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Sorption of Gases and Vapors in an Amorphous Glassy Perfluorodioxole Copolymer

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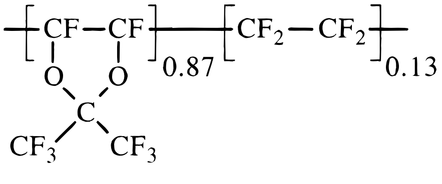
ABSTRACT: Gas and vapor sorption properties of a random copolymer of 87 mol % 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole and 13% tetrafluoroethylene (AF2400) are reported. Using both pressure decay and inverse gas chromatography (IGC) methods, a wide range of solutes was studied: He, N_2, O_2, CO_2, C_1-C_{13} *n*-alkanes, CF_4, C_2F_6, C_6F_6, and $C_6F_5CF_3$. These solutes have critical temperatures ranging from 5 to 677 K. AF2400 has very large solubility coefficients, *S*, relative to other glassy and rubbery polymers. Only poly(1-trimethylsilyl-1-propyne), the most permeable polymer known, exhibits higher solubility coefficients. The large solubility coefficients in AF2400 are mainly due to high Henry's law solubility coefficients. Fluorocarbon solutes exhibit higher solubility than their hydrocarbon analogues. A novel linear correlation between the logarithm of *S* and T_c^2, where T_c is the solute critical temperature, was observed. On the basis of IGC results, the microcavity size in this perfluoropolymer is larger than in conventional hydrocarbon-based glassy polymers.

Introduction

Poly(1-trimethylsilyl-1-propyne) (PTMSP), the most permeable polymer known, exhibits extremely high gas solubility and diffusivity[1−3] as well as very large free volume.[4] Moreover, other glassy polymers containing bulky $Si(CH_3)_3$ groups are also extremely permeable,[5] suggesting that this substituent could be a uniquely effective way to prepare highly permeable glassy polymers. Therefore, the discovery of another glassy polymer that is almost as permeable as PTMSP,[6−8] but is based on an entirely different repeat unit, has stimulated much interest. As shown below, this random copolymer is composed of 13 mol % tetrafluoroethylene and 87 mol % 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole (AF2400, Du Pont, Wilmington, DE):



This polymer has a glass transition temperature of 240 °C,[9] and its gas permeation properties have been described in several recent publications.[7,8,10−12] However, much less information is available regarding gas and vapor sorption properties of this polymer.[11] Therefore, this paper reports sorption properties of AF2400 for a wide range of gases and vapors. These results are compared with those of PTMSP as well as conventional, low free volume glassy polymers in order to rationalize structure/property relations in AF2400.

Experimental Section

Film Preparation and Characterization. Uniformly thick films of AF2400 (15−60 μm thick) were cast from a 1.5 wt % solution in PF 5060 (a mixture of perfluorohexane isomers supplied by 3M (Minneapolis, MN)). The film density, ρ, was determined by immersing samples in aqueous calcium nitrate solutions.

High-Pressure Sorption. Gas sorption over the range 0−28 atm was determined using a barometric (pressure-decay), dual-volume, dual-transducer instrument.[13] First cycle sorption isotherms were measured in the following order: He, N_2, O_2, and CH_4 (up to 27 atm); CO_2 and C_2H_6 (up to 5 atm). Then, second cycle sorption experiments were performed, and the gases were studied in the following order at pressures up to 28 atm or up to the vapor pressure of the solute when it was lower than 28 atm: CO_2, C_2H_6, He, CF_4, C_2F_6, N_2, C_3H_8, *n*-C_4H_{10}, and O_2. On the basis of a comparison of He, N_2, and O_2 isotherms from first and second cycles, there were no significant, long-term conditioning effects. Except for CH_4, all results reported in this work were obtained from second cycle measurements.

CO_2 and O_2 were purchased from Linde. He, N_2, C_2H_6, C_3H_8, and *n*-C_4H_{10} were obtained from National Specialty Gases. CF_4 and C_2F_6 were kindly provided by Dr. J. Greuneveld of 3M Co. Both fluorocarbons had a purity >99.5%. All gases were used as received.

Inverse Gas Chromatography. The infinite dilution solubility and enthalpy change of sorption for a series of *n*-alkanes (*n*-C_4H_{10} to *n*-$C_{13}H_{28}$) and perfluorinated solutes (C_6F_6 and $C_6F_5CF_3$) were determined by inverse gas chromatography (IGC). The gas chromatograph (GC) was a LKhM-8MD equipped with a flame ionization detector. The stainless steel column was 1 mm × 1 m (inside diameter × length) and was packed with SUPERINERTON (0.125−0.160 mm) as the solid support for the polymer. Three columns, containing 5.0, 9.5, and 20.1 g of AF2400/100 g of support, were prepared. To coat the support, a known amount of AF2400 was dissolved in perfluorotoluene with constant stirring and low heat. A fixed amount of SUPERINERTON was slowly added to the stirred solution, and the solvent was evaporated. The polymer-coated support was loaded into the column, which was installed in the GC.

Methane was used as a nonsorbing gas to account for the dead volume of the chromatographic system, and He was used

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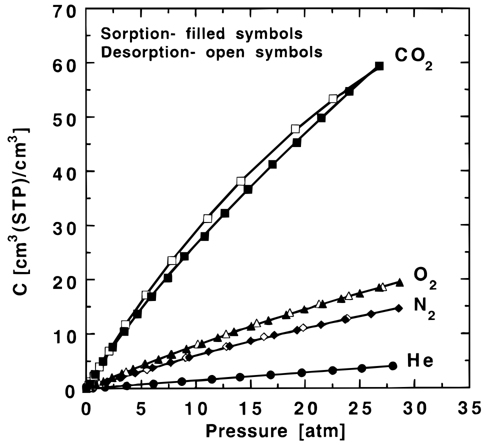

Figure 1. Sorption of permanent gases in AF2400 at 35 °C.

as the carrier gas. Inlet and outlet pressures of the column, measured by precision manometers, were used to correct retention volumes. For each solute, retention volumes were independent of sample size and flow rate, indicating that sorption equilibrium in the column characterized infinite dilution conditions and diffusion limitations did not distort the measured solubility coefficients.

Liquid solutes were purchased from Reakhim Co. (Kharkiv, Ukraine). Hydrocarbon gases were kindly provided by Institute of Chemistry (N. Novgorod State University, Russia). These solutes were used as received.

Results and Discussion

Density and Fractional Free Volume. The film sample density was 1.77 ± 0.01 g/cm^3 at 25 °C, which is in good agreement with the value of 1.74 g/cm^3 from dilatometry considering that our films were processed differently from the sample used for dilatometry studies.[9] Fractional free volume, FFV [cm^3 of free volume/cm^3 of polymer], is commonly used to characterize the efficiency of chain packing and is widely used as a correlating parameter for polymer permeation properties:[14]

$$\mathrm{FFV} = \frac{1/\rho - 1.3v_\mathrm{W}}{1/\rho} \qquad (1)$$

where v_W is the van der Waals volume of the repeat unit. On the basis of eq 1, the fractional free volume of AF2400 is 0.32, the highest value reported for a perfluoropolymer. For comparison, the FFV values of PTMSP (the most permeable polymer), polysulfone (a glassy polymer used commercially for gas separation), and poly(dimethylsiloxane) (a rubbery polymer used for vapor separation) are approximately 0.3, 0.14, and 0.18, respectively.[15]

High-Pressure Sorption. Sorption isotherms for He, N_2, O_2, and CO_2 at 35 °C are presented in Figure 1. With the exception of helium, all sorption isotherms are concave to the pressure axis, a feature commonly observed in glassy polymers.[16] The closed and open symbols in Figure 1 represent sorption data obtained on increasing and decreasing pressure, respectively. The lines through the data points for the gases other than helium represent nonlinear least-squares fits of the dual-mode sorption model to the experimental data. The model is given by[16]

$$C = k_\mathrm{D}p + C'_\mathrm{H}\frac{bp}{1 + bp} \qquad (2)$$

Table 1. Dual-Mode Sorption Parameters in AF2400 at 35 °C

gas	k_D (cm^3(STP)/(cm^{3}atm))	C'_H (cm^3(STP)/cm^3)	b (atm^{-1})	$C'_\mathrm{H}b/k_\mathrm{D}$
He[a]	0.15			
N_2	0.15	37.6	0.015	3.8
O_2	0.44	13.3	0.033	1.0
CH_4	0.35	24.5	0.036	2.5
CO_2	1.6	25.5	0.07	1.1
CF_4	0.45	29.3	0.082	5.3
C_2H_6	1.5	16.2	0.22	2.4
C_2F_6	1.6	17.8	0.59	6.6
C_3H_8	4.2	13.2	0.83	2.6
C_4H_{10}	8.5	18.6	1.2	2.6

[a] For helium, since the sorption isotherm is linear, it is not possible to extract all three dual-mode parameters. In this case, solubility is characterized by an effective Henry's law coefficient.

where k_D is the Henry's law parameter characterizing sorption into the densified equilibrium matrix of the glassy polymer, C'_H is the Langmuir sorption capacity, which characterizes sorption into the nonequilibrium excess volume associated with the glassy state, and b is the Langmuir affinity parameter. For the solutes in Figure 1 and for all other solutes considered in this study, the model parameters estimated from the data obtained on increasing pressure are recorded in Table 1. Since the helium isotherm is linear, it is not possible to extract estimates of all three dual-mode model parameters, so the slope of the helium isotherm is reported in Table 1 as an effective Henry's law parameter k_D^*, where $k_\mathrm{D}^* = k_\mathrm{D} + C'_\mathrm{H}b$.

For all of the solutes in Figure 1 except CO_2, the sorption and desorption isotherms are essentially identical. The CO_2 concentration is somewhat higher on desorption than on sorption. This behavior is typical for CO_2 sorption in other glassy polymers and is commonly ascribed to disruption of polymer chain packing by the solute, which leads to higher sorption levels during the desorption cycle of sorption measurements.[17] As indicated in the Experimental Section, in the absence of solute, the polymer reorganizes rather rapidly to a common, pseudoequilibrium state. Sorption isotherms of the light gases (He, N_2, and O_2) measured after exposure of the polymer to all gases were the same as those measured before exposure to CO_2, hydrocarbon, or fluorocarbon solutes, suggesting that the observed hysteresis was short-lived.

Figure 2 presents sorption isotherms for a series of hydrocarbons at 35 °C. Sorption levels are in the following order: n-C_4H_{10} > C_3H_8 > C_2H_6 > CH_4, consistent with decreasing solute condensability as the chain length is reduced. All sorption isotherms in this figure are well described by the dual-mode sorption model, and the corresponding parameters are recorded in Table 1. For the higher hydrocarbons (ethane, propane, and butane), gas sorption levels are somewhat higher on desorption than on sorption, consistent with the CO_2 results.

Sorption isotherms for CF_4 and C_2F_6 at 35 °C are presented in Figure 3. Like the corresponding hydrocarbons, at the same gas pressure, C_2F_6 is more soluble than CF_4. As noted earlier by Merkel et al.,[3] the fluorocarbons are more soluble in the polymer matrix than their hydrocarbon analogues. Similar to the higher hydrocarbon sorption isotherms in Figure 2, the more soluble fluorocarbon vapor in Figure 3, C_2F_6, exhibits hysteresis on desorption.

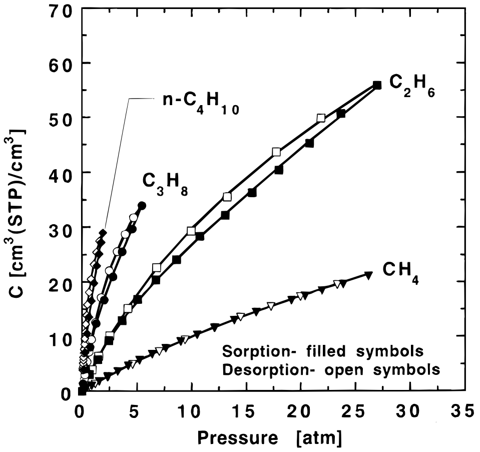

Figure 2. Hydrocarbon sorption in AF2400 at 35 °C.

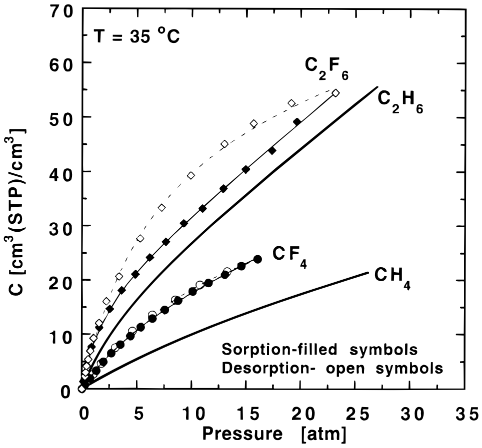

Figure 3. Fluorocarbon sorption in AF2400 at 35 °C. For comparison, sorption isotherms for hydrocarbon analogues are included from Figure 2. The solid and dashed lines represent fits of the dual mode model to the experimental sorption and desorption data, respectively.

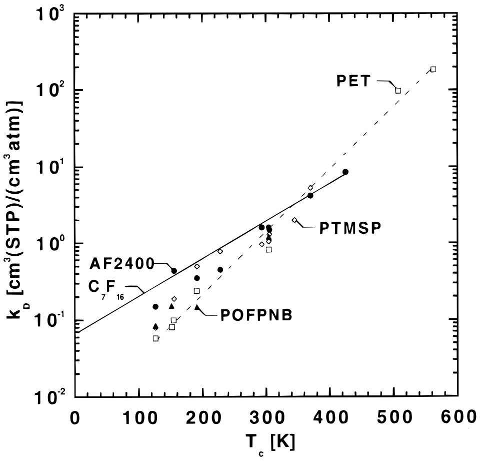

Figure 4. Correlation of Henry's law solubility coefficient at 35 °C with solute critical temperature in PTMSP,[3] POFPNB,[18] amorphous poly(ethylene terephthalate) [PET],[19] and C_7F_{16}.[20]

Figure 4 presents Henry's law coefficients at 35 °C from Table 1 as a function of gas critical temperature, T_c. For comparison, k_D values for gas sorption in other polymers[3,18,19] and in liquid perfluoroheptane[20] are included in this figure. For solutes that do not undergo specific interactions with the polymer or liquid matrix, solubility usually scales with measures of solute condensability such as solute boiling point, critical temperature, or the force constant in the Lennard-Jones intermolecular potential.[21−23] For such cases, the following relation between solute critical temperature and Henry's law coefficients was derived using a classical thermodynamics model:[23−25]

$$\log k_D = \log k^o_D + aT_c \tag{3}$$

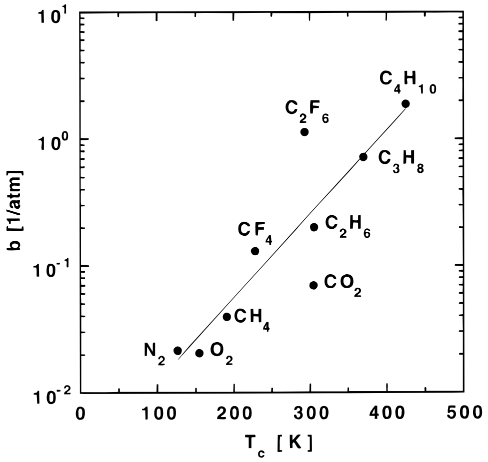

Figure 5. Langmuir affinity parameter, *b*, as a function of gas critical temperature in AF2400.

The parameters of this equation depend on the nature of the matrix and the solute. Henry's law solubility coefficients in AF2400 are very large, comparable to the values observed for PTMSP, and they are quite similar to the Henry's law solubility coefficients reported for perfluoroheptane. Kobatake and Hildebrand[20] observed that the parameter *a*, the slope of the correlation lines in Figure 4, is lower for gas dissolution in fluorinated liquids than for gas dissolution into hydrocarbon-based liquids. These phenomena (i.e., high Henry's law solubility coefficients and a weak dependence of k_D on T_c) have also been reported for gas dissolution in partially fluorinated polymers[18] and are ascribed to intermolecular interaction energies being much lower in fluorinated media than in hydrocarbon-based liquids and polymers. Consistent with these findings, the conventional, low free volume polymer, poly(ethylene terephthalate) [PET], exhibits a significantly higher slope than any of the fluorinated materials presented in Figure 4. Critical temperature is well correlated with critical volume of gas molecules.[26] Therefore, correlations of solubility with critical volume could also be considered. In AF2400, k_D changes relatively slowly with increasing T_c (or, equivalently, V_c), suggesting that the process of moving polymer chain segments to accommodate sorbed gas molecules requires less work in perfluorinated polymers and liquids than in conventional hydrocarbon-based polymers and liquids.

Figure 5 presents AF2400 Langmuir affinity parameter values at 35 °C (from Table 1) as a function of solute critical temperature. This parameter characterizes the relative rates of gas sorption and desorption in the excess free volume associated with the glassy state. The logarithm of *b* generally increases with increasing solute critical temperature, consistent with previous results for gas sorption in glassy polymers.[13]

Selected Langmuir affinity parameter values for several polymers are given in Table 2. The logarithm of this parameter increases with increasing T_c in AF2400 and in the other polymers. However, the Lang-

Table 2. Langmuir Affinity Parameters in AF2400 and Other Glassy Polymers[a]

	Langmuir affinity parameter, b, (atm^{-1})						
gas	AF2400	PTMSP[3,47]	PC[48,49]	PSF[50]	PVC[51]	PFMNB[b,18]	PVTMS[b,52]
N_2	0.015	0.014	0.056	0.016	0.045	0.019	0.014
CH_4	0.036	0.05	0.084	0.07	0.062	0.043	0.045
CO_2	0.070	0.04	0.26	0.326	0.209	0.171	0.16
C_2H_6	0.22	0.31			−0.30	0.5	

[a] The data are reported at 35 °C unless otherwise indicated. PTMSP = poly(1-trimethylsilyl-1-propyne), PC = bisphenol A polycarbonate, PSF = polysulfone, PVC = poly(vinyl chloride), PFMNB = poly(fluoromethylnorbornene), PVTMS = poly(vinyltrimethylsilane). [b] 25 °C.

muir affinity parameter of CO_2 for both AF2400 and PTMSP are systematically lower than those of the other polymers. These two polymers have extremely high values of nonequilibrium excess volume. For example, the fraction of the total specific volume present as nonequilibrium excess volume in AF2400 and PTMSP is estimated to be 0.20−0.25 (from solute sorption studies)[27] and 0.22 (by volume dilatometry),[11] respectively. In conventional glassy polymers, such as polycarbonate, polysulfone, and poly(vinyl chloride), the fraction of the total volume present as nonequilibrium excess volume is 0.051, 0.0705, and 0.012, respectively, at 25 °C (from volume dilatometry).[28] Langmuir sorption occurs in the nonequilibrium excess volume of glassy polymers. Srinivasan et al.[29] noted that the CO_2 Langmuir affinity constant for PTMSP is small relative to those for other glassy polymers. They linked the low CO_2 Langmuir affinity parameters to large Langmuir sorption sites, which presumably permits more facile sorption into the Langmuir sites. Low values of b in two high free volume glassy materials (AF2400 and PTMSP) corroborate the hypothesis of Srinivasan et al.[29] that weaker Langmuir affinity parameters can serve as an indication that the sorption sites in the Langmuir mode are larger than those in conventional glassy polymers.

Neither we nor Srinivasan observed large, systematic differences in Langmuir affinity parameter values for other light gas solutes between these high free volume polymers and conventional, low free volume glassy polymers. This may be related to the lower absolute values of heats of sorption of these light gases in comparison with carbon dioxide. Since the absolute value of CO_2 heat of sorption is larger than that of the light gas solutes, carbon dioxide may be more sensitive to the local environment inside the microvoids (e.g., interaction with the microvoid surface) than other, less condensable solutes. However, this effect is small and warrants further study.

Unexpectedly, AF2400 Langmuir affinity constants for several solutes with similar critical temperatures, i.e., CO_2, C_2H_6, and C_2F_6, differ by nearly an order of magnitude. The lowest value is observed for CO_2, whereas the highest is observed for C_2F_6. The lower the value of the Langmuir affinity constant, the more the Langmuir adsorption equilibrium is shifted toward dissociation of the "sorbed gas-site complex". In other words, the affinity of AF2400 for carbon dioxide is less than might be anticipated for a gas with such a T_c value. In contrast, the Langmuir affinity parameter of C_2F_6 is substantially larger than expected on the basis of the trend line in Figure 5.

Infinite dilution gas solubility coefficients ($S = k_D + C'_Hb$) in AF2400 at 35 °C are presented in Figure 6 as a function of T_c. For comparison, the solubility coefficients in several other glassy polymers[3,18,30] are also included. The dual-mode sorption parameters used to estimate S are reported in Table 1. There is a reasonable correlation between S and T_c. With the exception of PTMSP, solubility coefficients are consistently higher in AF2400 than in the other polymers. Interestingly, AF2400 has Henry's law solubility coefficients that are similar in magnitude to those of PTMSP (cf. Figure 4), but overall gas solubility is significantly higher in PTMSP than in AF2400 (cf. Figure 6). Therefore, the higher gas solubilities in PTMSP, relative to AF2400, are a result of much higher solute sorption in the nonequilibrium excess volume (Langmuir sites) in PTMSP than in AF2400.[11] Extremely high Langmuir capacity parameters for penetrants in PTMSP relative to penetrants in conventional polymers have been noted previously.[27,29] In addition, the apparent inaccessibility of Langmuir microvoids in AF2400 has been reported.[11] The slopes of the least squares lines drawn through the data in Figure 6 are somewhat steeper in the hydrocarbon-based polymers (PTMSP, PET) than in the fluorinated materials (AF2400, POFPNB). However, this difference is very subtle, particularly for POFPNB and PTMSP. In glassy polymers, infinite dilution solubility is determined predominantly by the Langmuir contribution to solubility since C'_Hb is usually much larger than k_D.[16] For AF2400, the weaker dependence of S on T_c is due to weaker correlations of both k_D and C'_Hb with T_c.

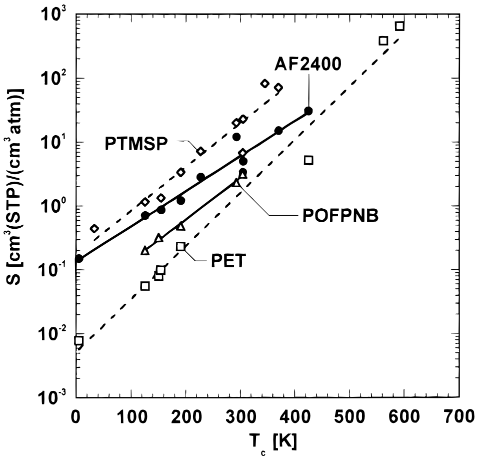

Figure 6. Correlation of solubility coefficients S with gas critical temperature T_c in AF2400, PTMSP,[3] POFPNB,[18] amorphous PET.[30]

The ratio C'_Hb/k_D characterizes the ratio of sorption in the nonequilibrium Langmuir sites to that in the Henry's law sites at infinite dilution. On the basis of the results in Table 1, a relation between the magnitude of C'_Hb/k_D in AF2400 and solute nature is observed. All hydrocarbon gases have C'_Hbk_D values close to 2.5. The ratio is substantially larger for the fluorocarbon gases (5.3 for CF_4 and 6.6 for C_2F_6). An especially low value of C'_Hb/k_D, 1.1, was observed for carbon dioxide, which is ascribed to its very low b value. This ratio is also unusually low for O_2, another oxygen-containing solute. The reason for the observed grouping of $C'_H b/k_D$ values with penetrant type is not well understood and is not predicted by current theoretical models of gas sorption in glassy polymers.

Inverse Gas Chromatographic Sorption. Inverse gas chromatography allows a direct determination of many thermodynamic parameters of sorption by measuring retention time, t_r, and net retention volume, v_n:

$$v_n = (t_r - t_a)J_n^{\,m}F_c(273/T_{col}) \tag{4}$$

where t_a is the retention time of a so-called "nonsorbed" component (CH_4 in this work) that serves as a measure of the dead volume of the chromatographic system, $J_n^{\,m}$ is the correction for pressure drop in the column, F_c is the carrier gas flow rate, and T_{col} is the column temperature. Tabulated values[31] of $J_n^{\,m}$ were used. The specific retention volume, v_g, was calculated from

$$v_g = v_n/w_1 \tag{5}$$

where w_l is the weight of the polymer in the column.

In principle, v_g values can include contributions of bulk sorption (absorption) in the polymer phase and surface adsorption at the "polymer−gas", "solid support−gas", and "polymer−solid support" boundaries. However, if v_g is independent of w_l, as in this work, the two latter contributions are negligible. This result was also confirmed by negligibly small retention times observed in the column with pure solid support. The observed v_g values characterize equilibrium sorption because t_r and v_n did not depend on the carrier gas flow rate (2−20 mL/min). Thus, for the amount of AF2400 in the three columns and for the set of solutes studied, diffusion limitations do not prevent the attainment of equilibrium sorption in the whole volume of the AF2400 film on the surface of the SUPERINERTON solid support. Such behavior is typical for polymers above their glass transition temperature.[32] However, for polymers with high diffusivity (e.g., poly(vinyltrimethylsilane)[33] or poly(phenylene oxide))[34] no diffusion limitation can be observed even in the glassy state. Additionally, the v_g values did not depend on the size of sample injected into the column, so these values characterized the initial slope of the sorption isotherm (i.e., infinite dilution conditions).

Figure 7 shows a retention diagram (i.e., temperature dependence of v_g) of n-heptane on three columns with different contents of AF2400 over a temperature range from 52 to 232 °C. The excellent coincidence of the points proves that only volumetric or bulk sorption takes place in the chromatographic columns containing this polymer. No hysteresis was observed when retention was measured upon heating or cooling. The relatively rapid attainment of sorption equilibrium in AF2400 is in agreement with reports of high solute diffusivity in this material.[12]

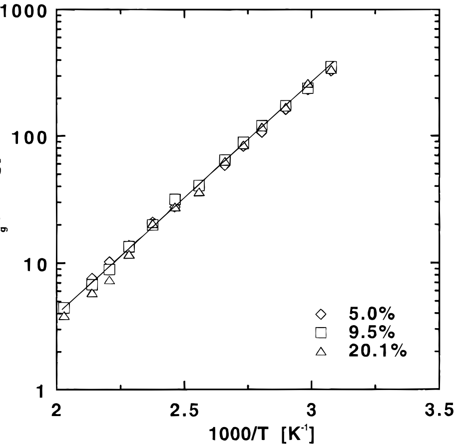

Figure 7. Retention diagram of n-heptane in columns coated with varying amounts of AF2400. The weight fraction of AF2400 on the columns was 5.0% (◇), 9.5% (□), and 20.1% (△).

Table 3. Comparison of Inverse Gas Chromatography Hydrocarbon Retention Volumes in AF2400 and Other Glassy Polymers at 150 °C

	retention volume, v_g (cm^3/g)		
solute	AF2400[a]	polysulfone[37]	poly(vinyltrimethylsilane)[36]
pentane	6.0	0.44	2.8
hexane	10.0	0.64	5.1
heptane	25	0.88	10.3
benzene	24	4.3	8.9

[a] Column containing 20.1 wt % AF2400.

The specific retention volume can be used to calculate the infinite dilution solubility coefficient as follows:[35]

$$S = v_g\, p^o \rho_1 \tag{6}$$

where the standard pressure, p^o, is 1 atm and ρ_l is the density of the polymer phase at the temperature of the measurement. In this equation, the term accounting for nonideal gas phase behavior of the solutes was neglected. However, this term is approximately unity for nonpolar and non-hydrogen-bonding solutes such as those considered in this study.[36]

IGC was used to determine the solubility coefficients for a series of solutes having critical temperatures from 425 K (n-butane) to 677 K (tridecane). Data obtained using the pressure decay technique provided S values for gases from He (T_c = 5.3 K) to n-butane. The solubility coefficients of n-butane at 35 °C by the pressure decay and IGC methods were 31 and 52 cm^3 (STP)/(cm^3 atm), respectively. While these values differ by approximately 40%, they are considered to be in reasonable agreement given the large differences in the experimental methodologies and differences in sample preparation protocols.

Table 3 presents a comparison of v_g values in AF2400 with those reported for other glassy polymers. These values reflect equilibrium bulk sorption (i.e., no surface adsorption or diffusion limitations) in polymers below their T_g. From these data, AF2400 retention volumes are several times larger than those in other glassy polymers. The difference is largest for PSF, a conventional, low free volume glassy polymer. Retention volume values in AF2400 are compared with those of several rubbers in Table 4. Again, AF2400 is distinguished by much higher solubility coefficients than other polymers, consistent with the gas sorption results already discussed.

The temperature dependence of v_g is used to determine the enthalpy of sorption, ΔH_s, as shown below:

$$\frac{d \ln v_g}{d(1/T)} = -\frac{\Delta H_s}{R} \tag{7}$$

An example of the hydrocarbon retention diagrams is

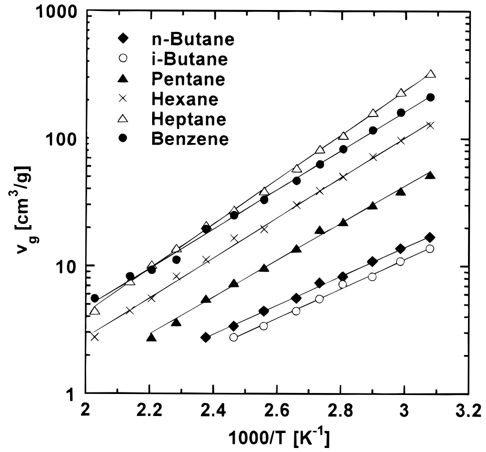

Figure 8. Retention diagram of hydrocarbons in a column containing 5.0 wt % AF2400.

Table 4. Comparison of Inverse Gas Chromatography Hydrocarbon Retention Volumes in AF2400 and in Rubbery Polymers at 100 °C

	retention volume, v_g (cm^3/g)				
solute	AF2400	poly(dimethylsiloxane)[53]	poly(diethylsiloxane)[53]	natural rubber[54]	polyisobutylene[55]
hexane	35	19	18	14	15
heptane	71	37	37	36	
benzene	52	28	29	33	27

Table 5. Enthalpies of Sorption in AF2400 and Enthalpies of Condensation of Solutes

AF2400 loading in column (wt %)	$-\Delta H_s$ (kcal/mol)			$-\Delta H_c$ (kcal/mol)[46]
	5.0	9.5	20.1	
n-butane	5.23	4.08	5.05	5.35
isobutane	5.30	4.85	5.96	5.09
n-pentane	6.68	6.38	6.48	6.16
n-hexane	7.21	7.55	7.58	6.90
n-heptane	8.03	8.36	8.68	7.58
benzene	7.04	7.05	7.16	7.35
C_6F_6			9.0	7.57
$C_6F_5CF_3$			10.6	7.056
n-nonane	9.20			9.03
n-decane	10.6			9.39
n-undecane	11.3			9.92
n-dodecane	10.6			10.43
n-tridecane	9.8			10.91

presented in Figure 8. The widest temperature range studied was from 52 to 232 °C. However, this range was narrower for certain solutes. The accessible temperature range was limited from above by v_n values too small to detect accurately at higher temperatures and from below by the appearance of diffusion limitations for larger solutes at lower temperatures.

The linear dependence of the logarithm of v_g on $1/T$ presented in Figures 7 and 8 indicates that the enthalpy of sorption, ΔH_s, does not vary significantly with temperature. ΔH_s can be represented as a sum of two contributions:[21]

$$\Delta H_s = \Delta H_m + \Delta H_c \tag{8}$$

where ΔH_m is the excess enthalpy of mixing and ΔH_c is the enthalpy of condensation. The enthalpies of sorption and condensation are recorded in Table 5. On the basis of these data, ΔH_s values obtained using columns with different polymer contents are, in most cases, in very good agreement. All of the enthalpies of sorption are negative, and the main contributions to ΔH_s are the enthalpies of condensation. Therefore, the systematic increase in $|\Delta H_s|$ with increasing solute size is primarily due to the increase in $|\Delta H_c|$ with size.

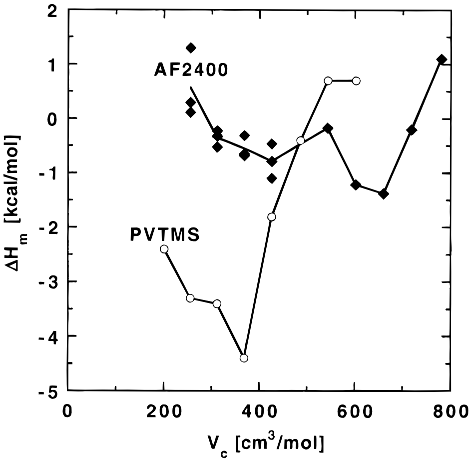

Figure 9. Influence of solute size on enthalpy of mixing *n*-alkane solutes and polymer segments in AF2400 and poly(vinyltrimethylsilane).[33]

Table 6. Solute Sizes Corresponding to the Minimum Enthalpy of Mixing for Hydrocarbons, Fractional Free Volume, and Apparent Radius of Free Volume Elements in Glassy Polymers

polymer	$V_{c,min}$ (cm^3/mol)	FFV	R_0 (Å)[a]
polysulfone[37]	220	0.15	4.357
poly(phenylene oxide)[34]	300	0.18	5.257
poly(vinyltrimethylsilane)[33]	365	0.17	4.757
AF2400	660	0.32	6.5−7.0[12]

[a] From positron annihilation lifetime spectroscopy.

The excess enthalpy of mixing contains information regarding interactions between sorbed solute molecules and the polymer. The ΔH_m values found using three different columns are presented in Figure 9 as a function of solute size, which is characterized by critical volume, V_c. Because ΔH_m values are computed from the difference between two much larger quantities (ΔH_s and ΔH_c), the uncertainty in ΔH_m ranges from 0.08 to 0.4 kcal/mol, depending on the solute. Nevertheless, ΔH_m values exhibit a distinct trend with solute size for the *n*-alkanes. For the lightest hydrocarbon, *n*-butane, the mixing process is slightly endothermic. As the size of the solutes increases, mixing becomes exothermic. When solute size is even larger (i.e., C_{10} and C_{11} alkanes), the mixing process is markedly more exothermic. With further increases in solute size, ΔH_m passes through a minimum before becoming endothermic again.

This dependence of ΔH_m on solute size has been obtained for several glassy polymers, such as polysulfone,[37] poly(phenylene oxide),[34] and poly(vinyltrimethylsilane).[33] Data for poly(vinyltrimethylsilane), a high free volume, glassy, hydrocarbon-based polymer, are included in Figure 9 for comparison. The value of V_c at the minimum of ΔH_m is interpreted as an approximate size of accessible Langmuir microcavities in the polymer.[38] Interestingly, for the polymers listed above, the fractional free volume (or gas diffusion coefficients, which depend strongly on free volume) varies in approximately the same order as the V_c values corresponding to these minima. These data are presented in Table 6. On the basis of the data in this table, AF2400 has an especially large $V_{c,min}$ value at the minimum and, relative to the data for PVTMS in Figure 9, has a very shallow minimum.

As discussed in more detail elsewhere,[33,38] mixing low molecular weight solutes with glassy polymers has much in common with the dissolution of gases and vapors in associated liquids such as water or lower alcohols. Their features are a strong exothermic character of mixing, large negative entropy of mixing and sensitivity of the excess functions of mixing to solute size. In terms of liquid solution theory,[39,40] such systems are called interstitial solutions. When the solute size becomes larger, the mixing process becomes less and less exothermic until it is characterized by near zero or slightly positive enthalpies of mixing. This behavior is consistent with mixing solutes with polymers above their glass transition temperatures, dissolution of solutes in nonassociated liquids such as hydrocarbons, and, generally speaking, formation of so-called displacement solutions.[39,40]

For perfluorinated AF2400, a rather shallow minimum in ΔH_m is observed relative to those found for hydrogen-containing polymers such as PVTMS (cf. Figure 9). This result suggests weak energetic interactions between hydrocarbon solutes and the perfluorinated environment of a Langmuir site or free volume element within the polymer. The excess enthalpies of mixing with two fluorocarbons studied in this work are much more negative than those of similar sized hydrocarbons (−1.4 and −3.6 kcal/mol for C_6F_6 and $C_6F_5CF_3$, respectively, (cf. Table 5)), indicating stronger favorable interactions between these solutes and the polymer matrix than between hydrocarbon-based solutes of similar critical temperature and the polymer matrix.

Correlation of Solubility with Solute Properties. The pressure decay technique was used to determine solute solubility of small gases and vapors, and the IGC technique was used to probe solubility of larger solutes; this combination has permitted characterization of solubility coefficients ranging from He to n-$C_{13}H_{28}$. Solubility in AF2400 varies by more than 5 orders of magnitude across this range of solutes. Therefore, it is possible to critically test correlations between solubility and solute properties. A test of two such correlations is presented in Figure 10. In Figure 10A, the logarithm of infinite dilution solubility is presented as a function of solute critical temperature. For many polymers and liquids, gas solubility over short ranges of critical temperature are well-described by a linear relation between the logarithm of solubility and critical temperature or some other measure of solute condensability, such as normal boiling point or the Lennard-Jones energy parameter, ϵ/k.[23] Such a relationship for gas solubility in polymers is predicted from simple, classical solution thermodynamics.[24] However, this correlation is not valid over the extremely wide range of critical temperature explored in this study.

The logarithm of S was observed to be a linear function of $(T_C/T)^2$ for a wide range of solutes in polyethylene and poly(dimethylsiloxane).[41,42] Because the solubility coefficients were obtained at different temperatures in these studies, the reduced temperature, $(T_c/T)^2$, was used in the correlation:

$$\log S = M + N\left(\frac{T_C}{T}\right)^2 \tag{9}$$

where N and M are parameters. A theoretical justification of this equation is provided in Appendix A. A least-squares fit of the data for AF2400 yielded the straight line presented in Figure 10B. The parameters for this equation are presented in Table 7, where they are compared with results for poly(dimethylsiloxane) and amorphous polyethylene. Large deviations from this correlation are observed for some gases. For example, solubility coefficients of helium are several times lower than those predicted by the correlation for AF2400 and polyethylene. Helium is the least condensable penetrant and is, therefore, expected to have the smallest contribution of penetrant condensability to overall enthalpy change of sorption. For this case, it would not be surprising if the approximation that $|\Delta H_c| \gg |\Delta H_m|$, which underpins the scaling of solubility with measures of penetrant condensability (cf. Appendix), was not valid. In AF2400, the solubility coefficients of the four fluorocarbons studied in the present work lie above the overall correlation line, suggesting an affinity for these solutes and the perfluorinated matrix. This result is consistent with the stronger exothermic mixing with these solutes. In polyethylene, sulfur hexafluoride ex-

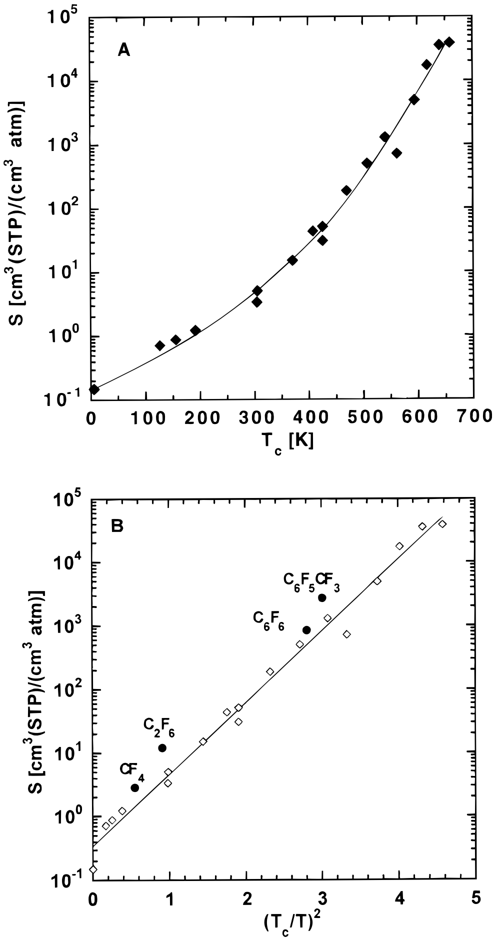

Figure 10. Correlation of infinite dilution solute solubility in AF2400 at 35 °C with (A) solute critical temperature and (B) the square of critical temperature. In (B), a straight line is obtained with a correlation coefficient of 0.9940.

Table 7. Comparison of Parameters in Solubility Correlation[a]

polymer	N	M
polyethylene	1.14	−1.29[b]
poly(dimethylsiloxane)	1.075	−0.75[c]
AF2400	1.11	0.17

[a] Solubility units are cm^3 (STP)/(cm^3 atm). [b] Calculated using an amorphous polyethylene density of 0.85 g/cm^3.[43] [c] Calculated using a poly(dimethylsiloxane) density of 1.138 g/cm^3.[42]

hibited sharply lower solubilities than expected on the basis of the correlation, indicating a decreased affinity between SF_6 and the hydrocarbon-rich polyethylene chains.[43] Similar results have also recently been reported by Merkel et al., who observed much lower solubilities of perfluorocarbons in hydrocarbon-based poly(dimethylsiloxane) than anticipated on the basis of the critical temperature of these solutes.[3] A combined analysis of the results for AF2400 and polyethylene shows that the conclusion by Stern et al. that such a correlation cannot be "expected to hold below the glass transition temperature of the polymer" is not correct.[41]

Conclusions

Sorption of a series of gases and vapors, from helium to tridecane, was characterized in AF2400 using pressure decay and inverse gas chromatography methods. Relative to conventional, hydrocarbon-based polymers, AF2400 has very high solubility coefficients and Henry's law solubility coefficients. Relative to other glassy polymers, the dependence of solubility coefficients and Henry's law solubility coefficients on critical temperature is weaker in AF2400. Although AF2400 is a high glass transition temperature polymer, a large contribution of the total infinite dilution gas solubility is due to sorption in the Henry's law mode. An investigation of an especially large series of solutes (with critical temperatures from 5 to 660 K) demonstrated an excellent linear correlation between the logarithm of S and $(T_C/T)^2$.

A study of the thermodynamics of sorption of C_4-C_{13} *n*-alkanes in AF2400 by inverse gas chromatography showed that excess enthalpies of mixing exhibit a minimum as a function of solute size. This minimum provides an estimate of the intrinsic size of accessible Langmuir microvoids in the polymer. The microvoid size in AF2400 estimated this way is larger than that in other lower free volume glassy polymers.

One goal of this work was to compare sorption properties of the two amorphous glassy polymers having the highest gas permeation and free volume parameters: PTMSP and AF2400. AF2400, like PTMSP, has very large gas and vapor solubility coefficients. However, for PTMSP, the main reason for high gas solubility is extremely large Langmuir capacity parameters. On the other hand, for AF2400, Langmuir capacity parameter values do not exceed those of other glassy polymers. Sorption levels in AF2400 are high due to large values of Henry's law solubility coefficients, which can be related to the weak interchain interactions in this fluorocarbon material.

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Appendix

The dependence of the logarithm of solute solubility on the square of solute critical temperature (cf. eq 9) can be derived by writing the infinite dilution solubility coefficient in terms of the enthalpy and entropy changes of sorption:[44]

$$S = e^{\Delta S_S/R} e^{-\Delta H_s/RT} \tag{A1}$$

where ΔS_S is the entropy change on solution. At constant temperature (i.e., 308 K), variations in solubility among a family of solutes is determined by changes in ΔS_S and ΔH_S. Linear thermodynamic correlations of the type

$$\Delta S_s = \alpha \Delta H_s + \beta \tag{A2}$$

where α and β are parameters, are valid for solute sorption in polymers and in organic solvents.[38,45] Combining eqs A1 and A2 gives

$$S = \exp[\beta/R] \exp[-\Delta H_s[1/RT - \alpha/R]] \tag{A3}$$

As indicated previously, $\Delta H_s = \Delta H_c + \Delta H_m$, so eq A3 can be rewritten as follows:

$$\log S = \frac{\beta}{2.3R} - \frac{\Delta H_c + \Delta H_m}{2.3R}\left[\frac{1}{T} - \alpha\right] \tag{A4}$$

Typically, $|\Delta H_c| \gg |\Delta H_m|$, for vapor sorption in polymers. As shown in Table 5, ΔH_c and ΔH_s values are rather similar in AF2400; hence this inequality is obeyed. With this approximation, eq A4 can be written as

$$\log S = \frac{\beta}{2.3R} - \frac{\Delta H_c}{2.3R}\left[\frac{1}{T} - \alpha\right] \tag{A5}$$

According to Stull et al.,[46] values of ΔH_c are well-correlated with T_c^2, the square of the solute critical temperature. For example, the enthalpies of condensation of the *n*-alkanes from C_1 to C_{12} (at their normal boiling points) are given by the following equation (correlation coefficient = 0.9991):

$$\Delta H_c = -2.1106 \times 10^{-5} T_c^{\ 2} - 1.4076 \tag{A6}$$

where ΔH_c and T_c are expressed in kcal/mol and K, respectively. Combining eqs A5 and A6 yields the following expression for the infinite dilution solubility coefficient:

$$\log S = \left[\frac{\beta}{2.3R} + \frac{1.4076}{2.3R}\left(\frac{1}{T} - \alpha\right)\right] + \left[(T - \alpha T^2)\frac{2.1106 \times 10^{-5}}{2.3R}\right]\left(\frac{T_c}{T}\right)^2 \tag{A7}$$

Equation A7 has the same form as eq 9 if M and N are identified as follows:

$$M = \frac{\beta}{2.3R} + \frac{1.4076}{2.3R}\left(\frac{1}{T} - \alpha\right) \tag{A8}$$

and

$$N = (T - \alpha T^2)\frac{2.1106 \times 10^{-5}}{2.3R} \tag{A9}$$

On the basis of these considerations, the logarithm of infinite dilution solubility should be proportional to T_c^2. Since this analysis is of general character, it suggests that linear correlations of log S with T_c, T_b, and ϵ/k

(including the one shown in Figure 6) are only obeyed over a narrow range of solute critical temperature.

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