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Correlation between Gas Diffusion Coefficient and Positron Annihilation Lifetime in Polymers with Rigid Polymer Chains

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ABSTRACT: Diffusion coefficients D of CO_2 and CH_4 and lifetimes of orthopositronium (o-Ps) τ_3 were measured at temperatures from 308 to 473 K for polyimides, a polybenzoxazole, and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with high glass transition temperatures T_g's above 488 K. The plots of log(D/T) and τ_3 for these polymers at 308 K were below the correlation line observed for polymers with relatively low T_g's at temperatures from $T_g - 90$ K to $T_g + 70$ K and interpreted by the free volume theory for diffusion. The lower D values for these high-T_g polymers were attributed to the restricted local motion of their polymer chains. With increasing temperature, the plots for PPO and a polyimide became close to the correlation line.

Introduction

It is important for development and selection of polymer membrane materials for gas separation to understand structural factors controlling diffusion of gas molecules in polymers. Diffusion in rubbery polymers is often interpreted by means of free volume theory.[1−3] Originally Cohen and Turnbull derived the following equation for self-diffusion of hypothetical liquids of hard-sphere molecules on the basis of the assumption that diffusion jumps result from a redistribution of the free volume within the liquid.[4]

$$D = ART\exp(-B/v_f) \tag{1}$$

where A and B are the parameters dependent on size and shape of the molecule, R is the gas constant, T is temperature, and v_f is an average free volume per molecule. Fujita applied the Cohen and Turnbull formulation to the polymer−penetrant systems by replacing quantity v_f with measurable fractional free volume, f.

$$D = A_dRT\exp(-B_d/f) \tag{2}$$

The fractional free volume is generally expressed by

$$f = f_g + (\alpha_l - \alpha_g)(T - T_g) \tag{3}$$

where f_g is the fractional free volume at the glass transition temperature T_g, and α_l and α_g are the thermal expansion coefficients above and below T_g, respectively. The Williams−Landel−Ferry (WLF) fractional free volume derived from the viscosity theory,[5] f_{WLF}, in which f_g is taken as 0.025, is often used as f. Equation 2 with f_{WLF} satisfactorily describes the temperature dependence of D. A linear correlation between log(D/T) and f_{WLF}^{-1} has been observed for a given gas−polymer system at a rubbery state.[5] However, the log(D/T) values at a given f_{WLF} value have been often different from polymer to polymer.[6]

Another type of fractional free volume can be calculated from the following equation.

$$V_F = (V_T - V_0)/V_T \tag{4}$$

where V_T is the molar volume at temperature T and V_0 is the volume occupied by the molecules at 0 K per mole of repeat unit of the polymer. V_T is calculated from density data. V_0 is estimated to be 1.3 times[7] the van der Waals volume calculated by the group contribution method of Bondi.[8] The V_F corresponds to the volume fraction of the "expansion volume",[9] which is considered to be composed of a spectrum of microcavities among polymer chains caused by thermal motions of polymer chains. In this study, the microcavities are referred to as "free volume holes". For rubbery polymers, log(D/T) has been correlated to V_F^{-1}.[6] This correlation is better than that between log(D/T) and f_{WLF}. This means that a portion of the distribution of the free volume holes involved in diffusion is not necessarily identical with that in viscosity.[3]

Diffusion in a glassy state cannot be interpreted by eq 2 with f_{WLF} because of nonequilibrium state. However, the formulation of the free volume theory is often used to explain the difference in D at a temperature. There is a rough correlation between log D at a given temperature below T_g and the V_F^{-1} of polymers.[10,11] Deviations from the correlation have been also observed for several polymers. Size distribution of free volume holes and local mobility of polymer chains have been considered as another factors controlling D in glassy polymers.[12]

The f_{WLF} and V_F are macroscopic quantities calculated indirectly from viscosity and density data, respectively. The positron annihilation (PA) is the most promising technique to observe microvacancies in polymers directly.[13] PA lifetime spectra of polymers have a long-lived component which is attributed to orthopositronium (o-Ps) formed and annihilated in amorphous regions. The lifetime of the component, τ_3, is a measure of the size of the microvacancy where o-Ps is trapped. The microvacancies seen by o-Ps in polymers are presumed

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to be free volume holes. The average size of free volume holes probed by o-Ps, $v_{h,Ps}$ [$= {}^4/_3\pi R^3$], is often calculated by the following expression for τ_3 in a spherical microvacancy of radius, R [nm].[14,15]

$$\tau_3 = {}^1/_2\left[1 - R/R_0 + \frac{1}{2\pi}\sin(2\pi R/R_0)\right]^{-1} \qquad (5)$$

where $R_0 = R + \Delta R$, $\Delta R = 0.166$ nm. The intensity of the component, I_3, includes information about the number of the free volume holes. It is not mature to correlate I_3 with the number of free volume holes. Although the I_3 data have linearly correlated with numbers of free volume holes for some polymers, the proportionality constants depended on kinds of polymers.[16−19]

There have been several studies dealing with the correlation between D and PA properties.[6,20−28] Volkov et al. reported that the value of $\tau_3 I_3$ reflected free volume fraction and that D of H_2 and CH_4 for rubbery polymers correlated with $\tau_3 I_3$, but not for glassy polymers.[22] They correlated D for glassy polymers with another factor. Kobayashi et al. reported on a correlation between D of Ar and τ_3 for liquids and polymers, but they did not discuss the reason for the correlation.[23] Jean et al. reported that a broader lifetime distribution was observed for the polymer with larger D for four kinds of polycarbonates.[24]

In previous papers,[6,25−28] we have reported on the correlation between D and PA properties using the data measured at different temperatures for a variety of polymers. The plots of $\log(D/T)$ of CO_2 or CH_4 versus τ_3 for eight rubbery polymers at temperatures from glass transition temperature T_g to $T_g + 70$ K lay on a correlation line. We also found that the plots for five glassy polymers including polysulfone (PSF), polycarbonate (PC), and polystyrene (PS) at temperatures from $T_g - 90$ K to T_g lay on the same correlation line as obtained for the rubbery polymers.[28] It is interesting that the same correlation line describes the diffusion of a penetrant at temperatures below and above T_g.

The polymers with high T_g's as a result of rigid polymer chains such as aromatic polyimides (PIs) and polybenzoxazoles (PBOx) have attracted much attention as membrane materials for gas separation because of their higher gas permselectivity compared with other polymers with similar gas permeability.[11,12,29,30] In this study, the correlation between D and τ_3 for such polymers with high T_g's is investigated at a wide range of temperatures in comparison with that for ordinary polymers previously reported.

Experimental Section

Figure 1 shows the chemical structures of polymers used. Preparation of the films of 6FDA-TeMPD, 6FDA-BAAF, BPDA-BAAF, 6FDA-ODA, and 6FDA-mpODA polyimides and polybenzoxazole (PBO) were described in previous papers.[11,12,29] All polyimide films were dried at 473 K for 20 h in a vacuum. PBO film was subjected to thermal cyclodehydration at 553−573 K for 10 h under a stream of nitrogen and dried at 443 K for 20 h in a vacuum. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was purchased from Aldrich Chemical Co. Inc. Its film was prepared by casting the chloroform solution onto a glass plate and then by drying at 373 K for 10 h. 6FDA-mpODA polyimide and PPO films were finally heated above their T_g (at 553 and 493 K, respectively) for 1 h in a vacuum prior to experiments.

The permeability coefficient P was measured by a vacuum method. The solubility coefficient S was measured using an electric microbalance (S3D-P, Sartorius). P and S for CO_2 and CH_4 were measured at 1 atm. The D values were determined by $D = P/S$ at 308 K for every polymers and at temperatures up to 473 K for 6FDA-mpODA polyimide and PPO.

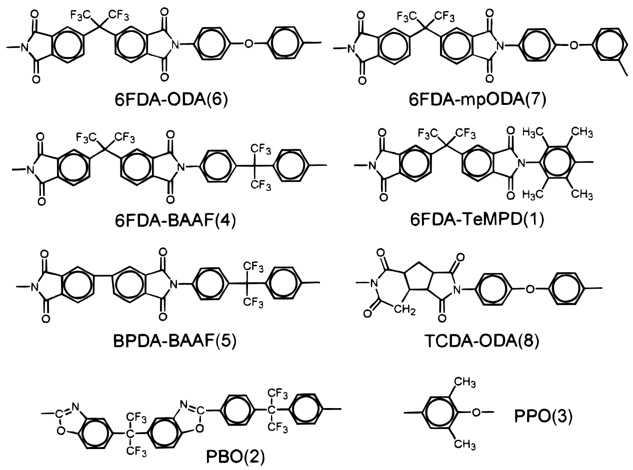

Figure 1. Chemical structures of polymers.

The PA lifetime measurement was carried out at the Inter-University Laboratory for Common Use of JAERI facilities. The details are described in a previous paper.[25] Each spectrum having more than 1 million total counts was analyzed into three lifetime components using the computer program PATFIT.[31] The PA spectra were measured in the same temperature range as D.

Results and Discussion

Characterization. Table 1 lists characterization results of the polymers. All these polymers have high T_g's. Their wide-angle X-ray diffraction curves were broad and structureless, indicating that they were amorphous. The V_F values were calculated from eq 2. The D values of CO_2 and CH_4, D_{CO_2} and D_{CH_4}, and PA properties at 308 K are also listed in Table 1. The D_{CO_2} values ranged between 10^{-9} and 10^{-7} cm^2 s^{-1}.

Figure 2 shows the plots of $\log(D/T)$ for CO_2 and CH_4 versus τ_3 at 308 K for the polymers listed in Table 1 together with the data previously reported for the ordinary polymers.[6,28] The plots for the polymers with high T_g are much below the correlation line obtained for the ordinary polymers at the temperatures from $T_g - 90$ K to $T_g + 70$ K.

To understand the meaning of the correlation between D and τ_3 at temperatures not much below T_g, we plotted $\log(D/T)$ against the reciprocal of $v_{h,Ps}$ in Figure 3. There is a good linear correlation between $\log(D/T)$ vs $v_{h,Ps}{}^{-1}$. This linear correlation is described by the following equation:

$$D = ART\exp(-B/v_{h,Ps}) \qquad (6)$$

This is the same as eq 1 derived by Cohen and Turnbull[4] when the average free volume per molecule v_f is replaced by $v_{h,Ps}$. The linear correlation means that the free volume model for diffusion in terms of an average size of free volume probed by o-Ps can be applied to diffusion of gas molecules in polymers even in fairly wide range of temperatures below T_g.

In a rubbery polymer the segmental motion frequently generates and dissipates free volume holes, allowing a penetrant to have frequent chances of diffusion jump. In this case, the factor controlling D is the probability that the penetrant finds the free volume holes large enough to pass through. The probability is equivalent

Table 1. Physical Properties of Polymers[a]

no.	polymer	T_g [K]	density [g cm^{-3}]	V_F	D_{CO_2} [10^{-8} cm^2 s^{-1}]	D_{CH_4}	τ_3 [ns]	I_3 [%]
1	6FDA-TeMPD	693	1.330	0.182	25	5.1	3.94	18
2	PBO	563	1.461	0.207	9.3	1.1	3.24	22
3	PPO	488	1.066	0.206	9.0	1.8	2.68	33
4	6FDA-BAAF	578	1.480	0.182	3.5		2.98	17
5	BPDA-BAAF	602	1.424	0.157	2.0		2.67	12
6	6FDA-ODA	572	1.432	0.165	1.0		2.40	9.4
7	6FDA-mp′ODA	533	1.438	0.162	0.39	0.051	2.21	7.8
8	TCDA-ODA	623	1.357	0.124	0.098		1.91	21

[a] D_{CO_2} and D_{CH_4} are at 308 K and 1 atm. τ_3 and I_3 are at 308 K.

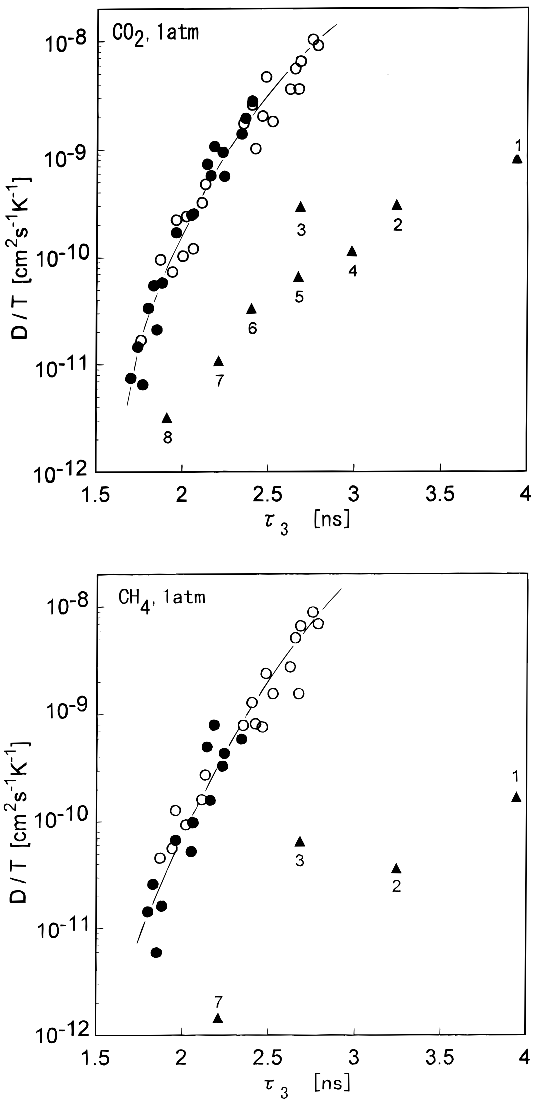

Figure 2. Plots of log(D/T) of CO_2 (a) and CH_4 (b) versus τ_3 for polymers with high T_g's at 308 K and 1 atm (▲) together with the data for ordinary polymers at temperatures between $T_g - 90$ K (○) and $T_g + 70$ K (●) and at 1 atm.[6,28] The numbers near the symbols refer to number of the polymers shown in Table 1.

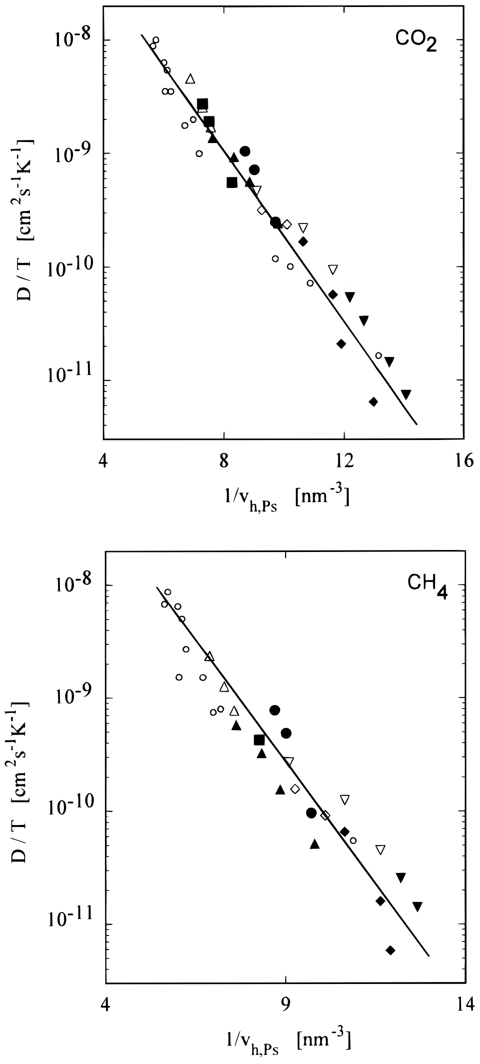

Figure 3. Plots of log(D/T) of CO_2 (a) and CH_4 (b) versus $v_{h,Ps}^{-1}$ for ordinary polymers at temperatures between $T_g - 90$ K and $T_g + 70$ K.[6,28] Open and closed symbols are for rubbery and glassy states, respectively: (●) polysulfone (PSF); (■) polycarbonate (PC); (◇, ◆) polyimide from 6FDA and 1,6-diaminohexane (6FDA-DAH); (△, ▲) polystyrene (PS); (▽, ▼) poly(ethylene terephthalate) (PET). Small circles are for other rubbery polymers.

to a fraction of free volume holes larger than the size of the penetrant. The equation derived by Cohen and Turnbull means that the distribution is characterized by the only an average free volume per molecule. The linear correlation obtained in Figure 3 shows the average size $v_{h,Ps}$ evaluated by τ_3 can be the characteristic parameter to interpret the dependence of D on temperature from $T_g - 90$ K to $T_g + 70$ K for some polymers. Generation and dissipation of small free volume holes may occur frequently in concert with local motion of polymer chains and side groups even at the glassy state. The small free volume holes may be available for diffusion of gas molecules in polymers at the glassy state.

Figure 4 shows the plots of log(D/T) versus τ_3 for polysulfone (PSF) and polycarbonate (PC) at temperature below $T_g - 90$ K in addition to the data shown in Figure 2. The plots for PSF and PC below $T_g - 90$ K seem to deviate downward from the correlation line. As temperature decreases, the generation and dissipation

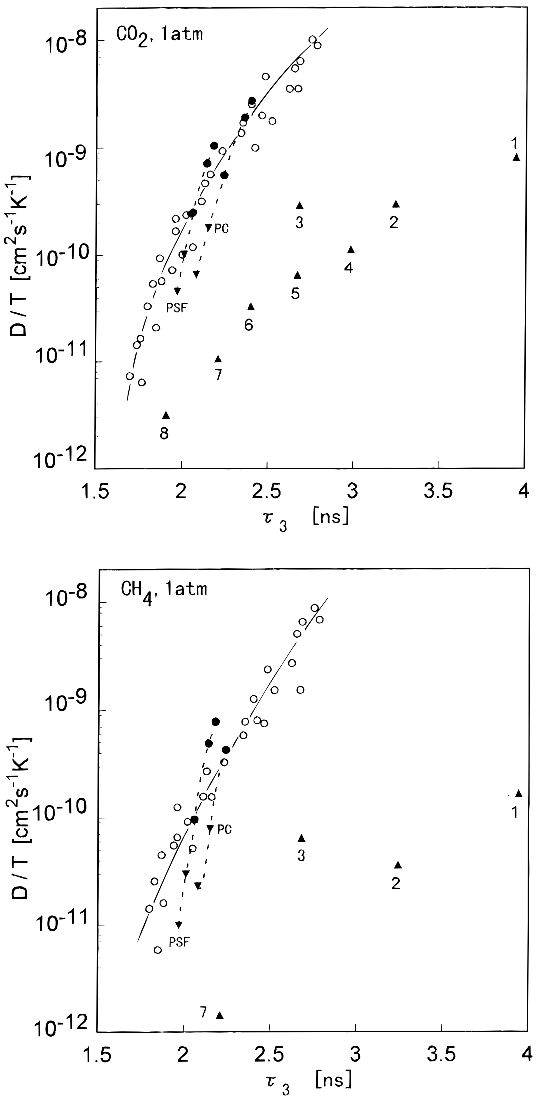

Figure 4. Plots of log(D/T) of CO_2 (a) and CH_4 (b) versus τ_3 for PSF and PC at temperatures from $T_g - 150$ K to $T_g - 90$ K together with the data shown in Figure 2: (▲) polymers with high T_g; (○) ordinary polymers except for PSF and PC; (● and ▼) PSF and PC at temperatures above and below $T_g - 90$ K, respectively.

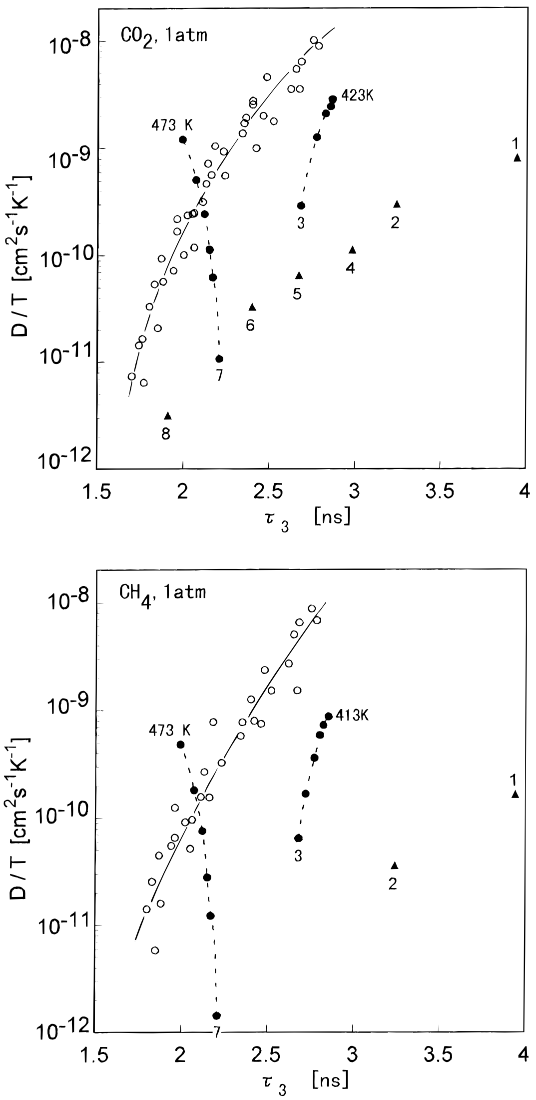

Figure 5. Plots of log(D/T) of CO_2 (a) and CH_4 (b) versus τ_3 for PPO and 6FDA-mPD polyimide at temperatures from 308 to 473 K and 1 atm together with the data shown in Figure 2: (▲) polymers with high T_g except for PPO (no. 3) and 6FDA-mPD polyimide (no. 7); (○) ordinary polymers except for PSF and PC; (●) PPO and 6FDA-mPD polyimide at temperatures from 308 to 473 K.

of small free volume holes become less frequent because of more restricted local motion of polymer chains. This seems the reason that the plots for the polymers below $T_g - 90$ K deviated downward from the correlation line based on the free volume theory in Figure 3. Local mobility of polymer chains is considered to become another dominant factor controlling the successful diffusion jump at temperatures much below T_g.

The plots for PIs, PBO, and PPO at 308 K were further below the correlation line as shown in Figure 2. The measurement temperatures for these polymers are below $T_g - 180$ K. At this temperature range, local motion of polymer chains is much more restricted, and as a result, the small free volume holes for molecules to pass through is frozen. In this situation the gas molecules mainly migrate in the preexisting free volume holes large enough to pass through. This is quite different from the mechanism that is described by the free volume model. In the latter case, displacement of molecules results from exchange of position occupied by the molecules and polymer chains.

It is known that the restricted local motion of polymer chains enhances the D ratio of CO_2 over CH_4, D_{CO_2}/D_{CH_4}.[11,12,32] The D_{CO_2}/D_{CH_4} values for 6FDA-mpODA, 6FDA-TeMPD, PBO, and PPO are between 5 and 9 at 1 atm and 308 K. These values are higher than the D ratios between 1 and 5 for ordinary polymers whose plots lie on the correlation.

Figure 5 shows the plots of log(D/T) versus τ_3 for PPO and 6FDA-mpODA polyimide at temperatures from 308 to 473 K together with the plots in Figure 3, and the data are also listed in Table 2. With increasing temperature, the plots for PPO approached the correlation line. This may be due to an increase in frequency of generation and dissipation of free volume holes caused by less-restricted local mobility. However, the plots at temperatures from $T_g - 90$ K to $T_g - 65$ K were still apart from the correlation line.

With increasing temperatures, the plots of log(D/T) versus τ_3 for 6FDA-mPD polyimide approached the correlation line for the ordinary polymers. However, the plots went across the correlation line with further

Table 2. Lifetime and Intensity of o-Ps, τ_3, and I_3, Diffusion Coefficient D, and Activation Energy E_D for 6FDA-mpODA Polyimide at Temperatures from 308 to 473 K[a]

				CO_2		CH_4	
polymers	T [K]	τ_3 [ns]	I_3 [%]	D	E_D	D	E_D
6FDA-mpODA	308	2.21	7.8	0.33	37	0.044	46
	353	2.17	9.3	2.2		0.43	
	373	2.15	10	4.22		1.0	
	403	2.12	11	9.8		3.1	
	433	2.07	12	22		7.9	
	473	1.99	13	57		23	
PPO	308	2.68	33	9.0	24	2.0	29
	343	2.72	34			5.8	
	373	2.77	35	47		14	
	393	2.80	35			23	
	403	2.82	35	85		30	
	413	2.85	35	101		36	
	423	2.86	36	120			

[a] D is in 10^{-8} cm^2 s^{-1} and E_D is in kJ mol^{-1}.

increasing temperature, and the plot at 473 K ($T_g - 60$ K) lay above the line. The temperature dependence of D was described by the Arrhenius type with an activation energy E_D listed in Table 2. The values of E_D were similar to those for other glassy polymers.[28] However, the temperature dependence of τ_3 was anomalous. For 6FDA-mpODA polyimide τ_3 decreased with an increase in T below T_g and turned to increase at T_g, whereas I_3 increased both below and above T_g. This temperature dependence was reproducible in both heating and cooling runs. The decrease in τ_3 has been also observed for other polyimides and considered to be unique to aromatic polyimides, as reported elsewhere.[33] The reason has not been clearly known. This decrease in τ_3 was not considered to mean the decrease in the size of free volume holes because the specific volume of 6FDA-mpODA polyimide increased with a thermal expansion coefficient of 1.5×10^{-4} K^{-1} below T_g,[33] which was similar to the values for other glassy polymers.[28] If the τ_3 value for 6FDA-mpODA polyimide increases at a rate similar to that for the other glassy polymers, the plots at 473 K will be close to or on the correlation line for the ordinary polymers. The unexpected overrunning of the plot near T_g for 6FDA-mpODA in Figure 5 was attributed to the anomalous temperature dependence of τ_3.

Conclusion

The correlation between D of gases and τ_3 was examined for the polymers with high T_g above 488 K. The plots of log(D/T) versus τ_3 for these polymers at 308 K were much below the correlation line for ordinary polymers at temperatures from $T_g - 90$ K to $T_g + 70$ K. The correlation line was interpreted by the equation of free volume model for diffusion derived by Cohen and Turnbull. The probability that penetrants find the free volume holes large enough to pass through determined log(D/T), and it was characterized by an average size of free volume holes. The τ_3 was used to evaluate an average size of free volume holes. The correlation line indicated the free volume model would be also applied for diffusion in the polymers at temperatures not much below T_g, where local motion of polymer chains could cause frequent generation and dissipation of free volume holes. However, the downward deviation of the plots for high-T_g polymers indicated that the mechanism for diffusion in polymers at temperatures much below T_g was different from one above $T_g - 90$ K because of much more restricted local mobility. The plots log(D/T) versus τ_3 for PPO and an aromatic polyimide above $T_g - 90$ K were close to the correlation line.

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