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Sorption and Dilation of Poly(1-(trimethylsilyl)-1-propyne) by Carbon Dioxide and Methane

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ABSTRACT: Poly(1-(trimethylsilyl)-1-propyne), PMSP, is known to absorb large amounts of fixed gases such as carbon dioxide and methane, presumably due to the inherently large free volume of PMSP. Exposure to carbon dioxide at pressures as high as 1000 psia apparently increases chain mobility, allowing for relaxation of excess volume in the polymer matrix induced by toluene solution casting. These volumetric relaxations, determined with a three-dimensional dilatometer, appear in the form of a time-dependent decrease in the overall polymer volume upon depressurization of the carbon dioxide. Repeated exposures to carbon dioxide show no further decrease in sorption capacity and essentially no further decrease in overall volume. PMSP did not exhibit the typical conditioning behavior in which volume and sorption capacity increase upon subsequent repressurization following desorption. This absence of "normal" conditioning behavior was attributed to residual "preconditioning" by the toluene casting solvent. The PMSP stiff chain backbone relaxes so slowly after casting that the polymer retains massive amounts of excess volume even after initial exposure to plasticizing carbon dioxide.

Introduction

Gas separations by polymer membranes are becoming increasingly attractive for removing carbon dioxide, hydrogen sulfide, and water vapor in many natural gas treating operations.[1] Several advantages of the membrane system over more conventional systems include low capital cost, ease of operation, low maintenance, and adaptability.

Advancements are continually being made, especially in the membrane material itself. Research into understanding the role certain functional groups on the polymer backbone play in the separation process has been undertaken with the polycarbonate and polyimide families.[2–5] In addition, studies of in situ modifications to membranes to enhance separation and permeation properties have also been performed which include exposure of the membrane to highly swelling gases and vapors.[6–8]

A highly desirable membrane would be extremely selective by completely rejecting unwanted components in a gas stream while allowing product to permeate freely. In addition, the membrane would exhibit a large absolute permeability to increase the productivity of the process. Recently, poly(1-(trimethylsilyl)-1-propyne) or PMSP has been synthesized which displays extremely high gas permeabilities.[11–15] These high permeabilities motivate further characterization of PMSP.

This study was performed to determine the sorption and dilation characteristics of PMSP under high pressures of carbon dioxide and methane. Another objective was to determine if PMSP exhibits the conditioning response observed with other glassy polymers where preliminary exposure to a highly swelling gas causes subsequently higher sorption, dilation, and permeation properties.[6–10]

Background

Sorption of gases and vapors into glassy polymers has been a subject area studied for several years. Numerous models have been proposed to explain the unique sorption isotherm characteristics exhibited by these polymers.[16–23] One of the original models which has gained wide acceptance was termed the dual mode model of sorption and is shown by eq 1,[23] where C is total sorption, C_D and

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

C_H are sorption contributions by the dissolved and the hole-filling modes respectively, k_D is the Henry's law parameter, p is pressure, C_H' is the Langmuir capacity constant, and b is the Langmuir affinity constant. The development of the model was based on the hypothesis that the concave curvature of a plot of penetrant concentration versus penetrant pressure was due to sorption into two distinct environments. Penetrant molecules sorbed into one of these environments were classified as existing in a dissolved state where the molecule occupied a volume much as it would in a rubbery polymer. This population of sorbed penetrants was described by Henry's law. Penetrant molecules sorbed in the second environment were described as existing in molecular scale defects which could accommodate a sorbed penetrant without any movement of chains. This population of penetrants was described by a Langmuir isotherm. A wide variety of gas/polymer systems have been successfully modeled using the dual mode of sorption approach.[8,21,24–26]

Further physical evidence supporting the dual mode sorption model was obtained using penetrant-induced dilation of glassy polymers.[25] In one study, Fleming and Koros stated that according to the dual mode model, only the dissolved, or Henry's law, population should contribute to dilation.[25] The volume dilation data was described using a combination of the Henry's law parameter obtained from fitting sorption data to the dual mode model along with an estimated molecular volume of the penetrant. The data seemed to provide convincing physical evidence of the applicability of the dual mode model. The model provides the basis for arguments to be presented in a later section.

Many glassy polymers exhibit a phenomenon which has been termed conditioning behavior.[6–10] Conditioning refers to the dilation of a polymer resulting in higher values of sorption and permeation after exposure to a highly

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swelling gas or vapor compared with an unexposed sample.[6-10] The magnitude of these increases has been shown to depend on a number of factors including the amount of swelling induced during the conditioning step and the free volume characteristics of the original polymer.[6] Explanations of the conditioning behavior have centered around the hypothesis that as the polymer matrix is swelled, chain mobility is increased, allowing subtle chain-packing disruptions to be introduced into the matrix. These disruptions then provide localized areas of more favored sorption sites due to lowered energy requirements for sorption. The conditioning of a sample has been found to be reversible by annealing which involves heating the sample to temperatures just below the glass transition or heating above the glass transition combined with slow cooling.[27] These thermal processes are thought to remove the disruptions introduced by the swelling penetrant.

Experimental Section

Procedures. Sorption Measurements. Sorption measurements were performed by two methods. The pressure decay method has been described in detail by others.[28,29] Briefly, the pressure decay apparatus consists of two carefully calibrated chambers each fitted with a pressure transducer. These two chambers are connected by tubing with an intervening valve allowing isolation of each chamber. Typically, 2 cm^3 of polymer sample are placed in the designated polymer chamber and the apparatus is evacuated with a vacuum pump. The polymer sample is isolated by shutting the intervening valve, and the gas reservoir chamber is charged with gas with the pressure being measured to determine the amount injected. The intervening valve is opened, and the polymer sample is exposed to gas. By monitoring the pressure decrease, the equilibrium sorption value is determined from a mass balance.

The second method of sorption involved a direct measurement of mass uptake using a quartz spring. This method has been described in detail previously as well.[30] Briefly, the sample is suspended on a quartz spring in a high-pressure chamber fitted with a view window. The distention of the spring is measured at various pressures, and the sorption is calculated using the spring distention and calibrated spring constant.

Procedures. Dilation Measurements. The volume dilation of the polymer samples was measured using direct optical techniques. The equipment for length and thickness measurement has been described elsewhere and will only be briefly described here.[24,31] The length dilation was measured using a thin polymer strip approximately 25 cm in length. This strip was mounted in a holder which prevented the strip from curling but caused no restriction in vertical movement and was placed in a high-pressure chamber fitted with a view window. The upper and lower edges were then viewed directly with a cathetometer.

The thickness measurements were performed on films approximately 10–15 mil thick viewed edge on. Due to the small dimensions, the thickness measurement required high magnification and therefore used a video camera fitted with magnifying optics capable of magnification of 500×. The edge of the mounted film was displayed on a video monitor with the thickness measured directly on screen using a set of markers and digital readouts displayed on screen.

Materials. PMSP was obtained in powder form from Air Products and Chemicals Inc. Films were cast from a 2–3 wt % solution of PMSP in toluene on a glass plate in a glovebag. A beaker filled with toluene was placed inside the glovebog to control evaporation. The film required approximately 2 weeks to dry and was then removed by immersion of the glass plate in distilled water. The resulting films were dried under vacuum at ambient temperature in a vacuum oven over a period of 7 days. DSC scans showed that all of the toluene had been removed. No glass transition temperature, T_g, was found for PMSP below 300 °C. The PMSP density was found to be 0.779 g/cm^3, as determined using a pycnometer with methanol.

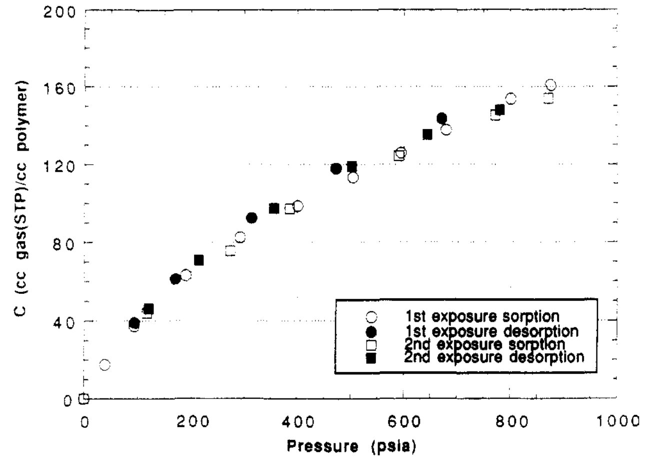

Figure 1. Sorption/desorption of carbon dioxide in PMSP for first and second exposures.

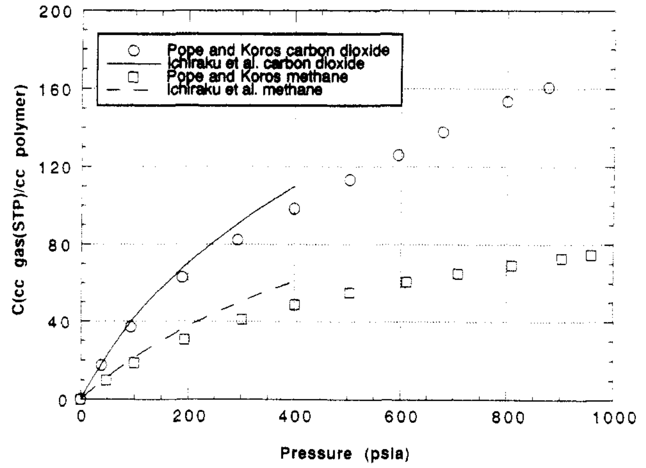

Figure 2. Comparison of carbon dioxide and methane sorption—present study versus Ichiraku and Stern.[15]

Carbon dioxide and methane were purchased from Linde, Inc. at purities of at least 99.99% and 99.97%, respectively, and were used as-received.

Results and Discussion

Two cycles of equilibrium carbon dioxide sorption/desorption isotherms for PMSP are shown in Figure 1. Figure 2 compares the first exposure sorption data for carbon dioxide and methane with previously published data by Ichiraku and Stern who performed sorption studies up to 400 psia.[15] The solid line represents the Ichiraku and Stern data as calculated from their reported dual mode parameter values. The data points from this study fall close to the published data at low pressures but show lower sorption values above 200 psia. These slight differences are most likely due to differences in the PMSP samples and samples histories. The PMSP in the Ichiraku and Stern study was obtained from Sanyo Chemical Industries in the form of beads with a density of 0.938 g/cm^3. Since the previous gas exposure history and formation techniques for these beads are unknown, they could contain a very different free volume distribution compared to the solution cast films used for this study. Most importantly, however, both studies reveal high sorption levels.

Several features of the sorption isotherms from the current study are apparent. The sorption isotherms follow classic dual mode behavior with the sorption curve concave to the pressure axis. The second exposure isotherm does not suggest conditioning. As discussed previously, many glassy polymers will display higher sorption values at the same pressure after having been exposed to a highly sorbing gas or vapor.[6-10] These same polymers also normally display a substantial amount of hysteresis between the sorption and desorption cycles. However, observation of the desorption cycles for PMSP indicates that only a very slight amount of hysteresis occurs.

A number of reasons may explain this absence of conditioning behavior. The most likely explanation involves the method of polymer film formation. The films were cast from solutions of PMSP in toluene which were placed in a glovebag and allowed to dry for 2 weeks. The films were then removed from the molds and placed in a vacuum oven to dry under vacuum at ambient temperature for 1 week. Normally, the cast film would be gradually heated to approximately 10–15 deg above the glass transition temperature to remove any residual solvent and then cooled back to ambient temperature. However, the T_g of the PMSP is above 300 °C which was above the temperature limit of the vacuum oven. Therefore, the toluene may have left the PMSP film in a conditioned state far beyond the level which could be induced by carbon dioxide.

In conjunction with the possible preconditioning by toluene, the nature of the polymer itself may have contributed to the lack of conditioning by carbon dioxide. As mentioned, the T_g of PMSP is above 300 °C due primarily to the extremely stiff PMSP chain backbone. As noted by Ichiraku and Stern, PMSP is made up of rigid molecules separated by large trimethylsilyl side chains.[15] Therefore, the stiffness comes from a combination of alternating double bonds in the backbone and hindrance of segmented rotation by the side groups. Except at very high penetrant concentrations, this chain stiffness would impede the carbon dioxide-induced dilation and therefore prevent the matrix from being conditioned. PMSP has a calculated fractional free volume of 0.3213 which is described by Bondi as a measure of the fraction of the volume of the sample not directly occupied by atoms.[32] Methods for calculating the fractional free volumes have been described in the literature using a group contribution theory.[32] A study by Pope *et al.* showed qualitatively that the level of conditioning or subsequent increase in sorption and dilation compared to untreated values depended on the swelling of the polymer matrix (conditioning level) and the inherent fractional free volume of the polymer.[6] At equivalent dilation levels (conditioning levels), the polymers with larger fractional free volumes showed less conditioning behavior. Polymers with higher fractional free volumes experience less of a percent increase in volume and hence less of an opportunity for additional packing disruptions to be introduced. Less additional packing disruptions then translates into less conditioning of the polymer matrix. The largest fractional free volume in that study of 0.216 is significantly lower than the value of 0.321 calculated for PMSP. Therefore, the absence of conditioning for the PMSP is not altogether surprising.

To explore whether the carbon dioxide had conditioned the matrix for other penetrants, methane sorption experiments were conducted in an as-cast sample and one which had been exposed to 900 psia carbon dioxide. These data are shown in Figure 3. As with the carbon dioxide, the methane sorption levels are unchanged after the sample has been exposed to high concentrations of carbon dioxide. Again, these results imply that the carbon dioxide has not introduced any additional disruptions. The absence of conditioning for methane sorption is consistent with the carbon dioxide sorption behavior, providing additional support for the interpretation presented earlier to explain carbon dioxide sorption.

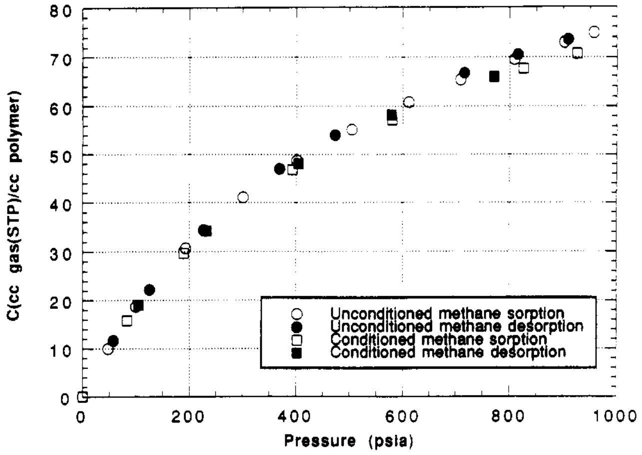

Figure 3. Sorption/desorption of methane by unconditioned and 900 psia carbon dioxide-exposed (conditioned) PMSP.

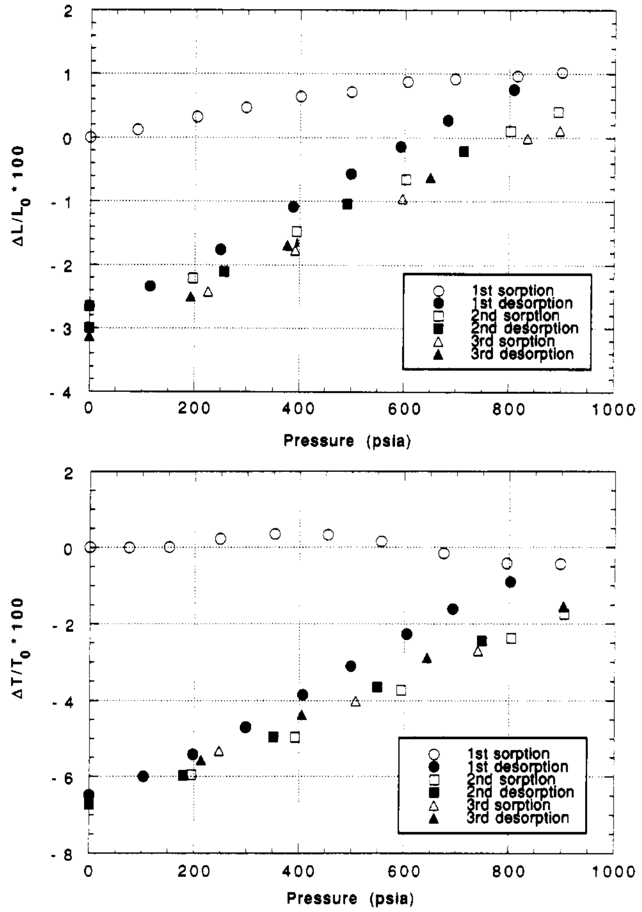

Figure 4. (a) Carbon dioxide-induced length dilation of PMSP. (b) Carbon dioxide-induced thickness dilation of PMSP.

The equilibrium carbon dioxide-induced dilation of the PMSP sample is shown in Figures 4a, 4b, and 5 as percent increase in length, thickness, and overall volume versus pressure in psia, respectively. Typically, most glassy polymers will expand equally in all directions if no residual stresses are present. However, parts a and b of Figure 4 show that is not the case for the solution-cast PMSP. The length dilation isotherm shows an approximately linear increase with pressure up to about 1% at 900 psia. In contrast, the thickness remains essentially unchanged during the initial pressurization cycle. Upon depressurization, the length decreases to approximately 97% of its original value and the thickness decreases to ap-

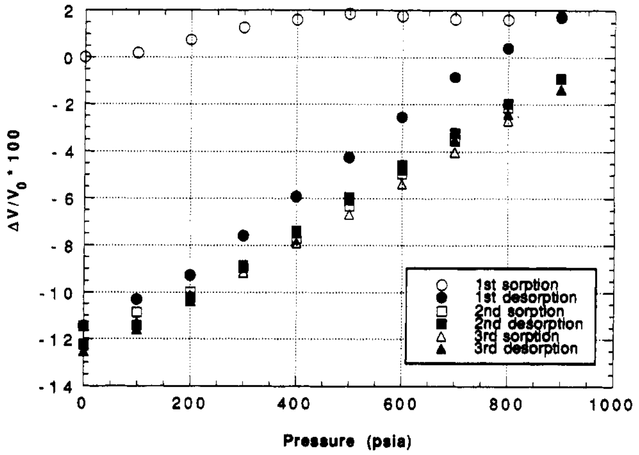

Figure 5. Carbon dioxide-induced total dilation of PMSP.

proximately 94% of its original value. Repeated pressurization/depressurization cycles give approximately linear isotherms, with the third cycle giving reproducible values. The overall volume dilation isotherms combining the length and thickness data are shown in Figure 5. Apparently, some type of residual volume remained in the polymer matrix after casting in toluene and drying under ambient conditions, with final drying under vacuum. This volume seems to have relaxed out after repeated exposures to high levels of sorbed carbon dioxide.

This unusual decrease in volume has been documented for PMSP with other pentrants as described by Witchey *et al.* for nonane-induced dilation of PMSP in a recent study.[33] The data indicated a contraction in one of the coordinate dimensions below the original value after exposure to the nonane. However, the authors assumed that the overall volume was not changed by hypothesizing that an increase in the sample thickness offset the decrease in sample length and width. Measurements were made of the initial and final thicknesses using a relatively insensitive digital micrometer capable of measuring to within 0.05 mil. The discrepancy in trends of thickness changes between the work of Witchey *et al.* and the present study may have been due to differences in film-casting technique or type of penetrant sorbed; however, the measurement technique of Witchey *et al.* would not be expected to reveal the subtle changes in thickness observed in this study.

At first glance, the decrease in volume of the original sample coupled with no decrease in sorption capacity for repeated exposure may seem contradictory. However, a number of scenarios may be offered to explain these observations. One of these explanations again involves the method of film preparation. As discussed previously, the cast film may be thought of as initially existing in an out of equilibrium stressed state due to expanded chain-packing disruptions and chain-packing defects left in the polymer matrix by the evaporating toluene. In this context, a packing defect may be thought of as a volume element in the polymer matrix capable of accommodating a penetrant molecule with no additional dilation required and a packing disruption may be thought of as a localized area of disordered chains providing a sorption site with reduced sorption energy requirements which normally requires some movement of chains to accommodate the penetrant. Upon initial exposure to carbon dioxide, the penetrant molecules take advantage of the many sites for sorption, most of which require no polymer chain movement, i.e. dilation, for accommodation. These sites may consist of both packing defects and large packing disruptions, as caused by the toluene casting procedure. As the concentration of carbon dioxide increases in the matrix, eventually some mobility is added to the polymer chains due to the presence of the carbon dioxide. As the pressure is reduced and carbon dioxide leaves the matrix, the chains are able to reorient to a more stable or equilibrium state which might involve the loss of volume from some of the larger packing disruptions. However, these areas most likely will not return to a close packed or most favored packing state but will remain as an out-of-equilibrium site and, therefore, provide an energetically favorable site for sorption during the next pressurization cycle. Considering these possibilities, the carbon dioxide could cause a reduction in overall volume while maintaining a constant number of sites for sorption.

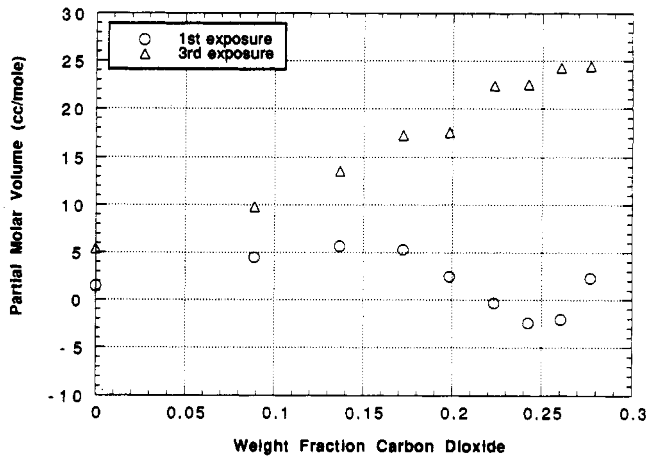

Figure 6. Partial molar volume of carbon dioxide in PMSP—first and third exposures.

Some evidence of this reordering of volume may be seen when the data are interpreted in terms of the partial molar volume of carbon dioxide in the polymer/penetrant mixture. The basic definition of the partial molar volume of a component in a mixture is given by eq 2,[34] where $\bar{v}_i$

$$\bar{v}_i = \left(\frac{\mathrm{d}V}{\mathrm{d}n_i}\right)_{T,p,n_j} \tag{2}$$

is the partial molar volume of component i, V is the total volume of the system, n_i is the number of moles of component i, T is temperature, p is pressure, and n_j is the number of moles of other components. When used for a binary mixture, as in this case, the partial molar volume of carbon dioxide is given by eq 3,[24] where $\bar{v}_1$ is the partial

$$\bar{v}_1 = V + (1 - \omega_1)\left[\left(\frac{\partial V}{\partial \omega_1}\right)_T + V\beta\left(\frac{\partial p}{\partial \omega_1}\right)_T\right] \tag{3}$$

molar volume of carbon dioxide, ω_1 is the weight fraction of carbon dioxide in the system, and β is the isothermal compressibility of the system which is usually small enough to be neglected.

By combination of the sorption and dilation data, the partial molar volume of carbon dioxide at various sorption levels in the mixture was calculated for the first and third pressurization cycles. The results are shown in Figure 6 which is a plot of carbon dioxide partial molar volume in cubic centimeters per mole versus the carbon dioxide weight fraction in the mixture. The partial molar volume for carbon dioxide during the first exposure gradually increases from an infinite dilution value of approximately 2.6 cm^3/mol to almost 6 cm^3/mol at a carbon dioxide weight fraction of 0.17. At higher weight fractions, the partial molar volume begins to decrease to a low of approximately −2 cm^3/mol. This decrease in values would seem to indicate that the concentration of carbon dioxide in the matrix reached a point at which the mobility of chains had been increased enough to begin relaxing out the extra volume mentioned earlier. As more carbon dioxide is added, the chains gain more mobility and relax further, resulting in a decreasing partial molar volume of carbon dioxide in the mixture. However, the third exposure gives constantly increasing values from an infinite dilution value of approximately 5 to 24 cm^3/mol at a carbon dioxide weight fraction of 0.3. The carbon dioxide partial molar volume does not appear to level off by a weight fraction of 0.3, indicating that all of the packing defects have not been filled, which may be explained in the context of the dual mode sorption model.

The dual mode sorption model states that two populations exist in the polymer environment. In its strictest sense, only the Henry's law population contributes to dilation of the polymer matrix by separating chains in order to be accommodated. The Langmuir population is said to reside in molecular scale packing defects which are capable of accommodating a sorbed penetrant with no movement of chains. Therefore, one would expect a partial molar volume initially at a low value due to the sorbing molecules entering both environments with only one contributing to dilation of the matrix. The penetrant partial molar volume would then increase as the defect sites are filled and then level off to a constant value once the defects had been saturated, and all remaining sorption occurs in the dissolved state. This final value indicates the volume required to accommodate penetrant in the dissolved state within the matrix. Therefore, the increasing carbon dioxide partial molar volume in PMSP is reasonable and might be expected to reach a plateau at around 30 cm^3/mol, as was seen in a previous study with polycarbonate.[24]

The differences between the partial molar volumes for the first and third isotherms support the idea presented earlier where excess volume is located around packing disruptions. During the initial exposure, these disruptions may be thought of as existing in an expanded state requiring little chain movement to accommodate a penetrant, resulting in a relatively low carbon dioxide partial molar volume. However, the chain configuration at these sites is not necessarily stable. Therefore, the dissolved carbon dioxide could provide enough mobility to relax the chains and reduce this excess volume, as shown by the decreasing carbon dioxide partial molar volume above a weight fraction of 0.17. On the next pressurization, however, the chains would have to be separated to accommodate the penetrant, thereby causing dilation. This dilation is shown as a constantly increasing partial molar volume for the third pressurization cycle.

Conclusions

PMSP sorbs carbon dioxide and methane in high amounts. These high sorption values can be attributed to the inherently large PMSP free volume. Initial exposure to carbon dioxide apparently increases chain mobility and therefore relieves stresses and excess volume in the polymer matrix induced by toluene solution casting. These relaxations appear in the form of a decreased overall volume upon depressurization. Repeated exposures to carbon dioxide do not result in subsequent relaxations. These findings were described in terms of some excess volume relaxing around packing disruptions but leaving the disruptions as sorption sites with lowered sorption energy requirements. PMSP did not exhibit conditioning behavior after exposure to high pressure of carbon dioxide. Subsequent carbon dioxide and methane sorption isotherms showed no increase in sorption levels when compared to samples which had not been exposed to carbon dioxide. This absence of conditioning was attributed to preconditioning by the toluene solvent and by the stiff chain backbone which is less susceptible to disruption formation in the chain packing.

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References and Notes

(1) Markiewicz, G. S.; Martinez, J. M. *Membrane Systems Gaining Gas Treating Converts. Am. Oil Gas Reporter*, May (1991).

(2) Hellums, M. W. Gas Permeation and Sorption in a Series of Aromatic Polycarbonates. Dissertation, The University of Texas at Austin, 1990.

(3) Coleman, M. R.; Koros, W. J. Isomeric Polyimides Based on Fluorinated Dianhydrides and Diamines for Gas Separation Applications. *J. Membr. Sci.* **1990**, *50*, 285.

(4) Jordan, S. M.; Koros, W. J. Characterization of Carbon Dioxide-Induced conditioning of Substituted Polycarbonates Using Various "Exchange" Penetrants. *J. Membr. Sci.* **1990**, *51*, 233.

(5) Hellums, M. W.; Koros, W. J.; Husk, G. R.; Paul, D. R. Fluorinated Polycarbonates for Gas Separation Applications. *J. Membr. Sci.* **1989**, *46*, 93.

(6) Pope, D. S.; Fleming, G. K.; Koros, W. J. Effect of Various Exposure Histories on Sorption and Dilation in a Family of Polycarbonates. *Macromolecules* **1990**, *23*, 2988.

(7) Jordan, S. M.; Koros, W. J.; Fleming, G. K. The Effects of CO_2 Exposure on Pure and Mixed Gas Permeation Behavior: Comparison of Glassy Polycarbonate and Silicone Rubber. *J. Membr. Sci.* **1987**, *30*, 191.

(8) Jordan, S. M. The Effects of Carbon Dioxide Exposure on Permeation Behavior in Silicone Rubber and Glassy Polycarbonates. Dissertation, The University of Texas at Austin, 1989.

(9) Chiou, J. S.; Paul, D. R. Effects of CO_2 Exposure on Gas Transport Properties of Glassy Polymers. *J. Membr. Sci.* **1987**, *32*, 195.

(10) Wonders, A. G.; Paul, D. R. Effect of CO_2 Exposure History on Sorption and Transport in Polycarbonates. *J. Membr. Sci.* **1979**, *5*, 63.

(11) Masuda, T.; Isobe, E.; Higashimura, T.; Takada, K. Poly[1-(trimethylsilyl)-1-propyne]: A New High Polymer Synthesized with Transition-Metal Catalysts and Characterized by Extremely High Gas Permeability. *J. Am. Chem. Soc.* **1983**, *105*, 7473.

(12) Masuda, H.; Nakata, Y.; Takada, K. Application of the Substituted Poly(acetylene) to a Semi-permeable Membrane. *Polym. Prepr. Jpn.* **1983**, *32*, 2925.

(13) Masuda, T.; Isobe, E.; Higashimura, T. Polymerization of 1-(trimethylsilyl)-2-propyne by Halides of Niobium(V) and Tantalum(V) and Polymer Properties. *Macromolecules* **1985**, *18*, 841.

(14) Takada, K.; Matsuya, H.; Higashimura, T. Gas Permeability of Polyacrylates Carrying Substituents. *J. Appl. Polym. Sci.* **1985**, *30*, 1605.

(15) Ichiraku, Y.; Stern, S. A. An Investigation of the High Gas Permeability of Poly(1-Trimethylsilyl-1-Propyne). *J. Membr. Sci.* **1987**, *34*, 5.

(16) Vrentas, J. S.; Vrentas, C. M. Sorption in Glassy Polymers. *Macromolecules* **1991**, *24*, 2404.

(17) Conforti, R. M.; Barbari, T. A.; Vimalchand, P.; Donohue, M. D. A Lattice-Based Activity Coefficient Model for Gas Sorption in Glassy Polymers. *Macromolecules* **1991**, *24*, 3388.

(18) Lipscomb, G. G. Unified Thermodynamic Analysis of Sorption in Rubbery and Glassy Materials. *AIChE J.* **1990**, *36*, 1505.

(19) Mi, Y. S.; Zhou, S.; Stern, S. A. Representation of Gas Solubility in Glassy Polymers by a Concentration-Temperature Superposition Principle. *Macromolecules* **1991**, *24*, 2361.

(20) Wissinger, R. G.; Paulaitis, M. E. A Molecular Thermodynamic Model for Sorption and Swelling in Glassy Polymer-CO_2 Systems at Elevated Pressures. *Ind. Eng. Chem. Res.* **1991**, *30*, 842.

(21) Koros, W. J.; Chan, A. H.; Paul, D. R. Sorption and Transport of Various Gases in Polycarbonate. *J. Membr. Sci.* **1977**, *2*, 165.

(22) Kamiya, Y.; Mizoguchi, K.; Hirose, T.; Naito, Y. Sorption and Dilation in Poly(ethylmethacrylate)-Carbon Dioxide System. *J. Polym. Sci., Part B: Polym. Phys.* **1989**, *27*, 879.

(23) Chiou, J. S.; Paul, D. R. Gas Sorption and Permeation in Poly(ethyl methacrylate). *J. Membr. Sci.* **1989**, *45*, 167.

(24) Fleming, G. K. Dilation of Silicon Rubber and Glassy Polycarbonates Due to High Pressure Gas Sorption. Dissertation, The University of Texas at Austin, 1988.

(25) Fleming, G. K.; Koros, W. J. Dilation of Polymers by Sorption of Carbon Dioxide at Elevated Pressures. 1. Silicone Rubber and Unconditioned Polycarbonate. *Macromolecules* **1986**, *19*, 2285.

(26) Jordan, S. M.; Koros, W. J.; Beasley, J. K. Characterization of CO_2-Induced Conditioning of Polycarboante Films Using Penetrants with Different Solubilities. *J. Membr. Sci.* **1989**, *43*, 103.

(27) Moe, M. B.; Koros, W. J.; Paul, D. R. Effects of Molecular Structure and Thermal Annealing on Gas Transport in Two Tetramethyl Bisphenol-A-Polymers. *J. Polym. Sci., Part B: Poly. Phys.* **1988**, *26*, 1931.

(28) Koros, W. J. Sorption and Transport of Gases in Glassy Polymers. Dissertation, University of Texas at Austin, 1977.

(29) Koros, W. J.; Paul, D. R. Design Considerations for Measurement of Gas Sorption in Polymers by Pressure Decay. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1903.

(30) Pope, D. S. The Effects of Conditioning on Sorption and Volume Dilation in Rubbery and Glassy Polymers. Dissertation, The University of Texas at Austin, 1991.

(31) Pope, D. S.; Koros, W. J.; Fleming, G. K. Measurement of Thickness Dilation in Polymer Films. *J. Polym. Sci., Part B: Polym. Phys.* **1989**, *27*, 1173.

(32) van Krevelen, D. W.; Joftyzer, P. J. *Properties of Polymers, 2nd ed.*; Elsevier: New York, 1976.

(33) Witchey, L.; Hopfenberg, H. B.; Chern, R. T. Sorption of n-Nonane In and Concomitant Dilation of Poly(1-Trimethylsilyl-1-propyne). *J. Membr. Sci.*, in press.

(34) Prausnitz, J. M.; Lichtenthaler, R. N.; Gomes de Azevedo, E. *Molecular Thermodynamics of Fluid-Phase* Equilibria, 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1986.