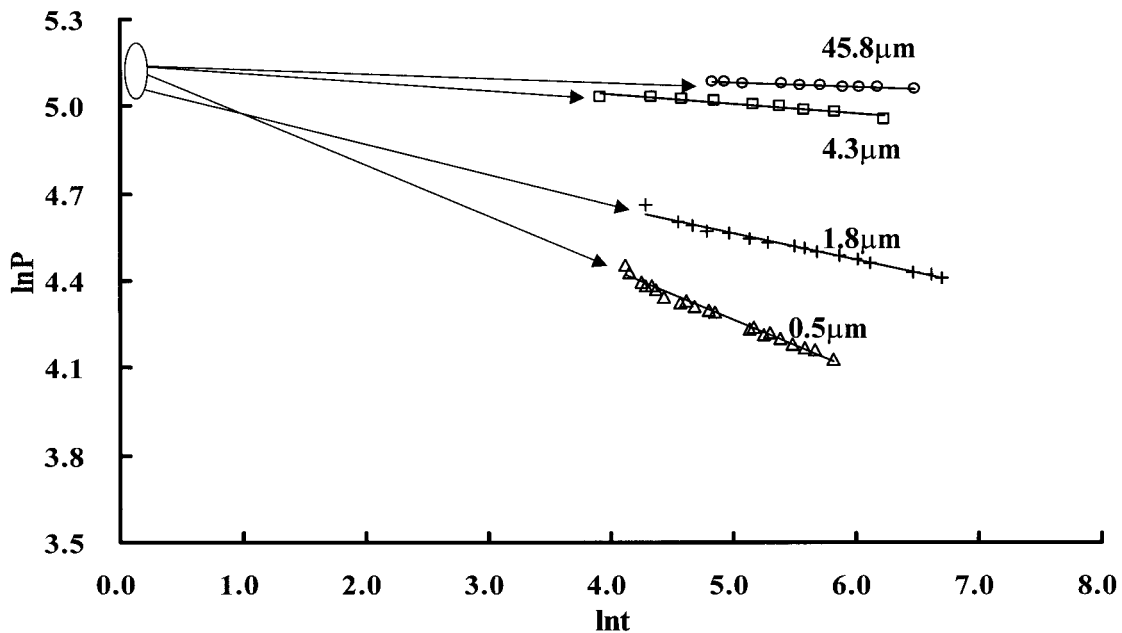

Figure 4 The double logarithmic curve of permeability and aging time for films with different thickness.

TABLE I
Values of B(T) and A for Films with Different Thicknesses

Thickness (μm)	$B(T)$	A
48.5	−0.016	5.16
4.3	−0.034	5.18
1.8	−0.093	5.03
0.5	−0.175	5.14

process of the polyimide used. The starting point of the relative aging time is defined as the moment when the heat treatment ends [i.e., after approximate 35 h sub-T_g annealing as shown in x-axis of Fig. 2(A)]. The oval represents the possible values of real aging starting points for different samples. Clearly, for the thick film (45.8 μm), the permeability values are virtually not changing with time. For the intermediate film (4.3 μm), a slow and gradual decrease of O_2 permeability is observed when compared with the more much significant O_2 permeability loss as a function of time observed for the thin films (1.8 and 0.5 μm). As the films age, the permeability approaches an equilibrium value for each film on our observation time scale. A similar trend was found for the change of N_2 permeability as a function of time for different samples. Figure 2(B) further provides impressive evidence of the accelerated aging process in the polyimide thin films, where maximum total O_2 permeability loss was found for the thin film of 0.5 μm studied, and the trend of another thin film (1.8 μm) is less significant,

while for the intermediate and thick films, the loss of permeability is very limited. An accelerating aging process is obvious for the intermediate and thin films, which is strongly size-dependent.

$B(T)$ versus $-\ln(1/l^2)$ is shown in Figure 3. As mentioned above, the value of $B(T)$ should scale as $-\ln(1/l^2)$ if diffusion concepts were to be applied for the adjustable parameter $B(T)$ in eq. (9). The fitting shows that the trend is clear for the corresponding data points. The deviation might be due to the following differences: first and most important, the scalability of permeability and $1/l^2$ was reported for a quenching system,[23] in which the heat history of the samples is removed and the chains are frozen in a fully relaxed state; the diffusion of free volume, therefore, starts from a maximum state, while in our system all the samples undergo a sub-T_g annealing, which have densified the polymer and reduced the FFV,[38] especially for the thin films. Second, from the view point of the materials studied in both systems, the chain rigidity and conformation of our polyimide in our densifying system might greatly hinder the change of chain configuration in the way it should be to accommodate the change in free volume after the annealing than polyarylate. Table I lists the values of constant A and $B(T)$ for films with different thicknesses plotted in Figure 4. The values of constant A meaning starting value for the four films compared are nearly the same, which indicates to some extent that the O_2 permeability value may be traced back to approximately close starting points after the same sub-T_g annealing. Because the
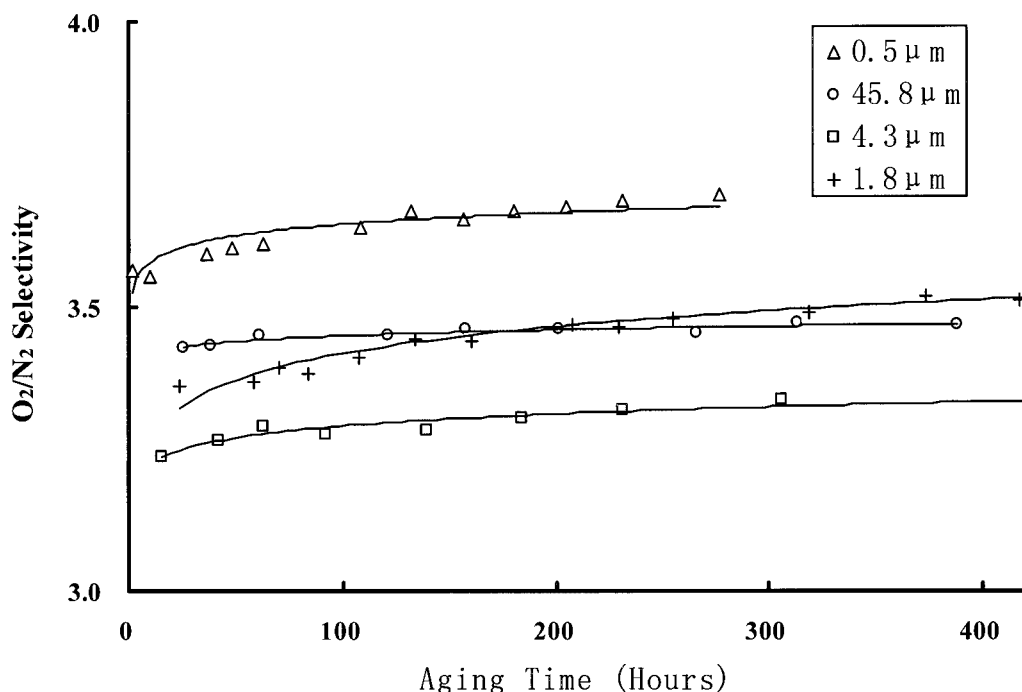

Figure 5 O_2/N_2 permselectivity vs. aging time for films with different thickness.

constant $B(T)$ can be considered as a parameter associated with the thickness and the aging rate, as the sample thickness decreases, the absolute value of $B(T)$ increases from 0.016 to 0.175, suggesting that the aging rate is inversely proportional to the thickness of the sample. In view of the fact that this equation is principally derived from the segmental mobility, this trend may be explained by the difference of mobility of polymer segments/chains in thin and thick film samples: the mobility of the polymer segment/chain in thin films might be much bigger than that in thick films, which can probably be reinforced by the report of the significant decreased T_g with the reduction of thickness for thin films,[39] so the aging rate is much faster for thin films. From another point of view, this trend is consistent with the idea of free volume diffusion: the thinner the films, the less time it takes for the total amount of free volume to diffuse out from the polymer chains toward both surfaces under identical circumstances.

In an up-to-date modified dual mechanism model,[23] whereby the authors attempted to correlate the permeation coefficient and thickness-normalized aging time of polyarylate, a huge deviation for the early stage of the aging is still obvious. Although as shown in Figure 3, the aging process of 6FDA-Durene films can be described by the proposed simple equation based on the segmental mobility throughout the aging process, which sets this work apart from those that rely on the complicated derivation of the diffusion of free volume and/or lattice contraction. However, further systematic studies are needed to fully understand the situation. It seems that this equation is suitable for describing the aging of less flexible polyimides with huge rotational resistance of —$C(CF_3)_2$— group in a densifying system.

Figure 5 shows the change of ideal permselectivity for O_2 over N_2 as a function of time for films with different thicknesses. Because the selectivity remains the same, it defies the possibility that the observed significant permeability loss is due to the existence of defects or the residual solvent. A possible explanation for the moderate change of selectivity might be that within the microscopic entity of the sample, the relaxation/densification of segments/chains retard the total passage of different gas molecules, resulting in the reduction of permeability coefficient, but the minimum threshold pass way to differentiate the size difference of gases might not be affected because of the very bulky CF_3— side group; therefore, an unaffected or slight change of selectivity should be observed.

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