Thickness-Dependent Sorption and Effects of Physical Aging in a Polyimide Sample

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ABSTRACT: The solubility of a relatively noninteracting gas (CH_4) was measured and compared for samples of vastly different thicknesses (25.4 vs 0.1 μm) to investigate the possibility of thickness-dependent sorption and physical aging in glassy polymers. Changes in the sorption due to physical aging in these dense samples were observed and compared. To further compare the tendency of free-volume relaxations in samples of different thicknesses, a variety of conditioning sorption tests were performed in which increases in the CH_4 sorption due to high-pressure CO_2 exposure were observed and then compared after sample degassing. The reduction in CH_4 solubility was related to excess free-volume relaxations, and response comparisons of samples of widely different film thicknesses supported the notion of thickness-dependent physical aging in glassy polymers. To the authors' knowledge, this was the first direct observation of a significant differences in gas solubility in glassy polymers due to the film thickness and aging time. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1115–1121, 2005

Key words: ageing; glass transition; membranes; thin films

INTRODUCTION

The solubility of gases in glassy polymers plays an important role in a number of applications, particularly in polymeric gas-separation membranes. Early research conducted by Kovacs[1,2] showed that physical aging in glassy polymers is independent of the sample dimensions. However, other studies[3,4] have shown differences in the aging rate of permeability in glassy-polymer samples of different thicknesses, and this suggests the need for reinvestigating the conclusions of Kovacs. Gas diffusivity and solubility rely heavily on the amount of free volume, which is directly affected by physical aging. This study provides additional information relevant to such an investigation and expands the understanding of the glassy state and its interaction with penetrant species. This improved understanding can help us in defining strategies to control physical-aging-related problems in finely structured glassy morphologies, such as those found in asymmetric polymeric gas-separation membranes.

The motivation for this work lies in gas-separation membrane technology, in which a thin, selective layer (~1000 Å thick) is used to separate gases according to differences in the permeability. Strong departures from bulk film permeabilities have been observed for these so-called asymmetric membranes, and the reasons for these nonidealities are not well understood. This work focuses on the possible thickness dependence of glassy-polymer gas solubility (one of the two aspects of permeability, the other being diffusivity). The heterogeneous morphology of gas-separation membranes, however, makes such samples difficult to characterize. These membranes possess a broad density gradient along their thickness, which ranges from a highly dense selective skin to a mechanically robust spongy support layer and actually makes up greater than 99.9% of the volume of the membranes. In contrast, the sample types considered in this work are dense films formed via the slow and controlled evaporation of a volatile solvent from solution. These films have a well-defined processing history and are homogeneous in their morphology. Such dense films provide a reference point for studying asymmetric membranes. Substrate effects are avoided in all sample types with only freestanding films, even for the thin samples (~0.1 μm). Thus, the dense films studied here are used to observe the dependence of gas sorption on the sample thickness alone.

A considerable amount of research has already been devoted to understanding the thickness dependence of transport properties due to physical aging in amorphous glassy-polymer films, but mainly with respect to permeation properties.[4,5] Differences in the permeation properties between asymmetric membranes and thick, dense films have also been documented.[3,6] Reductions in gas permeability and increases in He/N_2 permeation selectivity over time have been reported to

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be stronger in asymmetric membranes than in thick, dense films. Rezac and coworkers[4] attributed these trends to physical aging because physical aging tends to reduce the amount of excess free volume in a glassy polymer over time, and this is consistent with suppressed permeabilities and enhanced selectivities.

To elucidate the behavior of thin, selective skins, investigators have studied the time-dependent permeabilities of thin, dense films and found results qualitatively similar to those of asymmetric, flat-sheet membranes.[4] Moreover, they have observed significantly lower permeation isotherms for ultrathin, dense polyimide films in comparison with those measured for thicker dense films. Permeability is the product of the diffusion and sorption coefficients. It has been hypothesized that thinner samples possess a lower diffusion coefficient and lower solubility. Here we focus on the direct observation of gas sorption isotherms in both thick and thin samples to evaluate this hypothesis.

Model for gas sorption

The dual-mode sorption model provides a useful framework for interpreting sorption measurements and may be used to gain insight into the relationship between the glassy-polymer free volume and sorption capacity.[7] This model is the simplest and most widely employed model of gas sorption in glassy polymers and has been demonstrated by many authors to describe sorption with excellent success.[8,9] The dual modes refer to two distinct, though idealized, environments in which sorption can occur. The first mode represents liquidlike sorption, in which the closely packed polymer segments are parted to accommodate the penetrant. This mode gives rise to a dissolved population and follows a solubility expression of Henry's law. The second is a result of the nonequilibrium glassy state, in which pockets of excess free volume, or packing defects, serve as ready-made sites for sorption. This mode gives rise to a hole-filling population and follows a Langmuir-type expression. The mathematical expression of the model is

$$c = k_D p + \frac{C'_H b p}{1 + b p} \qquad (1)$$

where c is the penetrant concentration within the polymer, p is the external penetrant pressure, k_D is Henry's law constant, C'_H is the Langmuir capacity constant, and b is the Langmuir affinity constant. The first term of the equation represents Henry's law (i.e., liquidlike) sorption, whereas the second term represents Langmuir (i.e., hole filling) sorption. The dual-mode theory postulates that there is a finite number of Langmuir sites that ultimately can be saturated as sorption increases. The total amount of unrelaxed volume in the
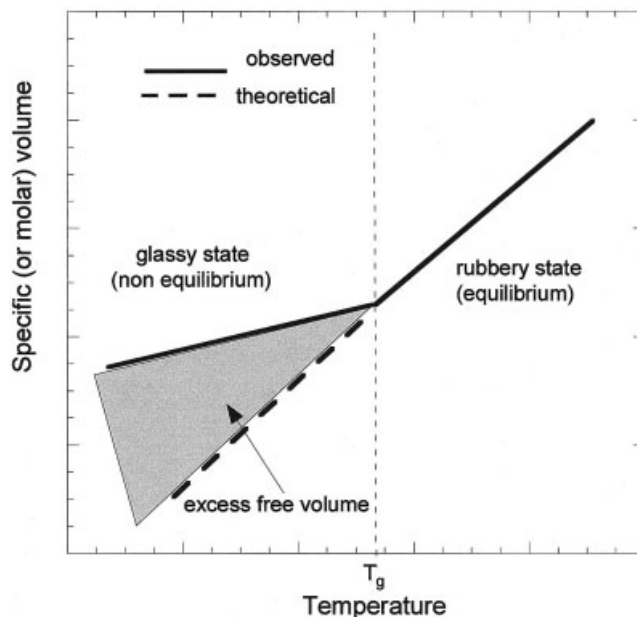

Figure 1 Specific (or molar) volume versus the temperature for a glassy polymer.

glassy polymer is visualized as being available for additional sorption above that which would be possible in a corresponding equilibrium matrix with properties extrapolated from above the glass-transition temperature (T_g). As stated previously, because the excess free volume is distributed between the hypothetical Langmuir sites, reductions in the excess free volume due to physical aging should be signaled by reductions in C'_H.

Figure 1 illustrates this concept of excess free volume in glassy polymers. Above T_g, the polymer exists in the rubbery state, in which the polymer chains possess long-range mobility and easily attain low free-energy conformations. Satisfyingly, the plot of the specific volume versus the temperature for rubbery polymers is reasonably well predicted by lattice–fluid equations of state based on equilibrium conditions of the polymer chains.[10] In contrast, the specific volume of a glassy polymer is usually higher than what is expected from an extrapolation of the plot below T_g. Unlike in the rubbery state, it is believed that the long-range mobility of polymer chains below T_g is severely restricted, and only segmental motion occurs with any significant frequency. As a result, regions of the matrix that are not well packed remain as long-lived segmental-scale voids, which are here called Langmuir sites. The collective sum of these voids ideally makes up the excess free volume, which is also sometimes called the unrelaxed volume.

Mechanisms for physical aging and the origin of thickness dependence

Two primary mechanisms have been proposed to explain the removal of the unrelaxed volume trapped in

glassy matrices during quenching from above T_g to room temperature. The first mechanism, lattice contraction, refers to a generalized collapse of all of the segments comprising the dilated matrix.[11] Simplistically, this is analogous to the nearly instantaneous collapse of a fluid from one volume to another in response to a change in temperature at constant pressure. An extension of this idea would be to envision a high viscosity retarding the collapse, but in either case, the key element of this mechanism is its independence of the sample size.

More relevant to the hypothesized dimension dependence is the so-called diffusion-of-free-volume mechanism. In this case, unrelaxed regions of excess free volume are envisioned as leaving the sample via diffusion. Because the diffusion process is itself enabled by the presence of the free volume, which allows segmental motion and rearrangement, the effective diffusion coefficient for the free volume decreases as the sample ages.[12] This process is analogous to the concentration-dependent diffusion of a penetrant; however, in this case, the penetrant is a packet of free volume. Because this mechanism involves diffusion, the timescale of the process scales with the square of the effective thickness of the sample dimension.[5]

Samples of any geometry may approach their equilibrium state via lattice contraction because it occurs independently of the sample dimension. However, the effect of the diffusion of the free volume is practically only detectable in reasonable timescales in samples approximately 0.1 μm thick or less. As shown later, this concept may explain why ultrathin samples (<0.1 μm) have an intrinsically lower sorption capacity than otherwise identical thick samples (~25.4 μm).

Conditioning experiments: Alternative experiments for observing free-volume relaxations

Although gas-probe sorption studies on virgin samples have yielded much insight into the presence of excess free volume in glassy polymers, unrelaxed volume can be effectively introduced into glassy-polymer samples through a process called conditioning. In this process, the sample is exposed to high activities of a strongly sorbing penetrant and then is completely degassed. If the sample is subsequently examined by sorption probing with a noninteracting gas (e.g., N_2 or CH_4), an elevated C'_H value is observed that indicates an increased amount of unrelaxed volume.[13,14] Moreover, if a polymer sample is probed with sorption measurements while it is still swollen by the original conditioning agent in a procedure called exchange conditioning, even greater increases in solubility will be observed. Conditioning analysis has been conducted extensively in previous works to study the lasting effects of highly sorbing species. In this work, conditioning experiments have been used to compare

the extent to which the introduced unrelaxed volume is lost in samples of different film thicknesses.

EXPERIMENTAL

Sample preparation

The polymer studied in this work was Matrimid 5218 (benzophenone tetra carboxylic dianhydride-diamino phenylindane), a high-T_g (~313°C) polyimide from Ciba–Geigy Corp. (Tarrytown, NY) that is well known for its attractive gas-separation properties. All the thick films (~25.4 μm) were prepared via the uniform spreading of a solution of the material over a flat mirror surface with a doctor blade. The solvent was dichloromethane (CH_2Cl_2; bp = 39.8°C). An 8 wt % polymer solution produced the ideal fluid viscosity for casting. The resulting film thickness for this procedure was adjusted to approximately 1 mil (25.4 μm). The films were then placed in a vacuum oven and heated at 100°C for 24 h. The films prepared this way are called "as cast" in this work.

For thin freestanding films, a mold-casting technique was used. A stock solution of 104 mg of the polymer per 150 cc of the solvent was prepared. An appropriate volume of this dilute solution was poured into a metal ring mold (7 cm in diameter) that rested flatly on a bare silicon wafer. A glove bag was used to control the rate of solvent evaporation. A level surface was ensured before the casting so that a uniform thickness would be achieved throughout the films. The films were then removed from the substrate through the delicate submersion of the samples in water. The water displaced the films from contact with the silicon surface. This procedure is discussed in depth elsewhere,[3] and the same steps were closely followed. A labile wire hoop was used to support the thin, delicate films, and this allowed the samples to remain free of any substrate effects or mechanical stresses. These films were also placed in a vacuum oven and heated at 100°C for 24 h. The film thickness of the samples was 0.098 μm, as measured by profilometry, before the removal of the films from the substrate. Because both the thick and thin samples were fabricated by slow solvent evaporation, the morphologies of both types were reasonably homogeneous and dense. Second-order effects, such as residual solvent and polymer chain orientation, from the heating of the samples above their T_g are now discussed.

Sample annealing protocol

In any study of the physical aging of glassy polymers, it is important to clearly define a time-zero event to which the reported aging time is referenced. Because physical aging is a phenomenon that occurs only in the glassy state, previous researchers in this area have

appropriately heated samples above their T_g and then quickly cooled them to room temperature.[4,5] Moreover, through the heating of a sample above its T_g (in an inert environment), potentially spurious effects from artifacts, such as residual solvent and polymer-chain orientation, due to the casting technique or solvent evaporation are removed. Unfortunately, this makes sample preparation for the study of high-T_g polyimides, such as Matrimid, particularly difficult because most conventional vacuum ovens can rarely reliably operate above 300°C. To achieve a highly controllable, repeatable, high-temperature, inert environment, a programmable gas chromatograph oven with an ultrahigh-purity nitrogen purge was used to conduct sample annealing. The super-T_g annealing temperature was selected to be 340°C. This experimental procedure was conducted for both thick (25.4-μm) and thin (0.1-μm) Matrimid samples. Therefore, these two dense film samples of different thicknesses experienced the same processing history and possessed a clearly defined time zero for aging experiments. The cooling time was held to a minimum to reduce the effect of near-T_g and sub-T_g annealing. Ideally, a step change in the temperature from T_g to the experimental temperature would be used. For the apparatus used in this experiment, the absolute minimum cooling time achieved was approximately 15 min (i.e., a quench rate of approximately 20°C/min).

To examine potential chemical changes in the super-T_g heated samples, we redissolved the samples in the original solvent and performed infrared spectroscopy. The samples easily redissolved, and this demonstrated that no significant thermal crosslinking took place. Moreover, no substantial change in the Fourier transform infrared spectrum was found.

Sorption measurements

The well-known dual-volume pressure decay technique[8,9] was used to measure the gas solubility of the thick film samples. The resolution of the measurements was approximately ±0.005 cc (STP). Additionally, the volumes of the reservoir and cell were known to within ±0.005 cm^3. Combining these two major sources of error, for a typical sample volume of 1 cm^3 (~1.2 g), we found that the sorption concentration could be determined to within ±0.5%.[15]

For the thin-film samples, sample masses of approximately 10 mg were realistically attainable. Therefore, a technique capable of measuring sorption for smaller samples was necessary. Gravimetric sorption with a highly sensitive spring was a suitable technique for this purpose. A quartz spring, purchased from Ruska Instruments (Houston, TX), had a spring constant of 0.41 cm/mg. The measurement of the spring elongation was performed with a Bausch and Lomb optical reader (Rochester, NY) and could be observed to

within 5 μm. This displacement translated into an experimental tolerance of roughly 3% of the measured value.

The buoyancy effects were strong at moderate and high pressures and had to be taken into account for accurate measurements of the sorption. All three bodies (the spring, sample holder, and polymer sample) were affected by the buoyancy. The force of buoyancy on the samples and sample holders could be explained with the following expression:

$$F_{\text{bouyancy}} = m_{\text{solid}}\left(\frac{\rho_{\text{gas}}}{\rho_{\text{solid}}}\right)g \qquad (2)$$

where m_{solid} and ρ_{solid} are the mass and density of the object (sample or sample holder), respectively; ρ_{gas} is the gas density (pressure- and virial-coefficient-dependent); and g is the acceleration of gravity.

Using control studies with nonsorbing aluminum foil weights, we found that the effect of buoyancy on the spring was highly nonlinear and could not be analytically calculated with eq. (2). Therefore, the displacement of the spring resulting solely from its own buoyancy had to be empirically determined. Experimental verification of this treatment of buoyancy effects was successful because zero solubility was calculated for blank runs. The overall deviations between the gravimetric and pressure decay techniques were found to be at most ±0.5 cc (STP). All measurements were conducted at 35 ± 0.1°C instead of room temperature to ensure the thermal stability of the experimental apparatus.

With respect to a statistical approach for the study of this phenomenon, we note that the sample fabrication of a 1000-Å freestanding thin film was highly nontrivial. The use of freestanding films ensured that there were no substrate effects on the films, and this was critical for this work. The process of fabricating a sufficient amount of a sample so that sorption measurements could be obtained was highly labor-intensive, and so such measurements were not optimally suited for a statistical study at this exploratory stage. The approach that we took in this study involved conducting control experiments, which ensured that any differences in the sorption observed between the thick and thin films were not experimental artifacts of the measurement technique or sample preparation.

Conditioning and exchange-conditioning protocol

As noted earlier, conditioning experiments are simply sorption measurements made on samples that have previously been exposed to high activities of a swelling penetrant. For the conventionally conditioned samples, the CH$_4$ solubility was first measured on virgin samples. The samples were depressurized, de-

gassed, and exposed to the conditioning agent (800 psia CO_2) until equilibrium was reached. The samples were then degassed completely, and the CH_4 solubility was tested again. CO_2 was depressurized gradually (from 800 to 14.7 psia over 24 h). This was done to prevent foaming of the polymer, which is known to happen if a highly swelling penetrant is removed too quickly from a polymer sample.[9]

The exchange-conditioned samples were tested identically, with one exception: there was no depressurization step between the conditioning exposure and the second observation of CH_4 solubility. We did this by opening a vent line in the sorption sample chamber and simultaneously purging the sample chamber of the conditioning agent with the probe gas (CH_4) at a constant pressure until the sample was completely rid of the conditioning agent (CO_2). Then, the sorption curve was measured from this pressure down to a vacuum. In practice, the unconditioned sorption curves were first measured. Then, when the exchange-conditioning pressure was reached, the exchange-conditioned sorption isotherm was obtained. Finally, the samples were degassed, and the samples were retested to obtain the conventionally conditioned isotherms.

RESULTS AND DISCUSSION

Comparison of physical aging and sorption isotherms of thick films versus thin films

Samples 0.1 and 24.5 μm thick were tested after 240 h of aging at room temperature. The CH_4 sorption isotherms obtained for all the samples are given in Figure 2.

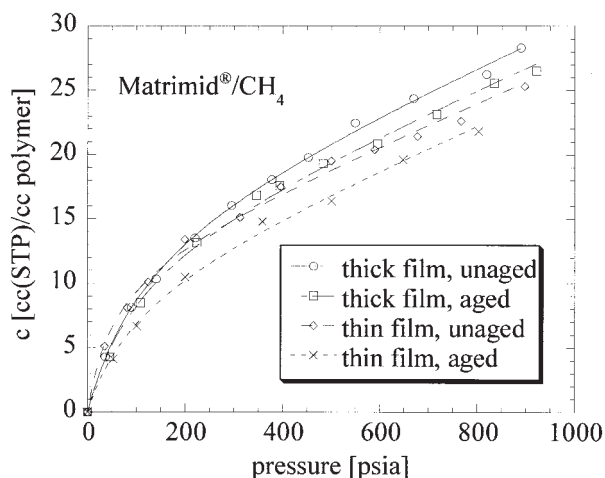The thin-film sorption isotherms lay significantly below those of the thicker films. Moreover, the effect

TABLE I
CH_4 Langmuir Capacity for Thick and Thin Matrimid Dense Films[a]

	C'_H [cc (STP)/cc of polymer]	
	Unaged	Aged
Thick film (l = 25.4 μm)	16.0 $\pm$ 0.5	13.8 $\pm$ 0.5
Thin film (l = 0.098 μm)	12.0 $\pm$ 0.5	10.6 $\pm$ 0.5

[a] With a Common k_D Value of 0.16 cc (STP)/cc of polymer psia for all data sets.

of 240 h of physical aging at room temperature was readily observed for samples of both thicknesses. To our knowledge, this was the first direct observation of significant differences in the gas solubility of glassy polymers due to film thickness and aging time. Although the thickness effect was indeed subtle, the differences in the sorption measured for the two samples of different thicknesses were well beyond the observed experimental tolerances discussed previously.

Satisfyingly, the slopes of all the sorption isotherms in the higher pressure regimes appeared to be identical, and this was consistent with the dual-mode sorption theory. The sorption isotherm slope in the linear (higher pressure) regime was equal to k_D and was theoretically an intrinsic polymer-penetrant parameter. The extracted k_D values and dual-mode parameters from the curves in Figure 2 are listed in Table I. A constraint of a common value for k_D [0.16 cc (STP)/cc of polymer psia] was used to simplify the analysis. For all data sets, R^2 was at least 0.996, and the average χ^2 value was 1.77. This suggests that the data were reasonably well described by the constrained dual-mode analysis.

Because the Langmuir sorption capacity of the thinner films was approximately 22% lower than that of the thicker films, we inferred that the thin-film samples contained less unrelaxed volume than the thicker samples and rationalized this phenomena by the theory of free-volume diffusion. However, we also expected, on the basis of the theory of free-volume diffusion, that the decline in C'_H would be much greater for the thinner samples as well. On the contrary, the reduction in C'_H was roughly 1.4 cc (STP)/cc of the polymer in the thin films and 2.2 cc (STP)/cc of the polymer in the thicker films. Because of the experimental and numerical uncertainties, these changes in C'_H were essentially indistinguishable.

To explain these unexpected results, we speculate that a significant fraction of the initially present excess free volume might have diffused out during the cooling process from above T_g for the thin sample but not for the thick sample. To understand this point, we note that the free-volume diffusion from the 25.4-μm sample (vs the 0.1-μm sample) occurred $25.4^2/0.1^2 = 64{,}500$ times faster than for the thick film, and we

Figure 2 Comparison of the CH_4 sorption isotherms and associated physical aging effects on thick and thin Matrimid films.

made use of the fact that the diffusion process scaled directly with the square of the diffusion length (technically, the half-thickness should be used, but in this case, the factor of 1/2 simply cancelled out). In relative terms, aging due to the free-volume diffusion during cooling from above T_g was relatively unimportant for the thick sample because of the much longer effective diffusion timescale for the thick sample. Nevertheless, significant free-volume diffusion aging could occur during the drift cooling of the thin sample. Such accelerated aging in the thin sample (as shown by the overall lower sorption values for the thin film) could then prevent subsequent aging under the controlled 35°C aging study and produce the nonintuitive result observed. The process of physical aging is self-retarding,[12] and as the excess free volume is relaxed out of a sample, the effective diffusion coefficient of the surviving regions of unrelaxed volume is reduced. For example, during the 15-min cooling process from above T_g experienced by the dense film, the thin film had already experienced equivalent free-volume diffusion aging that was 64,500 times longer (roughly equivalent to 2 years). Conversely, the thin film with only 240 h of additional aging at 35°C after its simple 15-min cooling preaging should have approximately reflected the aging expected in the thick film after 1770 years (240 × 64,500 h).

Conditioning results for thick and thin films

Marked differences in the CH_4 sorption conditioning responses were observed between the thick and thin, dense polymer samples, as shown in Figure 3. For CH_4, which is a low-sorbing, noncondensable gas, there is typically no hysteresis in sorption curves. However, as shown in the figure, the CH_4 solubility clearly increased as a result of the conditioning procedure. The CH_4 concentration during the exchange conditioning at the highest pressure was observed to be as high as approximately 40 cc (STP)/cc of polymer, which is unusually high for methane.

For the two samples of different thicknesses, the trends of the three treatments were similar to those found in a similar study.[14] In that work, Pope found that for simple thick polycarbonate films (>25 μm), conventionally conditioned samples exhibited higher solubility than virgin samples, and exchange-conditioned samples exhibited higher solubility than conventionally conditioned samples. As discussed earlier, the elevated solubility for conventionally conditioned samples is caused by the lasting rearrangement of the polymer-penetrant environment by the conditioning agent. Such rearrangements may be viewed as an increase in the excess free volume of the polymer. When the probe gas (CH_4) was exchanged at a constant applied pressure with the conditioning agent (CO_2), the timescale for the collapse of the polymer
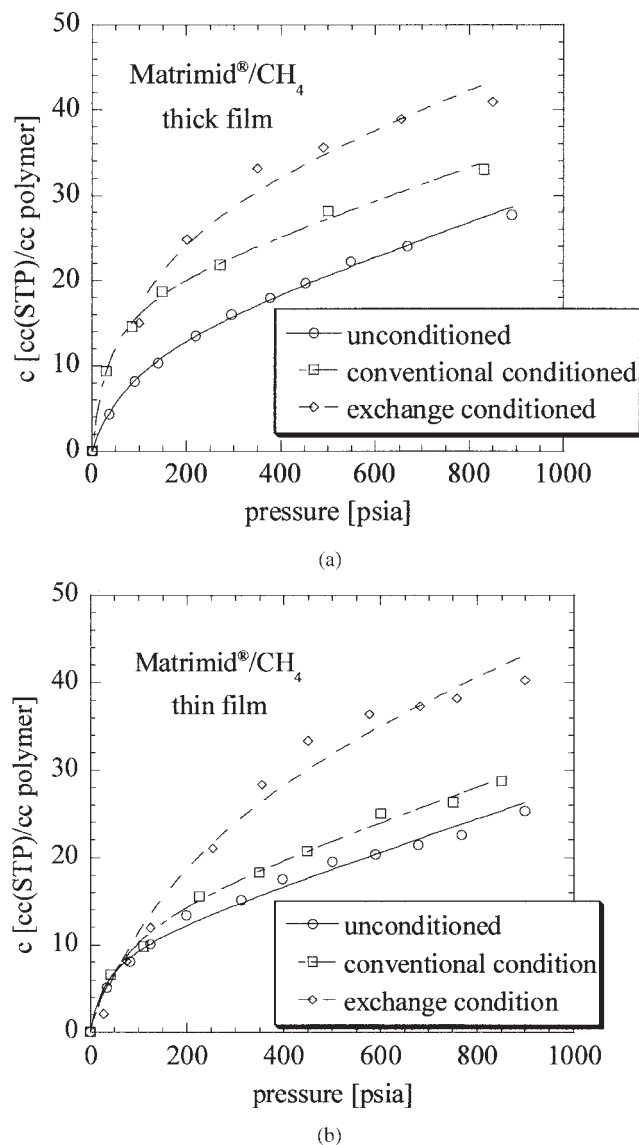

(a)

(b)

Figure 3 Effects of conventional and exchange conditioning on (a) thick and (b) thin films.

network was dramatically reduced, if not completely eliminated, and so even higher sorption curves were observed for the exchange-conditioned samples. When the thickness of the polymer samples was reduced to approximately 1000 Å, we observed some very interesting effects.

In Figure 3, we see that for unconditioned samples, the thin sample possessed a low sorption curve. This observation has already been noted in a previous section. Moreover, very similar exchange-conditioned sorption curves were observed for the thick and thin samples. This suggested that the swollen, unprotracted polymer-penetrant environment, as affected by the conditioning agent, was similarly independent of the sample size. However, once all the penetrants were removed, the sample was degassed, and conventionally conditioned sorption curves were obtained; a

larger reduction in the sorption capacity was observed for the thinner film, with the thicker film retaining more of its induced free volume.

CONCLUSIONS

Methane sorption isotherms were measured for both thick and thin Matrimid samples with identical thermal and aging histories. The theory of free-volume diffusion suggests that the thinner samples had less excess free volume than the thicker samples; this inference was consistent with the observation that the thin samples possessed a lower Langmuir sorption capacity than the thick, dense films (~22% lower) because the Langmuir sorption capacity is known to be intimately related to the amount of excess free volume. It was also observed that thinner films of the polyimide exhibited less pronounced conditioning effects. This observation also supported the notion that the thinner films could more readily relax out the free volume; for the conditioning experiments, this was induced by the conditioning agent.

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