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MONTE CARLO SIMULATION OF THE SORPTION OF PURE AND MIXED ALKANES IN POLY[1-(TRIMETHYLSILYL)-1-PROPYNE]

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ABSTRACT

The sorption of alkanes (methane, ethane, propane, and *n*-butane) and alkane mixtures in poly[1-(trimethylsilyl)-1-propyne] (PTMSP) has been studied by means of Grand Canonical Monte Carlo (GCMC) simulations at low pressure. Sorption isotherms for the four alkanes in PTMSP were obtained by fixed-pressure GCMC simulation at several temperatures. The sorption isotherms followed dual-mode sorption behavior, often observed for gases and some vapors in glassy polymers; however, sorbate concentrations were consistently lower than experimental values with increasing pressure. On the other hand, solubility coefficients calculated by extrapolating the ratio, cell loading/*p*, to zero pressure were in good agreement with those reported from gravimetric measurements. Heats of sorption determined from plots of simulation solubility coefficients against reciprocal temperature were large and negative and, at least in the case of methane where data was available, there was good agreement with experiment. In the case of the alkane mixtures, GCMC simulation showed that the more condensable component was preferentially sorbed. The high free volume and large free-volume distribution which contribute to the high solubility of gases in PTMSP were investigated by the Voorintholt method. The large fractional free volume of 0.35 obtained from this simulation was consistent with positron annihilation measurements and with Bondi group contribution calculations. Simulation views of the free volume sites revealed a broad distribution of small and large elements.

Key Words: Poly[1-(trimethylsilyl)-1-propyne]; Monte Carlo simulation; Alkane; Solubility.

INTRODUCTION

Poly[1-(trimethylsilyl)-1-propyne] (PTMSP) is a highly permeable, high-T_g amorphous glassy polymer[1] reported to absorb large amounts of gases and condensable vapors. The high gas permeability of PTMSP may be attributed, in part, to its high gas solubility resulting from extremely large excess free volume. In contrast with conventional glassy polymers such as polysulfone, PTMSP is significantly more permeable to large, condensable vapors (e.g., C_2 to C_4 alkanes) than to small, permanent gases. This has been attributed to extremely high solubility of the more condensable permeants. Of significant interest is the observation[2] that PTMSP shows both the highest C_{3+} hydrocarbon permeability and the highest C_{3+}/methane and C_{3+}/hydrogen permselectivity of any polymer. This high permselectivity of PTMSP to hydrocarbons has been attributed to pore blocking by the larger, more condensable sorbate molecules in the large free volume cavities of PTMSP. To better understand the molecular basis for this unusual behavior, the sorption of pure and mixed alkanes (CH_4, C_2H_6, C_3H_8, and n-C_4H_{10}) in PTMSP has been investigated by means of Grand Canonical Monte Carlo (GCMC) simulation.

MOLECULAR SIMULATION METHODS

Amorphous Cell Generation

Simulations were performed using the Open Force Field (OFF) module of Cerius^2 (release 3.5, Molecular Simulations, Inc.). The DREIDINGII force field[3] parameterized for PTMSP[4] was used for atomistic simulation of PTMSP and the alkanes. Calculated torsional potential energies were used to formulate a Rotational Isomeric State (RIS) model for building amorphous cells from a single 160-mer chain of PTMSP. A cycle of energy minimization (1000 steps) and NPT

Table I. Cell Densities and Solubility Coefficients, S, of Alkanes at Different Temperatures in PTMSP (80-mer, 27 Å cell length)

		S [cm^3(STP)/cm^3(polymer)-cmHg]			
T (K)	ρ (g cm^{-3})	CH_4	C_2H_6	C_3H_8	n-C_4H_{10}
308	0.773	0.037	0.196	0.703	1.333
320	0.764	0.025	0.126	0.343	0.953
340	0.754	0.020	0.087	0.286	0.690
360	0.742	0.017	0.063	0.217	0.539
400	0.735	0.011	0.027	0.060	0.162

molecular dynamics annealing (300 to 600 K, 1 atm, 1000 periods) and relaxation (300 K, 1 atm, 100 ps) was used to equilibrate the amorphous periodic cells (ca. 34.5 Å on a side). The cutoff distance was 10 Å with a spline width of 1.0 Å. Cells prepared in this way had an average density of 0.76 g cm^{-3} which compares well with experimental values reported[5,6,7] in the range from 0.75 to 0.81 g cm^{-3}. In addition, smaller amorphous PTMSP cells (ca. 27 Å in length), were built from a single 80-mer at five other temperatures (308 K, 320 K, 340 K, 360 K, and 400 K) to determine heats of solution. The smaller cell size was used to shorten computational time. Densities of these equilibrated cells are given in Table I.

Grand Canonical Monte Carlo Simulations

Sorption isotherms were obtained from GCMC (μ,T, p) simulation by calculating the average number of sorbate molecules contained per unit cell at thermodynamic equlibrium (i.e., when the chemical potential of the sorbed gas equaled that of the bulk gas). The program for GCMC simulation was provided within the Sorption module of Cerius^2 (Molecular Simulations, Inc.).

In the GCMC simulation procedure,[8] the first step is the random selection and insertion of a sorbate molecule into the simulation cell. The decision whether to translate or reorient the molecule is totally random. The potential energy of the new configuration is then calculated. A decision is then made whether to accept the move or to return to the old configuration based on the probability

$$p_{\mathrm{move}} = \min[\exp(-\Delta U/kT);1] \quad (1)$$

where ΔU is the difference in potential energy between the old and new configurations. To make this decision, a random number between 0 and 1 is generated and is compared to the p_{move}. If the random number is less than p_{move}, the new configuration is accepted. If the random number is greater than p_{move}, the system is returned to the old configuration.

The second step in the simulation cycle is the decision whether to add or subtract a molecule. This decision is made at random with equal probability. If an addition is attempted, then the third step begins with the random generation of a position and an orientation vector for the new molecule. The potential of the new configuration is calculated and the addition is accepted or rejected based on the probability

$$p_{\text{add}} = \min\left[\frac{1}{(N+1)}\frac{pV}{kT}\exp(-\Delta U/kT);1\right] \tag{2}$$

where N is the number of molecules before the addition, p is the pressure of the bulk gas, and V is the volume of the cell. If the addition is accepted, the new molecule is retained. If the addition is rejected, the new molecule is deleted and the system returns to the old configuration. If a subtraction is attempted, the third step then begins with the deletion of a randomly chosen sorbate molecule. The potential of the new configuration is calculated and the subtraction is accepted or rejected based on the probability

$$p_{\text{sub}} = \min\left[\frac{Nkt}{pV}\exp(-\Delta U/kT);1\right] \tag{3}$$

where N is the number of molecules before the subtraction. If the subtraction is accepted, then the deletion is made permanent. If the subtraction is rejected, the deleted molecule is then returned to its old position. In the final step of the cycle, the number of sorbate molecules and the total potential energy are recorded.

Several modifications were required to calculate sorption isotherms for gas mixtures from GCMC simulation. First, the pressure in the probability expressions was replaced by the partial pressure of the gas molecule being added or subtracted. For example, when the total pressure was 10 kPa and the gas mixture consisted of 50 mol% methane and 50 mol% *n*-butane, the partial pressures of the two gases were taken to be 5 kPa each. This makes the assumption of an ideal gas mixture as has been shown to be reasonable at low pressure and temperature for the mixtures of simple alkanes used in this study.[9] In addition to this change in the probability expression, a decision must be made at each simulation step to determine which type of sorbate molecule to move, add, or subtract. This decision was made randomly with equal probability.

GCMC simulations of sorption in PTMSP were run up to 1,000,000 cycles for methane, up to 2,000,000 cycles for ethane, up to 4,000,000 cycles for propane, and up to 5,000,000 cycles for *n*-butane. These large simulation runs were required to ensure sorption equilibrium (i.e., gas loading approaches a constant value), especially at higher pressures. Generally, more trials were required to achieve equilibrium at high pressures than at low pressures and for sorption of a mixture compared to sorption of a pure component. A representative 4-million step sorption run for *n*-butane at 50 kPa (0.5 atm) is shown in Figure 1.

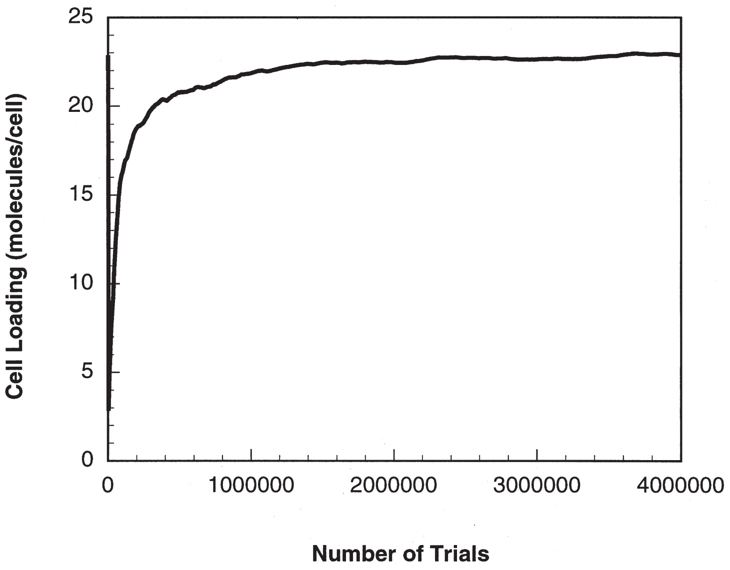

Figure 1. Concentration (molecules/cell) of *n*-butane sorbed in a 160-mer cell of PTMSP as a function of the number of MC steps.

Fixed-pressure calculations were performed in the pressure range from 2 kPa to 50 kPa (0.02 to 0.5 atm). Solubility coefficients, S, were calculated by extrapolating the ratio, cell loading/p, to zero pressure

$$S = \lim_{p \to 0} \frac{C}{p} \tag{4}$$

where C is gas molecule concentration (molecules/cell).

High overall free volume and free volume distribution that contribute to high solubility of gases in PTMSP was studied by the Voorintholt method.[10] This method generates a smooth van der Waals surface of the polymer chain by a grid mapping procedure. The free volume was then obtained as the difference between the cell volume and the total polymer volume. Accessible free volume was obtained by determining the surface volume of the polymer chain accessible to a probe molecule (e.g., gas molecule) of specified volume. In this approach, a simple geometric algorithm was used to calculate a value describing the distance of the probe molecule at a grid point to the nearest atom. This value was set to a maximum when the distance from the grid point to the nearest atom was within the van der Waals radius of the atom. The value was 0 if the grid point was further from the nearest atom than the sum of the van der Waals radii of guest and host atom; otherwise, the value fell between 0 and the maximum.

RESULTS

GCMC simulations were conducted to obtain sorption isotherms for pure and mixed alkanes in PTMSP at 300 K. Pure gas simulations were performed for hydrogen, methane, ethane, propane, and *n*-butane at 300 K over a pressure range from 2 kPa to 50 kPa (0.02 atm to 0.5 atm). Pure gas simulations were also performed using the smaller simulation cells for methane, ethane, propane, and *n*-butane at 308 K, 320 K, 340 K, 360 K, and 400 K. Multicomponent simulation of sorption isotherms at 300 K are reported for three binary (50/50 mol%) mixtures — hydrogen/propane, hydrogen/*n*-butane, and *n*-butane/methane.

Representative isotherms for methane, ethane, propane, and *n*-butane at 300 K are given in Figure 2. As shown, all isotherms are concave to the pressure axis as typical of sorption in glassy polymers at low to moderate sorbate concentrations. It is also evident that PTMSP absorbs very large concentrations of *n*-butane and propane compared to methane and ethane at moderate pressure. Comparison between simulation and the experimental isotherm reported by Merkel et al.[11] for propane as a representative case is made in Figure 3. At low pressures (<0.1 atm), there is very good agreement between simulation and experiment; however, the sorbate concentrations obtained by simulation at higher pressures are substantially lower than the experimental values. Similar results were obtained for the other sorbates. Reasons for this behavior are discussed in the next section.

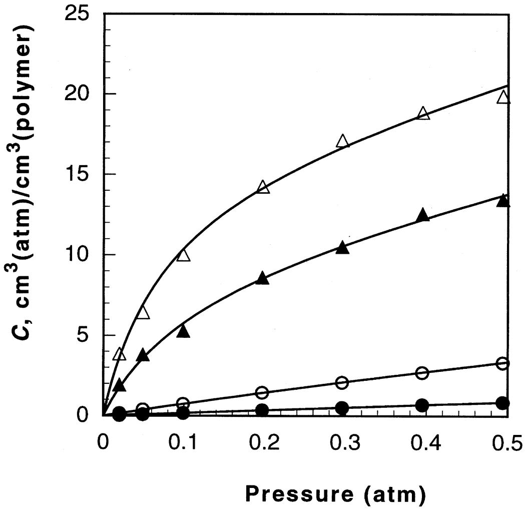

Figure 2. GCMC concentration of sorbed hydrocarbons as a function of pressure at 300 K (160-mer cell). (●) methane; (○) ethane; (▲) propane; (△) *n*-butane. Curves represent dual-mode model fit of simulation data using parameters given in Table III.

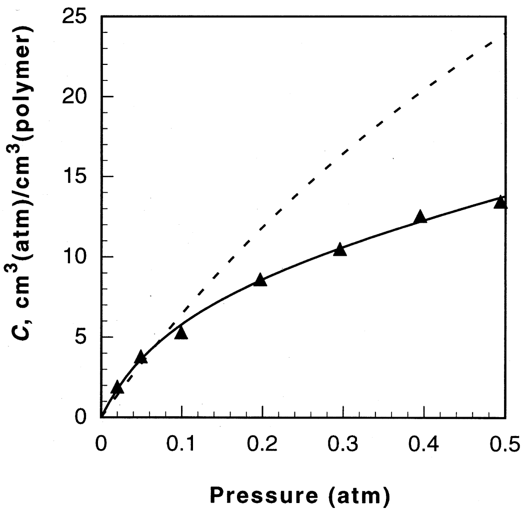

Figure 3. Comparison between propane sorption isotherms from experiment (308 K) and from simulation (160-mer cell, 300 K). (▲) GCMC results. The curve represents dual-mode model fit of simulation data using parameters given in Table III; the broken line is the experimental sorption isotherm drawn using the dual-mode parameters reported by Merkel et al.[11]

In Figure 4, solubility coefficients are plotted against the Lennard-Jones potential well depth parameter,[12] ε/k, in the form[13]

$$\log S = K_1 + K_2(\varepsilon/k) \tag{5}$$

where K_1 and K_2 are empirical constants and k is the Boltzmann constant. As shown, the solubility coefficients increase with increasing condensability of the sorbate molecule (i.e., increasing value of ε/k) and there is excellent agreement between the simulation and experimental[11] (gravimetric) values. In our earlier publication,[4] similarly good agreement between simulation and experimental data was reported for the solubility of methane and five gases (He, H_2, N_2, O_2, and CO_2) in PTMSP.

Figure 5 shows sorption isotherms obtained for methane at five different temperatures using a 80-mer cell. As expected for this glassy polymer, sorbate concentrations decrease with increasing temperature from 308 K to 400 K. Similar results were obtained for the three other alkanes. As mentioned earlier, a smaller cell (80 mer, 27 Å) was used to reduce computation time in order to obtain a sufficient number of simulation runs to calculate the heat of solution, ΔH_s, from the van't Hoff expression

$$S = S_0 \exp(-\Delta H_s/RT). \tag{6}$$

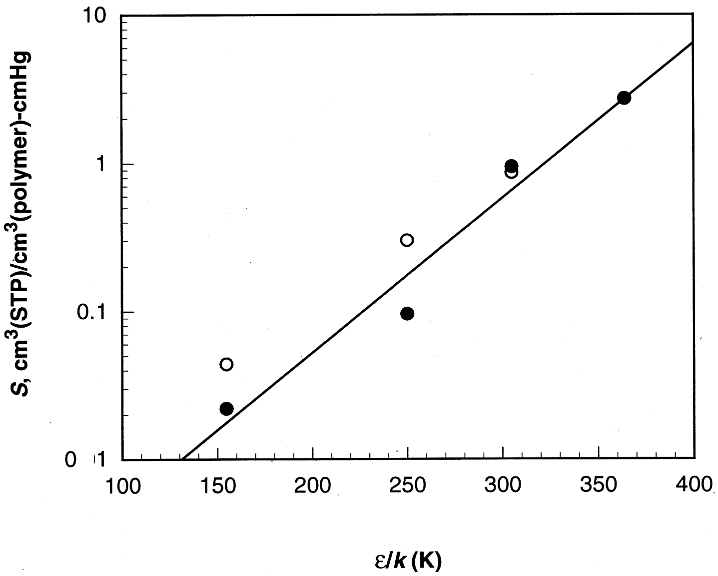

Figure 4. Semilogarithmic plot of solubility coefficents, S, as a function of the Lennard-Jones potential well-depth parameter, ϵ/k, for methane, ethane, propane, and n-butane. Solubility coefficients include results of GCMC simulations (●) at 300 K (160-mer cell) and experimental values (○) reported by Merkel et al.[11] Line is the least-squares fit of simulation values.

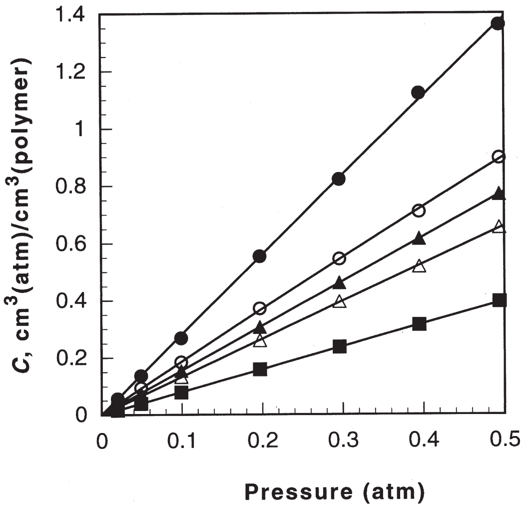

Figure 5. Sorption isotherms for methane obtained at different temperatures (80-mer cell). (●) 308 K; (○) 320 K; (▲) 340 K; (△) 360 K; (■) 400 K. Curves represents dual-mode model fit of simulation data.

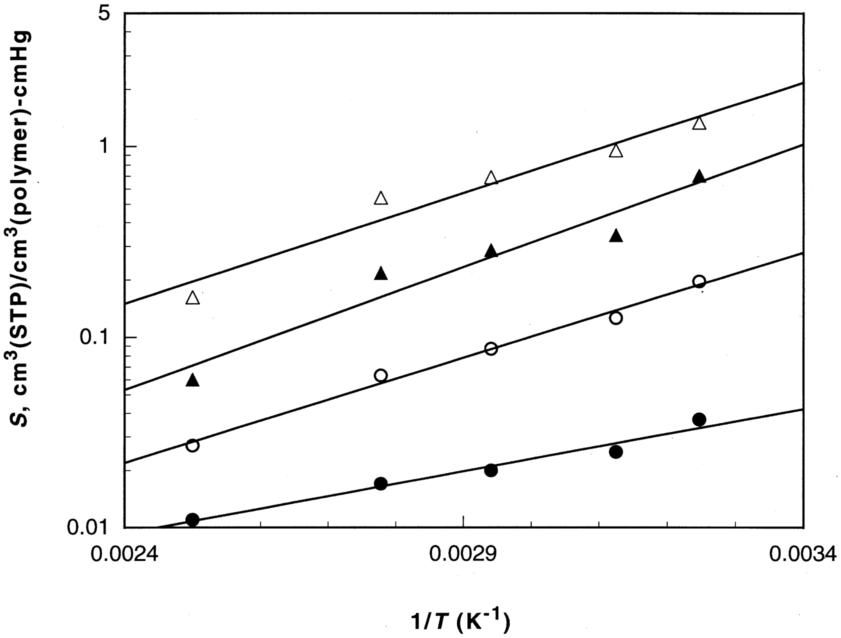

Figure 6. Semilogarithmic plot of solubility coefficients, *S*, obtained from GCMC simulation at different temperatures for methane (●), ethane (○), propane (▲), and *n*-butane (△).

Plots of ln *S* versus reciprocal temperature are shown in Figure 6. Unfortunately, experimental data were available only for methane for which ΔH_s was reported by Starannikova and Teplyakov[14] to be –3.3 kcal mol^{-1}. This value compares very favorably with the simulation value of -3.08 kcal mol^{-1}.

In the dual-mode model for sorption in glassy polymers,[15] the concentration of a sorbed gas or vapor is given as

$$C = k_D p + \frac{C'_H bp}{1 + bp} \qquad (7)$$

where C is the total sorbate concentration, k_D is the Henry's law constant, C'_H is the Langmuir capacity constant, and b is the hole affinity constant. Dual-mode pa-

Table II. Heats of Sorption for Alkanes in PTMSP Obtained from GCMC Simulation (80-mer cell)

Gas	CH_4	C_2H_6	C_3H_8	n-C_4H_{10}
ΔH_S (kcal mol^{-1})	−3.075	−5.064	−5.892	−5.309

rameters (k_D, C'_H and b given in Table III) for the pure alkanes were obtained by a least-squares fit of the sorption isotherms (Figure 2) using eq. 7. There is reasonable agreement between simulation and experimental results for k_D and, to a lesser extent, for b. By comparison, the simulation values of C'_H for ethane, propane, and *n*-butane are significantly smaller than those obtained from the fit of gravimetric data. These results may be attributed to the inability of the simulation method to model sorption at higher pressure as mentioned earlier and discussed in the next section. The lower sorbate concentration obtained from simulation results in a lower predicted value for C'_H.

Sorption isotherms were obtained for several alkane mixtures at 300 K from GCMC simulation. Figure 7 shows a comparison between the sorption isotherms obtained for hydrogen and for hydrogen in two gas mixtures (50/50 mol%)—hydrogen/propane and hydrogen/*n*-butane. The concentration of sorbed hydrogen in PTMSP is very low compared to that of the alkanes (Figure 2). The simulation results show that when hydrogen is mixed with propane and *n*-butane, hydrogen sorption is suppressed due to competition by the more condensable alkane. By comparison, the high solubility of *n*-butane is nearly unaffected by mixing with the less condensable alkanes, methane and propane, as shown in Figure 8. This competition for sorption sites by the more condensable alkanes contributes to the high permselectivity of PTMSP for alkanes over the permanent gases.

The fractional free volume (FFV) of PTMSP was determined to be 0.35 by the Voorintholt geometric method. This favorably compares with a value of 0.32

Table III. Comparison of Dual-mode Model Parameters (eq. 7) for Alkanes in PTMSP (160-mer)

Gas	k_D $cm^3(STP)/cm^3$ atm	b atm^{-1}	C'_H $cm^3(STP)/cm^3$	T K	Reference
H_2	0.07	0.006	61	308	Merkel et al.[11]
	0.014	0.006	81	300	This work[a]
CH_4	0.633	0.058	58.87	298	Srinivasan et al.[19]
	0.500	0.050	62.00	308	Merkel et al.[11]
	0.461	0.043	29.8	300	This work[a]
C_2H_6	1.300	0.310	71.00	308	Merkel et al.[11]
	3.13	0.507	8.86	300	This work[a]
C_3H_8	5.776	2.508	49.70	308	Morisato et al.[20]
	5.300	1.100	60.00	308	Merkel et al.[11]
	11.61	9.087	9.74	300	This work[a]
n-C_4H_{10}	27.664	14.744	43.50	308	Morisato et al.[20]
	13.72	13.44	15.77	300	This work[a]

a. Parameters were obtained from best fit of low-pressure (< 0.5 atm) simulation data.

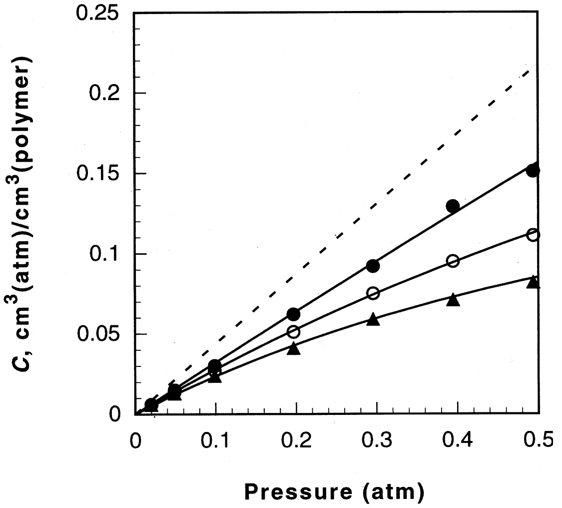

Figure 7. Sorption isotherms for hydrogen and hydrogen mixtures (50/50 mol%) obtained from GCMC simulation at 300 K (160-mer cell). (●) hydrogen; (○) hydrogen/propane: (▲) hydrogen/*n*-butane. Curves represent dual-mode fit of simulation values. Broken line is a plot of experimental data for hydrogen at 308 K (drawn using the dual-mode parameters reported by Merkel et al.[11]).

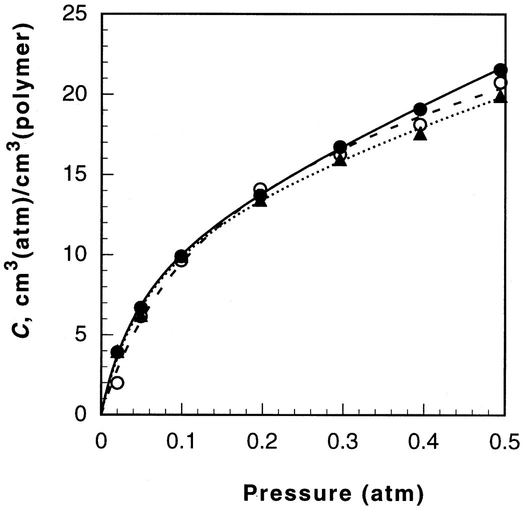

Figure 8. Sorption isotherms for *n*-butane and *n*-butane mixtures (50/50 mol%) obtained from GCMC simulation at 300 K (160-mer cell). (●) *n*-butane; (○) *n*-butane/hydrogen; (▲) *n*-butane/methane. Curves represent dual-mode fit of simulation data. (—) *n*-butane; (¯) n-butane/hydrogen; (.....) *n*-butane/methane.

obtained from the Bondi group contribution method.[16] From inspection of the gas diffusion-accessible surface (shown in Figure 9) generated by the Voorintholt method for methane, the free volume sites in PTMSP have a broad distribution of small and large free volume elements. The small free volume sites are dispersed in the polymer matrix, while the large elements are interconnected to form continuous channels. The fractional free volume of PTMSP reported in the literature and confirmed in the current simulation indicates a highly porous glassy polymer. For example, positron annihilation experiments[17] indicate the presence of pores having diameters of 6 to 12 Å. As shown in Figure 10, a 5 Å thick slice cut from the periodic cell reveals cavities with dimensions as large as 8 to 16 Å in good agreement with the positron annihilation results. This high fractional free volume of PTMSP is due to a combination of factors, particularly a relatively rigid backbone separated by flexible trimethylsilyl side groups. The rigidity of the PTMSP

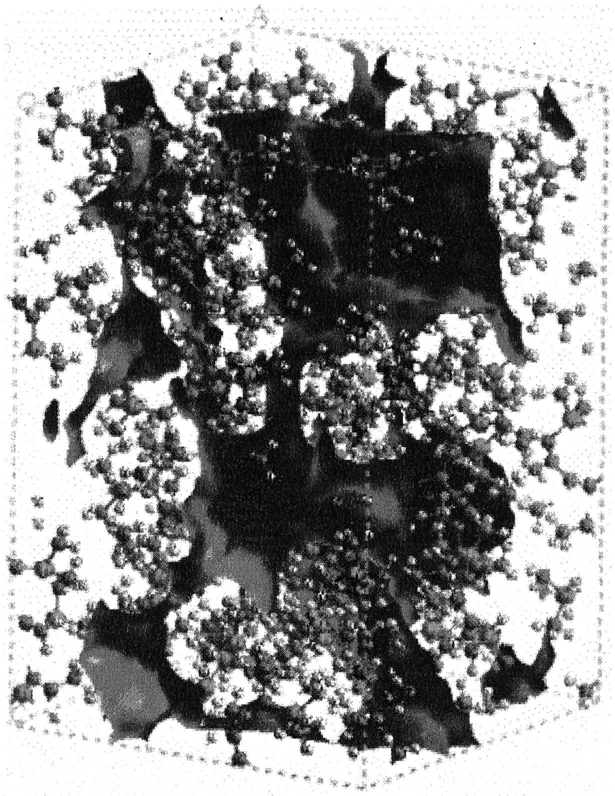

Figure 9. Methane accessible free volume regions in PTMSP determined by the Voorintholt method.

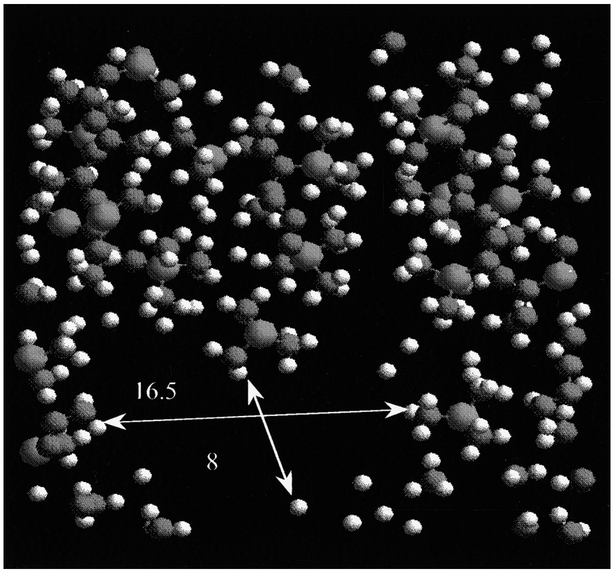

Figure 10. View of a slice (5 Å thick) cut through a periodic cell of PTMSP showing a large cavity with a long diameter of approximately 16.5 Å and a short axis of 8 Å.

molecules arises in part from alternating double bonds in the polymer backbone and in part from the fact that segmental rotation is sterically hindered by presence of the bulky trimethylsilyl groups. The high gas solubility of PTMSP is directly attributed to this high fractional free volume.

DISCUSSION AND CONCLUSIONS

GCMC simulations clearly demonstrated that sorption of alkanes in PTMSP follow the dual-mode behavior observed for gases and vapors in glassy polymers. Sorbate solubility in PTMSP decreased with increasing temperature and heats of sorption for the large condensable vapors were higher than those of gases. The high gas solubility characteristic of PTMSP can be attributed to the large fractional free volume of this glassy polymer as explored by simulation. In mixtures of alkanes, the larger, more condensable sorbate molecule was preferentially sorbed.

Although the GCMC method provided good values of solubility at low pressure and consistent heats of solution for alkanes in PTMSP, this method did not adequately reproduce sorption isotherms at high pressure (sorbate concentration).

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There may be several reasons for this inadequacy. One factor could be the force field; however, the DREIDINGII force field parameterized using AM1 semiempirical quantum chemistry calculations of the dimer,[4] has successfully reproduced x-ray diffraction patterns, amorphous cell densities, diffusion coefficients, and fractional free volume.[4,9] A second reason may be related to cell size. In a study of the effect of cell size on the simulation of gas solubility in polystyrene, Cuthbert et al.[18] have shown that very cells may not adequate represent the statistical distribution of larger sorption sites and, therefore, underestimate the solubility of larger molecules such as carbon dioxide or methane. In that study of gas sorption in polystyrene, size appeared to be no longer a significant factor for cells approaching 40 Å in length which is close to the 34.5 Å cells (160 mer) used for the isotherms. It is reasonable to assume that as the sorbate molecules increases in size (e.g., *n*-butane), a true statistical population of sorption sites may be even more difficult to achieve and it becomes increasingly more difficult to place a sorbate molecule within a small cell as sorbate concentration increases. It is noted that the discrepancy between simulation and experimental isotherms for the smallest sorbate molecules, hydrogen, as shown in Figure 7, was much smaller than observed for propane (Figure 3). In addition, the fixed-volume constraint of the GCMC method, although reasonable for simulation of sorption in the fixed framework of high-porosity zeolites,[7] would not accommodate volume changes associated with the swelling of a real polymer film during sorption of condensable sorbate molecules at higher pressures. Unfortunately, the dilation stuides for PTMSP have not been reported as yet.

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