Relaxation Dynamics of CO_2 Diffusion, Sorption, and Polymer Swelling for Plasticized Polyimide Membranes

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ABSTRACT: The CO_2 permeability, solubility, and dilation of 6FDA-DAM:DABA 2:1 polyimide membranes exposed to pure CO_2 at 40 atm and 35 °C were investigated over long times (up to 20 days). Swelling and sorption measurements were performed on 120 nm films with in situ spectroscopic ellipsometry. The sorption measurements by ellipsometry are compared with sorption into thick films (40−70 μm) by the pressure-decay technique. There is a strong correlation between the CO_2 diffusion coefficient and the film swelling. Solid-state covalent cross-linking of the membranes with 1,4-cyclohexanedimethanol and thermal annealing of the polymer films with free acid groups leads to significantly improved ability to maintain a relatively constant CO_2 diffusion coefficient over long times. Annealing at temperatures between 100 and 295 °C leads to similar sorption behavior but significantly different diffusion and swelling. Relaxation functions are fit to the permeation, sorption, and swelling data to quantify the relationships between these parameters. There is a correlation between the permeation and swelling relaxation times and the magnitude of the increase in each parameter due to the relaxations with respect to the annealing temperature of the film. However, the relaxation times in the thin film swelling are an order of magnitude faster than in the permeation through thick films. Cross-linking tends to slow down the polymer chain relaxations while decreasing the polymer swelling and stabilizing the CO_2 diffusion coefficient under high CO_2 feed pressures. Spectroscopic ellipsometry allows for rapid measurement of swelling and sorption of thin films on the length scale of the permselective skin of practical asymmetric membranes (0.1 μm).

Introduction

Membrane applications could be expanded considerably (e.g., natural gas purification, propylene/propane,[1] butadiene/butane,[2] and aromatic/aliphatic[3] separations) if they can be made more stable and robust. In natural gas separations, high partial pressures of CO_2 and condensable hydrocarbons can result in unstable and unpredictable membrane performance and increased losses of methane to the permeate stream (i.e., lost revenue) due to declines in permselectivity. In membrane separations, plasticization is generally defined to be an increase in the permeability of a penetrant molecule due to increased polymer chain segmental mobility facilitated by the presence of other penetrant molecules.[4] A penetrant's diffusion coefficient in a glassy polymeric membrane depends on the size and shape of the diffusing molecule and on the polymer free volume and segmental mobility of the polymer chains. Slow polymer chain relaxations can have a significant impact on the membrane transport properties (both equilibrium and polymer relaxation-controlled permeability).

Since glassy polymers are nonequilibrium materials, the CO_2 permeation,[5] sorption, and dilation isotherms can all show hysteresis, (i.e., nonreversibility with respect to CO_2 pressure). This hysteresis is problematic for membranes, since the performance can be significantly altered by an operational upset (e.g., feed pretreatment failure and subsequent exposure to heavy hydrocarbons), even if it is only for a short duration. Field tests on cellulose acetate membranes have shown significant performance declines over an 8 month operating period.[6] Though cellulose acetate is the dominant membrane material for natural gas separations, it is very susceptible to plasticization.[7] The time dependence of permeation[8−11] and sorption/swelling[12,13] have been investigated for various polymers, but the relationships between all of these parameters and the polymer physical properties have not been reported. Wessling et al. have shown exponential relaxations for permeation[9] and dilation[12] on the same polyimide (6FDA-MDA), but an explicit relationship between the two processes was not developed. They have also looked at the relationship between the long-term kinetics of sorption and dilation, but this was on different polymers than the other studies.[8] Moreover, the longest time scales considered were 2 days and the highest pressures were 20 bar. Bohning and Springer observed significant differences in the short-term and long-term values of the partial molar volume of CO_2 and N_2O in polysulfone and poly(ether sulfone) for sorbed partial molar volumes exceeding ∼30 cm^3 (STP)/mol.[13] This is consistent with the sorbed CO_2 partial molar volume where plasticization is seen in permeation experiments with the polyimides used in this study.[14] No long-term dependence was observed for CH_4 sorption in these polymers, consistent with the fact that CH_4 is not a significant plasticizing agent.

The objective of this paper is to understand how the time dependence of CO_2 diffusivity, solubility, and membrane swelling are coupled in a plasticized membrane and how the membrane structure may be tailored by thermal annealing and cross-linking to minimize plasticization effects. To achieve this, the polymer

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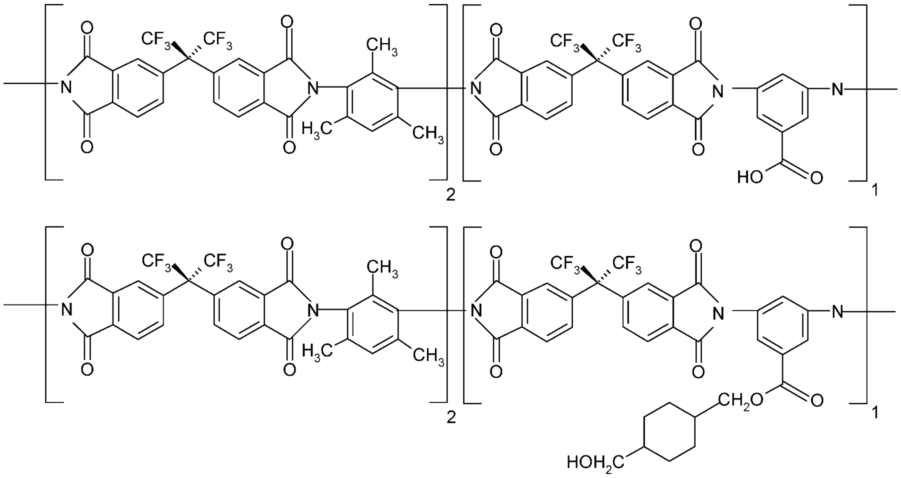

Figure 1. Polymer structures (6FDA-DAM:DABA 2:1): free acid and cyclohexanedimethanol (CHDM) monoester.

structure was systematically varied to develop a quantitative and physical description of the coupling of the permeation, sorption, and dilation with respect to the polymer structure.

The kinetics of CO_2 permeation and sorption in both un-cross-linked and cross-linked free-standing 6FDA-DAM:DABA 2:1 polyimide films were measured over long times of up to 25 days at 40 atm CO_2 pressure and 35 °C. Furthermore, dilation kinetics were measured on supported thin films (~120 nm) with in situ spectroscopic ellipsometry. The thickness of these films is on the order of that of the permselective skin in asymmetric membranes. Although the transport properties and polymer relaxations may be expected to be different for thin films vs bulk polymers, few studies have investigated submicron thin films. Comparisons of the permeation, sorption, and dilation kinetics are made to assess the effects of thermal annealing and chemical cross-linking on the CO_2 diffusivity and to determine its importance in controlling membrane plasticization. Relaxation functions are fit to the kinetic curves for permeation, sorption, and swelling to quantify the effects of thermal annealing and covalent cross-linking on the slow, long-term polymer chain relaxations.

Experimental Section

The experimental details for most of the material preparation were reported elsewhere.[14] The polymer structures of the 6FDA-DAM:DABA 2:1 polyimide (untreated and 1,4-cyclohexanedimethanol (CHDM) monoester) are shown in Figure 1. The CHDM monoester must be annealed at temperatures greater than ~160 °C for cross-linking to occur. The cast films used for permeation and sorption measurements were 40−60 μm thick.

To quantify the time-dependent effects of plasticization on the CO_2 permeability, the CO_2 feed pressure at 35 °C was increased to 40 atm over a 4 h period, and the permeability was recorded over a period of up to 25 days. The 4 h pressure ramp was chosen in order to prevent breaking the membrane from a pressure surge. All membranes were virgin before exposure to CO_2 at 40 atm. The relative permeability (P_t/P_0) is defined as the permeability at any time normalized by the permeability at effective time zero (i.e., after the 4 h pressure ramp). The permeation lag time for these membranes is less than 1 h, so the changes in the permeability were due to polymer chain relaxations and not to Fickian transient mass uptake after the 4 h initial period.

The kinetic swelling measurements were made on supported thin films (~120 nm) with in situ spectroscopic ellipsometry, as reported previously.[14] The nominal Fickian half-times for CO_2 diffusion are less than 10 s for these films, for a typical CO_2 diffusion coefficient of 1×10^{-7} cm^2/s, so the increases in film swelling were also driven by polymer chain relaxations. The films were exposed to a CO_2 pressure of 40 atm, and the film swelling was monitored over a 24 h period. Kinetic sorption measurements were made on the free-standing films using the pressure-decay method[15] and on the supported thin films using the Clausius−Mosotti equation based on refractive index measurements from the ellipsometry data.[14]

Results

Permeation. Plasticization is often associated with protracted polymer chain relaxations that tend to increase permeabilities and reduce the separation efficiency for glassy polymeric membranes, producing unpredictable long-term performance. Figure 2 shows the effect of thermal annealing and cross-linking on the relaxation-controlled permeation at 40 atm feed pressure and 35 °C. For the films treated at 100 and 130 °C, the initial permeability was chosen as the permeability measured at 8 atm feed pressure (below the plasticization pressure), since the films showed significant increases in the permeability even within the 4 h time period it took to increase the pressure to 40 atm.

For both the polymer with free acid groups and monoesterified with CHDM (i.e., cross-linkable), higher annealing temperatures led to better stability in the presence of CO_2. At the low-temperature treatments, both membranes were quite unstable. With a 220 °C treatment, the untreated film was completely soluble in NMP and showed a more significant increase in the CO_2 permeability over time than the insoluble, cross-linked membrane annealed at the same temperature. For a 295 °C treatment, both films (cross-linked and with free acid groups) were insoluble in NMP and showed good stability against CO_2 plasticization.

Swelling. The kinetic dilation experiments in Figure 3 show that the films continue to swell over long times. This underscores the importance of experimental time scales in assessing polymer properties under conditions of plasticization. It is difficult to compare the absolute time scales of the relaxation-controlled permeation, sorption, and swelling because in the swelling experiments the films are very thin and supported on a substrate. Contrary to Fickian behavior, the characteristic times cannot be scaled on the basis of the square of the film thicknesses due to the complex nature of the relaxations. Furthermore, in the permeation experi-

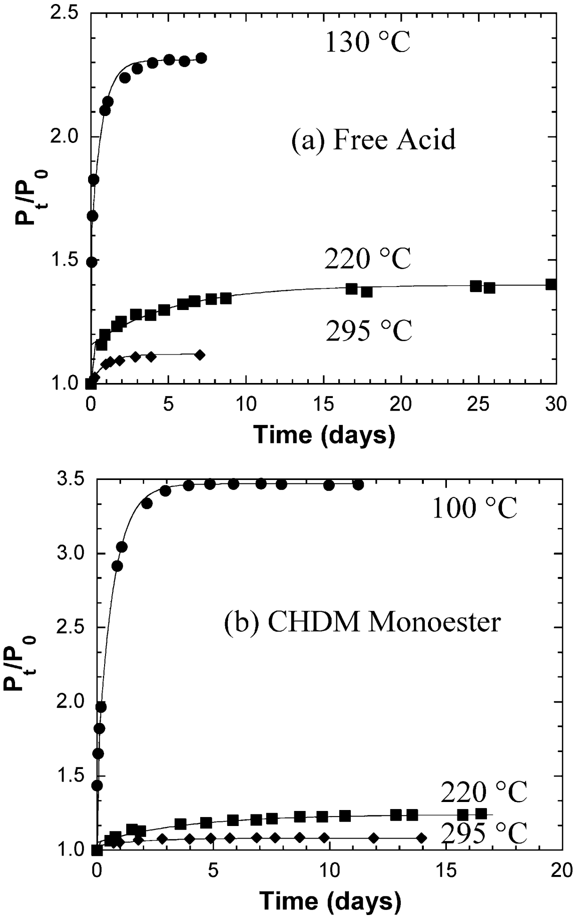

Figure 2. Relaxation-controlled permeation (6FDA-DAM:DABA 2:1): (a) free acid and (b) cyclohexanedimethanol (CHDM) monoester annealed at various temperatures. Curves are best fits from eqs 2 and 3.

ment, there is a concentration gradient across the film so the plasticization effects (e.g, polymer relaxations, changes in free volume) and the relaxations may be different than if the pressure is isotropic, as it is in the sorption and dilation experiments. Nevertheless, there are some important observations regarding the coupling of the CO_2 permeability and the polymer swelling, namely the asymptotic limits of swelling and permeability, along with the kinetics of approaching this asymptote.

Increased annealing temperatures for both the free acid-containing polymer and CHDM-cross-linked films lead to better stability, in both permeation and swelling. There is a direct correlation between the asymptotic values of permeability and swelling at 40 atm with respect to annealing temperature for both polymers. Moreover, the kinetic trajectory at which the swelling approaches this asymptotic value is related to the polymer's resistance to plasticization. The films annealed at 130 and 100 °C are much less resistant to plasticization, presumably because they do not have cross-links[16] or strong intermolecular interactions[14] acting to retard swelling. Therefore, they reach their pseudo-steady-state values very quickly. This is directly analogous to the permeability behavior shown in Figure 2, where the membranes annealed at low temperatures become unstable very quickly *and* the amplitude of this instability is large. Thermal annealing and/or cross-linking are effective in suppressing these instabilities, leading to more robust membrane performance in the presence of aggressive feed streams. Not only is the absolute final magnitude of the "permeability creep" suppressed, but also the time to reach this ultimate creep is protracted by annealing and/or cross-linking. A quantitative analysis of the relaxation phenomena describes the time scales and magnitude of the relaxation processes occurring with permeation, sorption, and swelling, as shown later in this paper.

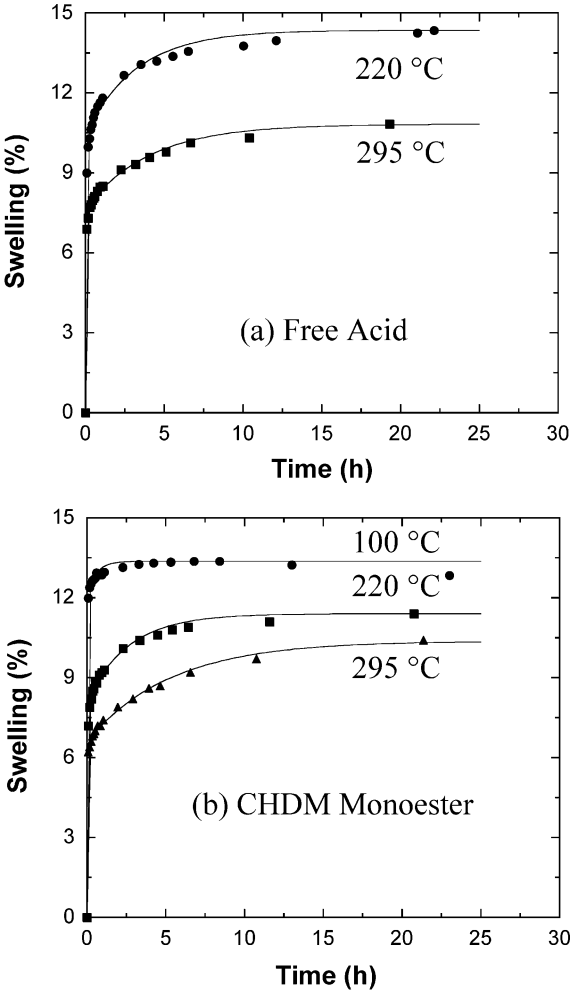

Figure 3. Relaxation-controlled swelling (6FDA-DAM:DABA 2:1): (a) free acid and (b) cyclohexanedimethanol (CHDM) monoester annealed at various temperatures. Curves are best fits from eqs 2 and 3.

Sorption by Pressure-Decay. Figure 4 shows the kinetic sorption at 40 atm for the CHDM monoester annealed at 100 and 295 °C. The annealing temperature does not have a large impact on the equilibrium CO_2 concentrations or the kinetic path taken to reach these equilibrium values. This is quite different from the permeation and swelling behavior, where the films annealed at higher temperatures have much more stable CO_2 permeabilities and do not swell as much. At higher pressures, the time taken to reach equilibrium for the thick films can be quite protracted, but the amount of excess gas sorbed as a result of these relaxations is small in comparison to the corresponding non-Fickian swelling and permeability increases. Since the long-term sorption does not depend strongly on the annealing temperature for the CHDM monoester, it appears reasonable to assume that the increases in CO_2 permeability are caused by increases in the film swelling from polymer chain relaxations that are facilitated by the sorbed CO_2.

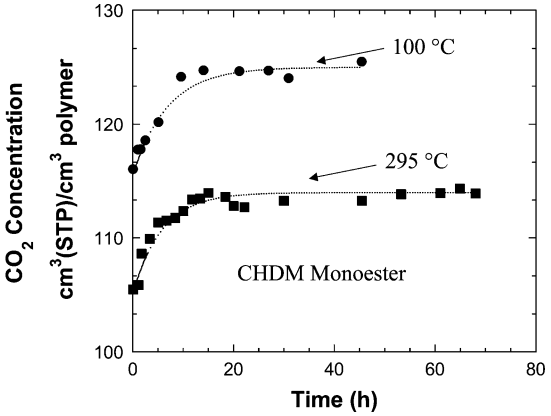

Figure 4. Relaxation-controlled sorption of bulk films by pressure-decay at 35 °C and 40 atm: CHDM monoester annealed at 100 and 295 °C. Curves are best fits from eqs 2 and 3.

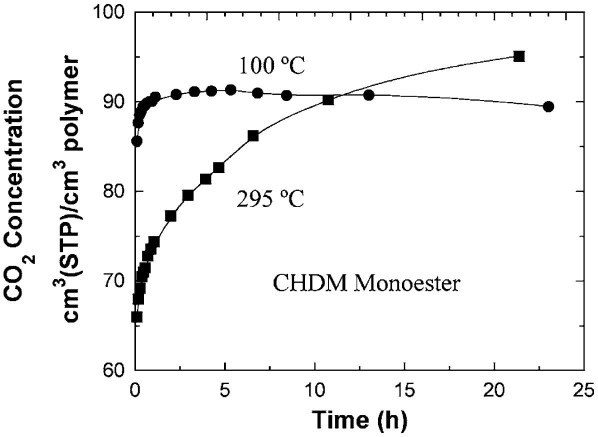

Figure 5. Relaxation-controlled sorption of thin, supported films by ellipsometry at 35 °C and 40 atm: CHDM monoester annealed at 100 and 295 °C. The curves highlight the trends in the data.

Sorption from Refractive Index. The CO_2 sorption in the glassy polymer can be estimated from the refractive index of the swollen film using the Clausius–Mosotti equation.[14,17,18] For the polyimides studied here, this technique gives a reasonable estimate of the sorption isotherms.[14] Figure 5 shows the long-term sorption at 40 atm for the CHDM monoester, annealed at 100 and 295 °C. The optical technique for the thin films shows much different behavior than that for the pressure-decay measurements of bulk films.

Both chain relaxation-induced swelling and dissolution of CO_2 in the polymer cause decreases in the swollen film refractive index. The film annealed at 295 °C appears to have much more sorption over long times, but it is likely that this result arises from the protracted swelling of the film, due to increased segmental mobility, not from large amounts of CO_2 sorption, considering the film annealed at 100 °C and the pressure-decay sorption data in Figure 4. It could be that some of the assumptions in the empirical Clausius–Mosotti model, such as a constant molar refractivity for the components, may be too simplistic to accurately model the subtleties of this complex relaxation-based dilation and residual sorption behavior. In addition, the Clausius–Mosotti model is quite sensitive to the film refractive index, where small errors (~1%) in the refractive index can propagate to larger errors (~10%) in the calculated sorption (although the error in both the thickness and the refractive index determined using the ellipsometer is less than 1%). It has been shown for other glassy polymers (100 μm melt extruded films of polysulfone and poly(ether sulfone)) that over long times the film can continue to swell without much additional sorption.[13] The same behavior is observed here (assuming the thin supported films behave in the same way as the thicker bulk films), but the optical technique is unable to show this completely because of some correlation between swelling and the calculated sorption. However, differences in the relaxation-controlled sorption between the ultrathin supported films and the thicker bulk films cannot be ruled out. Future work will focus on quantifying the effects of film thickness on the long-term sorption behavior. This is a very important issue since the thicknesses of permselective skins of practical asymmetric membranes are also ultrathin (~0.1 μm).

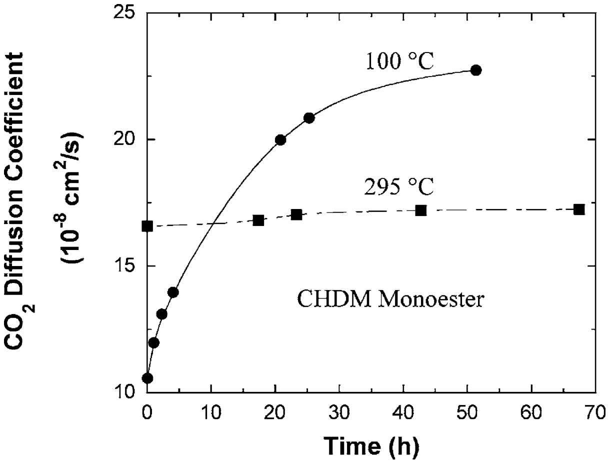

Figure 6. Relaxation-controlled CO_2 diffusion coefficient at 35 °C and 40 atm: CHDM monoester annealed at 100 and 295 °C. The curves highlight the trends in the data.

Discussion

Figure 6 shows the diffusion coefficient at the upstream face of the membrane for the CHDM film treated at 100 and 295 °C. The diffusion coefficient is calculated from the permeability and sorption coefficient, determined from the pressure-decay measurement ($D = P/S$, where P is the permeability and S is the sorption coefficient). As noted earlier, the 100 °C sample is un-cross-linked and the 295 °C sample is cross-linked and insoluble in THF and NMP. Cross-linking leads to very stable diffusion coefficients because the segmental mobility is controlled by the cross-linking, and the film swelling is reduced significantly due to the decreased mobility. Increases in the permeability for the cross-linked membrane (Figure 2) appear to be *primarily* due to increases in the sorption. For the un-cross-linked monoester (annealed at 100 °C where there is insufficient mobility for the cross-linking reaction to occur), increases in the permeability (Figure 2) are mainly due to strong increases in the CO_2 diffusion coefficient, since Figure 4 shows only moderate (~8%) increases in sorption over time.

It has been suggested that a penetrant's diffusion coefficient in rubbery polymers is related to its partial molar volume in the polymer.[19] In another study, we found that the plasticization pressure in permeation experiments correlated with a sorbed CO_2 partial molar volume of 29 ± 2 cm^3/mol for these polyimides (based on ellipsometry data), since an increase in the segmental

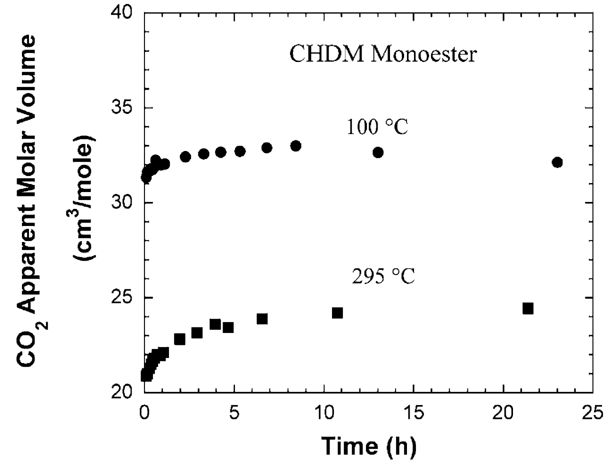

Figure 7. Long-term sorbed CO_2 apparent molar volume at 35 °C and 40 atm: ellipsometry data for CHDM monoester annealed at 100 and 295 °C.

mobility results in an upturn in the swelling and, hence, an increase in the partial molar volume.[14]

When analyzing the time dependence of the sorbed CO_2 molar volume, it is necessary to analyze the apparent molar volume instead of the partial molar volume[20]

$$\phi_{V_{CO_2}} = 22400\left[\frac{h/h_0 - 1}{C}\right]_{T,p} \tag{1}$$

The apparent molar volume of a sorbed penetrant refers to the average volume occupied per mole, as opposed to the differential volume change that is characterized by the partial molar volume. For the kinetic data (at constant pressure) considered here, changes in the apparent molar volume can be used to characterize changes in sorption and swelling for various polymer structures. The apparent molar volume is a good way to compare the effect of CO_2 sorption on different polymers because the swelling is normalized by the penetrant concentration. In the apparent molar volume calculation, the volume change in the swollen polymer upon sorption of CO_2 is attributed to volume occupied by the CO_2; however, increased occupied volume by the polymer segments due to increased mobility (rotational, vibrational etc.) facilitated by the sorbed CO_2 may also contribute to the swelling.

Figure 7 shows the CO_2 apparent molar volumes for the CHDM monoester annealed at 100 and 295 °C for sorption based on the refractive index data. Cross-linking causes a lower CO_2 molar volume for two main reasons: (I) higher starting polymer free volume[14] with higher Langmuir sorption which leads to lower swelling than sorption via a dissolution mechanism (Henry's law)[21] and (II) restricted polymer mobility that limits swelling.

For the film annealed at 100 °C, the molar volume does not change appreciably over time because the swelling reaches its asymptotic values quickly because the swelling is not retarded by cross-links. The film annealed at 295 °C shows an increase in the apparent molar volume over time as the film swells more slowly, but it remains much lower than that of the film annealed at 100 °C.

To quantify the effects of chemical cross-linking and thermal annealing on the long-term relaxation of the polymer chains, the sorption, dilation, and permeation kinetics were fit to a semiempirical model[12,22] that accounts for the Fickian diffusion and the considerably slower relaxation phenomena:

Table 1. Sorption,[a] Permeation, and Swelling Relaxation Times for CHDM Monoester Annealed at 100 and 295 °C

annealing temp (°C)	sorption (h)	permeation (h)	swelling (h)
100	6.8	16	0.57
295	5.8	47	5.3

[a] Pressure-decay technique.

$$\frac{Y(t) - Y_0}{Y_\infty - Y_0} = \phi_F + \phi_R(t) \tag{2}$$

where $Y(t)$ is the measured quantity (e.g., sorption, thickness, or permeation), ϕ_F is the Fickian contribution to $(Y(t) - Y_0)/(Y_\infty - Y_0)$, and $\phi_R(t)$ is the relaxational contribution. Furthermore, $\phi_R(t)$ can be calculated as follows:

$$\phi_R(t) = \phi_R\left[1 - \exp\left(-\frac{t}{\tau_R}\right)\right] \tag{3}$$

Equations 2 and 3 were fit to the experimental data by varying τ_R to minimize the mean-square error between the experimental and calculated data. The Fickian fraction, ϕ_F, was held constant since the Fickian contribution to the kinetic data occurs too rapidly to capture with our experimental setup.

Table 1 shows the effect of covalent cross-linking and thermal annealing on the relaxation times for the CHDM films annealed at 100 and 295 °C. Interestingly, the relaxation time, based on the swelling kinetics, increases by an order of magnitude when the annealing temperature is increased from 100 to 295 °C. This marked increase is consistent with the chains being more rigid due to cross-linking, making it more difficult for the chains to relax the strains imposed by the penetrant molecules and, hence, leading to better plasticization resistance. Moreover, the more rigid chains appear to show less ultimate swelling as well. Table 1 also shows that the relaxation times based on the pressure-decay sorption kinetics do not show a significant change with annealing temperature. However, the relaxation times based on the permeation kinetics do show a significant increase, similar to the swelling kinetics. This result suggests that the effects of covalent cross-linking and annealing temperature on the swelling behavior correlate with the effects on the permeation behavior.

The relaxation times for the permeation kinetics in Table 1 are systematically larger than the times derived from the swelling kinetics. There are a couple of possible reasons for the difference in relaxation times. First, the swelling kinetics experiments were performed on thin films (~120 nm) whereas the permeation kinetics were for much thicker films (~50 000 nm). Simulations and experiments have shown that thin films can often have lower glass transition temperatures (T_g) than the corresponding bulk films.[23,24] Others have attributed the origin of this lower T_g to a region of increased mobility at the free surface that arises from an increase in configurational freedom of the polymer chains.[23,25] When the film becomes sufficiently thin, the length scale associated with this region of increased configurational entropy becomes comparable to the total film thickness and can affect the observed film properties (i.e., finite size effects become important). Typically for supported thin films, deviations for the neat polymer T_g occur at film thicknesses below 40−50 nm. However, in the presence of a solvent, the length scales at which confinement affects other properties, such as permeation, sorption, and dilation, are unknown. Thin films, an order of magnitude thicker than those used in this study, have been shown to plasticize at lower CO_2 pressures than thick films.[26] Therefore, it is reasonable to expect that the thin films used in the swelling experiments will have faster relaxation times relative to the thicker films used in the permeation experiments.

An additional reason for the increased relaxation times in the permeation measurements is likely due to the concentration gradient that exists in these experiments as opposed to the swelling experiments, where the pressure is isotropic around the film. With a concentration gradient, the observed relaxation time is composed of the sum of relaxation times for polymer chains exposed to different CO_2 concentrations within the film. It appears that lower CO_2 concentrations may lead to longer effective relaxation times since the polymer chain mobility is lower. For example, when the polymer with free acid groups was annealed at 220 °C and exposed to 40 and 92 atm of CO_2 in separate experiments, the swelling relaxation times were 3.3 and 1.6 h, respectively. Near the downstream face of the membrane, the relaxations are negligible due to the low CO_2 concentrations. This gradient, coupled with the possible thin film effects, likely explains the differences in the permeation and dilation relaxation times.

The permeation, sorption, and dilation isotherms of glassy polymers all show hysteresis. This behavior is typical for glassy polymers that are exposed to plasticizing penetrants, where the polymer is unable to rapidly relax back to its unconditioned state once the plasticizer is removed. This is particularly damaging to a membrane operation, where an “operational upset” (e.g., feed pretreatment failure) can expose the membrane to plasticizing components, and the effect of this will be seen for periods well beyond just the exposure time. The permeation and sorption kinetics show that heat treatment and covalent cross-linking are effective at minimizing instabilities in the CO_2 diffusion coefficient, in terms of both the amplitude and time scales of this disturbance. Therefore, cross-linking makes the membrane operation more stable over wider operating conditions, and the membranes are better able to sustain operation under upset conditions.

Conclusions

The time dependence of CO_2-induced polymer chain relaxations has been investigated through measurements of the permeation, sorption, and swelling kinetics of polyimide membranes. The permeability and swelling can be stabilized by simple thermal annealing of the 6FDA-DAM:DABA 2:1 with free carboxylic acid groups. These COOH groups were also esterified with 1,4-cyclohexanedimethanol and cross-linked at sufficiently high annealing temperatures. Cross-linking presumably increases the rigidity of the chains, leading to a significant increase in the stability of the CO_2 permeability and a decrease in the sorbed CO_2 apparent molar volume.

The magnitudes of the relaxation-induced increases in swelling and CO_2 diffusion can be correlated with respect to the polymer annealing temperature. Moreover, relaxation times derived from the kinetic data increase with increased cross-linking. Furthermore, analogous trends are observed between the relaxation times determined from the permeation kinetics and those determined from the swelling kinetics, with respect to annealing temperature. However, the swelling relaxation times are faster than the permeation relaxation times. This difference is likely due to the presence of a concentration gradient in the permeation experiment and increased chain mobility at the free surface. This mobility at the free surface is a more significant factor in determining the polymer relaxations for the much thinner films used in the swelling experiments than for the bulk films used in the permeation and pressure-decay sorption experiments. The permeation relaxations in ultrathin asymmetric membranes may be accelerated due to these thin-film effects.

Pressure-decay sorption measurements indicate that polymer film swelling (without corresponding levels of CO_2 sorption) is responsible for the plasticization observed in permeation experiments. Thus, sorption is not the best indicator of the long-term membrane plasticization resistance. Swelling of the polymer causes an increase in the CO_2 diffusion coefficient. Cross-linking and thermal annealing reduce swelling to stabilize the CO_2 diffusion coefficient, thus making the membrane performance more robust and predictable.

Since thin films plasticize at lower pressures than thick films, and we have correlated plasticization with polymer swelling, it is natural to expect that the dynamics of permeation and swelling would be affected by the film thickness. Spectroscopic ellipsometry can be used to obtain rapid kinetic measurements on length scales that are on the order of that of the selective skin in asymmetric hollow fiber membranes. An understanding how the plasticization-induced instabilities depend on the film thickness and polymer structure is of great fundamental and practical interest.

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