Effect of Chain Flexibility on Selectivity in the Gas Separation Process: Molecular Dynamics Simulation

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ABSTRACT: We have investigated the effect of chain flexibility on the sieving ability of polymers by means of a molecular dynamics simulation method. As the size of penetrants and the rigidity of chains increase, the diffusion coefficients decrease. The more rigid chains give a greater difference between the diffusion coefficients of smaller and larger penetrants, which results in an improvement of selectivity. In the case of the penetrant whose size is smaller than that of the polymer segment, it is observed that the condition with an optimum selectivity and permeability exists resulting from a competition between the effect of the redistribution of dynamic free volume and that of the amount of static free volume on the diffusion of penetrants. One must take both the available free volume and the chain flexibility into account when designing a membrane for gas separation process.

Introduction

Diffusion behaviors of gas penetrants in polymers are important, especially in membrane separation processes. During the last few decades, several approaches based on molecular theory and free volume theory have been made to give a microscopic description of diffusion phenomena.[1] Molecular dynamics (MD) simulations have been frequently performed for the purpose of further theoretical understanding.[2−9]

Diffusion is assumed to be a process in which polymer segments separate in front of a diffusing gas molecule, forming a hole through which the gas can jump.[1] The difference in diffusion rates for gases of different sizes has been attributed to a distribution of hole sizes, or free volume, in the polymer. According to the standard free volume theories of diffusion, there is at each instant a distribution of holes due to thermal density fluctuations. Each gas molecule can jump through any hole equal to or larger than its effective size. At each step the smallest molecules will find the largest number of accessible diffusion jumps and therefore have the highest diffusion rate. Thus, the polymer acts as a sieve.

It is reported that removal of the rotational restriction of polymer chains increases the mobility of chain segments and affects the dynamic free volume distribution.[2,3] The most dominant factor that has an effect on the diffusion rate is, of course, the amount of free volume. However, the distribution and dynamics of free volume, which depend on the chain flexibility, clearly affect the diffusion for a fixed amount of free volume. The high chain flexibility causes large diffusion coefficients and a low apparent activation energy of diffusion. The diffusion of small molecules is affected by the free volume distribution and its dynamics depending on the chain flexibility.

In this report, we have investigated the effects of chain flexibility and penetrant size on the sieving ability of the polymers by means of a MD simulation method. The main objective of this study is to understand the chain flexibility effect on the diffusion process and to obtain information on designing membranes with an optimum selectivity and permeability.

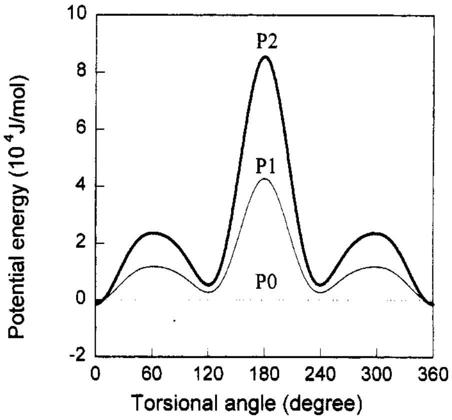

Figure 1. Torsional potentials employed for model polymers P0, P1, and P2.

Model and Simulation

The model system is composed of 24 polyethylene (PE) chains, which have a total of 480 methylene groups as united atoms, and the side length of the periodic box is 23.8 Å so that the density of the model polymer corresponds to about 0.83 g/cm^3. This density is maintained throughout overall simulation. Four kinds of gas molecules having the size of hydrogen (H), methane (M), ethane (E), or propane (P) are introduced into the box as penetrants. Their physical parameters are modified to have the same values except for their sizes. To impose the chain flexibility effect, three types of chain molecules are prepared. One (P0) has no rotational barrier so that it behaves like a freely rotating chain, another (P1) has the normal rotational barrier,[10] and the third (P2) has double the height of the normal rotational barrier so that its rotational movement is extremely limited (Figure 1). While the model polymer P1 corresponds to a normal PE chain, P0 and P2 represent the more flexible and the more rigid chains, respectively. In addition to the rotational restriction, the potential energies describing the bond length, the valence angle, and the nonbonded Lennard-Jones interaction are employed.[11]

A common method of preparing equilibrium samples of atomic liquids for computer simulation is to melt a crystal configuration.[12] However, the structure developed from a lattice is far away from the amorphous

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Table 1. Parameters Used in the Simulation

		σ^* (Å)	k_ϕ (J/mol)
polymer	P0	3.8	0
	P1	3.8	9000
	P2	3.8	18000
penetrant	H	2.9	
	M	3.8	
	E	4.4	
	P	5.1	
	Δt (s)	1.0×10^{-15}	
	T_r (K)	400	

polymer state, and thus more equilibration time is required. To overcome this disadvantage, the modified self–avoiding random walk technique[13] has been developed, which is a method generating an amorphous structure close to equilibrium. The method generates the linear chain sequentially site by site with an acceptance criterion very similar to the Monte Carlo method. At each step, the next position is randomly proposed from the previous position and equilibrium bond length, and then the potential energy change due to the introduction of a new segment is calculated. Consequently, it is determined by the Metropolis rule[14] whether the new position is accepted or rejected. Until all the segments are generated, the above procedures are repeated. After the initial configuration of chains is generated, the positions of 10 penetrants are determined with limited randomness: Randomly produced positions are accepted or rejected by Metropolis criterion to avoid unrealistic overlap. As the last procedure, the initial set of velocities for both polymer segments and gas molecules corresponding to the desired temperature is created to have the Gaussian distribution. Adopting this method, the nonphysical overlap of the segments, which might cause a serious problem, can be avoided. In the Lennard-Jones potential, the overlap could cause extremely large forces and thus make the differential equation difficult to solve. The successive equilibration step makes a realistic amorphous chain from the freely jointed ideal chain initially generated.

The configuration generated initially does not still have the exact nature of the amorphous polymer chain. The valence angle and dihedral angle distributions are far away from the equilibrium state. By imposing the potential energy restricting the angles as well as the bond length, and nonbonded interaction, and by running for a certain time the equilibrated chains can be obtained. Three different potential energies restricting the dihedral angle are used for the three polymer models, P0, P1, and P2. The system equilibration is monitored by calculating the total potential energy, the force, the kinetic temperature, and the total momentum at each time step. After 10 000 steps, it is assured that the systematic drift has ceased and the system is stabilized. It is confirmed that the system itself does not drift by the very small value of the total force and total momentum as compared to the root-mean-square force and momentum.

Conventionally, MD simulations of liquids at equilibrium are performed using the (*N*, *V*, *E*) ensemble. But, several schemes[15] have been proposed recently for performing MD calculations in other ensembles more comparable with the usual laboratory conditions of constant temperature and/or constant pressure. It is known that the constant-temperature and/or constant-pressure algorithms produce results nearly identical, within statistical accuracy, to those obtained using the constant-energy ensemble for mass transport properties. Thus, the diffusion coefficients in the (*N*, *V*, *T*) ensemble with *ad hoc* scaling of velocities adopted here are comparable to those from the (*N*, *V*, *E*) or (*N*, *P*, *T*) ensemble. It is confirmed that the diffusion coefficients calculated in the (*N*, *V*, *T*) ensemble with *ad hoc* scaling are comparable to those in the (*N*, *V*, *E*) ensemble with a difference of less than 8%. The basic equation of motion for the (*N*, *V*, *T*) ensemble, using the leapfrog form of the Verlet algorithm, can be found in ref 15.

Forces originate from such imposed potentials as

$$E(r_{ij}) = 4\epsilon_{ij}^*\left[\left(\frac{\sigma_{ij}^*}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}^*}{r_{ij}}\right)^{6}\right] \quad (1)$$

$$E(l) = {}^1/_2 k_b (l - l_0)^2 \quad (2)$$

$$E(\theta) = {}^1/_2 k_\theta (\cos\theta - \cos\theta_0)^2 \quad (3)$$

$$E(\phi) = k_\phi \sum_{n=0}^{5} a_n \cos^n \phi \quad (4)$$

where r_{ij} is the distance between particle i and j, l is the bond length, θ is the valence angle, and ϕ is the dihedral angle. Typically, the torsional potential is given as

$$E(\phi) = k_\phi(1 + s\cos n\phi) \quad (5)$$

But eq 5 does not contain the information on the difference in the conformational transitions between gauche to gauche and trans to gauche. When dealing with polymers whose force field is not clearly revealed, the potential of eq 5 can be used. This is because the torsional potential naturally arises from the interaction of the electrons and nuclei of atoms, and thus the torsional potential is indirectly included in the nonbonded interactions such as Lennard-Jones potential. However, the torsional potential of PE of the united atom model has been studied extensively and thus the well-known potential of eq 4 is used. By a simple relation, the force is expressed as a gradient of energy:

$$\vec{F}_i = -\vec{\nabla}_i E_{\text{total}} \quad (6)$$

Three types of polymers have different k_ϕ values, i.e., $k_\phi(\text{P0}) = 0$, $2k_\phi(\text{P1}) = k_\phi(\text{P2})$, and three types of penetrants have different σ^*. For a pair of different particles, i.e., between the polymer segments and gas molecules, the Lorentz–Berthelot mixing rule is employed.

$$\sigma_{ij}^* = {}^1/_2(\sigma_{ii}^* + \sigma_{jj}^*) \quad (7)$$

$$\epsilon_{ij}^* = \sqrt{\epsilon_{ii}^*\epsilon_{jj}^*} \quad (8)$$

The parameters used in this simulation are listed in Table 1. Other parameters are taken from ref 11. The bond potential is weakened to increase the time step as done in ref 11. Though the spring is softer than the real chain, it has much stiffer movement than the torsion. Therefore, the weak bond will not affect the results. Cubic periodic boundary conditions are imposed to eliminate surface effects.

Results and Discussion

The equilibrated velocities of the particles in the system have a Maxwell–Boltzmann distribution, from

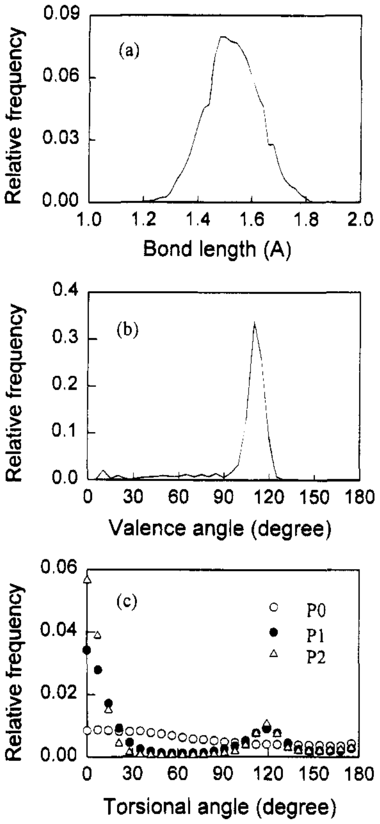

Figure 2. (a) Bond length distribution of polymer chains. Equilibrium value is 1.52 Å. (b) Valence angle distribution of polymer chains. Equilibrium value is 109.5°. (c) Torsional angle distribution of polymer chains. 0° corresponds to trans state and 120° to gauche state.

which the desired temperature of 400 K is determined. The temperature is chosen to be higher than room temperature so as to give rise to faster movement, which enables us to observe the diffusion phenomena at room temperature for longer time according to the time–temperature superposition principle. The trick is reasonable because our major interests lie in the qualitative trends, no in the quantitative prediction. By imposing potential energy restrictions as mentioned above, most of bond lengths (Figure 2a), valence angles (Figure 2b), and torsional angles (Figure 2c) are forced to remain in their equilibrium state. The conformation of more rigid chains prefers the trans and gauche state, as shown in Figure 2c. A freely rotating chain (P0) has nearly uniform distribution, while the most rigid chain of the three (P2) has a strong tendency to lie in the trans and gauche states. The conformational transition seems to happen within a 0.01 ps range. Thus, the cooperative motion between polymers and penetrants, which causes the macroscopic diffusion behavior according to the free volume model, also happens within a short period. The center of gravity of a chain seldom moves around, because the chain connectivity restricts the mobility of chain segments, resulting in vibrating at the same position for a relatively very long time.

The frequent collision of the penetrant with its neighbors can be deduced from the analysis of the velocity of a penetrant (Figure 3). If the inner product of two unit vectors is −1, the two vectors have the opposite direction to each other. Using this simple idea, the direction of the penetrant after the collision can be monitored.[5] Figure 4 shows that the diffusant collides frequently and remain there for a long time relative to the time for the jump to another vibrating site. Figure 5 shows traces of jump motion of penetrants. Even though the penetrant travels long distances, the net displacement of the movement is very small. The region where the penetrant sweeps becomes wider the smaller the penetrant size and more flexible the polymer chain.

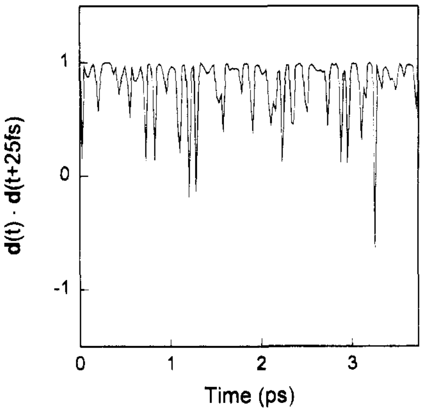

Figure 3. Inner product of unit vectors of velocities of penetrant molecule P in polymer P2 at time t and those of 25 fs later.

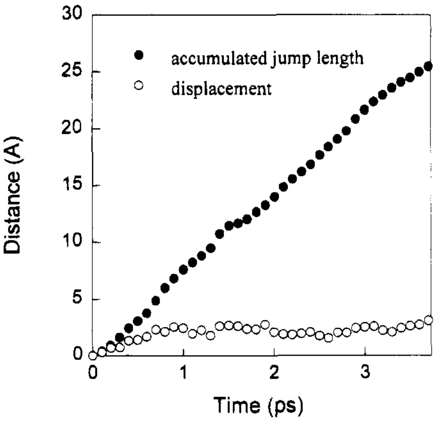

Figure 4. Vibrational motion of penetrant P in polymer P2.

The dynamics for a change in the conformational state can be investigated by the time autocorrelation function of torsional angle, $R_\phi(\tau)$, as given by eq 9:[2,5]

$$R_\phi(\tau) = \frac{\langle \cos \phi(t-\tau) \cos \phi(t) \rangle - \langle \cos \phi(t) \rangle^2}{\langle \cos^2 \phi(t) \rangle - \langle \cos \phi(t) \rangle^2} \qquad (9)$$

The curve can be fitted using an exponential function:

$$R_\phi(\tau) = \exp(-(\tau/\tau_e)) \qquad (10)$$

where τ_e is the rotational relaxation time. The relaxation time that characterizes how fast or slowly it decays gives information about the rotational mobility. The larger rotational mobility may cause faster "memory lost" and shorter relaxation time. In other words, the more rigid the chain is, the slower the decay is, as shown in Figure 6. The relaxation times of polymers P0, P1, and P2 are found to be 0.346, 1.68, and 2.30 ps, respectively, by nonlinear-least-squares curve fit. The rotational mobility obviously has a strong effect on the dynamics of free volume distribution. Faster redistribution of free volume may occur for the system composed of more flexible chains. The opening of the "cage" in more flexible chains becomes more frequent, and the diffusion rate is increased by the activated redistribution.

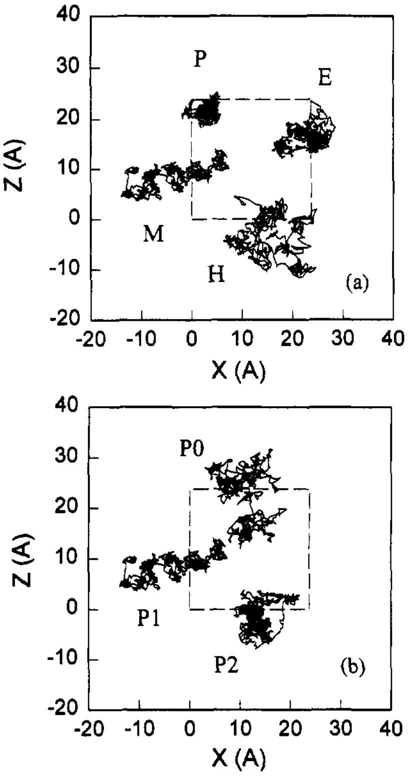

Figure 5. (a) Traces of jump motion of penetrants. Dashed line represents the periodic box, and the traces for separate diffusion processes are assembled for illustration ($x-z$ plane). (b) Traces of jump motion of penetrant M in polymers P0, P1, and P2 ($x-z$ plane).

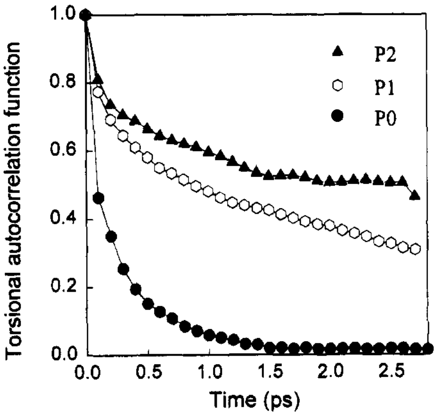

Figure 6. Decay of torsional autocorrelation function for polymers P0, P1, and P2.

The structure of a liquid can be characterized by a set of distribution function for the atom positions, the simplest of which is the radial distribution function.[12] The function gives the probability of finding a pair of atoms at a distance r apart, relative to the probability expected for a completely random distribution at the same density. After calculating the radial distribution function for all the segments and then the function between intrachain segments, the subtraction of the latter from the former gives the interchain distribution function. In Figure 7, the peaks in the intrachain components imply the regular spatial arrangement of segment along with the polymer chain. The first peak from the left is thought to arise from the closest bonded neighboring segment, the second peak from the next neighbor, and so on. The order is rapidly vanishing as the distance expands outward in the radial direction. As the flexibility of the polymer increases, the peaks become dull, which means the loss of intrachain regularity. Figure 8 shows the interchain radial distribution function. The separation distance of chains can be estimated from the position of the first peak, from which it is deduced that a more rigid polymer gives more close-packed structure. This is consistent with the fact that a more rigid chain has better intrachain order.

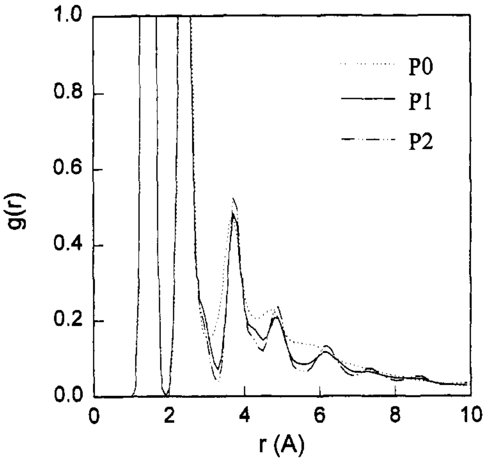

Figure 7. Intrachain radial distribution function for polymers P0, P1, and P2.

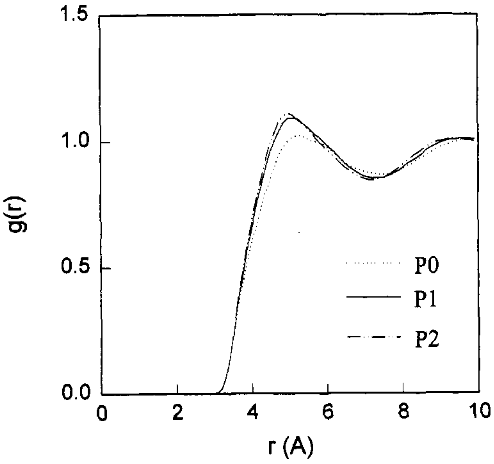

Figure 8. Interchain radial distribution function for polymers P0, P1, and P2.

To evaluate the free volume, the system is divided into a certain number of cubic lattices, each of which is labeled as "occupied" or "unoccupied" by polymer segment. Free volume is then defined as a set of unoccupied lattices. The fraction of free volume is obtained by enumerating the unoccupied lattices and evaluating their volume. As the number of cubic lattices increases, a more accurate result can be obtained. All the free volume fraction is obtained with 34^3 lattices, since the amount of free volume converges at above 34^3 lattices. The system of density of 0.83 g/cm^3 has about 39% free volume. Of course, the free volume has its distribution in size. Therefore, all the free volume is not available to penetrant molecules. Table 2 tells us that smaller penetrant, as could be known intuitively, can easily find the space to jump in and that a more rigid chain provides more free space, which is consistent with the results from the radial distribution function. However, this contradicts the fact that the enhanced rotational mobility makes the redistribution of free volume feasible and contributes to the easy jump of penetrants to another vibrating site. Therefore, it is thought that there must be a competition between the effect of the

Table 2. Fractions of Total Free Volume and Available Free Volume for Penetrants (10^{-4})

	polymer P0	polymer P1	polymer P2
total	3893.00 ± 1.30[a]	3914.00 ± 1.10	3919.00 ± 1.10
H	78.28 ± 0.47	94.04 ± 0.43	96.64 ± 0.59
M	18.72 ± 0.17	23.09 ± 0.18	28.15 ± 0.26
E	7.08 ± 0.10	10.11 ± 0.13	11.57 ± 0.16
P	2.40 ± 0.05	3.30 ± 0.07	4.38 ± 0.10

[a] Standard error.

Table 3. Diffusion Coefficient Calculated from the Mean Square Displacement (A^2/ps)

	polymer P0	polymer P1	polymer P2
H	0.995 (0.998)[a]	0.702 (0.999)	0.813 (0.999)
M	0.703 (0.998)	0.387 (0.998)	0.255 (0.987)
E	0.627 (0.997)	0.277 (0.998)	0.0942 (0.985)
P	0.435 (0.995)	0.0985 (0.996)	0.0323 (0.986)

[a] Square of correlation coefficient.

Table 4. Selectivity of Polymers for Various Gases

	ratio of volume	polymer P0	polymer P1	polymer P2
M/E	0.644	1.121	1.395	2.706
E/P	0.642	1.443	2.817	2.915
M/P	0.414	1.618	3.947	7.888
H/M	0.444	1.415	1.814	3.188
H/E	0.286	1.587	2.534	8.631
H/P	0.184	2.287	7.127	25.17

redistribution of dynamic free volume and that of the amount of static free volume on the diffusion of penetrants.

The self-diffusion coefficient of a component in a mixture[4] can be calculated from the Einstein relation:

$$D_a = \frac{1}{6N_a}\lim_{t\to\infty}\frac{d}{dt}\sum_{i=1}^{N_a}\langle[\vec{R}_i(0) - \vec{R}_i(t)]^2\rangle \qquad (11)$$

where $\vec{R}_i$ is the position of particle, N_a is the number of particles of type a, and the broken brackets denote averaging over all choices of time origin.

Similar to relative volatility in distillation, the separation factor of a binary mixture is expressed by the selectivity, defined as the ratio of permeation fluxes of the two components as measured by permeation of the mixture.[16] For dilute solutions of fluid in an isotropic membrane, the selectivity is independent of membrane thickness and is equal to the ratio of the permeabilities of the pure components:

$$\alpha_{Aj,Bj} = P_{Aj}/P_{Bj} \qquad (12)$$

where the permeability P_{ij} is related to the solubility coefficient k and the diffusion coefficient D_{ij} by

$$P_{ij} = kD_{ij} \qquad (13)$$

Because we focus on the sieving ability arising from the size difference of penetrants, which is the main viewpoint of free volume theory, the penetrants, H, M, E, and P are modeled to have the same spherical geometry and the same energy parameter, which results in the assumption of the same solubility. Thus the selectivity becomes equal to the ratio of the diffusion coefficients.

$$\alpha_{Aj,Bj} = D_{Aj}/D_{Bj} \qquad (14)$$

where D_{ij} is a self–diffusion coefficient of penetrant i in polymer j. In addition, this study excludes the strong interaction between penetrants so that the diffusion coefficients obtained for the diffusion process of one species are able to replace those in a mixture diffusant system. This approximation is, however, applicable to give qualitative information of selectivity. The ratio of self-diffusion coefficients gives information on the sieving ability of the polymer and/or the retardation effect of penetrant diffusion in a rigid polymer.

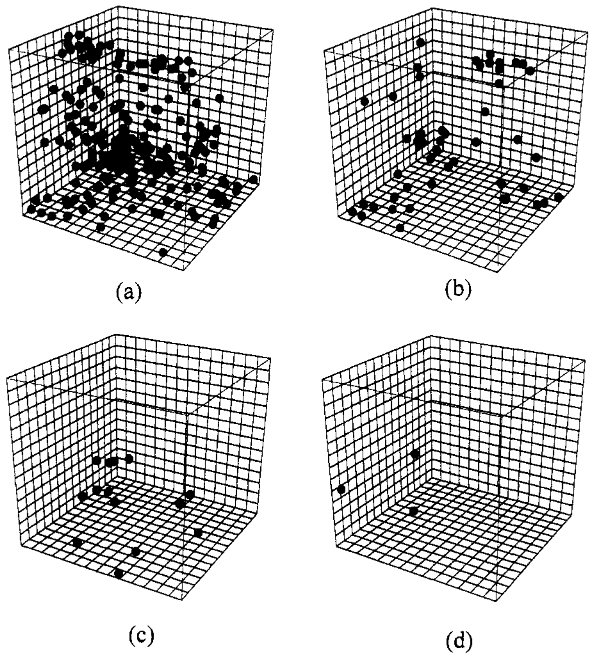

Figure 9. Snapshots of the distribution of free volume available to (a) H, (b) M, (c) E, and (d) P.

It is noteworthy that the chain itself shows a much lower diffusion rate due to the chain connectivity rather than the penetrants. Generally, the mean square displacement of penetrant in a polymer shows lower mobility as the size of the penetrant increases, and larger flexibility of the polymer chain enhances the mobility of penetrant. The self-diffusion coefficients are calculated from the mean square displacement over 100 ps by the Einstein relation and are listed in Table 3. As the flexibility of the polymers decreases, the diffusion coefficient decreaces more remarkably with the increase of penetrant size. This means that the mobility of the penetrant is much affected by its size, when the polymer is rigid. As a result, the rigidity of the polymer chain improves the selectivity, as shown in Table 4. The penetrants M, E, and P diffuse faster through more flexible polymer. However, H can diffuse faster through P2 than through P1. It is thought that this behavior originates from the competition between the effect of dynamic free volume redistribution and that of static free volume amount on the diffusion of penetrants. When the polymer chain is rigid, the rotational motion of the chain is so slow that it can make the diffusion of penetrant difficult, but at the same time the free volume that the penetrant can jump into will increase and allow the diffusion to be feasible due to the regular packing over a short range. However, because the free volume available to a large gas molecule is quite little and rather sparse, and forms a cluster which is locally concentrated, the gas molecule can rarely find the cluster around its neighboring sites (Figure 9). Therefore, the effect of dynamic redistribution of the free volume on gas diffusion is dominant for larger pen-

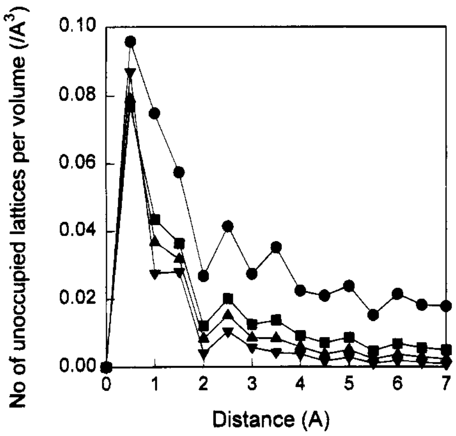

Figure 10. Number of unoccupied lattices available to penetrant P (▼), E (▲), M (■), and H (●) in unit volume of polymer P1 in the radial direction. The same trends are observed in the case of P0 and P2.

etrants such as P, E, and M. In the case of H, which is smaller than that of a polymer segment, it has a relatively larger amount of the available free volume than the others (Figure 10), and thus the unoccupied lattices become greater and they are interconnected. Therefore, the static aspects of free volume may play an important role, and the competition between the dynamic and static features can be observed.

The selectivity of P2 is much higher than P1 even though the permeability of H through P2 is also higher than that through P1. This implies that it is of great significance to take both the available free volume and the chain flexibility into account when designing a membrane for gas separation process. A membrane, which is rigid in the dynamical sense and has much free volume accessible to only one gas component, is desirable to obtain the optimum permeability and selectivity. It is suggested that this can be accomplished by introducing bulky side groups into rigid polymer chains.

Conclusions

The mobility of penetrant is much affected by its size, especially when the polymer is rigid, which will undoubtedly improve the selectivity. The more rigid chain provides more free volume, which is consistent with the results from the radial distribution function. However, this contradicts the fact that the enhanced rotational mobility makes the redistribution of free volume feasible and contributes to the easy jump of penetrants to another vibrating site. Therefore, it is thought that there must be a competition between the effect of dynamic free volume redistribution and that of static free volume amount on the diffusion of penetrants. It is of great significance to take both the available free volume as a static aspect and the chain flexibility as a dynamic one into account when designing a membrane for gas separation process.

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