Macromolecules 1990, 23, 1353-1360

Carbon Dioxide Conditioning Effects on Sorption and Volume Dilation Behavior for Bisphenol A-Polycarbonate

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Received March 22, 1989

ABSTRACT: Sorption/desorption and volume dilation/consolidation measurements are reported for Bisphenol A-polycarbonate in the presence of carbon dioxide pressures up to 900 psia at 35 °C. Second-exposure sorption and desorption isotherms are presented after conditioning samples at 300, 600, and 900 psia. The sorption and volume-dilation data are used to calculate the partial specific volumes of the polymer and penetrant as functions of sorption level. Qualitative physical arguments concerning the nature of the conditioning effect are presented based on this thermodynamic analysis of the gas-glassy polymer system. A fugacity-based dual-mode sorption model is shown to be very useful for describing the sorption and volume-dilation results. The increase in solubility observed during the desorption hysteresis cycle does not appear to be due to the simple introduction of additional packing defects responsible for the Langmuir-like sorption in the as-received sample. Specifically, more subtle and generalized intersegmental, residual dilation appears to be responsible for the enhanced sorption during the desorption process. After total removal of the sorbed gas, however, evidence of a small amount of additional packing defects can be detected with subsequent resorption. This small conditioning effect is shown to be reversed by annealing the polycarbonate sample at 135 °C.

Introduction

Changes in the physical properties of glassy polymers caused by so-called "conditioning" treatments during the initial exposure of the polymer to high activities of a penetrant have been reported in earlier studies.[1-10] Following the initial exposure to the penetrant, the sorption behaviors of penetrant-glassy polymer systems have been shown to be reproducible for multiple exposures.[6,9,10-13] This study presents an investigation of the effects of different maximum CO_2 conditioning pressures, ranging from 300 to 900 psia, on solubility and volume-dilation behavior measured during a second exposure of the sample to CO_2.

In our earlier study[1] results were presented for hysteresis in sorption and volume dilation for polycarbonate exposed to CO_2 pressures as high as 900 psia, and Kamiya et al.[13] have also reported smaller but still significant sorption hysteresis effects for polycarbonate exposed to CO_2 pressures as high as 735 psia. It is reasonable to expect that, at a fixed temperature, the magnitude of the hysteresis observed for polycarbonate is related to the sorption level at the highest penetrant pressure experienced by that sample. In this context, solubility and volume hysteresis data were collected during repressurization following the first exposure for each of the three maximum exposure pressure cases to provide a systematic characterization of the hysteresis process and allow testing of hypotheses concerning the cause of the effect.

By combining the sorption and volume-dilation measurements, one can determine the volume change on mixing for the gas-polymer system and, hence, the partial specific volumes of both the penetrant and polymer as a function of the CO_2 sorption level. These partial specific volume determinations were made under conditions of both the first and second exposure to CO_2 as well as during desorption hysteresis following equilibration at each maximum exposure pressure.

Finally, Chan and Paul[9] have shown that sub-T_g annealing of as-received polycarbonate reduces the solubility and enthalpy while increasing the sample density. The effect of such thermal treatments on the conditioned samples prepared here was studied to determine the degree of thermal reversibility of the CO_2-induced conditioning process.

Background

For many years the so-called dual-mode model has been used to describe gas sorption into glassy polymers. Inherent in the dual-mode model is the concept of sorption into two idealized environments.[14-16] One population of sorption (C_D) is viewed as arising from uptake into a dissolved state. This behavior is visualized as being similar to sorption in rubbery polymers and low molecular weight liquids and is described by Henry's Law sorption. The second population of sorption (C_H) is viewed as being due to uptake into molecular scale berths or "microvoids", which are present due to the nonequilibrium nature of glassy polymers. This mode of sorption is described by a Langmuir isotherm. The model is represented mathematically by

$$C = C_D + C_H \tag{1a}$$

$$C = k_D p + C_H' bp/(1 + bp) \tag{1b}$$

where k_D is the Henry's Law constant, in cubic centimeters at STP per cubic centimeters of the polymer atmosphere, b is the Langmuir affinity constant, in reciprocal atmospheres, and C_H' is the Langmuir capacity parameter, in cubic centimeters at STP per cubic centimeters of the polymer. In cases where nonideal vapor-phase behavior is significant, eq 1b can be expressed in terms of penetrant fugacity rather than pressure. In this case, the parameters in the above expression are generally denoted as k_D^*, b^*, and $C_H'^*$, respectively to designate a fugacity fit.

Experimental Section

The Bisphenol A-polycarbonate used in this study was supplied by the General Electric Co. in film form. The density of the film samples was determined by aqueous density gradient column to be 1.200 ± 0.001 g/cm^3. The thickness of the films used was nominally 3 mil (0.076 mm) to 5 mil (0.13 mm).

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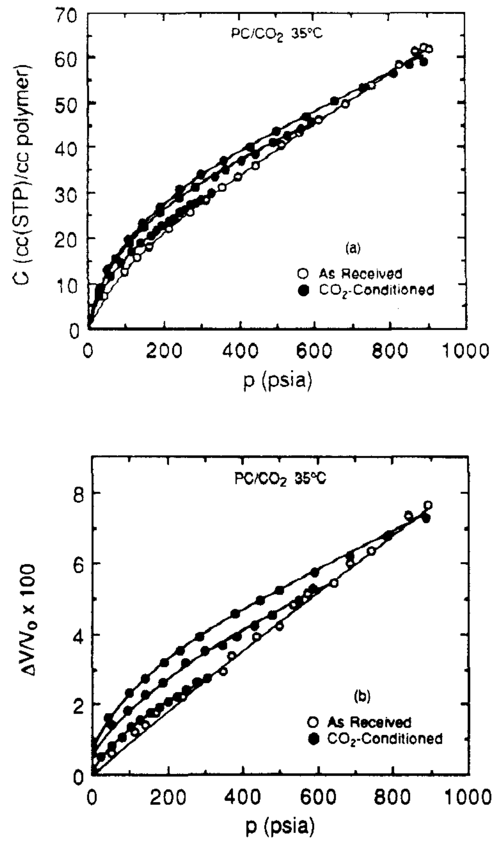

Figure 1. (a) CO_2 sorption isotherms for conditioning pressures of 300, 600, and 900 psia. Solid lines represent fits based on eq 1b. (b) CO_2 volume-dilation isotherms for conditioning pressures of 300, 600 and 900 psia.

The carbon dioxide used in this study was supplied by Linde, Inc., at a purity of 99.99%.

Pure gas sorption measurements were made with a dual volume pressure decay cell. The procedures for using this sorption cell for measurements up to 68 atm (1000 psia) have been described earlier.[1] Procedures for volume-dilation measurements are also identical with those described in an earlier study.[1]

In all cases for sorption and desorption, extremely long times were allowed to ensure that the gas–polymer system had reached equilibrium. For sorption and desorption measurements, typically 24–48 h were allowed after any detectable change in sorption or volume-dilation level. Also on several occasions the sorption and volume-dilation levels were monitored for periods up to 1 week during the depressurization process with no significant consolidation (<0.02%) back to the level measured during pressurization. Additionally, a similar study of CO_2 permeability in polycarbonate by Jordan et al.[2] showed stable increases in permeability for periods up to 8 weeks. Because of the extremely protracted relaxation times observed during the depressurization process, it appears that more than one semipermanent state exists for the gas–polymer system over a time scale of days or weeks.

Results and Discussion

Sorption and Volume Measurements for Polycarbonate Conditioned at Different CO_2 Pressures. In this section only isotherms measured for increasing increments of pressure will be discussed. The following section will report history-dependent results for decreasing pressure increments after preswelling with high-pressure CO_2. The second-exposure isotherms, measured during pressurization, will be referred to as "conditioned" isotherms. Sorption and volume-dilation isotherms are presented in Figure 1 for polycarbonate samples conditioned at maximum pressures of 300, 600, and 900 psia as well as measurements for an as-received or unconditioned sample. It is apparent from parts a and b of Figure 1 that conditioning effects reported by previous authors for pressures as high as 300 psia are much smaller than increases in the sorption or volume-dilation level that can be realized by conditioning at pressures as high as 900 psia.[6,9,11]

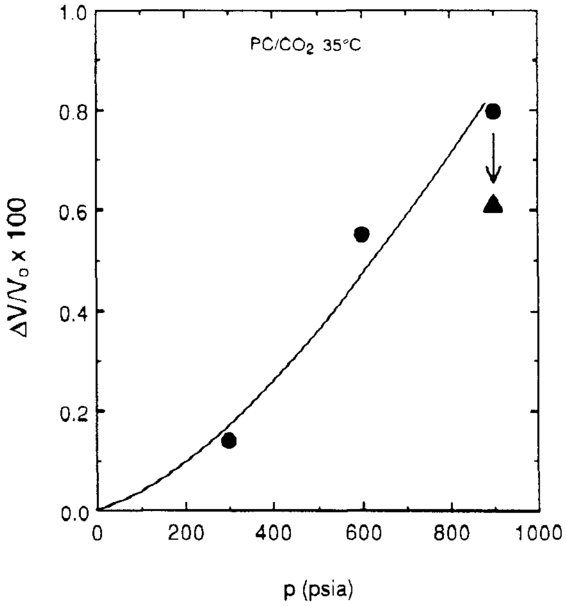

Figure 2. Excess residual volume in penetrant-free polycarbonate versus CO_2 conditioning pressure following total removal of CO_2. (▲) Volume-dilation level after 3 mo in the depressurized state.

The sorption and volume-dilation measurements for the conditioned samples intersect the data for the unconditioned sample at the conditioning pressure in all cases. Presumably, measurements for samples conditioned at any pressure between zero and 900 psia would also intersect the unconditioned first-exposure isotherm at the conditioning pressure considered. The magnitude of the conditioning effect is, therefore, directly related to the level of the preswelling agent used to condition the glassy polymer. A physical interpretation for this observation was offered earlier in terms of the introduction of excess volume in the glassy sample during the conditioning treatment step.[1] This concept will be developed further in later discussions.

For the CO_2-conditioned samples, the volume-dilation behavior is more complicated than the sorption behavior. This added complexity is presumably related to the observation that the volume dilation for the conditioned samples is not zero at the zero-pressure intercept. Aqueous density gradient column measurements confirmed that the density of the 900 psia CO_2-conditioned PC sample had decreased to 1.194 g/cm^3. This represents a 0.5% decrease in density as compared to the as-received sample (ρ = 1.200 g/cm^3). Figure 2 shows results for the semipermanent excess volume introduced into PC after removal of CO_2 following conditioning at 300, 600, and 900 psia. It is apparent that as the conditioning pressure is increased the excess volume introduced into the polymer increases dramatically. The residual volume-dilation values reported here were measured after 48 h under vacuum, and the volume continues to consolidate very slowly in the *absence* of penetrant. We have found, however, that even after 3 mo in the depressurized state, most (>75%) of the volume introduced by conditioning with 900 psia CO_2 is retained by the polymer. Relax-

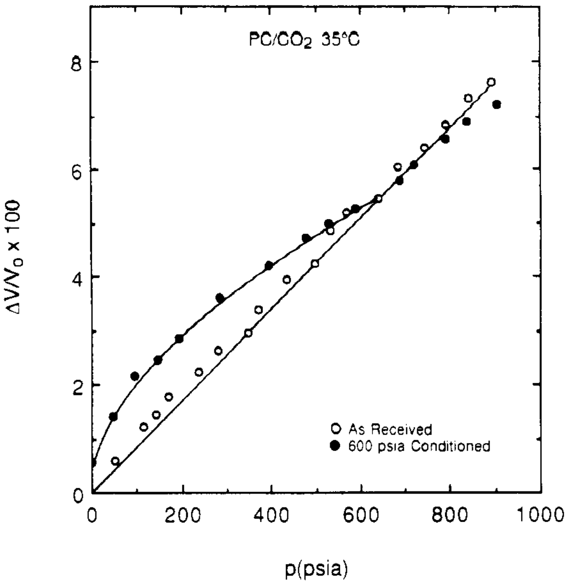

Figure 3. Second CO_2 volume-dilation isotherm after 600 psia CO_2 conditioning.

ation times are extremely long in the glassy state; therefore, chain packing perturbations introduced by volume swelling with CO_2 tend to become a semipermanent feature of the glass[6] even in the absence of the penetrant. In the presence of the conditioning penetrant, the relaxations are even more effectively suppressed and appear to be prevented over extended periods of over 1 mo[2] even though simple diffusive equilibration occurs over a time frame of several hours.

To simplify the comparison of polycarbonate conditioned at different CO_2 pressures, the volume dilation was calculated on the basis of the initial volume for the as-received sample. This approach allows one to make a more convenient comparison of the conditioning effect because the volume dilation for all conditioning pretreatments can be easily related to the actual volume of the gas-polymer system. For instance, the excess volume introduced into the sample by conditioning at 900 psia is approximately 0.8%. If the volume-dilation values for the 900 psia conditioned sample were plotted using a redefined initial volume, the volume dilation at 900 psia would be only 6.4% instead of 7.5%. This would be misleading since it would suggest that the volume isotherm for the conditioned sample is lower than the volume-dilation isotherm for the unconditioned sample. However, in fact, the *volumes* of both the unconditioned and conditioned samples are essentially *equivalent* at 900 psia. Using the as-received volume basis to report dilation data also makes it clear that the dilation isotherms for 300 and 600 psia conditioning intersect the unconditioned isotherm at their respective conditioning pressures.

For unconditioned PC, the volume-dilation isotherm is essentially linear with increasing pressure. In contrast, the volume-dilation isotherms for the conditioned samples are slightly concave to the pressure axis at pressures below the conditioning pressure. The volume-dilation measurements for a second exposure after 600 psia CO_2 conditioning, shown in Figure 3, are concave to the pressure axis below the conditioning pressure, but above the conditioning pressure the response again tracks along the same linear relationship as was found for the first exposure. Consequently, it appears that the relationship between volume dilation and pressure for glassy polymers can be either concave or essentially linear with pressure depending on the conditioning protocol for that sample. However, it appears that the volume-dilation isotherm will only be concave to the pressure axis at pressures lower than a prior conditioning pressure for that sample. The implications of this phenomenon and a physical rationalization of the volume response for glassy polymers due to the conditioning process will be discussed further below.

Partial Molar Volume Determinations for Pressurization with CO_2. The polymer and penetrant partial specific volumes shown in parts a-c of Figure 4 were determined graphically by the tangent slopes of specific volume data calculated using the sorption and volume-dilation measurements in parts a and b of Figure 1. Figure 4 shows that the partial specific volume of the polymer, V_p, changes only slightly as the sorption level of CO_2 is increased. On the other hand, the partial specific volume of CO_2 is a strong function of the CO_2 sorption level. As noted earlier,[1] the partial specific volume of CO_2 at infinite dilution in unconditioned polycarbonate is some 70% lower than a typical value for CO_2 in organic liquids and rubbery polymers. The partial specific volume increases significantly with increasing mass fraction of sorbed CO_2. However, even at a mass fraction of 8%, the partial specific volume for CO_2 is still some 20–25% lower than for that CO_2 in organic liquid or rubbery polymer environments. The large depression in the partial specific volume of CO_2 in glassy polycarbonate can be rationalized in terms of accommodation of some of the CO_2 molecules in a fixed number of molecular scale packing defects present in quenched glasses.[1] Such observations are clearly consistent with the concept of molecular scale gap filling implicit in the so-called dual-mode sorption model.

Data in Figure 2 indicate that the semipermanent excess volume introduced by CO_2 conditioning increases with conditioning pressure. The introduction of additional excess volume in the conditioned glassy samples appears to cause a small but experimentally significant depression of the CO_2 partial specific volume as the conditioning pressure is increased. This effect can be rationalized physically as being due to an increase in the fraction of sorption, which occurs in preexisting packing defects in the conditioned glassy solid as the conditioning process becomes more extensive. For instance, the CO_2 infinite dilution partial specific volume for the unconditioned sample is approximately 0.30 cm^3/g while the CO_2 infinite dilution partial specific volume for the 900 psia CO_2-conditioned sample is reduced to 0.25 cm^3/g. The CO_2 infinite dilution partial specific volumes for the other two conditioning pressures also fall within this range.

A depression in the partial specific volume of CO_2 due to conditioning is consistent with the qualitative viewpoint that sorption into additional excess volume, which has been introduced into the glassy samples by conditioning, allows for increases in the sorption level with minimal increases in volume dilation. This is because extra gas can sorb into additional volume packing defects in the conditioned polymer without the need to separate the polymer chains as much as was necessary for the unconditioned sample.

Dual-Mode Analysis. The so-called "dual-mode" sorption model provides a simple but very useful framework for discussion of gas and vapor sorption in glassy polymers. Shown in Table I are dual-mode parameters determined from the experimental data for the CO_2-conditioned samples using a nonlinear Marquardt algorithm.[17] Figure 1a shows the experimental data along with solid lines that represent sorption calculations from the dual-mode model using the parameters in Table I.

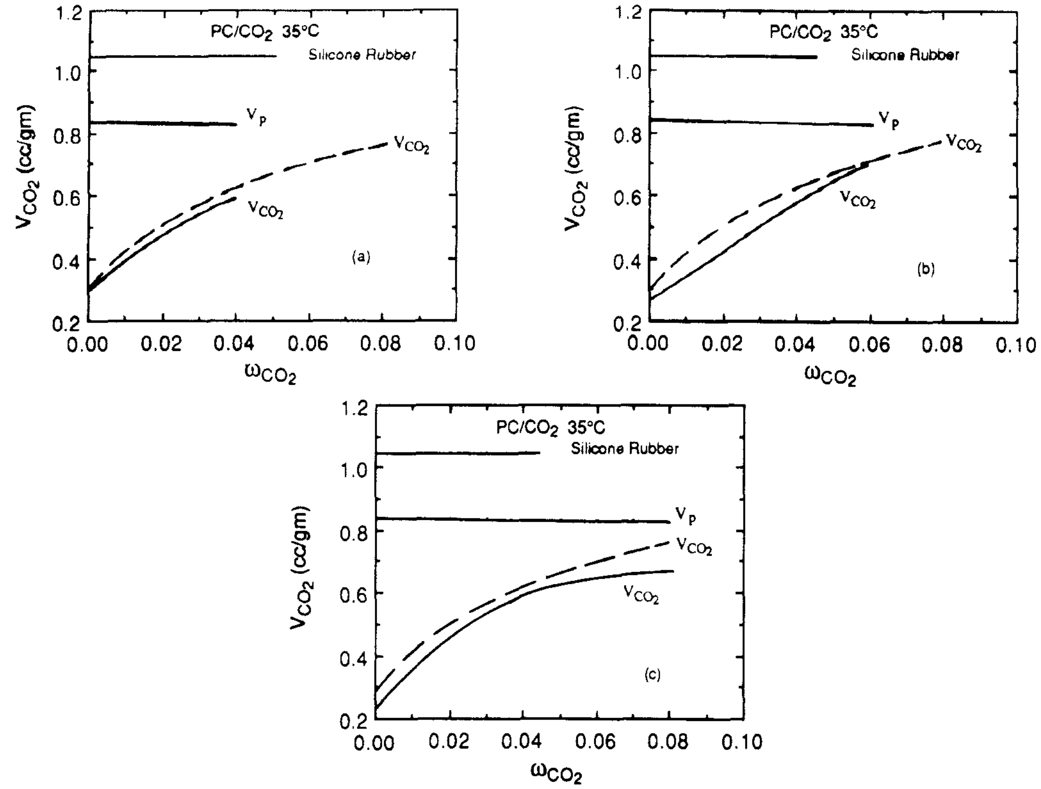

Figure 4. Partial specific volume of CO_2 and polycarbonate as a function of CO_2 mass fraction: (a) 300 psia conditioned sample, (b) 600 psia conditioned sample, (c) 900 psia conditioned sample; (– –) CO_2 partial specific volumes measured in unconditioned PC, (—) CO_2 partial specific volumes measured in CO_2-conditioned samples. The CO_2 partial specific volume measured in silicone rubber[1] is also indicated.

Table I
Dual-Mode Sorption Parameters for CO_2 Sorption in Polycarbonate at 35 °C

condition pressure, psia	basis	k_D, cm^3(STP)/cm^3 atm	C_H', cm^3(STP)/cm^3	b, atm^{-1}
440[a,b] (30 atm)	pressure	0.685	18.80	0.262
440[a,b] (30 atm)	fugacity	0.833	17.04	0.290
300[a]	pressure	0.634	17.91	0.252
300[a]	fugacity	0.788	15.88	0.288
300	pressure	0.681	17.30	0.261
300	fugacity	0.844	15.16	0.303
600	pressure	0.587	29.61	0.194
600	fugacity	0.843	19.42	0.265
900	pressure	0.542	29.21	0.167
900	fugacity	0.868	21.24	0.257

[a] Data not corrected for a small change in the volume of the sample. This has been shown to be a small factor at these pressures.[1]
[b] As determined by Koros et al.[18]

The dual-mode parameters listed in Table I are for both a pressure-based model and a fugacity-based model. Because CO_2 is highly nonideal at high pressures, a fugacity basis is preferred to compare parameters for the different conditioning treatments. Using a fugacity basis rather than a pressure basis decouples the nonideal gas-phase effects from the more complex phenomena for the polymer phase. Therefore, using a fugacity-based fit allows a thermodynamically rigorous comparison of the dual-mode parameters for different conditioning protocols.

Increases in sorption after conditioning would be expected to arise from increases in the Langmuir capacity parameter, C_H', with little change in k_D or b in eq 1.[6] Indeed, the dual-mode parameters in Table I determined for different CO_2-conditioning protocols support the earlier notion that conditioning principally affects the Langmuir capacity parameter with relatively little dependence of k_D and b on the conditioning pressure.

In an earlier study assumptions inherent in the dual mode were used to predict the volume-dilation behavior of glassy polymers.[1] The volume-dilation predictions are based on the assumption that the Langmuir sorption term in the dual-mode model corresponds to a true hole-filling process. The volume dilation is, therefore, predictable in terms of the fraction of CO_2 sorbed according to the linear sorption term k_Dp in eq 1b. For this prediction the partial molar volume of CO_2 is taken to be $\bar{V}_{CO_2}$ = 46 cm^3/mol, which is equivalent to the average value measured in various organic liquids[19] as well as the value measured in silicone rubber.[1] If one assumes this volume also applies to the polymer state at 35 °C and is essentially constant, one can predict the volume dilation based on either the total penetrant concentration, C_T, or the dissolved concentration, C_D, as shown in eqs 2a and 2b, respectively.

$$\frac{\Delta V}{V_o} = \left[k_Dp + \left(\frac{C_H'bp}{1+bp}\right)\right]\left(\frac{\bar{V}_{CO_2}}{22415}\right) \tag{2a}$$

$$\frac{\Delta V}{V_o} = k_Dp\left(\frac{\bar{V}_{CO_2}}{22415}\right) \tag{2b}$$

Similar to eq 1b, nonideal gas-phase effects can be treated by expressing eq 2 in terms of penetrant fugacity rather than pressure as shown in eqs 3a and 3b.

$$\frac{\Delta V}{V_o} = \left[k_D^*f + \left(\frac{C_H'^*b^*f}{1+b^*f}\right)\right]\left(\frac{\bar{V}_{CO_2}}{22415}\right) \tag{3a}$$

$$\Delta V V_o = k_D^*f\left(\frac{\bar{V}_{CO_2}}{22415}\right) \tag{3b}$$

Figure 5a shows that the volume dilation for the unconditioned sample is represented very well for the entire

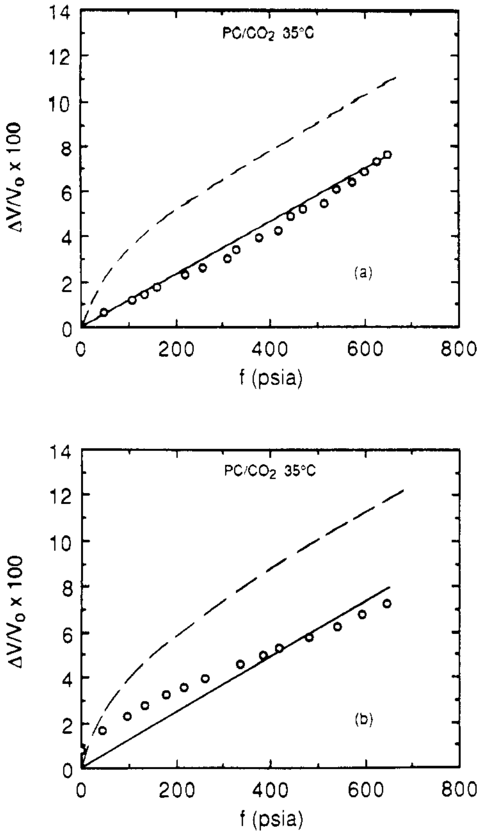

Figure 5. Volume-dilation predictions based on the dual-mode model for (a) as-received PC and (b) 900 psia CO_2-conditioned PC: (- -) based on C_T; (—) based on C_D.

range studied using the fugacity-based k_D^*. In the earlier study it was noted that there was a tendency for the volume-dilation data to fall below the dual-mode prediction at high pressures. However, Figure 5a shows that the data agree quite well with the prediction when plotted versus fugacity because fugacity more accurately reflects the true activity of the gas at high pressures.

Figure 5b shows the volume-dilation results for the 900 psia CO_2-conditioned sample as compared to the fugacity-based dual-mode prediction (eq 3b). Also, the predictions of eq 3a are shown as the dashed line for comparison. It is apparent that the volume-dilation results for the 900 psia CO_2-conditioned sample are more strongly concave to the pressure axis than dilation for the unconditioned sample. Hence, the dual-mode prediction does not provide as good a description of the volume-dilation behavior for this case.

Assuming the unrelaxed volume introduced into the sample during conditioning simply augmented that present in the original sample with no change in the Henry's Law environment, the volume dilation during the second sorption would not return to the same volume observed during the initial exposure at the maximum conditioning pressure. As noted earlier, however, the volumes do, in fact, return to the same points at each of the maximum conditioning pressures considered (i.e., 300, 600, or 900 psia). It appears, therefore, that the additional unrelaxed volume present in the conditioned glass after removal of penetrant is redistributed during the second exposure to the penetrant. Thus, while on the basis of sorption alone, one can formally assign sorption increases observed during the second cycle to simple Langmuir saturation of additional packing defects, the volume data suggest that more complex phenomena are at play.

Hypothetical Explanation of Second-Exposure Dilation Results. Consider the residual volume introduced during conditioning and subsequent removal of penetrant (zero-pressure intercept in $\Delta V/V_o$ in Figure 1b). We speculate that this volume can be attributed to introduction of residual packing disruptions in the matrix that are too small to accommodate a penetrant. Further, we suggest that these disruptions serve as sources of local volume to reduce the need to dilate the matrix by the full amount, ΔV^*, needed to accommodate a given dissolved penetrant. The process of sorption and desorption of the gas, while disruptive, is much less dramatic than the quenching process from the rubbery to the glassy state. Presumably, packing disruptions resulting from the gas-exposure conditioning process are correspondingly more subtle than the rubber-to-glass quenching process. The higher the conditioning pressure, of course, the larger the number of disturbances.

Upon resorption to the original conditioning pressure, it seems reasonable that energetic considerations would favor reutilization of such locally available volume rather than requiring the molecule to overcome the full cohesive energy resistance of the matrix by opening totally new gaps of the required ΔV^* for dissolution. This later, less favorable, situation would result in a larger ultimate volume on the second sorption. The hypothetical tendency for the excess volume introduced by conditioning to be reutilized for dissolution of additional penetrant sorbed during the second-exposure cycle is consistent with the above observations that indeeed the same ultimate volume is achieved on the first and second cycles.

Moreover, since there is only a fixed amount of the newly introduced volume which is eventually allocated as resorption occurs, one can understand the tendency of the sample to return to the same volume and sorption level as in the original conditioning exposure. This is true whether the original conditioning was done at 300, 600, or 900 psia. Since after the newly available volume has been reallocated to aid in accommodating resorbing penetrants in dissolved environments, additional sorption above the maximum previous exposure pressure again requires the introduction of additional ΔV^* per dissolved penetrant.

As time passes in the absence of penetrant, these already subtle disruptions will tend to dissipate further to be uniformly distributed throughout the matrix, and they will eventually relax totally out of the sample. Measurements shown above for a sample allowed to relax in the penetrant-free state for 3 mo indicated that very little relaxation had taken place over this time frame. Thus, total relaxation of disturbances created by CO_2 conditioning appears to require an extremely long time.

Hysteretic Behavior of Sorption and Volume Dilation for Polycarbonate Conditioned with High-Pressure Carbon Dioxide. Parts a and b of Figure 6 show desorption and volume consolidation results for the three conditioning cycles along with the initial sorption isotherm for the unconditioned or "as-received" polycarbonate sample. It is apparent that the desorption values for solubility and volume are significantly greater than either the first or conditioned sorption resonse shown earlier in parts a and b of Figure 1. Two sets of points are shown for 600 and 900 psia desorption, indicating that the desorption hysteresis is reproducible. Furthermore, parts a and b of Figure 6 show that the desorption hysteresis at 900 psia is much larger than that for either 300 or 600 psia cycles.

Parts a–c of Figure 7 show CO_2 partial specific volumes determined from the tangent slope of total specific volume data calculated from the desorption and volume

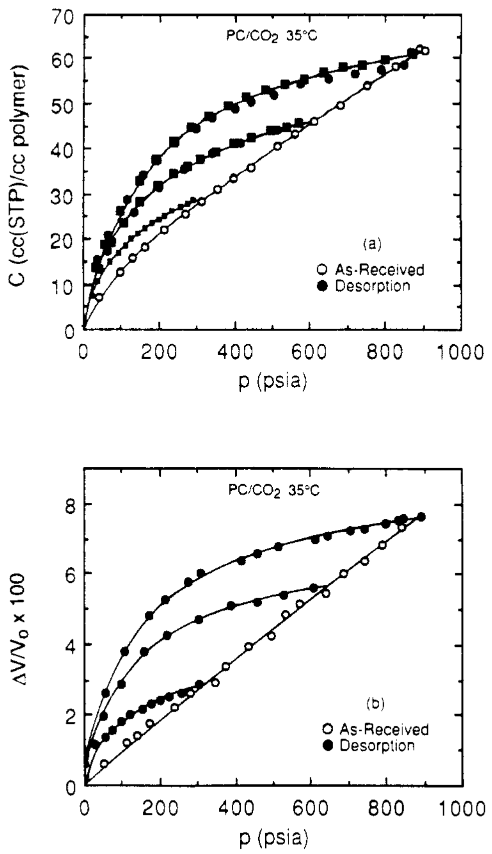

Figure 6. (a) Initial CO_2 sorption and desorption after conditioning pressures of 300, 600, and 900 psia. (b) Initial volume dilation and consolidation after conditioning pressures of 300, 600, and 900 psia.

consolidation measurements shown in parts a and b of Figure 6. Clearly, the CO_2 partial specific volume behavior is complex and displays a maximum value not seen in the case of pressurization. Because the partial specific volume behavior is similar during depressurization for all three conditioning pressures, results for the 900 psia cycle in Figure 7c will be used for discussion purposes since this isotherm shows the largest hysteresis effects. Figure 7c shows that at a mass fraction of 0.08 the partial specific volume is approximately 0.57 cm^3/g. As the pressure is lowered, the partial specific volume increases to a value of approximately 0.68 cm^3/g at a mass fraction of 0.048. A mass fraction of 0.048 corresponds to a pressure of 108 psia. As the pressure is lowered further, the partial specific volume decreases rapidly to a value of approximately 0.38 cm^3/g at infinite dilution.

The increase in the partial specific volume as the pressure is initially decreased may reflect the fact that, in the initial stages of depressurization, where significant penetrant is still present, the excess volume in the polymer relaxes easily. The maximum in the partial specific volume is reached at a relatively low pressure (approximately 100 psia). At this point the fraction of gas residing in packing defects or molecular scale void volume in the glass is presumably increasing quite rapidly. Hence, the fraction of gas that contributes to significant volume contraction upon desorption becomes a smaller fraction of the total gas population in the polymer. This, of course, will tend to make the apparent average partial specific volume decrease rapidly. At infinite dilution, however, the partial specific volume for depressurization is still 50% greater than the partial specific volume for pressurization.

Examination of the Hysteresis Behavior. Applicability of the Dual-Mode Model. Although several authors have measured hysteresis in solubility and volume dilation for high-pressure CO_2 sorption in glassy polymers, no one has offered a clear explanation for such behavior. Using the physically based parameters of the dual-mode model, the behavior of gas sorption in glassy polymers has been shown to be described very well at pressures as high as 900 psia. Table II shows dual-mode parameters determined for both pressurization and depressurization for CO_2 sorption in PC at various conditioning pressures. The physical, rational consistency of the pressurization parameters has been discussed in the previous section. However, in all cases for the depressurization cycle it is apparent that the parameters determined from a nonlinear regression are very different from the pressurization cycle. The most striking characteristics of the depressurization parameters are the large increases in the Langmuir capacity, C_H', and large decreases in the Henry's Law coefficients, k_D. Indeed, if one considers the solubility isotherm for desorption, it is apparent that there is an increase in the curvature of the isotherm as compared to the pressurization case. However, we feel such an "ad hoc" use of the dual-mode model may not be justified, and one must more carefully consider the details of the behavior of the polymer–gas system during depressurization.

Even though the parameters determined from a nonlinear regression suggest there is a large increase in the Langmuir concentration, C_H', along with a large decrease in the dissolution concentration, k_D, Figure 7 above shows that during depressurization the magnitude of the partial specific volume is very similar to the partial specific volume during pressurization. If there was such a large shift in the fraction of the gas residing in Langmuir and dissolution sites, one would expect a corresponding large depression in the partial specific volume during depressurization. The absence of such a large depression in the partial specific volume indicates that this simple explanation is not satisfactory.

Jordan et al.[2] have shown that during depressurization the permeability increases steadily as the pressure is reduced. At low pressures, the permeability is on the order of 100% greater than the permeability measured for the pressurization case. Such large increases in permeability cannot be explained by such a large increase in the lower mobility Langmuir population. These large increases in permeability for CO_2 in PC, however, are consistent with significant increases in the dissolution solubility, C_D, and only minor enhancement in the Langmuir solubility, C_H.

It is possible that the high degree of swelling of the polymer by the gas at high CO_2 pressures has changed the microenvironment of the glassy sample. This change has occurred by effectively lowering the cohesive energy density of the glass. That is, CO_2 conditioning has introduced subtle submolecular scale disruptions into the glassy sample making it energetically easier for more gas to exist in the polymer at any penetrant pressure during depressurization.

Sub-T_g Annealing of CO_2-Conditioned PC. The CO_2-conditioning process is believed to be caused by perturbation of interchain packing accompanied by inhibition of the polymer morphology to return to its original conformation. Hence, the conditioning process should be reversible by increasing the thermal energy of the polymer chains to facilitate motions necessary to return to a more densely packed arrangement. Thermal treatment

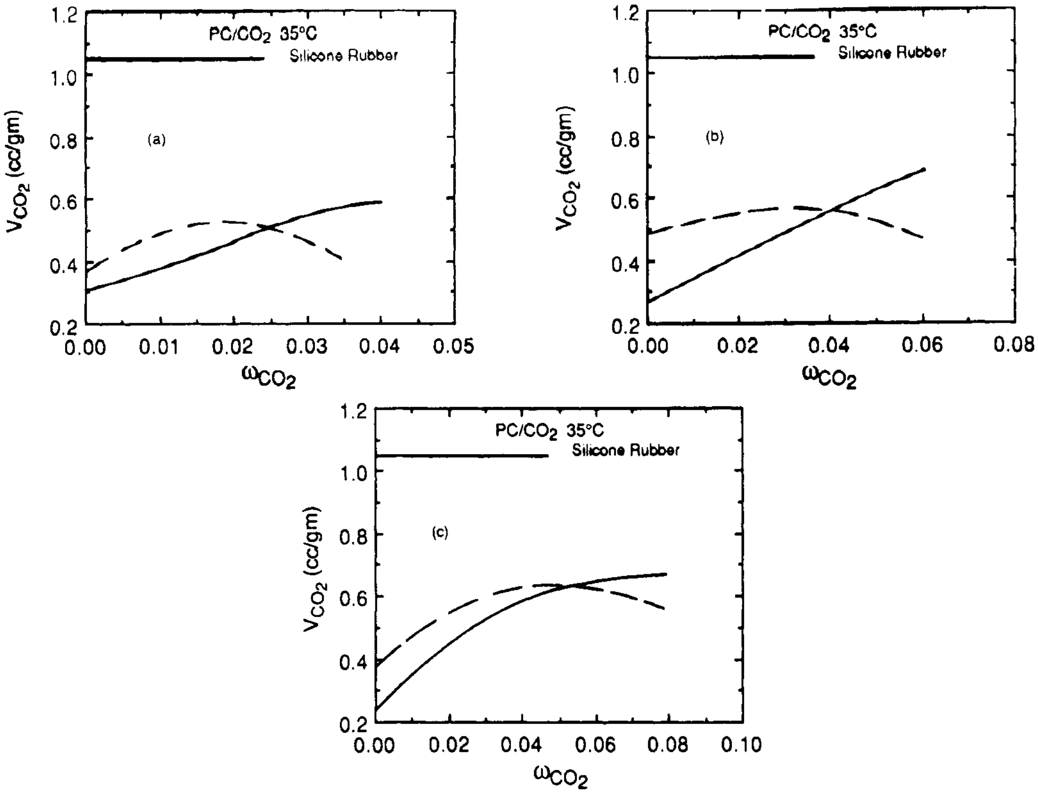

Figure 7. Partial specific volume of CO_2 as a function of CO_2 mass fraction: (- -) sorption, (—) desorption. Also represented is the CO_2 partial specific volume measured in silicone rubber.[1]

Table II
Dual-Mode Parameters for PC/CO_2 at 35 °C for Conditioning at Various Pressures[a]

condition pressure, psia	$P\uparrow$ or $P\downarrow$	$k_D{}^{\ddagger}$, cm^3(STP)/cm^3 atm	$C_H{}'^{\ddagger}$, cm^3(STP)/cm^3	$b^{\ddagger}$, atm^{-1}
300	$P\uparrow$	0.844	15.16	0.303
	$P\downarrow$	0.617	21.00	0.285
600	$P\uparrow$	0.843	19.42	0.265
	$P\downarrow$	0.254	46.59	0.125
900	$P\uparrow$	0.868	21.24	0.257
	$P\downarrow$	0.261	59.50	0.117

[a] The superscript ‡ indicates a fit to fugacity-based model.

at temperatures slightly less than the glass transition temperature, T_g, is commonly referred to as annealing, and such treatments tend to reduce the excess volume in a glassy polymer.

A polycarbonate sample was first conditioned under 900 psia CO_2. Then the sample was annealed at 135 °C for approximately 3 weeks. Chan[9] found that the solubility of CO_2 was reduced in PC due to annealing at both 125 and 135 °C. Reductions in solubility for these annealed samples was attributed primarily to decreases in excess volume for the nonequilibrium glassy solid.

It was found that the density of the CO_2-conditioned sample was increased due to the annealing treatment. Density gradient column measurements for a CO_2-conditioned sample showed that the density of the sample was 1.194 g/cm^3. Similar density measurements after annealing the CO_2-conditioned sample show that the density had increased to 1.198 g/cm^3. The density of an as-received sample was determined to be approximately 1.200 g/cm^3. Although the density of the annealed sample did not increase to the level of the as-received sample, these small changes in density are shown below to have a large effect on the sorption and volume-dilation behavior.

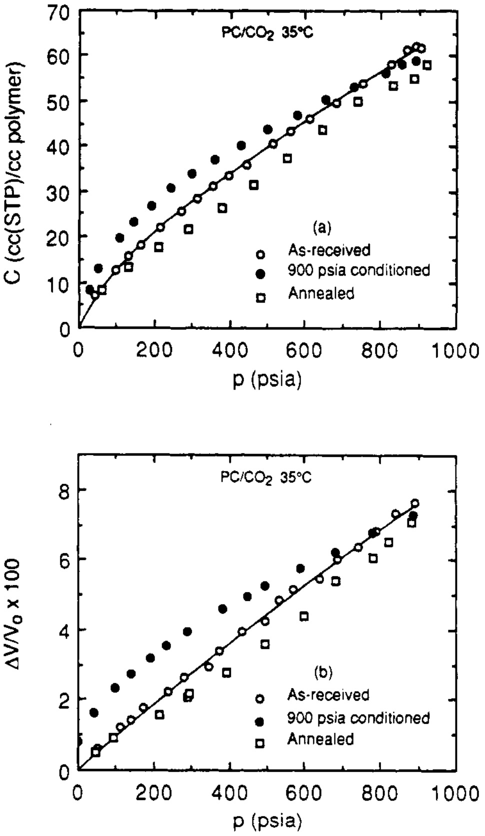

Figure 8. Sorption isotherms for CO_2 at 35 °C in CO_2-conditioned, as-received, and annealed polycarbonate. The annealed sample was first CO_2-conditioned at 900 psia and then annealed at 135 °C for 500 h under vacuum.

Carbon dioxide sorption isotherms are presented in Figure 8a for the as-received, CO_2-conditioned and annealed PC samples. Figure 8b shows volume-dilation measurements for the as-received, CO_2-conditioned and annealed samples, as well. The sorption and volume-dilation isotherms for the annealed samples are depressed far below the previous CO_2-conditioned level and are in fact slightly below the as-received level at low pressures. At higher pressures the sorption and dilation isotherms are slightly convex to the pressure axis, and finally at approximately 900 psia the sorption and volume-dilation measurements for the annealed sample approach the level of the unconditioned sample. It appears that the effect of high sorption levels of CO_2 acts to plasticize the polymer somewhat and helps reverse the annealing effect. Because of the small but significant increases in density for the annealed sample, it is not surprising that the volume dilation and sorption behavior for the annealed samples are significantly depressed below that measured for the CO_2-conditioned samples.

Conclusions

Sorption and desorption measurements after conditioning at different carbon dioxide pressures show that the history dependence of glassy polycarbonate is related to the volume-dilation level induced in the polymer at the conditioning pressure. Higher levels of volume dilation during conditioning at progressively higher pressures lead to greater increases in mass uptake and volume dilation on subsequent sorption isotherms. Also, greater volume dilation during conditioning leads to larger hysteresis during depressurization with the glassy polymer. It has also been shown that the penetrant-free volume of the conditioned glassy sample is related to the conditioning pressure as well, and long-term measurements over several months indicate that the excess volume introduced in the polymer by CO_2 conditioning is long-lived. Partial molar volumes for CO_2 in a conditioned sample are slightly depressed below those measured in the as-received sample. This effect can be explained qualitatively as being due to an increase in the fraction of sorption into molecular scale packing defects in the glassy polymer.

Similarity in the partial specific volumes determined for both sorption and desorption measurements indicates that the primary reason for the desorption hysteresis is not a large increase in molecular scale unrelaxed defects in the glass as would be predicted by an ad hoc application of the dual-mode model in its present form. Although the behavior of the partial specific volume during depressurization is found to be more complicated than that for the pressurization case, the level of the partial specific volume seems to indicate that increases in mass uptake during depressurization are largely due to increases in the dissolved sorption level.

Finally, annealing the glassy sample below its T_g is shown to reverse the conditioning effect. After annealing the 900 psia CO_2-conditioned polycarbonate sample for 3 weeks at 135 °C, both the sorption level and the volume-dilation level are shown to be equal to or below the level measured for the as-received sample.

Acknowledgment. The authors gratefully acknowledge the support of the National Science Foundation Grants No. CBT-8516148 and No. CBT-8351932.

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Registry No. CO_2, 124-38-9; (Bisphenol A)(PC) (copolymers), 25037-45-0; (Bisphenol A)(PC) (SRU), 24936-68-3.