Effect of Various Exposure Histories on Sorption and Dilation in a Family of Polycarbonates

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ABSTRACT: Methane sorption and dilation isotherms along with their dependence on sample exposure history are presented for three systematically varied polycarbonates. Sorption and dilation levels of CH_4 in the various polycarbonates are shown to be increased by two methods of exposure to CO_2 termed "conventional conditioning" and "exchange conditioning". The exchange-conditioning procedure produces the largest increases for all three polycarbonate samples. The largest percentage changes in properties are noted for the well-packed unsubstituted bisphenol-A polycarbonate (PC), which displays a 44% increase in sorption and a corresponding 58% increase in dilation with the conventional-conditioning protocols. This polymer also showed the largest changes in properties for the exchange-conditioning procedure, with a 79% increase in sorption and a corresponding 167% increase in dilation over unconditioned values. Qualitatively, the substituted materials, with less efficiently packed matrices and higher T_g values, showed smaller increases under both conditioning protocols as compared to standard PC, indicating a trend of smaller sorption and dilation enhancements for samples that experience smaller increases in fractional free volume as induced by the conditioning treatments.

Introduction

Glassy polymers differ from rubbery polymers in their tendency to display an apparently permanent sorption/desorption hysteresis effect when exposed to a moderately to strongly sorbing penetrant under certain controlled conditions.[1] The penetrants that have been shown to cause this hysteresis effect are said to alter the polymer by a process known as "conditioning". The conditioning effect causes a significant increase of penetrant sorption in and permeation through a sample, as well as a significant increase in its volume dilation.[2-4] These increases can also be noted for low-sorbing penetrants in a conditioned glassy sample even after the conditioning agent has been removed and the sample has been exposed to an intervening vacuum. In the case of permeation characterization, a peculiar aspect of the phenomenon is the observation that some components (e.g., CH_4, N_2, air) are able to maintain the conditioning response following a complete gas exchange to remove the conditioning agent although they are not able to induce the conditioning response themselves.[5]

Previous sorption and dilation studies have focused on protocols (termed "conventional conditioning") in which the sample is evacuated after exposure to the conditioning agent before introduction of the secondary penetrant. The present work, however, will explore an additional method of conditioning in which the polymer sample is *never* exposed to an intervening vacuum. This "exchange-conditioning" procedure involves replacing the conditioning agent by a secondary penetrant at a constant pressure. The effects of the various conditioning procedures on the sorption and dilation levels of a family of systematically varied polycarbonates will be compared. It was expected that significant differences would result between the conventional and gas-exchange conditioning procedures since rapid relaxations occur in the highly dilated sample during the evacuation step of the conventional-conditioning procedure as opposed to the exchange-conditioning procedure, which does not involve an intermediate evacuation step.

The understanding and application of conditioning phenomena will benefit a number of areas involving gas separations and barrier research. The increased sorption levels produced by the various methods of conditioning provide a possible means of increased gas permeability and, consequently, increased productivity. Potentially, understanding the various conditioning effects on sorption and dilation levels in polymers with similar backbones, but different substituent groups, could help provide a basis for the synthesis of polymers that can take maximum advantage of the conditioning effect. On the other hand, this knowledge could also be useful in producing polymers that are immune to the conditioning effect, which would be desirable to avoid system upsets in a separation process or barrier application where permeability changes are considered undesirable. An illustration in this area is the loss in barrier efficacy for samples exposed to conditioning agents such as steam used for retorting food-packaging resins such as ethylene–vinyl alcohol.[6] The conditioning effect therefore presents an interesting phenomena that merits considerable study both from the standpoint of the basic physics of the glassy state and in terms of practical processes involving polymers for membrane and barrier applications.

Background

Although conventional conditions has been studied in some depth, the effects of the exchange-conditioning process have just recently been observed.[5] To eliminate confusion, the various types of samples studied are defined in detail below.

The first type of sample is termed "unconditioned", which refers to samples with no prior gas exposure history other than normal atmospheric storage.

The second type of sample is termed "conventionally conditioned" and refers to the case in which a highly sorbing penetrant is equilibrated at a predetermined pressure with the sample and then evacuated completely before exposure to the secondary penetrant.

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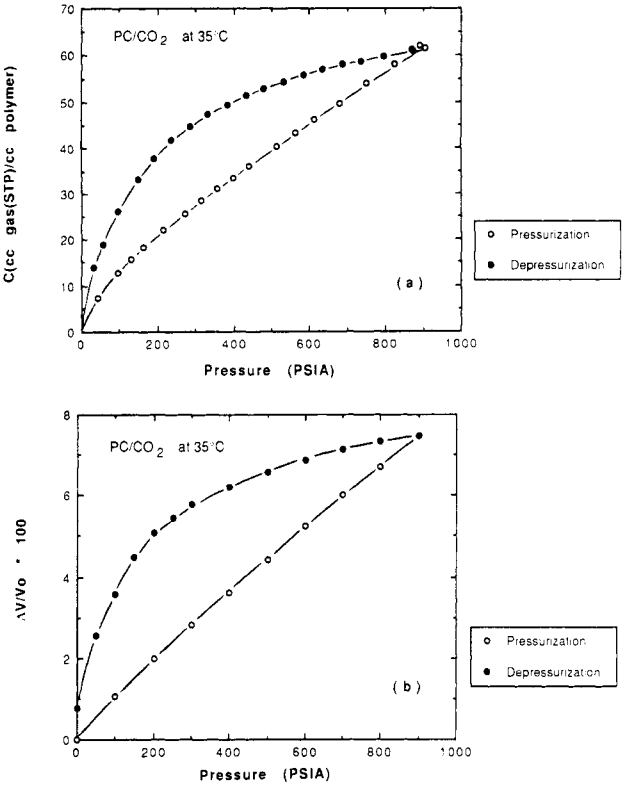

Figure 1. Examples of sorption and dilation hysteresis for PC/CO_2.

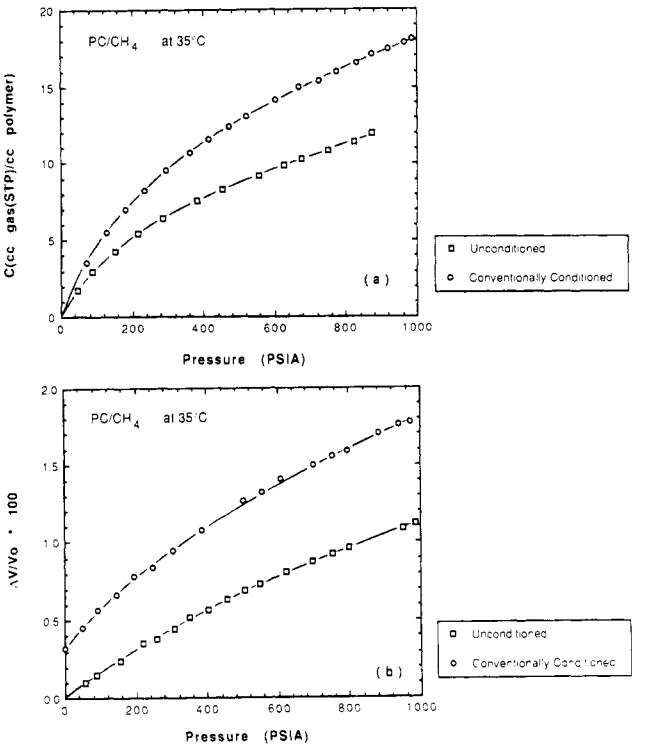

Figure 2. Examples of CO_2 conventional conditioning for PC/CH_4.

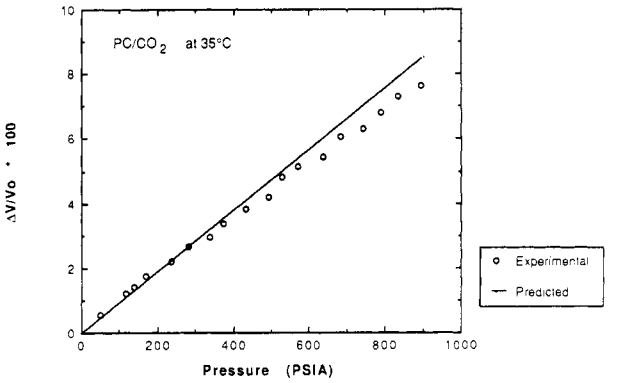

Figure 3. Application of dual-mode theory in predicting dilation of PC by CO_2.

The final type of sample is termed "exchange conditioned". Exchange conditioning involves exposing the sample to a highly sorbing penetrant at a predetermined pressure; however, instead of evacuating the sample, the secondary penetrant is swept through the sample chamber to completely replace the conditioning agent at a constant pressure. Purging is continued until all of the conditioning agent has been removed from the polymer sample as well as the gas space.

Since glassy polymers are known to be nonequilibrium materials, the manner in which the samples have been treated will affect their sorption, transport, and other physical properties. Previous studies have shown that exposure to high gas sorption levels will cause a hysteresis between the pressurization and depressurization cycles for sorption and volume dilation isotherms.[7] Typical hysteretic responses are shown in Figure 1 for the CO_2/polycarbonate system, where C refers to the concentration of gas in the polymer and $\Delta V/V_0 \times 100$ refers to the percentage increase in polymer volume. This exposure to a highly sorbing gas (i.e., conventional-conditioning procedure) has also been shown to increase subsequent sorption and dilation levels as compared to levels in an as-received or unconditioned sample. A typical conventional-conditioning response is shown in Figure 2 for CH_4 sorption in 900 psia CO_2 conditioned polycarbonate. These phenomena have been described by several authors and have been explained in part by attributing the increase in subsequent sorption and dilation levels to an increased number of subtle packing disruptions in the polymer matrix which makes it energetically easier for penetrant molecules to be sorbed.[8,9] This study shows that the conditioning effect is even more pronounced if the secondary penetrant is introduced while the sample is still exposed to the conditioning agent, i.e., using a "gas-exchange" protocol as described above.

Previous studies have shown that gas sorption into glassy polymers can be conveniently described by the dual-mode theory, which postulates that the penetrant molecules exist in equilibrium between two idealized molecular environments.[10-12] One population of molecules is viewed as arising from uptake into a dissolved state similar to sorption in rubbery polymers or low molecular weight liquids. These so-called "dissolved" molecules may be described by a Henry's law term. The other population is postulated to exist in molecular-scale defects that are present due to the nonequilibrium nature of glassy polymers and may be described by a Langmuir type of expression. The combination of sorption in these two environments leads to the dual-mode sorption expression given by

$$C = k_D p + \frac{bC'_H p}{1 + bp} \quad (1)$$

where C is the sorption level, k_D is the Henry's law constant, b is the Langmuir affinity constant, and C'_H is the Langmuir capacity parameter. Other studies have shown that this theory is also useful in describing the volume dilation of glassy polymers as shown in Figure 3 for the PC/CO_2 system.[7] To describe the dilation of the polymer, it was assumed that the molecules in the dissolved

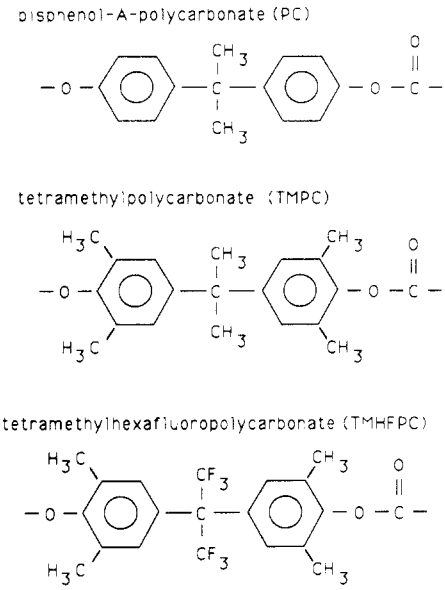

Figure 4. Structures of study materials.

Table I
Physical Properties of Polycarbonates

polymer	T_g, °C	density, g/cm³	v_f
PC	150[a]	1.200	0.1643
TMPC	203[a]	1.08	0.1821
TMHFPC	208[b]	1.286[b]	0.2162

[a] From Yee and Smith.[14] [b] From Hellums et al.[13]

environment are the only contributors to the dilation of the sample since these molecules must separate chains to be accommodated into the matrix while those in the penetrant-size packing defects cause essentially no net dilation. It was also suggested that each dissolved molecule contributes essentially an equal amount of dilation; therefore, at a given dilation, each sample should have an equivalent dissolved population. While this is clearly an idealized representation, it permits one to make useful predictions of basic properties such as the dilation behavior of the complex nonequilibrium glass.

To accurately compare conditioning treatments on sorption and dilation levels of the various polycarbonates, the samples were exposed at a conditioning pressure that gives an *equivalent volume dilation* of the various samples and hence an equivalent dissolved molecule population. Since additional sorption in unrelaxed packing defects contributes to sorption but not dilation, the total sorption level need not be identical for different polymers containing different levels of packing defects. Explicit consideration of this additional factor allows rationalization of otherwise confusing data for the various samples.

Experimental Section

Materials. Three types of polymers were used in this study. The bisphenol-A polycarbonate (PC) was provided by General Electric Co., the tetramethylpolycarbonate (TMPC) was provided by Dow Chemical Co., and the tetramethylhexafluoropolycarbonate (TMHFPC) was synthesized in our laboratory.[13] The structures of these polycarbonates are shown in Figure 4 with various physical properties listed in Table I. The glass transition temperatures were measured by DSC, and the densities of the materials were measured by a density gradient column.[13,14] The PC was used as received in extruded form in sample thicknesses of 2, 3, and 5 mils. The TMPC and TMHFPC were each solution cast from a 5 wt % solution in methylene chloride on glass plates, resulting in films of ca. 5 mils in thickness. These films were dried in a vacuum oven at ca. 10 °C above T_g to completely remove the solvent and then slow cooled to room temperature under vacuum.

The CO_2 and CH_4 were supplied by Linde, Inc., at purities of at least 99.99% and were used as received.

Equipment and Procedures. Sorption measurements were made by both mass balance and gravimetric techniques. For unconditioned and conventionally conditioned isotherms, standard pressure decay cells were used as have been described by others.[15,16] For the exchange-conditioned sorption isotherms, a quartz spring in a high-pressure Jerguson liquid level gage was used. The sample was suspended directly on the spring and its extension was measured with a high-accuracy filar eyepiece. After the buoyancy of the sample in the high-pressure gas was accounted for,[17-19] the sorption level was determined. By performing sorption isotherms on several different polymer/gas systems, we found the two methods of sorption measurement to give identical sorption values.

Dilation measurements were conducted by using equipment that has been described previously.[7] Briefly, strips of polymer film were suspended between brass guides that prevent curling but cause no restriction of linear expansion movement. This assembly was then placed in a high-pressure Jerguson gage where the sample length was measured optically with a cathetometer.

Although, the methods for measuring sorption and dilation isotherms of unconditioned and conventionally conditioned samples have been well described,[4,15,16] the exchange-conditioning procedure is somewhat more involved. The exchange-conditioning procedures for sorption and dilation measurements were analogous and involved placing the unconditioned sample in the Jerguson gage and evacuating for 24–48 h. After the sample length was measured at zero pressure, the sample chamber was pressurized to a predetermined conditioning level. Upon reaching equilibrium, the pressurized sample was isolated while the conditioning agent supply cylinder was replaced with the exchange penetrant supply cylinder and the supply lines were evacuated. Then at a constant pressure, the conditioning agent was purged out of the sample chamber by introducing the exchange penetrant. The exchange process normally required ca. 2 h, with confirmation of a complete gas exchange being obtained from analysis of the gas in the sample chamber by a gas chromatograph.

Measurements of all sorption and dilation isotherms were performed at 35 °C.

Results and Discussion

Initially, sorption and dilation isotherms of CH_4 in PC for the various conditioning procedures were studied. As stated earlier, the unconditioned sample had no prior gas treatment. For the CH_4/PC system, the conventionally-conditioned sample was equilibrated with 900 psia CO_2, depressurized over a period of 2–3 h, and then held under vacuum for ca. 48 h before exposure to the CH_4. This conditioning level represents the maximum delivery pressure of the available CO_2 cylinders and corresponds to a volume dilation level of ca. 7.8%. The 7.8% dilation level was then used as the conditioning level for all samples. The exchange-conditioned sample was also equilibrated with 900 psia CO_2 and then exchanged for 900 psia CH_4 at a constant pressure.

In Figure 5 CH_4 sorption and dilation values in PC for the various conditioning procedures are shown. The lowest sorption and dilation levels at 900 psia are noted for the unconditioned sample, while the sorption level of the conventionally conditioned sample occurs ca. 44% higher with a corresponding 58% increase in dilation. The highest sorption level is noted for the exchange-conditioned sample, with a level 79% higher than that of the unconditioned sample and a corresponding 167% increase in dilation. These values are summarized in Table II. As noted earlier, rigorous steps were taken to ensure that no residual CO_2 existed in the sample or external gas phase. In addition, the samples were held at each pressure until no significant changes in the sorption or dilation levels were observed. Typically, samples reached equilibrium within 8–12 h; however, some samples were

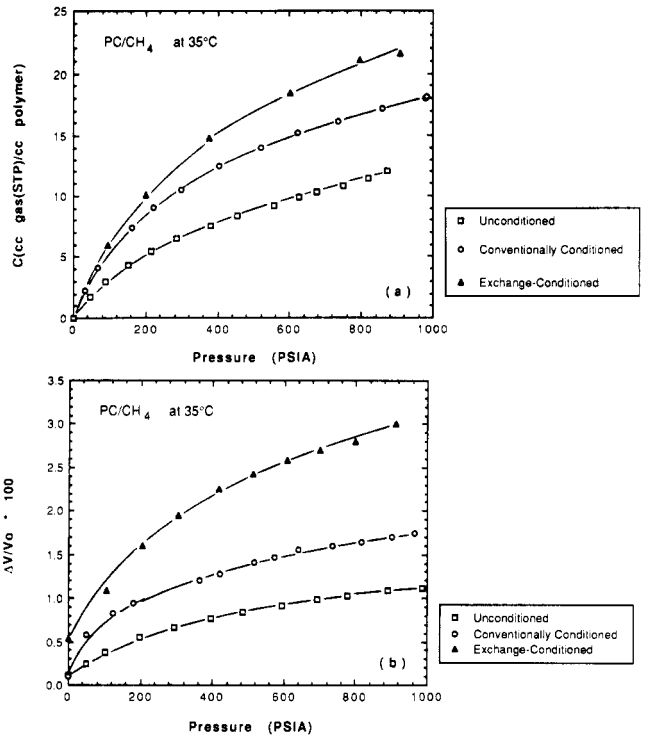

Figure 5. (a) Sorption isotherms for various exposure histories for PC/CH_4 at 35 °C. (b) Dilation isotherms for various exposure histories for PC/CH_4 at 35 °C.

Table II
CH_4 Sorption and Dilation Values and Percentage Increases for the Conditioning Procedures on the Polycarbonates

		sorption		dilation	
polymer	history	C^a	% incr over unconditioned	$\Delta V/V_0 \times 100^b$	% incr over unconditioned
PC	unconditioned	12.08		1.07	
(at 900 psi and	conventionally conditioned	17.38	43.9	1.70	58.3
35 °C)	exchanged conditioned	21.57	78.6	2.86	166.9
TMPC	unconditioned	20.51		1.28	
(at 654 psi and	conventionally conditioned	26.10	27.2	2.37	85.1
35 °C)	exchange conditioned	32.47	58.3	3.38	163.8
TMHFPC	unconditioned	22.0		1.23	
(at 386 psi and	conventionally conditioned	26.0	18.2	1.84	49.6
35 °C)	exchange conditioned	28.4	29.0	2.71	120.3

[a] In units of (cm^3 of gas (STP)/cm^3 of polymer. [b] ΔV = change in volume, V_0 = original volume.

allowed to remain at the exchange pressure for as long as 10 days to confirm that equilibrium had truly occurred.

A relatively simple physical picture can be used to explain the shape of the sorption and dilation isotherms and their changes as functions of pressure for the various samples. A useful idealized representation of the as-received glass considers two subtly different molecular environments such as that described in the context of the dual-mode sorption model. The majority of the matrix is visualized to be comprised of regions in which the chains are randomly oriented but well packed and "nested" to provide the characteristically high densities of glassy solids. In addition to the well-packed regions, a small number of out of equilibrium, or unnested segmental sites also can be envisioned, some of which are sufficiently large to accommodate an individual penetrant with no net dilation of the matrix. Combined sorption, dilation, and permeation data taken during the depressurization of polycarbonate exposed to 900 psia CO_2 have suggested that a generalized disruption of the matrix packing has occurred during the conditioning process.[1,4,7] This disruption is envisioned to be much more subtle and uniformly distributed than the aforementioned "packing defects" which are capable of accommodating a penetrant without net dilation of the matrix.

Consistent with reports by Hopfenberg et al. for perturbations of glasses with vapors,[20] such subtle disruptions persist in the presence of a small pressure of the conditioning agent or even a nonconditioning agent such as CH_4 in the present study. Very slow relaxation rates are apparent for the long-lived packing defects present in the as-received sample as is reflected by the similar sorption isotherms observed for as-received samples that differ in age by several years. Thus, we will focus the present discussion concerning gas exchange conditioning on the alteration of the more or less densified matrix caused by the introduction of hypothetical subtle packing disruptions.

Sorption includes an exothermic process to bring the gaseous sorbate to a condition with its near-liquid-like volume plus an endothermic contribution for formation of a sorbed cage for the penetrant, and a small interaction energy due to contact between the sorbate and the polymer segments comprising its sorbed cage. We speculate that when a sample is treated with a highly sorbing gas (CO_2 in this study), the matrix becomes sufficiently dilated to allow bond rotations to occur, thereby disrupting the close-packed structure of the as-received glass matrix. Once the CO_2 is removed, some "subtle disruptions" remain due to the extremely slow relaxation times characteristic of glassy polymers. This more disrupted matrix then results in lower endothermic energy requirements for generating a cavity for CH_4 placement in the matrix, thereby making the overall enthalpy of sorption more negative and leading to higher sorption and dilation levels for the conventionally conditioned samples as compared to the unconditioned.

This same type of rationale may be used to explain the even larger sorption and dilation increases observed for the exchange-conditioned samples. When exposed to CO_2, the PC is highly dilated with many packing disruptions present. During the exchange procedure, the entering CH_4 molecules can presumably take advantage of this highly open structure and thereby require even less energy to be placed within the matrix. This lowered energy requirement therefore results in further increased CH_4 sorption and dilation isotherms as compared to both the unconditioned and conventionally conditioned samples. Moreover, the exchange-conditioned samples have larger increases in sorption and volume dilation compared to the conventionally conditioned samples because the exchange-conditioning protocol eliminates the loss in free volume that occurs during exposure to vacuum in the conventional conditioning process.

Sorption and dilation isotherms for CH_4 in TMPC are shown in Figure 6. Conditioning treatments similar to those used for PC were applied to the TMPC samples; however, the CO_2 pressure required to give the 7.8% dilation level was 654 psia, somewhat lower than for PC. Both the conventionally conditioned and exchange-conditioned samples were treated with 654 psia CO_2, which was also used as the CH_4 exchange pressure. The same trends were observed for the TMPC/CH_4 system as were observed for the PC/CH_4 system. A summary of the increases of CH_4 sorption in and dilation of TMPC for

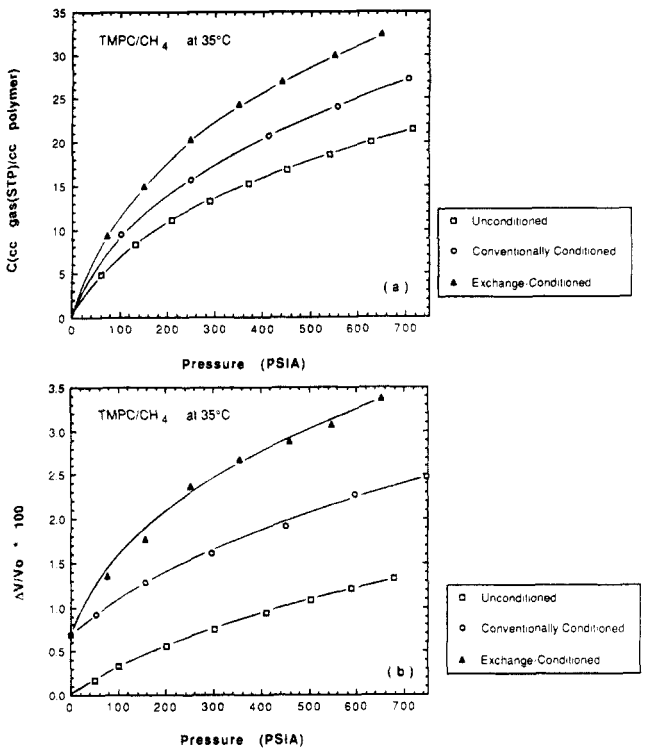

Figure 6. (a) Sorption isotherms for various exposure histories for TMPC/CH_4 at 35 °C. (b) Dilation isotherms for various exposure histories for TMPC/CH_4 at 35 °C.

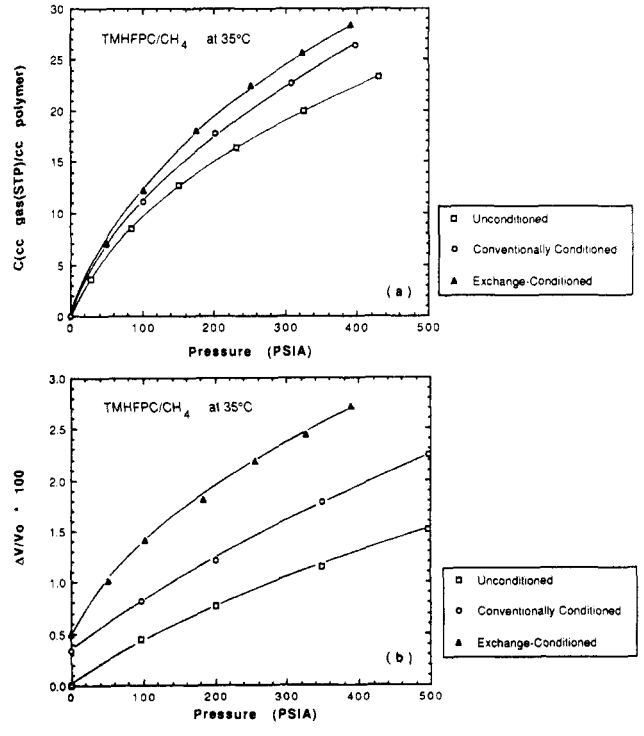

Figure 7. (a) Sorption isotherms for various exposure histories for TMHFPC/CH_4 at 35 °C. (b) Dilation isotherms for various exposure histories for TMHFPC/CH_4 at 35 °C.

the exchange-conditioned and conventionally conditioned levels over the unconditioned isotherm levels is presented in Table II.

Figure 7 shows sorption and dilation isotherms for CH_4 in TMHFPC. The CO_2 conditioning pressure corresponding to the 7.8% volume dilation for the TMHFPC was 386 psia, which was also used as the exchange pressure for the exchange-conditioned samples. As with PC and TMPC, TMHFPC also displays increases in CH_4 sorption and dilation for the exchange-conditioned and conventionally conditioned samples as compared to the unconditioned samples. These percentage increases are summarized in Table II. The same physical arguments used to explain the trends in the PC/CH_4 system can be used for both the TMPC/CH_4 and TMHFPC/CH_4 systems.

Table III
Percentage Increases in Fractional Free Volume with Corresponding Sorption and Dilation Increases at the Exchange Pressures

polymer	% incr in v_f	% incr in sorption	% incr in dilation
PC	36.8	78.6	166.9
TMPC	32.5	58.3	163.8
TMHFPC	26.2	29.0	120.3

Although all three of the equally dilated polymers show increases in CH_4 sorption and dilation levels after the conditioning procedures, the relative increases were systemically different. The increases in dilation and CH_4 sorption, evaluated at the pressure at which the conditioning treatments were performed, are summarized in Table III for the conventionally conditioned and exchange-conditioned samples. All three equally dilated samples are presumed to involve the same number of dissolved CO_2 molecules at their respective maximum conditioning points as represented by the product of the Henry's law constant and the pressure. Therefore, the actual fraction of the total volume increase that is occupied by CO_2 molecules is the same for all three materials and consequently, the absolute amount of additional free volume added to each of the matrices should be the same. Additional free volume is used here to refer to the total 7.8% increase in volume minus the actual volume occupied by sorbed CO_2 at the maximum conditioning pressure for each sample.

On a fractional basis, however, the increase in free volume is much larger for the well-packed polycarbonate as opposed to the TMPC and TMHFPC. For a more quantitative correlation, the as-received fractional free volume of each sample was estimated by the group contribution method of Bondi where the free volume refers to the volume of the sample not directly occupied by atoms.[21] This value is not to be confused with a free volume that only measures the difference in volume between the glassy and extrapolated rubbery state, which we prefer to refer to as "unrelaxed" volume that characterizes deviation of the glass from its equilibrium packing. A sample calculation for determining the fractional free volume of PC is described below.

With the structure of PC as given in Figure 4, a specific van der Waals volume (V_W) of 0.5357 cm^3/g may be calculated by summing the individual molecular contributions as tabulated by van Krevelen.[21] A specific occupied volume (V_0) is then defined as $1.3V_W$, which gives V_0 = 0.6964 cm^3/g. The fractional free volume (v_f) is then calculated, using a PC density (ρ_{PC}) of 1.2 g/cm^3, as follows:

$$v_f = \frac{1/\rho_{PC} - V_0}{1/\rho_{PC}} = 0.1643 \qquad (2)$$

In Figure 8 percentage increases in sorption and dilation are plotted versus the as-received inverse fractional free volume of each sample. Since each sample is dilated by an equivalent amount, the as-received inverse fractional free volume of each sample is proportional to the percentage increase in fractional free volume introduced into each sample during the conditioning procedure. From Figure 8, a tendency of increased sorption and dilation enhancement for the better packed samples can be seen.

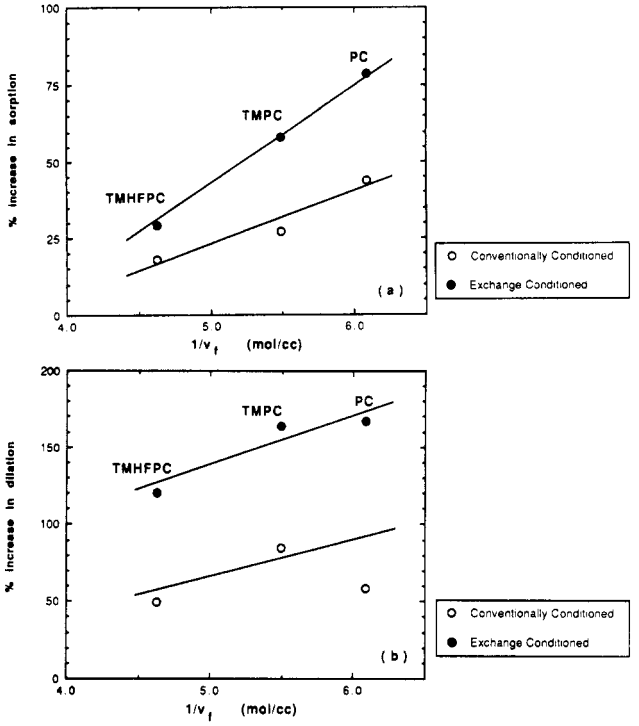

Figure 8. (a) Conventionally conditioned and exchange-conditioned sorption enhancements versus as-received fractional free volume for the series of polycarbonates. (b) Conventionally conditioned and exchange-conditioned dilation enhancements versus as-received fractional free volume for the series of polycarbonates.

In addition, the exchange-conditioned samples are seen to produce even larger enhancements than the conventionally conditioned samples while still displaying the same trends.

Although the general trends are clear, the dilation enhancement of the conventionally conditioned PC seems to fall somewhat below the expected value. However, if the data are analyzed more closely, this lower than expected enhancement may be explained. Upon removal of the conditioning agent, CO_2, during the conventional-conditioning procedure, a small amount of residual volume dilation remains in the polymer sample. This residual volume has been shown to remain over extended periods of time and has been attributed to the introduction of new packing defects and disruptions in the evacuated conditioned sample.[4,7] If this residual volume is accounted for in each of the polycarbonate samples, corrected dilation enhancements may be determined that use the *conditioned volume* at zero pressure as the new base volume. These corrected values are shown as functions of the inverse fractional free volume in Figure 9. Here the expected trend of increased enhancement for the better packed PC is much clearer. In contrast to conventional conditioning where the sample is exposed to an intervening vacuum, corrections are not needed for the exchange-conditioned samples since the polymer matrix undergoes no relaxation between penetrant exposures.

The conditioning treatment effects are believed to be the most significant for the most efficiently packed member of the family for reasons discussed earlier concerning the endothermic term required for formation of the sorbed cage for the gas. For systematically related polymers with similar intermolecular attractions, the energy required to generate equal-sized cavities to accommodate a sorbate should be the highest for the one with the highest packing density, or lowest fractional free volume. In this case, the enthalpy of sorption of gases in

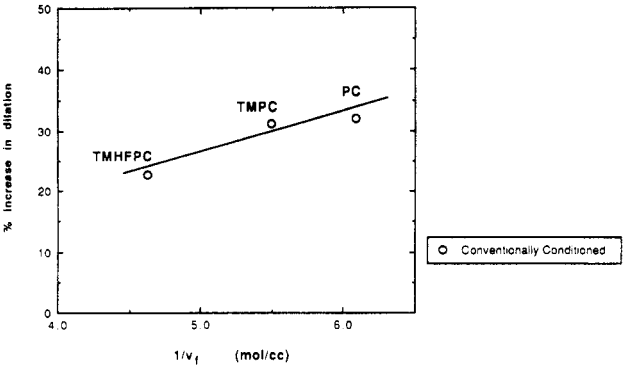

Figure 9. Corrected conventionally conditioned dilation enhancements versus as-received fractional free volume for the series of polycarbonates.

the as-received samples should be less exothermic and less favorable to sorption for the materials with well-packed matrices such as PC. We speculate that the introduction of the same amount of free volume produces a larger increase in the fractional free volume of the well-packed members of the family, so a proportionally larger increase in the exothermic net enthalpy of sorption also occurs. Since this enthalpy enters in an exponential fashion in determing sorption, small changes in the enthalpy can produce large effects on the apparent sorption and, hence, dilation in the conditioned sample. Careful studies of the enthalpies of sorption for methane in the as-received and conditioned samples of PC, TMPC, and TMHFPC would be needed to test the preceding explanation of the relative trends in the conditionability of the three materials studied here.

Another possible factor influencing the conditionability of the various polycarbonates involves the inherent "stiffness" of the polymer chains as reflected by the T_g values. The abilities of the substituted polymer chains to move and rotate are hindered as reflected by the higher T_g values of TMPC and TMHFPC. In this case it may be possible that the restoring force tending to eliminate packing disruptions in the three equally dilated matrices is larger for the higher T_g samples, thereby resulting in smaller sorption and dilation enhancements. A correlation between decreasing T_g and increasing sorption and dilation enhancement can, in fact, be seen in the above data, although this trend is not as clear as the correlation between increasing fractional free volume and increasing enhancement as shown in Figure 8. However, for the polycarbonate samples in this study, a trend of increasing T_g with increasing as-received fractional free volume occurs, thus preventing separate observations of the effects of varying the T_g and fractional free volume on conditioning enhancements.

To clarify the separate contributions of these two factors, another series of polymers needs to be studied where the fractional free volume is either held constant or decreases with increasing T_g through the polymer series. A possible candidate for this type of study is the polysulfone family. Methyl substitutions onto the phenyl rings of the bisphenol-A group are seen to simultaneously decrease the fractional free volume while increasing the T_g by over 40 °C.[22-24] However, a study of the polysulfone family and a detailed study of the enthalpies of sorption in as-received and conditioned samples of PC, TMPC, and TMHFPC are beyond the scope of the present work.

Conclusions

Each of the polycarbonate samples studied displayed highly different sorption and dilation values depending

on the history of the sample. The unconditioned samples displayed the lowest sorption and dilation values while the exchange-conditioned samples displayed the largest, presumably due to the lowered energy requirements for penetrant sorption. In addition, the largest enhancements of sorption of dilation over unconditioned values, at a given conditioning level, were noted for PC, with the smallest enhancements occurring for TMHFPC. This trend reflects larger enhancements for materials with larger percentage increases in fractional free volume and correspondingly smaller values of T_g as seen in the series PC, TMPC, and TMHFPC.

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Quasi-Scaling for Finite Lattice Polymers with Pair and Triplet Interactions

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ABSTRACT: To extract the sealing for finite polymers, we present general relations directly derived from the context of the renormalization group and examine their validity. The context asserts that, in the two-parameter model, any of the reduced moments is described solely by an arbitrary reduced moment. In the three-parameter model, it is described by two arbitrary reduced moments. Our basic relations are free from the artificial theoretical models and involve no specific reference point such as Θ-point. For finite polymers, the concepts of *scaling*, *master curve*, and *master surface* should be replaced by those of *quasi-scaling*, *master belt*, and *master shell*, respectively. The relations were critically examined by numerical experiments of lattice polymers with the nearest-neighbor pair and triplet intrachain interactions. In a restricted regime, we could identify universal master belts in two-dimensional plottings. In three-dimensional plottings, we could identify universal master shells, within which many of the two-dimensional non-quasi-scaling points fall. The convergence to the expected quasi-scaling is varied by the combinations of the reduced moments.

1. Introduction

Although the scaling concept for single polymers has been constructed in several ways, the correspondence of the theoretical models with actual and/or lattice polymers is not entirely clear. The model used in the conformational renormalization group (RG)[1] is a Gaussian molecule with two-body (and three-body) δ-function-like intrachain interaction. However, the polymer intrachain interaction is actually never so.[2] The correspondence of a self-avoiding walk with the zero-dimensional spin system[3] is merely mathematical. The polymer model used in the classical mean-field theory is much like a pre-averaged monomer cloud rather than a string of monomers.[4] To legitimate these models, we have to conceive extremely long, unpractical molecules. Then what hap-

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