1554 *Macromolecules* **2006,** *39,* 1554−1559

Physical Aging of Thin Glassy Polymer Films Monitored by Optical Properties

Y. Huang and D. R. Paul*

Department of Chemical Engineering and Texas Material Institute, The University of Texas at Austin, Austin, Texas 78712

Received March 12, 2005; Revised Manuscript Received December 21, 2005

ABSTRACT: The change in refractive index of thin films formed from three glassy polymers, polysulfone, a polyimide, and poly(2,6-dimethyl-1,4-phenylene oxide), measured by ellipsometry was used to track their physical aging. These thin films with thicknesses less than 1 μm were aged for up to 6000 h at 35 °C. A pronounced aging response via refractive index change, attributed to the densification of the glassy polymers, was observed for each film. The Lorentz−Lorenz equation was used to relate changes in refractive index to densification, or volume relaxation, with aging time. The volumetric aging rate was shown to be dependent on the polymer structure and the film thickness. These thin films age at rates orders of magnitude more rapid than expected for bulk or thick films.

1. Introduction

Physical aging of glassy polymers, which has been studied extensively for the bulk systems in the past years from many aspects, involves densification or loss of free volume as these nonequilibrium materials progress toward the equilibrium state.[1] However, the physical aging of thin films has been studied only recently. It has been observed via gas permeability measurements that thin glassy polymer films physically age at rates orders of magnitude more rapid than expected in bulk.[1−10] These observations have considerable relevance in the development and use of thin films as gas separation membranes; thus, more in-depth investigations of this behavior are of interest. However, measuring gas permeability of thin films as a means to monitor the aging process is both time-consuming and difficult because it requires the thin films (submicron) to be strictly defect-free and able to bear high pressures. In this paper, we show that the physical aging of thin glassy polymer films can be conveniently monitored by refractive index (n) changes using ellipsometry, and the trends parallel that seen by gas permeation.

One of the useful relationships in this context is the Lorentz−Lorenz equation[11]

$$\frac{n^2 - 1}{n^2 + 2} = \frac{\rho N_{av} \alpha}{3 M_0 \epsilon_0} \qquad (1)$$

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, ρ is the density of the polymer, and α is the average polarizability of the polymer repeat unit. This expression has been widely used and confirmed experimentally, especially with regard to its connection of refractive index to density except near the critical point of fluids.[12] From the Lorentz−Lorenz equation, one expects the refractive index to depend on wavelength/frequency due to its correlation with polarizability and on temperature via the density.

Even though refractive index can be used as a probe of the nonequilibrium nature of the aging process of glassy polymers, there are relatively few reports that have taken advantage of this possibility.[13,14] Roberston and Wilkes[13] monitored the physical aging of bulk samples of atactic polystyrene (PS) at 74 °C, following a quench from above the glass transition temperature, by measuring the refractive index using refractometry, and found the refractive index to increase linearly with the logarithm of aging time, t. This linear relationship was used to convert refractive index changes to the rate of volume relaxation which appears to be a quantitative alternative to dilatometry for following the kinetics of densification associated with physical aging. However, because of the limitations of conventional refractometry, it was not feasible to track a single sample at different aging times, which not only limits the accuracy of the measurement but also makes the aging study extremely laborious and difficult. In addition, conventional refractometry is not applicable for thin, submicron, films particularly when the variations during aging are very small and lie within the range of the detection limit of the measurements. In contrast, ellipsometry has the advantage of measuring the refractive index of a sample placed on a substrate where no damage or change to the sample occurs. This technique is specially designed for characterization of thin films with high accuracy, and the results obtained are representative of an average over a sufficiently large measurement area (0.5 mm by 1.2 mm). This is an elegant, efficient, and versatile measurement method that yields the refractive index along with other useful information in a rapid and quantitative manner for tracking a single sample over unlimited times. To our knowledge, this is the first use of ellipsometry for investigating physical aging of thin glassy polymer films by examining their refractive index change.

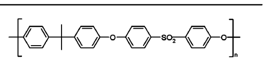
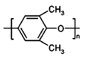
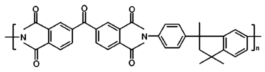
A quantitative link between the refractive index change and the volume relaxation rate is developed for three different glassy polymers. The higher aging rate observed in thin films compared to bulk polymers has been hypothesized to be the result of diffusion of the glassy polymer's free volume to the surface where it can escape, leading to a thickness dependence of the aging process.[2−4,6,8−10] While the current work does not establish proof of this mechanism, it does show convincing evidence that the prior observations on thin film aging by gas permeation are indeed paralleled by changes in density. Direct measurement of the expected densification during physical aging is not

---

* To whom all correspondence should be addressed: e-mail drp@che.utexas.edu; Tel +1-512-471-5392; Fax +1-512-471-0542.

10.1021/ma050533y CCC: $33.50

Table 1. Bulk Physical Properties and Chemical Structure of Polymers Studied

Polymer	ρ_b (g/cm³)	Refractive Index	T_g (°C)	Chemical structure
PSF	1.24	1.633	186	
PPO	1.069	1.573	213	
Matrimid®	1.20	1.653	310	

possible by conventional techniques for thin films with sufficient accuracy.

2. Experimental Methods

2.1. Materials. Three different glassy polymers were used in this work: the polysulfone based on bisphenol A (PSF), a polyimide known commercially as Matrimid 5128, and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). Detailed descriptions of these polymers have been given elsewhere,[1] and their bulk properties pertinent to this work and chemical structures are presented in Table 1. The first two polymers are commonly used to form asymmetric gas separation membranes employed in commercial separation processes; this is the primary motivation for the selection of these polymers for this study.

2.2. Film Preparation. In this work, thin films (below 1000 nm) were obtained using a spin-coating method as described previously.[1] The films were removed from the wafer surface using deionized water and transferred to a wire frame to give a free-standing thin film which was then annealed above T_g in an oven with a N_2 purge according to a protocol designed to remove prior thermal history and set the "aging clock" to time zero.[15] The "fresh" film sample was then placed onto the silicon wafer substrate, which was precleaved into squares of 10 mm × 10 mm in size, by gently rolling it over the wafer surface to avoid trapping air bubbles under the film, and the sample was left on the wafer surface during aging. However, such prepared thin films were not strongly bonded to the silicon wafer because they could be easily lifted off the wafer surface at any time. A perfect film/silicon wafer laminate should be free of corrugations or scratches with a homogeneous transparent surface as observed by an optical microscope on a 10 μm overview.[15] The sample was then marked with an arrow on the back of the wafer for indication of the direction of placement during the following measurements. Finally, the samples, which are continuously on the wafer, were placed in a storage chamber held in air at 35 °C for aging but were cooled to 25 °C periodically for refractive index measurement using ellipsometry (see below for details).

2.3. Cleaning of Silicon Wafers. The wafers used for spin-coating were cleaned by acetone, methanol, and deionized water. This cleaning process removes organic residues on the wafer surfaces but preserves the native oxide layer.

The wafer squares used to support the annealed film samples were cleaned in an ultrasonic bath of high-purity water for 10 min to remove dust, then rinsed with acetone, isopropyl alcohol, and deionized water, and blown off with dry nitrogen. They were then further cleaned for 15 min by irradiation with UV light to remove organic contaminants while not altering the native oxide features.

2.4. Ellipsometry. The ellipsometric technique has been widely used for measuring the thin film thickness and other related characterizations.[16−20] This technique is used here to measure the refractive index change due to densification of thin glassy polymer films using a variable angle spectroscopic ellipsometer (VASE), model 2000D from J.A. Woollam, which has an accuracy of 10^{-4} for refractive index measurement. The measurement temperature was maintained at 25 ± 0.1 °C. On the basis of the useful empirical "rule of thumb" for the similar temperature dependence of the refractive index of all polymers in the glassy state,[21] this temperature fluctuation is expected to result in a refractive index error of the order of 10^{-5}, a value negligible in comparison to the extent of refractive index change owing to physical aging to be detailed later. To eliminate sample error, it would be desirable to determine the refractive index at the same scan point on the film sample for measurement at each incremental aging time. This was achieved by carefully recording the wafer position on the ellipsometer measurement table for the first measurement and realigning the sample accurately to this original measurement position during the following tests. For each polymer film thickness, at least four samples were prepared and monitored simultaneously in order to verify the reproducibility of the measurement as well as the accuracy. However, no constraint was used in the data analysis process, and each individual measurement was treated completely independently. The thickness of the SiO_2 layer was predetermined before each film sample was attached to the silicon wafer. Within experimental uncertainty, we were able to reproduce numerical values of the refractive index measurement for samples with similar thickness for each polymer (see results in the next section). Because the preparation process should lead to unoriented films,[1] the refractive index in any direction should be equal to the average refractive index, i.e., the measured value. In this work, the refractive index measurement was conducted in the spectral range from 400 to 1000 nm. The procedures and methods of measurement are the same as described before.[1,15] The refractive index was calculated using the Cauchy theory, eq 2, at the sodium (Na) D wavelength (λ = 589.3 nm) under room temperature for each polymer film, where the parameters *A*, *B*, and *C* are constants obtained from the ellipsometry measurements as described before.[15]

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \tag{2}$$

The upper limit of film thickness with sufficient measurement accuracy by ellipsometer is about 1 μm; therefore, the thin films studied in this work had thicknesses of ∼400, 700, and 1000 nm. Thus, densification of films sufficiently thick to be regarded in the "bulk state" cannot be tracked by this technique.

3. Results and Discussion

Film samples of the three polymers were isothermally aged at 35 °C. At each aging measurement time, after removal from the aging chamber, the film samples were cooled to room temperature, and the refractive indices were determined at 25 °C within 5 min from the time of removal from the chamber. Any additional physical aging during this short time of measurement was assumed insignificant since the whole aging process persists for very long times.[1] Since the thin film is not strongly bonded to the silicon wafer, i.e., it can be easily lifted off the wafer surface at any time, and the difference between the aging temperature and measurement temperature is only 10 °C, any in-plane thermal stresses should be very small. The optical constants of all materials have some dispersion as a function of wavelength.[22] In this work, the refractive index obtained for each film decreases as the wavelength increases for the spectral range used, and the extinction/absorption coefficient (imaginary part of refraction), *k*, was found to be zero for all film samples during physical aging. An example is given in Figure 1 for a PSF film with thickness of ∼400 nm. The constant zero value of *k* verifies that all film samples are transparent, and the application of the Cauchy equation for refractive index calculation is valid. Since the refractive index measurement is very fast, such aging data could be collected at very short aging times, ∼0.1 h for each film sample.

The polarizability in the Lorentz−Lorenz equation refers to electronic polarizability (a temperature-independent parameter) because the refractive index is measured in the visible range of frequencies; i.e., the orientational polarizability (permanent

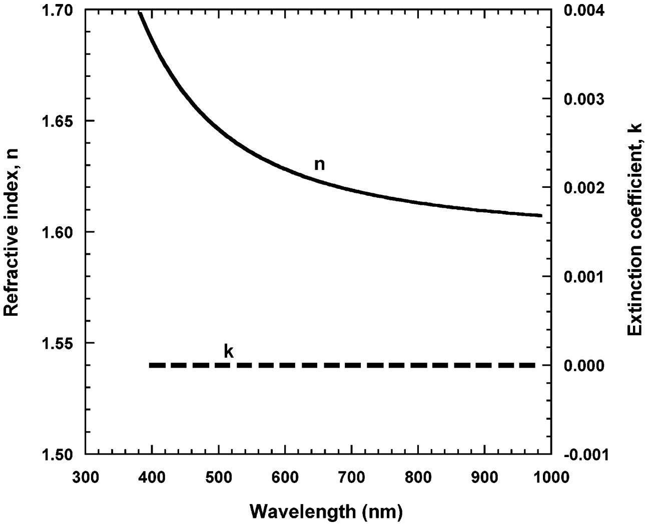


Figure 1. An example of optical data obtained for a PSF thin film on a silicon wafer.

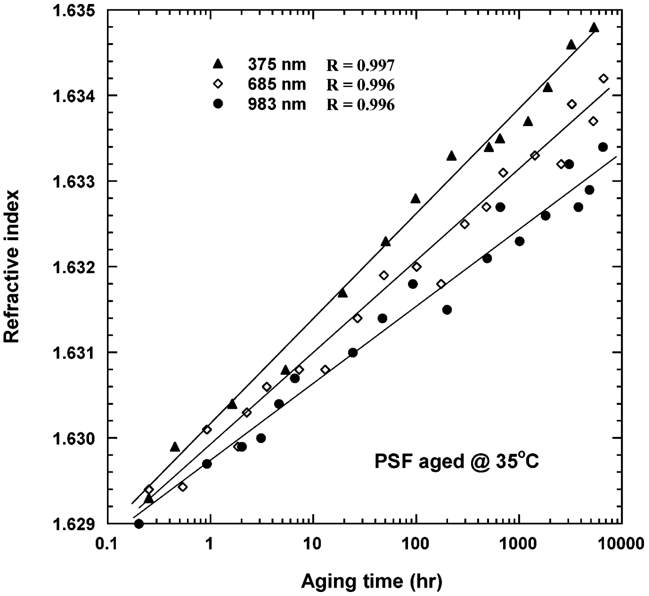


Figure 2. Refractive index measured at 25 °C for PSF thin films as a function of aging time at 35 °C.

dipole moment) is excluded.[23] During the aging process, electronic polarizability can be assumed constant because of its sole dependency on the distribution of the electronic cloud. On the other hand, irrespective of the changing thermodynamic state of the glassy polymer undergoing physical aging, the Lorentz−Lorenz expression should remain valid at any time. Thus, from the Lorentz−Lorenz equation, there should be a unique correlation between refractive index and density during the aging process.

3.1. Physical Aging Tracked by Refractive Index Change. Figures 2−4 show the evolution of the refractive index (obtained at 25 °C) for PSF, Matrimid 5128, and PPO isothermally aged at 35 °C vs aging time for films having thicknesses ~400, 700, and 1000 nm. Each figure clearly shows an increase of refractive index for each film over the period of investigation, and it seems the refractive index increases in a nearly linear fashion as a function of log *t* except during the initial stage of aging, similar to aging monitored by enthalpy recovery[24] and density.[25,26] The linearity is statistically significant as is evident from the fact that correlation coefficients (*R*) for the linear fit are higher than 0.99 for each sample. Therefore, one would expect the refractive index change to be related to the change in density. In fact, since $1.3 < n < 1.7$ for most polymers, correlations proposed for n^2 almost always find a simplified version with *n*, such as the Lorentz−Lorenz equation vs the Gladstone−Dale equation.[21] This refractive index trend is very similar to that observed by Roberston and Wilkes.[13] In the present case, there is a more rapid increase in refractive index for thinner films than for thicker films of the same polymer, while the aging pattern appears to be rather similar for the three polymers. Figure 5 gives a comparison of the relative refractive index (normalized by the corresponding refractive index at around 1 h of aging) change of the three polymer films with thickness ~400 nm during the process of aging; these relative quantities display the same trend reported earlier for gas permeability.[1] PPO shows the most rapid increase in refractive index with log *t*; at an aging time of 6000 h, the refractive index is increased by 0.87% for PPO followed by 0.60% for Matrimid and 0.35% for PSF. These increases correspond to density increases of 1.84%, 1.14%, and 0.69% for PPO, Matrimid, and PSF, respectively, which are much higher than expected for bulk systems.[1−10] Using a density

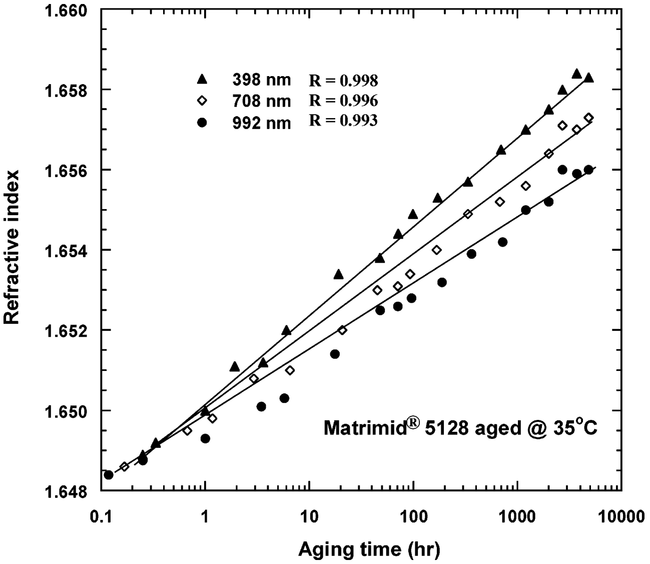


Figure 3. Refractive index measured at 25 °C for Matrimid thin films as a function of aging time at 35 °C.

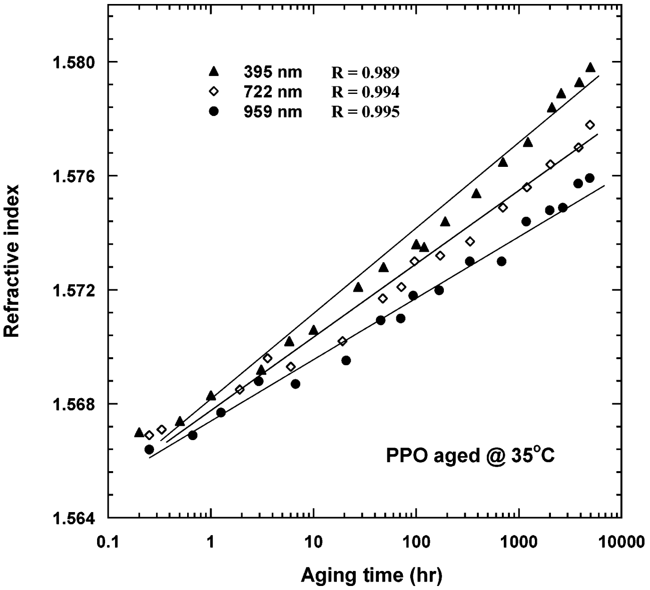


Figure 4. Refractive index measured at 25 °C for PPO thin films as a function of aging time at 35 °C.

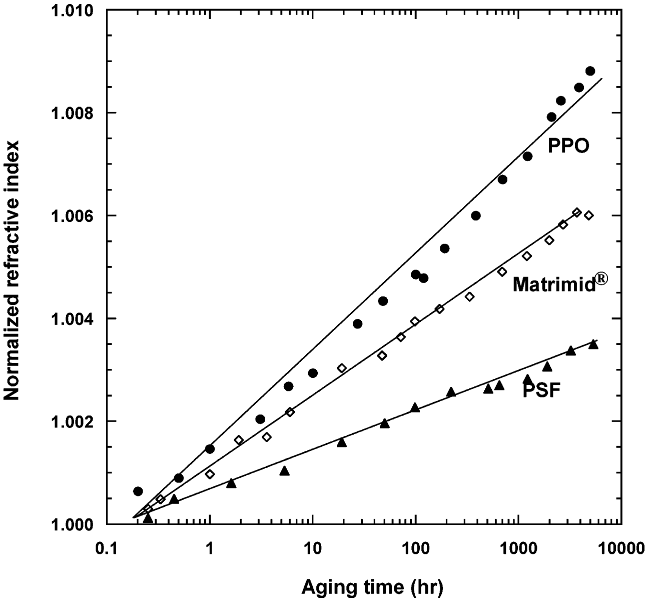


Figure 5. Normalized refractive indices for thin films (~400 nm) of the three polymers as a function of aging time.

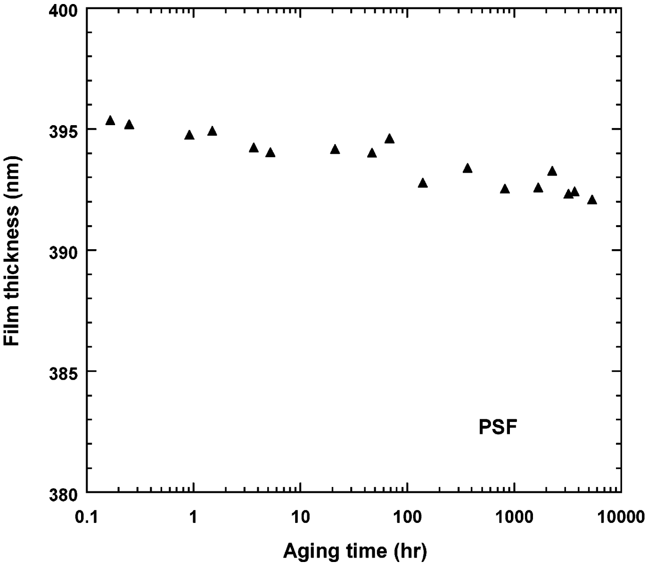


Figure 6. Effect of physical aging on film thickness for PSF film with thicknesses of ~400 nm.

gradient column technique, Pfromm estimated density changes of the order of 1−2% for a 0.5 μm PSF film aged for 236 days.[27] These increases in density represent about 15−20% of the progression from the initial density immediately after quenching from above T_g to the estimated equilibrium density; a more detailed analysis of this aging progress will be described in a subsequent paper.[28] For each polymer film, the refractive index values at very short aging times are about the same as documented earlier.[1]

In addition to the increase in refractive index observed during physical aging, there is a slight decrease in film thickness that accompanies aging as depicted in Figure 7 for a PSF film with an initial thickness of 395 nm. The change of thickness over 6000 h for this sample is ~0.8%. This is quite similar to the change in density calculated from refractive index, which suggests that the densification during aging is manifested by only a decrease in thickness and not in the film's lateral dimensions. A few selected measurements of thickness and refractive index made on samples aged in the free-standing state (but placed on the wafer for measurement) gave similar values as for samples aged on the wafer. Analyses of the ellipsometry observations by uniaxial vs nonuniaxial models revealed no statistically significant difference in thickness or refractive index. While it would be interesting to explore any deviations from isotropic densification, this may be beyond the resolution limits of the current techniques.

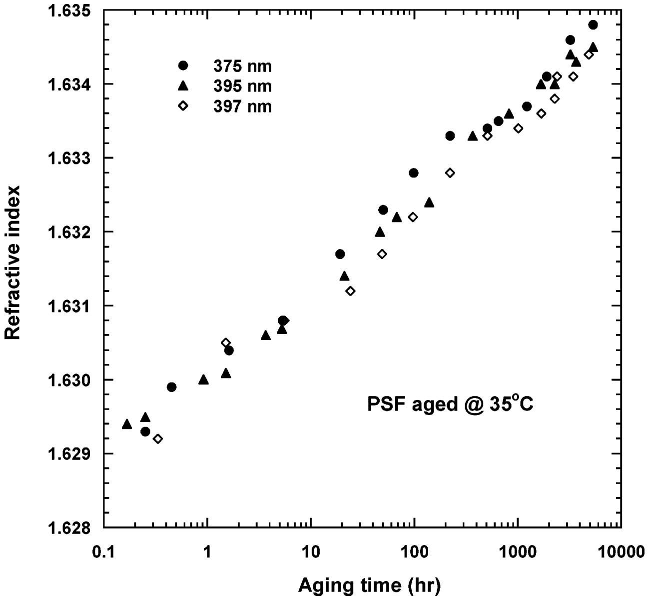


Figure 7. Demonstration of the reproducibility of refractive index change with aging for PSF films with thicknesses of ~400 nm.

3.2. Reproducibility of Refractive Index Measurement. By carefully recording the sample position on the ellipsometer measuring table, the data are highly reproducible for the multiple measurements at each aging time for each sample. Measurements on different samples with similar thicknesses show good reproducibility as may be seen by the representative example in Figure 7 for three PSF films with thickness ~400 nm. The slight differences among these data might be taken as one indicator of the sensitivity of the refractive index measurement. In general, the change in refractive index is much larger than the standard deviation about the mean value of the measurements for the three samples at any time during the aging process. The overall increase in refractive index proceeds smoothly and almost linearly with log *t*. For each refractive index plot in Figures 2−4, the slight scattering of the data about the linear line might also be considered as another indicator of the error of the measurement; clearly, these deviations do not overshadow the trend of the increase of refractive index in any of the cases examined.

3.3. Estimation of Volumetric Aging Rate from Refractive Index. From the above analysis, the change in refractive index is related to the change in density of the polymer film; thus, use of refractive index change to predict the volumetric aging rate seems justified.

The isothermal volumetric aging rate, *r*, is defined as follows:[29]

$$r = -\frac{1}{V}\left(\frac{\partial V}{\partial \ln t}\right)_{P,T} = \left(\frac{\partial \ln \rho}{\partial \ln t}\right)_{P,T} \tag{3}$$

where *V* is the material specific volume and *P* and *T* refer to the pressure and temperature during aging. The parameter *r* is widely used to compare the recovery kinetics for the time interval over which a linear relationship pertains.[30]

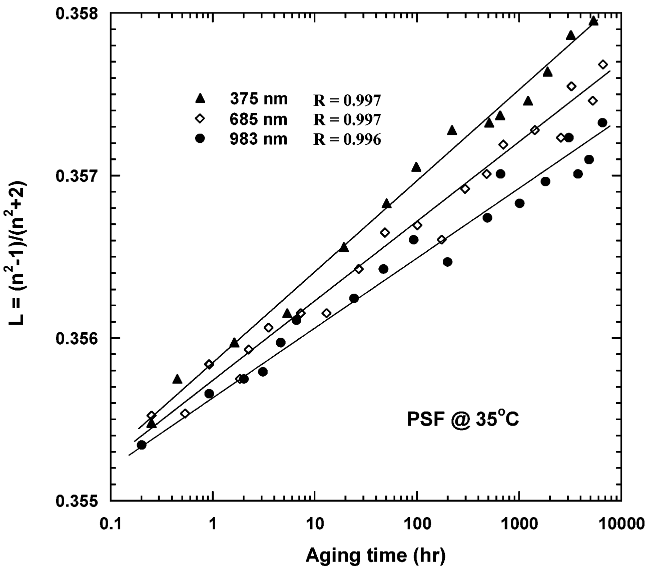


Figure 8. Refractive index change plotted in the form of the Lorentz−Lorenz parameter, L, for PSF thin films as a function of aging time.

The Lorentz−Lorenz equation can be reformatted as follows

$$L = \frac{n^2 - 1}{n^2 + 2} = \rho C \tag{4}$$

where L is defined as the Lorentz−Lorenz parameter; $C = N_{av}\alpha/3M_0\epsilon_0$ may be assumed to be constant during the aging process as discussed earlier. The Lorentz−Lorenz parameter is therefore a linear function of density; Figure 8 is an example of replotting the refractive index data in the form of the Lorentz−Lorenz parameter for PSF films. Since the change in refractive index during aging is quite small, L is also a linear function of log t as observed for the refractive index. Indeed, the volumetric aging rate can be calculated from the change of the Lorentz−Lorenz parameter as follows:

$$r = \left(\frac{\partial \ln \rho}{\partial \ln t}\right)_{P,T} = \left(\frac{\partial \ln L}{\partial \ln t}\right)_{P,T} = \left(\frac{\partial \log L}{\partial \log t}\right)_{P,T} \tag{5}$$

Excellent linear relationships were also observed for all film samples in the double-logarithmic plot of log L vs log t, whose slopes are the volumetric aging rates as shown by eq 5.

Figure 9 summarizes the optically measured aging rates vs film thickness for the three polymers studied. Clearly, the aging rate decreases as the film thickness increases for all these polymers; this is consistent with gas permeation studies where a much wider range of thicknesses have been examined.[1−10] As noted earlier, the aging rate ranks in the order of PPO > Matrimid > PSF for films with similar thickness which must reflect their chemical structures and free volume levels; this trend agrees with observations of aging tracked by gas permeability.[1] However, this order does not simply correlate with the difference between the polymer T_g and the aging temperature, $\Delta T = (T_g - T)$, since $\Delta T_{\mathrm{Matrimid}} > \Delta T_{\mathrm{PPO}} > \Delta T_{\mathrm{PSF}}$. Clearly, the aging rate for a given polymer depends on more than its T_g or the relative distance of the aging temperature to the T_g. We expect that the polymer's free volume is an important factor in the relative aging rates. The aging observations reported here were conducted at temperatures far below the respective T_g of each polymer where it is expected that the extent of aging for bulk samples, or thick films typically used to screen membrane materials, would be very insignificant.[1−10]

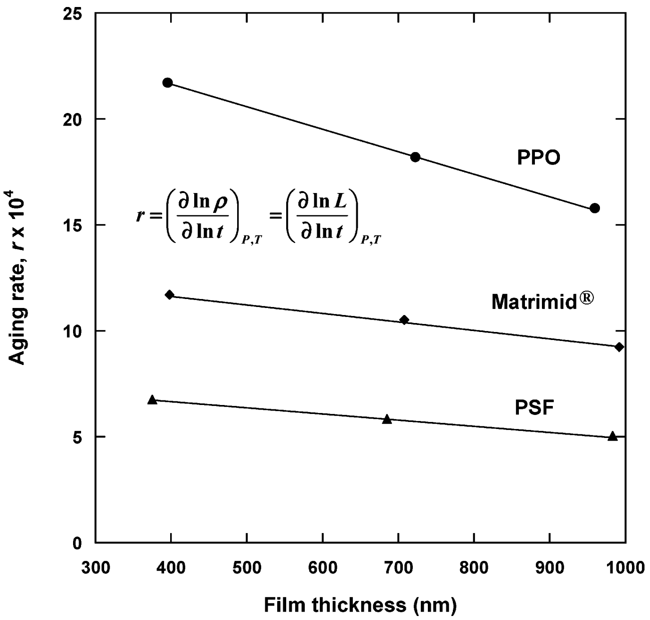


Figure 9. Volumetric aging rate, r, determined from the Lorentz−Lorenz equation vs film thickness for the three polymers.

4. Conclusions

Physical aging of glassy polymer films having thicknesses in the range of 400−1000 nm made from PSF, Matrimid 5128, and PPO, isothermally aged at 35 °C following a quench from above the glass transition temperature, is clearly manifested by changes in their refractive indices measured by ellipsometry. The refractive quantities in different forms were found to increase more or less linearly with log t during the densification process owing to physical aging. The volumetric aging rate, defined as $r = (\partial \ln \rho/\partial \ln t)_{P,T}$, was calculated by using the Lorentz−Lorenz equation. The results indicate that the volumetric aging rate is thickness dependent; thinner films age faster than thicker films as documented previously by other techniques.[1,6,10,31,32] The aging behavior monitored by refractive index is consistent with aging followed by gas permeability measurements.[1] It has been proposed in the literature that the faster aging of thin films than bulk polymers is due to the diffusion of free volume, in analogy to the diffusion of defects, to the surface of the film, thereby causing aging to be thickness dependent. However, to date, there is no direct confirmation of this hypothesis; other techniques that could detect any gradient of density across a film caused by such free volume diffusion need to be explored. The ellipsometry technique employed here does not seem to be sensitive enough to detect such a gradient. The aging rate clearly depends on polymer structure; PPO ages somewhat faster than Matrimid 5128 while PSF has the slowest aging rate. After 6000 h of observation there is no sign of stabilization of the aging process, indicating that the films are still far from equilibrium regardless of thickness, which is consistent with previous findings.[1]

Acknowledgment. The authors thank Dr. C. G. Willson and his research group for their help in using their ellipsometer. We are also grateful to Dr. Ping He and Dr. Greg Pribil from J.A. Woollam Co., Inc., for their help with ellipsometric analysis. The financial support from the Separations Research Program at the University of Texas at Austin and the National Science Foundation (Grant DMR-0238979 administered by the Division of Material Research−Polymer Program) is gratefully acknowledged.

References and Notes

(1) Huang, Y.; Paul, D. R. *Polymer* **2004**, *45*, 8377−8393.
(2) Rezac, M. E.; Pfromm, P. H.; Costello, L. M.; Koros, W. J. *Ind. Eng. Chem. Res.* **1994**, *32*, 1921−1926.
(3) Rezac, M. E. *Ind. Eng. Chem. Res.* **1995**, *34*, 3170−3172.
(4) Dorkenoo, K. D.; Pfromm, P. H. *J. Polym. Sci., Part B: Polym. Phys.* **1999**, *37*, 2239−2251.
(5) Reiter, G. *Macromolecules* **1994**, *27*, 3046−3052.
(6) McCaig, M. S.; Paul, D. R. *Polymer* **2000**, *41*, 629−637.
(7) Reiter, G.; de Gennes, P.-G. *Eur. Phys. J. E* **2001**, *6*, 25−28.
(8) Dorkenoo, K. D.; Pfromm, P. H. *Macromolecules* **2000**, *33*, 3747−3751.
(9) McCaig, M. S.; Paul, D. R.; Barlow, J. W. *Polymer* **2000**, *41*, 639−648.
(10) Pfromm, P. H.; Koros, W. J. *Polymer* **1995**, *36*, 2379−2387.
(11) Mills, N. J. 2nd ed.; Mark, H. F., Kroschwitz, J. I., Eds.; John Wiley and Sons: New York, 1987; Vol. 10.
(12) Larsen, S. Y.; Mountain, R. D.; Zwanzig, R. *J. Chem. Phys.* **1965**, *42*, 2187−2190.
(13) Robertson, C. G.; Wilkes, G. L. *Polymer* **1998**, *39*, 2129−2133.
(14) Boesch, L.; Napolitano, A.; Macedo, P. B. *J. Am. Ceram. Soc.* **1970**, *53*, 148−153.
(15) Huang, Y.; Paul, D. R. *J. Membr. Sci.* **2004**, *244*, 167−178.
(16) Kim, J. H.; Jang, J.; Zin, W.-C. *Langmuir* **2000**, *16*, 4064−4067.
(17) Grohens, Y.; Sacristan, J.; Hamon, L.; Reinecke, H.; Mijangos, C.; Guenet, J. M. *Polymer* **2001**, *42*, 6419−6423.
(18) Kawana, S.; Jones, R. A. L. *Phys. Rev. E* **2001**, *63*, 021501/021501−021501/021506.
(19) Pham, J. Q.; Green, P. F. *Macromolecules* **2003**, *36*, 1665−1669.
(20) Keddie, J. L.; Jones, R. A. L. *Isr. J. Chem.* **1995**, *35*, 21−26.
(21) Seferis, J. C. In *Polymer Handbook*, 4th ed.; Brandrup, J., Immergut, E. H., Grulke, E. A., Eds.; John Wiley & Sons: New York, 1999; pp VI/571−VI/582.
(22) J.A. Woollam Co., Inc., 2001.
(23) Israelachvili, J. N. *Intermolecular and Surface Forces*, 2nd ed.; Academic Press: London, 1991.
(24) Royal, J. S.; Torkelson, J. M. *Macromolecules* **1992**, *25*, 4792−4796.
(25) Tant, M. R.; Wilkes, G. L. *Polym. Eng. Sci.* **1981**, *21*, 325−330.
(26) Greiner, R.; Schwarzl, F. R. *Rheol. Acta* **1984**, *23*, 378−395.
(27) Pfromm, P. H. In *Chemical Engineering*; The University of Texas at Austin: Austin, 1994.
(28) Huang, Y.; Wang, X.; Paul, D. R. Submitted to *J. Membr. Sci.*
(29) Kovacs, A. J. *Fortschr. Hochpolym. Forsch.* **1964**, *3*, 394−508.
(30) Hutchinson, J. M. *Prog. Polym. Sci.* **1995**, *20*, 703−760.
(31) Pinnau, I.; Koros, W. J. *J. Appl. Polym. Sci.* **1991**, *43*, 1491−1502.
(32) Zhou, C.; Chung, T.-S.; Wang, R.; Goh, S. H. *J. Appl. Polym. Sci.* **2004**, *92*, 1758−1764.

MA050533Y