Diffusion of Gases in Silicone Polymers: Molecular Dynamics Simulations

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ABSTRACT: Diffusion coefficients of He, O_2, N_2, CO_2, and CH_4 at 300 K in four silicone polymers, namely, poly(dimethylsiloxane) (PDMS), poly(propylmethylsiloxane), poly((trifluoropropyl)methylsiloxane), and poly(phenylmethylsiloxane), have been estimated by molecular dynamics (MD) simulations. The estimated diffusion coefficients decrease with increasing size of the polymer side chains and of the penetrant molecules, as was also found experimentally. The estimated diffusion coefficient for He in PDMS is consistent with its experimental value. The values of the estimated diffusion coefficients for the other gas/silicone systems considered in this study are within ± 40−60% of the corresponding experimental values. The MD simulations revealed two types of motions of the penetrant molecules: (1) "jumps" from one cavity in a silicone matrix to another, and (2) "oscillating motions" inside cavities. The lengths of the jumps are of the order of 8−15 Å, whereas the oscillating motions are of the order of ≤5 Å. The total timeframe for the execution of a jump is about 5 ps (5×10^{-12} s). The number of jumps and the average length of a jump of a penetrant molecule inside a silicone matrix decrease as the size of the molecule and of the polymer side chain increase. Some problems associated with the estimation of gas diffusion coefficients in polymers by MD simulations are also discussed.

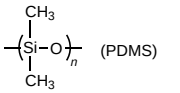
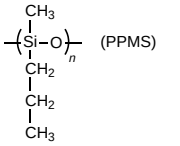
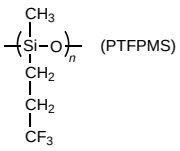
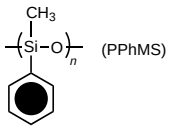
I. Introduction

A number of important practical applications depend on the diffusion of gases in polymers. These applications include the separation of gases by selective permeation through polymer membranes, food packaging, protective coatings, biomedical devices (e.g., the heart-lung machine), etc. The process of gas diffusion in polymers can often be described satisfactorily on a macroscopic (continuum) level by suitable solutions of Fick's laws.[1−4] In contrast, the mechanisms of diffusion on a molecular level are not well understood and have been formulated mainly by means of phenomenological models.[5] Such models, e.g., the free-volume[2,4−8] and the "dual-mode sorption" models,[3,9−14] are very useful for the correlation and comparison of gas diffusivity measurements. However, phenomenological models are not predictive because the model parameters are not directly related to the polymer structure.

A powerful new research tool has become available in this field in recent years, namely, the computer simulation of polymer microstructures. This has made possible the estimation of diffusion coefficients of gases in polymers via molecular dynamics (MD) simulation techniques.[15−19] Almost all the MD simulations of gas diffusion in polymers made up to now have been concerned with specific gas/polymer systems,[15−19] but the effect of systematic modifications in the polymer structure on the diffusion of penetrant gases does not appear to have been sufficiently examined.

Therefore, MD simulations were used in the present study to estimate the values of diffusion coefficients of He, O_2, N_2, CO_2, and CH_4 in four homologous silicone polymers, namely, poly(dimethylsiloxane) (PDMS), poly(propylmethylsiloxane) (PPMS), poly((trifluoropropyl)methylsiloxane) (PTFPMS), and poly(phenylmethylsiloxane) (PPhMS). The structures of these polymers differ with respect to the nature and size of their side chains. The "parent" polymer, PDMS, has two methyl groups attached to Si atoms. In PPMS one of the methyl groups in PDMS is substituted by a bulkier propyl group; in PTFPMS one methyl group in PDMS is substituted by an even bulkier trifluoropropyl group; and in PPhMS one methyl group in PDMS is substituted by a rigid phenyl group.

Table 1. Repeat Unit Structures of Polymers and Their Pertinent Properties

Polymer repeat unit	Glass-transition temp, T_g (°C)	Density,[a] ρ (g/cm^3)
 (PDMS)	−123	0.971
 (PPMS)	−120	0.916
 (PTFPMS)	−70	1.292
 (PPhMS)	−28	1.138

[a] Density at 25 °C.[27]

The structures of the repeat units of the above four silicone polymers are shown in Table 1 together with their physical properties pertinent to the present study. The methodology used in these simulations, the results

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of the simulations, and the significance of the results are discussed in the following sections.

II. Model and Simulation Method

A. Simulation of Polymer Microstructures. The MD simulations of polymer microstructures were made with a Silicon Graphics workstation (INDY). The workstation was networked to the Cray YMP supercomputer at the National Center for Supercomputing Applications (NCSA) at the University of Illinois, Urbana-Champaign, IL, and the SP2 supercomputer at the Cornell Theory Center, Cornell University, Ithaca, NY. The initial microstructure of a polymer containing penetrant gas molecules was generated by means of the "Amorphous Cell" module in the *Polymer* software (Version 6.0) of Biosym Technologies, Inc., of San Diego, CA.[20]

Previous studies[17,18] have indicated that the "united atom" model leads to an overestimate of the values of diffusion coefficients of small penetrant molecules in polymers. Therefore, an "all atom" model was used in the present study. The generation of an initial polymer microstructure was based on the "self-avoiding" random-walk method of Theodorou and Suter.[21] This method is described in detail in the Polymer User Guide of the Biosym Software, Part 1 (Version 6, December 1993). Briefly, according to this method, three backbone-chain atoms of a polymer together with their bonds are initially "placed" in a cubic unit cell in some random orientation. Next, the length of the backbone chain is increased stepwise by adding one atom at a time to the growing polymer chain. During this process, the allowed rotational states (orientations) of successive bonds between adjacent atoms are determined from probability functions, which are governed, in turn, by energy considerations.

The probability that a bond will be in a given rotational state, i.e., will assume a given orientation relative to an adjacent bond, depends on the rotational state of the adjacent bond. Thus, although an atom can be added to the growing polymer chain in a number of different orientations (rotational states), only the particular orientation that results in the smallest increase in the potential energy of the chain will have the highest probability. Polymer chains of desired length can be constructed by this method.

Periodic boundary conditions are imposed on the cubic unit cell in order to eliminate surface effects. The cubic unit cell is visualized as being surrounded on all sides by replicas of itself, thus forming an infinite three-dimensional microlattice. It was assumed that the PDMS microstructure generated in the present study contained eight polymer chains, and that the PPMS, PTFPMS, and PPhMS polymer microstructures contained six polymer chains. The number of chains in the microstructures was varied so that the total volume of the cubic cell remained approximately constant. All the microstructures were also assumed to contain four molecules of the same penetrant gas in each cell. Each polymer chain was built from 10 repeat units. The length of the sides of the cubic unit cells in this study was 20−22 Å.

Once the initial microstructure is generated, the next step is the calculation and minimization of the potential energy of the penetrant/polymer system. All interactions between the atoms of the polymer chains, between polymer chains and diffusing penetrant molecules, and between the penetrant molecules themselves must be taken into account. This was accomplished by means of the *Discover* software (Version 2.95) of Biosym Technologies.[22] All interaction potentials were simulated by means of the "CFF91" forcefield.[23] The "forcefield" describes the potential energy functions for all the different types of interactions involved in the diffusion of small penetrant molecules in a polymer matrix (bond stretching, bond angle bending, bond rotation, nonbonded van der Waals interactions, etc.). The CFF91 forcefield has been modified recently to include interaction parameters specific for the modeling of silicone polymers.[24]

The potential energy associated with bond stretching, i.e., with the deviation of bond lengths from their equilibrium values, is given by the relation

$$V_b = [\kappa_2(l - l_o)^2 + \kappa_3(l - l_o)^3 + \kappa_4(l - l_o)^4] \quad (1)$$

where l_o is the equilibrium bond length, l is the bond length in the simulated microstructure, and κ_2, κ_3, and κ_4 are force constants.

The potential energy associated with the deviation of bond angles from their equilibrium values was determined from the relation:

$$V_\theta = [H_2(\theta - \theta_o)^2 + H_3(\theta - \theta_o)^3 + H_4(\theta - \theta_o)^4] \quad (2)$$

where θ_o is the equilibrium (experimental) bond angle, θ is the bond angle in the simulated microstructure, and H_2, H_3, and H_4 are the corresponding force constants.

The dihedral (torsional) potential energy of the bonds was determined from the relation

$$V_\phi = \kappa_\phi[1 + \cos(n\phi - \delta)] \quad (3)$$

where κ_ϕ is a force constant, ϕ is the dihedral angle, n is a multiplicity factor, and δ is the phase shift. Values of the force constants in eqs 1−3 were taken from refs 23 and 24.

The nonbonded interactions (interactions between two atoms i and j not connected to one another by chemical bonds) were estimated from the following relation, which is the sum of a Lennard-Jones 6−9 potential and a term for electrostatic interactions:

$$V(r) = \frac{A_{ij}}{r^9} - \frac{B_{ij}}{r^6} + \frac{q_i q_j}{4\pi\epsilon_0 r} \quad (4)$$

where A_{ij} and B_{ij} are constants, q_i and q_j are the electrical charges of atoms i and j, respectively, and ϵ_0 is the dielectric constant in vacuum. In the present study, the potential energy function for the nonbonded interactions (eq 4) was "cut off" at an interatomic distance of 10 Å in order to decrease the computing time.

The *total* potential energy of an initial polymer microstructure generated randomly as described above is usually much higher than the potential energy of the polymer it simulates. This high energy is due to the nonbonded interactions between the atoms of the polymer chains, which arise from the overlap of atoms in the simulated initial microstructure. Also, at this stage of the simulation the cubic unit cell is not uniformly occupied by the atoms of the polymer microstructure. Therefore, the *total* energy of the initial microstructure must be minimized and the microstructure must be "equilibrated" before proceeding further to the estimation of the diffusion coefficients.

In the course of the energy minimization procedure, the simulation program seeks the local minimum of the potential energy surface of the microstructure by means of various algorithms (e.g., steepest descent, conjugate gradient, etc.). No kinetic energy is assigned to the atoms of the microstructure during this procedure.

The microstructure is next "equilibrated" by MD simulations in order to ensure that its minimized total energy remains constant with respect to the simulation time used. This is necessary because "rubbery" polymers, such as the silicone polymers of this study, are in a state of thermodynamic equilibrium; i.e., their structures are equilibrated. Equilibration in MD simulations is achieved by assigning random velocities (and, hence, kinetic energies) to all atoms of the polymer microstructure so that the velocity distribution is consistent with the Maxwell−Boltzmann distribution at a selected target temperature (300 K in the present study).

The equilibration step in this study consisted of a 50 ps (picosecond = 10^{-12} s) NVT molecular dynamics simulation (a simulation in which the number of atoms (N), the volume (V), and the temperature (T) of the system remain constant) using a standard Verlet algorithm.[25] The equilibration of the polymer microstructure is validated by plotting the kinetic and

Table 2. Estimated and Experimental Values of Cohesive Energy Density (CED) and Solubility Parameters (δ) for Silicone Polymers

polymer[a]	CED (exp) (J/cm^3)	CED (est) (J/cm^3)	δ (exp) [(J/cm^3)$^{0.5}$]	δ (est) [(J/cm^3)$^{0.5}$]
PDMS	223.0	209.0	14.9	14.5
PPMS	252.0	219.0	15.9	14.8
PTFPMS	319.6	293.0	17.9	17.1
PPhMS	388.8	352.0	19.7	18.8

[a] PDMS: poly(dimethylsiloxane). PPMS: poly(propylmethylsiloxane); PTFPMS: poly((trifluoropropyl)methylsiloxane). PPhMS: poly(phenylmethylsiloxane).

potential energies as functions of simulation time and verifying that they fluctuate randomly about constant mean values.

The equilibration of the microstructures was also validated by calculating the cohesive energy densities (CED) of the polymer microstructures. Table 2 lists the average values of estimated cohesive energy densities and the solubility parameter (δ) together with the corresponding experimental values. As seen from Table 2, the estimated values are in close agreement with the experimental values.[27b] These results confirm, in turn, that the simulated microstructures are equilibrated.

B. Estimation of Diffusion Coefficients. Diffusion coefficients of He, O_2, N_2, CO_2, and CH_4 at 300 K in the equilibrated microstructures of the four silicone polymers studied were determined from MD simulations with the aid of the *Discover* software (Version 2.95) of Biosym Technologies.[22] In such simulations, the succesive positions of a penetrant molecule diffusing in a polymer microstructure are computed as a function of time by solving Newton's equations of motion for that molecule. This computational procedure determines the "random walk" trajectory of the penetrant molecule in a given polymer microstructure. Diffusion coefficients were calculated from the mean-square displacement (MSD) of the penetrant molecules by means of the Einstein equation:

$$D = \lim_{t\to\infty} (1/6t)\langle[r(t) - r(0)]^2\rangle \qquad (5)$$

where $r(0)$ is an initial position coordinate of the penetrant molecule in the selected polymer microstructure, and $r(t)$ is the position coordinate of this molecule after a time t, $|r(t) - r(0)|$ represents the displacement of the penetrant molecule during time t. A time step of 1 fs (1×10^{-15} s) has been used in the present study. Equation 5 assumes that the diffusion coefficient, D, is constant, i.e., independent of the penetrant gas concentration in the polymer. Constant diffusion coefficients have been reported for the diffusion of light gases with low critical temperatures in many "rubbery" polymers. Such gases are very sparsely soluble in rubbery polymers even at elevated pressures. Therefore, in the computation of D the penetrant gas concentration in the polymer was assumed to be very low.

In the present study, mean-square displacements (MSD), $\langle|r(t) - r(0)|^2\rangle$, of He, O_2, N_2, CO_2, and CH_4 were calculated from the trajectories of four penetrant molecules of the same species in each of the four polymer microstructures, namely, PDMS, PPMS, PTFPMS, and PPhMS.

Several investigators have designated D in eq 5 as a "*self-diffusion*" coefficient when used to characterize the motion of penetrant gas molecules in a polymer matrix. Self-diffusion commonly describes the transport of one component in a two-component system of identical chemical composition, for example, the motion of radioactively-labeled molecules in a system of identical unlabeled molecules. Experimental measurements of gas diffusion in polymers yield *mutual* diffusion coefficients (denoted hereafter by $\bar{D}$) for two-component gas/polymer systems.[1−3] However, D determined from eq 5 and $\bar{D}$ should converge to the same value in the limit of zero penetrant concentration. As was mentioned above, the penetrant concentration was assumed to be very low in the described MD simulations (four penetrant molecules per cubic unit cell).

Table 3. Estimated and Experimental Diffusion Coefficients for He, O_2, N_2, CO_2, and CH_4 in PDMS, PPMS, PTFPMS, and PPhMS[a]

	PDMS ($V_f = 0.33$)		PPMS ($V_f = 0.32$)		PTFPMS ($V_f = 0.29$)		PPhMS ($V_f = 0.26$)	
gas	D_{est}	$\bar{D}_{exp}$	D_{est}	$\bar{D}_{exp}$	D_{est}	$\bar{D}_{exp}$	D_{est}	$\bar{D}_{exp}$
He	119	100	95		54		13	
O_2	18	41	16		6.7		1.1	
N_2	12	39	15		4.7		1.4	
CO_2	11	26	12	11	3.2	5.3	0.8	2.0
CH_4	9.4	24	13	8.1	2.3	5.6	0.5	1.2

[a] Units of diffusion coefficients, D: (cm^2/s) $\times 10^6$. V_f: fractional free volume calculated by the lattice-search method. The values of the estimated diffusion coefficients (D_{est}) are for the temperature of 300 K, whereas the experimental values ($\bar{D}_{exp}$) were obtained at 308 K. PDMS: poly(dimethylsiloxane). PPMS: poly(propylmethylsiloxane). PTFPMS: poly((trifluoropropyl)methylsiloxane). PPhMS: poly(phenylmethylsiloxane).

In the present study, mean-square displacements (MSD), $\langle[r(t) - r(0)]^2\rangle$, of He, O_2, N_2, CO_2, and CH_4 were calculated from 200 ps trajectories of four penetrant molecules of the same species in PDMS and PPMS, whereas in the case of PTFPMS and PPhMS the MSDs were calculated from 1000 ps (1 ns) trajectories of four penetrant molecules of the same species. The criteria employed for the estimation of diffusion coefficients using different lengths of trajectories of penetrant molecules in PDMS and PPMS as compared to those in PTFPMS and PPhMS are discussed below.

June, Bell, and Theodorou[26] have found that a penetrant molecule must travel a distance of at least one unit cell (≈20 Å) in a microstructure in order to pass from "anomalous" to "normal" (Einstein) diffusion. The time required by a penetrant molecule to travel such a distance increases with an increase in the rigidity of the polymer, i.e., with a decrease in its intrasegmental mobility, as reflected by a rise in the glass-transition temperature, T_g, of the polymer. Hence, the time necessary for the simulation of normal diffusive motion of a given penetrant molecule in a polymer also increases with an increase in the T_g of the polymer.

A simulation time of 200 ps appeared to be sufficient to obtain normal diffusive motion of the He, O_2, N_2, CO_2, and CH_4 molecules in PDMS and PPMS, because all the penetrant molecules could theoretically diffuse a distance of at least 1 unit cell within this timeframe. For diffusion in the two more rigid polymers, PTFPMS and PPhMS, a longer simulation time of at least 1 ns was necessary to obtain the same result. The T_g values of PDMS and PPMS are −123 and −120 °C, respectively, whereas the T_g values for PTFPMS and PPhMS are −70 and −28 °C, respectively.

III. Results and Discussion

A. General Considerations. Table 3 lists values of diffusion coefficients, D, at 300 K estimated from MD simulations for He, O_2, N_2, CO_2, and CH_4 in the silicone polymers PDMS, PPMS, PTFPMS, and PPhMS. Table 3 also lists for comparison the corresponding experimental values of diffusion coefficients, $\bar{D}$, reported in the literature.[27] The estimated values are averages for five different polymer microstructures; values determined from more than five different microstructures did not differ significantly. The MD simulations were made for a temperature of 300 K.

It should be noted that the estimated values of D are very sensitive to the density of the polymers. The densities of PDMS, PPMS, PTFPMS, and PPhMS listed in Table 1 are reported to have been measured at 298 K instead of 300 K; moreover, PDMS and PPhMS

contained 4.9 and 2.9 vol %, respectively, of a silica filler, whereas PPMS and PTFPMS were filler-free.[27] Therefore, the reported densities of PDMS and PPhMS are somewhat higher, and the estimated values of D are correspondingly lower, than would have been obtained for the filler-free polymers.

The accuracy of the estimated values of D depends also on the force field used, on the simulation time, on the "cutoff" of the potential energy function for nonbonded interactions, and on other assumptions and approximations embodied in the MD simulations. As mentioned previously, a modified CFF91 forcefield[24] was used in the present simulations.

The experimental values of the diffusion coefficients, $\bar{D}$, listed in Table 3 require some comments. No values of $\bar{D}$ for He, O_2, N_2, CO_2, or CH_4 in PDMS have been reported for the temperature of 300 K (27 °C) assumed in the present MD simulations. Nor have any values of $\bar{D}$ been reported for He, O_2, and N_2 in PPMS, PTFPMS, and PPhMS at any temperature. The values of $\bar{D}$ in Table 3, with the exception of $\bar{D}$ for He in PDMS, were determined only at 308 K (35 °C).[27] Moreover, these values were not directly measured but were calculated from the relation.[1−5,27]

$$\bar{D} = \bar{P}/S \tag{6}$$

where $\bar{P}$ is a mean permeability coefficient and S is a solubility coefficient. Consequently, the error in the values of $\bar{D}$ combines the experimental errors in the measurements of $\bar{P}$ and S, and could be as high as ±25%.

Values of $\bar{D}$ for He in PDMS have been determined by Barrer and Chio[28] by the "time-lag" method in the temperature range from 256 to 273 K (−17 to 0 °C). The value reported in Table 3 for He in PDMS was obtained by extrapolating the data of these investigators to 308 K (35 °C) for consistency with the other experimental $\bar{D}$ values in that table. In making this extrapolation, the reasonable assumption was made that the energy of activation for the diffusion of He in PDMS does not change significantly between 256 and 308 K.

B. Diffusion Coefficients of Gases in PDMS. Table 3 shows that the value of the diffusion coefficient (D) estimated from MD simulations for He in PDMS is 20% higher than the experimental value, whereas the estimated values of D for O_2, N_2, CO_2, and CH_4 in the same polymer are about 31−44% of the corresponding experimental values ($\bar{D}$). The estimated values of D may be viewed as consistent in magnitude with the experimental values considering the assumptions made in the MD simulations, the error in the experimental values, and the difference in the temperature at which the estimated and experimental values were determined (300 and 308 K, respectively).

MD simulations of the diffusion of CH_4 in PDMS at 300 K have also been reported by Tamai, Tanaka, and Nakanishi[29] and by Sok, Berendsen, and Gunsteren.[30] Both groups of investigators used in their simulations the GROMOS forcefield.[30] Tamai et al. obtained the value of 0.57×10^{-5} cm^2/s for the diffusion coefficient of CH_4 in PDMS, whereas Sok et al. reported a value of $2.1(\pm 0.8) \times 10^{-5}$ cm^2/s. These values are, respectively, about 23% and 86% of the experimental value of 2.45×10^{-5} cm^2/s. The value of 0.94×10^{-5} cm^2/s at 300 K estimated in the presented study (cf. Table 3) is intermediate between the values of Tamai et al. and of Sok et al.

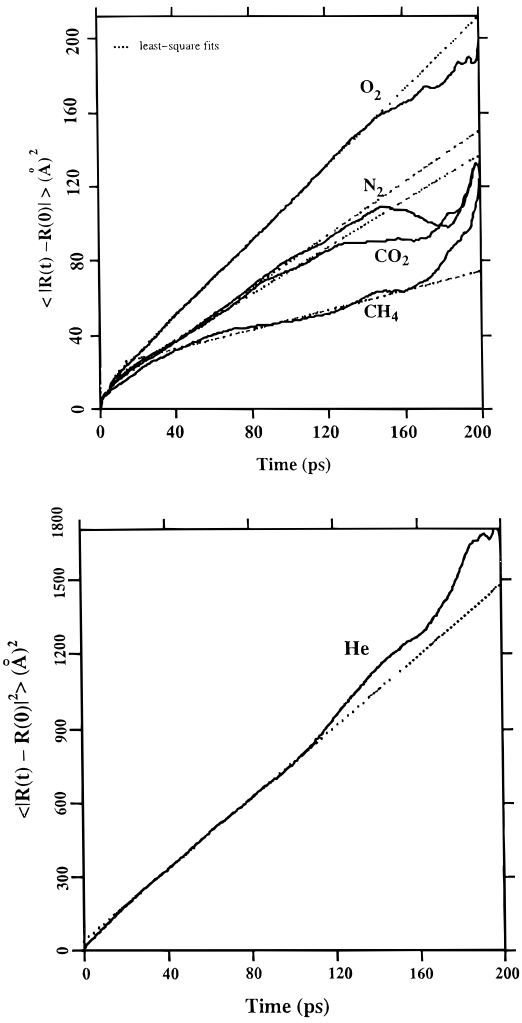

Figure 1. (a) Mean-square displacements of O_2, N_2, CO_2, and CH_4 molecules in a PDMS matrix as a function of time. The curves represent averages of the displacements of four molecules of each gas species. (b) Mean-square displacements of He atoms in a PDMS matrix as a function of time. The curve represents averages of the displacements of four He atoms. The dotted line is a least-squares fit to these data.

Plots of mean-square displacements (MSD) of CH_4, CO_2, N_2, and O_2 molecules in PDMS as a function of time, obtained from MD simulations, are shown in Figure 1(a). The corresponding plot for He in PDMS is shown separately in Figure l(b) because of the much larger MSD values of this small penetrant molecule. According to eq 5, a plot of MSD versus time should be linear if D is constant; i.e., the penetrant exhibits normal (Einstein) diffusion behavior. It is seen that the plots of MSD versus time are indeed linear for all penetrant gases over a period of time of about 100 ps. At longer times, however, the plots deviate from linearity due to the increasing statistical error involved in the calculations of MSD. All estimated diffusion coefficients, D, were determined from the slopes of such plots; cf. eq 5.

C. Diffusion Coefficients of Gases in PPMS, PTFPMS, and PPhMS. Table 3 shows that the estimated values of diffusion coefficients, D, for CO_2 and CH_4 in PTFPMS and PPhMS are 40−60% of the corresponding experimental values ($\bar{D}$). The particularly good agreement between the values of D and $\bar{D}$ for CO_2 in PPMS is probably fortuitous. No experimen-

tal diffusion coefficients have been reported for He, O_2, and N_2 in PPMS, PTFPMS, and PPhMS.

D. Comparison of Diffusion Coefficients of Gases in Different Silicone Polymers. The values of the estimated diffusion coefficients of all the above gases in the four silicone polymers studied decrease in the *gas* order

$$He > O_2 > N_2 > CO_2 > CH_4$$

this is also the order of increasing "kinetic" molecular diameters of these gases.[31]

The values of the estimated diffusion coefficients, D, of a given penetrant gas in different silicone polymers decrease in the *polymer* order

$$PDMS \geq PPMS > PTFPMS > PPhMS$$

The substitution of a bulkier or more rigid functional group in a polymer generally inhibits the intrasegmental (rotational) mobility of the polymer chains, which is commonly reflected by an increase in T_g. This reduces, in turn, the diffusivity of gases in the substituted polymer, because the rate of diffusion of a penetrant molecule depends on the cooperative motion and mobility of the surrounding polymer chains.[2−4]

The substitution of a methyl ($-CH_3$) group in the repeat units of PDMS with a propyl ($-C_3H_7$) group, to form PPMS, probably does not significantly reduce the mobility of the polymer chains, as is indicated by the fact that the T_g's of these two silicone polymers differ by only 3 °C; cf. Table 1. Consequently, the values of D of a given penetrant gas should not be very different in PDMS and PPMS at the same temperature. Table 3 shows that the values of D obtained from MD simulations for the five gases studied are indeed similar for PDMS and PPMS, at least within the accuracy of the simulations. However, the experimental diffusion coefficients for CO_2 and CH_4 in PPMS are significantly lower than reported for these gases in PDMS, possibly indicating that the experimental values are sensitive to small structural differences not accounted for in the MD simulations.

The substitution of a methyl ($-CH_3$) group in the repeat units of PDMS with the much bulkier trifluoropropyl ($-CH_2CH_2CF_3$) group reduces both the estimated and the experimental diffusion coefficients of penetrant gases. This behavior is expected from the fact that the T_g of PTFPMS is 53 °C higher than that of PDMS. Therefore, the intrasegmental mobility of PTFPMS should be more restricted than that of PDMS, and the gas diffusivity in the former polymer should be lower than in the latter.

The substitution of a methyl ($-CH_3$) group in the repeat units of PDMS with the bulky and even more rigid phenyl ($-C_6H_5$) group, to form PPhMS, further reduces both the estimated and experimental diffusion coefficients of all penetrants, as expected from the fact that the T_g of PPhMS is 95 °C higher than the T_g of PDMS; cf. Table 1.

E. Estimation of the Free Volume of Silicone Polymers. The diffusion coefficients of gases in polymers are also controlled by the amount of free volume, the free-volume distribution, and the dynamics of the free volume of the polymers. Therefore, the estimation and analysis of these polymer properties would enhance our understanding of the differences in the values of the diffusion coefficients of a given penetrant in structurally different polymers.

Preliminary estimates of the fractional free volume of polymers were obtained by means of a "lattice search" method. This method consisted in dividing the equilibrated microstructure of a given silicone polymer into 10^6 cubes or "cells"; i.e., the microstructure was divided into a three-dimensional lattice. The size of the cell was approximately 0.2 Å. Each cell was then examined to determine the presence of any part of an atom belonging to the polymer chain. If the cell was found to contain part of an atom, it was labeled "occupied"; otherwise the cell was labeled "unoccupied". It is seen from Table 3 that the fractional free volume decreases in the order PDMS > PPMS > PTFPMS > PPhMS. The diffusion coefficients for all the penetrant gases studied here decrease in the same order.

F. Mechanism of Gas Diffusion in Polymers. Previous studies by different investigators suggest the following mechanism of gas diffusion in polymers. Penetrant molecules reside most of the time in microcavities inside the polymer matrix. The microcavities are elements of "free volume" (or "empty" volume) between surrounding polymer chains. The size and shape of the microcavities in "rubbery" polymers, and hence the free-volume distribution, change with time much more frequently than in "glassy" polymers.

The diffusion of small penetrant molecules in a polymer can be visualized as occurring by a *hopping* mechanism.[2,3,5] A penetrant molecule oscillates inside a microcavity in the polymer matrix for a period of time that depends on the nature of the polymer and of the penetrant. From time to time, cooperative motions of the polymer chains surrounding this microcavity open a "tunnel" sufficiently wide to allow the penetrant molecule to "jump" into a neighboring microcavity, provided that the latter is not already occupied by another penetrant molecule. Thus, the overall diffusion process is a combination of random oscillations of the penetrant molecule inside microcavities, followed by occasional "jumps" into neighboring microcavities. The motion of a penetrant molecule inside a polymer (the trajectory of the penetrant) can be represented by tracing the displacement of the penetrant molecule from an original position $|r(t) - r(0)|$ as a function of time.

Figure 2(a) shows the trajectories of a He atom and of single O_2 and CH_4 molecules in PDMS, while Figure 2(b) shows the trajectories of single CO_2 molecules in three different silicone polymers, namely, PDMS, PTFPMS, and PPhMS. In Figure 2(a) the trajectories of He and O_2 in PDMS have been shifted upward by 20 and 10 Å, respectively, from the origin for greater clarity; similarly, in Figure 2(b) the trajectory of CO_2 in PPhMS has been shifted upward by 25 Å, and that of CO_2 in PTFPMS has been shifted upward by 10 Å.

Parts (a) and (b) of Figure 2 illustrate the "hopping" mechanism of penetrant molecules inside a polymer matrix. Thus, CH_4 molecules oscillate inside a polymer microcavity for a period of time of the order of 100 ps (1 ps = 10^{-12} s) before executing a jump into a neighboring microcavity. In contrast, the lighter He atoms execute frequent jumps in a much shorter period of time (≈5−10 ps). O_2 molecules exhibit an intermediate behavior. Similar plots have been reported by Smit et al.[32] for a CO_2 molecule in a polyimide matrix (6FDA-4,4′-PDA) and by Muller-Plathe[33] for H_2, O_2, and CH_4 molecules in polypropylene. The jumping motions of penetrant

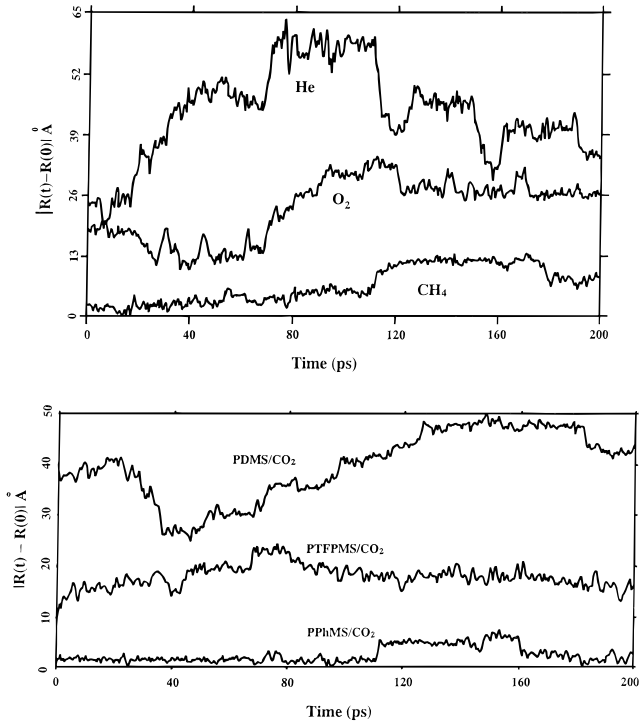

Figure 2. (a) Displacements of a He atom and of O_2 and CH_4 molecules from initial positions in a PDMS matrix. The displacements of the He atom and of the O_2 molecules are shifted upward by 20 and 10 Å, respectively, in order to avoid an overlapping of the plots. (b) Displacements of a CO_2 molecule from initial positions in PDMS, PTFPMS, and PPhMS matrixes. The displacements of the CO_2 molecule in PDMS and PTFPMS are shifted upward by 25 and 10 Å, respectively, in order to avoid an overlapping of the plots.

molecules in polymers have also been discussed in review articles by Gusev et al.[34] and by Muller-Plathe.[35]

Parts (a) and (b) of Figure 2 also show that the total timeframe for a diffusive "jump" is of the order of only about 5 ps. It should be noted that the lengths of diffusive jumps vary between about 8 and 15 Å, whereas the lengths of oscillating motions of penetrant molecules inside microcavities are shorter, being of the order of ≤5 Å. Both the number of jumps and the jump lengths decrease within the timeframe of the simulations (200 ps) in the *penetrant* order He > O_2 > N_2 ≥ CO_2 ≥ CH_4, i.e., with increasing penetrant size. The values of the estimated and experimental diffusion coefficients decrease in the same order.

Figure 2(b) also shows that the number of "jumps" executed by CO_2 molecules decreases in the *polymer* order PDMS > PTFPMS > PPhMS. The glass-transition temperature, T_g, of the polymers increases, and hence their intrasegmental mobility decreases, in the same order.

Another important aspect of the diffusion process is the distance traversed by penetrant molecules inside the cubic unit cell enclosing a simulated polymer microstructure. Figure 3(a) shows trajectories of a He atom and of O_2 and CH_4 molecules in a PDMS microstructure; the trajectories were obtained from three different simulations of 200 ps each. The arrow indicates the size of the unit cell. It is seen that in the case of PDMS (cf. Figure 3(a) the total distance traversed by the gas molecules in the polymer microstructure decrease in the penetrant order He > O_2 > CH_4.

Figure 3(b) represents similar projections of trajectories of CO_2 molecules in PDMS, PTFPMS, and PPhMS.

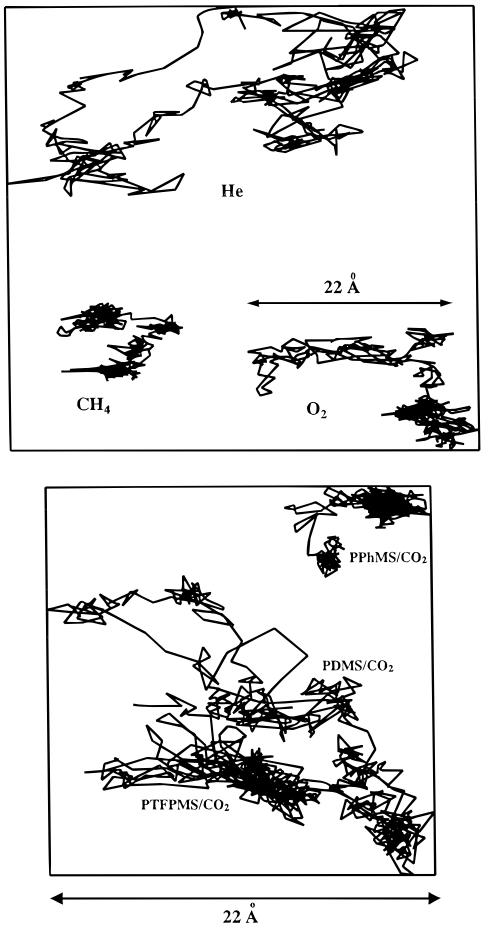

Figure 3. (a) Trajectories of a He atom and of O_2 and CH_4 molecules in a PDMS matrix during a period of 200 ps. The arrow indicates the size of the simulation box. (b) Trajectories of a CO_2 molecule in PDMS, PTFPMS, and PPhMS matrixes during a period of 200 ps. The arrow indicates the size of the simulation box.

It is seen that the length of the trajectory of a diffusing CO_2 molecule and the number of jumps decrease in the following *polymer* order: PDMS > PTFPMS > PPhMS. This order is likely due to the fact that the intrasegmental (rotational) mobility of the polymer chains decreases in the same order, as indicated by the corresponding increase in the T_g of these silicone polymers.

IV. Conclusions

Diffusion coefficients of He, O_2, N_2, CO_2, and CH_4 in four silicone polymers at 300 K have been estimated by molecular dynamics (MD) simulations. The silicone polymers are poly(dimethylsiloxane) (PDMS), poly(propylmethylsiloxane) (PPMS), poly((trifluoropropyl)methyl siloxane) (PTFPMS), and poly(phenylmethylsiloxane) (PPhMS).

The estimated diffusion coefficient for He in PDMS is in satisfactory agreement with the experimental value. The estimated diffusion coefficients for O_2, N_2, CO_2, and CH_4 in PDMS are 31−44% lower than the experimental values, depending on the penetrant gas. The estimated diffusion coefficients of CO_2 and CH_4 in PTFPMS and PPhMS are also lower, by 40−60%, than the experimental values. No experimental values of the diffusion coefficients of He, O_2, and N_2 in PPMS, PTFPMS, and PPhMS are available for comparison with the estimated values.

The above-mentioned differences between the estimated and experimental diffusion coefficients are not

unreasonable considering the assumptions made in the MD simulations and the errors in the experimental values. Moreover, the values of the estimated diffusion coefficients are for an assumed temperature of 300 K, whereas the experimental values were obtained at 308 K.

The diffusion coefficients estimated by means of the MD simulation software used in the present study do not appear to be sensitive to small differences in the structures of the silicone polymers, such as those between PDMS and PPMS.

The estimated diffusion coefficients of all five gases considered decrease in the *polymer* order: PDMS ≥ PPMS > PTFPMS > PPhMS. This is the order of increasing glass-transition temperature, T_g, of these polymers, and hence of decreasing intrasegmental mobility of the polymer chains. The estimated diffusion coefficients also decrease in the *penetrant* order: He > O_2 > N_2 > CO_2 > CH_4, i.e., with increasing size of the penetrant molecules.

The MD simulations revealed two types of motions of penetrant molecules inside the silicone polymers: (1) oscillating motions inside microcavities, and (2) "jumps" from one microcavity in a polymer matrix to another microcavity. The lengths of the oscillating motions are ≤5 Å, whereas the lengths of the "jumps" are of the order of 8−15 Å. The total timeframe for the execution of a molecular "jump" is about 5 ps (5×10^{-12} s). Both the frequency and length of the "jumps" decrease with decreasing intrasegmental mobility of the polymer chains and increasing size of the penetrant molecules.

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