Hydrocarbon and Perfluorocarbon Gas Sorption in Poly(dimethylsiloxane), Poly(1-trimethylsilyl-1-propyne), and Copolymers of Tetrafluoroethylene and 2,2-Bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole

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ABSTRACT: Sorption of a series of gases, perfluorocarbon vapors (CF_4, C_2F_6, and C_3F_8) and their hydrocarbon analogues in poly(dimethylsiloxane) [PDMS], poly(1-trimethylsilyl-1-propyne) [PTMSP], and two random copolymers of tetrafluoroethylene [TFE] and 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole [BDD] are reported as a function of penetrant pressure at 35 °C. Sorption isotherms for all penetrants in rubbery PDMS are linear or slightly convex to the pressure axis, while those in the glassy polymers are concave and are well described by the dual mode model. Fluorocarbon sorption levels are lower than sorption levels of their hydrocarbon analogues in the hydrocarbon-based PDMS and PTMSP matrixes, while the reverse is true in the fluorinated TFE/BDD copolymers. Exceptionally low fluorocarbon solubilities in PDMS are ascribed to poor penetrant/polymer energetic interactions.

Introduction

The separation and recovery of perfluorinated compounds, such as CF_4, C_2F_6, and C_3F_8, from permanent gases, such as nitrogen, has recently gained attention as an environmentally important and commercially viable application of membrane technology in the microelectronics industry.[1] However, there are few reports of the transport properties of perfluorocarbons in polymers. Systematic studies of the sorption of perfluorocarbons in polymeric matrixes are not available. A fundamental understanding of the relationship between polymer structure and fluorocarbon sorption, diffusion, and permeation properties is vital to optimize materials selection for this emerging membrane separation.

Four polymers were selected for study to provide fundamental structure/property data regarding perfluorocarbon and hydrocarbon sorption in hydrocarbon and fluorocarbon polymeric matrixes. The polymers investigated in this study included two random, glassy copolymers of tetrafluoroethylene [TFE] and 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole [BDD], rubbery poly(dimethylsiloxane) [PDMS], and poly(1-trimethylsilyl-1-propyne) [PTMSP]. The TFE/BDD fluorocopolymers have excellent chemical resistance and are among the most permeable polymers known.[2] The high permeability coefficients in these polymers are attributed, in part, to their extremely open matrixes, which are characterized by very large fractional free volumes (FFVs). For example, the FFVs of TFE/BDD65 and TFE/BDD87 are 0.30 and 0.33, respectively.[3] These values are among the highest FFVs reported for nonporous polymers. For comparison, both of these values are well above the FFV of 0.15 for polysulfone,[4] a common glassy polymer used for gas separations. PDMS, the most permeable rubbery polymer, is used commercially for membrane-based vapor separation applications.[5] PTMSP is a glassy, hydrocarbon-based polymer that is the most permeable polymer known.[6] Like the TFE/BDD copolymers, PTMSP has exceptionally high free volume. On the basis of a polymer density of 0.75 g/cm^3,[7] it has a FFV of 0.29, which is also among the highest values reported for dense (i.e. nonporous) polymers. In marked contrast, the fractional free volume of PDMS is only 0.16, based on the measured density of 0.98 g/cm^3.[8]

Background

The sorption of penetrant into a glassy polymer is frequently described by the dual mode model:[9]

$$C = k_D p + \frac{C'_H bp}{1 + bp} \tag{1}$$

where C is the equilibrium penetrant concentration in the polymer at pressure p. k_D is the Henry's law parameter describing penetrant dissolution into the equilibrium densified polymer matrix, and C'_H is the Langmuir capacity parameter, which describes the sorption capacity of the nonequilibrium excess free volume characteristic of the glassy state. The Langmuir affinity parameter, b, is an equilibrium constant describing the affinity of a penetrant for a Langmuir site.

The concentration of sparingly soluble gases and vapors in rubbery polymers generally exhibits a linear dependence on penetrant pressure. This isotherm is described analytically by Henry's law:[10]

$$C = k_D p \tag{2}$$

The solubility of a penetrant in a polymer is defined as the ratio of equilibrium penetrant concentration to penetrant pressure:[10]

$$S \equiv \frac{C}{p} \tag{3}$$

Experimental Section

Two random perfluorinated copolymers (DuPont, Newark, DE) were characterized in this study. The first, TFE/BDD65 (trade name AF1600), is synthesized from 65 mol % 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole [BDD] and 35

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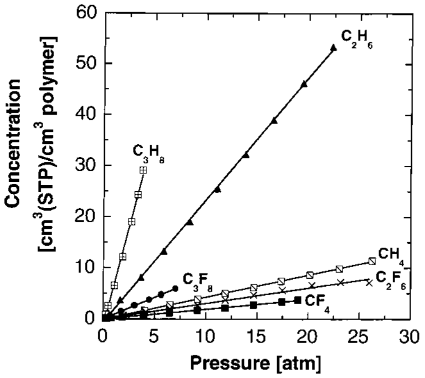

Figure 1. Hydrocarbon and fluorocarbon sorption isotherms at 35 °C in PDMS.

mol % tetrafluoroethylene [TFE]. The second, TFE/BDD87 (trade name AF2400), is prepared from 87 mol % BDD and 13 mol % TFE. Several 50 μm thick isotropic films of TFE/BDD65 and TFE/BDD87 were cast from 10 and 1 wt %, respectively, polymer solutions in PF 5060, a perfluorinated solvent supplied by 3M (Minneapolis, MN). The films were dried at ambient conditions until a constant weight was achieved (about 24 h).

A dense, filler-free poly(dimethylsiloxane) [PDMS] film, approximately 250 μm thick, was utilized for sorption experiments. This film was kindly prepared by Dr. Ingo Pinnau of Membrane Technology and Research, Inc. (Menlo Park, CA) using poly(dimethylsiloxane) supplied by Wacker Silicones Corp. (Adrian, MI). PDMS was cross-linked at 100 °C using a proprietary cross-linker/catalyst system provided by Wacker Silicones Corp. The cross-link density was estimated to be 7.8×10^{-5} mol/cm^3.[8] Singh et al. provide further characterization information for this sample.[8]

Poly(1-trimethylsilyl-1-propyne) [PTMSP] (Permea Inc., St. Louis, MI) films, approximately 90 μm thick, were prepared from a 2 wt % solution of polymer in toluene as described previously.[11] After casting and drying, the samples were stored in liquid methanol at ambient conditions until the day before use in order to prevent physical aging.[12] At this time, films were removed from methanol and dried at ambient conditions for 24 h.

Penetrant solubility was measured with a high-pressure barometric sorption apparatus.[13] Initially, each polymer film was placed in the sample chamber and exposed to vacuum overnight to remove air gases. For each gas, measurements were conducted stepwise from vacuum up to the maximum pressure (4 to 27 atm depending on the penetrant). The order of penetrant measurement in all polymers was H_2 (or He for the TFE/BDD copolymers), O_2, N_2, CH_4, C_2H_6, C_3H_8, CF_4, C_2F_6, and C_3F_8. Sorption equilibrium for all gases was reached within at most a few hours. After completion of these measurements, a low-pressure N_2 isotherm (up to 5 atm) was measured and compared to those obtained previously. For both TFE/BDD copolymers, these N_2 isotherms were the same, indicating no detectable long-term disruption of chain packing in these glassy copolymers. For PTMSP, there was no difference in N_2 isotherms determined before and after the sorption studies of the other penetrants. After each isotherm was collected, the polymer samples were degassed overnight.

Results and Discussion

Figures 1−4 present sorption isotherms for selected hydrocarbons and fluorocarbons in PDMS, PTMSP, and the TFE/BDD copolymers at 35 °C. The sorption isotherms for PDMS (cf. Figure 1) are linear or slightly convex to the pressure axis, which is consistent with previously reported gas and vapor sorption isotherms in PDMS[14] and in rubbery polymers in general.[10] For PTMSP (Figure 2) and the glassy fluorocopolymers (Figures 3 and 4) the characteristic concave shape of the isotherms relative to the pressure axis is well described by the dual mode model.[9] Sorption isotherms for the light gases (H_2, He, O_2, and N_2) are linear functions of pressure in all polymers.

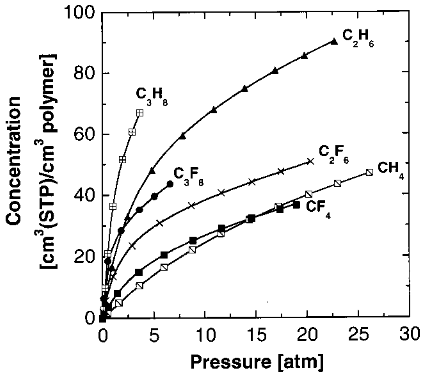

Figure 2. PTMSP sorption isotherms at 35 °C. The curves through the data points represent nonlinear least-squares fits of the sorption data to eq 1.

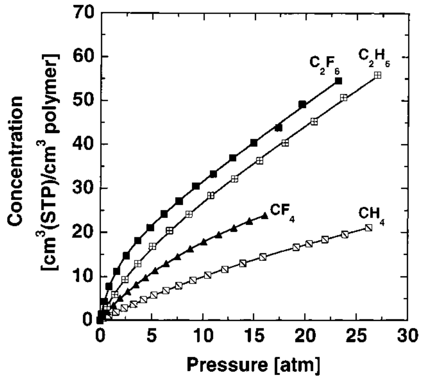

Figure 3. TFE/BDD87 Sorption isotherms at 35 °C. The curves through the data points represent nonlinear least-squares fits of the sorption data to eq 1.

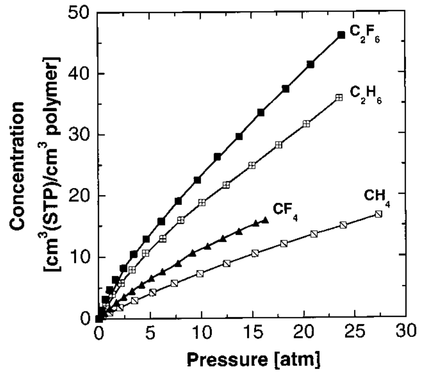

Figure 4. TFE/BDD65 Sorption isotherms at 35 °C. The curves through the data points represent nonlinear least-squares fits of the sorption data to eq 1.

On the basis of the isotherms in Figures 1 and 2, fluorocarbon penetrants are less soluble at the same pressure than the analogous hydrocarbon penetrants in the hydrocarbon-based polymers, PDMS and PTMSP. PDMS exhibits the largest difference between fluorocarbon and hydrocarbon sorption levels relative to the other polymers. For example, the concentration of C_2F_6 sorbed in PDMS is 7.4 times lower than that of C_2H_6 at 10 atm. In PTMSP, the concentration of C_2F_6 is 1.7 times less than that of C_2H_6 at 10 atm. In marked contrast, in both fluorocopolymers the fluorinated penetrants are more soluble than their hydrocarbon ana-

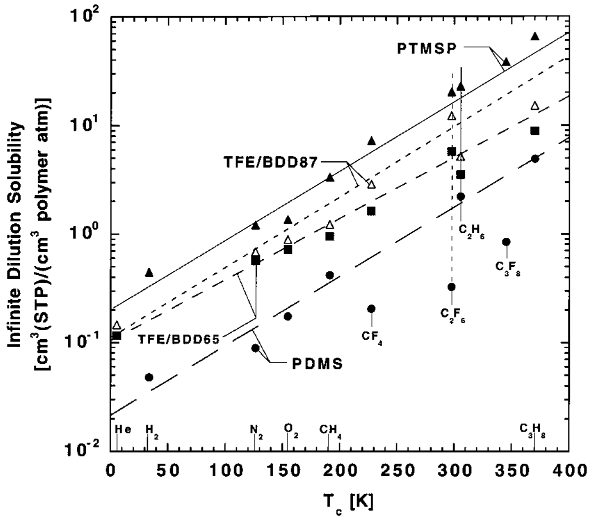

Figure 5. Infinite dilution solubility coefficients at 35 °C as a function of penetrant critical temperature. The line through the PTMSP data represents a best fit to the data for all penetrants. For the fluorinated TFE/BDD copolymers, the lines are the best fit to the permanent gases (He, N_2, and O_2) and fluorocarbons, and for PDMS, the line is the best fit to the permanent gases (H_2, N_2, and O_2) and hydrocarbons.

logues. For example, as shown in Figures 3 and 4, the concentration of C_2F_6 is approximately 1.2 times higher than that of C_2H_6 in both TFE/BDD65 and TFE/BDD87 at 10 atm.

These results are consistent with the solubility behavior of liquid mixtures of low molar mass fluorocarbons and hydrocarbons, which are known to demonstrate large positive deviations from ideal solution behavior.[15−17] Fluorocarbon liquids exhibit lower solubilities in typical hydrocarbon-based organic solvents than that usually associated with nonpolar liquids and are even immiscible in some hydrocarbons with similar carbon backbone structures.[18] For example, heptane/perfluoroheptane liquid mixtures phase separate around 50 °C.[16] This behavior agrees qualitatively with our observations that fluorocarbon penetrants are less soluble than their hydrocarbon analogues in a hydrocarbon environment (i.e. PDMS and PTMSP) and vice versa.

From these sorption data, infinite dilution solubility coefficients, S_0, were estimated for each penetrant by calculating the ratio of penetrant concentration to pressure in the limit as pressure approaches zero:

$$S_0 \equiv \lim_{p \to 0} \frac{C}{p} \tag{4}$$

Figure 5 presents these results as a function of penetrant critical temperature. Critical temperature, T_c, is frequently used as a scaling factor for penetrant condensability.[19] Generally, the larger T_c is for a penetrant, the more condensable and, therefore, the more soluble it is in a polymer. The logarithm of gas solubility in polymers often increases linearly with penetrant critical temperature.[19] We observe this trend in the solubility values of penetrants in PTMSP. In the TFE/BDD copolymers, in contrast, the larger hydrocarbon penetrants (C_2H_6 and C_3H_8) are less soluble than expected based on the best fit line through the permanent gas and fluorocarbon solubility data. In PDMS, the solubility coefficients of the fluorocarbon penetrants fall systematically below the predicted solubility level based on the solubility levels of permanent gases and hydrocarbons in this polymer. This result suggests unfavorable interactions between the fluorinated penetrants and the hydrocarbon-rich PDMS matrix and between hydrocarbons and the fluorocopolymers.

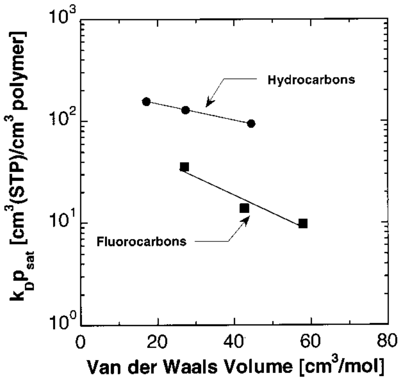

Figure 6. Activity-basis Henry's law coefficients as a function of penetrant size at 35 °C in PDMS.

Penetrant sorption into a polymer matrix may be viewed as a two step thermodynamic process: (1) penetrant condensation from a gas-phase density to a liquidlike density and (2) opening a gap in the polymer matrix to permit mixing of condensed penetrant (or, for supercritical gases, hypothetical condensed penetrant) with the polymer segments.[20] The first step of this process depends on the condensability of the penetrant at the temperature of interest, and the second step depends on the strength of polymer-penetrant interactions relative to polymer−polymer and penetrant-penetrant interactions.[21] To better understand the role of each step in determining penetrant solubility, it is desirable to separate these two effects. In this regard, condensability differences among penetrants can be accounted for by analyzing sorption data in terms of the product of gas solubility and penetrant vapor pressure, p_{sat}.[22] For rubbery PDMS, solubility at low pressure is equal to k_D, the Henry's law coefficient. The product of k_D p_{sat} is the activity-basis Henry's Law coefficient, k_D^a:

$$k_D^a \equiv k_D p_{sat} \tag{5}$$

The vapor pressures of gases whose critical temperatures are above 35 °C were calculated utilizing the Wagner equation with previously published constants.[23] The hypothetical vapor pressures of gases with critical temperatures below 35 °C were estimated by extrapolating the linear relation ln p_{sat} vs $1/T$ to above the critical point as suggested by Prausnitz[22] and Kamiya et al.[24]

Figure 6 presents k_D^a for hydrocarbons and fluorocarbons in PDMS as a function of the van der Waals volume of the penetrant. The van der Waals volume, a convenient measure of penetrant size, is calculated using Bondi's group contribution method.[25] On the basis of the data in Figure 6, the activity-basis Henry's Law coefficients for both hydrocarbons and fluorocarbons in PDMS decrease as penetrant size increases, consistent with more energy of mixing being required to open larger gaps in the polymer matrix to accommodate larger penetrants. The k_D^a values for fluorocarbons are nearly an order of magnitude lower than those of the hydrocarbons at the same penetrant size. This result indicates that insertion of a fluorocarbon molecule into

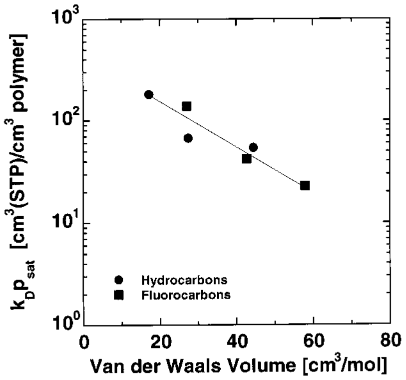

Figure 7. Activity-basis Henry's law coefficients as a function of penetrant size at 35 °C in PTMSP.

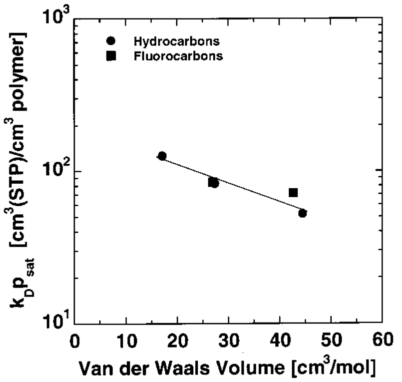

Figure 8. Activity-basis Henry's law coefficients as a function of penetrant size at 35 °C in TFE/BDD87.

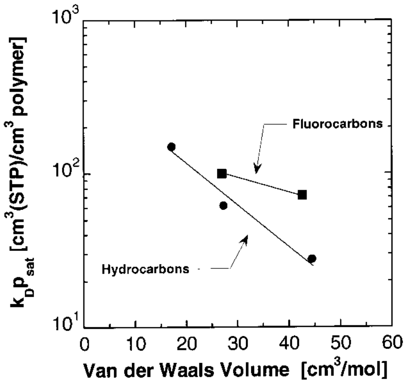

Figure 9. Activity-basis Henry's law coefficients as a function of penetrant size at 35 °C in TFE/BDD65.

the hydrocarbon, liquidlike, PDMS matrix requires substantially more energy than insertion of a hydrocarbon molecule of similar size and condensability, consistent with the strong nonideality of hydrocarbon–fluorocarbon liquid mixtures.

Penetrant sorption in a glassy polymer consists of the sum of contributions from Henry's Law sites and Langmuir sites, as indicated by eq 1. To focus on the effects of polymer–penetrant interactions and compare these with the trends observed in rubbery PDMS, we compare penetrant sorption only in the densified equilibrium polymer matrix of the glassy fluorocopolymers and PTMSP. In this regard, the sorption isotherms in Figures 2–4 were fit to the dual mode equation (eq 1), k_D^a values were calculated, and the results are presented in Figures 7–9. Similar to PDMS, k_D^a decreases with increasing penetrant size for all three glassy polymers. In contrast to PDMS, the ultrahigh free volume glassy polymers, PTMSP and TFE/BDD87, do not show significant differences (beyond those expected based on penetrant size) between hydrocarbon and fluorocarbon activity-basis solubilities. Only in TFE/BDD65, which has the lowest fractional free volume of the glassy polymers considered, does there appear to be a small systematic variation between the two families of penetrants. On the basis of fluorocarbon k_D^a values, which are higher than those of hydrocarbon penetrants of the same size, fluorinated penetrants experience more favorable interactions with the fluorinated TFE/BDD65 matrix than do the hydrocarbons. Nevertheless, differences in sorption levels among penetrants in the equilibrium-densified matrix of the glassy PTMSP and TFE/BDD87 polymers are predominately due to condensability and penetrant size effects. This result suggests that the poorer chain packing associated with these high free volume polymers provides relatively high energy sorption sites in the equilibrium densified Henry's Law regions which are easily accessible to the penetrant molecules and permits relatively nonspecific sorption. Temperature-dependent C_3H_8 and C_3F_8 sorption measurements in TFE/BDD87, which are used to characterize the enthalpy change on mixing, are consistent with this point of view.[26] The difference in enthalpy of mixing between hydrocarbons and fluorocarbons in TFE/BDD87 is near the uncertainty limit of the measurements at higher pressure, where most of the penetrant molecules are partitioning into the Henry's Law region of the polymer. Therefore, the higher hydrocarbons (ethane and propane) are more soluble than their fluorocarbon analogues in PTMSP (cf. Figure 2) primarily because the nonequilibrium excess volume in PTMSP is more accessible to hydrocarbons than fluorocarbons. In TFE/BDD87, the fluorinated penetrants are more soluble than their hydrocarbon analogues mainly because the nonequilibrium excess volume is more accessible to the fluorinated penetrants than to their hydrocarbon analogues. In TFE/BDD65, fluorocarbon penetrants are more soluble than their hydrocarbon analogues due to lower hydrocarbon sorption in the Henry's Law regions and, for CF_4, in the Langmuir sites as well.

Conclusions

The sorption isotherms of fluorocarbons and hydrocarbons in glassy PTMSP, TFE/BDD65, and TFE/BDD87 are consistent with the dual mode model. In rubbery PDMS, fluorocarbon penetrants are sparingly soluble and generally exhibit linear isotherms. In a fluorinated environment (the TFE/BDD copolymers), fluorocarbon penetrants are more soluble than their hydrocarbon analogues, while the reverse is true in a hydrocarbon matrix (PTMSP and PDMS). The extremely low fluorocarbon sorption levels in PDMS cannot be explained simply based on condensability or penetrant size effects. There appears to be an unfavorable interaction, consistent with the large positive deviation from ideal solution behavior exhibited by liquid mixtures of hydrocarbons and fluorocarbons, inhibiting the dissolution of fluorinated penetrants into the hydrocarbon-rich PDMS matrix.

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Supporting Information Available: Four tables consisting of Henry's Law coefficients and saturation vapor pressures of all penetrants studied in PDMS at 35 °C, and dual mode sorption parameters for all penetrants examined in PTMSP and the TFE/BDD copolymers (2 pages). Ordering and Internet access information is given on any current masthead page.

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