Sorption and Diffusion Characteristics of Water Vapor in Dense Polyimide Membranes

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Five kinds of polyimide membranes have been prepared using pyromellitic dianhydride (PMDA), 3,3′4,4′-benzophenonetetracarboxylic dianhydride (BTDA), 4,4′-diaminodiphenylether (ODA), 4,4′-diaminodiphenylmethane (MDA), and phenylenediamine (PDA) monomers, and the properties of polyimide membranes have been measured by experimental techniques. The dynamic sorption and desorption behavior of water vapor in the five polyimide membranes at 298 K and 308 K were investigated by experiments. According to the results and the fractal diffusion theory proposed by Chen, the diffusion of water vapor in BTDA + PDA polyimide membrane belongs to anomalous diffusion, and the anomalous diffusion factors are 2.38 at 298 K and 2.26 at 308 K. However, the diffusion behavior of water vapor in PMDA + ODA, PMDA + MDA, BTDA + ODA, and BTDA + MDA polyimide membranes obeys the Fickian diffusion law. The diffusion coefficients for Fickian diffusion of water vapor in PMDA + ODA, PMDA + MDA, BTDA + ODA, and BTDA + MDA polyimide membranes were calculated from the dynamic sorption data, following Fickian diffusion. The values of the diffusion coefficient for water vapor in all four polyimide membranes at 308 K are higher than those at 298 K, and those at the same temperature increase with the molar free volume of the polyimide membranes.

Introduction

The dynamic sorption and diffusion of small solvent molecules in dense polymeric membranes have gained great interest during the past decades.[1,2] This is mainly due to the fact that the dynamic sorption and diffusion of small molecule penetrants in dense polymer membranes is the prerequisite for membrane separation processes such as pervaporation, vapor permeation, and gas separation.[3,4] Hence predicting as well as analyzing sorption and diffusion is important to select appropriate membranes for a predefined task. Several models have been established to describe the sorption processes such as the Langmuir and Henry's Law Isotherms,[5] Solubility Parameter Theory,[6] Flory−Huggins Theory,[7] and the UNIQUAC Model.[8,9] Most of the models are of a semiempirical nature and try to predict the sorption behavior based on a minimum set of sorption experiments.

The diffusion of small molecules into amorphous polymers has been divided into three basic modes of transport, depending on the relative rates of penetrant diffusion and polymer chain relaxation:[10] (1) Case I or Fickian diffusion occurs when the diffusion rate of penetrant molecules is much slower than the polymer chain relaxation rate and the sorption equilibrium is established rapidly; (2) Case II diffusion occurs when the penetrant diffusion rate is much faster than the polymer chain relaxation; (3) Case III or anomalous diffusion occurs when the penetrant mobility and polymer chain relaxation rates are comparable. Among these three kinds of diffusion behavior, anomalous diffusion, which commonly occurs in the case of liquid penetrants diffusing into glassy polymer membranes, is the most complicated.

The key to membrane diffusion is the diffusion coefficient. Therefore, to obtain the diffusion coefficient a number of scientists have established many theories such as the Free Volume Theory and Dual Sorption Model. The free volume theory was developed by Fujita[11] to describe the mass transfer through polymeric membranes based on molecule movements from one place to another. The foundation of this theory is Fick's first law, which is commonly restricted to ideal systems, that is, binary systems. The fundamental assumption of the model is that the mobility of both polymer segments and solvent molecules is based on the available free volume in the membrane structure. The diffusion of molecules through membranes is caused by redistribution of the fractional free volume in the polymer−solvent system. On the basis of the assumption that sorption and desorption of a molecule are much faster than its diffusion through the membrane, the actual mass transport is completed when the equilibrium at the phase boundaries is adjusted. After being established by Fujita, the Free Volume Theory has been developed by a number of researchers including Fels and Huang,[12] Vrentas and Duda,[13] Rhim and Huang,[14] and so on.

Similar to the free volume model, the dual sorption model by Vieth and Sladek[15] and later extended by Vieth et al.[16] describes diffusion based on free spaces, the so-called microvoids, in the polymer structure. These microvoids or hollow spaces in the polymer structure are assumed to be uniformly distributed. In a case where a microvoid with an appropriate size is next to a solvent molecule, this microvoid can dissolve the molecule. The energy of this molecule has to be, therefore, high enough to enable it to move into the hole. Diffusion occurs if the free space of the moved molecule will be taken by another molecule. This mechanism is known as the Dual Sorption Model. Initially, it was developed for glassy polymers to describe negative deviations from Henry's Law concerning the absorption of gases into polymers.

Several experimental methods have been established to determine the sorption and diffusion behavior of small molecules

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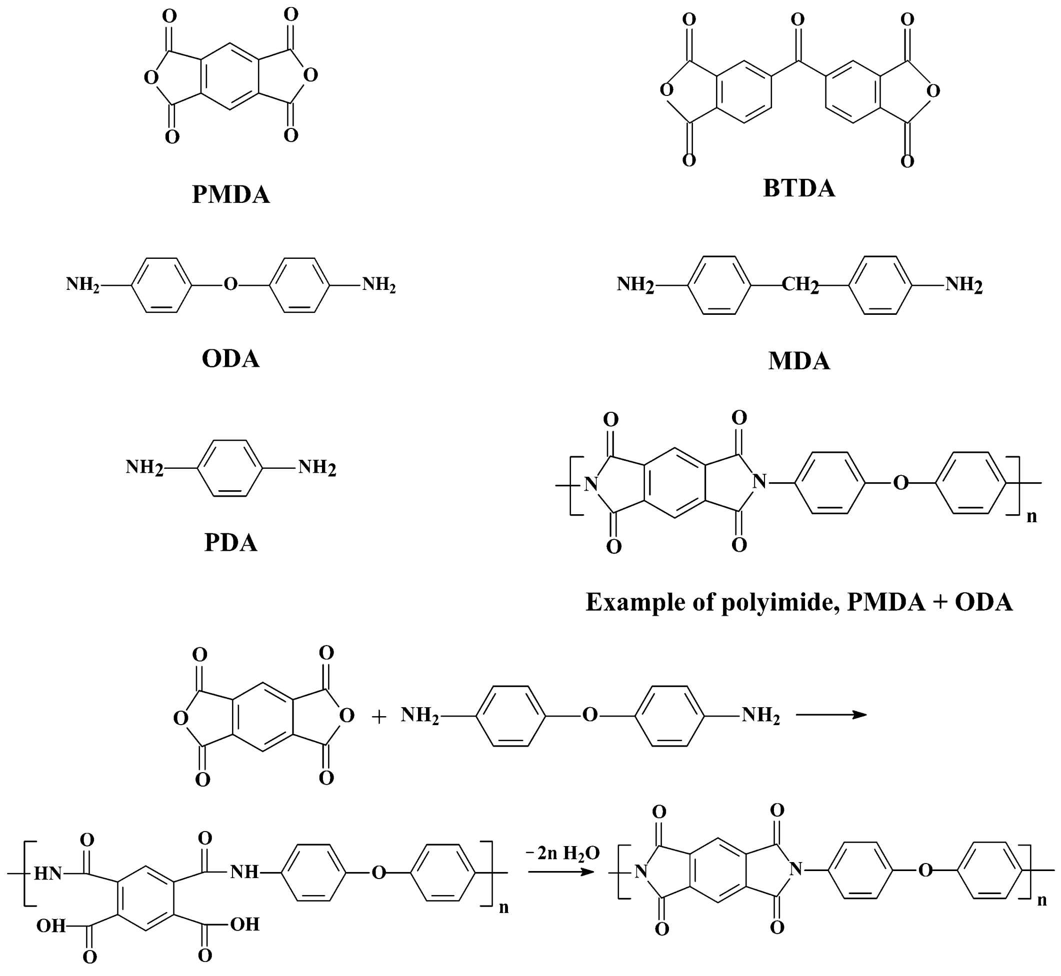

Example of polyimide, PMDA + ODA

Synthesize PMDA + ODA polyimide by two-step method

Figure 1. The structures of polyimide monomers.

in membranes. One of the most accurate approaches is sorption measurements using the membrane material and feed components. To determine the sorption isotherm, approaches such as gravimetric methods or the quartz crystal microbalance method can be used to estimate the time + dependence of the sorption process as well as the sorption equilibrium and, consequently, to predict the sorption isotherm. For modeling the pervaporation process at low-pressure conditions, the sorption data of saturated vapors of the pure components, as well as the mixtures, are useful.

In the present study, five kinds of polyimide membranes have been prepared using pyromellitic dianhydride (PMDA), 3,3′4,4′-benzophenonetetracarboxylic dianhydride (BTDA), 4,4′- diaminodiphenylether (ODA), 4,4′-diaminodiphenylmethane (MDA), and phenylenediamine (PDA) monomers, and the properties of polyimide membranes have been measured by experimental techniques. The dynamic sorption behavior of water vapor in the five polyimide membranes investigated, and the diffusion coefficient was also calculated.

Experimental Section

Materials. All chemicals were purchased from Acros Organics Inc. and the Fluka Chemical Corp. PMDA, ″BTDA, ′ODA, ′MDA, and PDA were purified before polymerization. The PMDA monomers were purified by recrystalization, and the BTDA, ODA, MDA, and PDA monomers were purified in a vacuum oven at different temperatures. *N*,*N*-dimethylformamide was obtained from the Beijing Yili Chemicals Co. Ltd., purified on distillation under reduced pressure over calcium hydride, and stored over molecular sieves (4 Å). All the monomers of polyimides are shown in Figure 1, and the structure of PMDA + ODA as an example of polyimide is also shown there.

The polyimide membrane was prepared by the so-called two-step method (Figure 1), that is, the polyamide acid (PAA) materials were synthesized by the condensation polymerization using the dianhydride and diamide monomers, and then the PAA membranes made by casting were heated at different temperatures to form the corresponding polyimide membranes. The details for the preparation and characterization of polyimide membranes have been described previously,[17] and the wide-angle X-ray diffraction (WAXD) pattern of BTDA−ODA polyimide is shown in Figure 2. In addition, the polyimides were analyzed by Fourier transform infrared (FTIR) spectra and were recorded on a Nicolet IR560 spectrometer with polymer membrane. Spectra in the optical range of 400 cm^{-1} to 4000 cm^{-1} were obtained by averaging 32 scans at a resolution of 4 cm^{-1}, and the spectra of the five polyimide used in this study are shown in Figure 3.

Dynamic Sorption Experiment. Figure 4 shows the dynamic sorption apparatus. It contains the vapor generator, the data recorder, the vacuum system, and the thermostat. The electrical balance (model BP211D, sensitivity 0.01 mg, made by Sartorius, Germany) is located in the thermostat. Prior to each sorption test, the membrane sample is hung vertically to the electrical

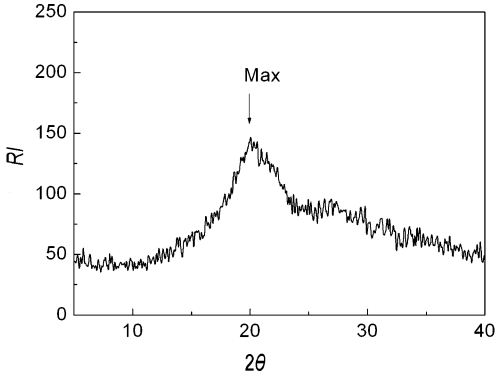

Figure 2. The WAXD pattern of BTDA + ODA polyimide: *RI* denotes the relative intensity.

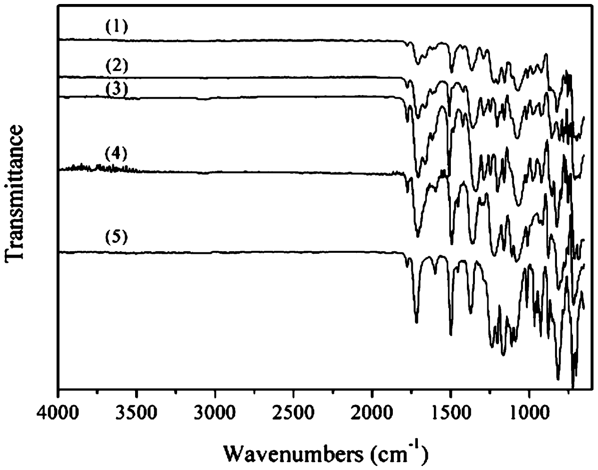

Figure 3. FTIR spectra of polyimide membranes: (1), BTDA + ODA; (2), BTDA + MDA; (3), BTDA + PDA; (4), PMDA + ODA; (5), PMDA + MDA.

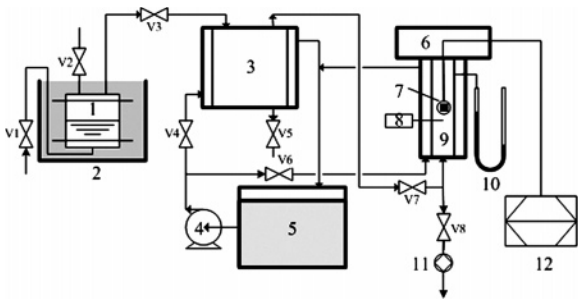

Figure 4. A schematic diagram of the apparatus used for measurement of the sorption and desorption behavior. 1, vapor generator; 2, thermostat; 3, cushion jar; 4, centrifugal pump; 5, thermostat; 6, electrical balance; 7, polymeric membrane; 8, thermometer; 9, balance compartment; 10, mercury barometer; 11, vacuum pump; 12, data processer (V1 to V8, valves).

balance by a small hook, and then the vacuum system is opened (pressure <0.1 Pa) to desorb gas from the membrane over 8 h. Simultaneously, the temperature of the thermostat was regulated to a given value. Then the vapor is introduced into the balance compartment and the sorption test begins. The mass of the membrane is recorded by the data recorder in time until the sorption equilibrium, which is determined when no measurable change is observed within an hour, is obtained. In this study, the sorption experiments were carried out at 298 K and 308 K.

Free Volume of Polymer Material. The free volume, expressing the total amount of free spaces in polymers, is a very important property of the polymer. In this paper, the molar free volume is obtained from Bondi's model of group contribution[18]

$$V_T = \frac{M}{\rho} \tag{1}$$

$$V_{0K} = 1.3V_w \tag{2}$$

$$V_F = V_T - V_{0K} \tag{3}$$

$$\text{FFV} = \frac{V_F}{V_T} \tag{4}$$

where V_T is the volume per mole of repeat unit at the temperature of interest, M is the molar weight of the repeat unit, V_w is the molar van der Waals volume of the repeat unit calculated from the group contribution method,[18] V_{0K} is the volume occupied by the molar repeat unit at 0 K, V_F is the molar free volume of the repeat unit, and FFV is the fractional free volume.

Theory

Fickian Diffusion Law. Diffusion is the process responsible for the movement of matter from one part of a system to another.[19] The first mathematical treatment of diffusion was established by Fick[11] who developed a law for diffusion in one dimension

$$J = -D\frac{\partial c}{\partial z} \tag{5}$$

where J is the flux per unit area, D *is* the diffusion coefficient, c *is* the concentration, z is the distance, and $(\partial c)/(\partial z)$ is the gradient of the concentration along the z-axis. This equation is also known as Fick's first law.

Fickian Diffusion. As mentioned in the Introduction, Fickian diffusion (Case I) is often observed in polymer networks when the temperature is well above the T_g of the polymer. According to the Fickian diffusion law, the permeation flux J is proportional to the reciprocal of membrane thickness L, and the percentage mass gain M_t/M_∞ in the early stage of sorption ($M_t/M_\infty < 1/2$) is proportional to the square root of time[19]

$$\frac{M_t}{M_\infty} = \left(\frac{16Dt}{\pi L^2}\right)^{1/2} \tag{6}$$

where M_t is the amount of solvent absorbed per unit area of polymer at time t, M_∞ is the saturated sorption amount, and L is the membrane thickness.

Equation 6 can be written as

$$D = \frac{\pi L^2}{16}k^2 \tag{7}$$

where

$$k = \frac{\partial(M_t/M_\infty)}{\partial(t^{1/2})} \tag{8}$$

k is the slope of the linear plot of M_t/M_∞ with $t^{1/2}$ in the early stage of the sorption curve.

Anomalous Diffusion. Anomalous diffusion is mainly observed in glassy polymers, that is, when the temperature of study is below the T_g of the polymer. At a specific temperature below T_g, the polymer chains are not sufficiently mobile to permit immediate penetration of the solvent in the polymer core.[20] For anomalous diffusion, the percentage mass gain M_t/M_∞ does not obey eq 2, that is, the percentage mass gain M_t/M_∞ in the early stage of sorption is not proportional to the square root of time.

Chen et al. proposed a new diffusion model describing the diffusion behavior of small molecule penetrants in dense

Table 1. Elemental Compositions of Polyimide Obtained by Elemental Analysis

polyimide	elemental analysis[a] (%) C	H	N
PMDA + ODA	67.30 (69.12)	2.50 (2.64)	7.32 (7.33)
PMDA + MDA	70.40 (71.05)	3.21 (3.18)	7.60 (7.37)
BTDA + PDA	69.63 (70.05)	2.64 (2.56)	7.25 (7.11)
BTDA + ODA	69.95 (71.60)	2.94 (2.90)	6.00 (5.76)
BTDA + MDA	72.13 (74.37)	3.38 (3.33)	5.80 (5.78)

[a] The data in brackets is the theoretical value calculated from the chemical structure.

polymer membranes.[21] Accordingly, a dense polymer is regarded as a "porous medium", where the "pores" are the local free volume. The transport of penetrants through a dense polymer membrane is similar to the fluid transport through a porous medium. The difference in these two cases is that the size and position of pores within the dense polymer membrane change with time, that is, a penetrant passes through a pore with a certain probability. To simplify the treatment, the dense polymer membrane is further described as a lattice. Each bond of the lattice represents a local free volume. A penetrant molecule passes through a bond with a certain probability. If penetrants can pass through the connected bonds from the upstream side of the membrane to the downstream side, the transport occurs. The passage allowing the penetrant to arrive at the downstream side of the membrane from the upstream one is called the diffusion passage. The transport behavior of penetrant through the dense polymer membrane is constituted of a series of continuous jumps in the diffusion passage.

According to the diffusion model proposed by Chen,[21] the percentage mass gain M_t/M_∞ in the early stage of sorption can be calculated using

$$\frac{M_t}{M_\infty} = \frac{K}{L} t^{1-[d_w(d_w-1)]^{-1}} \tag{9}$$

where K is a parameter, L is the membrane thickness, and d_w is the anomalous diffusion factor.[22] Note that d_w is the fractal dimension of the path of the random walker on the diffusion passage. The value of d_w can be obtained from the slope of the linear plot of $\ln(M_t/M_\infty)$ with $\ln t$. For Fickian diffusion, $d_w = 2$, and for anomalous diffusion $d_w > 2$. Therefore, when the diffusion belongs to Fickian diffusion, eq 9 becomes

$$\frac{M_t}{M_\infty} = \frac{K}{L} t^{1/2} \tag{10}$$

which is consistent with eq 6 deduced from Fickian law.

Results and Discussion

Characterization of Polyimide Membrane. Table 1 shows the results of elemental analysis, and it can be seen that the elemental compositions of polyimide membranes are in agreement with their theoretical values for the proposed chemical structure. FTIR spectra of polyimide membranes show peaks corresponding to wave numbers 1780 cm^{-1}, 1730 cm^{-1}, 1380 cm^{-1}, and 725 cm^{-1} as shown in Figure 3, and these peaks are all the characteristic peaks of the polyimides. In contrast, the characteristic peaks of polyamic acid are absent. That is to say, polyimide membranes show representative imide carbonyl peaks but no distinct amide groups, and this indicates that the polyamic acid materials have been fully imidized.

Table 2 presents other physical properties of the polyimide membranes used in this study. The free volume values of polyimide with the same dianhydride increase in the following order: PDA < ODA < MDA. It means that the free volume increases with the decreasing of density, and the higher the density, the lower the free volume is. The introducing of bridging atoms into diamines also contributes to the increase of free volume. Moreover, it also can be seen that with the same dianhydrides, the *d*-spacings of polyimide chains increase in the following order: PDA < ODA < MDA, which agrees with the decrease order of density. In comparison of T_g of polyimides composed of the same diamine components and different dianhydride components, PMDA polyimides show high T_g possibly because they are rigid and planer in structure.

Dynamic Sorption and Desorption. Figures 5−8 show the dynamic sorption curves of water vapor in polyimide membranes at different temperatures, and the dynamic desorption curve of water vapor in PMDA + based polyimide membrane at 298 K as an example of desorption curves is also shown in Figure 9. It can be seen that the time of penetrant reaching the saturated sorption in the same polyimide membrane decreases with an increase in temperature. For example, the percentage mass gain M_t/M_∞ of water vapor in the PMDA + ODA membrane at 308 K reaches 100 % in approximately 900 s, while that at 298 K reaches 100 % in approximately 2500 s. That is to say, the sorption of water vapor into the polyimide membrane becomes quicker with an increase in temperature. Furthermore, the sorption of water vapor into the polyimide membranes with the same dianhydrides and different diamines becomes slower following the order of MDA, ODA, and PDA, being consistent with the decreasing order of *d*-spacings, as shown in Table 2. This implies that the loose packaging of polymer chains is good for the sorption and diffusion of small molecules.

Anomalous Diffusion Factor. As mentioned in the section entitled Anomalous Diffusion, the anomalous diffusion factor d_w can be obtained from the slope of the linear plot of $\ln(M_t/M_\infty)$ with $\ln t$. Figures 10 and 11 show the relationships between $\ln(M_t/M_\infty)$ and $\ln t$ in PMDA-based and BTDA-based polyimide membranes at 308 K, respectively. All the anomalous diffusion factors of water vapor in five polyimide membranes at 298 K and 303 K are listed in Table 3.

As shown in Table 3, the values of anomalous diffusion factors for water vapor in the BTDA + PDA polyimide membrane at 298 K and 308 K are 2.38 and 2.26, respectively, while those in other polyimide membranes are all approximately equal to 2. This implies that the diffusion of water vapor in the BTDA + PDA polyimide membrane belongs to anomalous diffusion, and those in the PMDA + ODA, PMDA + MDA, BTDA + ODA, and BTDA + MDA polyimide membranes belong to Fickian diffusion. This is probably attributed to the chemical structure of the PDA monomer. In comparison to the polymer chains of ODA- and MDA-based polyimides, those of PDA-based polyimide show higher rigidity because of the phenyl structure and the lack of bridging atoms in the PDA monomer. This fact can also be confirmed from the values of T_g as given in Table 2, that is, the BTDA + PDA polyimide show the highest temperature of glass transition in BTDA-based polyimides. Because of the strong rigidity, polymer chains of the BTDA + PDA polyimide exhibit weak mobility and flexibility, and the *d*-spacing of the BTDA + PDA polyimide is the lowest. All of these factors will hinder the diffusion of small molecules in dense polymer membranes.

Diffusion Coefficient. The diffusion coefficient for Fickian diffusion can be calculated from eq 7, and the values of diffusion coefficient for water vapor in PMDA + ODA, PMDA + MDA, BTDA + ODA, and BTDA + MDA polyimide membranes at

Table 2. The Physical Property Parameters of Polyimide Membranes

polyimide	ρ $g\cdot cm^{-3}$	L^a μm	T_g K	M^b $g\cdot mol^{-1}$	*d*-spacing Å	$V_w{}^c$ $cm^3\cdot mol^{-1}$	V_F $cm^3\cdot mol^{-1}$	FFV
pmda + ODA	1.413	32.0	572	382.31	4.6	186.60	27.99	0.1034
PMDA + MDA	1.357	33.0	581	380.36	4.9	191.33	31.57	0.1126
BTDA + PDA	1.405	36.0	551	394.29	3.9	193.80	28.69	0.1024
BTDA + ODA	1.373	34.0	544	486.39	4.3	242.60	38.87	0.1097
BTDA + MDA	1.337	38.0	531	484.39	4.9	247.33	40.77	0.1125

[a] *L* is the thickness of the polyimide membrane. [b] *M* is the molar weight of the repeat unit. [c] V_w is the molar van der Waals volume of the repeat unit calculated from group contribution method.[18]

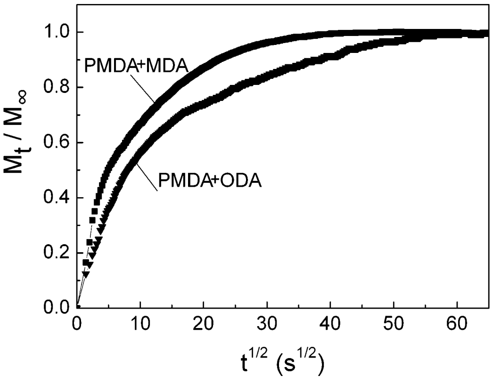

Figure 5. Dynamic sorption curve of water vapor in PMDA-based polyimide membranes at 298 K: ▼, PMDA + ODA; ■, PMDA + MDA.

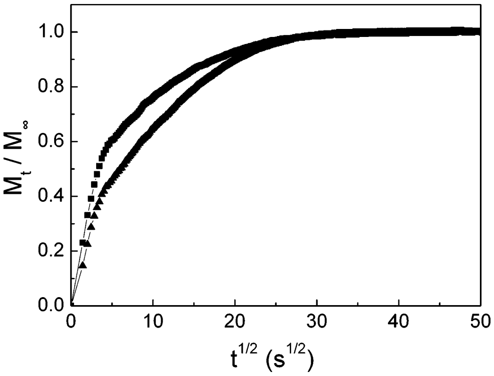

Figure 6. Dynamic sorption curve of water vapor in PMDA-based polyimide membranes at 308 K: ▲, PMDA + ODA; ■, PMDA + MDA.

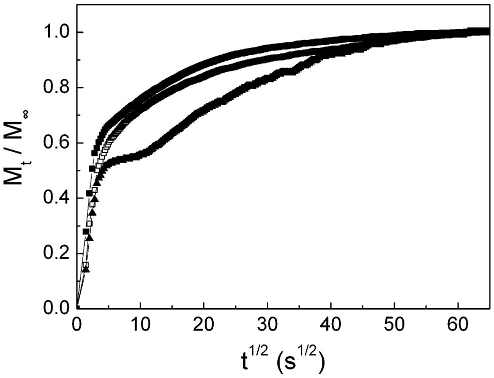

Figure 7. Dynamic sorption curve of water vapor in BTDA-based polyimide membranes at 298 K: □, BTDA + ODA; ■, BTDA + MDA; ▲, BTDA + PDA.

298 K and 308 K are listed in Table 4. It can be seen that the values of the diffusion coefficient for water vapor in all four polyimide membranes at 308 K are higher than those at 298 K. This result is consistent with the usual concept that an increase of temperature will be good for the diffusion.

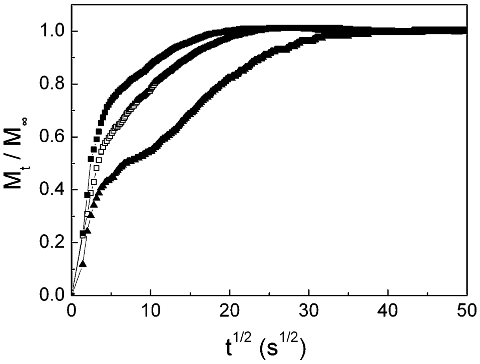

Figure 8. Dynamic sorption curve of water vapor in BTDA-based polyimide membranes at 308 K: □, BTDA + ODA; ■, BTDA + MDA; ▲, BTDA + PDA.

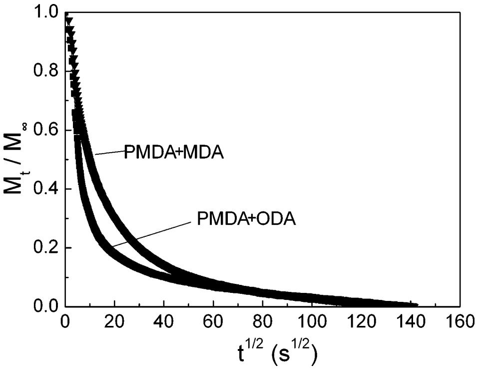

Figure 9. Dynamic desorption curve of water vapor in PMDA-based polyimide membranes at 298 K: ▼, PMDA + MDA; ■, PMDA + ODA.

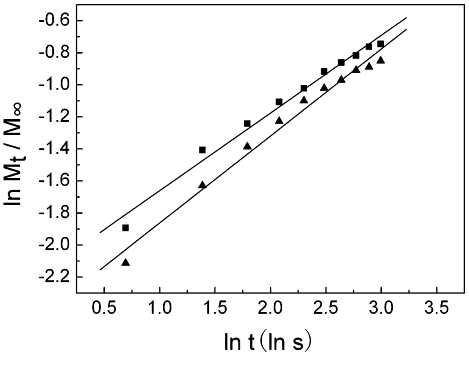

Figure 10. Relationships between the percentage mass gain and the time in PMDA-based polyimide membrane at 308 K: ■, PMDA + ODA; ▲, PMDA + MDA.

Furthermore, it can be found that the diffusion coefficients for water vapor in different polyimide membranes at the same temperature are different from each other. For example, the diffusion coefficient of water vapor in the PMDA + ODA polyimide membrane at 298 K is $1.741\cdot10^{-8}$ $cm^2\cdot s^{-1}$ while that

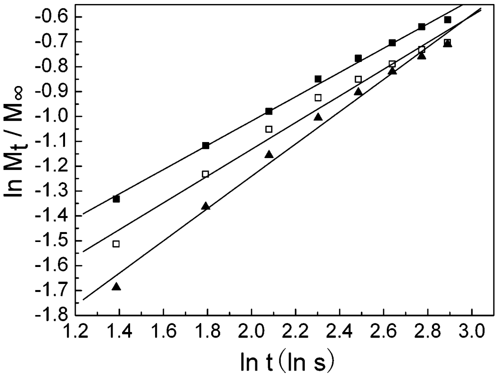

Figure 11. Relationships between the percentage mass gain and the time in BTDA-based polyimide membrane at 308 K: □, BTDA + ODA; ■, BTDA + MDA; ▲, BTDA + PDA.

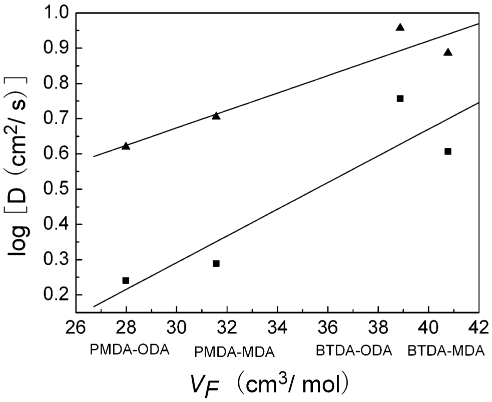

Figure 12. Relationships between the diffusion coefficient and free volume of polyimide membranes: ■, 298 K; ▲, 308 K.

Table 3. Values of Anomalous Diffusion Factor for Water Vapor in Polyimide Membranes

	d_w				
T (K)	PMDA + ODA	PMDA + MDA	BTDA + PDA	BTDA + ODA	BTDA + MDA
298	1.99	2.01	2.38	2.07	2.01
308	1.98	1.97	2.26	2.02	1.97

Table 4. Values of the Diffusion Coefficient for Water Vapor in Polyimide Membranes

	D (10^{-8} cm^2·s^{-1})			
T (K)	PMDA + ODA	PMDA + MDA	BTDA + ODA	BTDA + MDA
298	1.741	1.945	5.713	4.042
308	4.168	5.076	9.063	7.706

in the BTDA + ODA polyimide membrane is $5.713 \cdot 10^{-8}$ cm^2·s^{-1}. This is probably attributed to the chemical structure of the polymer material, and possibly the free volume of polymer material is one of the most important factors. Diffusion is assumed to be a process in which polymer segments separate in front of a diffusion penetrant molecule, forming a hole through which the penetrant molecule can jump. As shown in Figure 12, the values of the diffusion coefficient for water vapor in different polyimide membranes at the same temperature increase with the molar free volume, V_F, of polyimide membranes.

Conclusions

The dynamic sorption and desorption of water vapor in PMDA + ODA, PMDA + MDA, BTDA + ODA, BTDA + MDA, and BTDA + PDA polyimide membranes at 298 K and 308 K were investigated by experiments. In accordance to the results and the fractal diffusion theory proposed by Chen, the diffusion of water vapor in BTDA + PDA polyimide membranes belongs to anomalous diffusion, and the anomalous diffusion factors are 2.38 at 298 K and 2.26 at 308 K. However, the diffusion behaviors of water vapor in PMDA + ODA, PMDA + MDA, BTDA + ODA, and BTDA + MDA polyimide membranes obey the Fickian diffusion law. This is probably attributed to the chemical structure of the polymers. Moreover, the diffusion coefficient for Fickian diffusion of water vapor in PMDA + ODA, PMDA + MDA, BTDA + ODA, and BTDA + MDA polyimide membranes was calculated following the Fickian diffusion. The values of diffusion coefficient for water vapor in all four polyimide membranes at 308 K are higher than those at 298 K, and those at the same temperature increase with the molar free volume of polyimide membranes.

Literature Cited

(1) Liao, D. C.; Chen, Y. C.; Han, J. L.; Hsiesh, K. H. Swelling equilibrium and sorption kinetics of urethane-modified bismaleimides elastomer. *J. Polym. Sci., Part B: Polym. Phys.* **1997**, *35*, 1747−1755.

(2) Enneking, L.; Heintz, A.; Lichtenthaler, R. N. Sorption equilibria of the ternary mixture benzene/cyclohexene/cyclohexane in polyurethane- and PEBA-membrane polymers. *J. Membr. Sci.* **1996**, *115*, 161−170.

(3) Feng, X.; Huang, R. Y. M. Liquid separation by membrane pervaporation: a review. *Ind. Eng. Chem. Res.* **1997**, *36*, 1048−1066.

(4) Stern, S. A. Review: polymers for gas separations: the next decade. *J. Membr. Sci.* **1994**, *94*, 1−65.

(5) Prausnitz, J. M.; Lichtenthaler, R. N.; de Azevedo, E. G. Thermodynamics of fluid phase equilibria. In *International Series in the Physical and Chemical Engineering Science*; Englewood, C., Ed.; Prentice Hall: New Jersey, 1986.

(6) Nijhuis, H. H.; Mulder, M. H. V.; Smolders, C. A. Selection of elastomeric membranes for the removal of volatile organics from water. *J. Appl. Polym. Sci.* **1993**, *47*, 2227−2243.

(7) Nijhuis, H. H. Removal of organics from water by pervaporation. Ph.D. Thesis, University of Twente, The Netherlands, 1990.

(8) Abrams, D. S.; Prausnitz, J. M. Statistical thermodynamics of liquid mixtures: a new expression for the excess Gibbs energy of partly or completely miscible systems. *AIChE J.* **1975**, *21*, 116−128.

(9) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The properties of gases and liquids*; McGraw-Hill: New York, 1987.

(10) Shelden, R. A.; Thompson, E. V. Dependence of diffusive permeation rates on upstream and downstream pressures. III: membrane selectivity and implications for separation processes. *J. Membr. Sci.* **1978**, *4*, 115−127.

(11) Fujita, H. Diffusion in polymer-diluent systems. *Fortschr. Hochpolym− Forsch.* **1961**, *3*, 1−47.

(12) Fels, M.; Huang, R. Y. M. Diffusion coefficients of liquids in polymer membranes by a desorption method. *J. Appl. Polym. Sci.* **1970**, *14*, 523−536.

(13) Vrentas, J. S.; Duda, J. L. Molecular diffusion in polymer solutions. *AIChE J.* **1979**, *25*, 1−24.

(14) Rhim, J. W.; Huang, R. Y. M. On the prediction of separation factor and permeability in separation of binary mixtures by pervaporation. *J. Membr. Sci.* **1989**, *46*, 335−348.

(15) Vieth, W. R.; Sladek, K. J. Model for diffusion in a glassy polymer. *J. Colloid Sci.* **1965**, *20*, 1014−1033.

(16) Vieth, W. R.; Howell, J. M.; Hsieh, J. H. Dual sorption theory. *J. Membr. Sci.* **1976**, *1*, 177−120.

(17) Xu, Y. X.; Shang, T. G.; Chen, C. X.; Li, J. D. Dynamic sorption and anomalous diffusion of small molecules in dense polyimide membranes. *J. Chem. Eng. Data* **2006**, *51*, 2016−2021.

(18) Park, J. Y.; Paul, D. R. Correlation and prediction of gas permeability in glassy polymer membrane materials via a modified free volume based group contribution method. *J. Membr. Sci.* **1997**, *125*, 23−39.

(19) Crank, J. *The Mathematics of Diffusion*; Clarendon Press: Oxford, 1975.

(20) Grinsted, R. A.; Clark, L.; Koenig, J. L. Study of cyclic sorption-desorption into poly (methyl methacrolate) rods using NMR imaging. *Macromolecules* **1992**, *25*, 1235−1241.

(21) Chen, C. X.; Han, B. B.; Li, J. D.; Shang, T. G.; Zou, J.; Jiang, W. J. A new model on the diffusion of small molecule penetrants in dense polymer membranes. *J. Membr. Sci.* **2001**, *187*, 109−118.

(22) Havlin, S.; Bunde, A. Percolation I. In *Fractals and Disordered Systems*; Havlin, S., Bunde, A., Eds.; Springer-Verlag: New York, 1996; pp 59−110.

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