

A Molecular Dynamics Study on the Gas Permeation of Glassy Polymer

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Abstract: The gas permeation performance of commercially available polyetherimide (Ultem®) is simulated by means of molecular dynamics methods. By the observation of trajectory, long distance hopping of gas molecules is needed to transverse from top to bottom of membrane. Two possibilities mechanism of diffusion phenomena through glassy polymers can be issued. Diffusion coefficients were calculated by Einstein relation equation. In solubility simulation, the value of the constants C'_H and b for O_2 at 300 K were calculated. The diffusion and solubility coefficient of He for PEI were simulated in this simulation work. the permeability coefficient is 9.88 Barrer. This value is closed to experimental value of 9.4 Barrer.

Keywords: *molecular dynamic simulation, glassy polymer, gas separation*

1. Introduction

Commercially available polyetherimide (Ultem®) is well known as a high- T_g engineering thermoplastic polymer with a number of excellent physical properties including high permselectivity. There have been many attempts to adopt polyetherimide as a candidate material for gas separation membrane. The lack of experimental data demands trial and error procedures.

Molecular dynamics can provide the quantitative prediction of gas permeation properties. There has been development in the use of molecular dynamics methods for the simulation of gas permeation. Recently, molecular dynamics expanded its boundary to slower diffusion process. In dense polymeric membrane, Solution-diffusion mechanism postulates that permeation is controlled by diffusion of permeant gas in the membrane, which is assumed to be in thermodynamic solution

equilibrium with the gas at the interfaces.

The molecular structure and the morphology of glassy amorphous polymers has been the subject of numerous research efforts in the past. Motivation for this research is the need of a relation between the structure on a molecular level and bulk material properties. Especially, mechanical and mass transport properties of glassy as well as rubbery polymers have been investigated theoretically by molecular dynamics (MD) simulations. Mathematical incorporation of all bonded and non-bonded interactions between these molecules allows the study of the trajectory of any single atom in this system. For example, placing a single low molecular weight molecule in a polymeric host matrix and following the path of this molecule in time confirmed the hopping mechanism of diffusion in the polymer[1] as it was postulated some 40 years ago by Meares[2]. Advanced simulation techniques allow already the prediction of macroscopic diffusion coefficients for different polymers with an accuracy of one order of magnitude [3].

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Due to the recent development of improved force field, wide availability of commercial program packages and high speed computing facility, attention has begun to be directed to task of simulating the slow diffusional process through glassy polymer.

2. Theoretical Backgrounds

The most frequently used approach to obtain self-diffusion coefficients in molecular dynamics simulation is by means of the Einstein relationship. The Einstein relationship is as follows

$$D_0 = \frac{1}{6N_0} \lim_{t \rightarrow \infty} \frac{d}{dt} \sum_{i=1}^{N_0} \langle |r_i(t) - r_i(0)|^2 \rangle \quad (1)$$

where N is the number of diffusing particles of type are the initial and final position I over the time interval t and $\langle |r_i(t) - r_i(0)|^2 \rangle$ is the averaged mean-square displacement of the ensemble. The Einstein relationship assumes a random-walk motion for the diffusing particle.

It should be noted that the diffusion coefficient defined by obtained under equilibrium dynamics while diffusion coefficient typically reported in the literature are transport coefficient obtained from time-lag measurements. The connection between the self coefficient is often expressed by Darken equation.

$$D_{AB} = (D_A^* x_B + D_{BA}^* x_A) \left(\frac{d \ln f_A}{d \ln c_A} \right) \quad (2)$$

where f_a is the fugacity of diffusant A. In the limit of low concentration of the diffusant, Eq. (2) can be reduced to

$$D_{AB} = D_A^* \quad (3)$$

which is sometimes offered as an argument for the widely used practice of comparing self-diffusion coefficients obtained from time-lag measurements.

Solubility can be estimated from molecular simulation by several methods utilizing a molecular mechanics

force field. One approach is the determination of the Henry's law coefficient through the calculation of non-bonded potential energies of the sorbent molecules randomly inserted in a periodic cell representing the sorbent medium. Another approach is based on a grand canonical Monte Carlo method that uses a Metropolis algorithm for accepting or rejection configuration moves (rotational and translational of the sorbate molecule) as well as for sorbate insertion and deletion. By performing the simulation over a range of pressure or fugacity (for non-ideal gases) the sorption isotherm can be obtained as a plot of the concentration of sorbed gas, c , as a function of pressure (or fugacity) at constant temperature. The solubility coefficient, S , is then obtained from the limiting slope of the sorption isotherm at zero pressure.

2.1. Molecular Modeling Software and Hardware

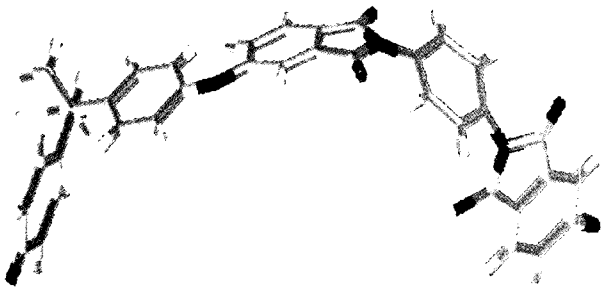
The amorphous state of polymer were built and simulated by means of amorphous builder of Cerius II of Molecular Simulation Inc. Cerius II pot the class II force field, COMPASS. The MD calculations were performed on Silicon Graphics workstation Octane SE equipped MIPS R10000 CPU.

2.2. Force Field

In this study, COMPASS (condensed phase optimized molecular potentials for atomistic simulation studies) force field was employed. COMPASS has been parameterized from *ab initio* computation of model compounds and optimized using condensed low molecular compounds and polymers. The potential terms of COMPASS force field are the same as the consistent force field CFF93. This force field was used to calculate and minimize the energy of a simulated system. Furthermore, it is possible to calculate the forces acting on each atom of a polymer, which can be utilized to solve equation of motion for MD simulations.

3. Model and Simulation Details

The repeating unit of polyetherimide and some of physical properties are shown in Figure 1. Procedure



Polyetherimide (PEI, Ultem, GE plastics)

| | T_g (°C)(Å) | d-space (g/cc) | density (V_f/V_p) | FFV |
|-------|------------------|-------------------|--------------------------|------|
| Ultem | 150 | 4.9 | 1.29 | 0.14 |

Fig. 1. The repeating unit of polyetherimide and some of physical properties.

of simulating the amorphous state of polymer is as follows. In the first stage, a cubic box using the density and the mass of polymer is built. A propagation process is begun in the center of the box to design one polymer conformation. And then, periodic boundary conditions (PBC) are imposed for saving CPU time. Polymer chains in PBC are located randomly with decisive parameters. These chains were optimized via two relaxation steps. After energy minimization by steepest descent method, polymer chains were relaxed with NVT dynamics for 10 ns simulation time.

To fit the simulated density of polymer matrix to experimental value, NPT dynamics at 300 K and 1 bar was performed. During our NPT MD, density of matrix converged into 1.25 g/cm^3 . This value is closed to reported density of 1.29 g/cm^3 .

3.1. Radial Distribution Function

The radial distribution function (RDF) can be determined from trajectory file data. This is the spherically averaged distribution of interatomic vector lengths. This type of information is useful in revealing overall structural properties such as packing, ordering, compressibility, and phase transitions. Because the system is assumed to be isotropic, the radial distribution function is centrosymmetric. The following expression is used to calculate the radial distribution function $G_{AB}(r)$ between two selected groups, A and B:

$$G_{AB}(r) = \frac{g_{AB}(r) \times V}{(N_A N_B - N_{AB}) 4\pi r^2 \Delta r} \quad (4)$$

where N_A = Number of atoms in group A.

N_B = Number of atoms in group B.

N_{AB} = Number of atoms common to both groups A and B.

V = Unit cell volume (for nonperiodic systems $V = 1$).

Groups A and B are specified by selecting the atoms in the model or by specifying particular elements or force field types. Groups A and B are the same for all or selected atoms but may be the same or different when elements or force field atom types are used.

3.2. Simulation of Diffusion Process

For diffusion simulation, three cells were selected for He, O₂ and N₂. Each gas molecules is inserted in each cell and the energy was minimized for 10 ps while the polymer chain coordinations were held fixed. Finally, 110~3000 ps NVT dynamics were carried out at 300 K. Cut-off distance was set to 10 Å. Diffusion coefficient were calculated using mean-square displacement over the range of simulation time where Einstein diffusion is observed.

4. Simulation Result and Discussion

4.1. Diffusion of Gas Molecules

Gas permeation properties of polyetherimide and other polymers are plotted in Figure 2. polyetherimide shows a outstanding high permselectivity of oxygen over nitrogen and a low permeability. Molecular dynamics simulation is only suitable for studying the fast diffusion of small gas molecules through polymer gels, solutions, and some rubbers or bulk amorphous materials above T_g . It is not recommended to study diffusion rates of less than $10^{-6} \text{ cm}^2/\text{sec}$. Only diffusion of small gas such as helium or hydrogen through polyetherimide could be simulated. If the slope of $\log(\text{MSD})$ against $\log(\text{time})$ graph is not close to 1.0 for the time seg-

Table 1. The Simulation Results of Diffusion Coefficients of He and H₂ for PEI

| Gas | D (10 ⁻⁶ cm ² /s) |
|----------------|---|
| He | 5.2 |
| H ₂ | 1.6 |

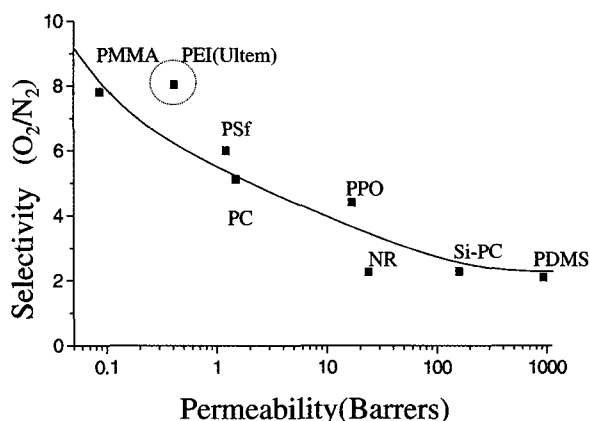


Fig. 2. Gas permeation properties of polyetherimide and other polymers are plotted.

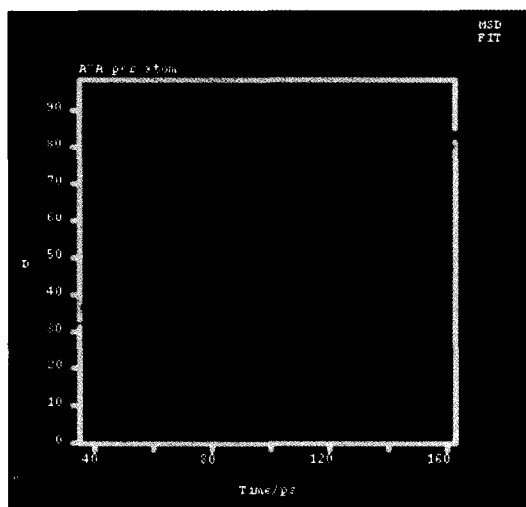


Fig. 3. The simulation results of diffusion coefficients.

ment analyzed, a longer simulation is required. The simulation results of diffusion coefficients are shown in Figure 3 and Table 1.

It is noted that the plots of simulated trajectory displacement versus time for both glassy and rubbery polymers, These plots show that a diffusant undergoes a rattling motion within small cages or cavities occupied with an occasional jump to other cavity in a time

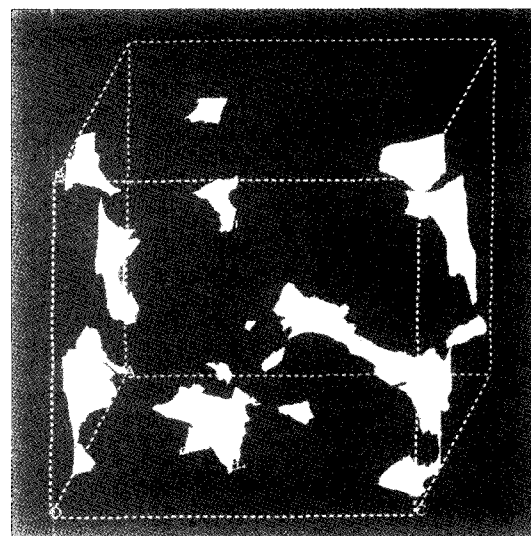


Fig. 4. The accessible free volume of polymer matrix can be analyzed by insertion of virtual 2 Å probe

frame that is short compared with the residence time in the cavity. It has been suggested that that this solid-like hopping mode can take place well above the glass transition temperature due to the short time nature of the diffusive jumps for small diffusants. Such a jump model of diffusion is consistent with a stochastic equation of Bueche based on a random walk model, as follows.

$$D = \frac{\delta^2}{6\tau} \tag{5}$$

where δ is the mean hopping distance and τ is the average time intervals between two hopping. Jumps of O₂ through PEI were detected by means of a long time simulation. Mean hopping distance and the average time intervals between two hopping were 5 Å and 800 ps, respectively. Fried et al. reported that the results for O₂ in PDMPO showed a jump length of 4-5 Å at intervals of 300-350 ps and hopping of CO₂ did not happen. In this case, hopping of CO₂ and N₂ could not be found for 2 ns simulation.

4.2. The Structure of Polymer as a Membrane Material

As shown in Figure 4, the accessible free volume of

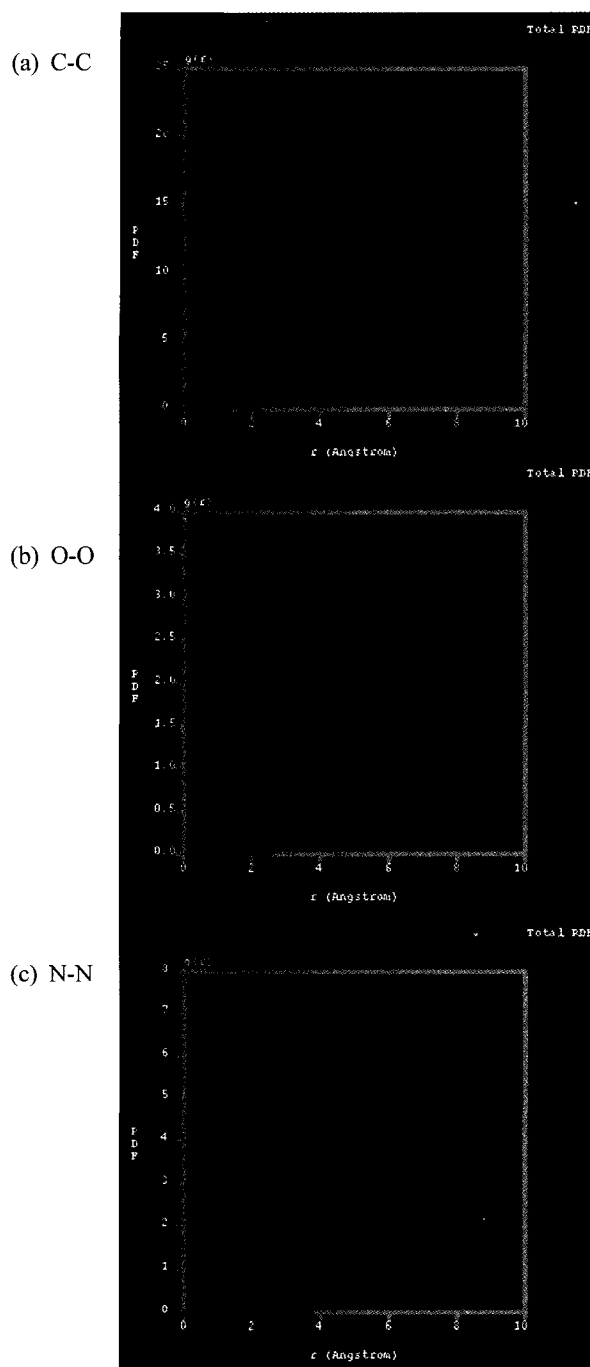


Fig. 5. Radial distribution function (RDF) of polymer matrix.

polymer matrix can be analyzed by insertion of virtual 2 Å probe. The accessible free volume shows a scattered structure, that is, each parts of free volume do not have a connectivity. Therefore, long distance hopping of gas molecules is needed to transverse from top

to bottom of membrane. Two possibility mechanism of diffusion phenomena through glassy polymers can be issued. First, there are preferred path might be the temporary opening by thermal fluctuation. That is the evidence of long distance hopping of gas molecules. Second, In diffusion simulation of CO₂ through PEI, long distance hopping could not be observed and diffusion coefficient from the Einstein equation is higher than the expected diffusion coefficient. It means that the gas molecule vibrate fast in a hole of polymer matrix. These observations provides clues to dual-mode behavior of gas permeation through a glassy polymer.

Radial distribution function (RDF) of polymer matrix are shown in Figure 5. These results provide some information on the structure and amorphous state of polymer matrix. In Figure 6, Pair correlation functions (RDF between two heteroatoms) of He and atoms in polymer matrix show that the access distance of He and carbons in polymer matrix is the closest than that of other atoms.

Typical results for the simulation of O₂ and N₂ solubility are shown in Figure 7 and Figure 8. The simulation value typically converged by 100,000 steps Henry's law coefficient were calculated by the insertion method of Bezus et al. the solubility parameter can be correlated with the condensibility of the gas as measured by the critical temperature, normal boiling temperature or the Lennard-Jones potential-well depth (ϵ/k). Meares have proposed the relationship

$$\log S = K_3 + K_4(\epsilon/k) \quad (6)$$

where the value of the constants K_3 and K_4 for PEI at 300 K are 3.54 and 0.01, respectively.

The solubility and transport properties of gases can be explained on the basis of the dual sorption model whereby the sorption isotherm is given as

$$C = k_D p + \frac{C_H b p}{1 + b p} \quad (7)$$

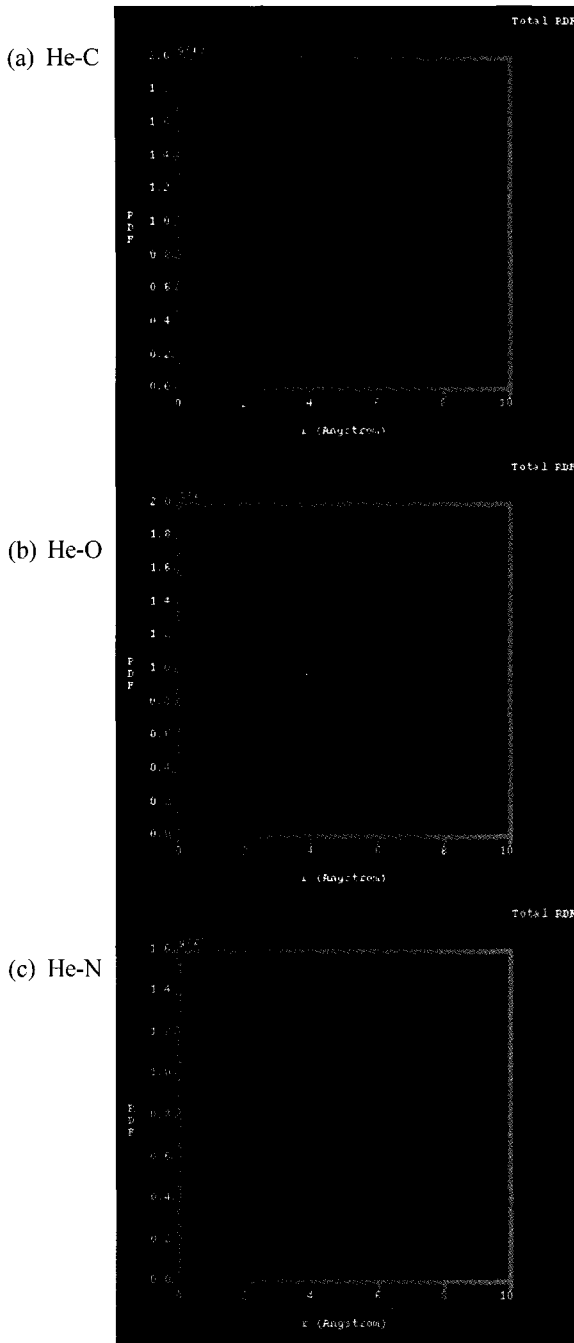


Fig. 6. Pair correlation functions (RDF between two heteroatoms) of He and atoms in polymer matrix.

where k_D is the Henry's law coefficient, C_H is the Langmuir or hole-filling capacity of the glass and b is a hole-affinity constant. The Langmuir capacity is equal to the maximum concentration of solute molecules in the relaxed domains of a glassy polymer can be mea-

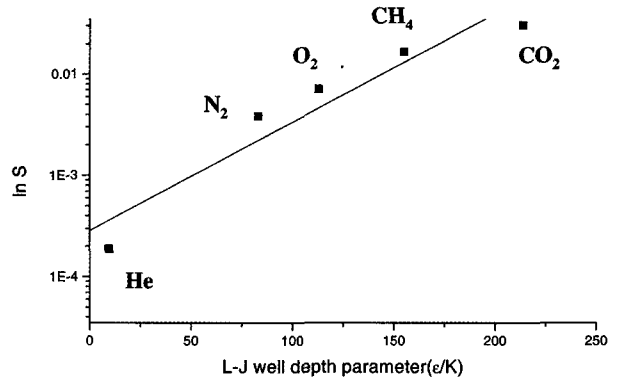


Fig. 7. Simulation result of Henry's constant.

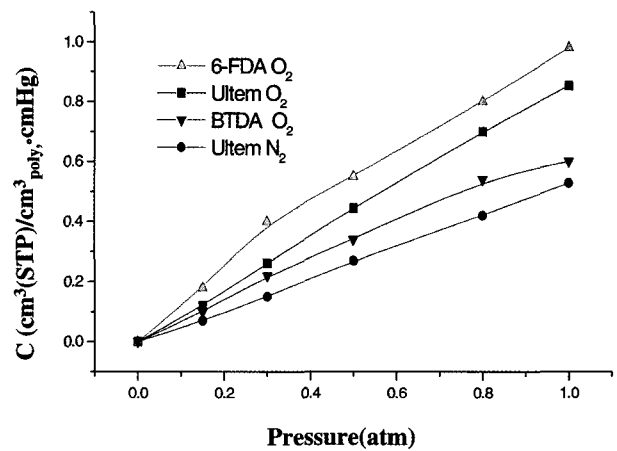


Fig. 8. Simulation result of Sorption isotherm and other experimental results of polyimide.

sure of excess free volume of a polymer. Fixed pressure (grand canonical ensemble) sorption computations were used to obtain the low pressure sorption isotherms from which dual-mode parameters were obtained by nonlinear regression fit of the simulation data. Sorption isotherms for O_2 with other results reported are shown in Figure. The value of the constants C_H and b for O_2 at 300 K are $10.5 \text{ cm}^3(\text{STP})/\text{cm}^3 \text{ poly.atm}$ and 0.11 atm^{-1} , respectively. This plot shows the simulated solubility data is range within a reasonable one.

For the purpose of comparison, the permeability of PEI was calculated with a simple equation of $P=D \times S$. The diffusion and solubility coefficient of He for PEI were $5.2 \times 10^{-6} \text{ cm}^2/\text{s}$ and $1.9 \times 10^{-4} \text{ cc}(\text{STP})/\text{cc cmHg}$ in this simulation work. Therefore, the permeability coefficient is 9.88 Barrer. This value is closed to

experimental value of 9.4 Barrer.

5. Conclusions

The gas permeation performance of commercially available polyetherimide (Utem[®]) is simulated by means of molecular dynamics methods. By the observation of trajectory, long distance hopping of gas molecules is needed to transverse from top to bottom of membrane. Two possibility mechanism of diffusion phenomena through glassy polymers can be issued. This is a evidence of the dual sorption model. Diffusion coefficient were calculated by Einstein relation equation. In solubility simulation, the value of the constants C'_H and b for O₂ at 300 K are $10.5 \text{ cm}^3(\text{STP})/\text{cm}^3_{\text{poly}}\text{atm}$ and 0.11 atm^{-1} , respectively. The diffusion and solubility coefficient of He for PEI were $5.2 \times 10^{-6} \text{ cm}^2/\text{s}$ and $1.9 \times 10^{-4} \text{ cc}(\text{STP})/\text{cc cmHg}$ in this simulation work. Therefore, the permeability coefficient is 9.88 Barrer. This value is closed to experimental value of 9.4 Barrer.

References

1. K. Toi, G. Morel, and D. R. Paul, "Gas sorption and transport in poly(phenylene oxide) and comparisons with other glassy polymers", *J. Appl. Polym. Sci.*, **27**, 2997 (1982).
2. R. T. Chern, F. R. Sheu, L. Jia, V. T. Stannet, and H. B. Hofenberg, "Transport of gases in unmodified and arylbrominated 2,6-dimethyl-1,4-poly(phenylene oxide)", *J. Membr. Sci.*, **35**, 103 (1987).
3. R. T. Chern, L. Jia, S. Shimoda, and H. B. Hofenberg, "A note on the effects of mono- and di-bromination on the transport properties of poly(2,6-dimethylphenylene oxide)", *J. Membr. Sci.*, **48**, 333 (1990).
4. J. R. Fried, M. Sadat-Akahavi, and J. E. Mark, "Molecular simulation of gas permeability: poly(2,6-dimethyl-1,4-phenylene oxide)", *J. Membr. Sci.*, **149**, 115 (1998).
5. D. Hoffman, J. Ulbrich, D. Fritsch, and D. Paul, "Molecular modeling simulation of gas transport in amorphous polyimide and poly(amide imide) membrane materials", *Polymer*, **37**, 4773 (1996).
6. D. Hoffman, L. Frotz, J. Ulbrich, and D. Paul, "Molecular modeling of amorphous membrane polymers", *Polymer*, **38**, 6145 (1997).