

Transport Parameters and Solubility Coefficients of Polymers at Their Glass Transition Temperatures

YU. P. YAMPOLSKII,¹ Y. KAMIYA,² A. YU. ALENTIEV¹

¹ A. V. Topchiev Institute of Petrochemical Chemistry, Russian Academy of Sciences, 29, Leninsky Pr., 117912, Moscow, Russia

² National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305, Japan

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ABSTRACT: Many parameters of polymers exhibit breaks when temperature passes through glass transition. It is also often assumed that fractional free volume (FFV) at the glass transition temperature (T_g) has a standard value (the isofree volume concept). As gas diffusion (D) and permeability (P) coefficients depend on FFV, and mechanism of sorption and permeation is different above and below T_g , a question can be asked if D and P parameters of various gases in polymers have standard values at corresponding T_g , and, if not, how the values of $D(T_g)$ and $P(T_g)$ vary with T_g in different polymers. To examine this problem, two approaches were used: (1) extrapolation to T_g of numerous P and D values measured at ambient temperatures; (2) an analysis of direct data obtained in different polymers at their T_g . In both cases, qualitatively similar results were obtained: the $D(T_g)$ and $P(T_g)$ values increase with growing T_g independently of the nature of gas. Permselectivity $P_i(T_g)/P_j(T_g)$ and selectivity of diffusion $D_i(T_g)/D_j(T_g)$ are reduced when T_g increases. The dependence of the solubility coefficients $S(T_g) = D(T_g)/P(T_g)$ is much weaker than those of $D(T_g)$ and $P(T_g)$. This conclusion was confirmed by the results of direct measurements of S in a wide range of temperature including T_g for several gas/polymer systems. An analysis of the results of positron annihilation studies of free volume in polymers led to the conclusion that the observed increases in the $D(T_g)$ and $P(T_g)$ values with T_g are caused mainly by thermal activation of diffusion processes at T_g . © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1691–1705, 2000

Key words: free volume; permeability coefficients; diffusion coefficients; solubility coefficients; glass transition temperatures

INTRODUCTION

The glass transition temperature (T_g) is, perhaps, the most important characteristic of linear high-molecular-mass polymers. At T_g , all the main functions of the state of a material, such as enthalpy and entropy, as well as specific volume, experience a break. Accordingly, the polymer ex-

hibits different values of the heat capacity Δc_p , thermal expansion coefficient α , the tangent of dielectric losses, and other properties below and above glass transition.^{1,2} Polymers have entirely different mechanical properties (the modulus, strain strength, elongation at break) above and below T_g .

It is known that the mechanism and regularities of sorption and diffusion of gases in polymers are different in glassy and rubbery state as well. The manifestation of it are in different shapes of sorption isotherms,³ in the changes in enthalpies

Correspondence to: Yu. P. Yampolskii.

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of sorption, and in the activation energies of gas diffusion and permeation^{4–7} a polymer experiences when temperature of measurement passes through T_g . The permeation of diffusants having different molecular masses or sizes is the mobility-controlled process below T_g or solubility-controlled process above T_g even in the same polymer.⁸

According to the concept of free volume in polymers,^{9,10} the glass transition occurs in polymers when the fractional free volume (FFV, the ratio of free volume and specific volume in polymers) reaches the standard value of $f_g = 0.025 \pm 0.003$. This statement is known as the Simha–Boyer isofree volume concept. Above T_g , that is, in the rubbery state, FFV increases linearly with temperature

$$\text{FFV} = f_g + (\alpha_l - \alpha_g)(T - T_g) \quad (1)$$

where α_l and α_g are thermal expansion coefficients in rubbery and glassy state, respectively. Below T_g (i.e., in the glassy state), FFV is thought to keep a constant value of f_g . On the other hand, unrelaxed free volume in the glassy state or the difference between the specific volume and equilibrium specific volume extrapolated from temperatures above T_g increases with the displacement of T ($< T_g$) from T_g . So two concepts of free volume in glassy polymers are seemingly in contradiction and this question remains subject to debate.

The concept of isofree volume at T_g as presented in such a straightforward manner was criticized¹¹ because the cases, when f_g is not constant, are frequent. However, it is generally accepted² that, at T_g in different polymers, f_g should be in the range 0.02–0.13. As free volume or f_g determine gas diffusion (D) and permeability (P) coefficients both in rubbery and glassy state of polymers, an important implication of the Simha–Boyer rule should be an approximate constancy of the P and D values at the corresponding T_g 's in polymers that can be as low as 150 K [e.g., in the case of poly(dimethyl siloxane)] or as high as 600–700 K (e.g., in the cases of various polyimides). This amazing prediction strongly requires experimental scrutiny and corroboration using a statistically reliable set of the data.

There is also an applied aspect of this problem. Membranes based on glassy polymers as selective materials are employed in most gas separation processes. Glassy polymers reveal better, in com-

parison with rubbers, a combination of permeability and permselectivity for separation of light gases. Stronger mechanical properties of glassy polymers provide better stability in the processes of application and storage. There are also some advantages in the formation of membranes from glassy polymers. On the other hand, a transition from ambient to elevated temperatures of the separation process performance is extremely important to expand the scope of applicability of membranes, because many industrial chemical processes are carried out at temperatures much higher than ambient. However, the membrane material should remain glassy in the whole temperature range of possible use. In this regard, a knowledge of the permeability coefficients of different gases $P_A(T_g)$ at the glass transition temperatures as well as the separation factors $P_A(T_g)/P_B(T_g)$ will be important as an estimate of the upper limit of permselective parameters of glassy polymers, potential membrane materials.

The aim of this work is to investigate possible variations of the $P(T_g)$ and $D(T_g)$ values with the T_g 's for various gases and polymers. For this purpose, numerous permeation parameters included in the database created in The Institute of Petrochemical Synthesis (TIPS) were used. An analysis of possible dependencies $S(T_g) = P(T_g)/D(T_g)$ on T_g was also performed by using: (1) the values $P(T_g)$ and $D(T_g)$ found as outlined above; (2) the results of direct measurements of the solubility coefficients in the temperature ranges including T_g in different polymers. Throughout this article, the permeability coefficients are expressed in Barrer and the diffusion coefficients in cm^2/s .

EXPERIMENTAL

Procedure

Sorption of gases, mainly CO_2 and Ar, in a wide range of temperatures including T_g 's of various polymers was measured by using an improved gravimetric apparatus of the Sartorius System (S3D-P). It consisted of an electronic microbalance placed in a pressure vessel with two chambers, a constant temperature air-bath, and auxiliary furnace. Measurements were performed at temperatures ranging from ambient temperature to 350°C and pressures < 20 atm. This procedure was described in detail elsewhere.¹²

DSC measurements of the T_g 's were carried out by using a Seiko Instrument (Model SSC5200) with a heating rate of 10 K/min.

Materials

Temperature dependencies of solubility coefficients in 10 polymers were obtained. In the present work, the results obtained for poly(vinyl trimethylsilane) (PVTMS) and poly(trimethylsilyl norbornene) (PTMSNB) will be described in more detail. The data on other amorphous polymers were reported earlier.¹²

PVTMS was prepared by anion polymerization. It had a density of 0.86 g/cm³ and the T_g in the range 152–163°C according to DSC.

PTMSNB was prepared by ring-opening metathesis polymerization in the presence of a WCl₆ catalyst. It had a density of 0.918 g/cm³ and T_g of 104°C.

A commercial sample of poly(methyl methacrylate) (PMMA) from Aldrich Chemical Co. (Milwaukee, WI), medium-molecular-weight grade, was used in a form of a film cast from benzene solutions. It had a density of 1.19 g/cm³ and T_g = 100°C. For other properties, see ref. 12.

A commercial sample of poly(vinyl chloride) (PVC) from the same company in the form of a powder had a density of 1.385 g/cm³ and T_g = 85°C.

UDEL polysulphone (PSF) of Nissan Chemical Industry Ltd. (Japan) was purchased in the form of a film with the density of 1.240 g/cm³ and T_g = 180°C. A detailed study of sorption of carbon dioxide in PSF was reported earlier.¹³

Bisphenol-A polycarbonate (PC) had a density of 1.194 g/cm³ and T_g = 144°C. Its gas sorption properties at 35–65°C were reported elsewhere.^{14,15}

Polystyrene (PS) of Aldrich Chemical Co. had a density of 1.047 g/cm³ and T_g = 100°C.

The sample of poly(ethyl methacrylate) (PEMA) was prepared by radical polymerization. It had a density of 1.120 g/cm³ and T_g = 61°C. See also earlier studies of gas sorption in this polymer.^{16,17}

Polyimides BPDA–BATPHF and 6FDA–BATPHF were kindly donated by Professor K. Okamoto. Their properties were described earlier.¹⁸ Briefly, their densities were 1.443 and 1.484 g/cm³ and T_g 's were 223 and 234°C, respectively.

In conclusion, the T_g 's varied from 61°C (for PEMA) to 234°C (for 6FDA polyimide) in the group of the polymers studied.

Search for $P(T_g)$ and $D(T_g)$ Values

The database in TIPS includes the gas permeation parameters (P , D) as well as activation

Table I The Number of Gas/Polymer Systems Used in the Extrapolations of D and P Values to Glass Transition Temperatures

Gas	D	P
He	16	27
H ₂	13	34
O ₂	44	51
N ₂	22	35
Ar	14	14
CO ₂	56	52
CH ₄	47	47

energies of permeation and diffusion (E_P , E_D) for about 20 gases and >300 amorphous glassy polymers. The data were originally reported at different temperatures mostly in the range 20–35°C, that is, at temperatures much lower than corresponding glass transitions. Two approaches were employed in finding the values of $P(T_g)$ and $D(T_g)$ for different gases in polymers having different T_g values.

1. Extrapolation of P_{ij} and D_{ij} (i th gas and j th polymer) to corresponding T_{gj} . This can be made for the gas–polymer systems the P_{ij} and D_{ij} values of which were measured at low-pressure limit (that is, pressure-independent P_{ij} and D_{ij} values) and if E_P and E_D values are available. This procedure is based on an assumption that the Arrhenius equations with constant E_P and E_D hold in a wide temperature range below glass transition. Some confirmation of this assumption can be found in the literature (see, e.g., refs. 19, 20); however, there are no grounds to suppose that it will be true for all gas–polymer systems. Hence, an uncontrolled source of errors can appear. On the other hand, in this treatment of the data, a range of variation of T_g and a number gas–polymer systems included in consideration are the largest. It is worth noting that expanding the range of variation of T_g by including in consideration negative (in °C) temperatures of glass transitions in rubbers is impossible because of nonlinear character of temperature dependencies of P_{ij} and D_{ij} for rubbers in Arrhenius coordinates.²¹

The numbers of gas–polymer systems the transport parameters of which were extrapolated to T_g are given in Table I. For other

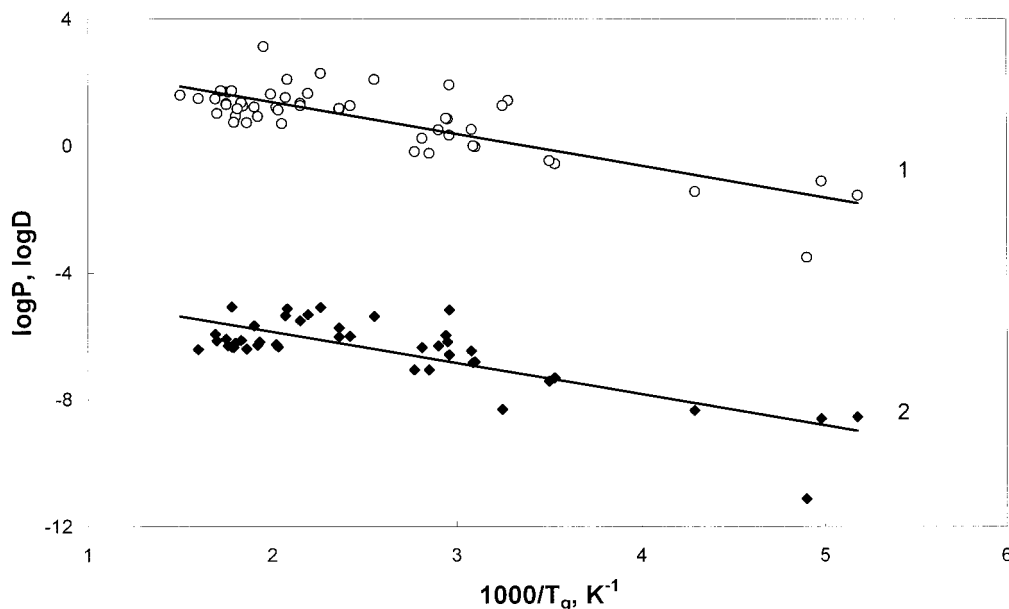


Figure 1 Dependence of $P(T_g)$ (1) and $D(T_g)$ (2) of oxygen on glass transition temperature T_g of different polymers: estimated with extrapolation.

gases, the data available were not sufficient for accurate extrapolation. Thus extrapolation was performed for the gases presented in Table I and polymers having T_g values in the range 10–394°C.

2. A number of articles report temperature dependencies of P_{ij} and D_{ij} values in a range of temperatures including corresponding T_g .^{4,6,19,20,22–29} This group of data enables a direct determination of P_{ij} and D_{ij} values at T_g . Here the data are less numerous but, apparently, more accurate. So the $P_{ij}(T_g)$ and $D_{ij}(T_g)$ values of five gases (He, O₂, N₂, CO₂, CH₄) in different amorphous polymers having T_g values in the range 32–320°C were analyzed. Those polymers belong to various classes (e.g., polyesters, polyimides, polycarbonate, etc.).

RESULTS AND DISCUSSION

Permeability and Diffusion Coefficients at T_{gj}

Temperature dependencies $P_{ij}(T_g)$ and $D_{ij}(T_g)$ were treated by using the equations

$$\log D_{ij}(T_g) = a_{Di}(1/T_{gj}) + b_{Di} \quad (2)$$

$$\log P_{ij}(T_g) = a_{Pi}(1/T_{gj}) + b_{Pi} \quad (3)$$

Figures 1 and 2 show examples of these dependencies for two gases obtained by extrapolation in Arrhenius coordinates. A large scatter of the points is obvious in both figures; the same is true for other gases. However, in all the cases the parameters of eqs. (2) and (3) indicate the growth of $P_{ij}(T_g)$ and $D_{ij}(T_g)$ when T_{gj} increases. This scatter seems to be related to the errors caused by wide temperature extrapolation from the measured P and D values and activation energies. The parameters of eqs. (2) and (3) obtained by the least-squares treatment are presented in Table II. The parameters a_{Di} and a_{Pi} are negative in all the cases in spite of the scatter. It means that $P_{ij}(T_g)$ and $D_{ij}(T_g)$ values are larger at higher T_{gj} .

Temperature dependencies $P_{ij}(T_g)$ and $D_{ij}(T_g)$ based on the direct measurements of these parameters at T_{gj} in different polymers are shown in Figures 3–6. It can be seen that the scatter here is substantially diminished, although the number of points is markedly less than in Figures 1 and 2. The parameters of eqs. (2) and (3) obtained by the least-squares treatment are given in Table III. The correlation factors shown in this table are larger than those in the analysis using temperature extrapolation. Again the parameters a_{Di} and a_{Pi} determine the increase in $P_{ij}(T_g)$ and $D_{ij}(T_g)$ values with in-

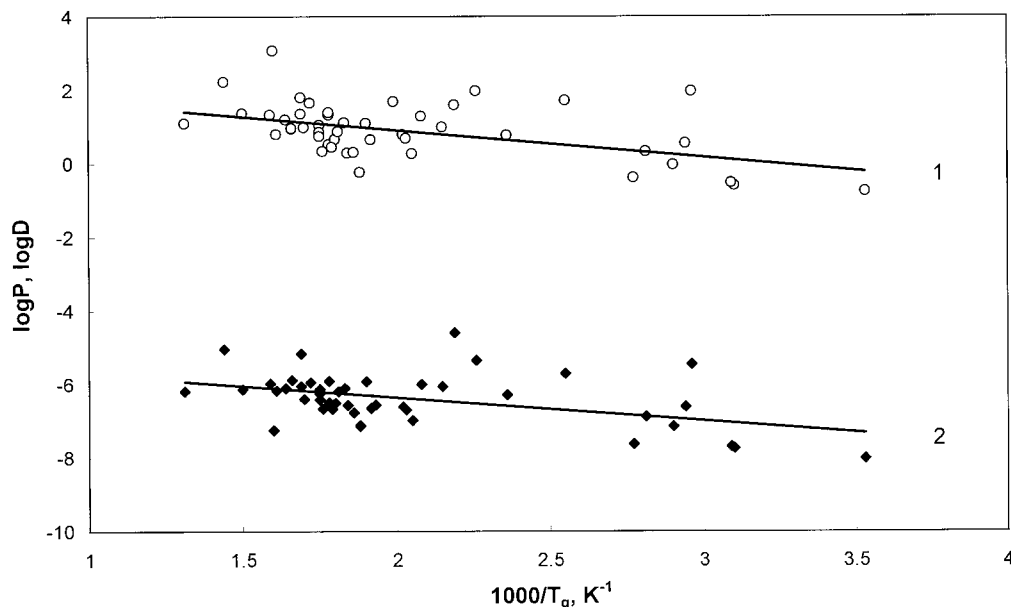


Figure 2 Dependence of $P(T_g)$ (1) and $D(T_g)$ (2) of methane on glass transition temperature T_g of different polymers: estimated with extrapolation.

creasing T_g in agreement with the conclusion made above.

By using the dependencies of $P_{ij}(T_g)$ and $D_{ij}(T_g)$, the ideal separation factors

$$\alpha_{AB}(T_{gj}) = P_A(T_{gj})/P_B(T_{gj}) \quad (4)$$

$$\alpha_{AB}^D(T_{gj}) = D_A(T_{gj})/D_B(T_{gj}) \quad (5)$$

for gas pairs A and B can be computed. The dependencies of $\alpha_{AB}(T_{gj})$ and $\alpha_{AB}^D(T_{gj})$ on T_{gj} were treated by using the similar equations the parameters of which are shown in Table IV:

$$\alpha_{AB}(T_{gj}) = a_\alpha(1/T_{gj}) + b_\alpha \quad (6)$$

$$\alpha_{AB}^D(T_{gj}) = a_\alpha^D(1/T_{gj}) + b_\alpha^D \quad (7)$$

Because in all the cases the values a_α and a_α^D that characterize the selectivity of permeation and diffusion are positive, permselectivity of polymers at T_{gj} decrease with increasing T_{gj} . Hence a common trade-off relation between permeability and permselectivity is observed in polymers at their T_g 's: at higher T_{gj} , permeability and diffusivity increase while selectivity decreases.

Solubility Coefficients at T_g

As is well-known, mobility and solubility coefficients can be distinguished in permeability coefficients, that is, $P = DS$. Again several ap-

Table II Obtained with Extrapolation Parameters of Temperature Dependences $P_{ij}(T_g)$ and $D_{ij}(T_g)$ and Correlation Factors ρ

Gas	a_{Pi}	b_{Pi}	ρ_{Pi}	a_{Di}	b_{Di}	ρ_{Di}
He	-1.03	4.47	0.78	-0.938	-1.87	0.81
H ₂	-0.722	3.61	0.60	-0.808	-2.70	0.72
O ₂	-0.998	3.37	0.80	-0.981	-3.91	0.78
N ₂	-0.654	2.31	0.51	-1.24	-2.90	0.77
Ar	-1.81	5.58	0.85	-1.59	-2.23	0.86
CO ₂	-0.316	2.12	0.26	-0.579	-5.00	0.53
CH ₄	-0.731	2.37	0.48	-0.625	-5.11	0.46

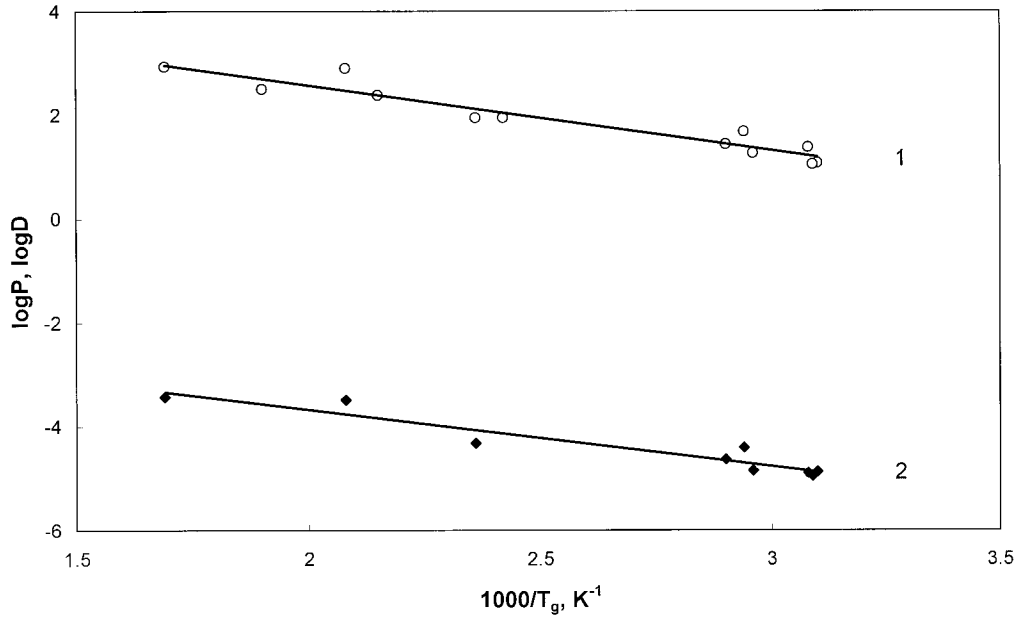


Figure 3 Dependence of $P(T_g)$ (1) and $D(T_g)$ (2) of helium on glass transition temperature T_g of different polymers: based on direct measurements.

proaches are possible to find solubility coefficients at the glass transition temperatures $S_{ij}(T_g)$.

By using the dependencies $P_{ij}(T_g)$ and $D_{ij}(T_g)$, one can find the parameters of the dependence

$$\log S_{ij}(T_g) = a_S(1/T_{g_j}) + b_S \quad (8)$$

As a_S and b_S values given below and based on the data from Table 3 indicate:

Gas	He	O ₂	CO ₂	N ₂	CH ₄
a_S	-0.16	0.17	0.54	0.12	0.09
b_S	-3.43	-3.42	-3.66	-3.39	-3.11

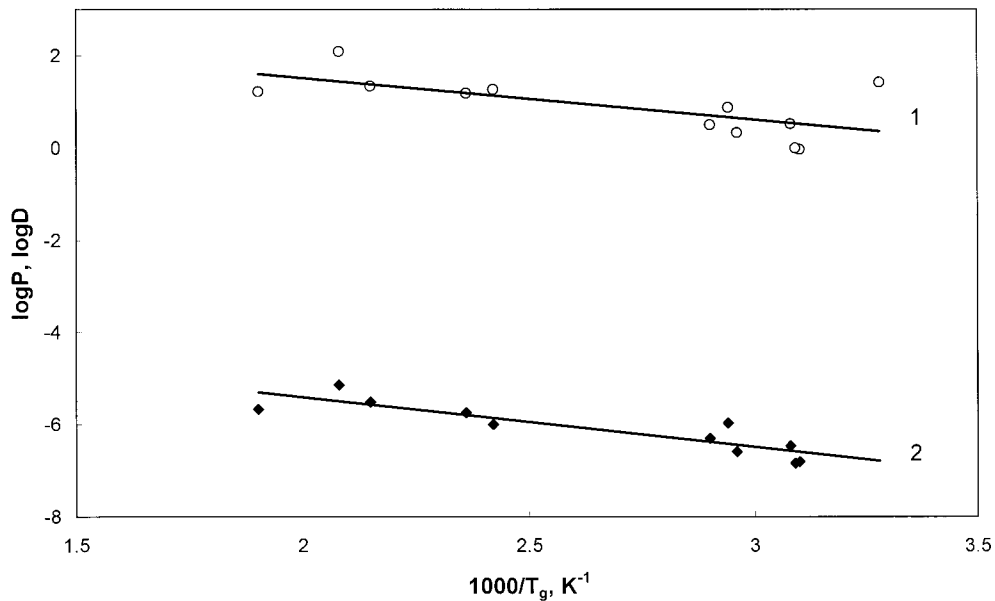


Figure 4 Dependence of $P(T_g)$ (1) and $D(T_g)$ (2) of oxygen on glass transition temperature T_g of different polymers: based on direct measurements.

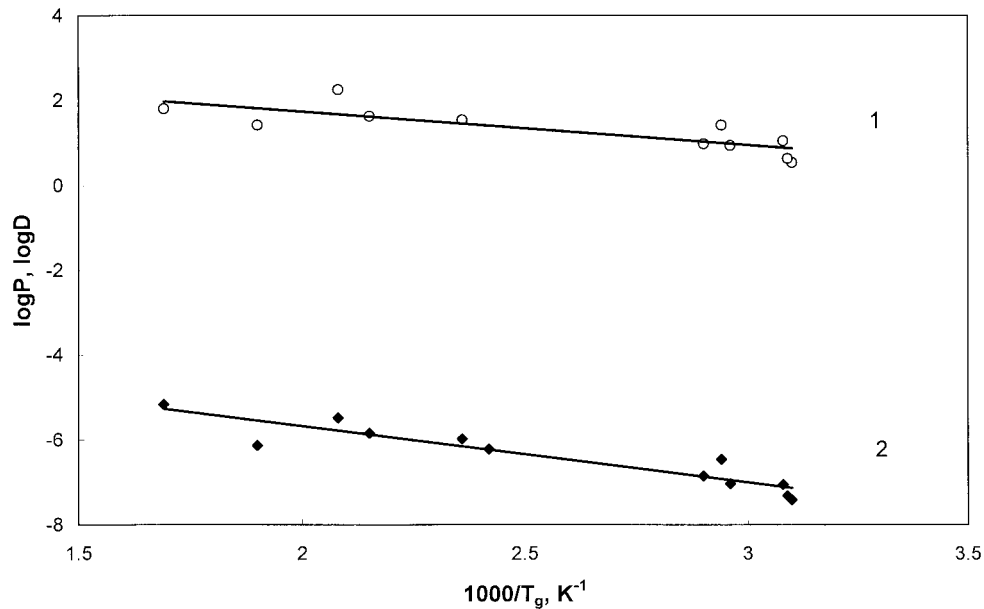


Figure 5 Dependence of $P(T_g)$ (1) and $D(T_g)$ (2) of carbon dioxide on glass transition temperature T_g of different polymers: based on direct measurements.

Several conclusions can be made: (1) The dependence of $S_{ij}(T_g)$ is much weaker than those of $P_{ij}(T_g)$ and $D_{ij}(T_g)$. (2) For all the gases except He, the $S_{ij}(T_g)$ values decrease when T_g increases, (3) b_S values for all the gases vary in a rather narrow range. In effect, this means that entropy of dissolution for different gases and polymers is approximately the same at T_g .

These conclusions were further checked by the results of experimental determination of solubility coefficients of two gases (CO_2 and Ar) in several polymers at different temperatures including the glass transitions. Figure 7 shows temperature dependence of the apparent solubility coefficients (or initial slope of sorption isotherms) $S = (C/p)_{p=0}$ of argon and carbon dioxide in PTMSNB.

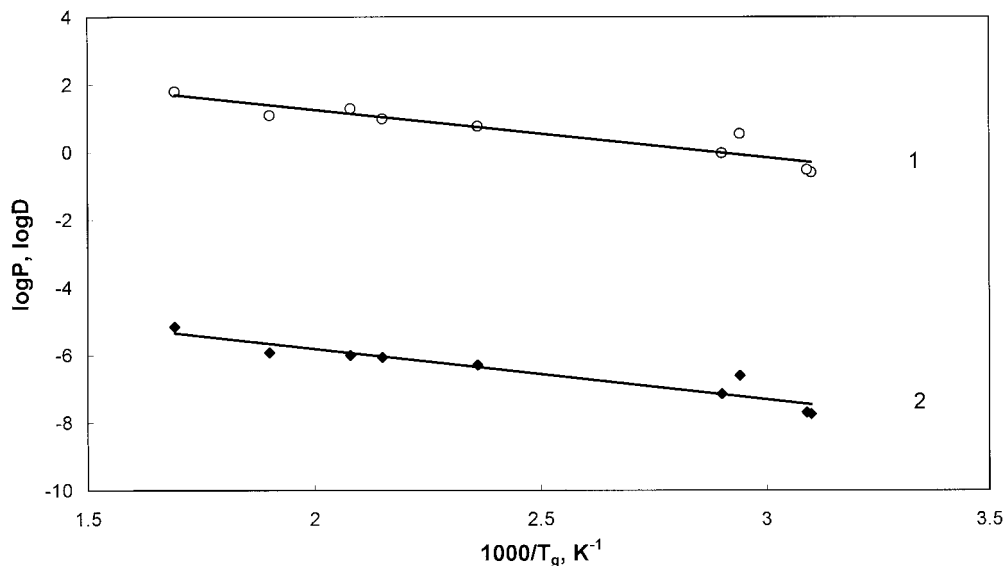


Figure 6 Dependence of $P(T_g)$ (1) and $D(T_g)$ (2) of methane on glass transition temperature T_g of different polymers: based on direct measurements.

Table III Parameters of Temperature Dependences $P_{ij}(T_g)$ and $D_{ij}(T_g)$ Based on Direct Measurements and Correlation Factors ρ

Gas	a_{Pi}	b_{Pi}	ρ_{Pi}	a_{Di}	b_{Di}	ρ_{Di}
He	-1.23	4.98	0.91	-1.16	-1.37	0.85
O ₂	-1.10	3.73	0.67	-1.48	-2.39	0.85
N ₂	-1.32	3.93	0.80	-1.44	-2.55	0.91
CO ₂	-0.778	3.29	0.66	-1.71	-2.16	0.83
CH ₄	-1.41	4.08	0.94	-1.50	-2.81	0.95

Two excellent linear dependencies are observed below and above the glass transition of this polymer with the break at 106–109°C that is very close to the T_g value of $104 \pm 2^\circ\text{C}$ observed by DSC method. Similar dependencies for PVTMS are shown in Figure 8. A peculiarity of the results obtained for PVTMS is that the break points in the temperature dependencies of S do not coincide with T_g as measured by DSC for the same sample. The slopes of the temperature dependence of S are changed at 171–175°C, whereas DSC method gives the values of $152 \pm 1^\circ\text{C}$ for onset temperatures and $163 \pm 1^\circ\text{C}$ for the end temperatures. The reason for this is not clear. Several temperature transitions were observed³⁰ for this polymer in the range 106–186°C; however, only one of them apparently influences gas sorption (Fig. 8).

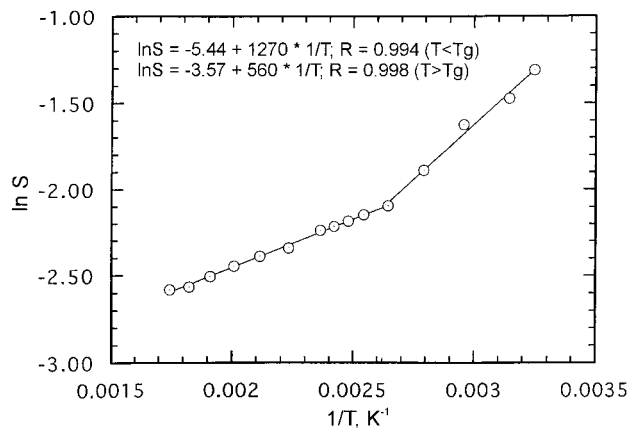
The S values at ambient temperature agree well with the solubility coefficients measured earlier by different methods (Table V). The slopes of the dependencies shown in Figures 7 and 8 enable one to calculate the enthalpies of sorption ΔH_S below and above T_g . In the glassy state of PVTMS, a reasonable agreement is reached between the values reported by Volkov et al.³³ for narrower temperature range and found in the present work.

It is common in the sorption thermodynamics to represent enthalpies of sorption as a sum of two

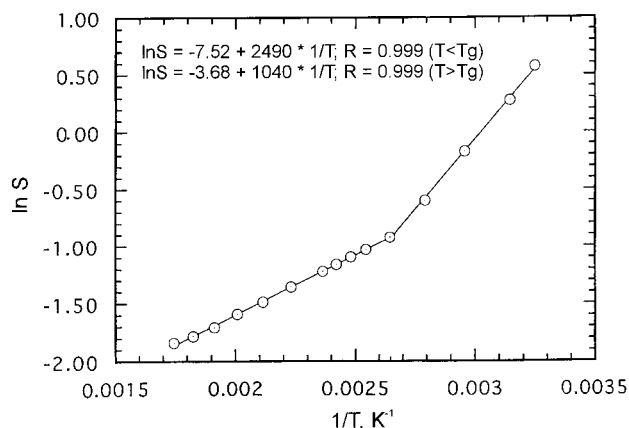
contributions, those of condensation ΔH_c and mixing ΔH_m :

$$\Delta H_S = \Delta H_c + \Delta H_m \quad (9)$$

Corresponding values of ΔH_c are tabulated.^{34,35} Because CO₂ sublimates and does not form a liquid



(a)



(b)

Table IV Parameters of Temperature Dependence of the Separation Factors $\alpha_{AB}(T_{gj})$ and $\alpha_{AB}^D(T_{gj})$

Gas Pair	a_α	b_α	α_α^D	b_α^D
He/N ₂	0.052	1.167	0.33	1.09
He/CH ₄	0.16	0.99	0.41	1.31
O ₂ /N ₂	0.40	-0.63	0.35	-0.67
CO ₂ /N ₂	0.52	-0.62	0.107	-0.465
CO ₂ /CH ₄	0.63	-0.79	0.187	-0.24

Figure 7 Temperature dependence of solubility coefficients ($\text{cm}^3(\text{STP})/\text{cm}^3 \cdot \text{atm}$) of (a) Ar and (b) CO₂ in poly(trimethylsilyl norbornene): temperature of the break is (a) 109°C and (b) 106°C.

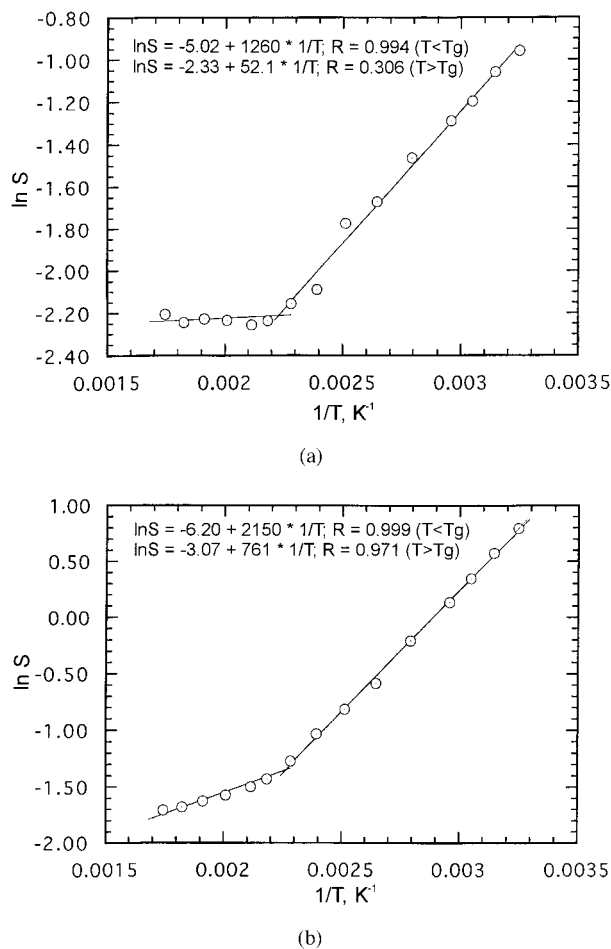


Figure 8 Temperature dependence of solubility coefficients ($\text{cm}^3(\text{STP})/\text{cm}^3 \cdot \text{atm}$) of (a) Ar and (b) CO_2 in poly(vinyl trimethyl silane): temperature of the break is (a) $175^\circ C$ and (b) $171^\circ C$.

phase at low pressure, the enthalpy of sublimation (equal to 3.93 kcal/mol ³⁵) was used in calculating ΔH_m . Table VI indicates that enthalpies of mixing of both gases are positive above T_g and negative in the glassy states of both polymers that is in agreement with the concept of filling preexisting microcavities in the glassy state and prevailing of the Langmuir sorption mechanism in dissolution at low pressure limit.

Temperature dependencies of the solubility coefficients of gases in other polymers also exhibit breaks in the vicinity of corresponding glass transitions.

Now using the values of $S_{ij}(T_{gj})$ for different polymers, it is possible to examine the effects of the T_g on $S_{ij}(T_{gj})$. Figure 9 gives an example of such a dependence for carbon dioxide. Three groups of data were used in preparation of this

graph: (1) the results of direct measurements of $S(CO_2)$ in various polymers at corresponding T_g (this work); (2) similar experimental data taken from the literature³⁶; and, (3) the dependence $S(T_{gj})$ obtained as a ratio of the permeability and diffusion coefficients of CO_2 at different T_g 's shown as a solid line in Figure 9. One can note that a reasonable agreement of these three groups of the results is achieved. The slope of the dependence that was obtained by using experimentally determined $S(CO_2)$ values at T_{gj} in this work gives the apparent enthalpy of sorption equal to -2.5 kcal/mol , a value consistent with typical enthalpies of sorption of carbon dioxide in polymers.³⁶

A similar analysis was performed for argon, and the results are shown in Table VII. No trend in $S(\text{Ar})$ at T_{gj} can be viewed within some scatter. Probably, it indicates that apparent enthalpy of sorption of argon in polymers at T_{gj} is smaller than that of CO_2 , an observation that can be anticipated.

Thus, both direct and indirect determinations of $S(T_{gj})$ indicate that solubility coefficients at T_g , in contrast to $P(T_{gj})$ and $D(T_{gj})$, are much weaker functions of T_g 's. It was shown, at least for carbon dioxide, that $S(T_{gj})$ in various polymers decreases when T_g increases, and apparent enthalpy of sorption found by linearization of $S(T_{gj})$ in van't Hoff coordinates is rather similar to usual enthalpies of sorption. Hence all the parameters involved in gas permeation and membrane gas separation (P , D , α , α^D , S) at T_g behave in the same manner as those parameters dependent on temperature. It should be emphasized, as an important observation, that unified dependencies of $P(T_{gj})$, $D(T_{gj})$, and $S(T_{gj})$ on the T_{gj} were obtained for a number of gases and polymers having entirely different chemical structure and properties.

Free Volume at T_g

Several models enable one to relate diffusivity of polymers with free volume V_f . Thus, according to

Table V Comparison of S [$\text{cm}^3(\text{STP})/\text{cm}^3 \text{ atm}$] at 298 K

Polymer	CO_2		Ar	
PVTMS	2.74 ^a	2.68 ³¹	0.45 ^a	0.49 ³¹
PTMSNB	2.28 ^a	3.15 ³²	0.31 ^a	0.31 ³²

^a This work.

Table VI Enthalpies of Sorption ΔH_s and Excess Enthalpies of Mixing ΔH_m (kcal/mol) at Different Temperatures

Gas	T	$-\Delta H_s$		ΔH_m	
		PVTMS	PTMSNB	PVTMS	PTMSNB
CO ₂	$>T_g$	1.51	2.07	2.4	1.9
	$<T_g$	4.27	4.95	-0.34	-1.02
Ar	$>T_g$	0.10	1.11	1.5	0.5
	$<T_g$	2.50	2.53	-0.9	-0.9

Cohen and Turnbull,³⁷ diffusion coefficients D are proportional to the probability of finding a microcavity the size of which is greater than the molecular size of B_D of the diffusant, hence,

$$D = A \exp(-\gamma B_D/V_f) \quad (10)$$

where $1 > \gamma > 0$ accounts for partial overlapping of microcavities. This equation does not specify any variation of V_f with temperature. A step in this direction was made in Fujita's model³⁸

$$D = A_a R T \exp(-B_D/V_f) \quad (11)$$

However, linear dependence of the preexponent is so weak, if compared with the exponential term,

that it can hardly be used for interpreting nonisothermal diffusivity data.

The free-volume model was extensively used in correlating diffusion coefficients of one gas in different glassy polymers³⁹ or various gases in a certain polymer⁴⁰ at constant temperature. However, to the knowledge of the authors, it has never been applied to interpretation of diffusion coefficients in glassy polymers at different temperatures. Neither eq. (10) nor (11) give explicit dependence of V_f on temperatures. There is little doubt that it should be changed at $T > T_g$ and, probably, in glassy state as well.

A more rigorous treatment of free-volume approach was made by Vrentas and Duda,⁴¹ who proposed including an energy term into the pre-

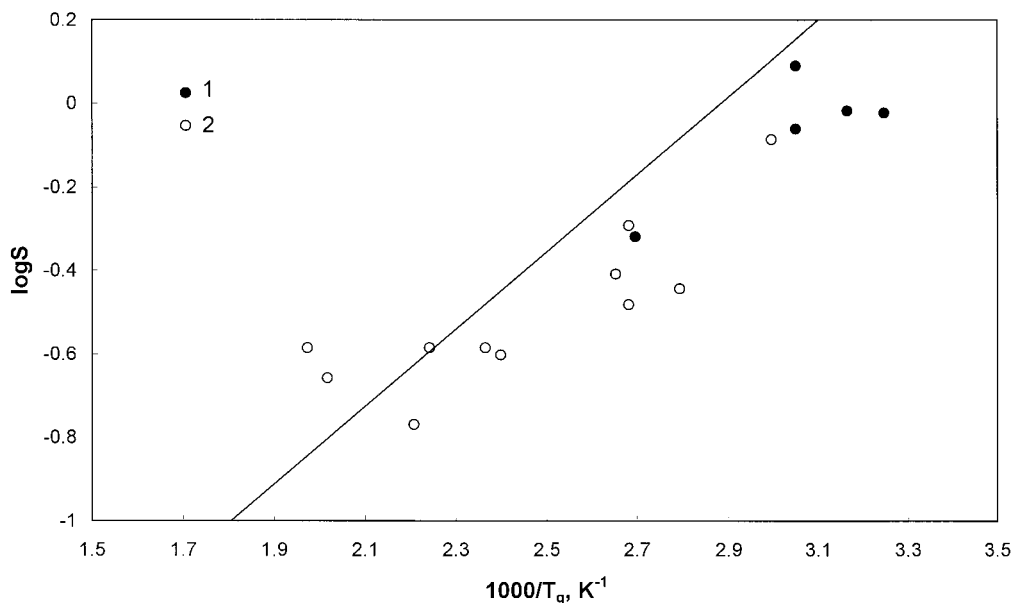


Figure 9 Dependence of $S(T_g)$ in $\text{cm}^3(\text{STP})/\text{cm}^3 \cdot \text{atm}$ of carbon dioxide on glass transition temperature T_g of different polymers: (1) direct measurements (this work); (2) direct measurements³⁶; solid line is based on estimation via $P(T_g)$ and $D(T_g)$ (Table III).

Table VII Solubility Coefficients S of Argon in Polymers at T_g

Polymer	T_g (°C)	S [cm ³ (STP)/cm ³ atm]
PEMA	61	0.097
PVC	85	0.051
PMMA	100	0.073
PS	100	0.069
PTMSNB	104	0.23
PC	144	0.057
PVTMS	157/173 ^a	0.11
PSF	180	0.050
BPDA-BATPHF	223	0.086
6FDA-BATPHF	234	0.10

^a The first value is according to DSC, the second value corresponds to the break in the temperature dependence of S .

exponent accounting for energy E needed for the diffusant molecule to jump into the opened microcavity. Their equation, however, included too many hardly defined parameters, so we shall use here a simpler equation suggested by Miyamoto and Shibayama⁴² for ionic conductivity of glassy polymers. According to these authors, the diffusion coefficient can be expressed by

$$D = \nu \alpha \exp(-E/RT) \exp(-\gamma B_D/V_f) \quad (12)$$

where ν is the vibrational frequency of diffusant molecule and α is a correlation (adjustable) parameter. Note that nothing is specified again on temperature dependence of V_f .

It is possible now to check the hypothesis of isofree volume at T_g and implications of the eqs. (10)–(12) on the basis of the observed increase in the $D_{ij}(T_{gj})$ and $P_{ij}(T_{gj})$ values with growing T_g 's. However, eq. (12) contains several conceivably temperature-dependent parameters, so some simplifications are required.

Free volume in the glassy state is assumed, in agreement with the isofree volume concept, to be constant. Then the dependence of $\log D_{ij}(T_{gj})$ and $\log P_{ij}(T_{gj})$ versus $1/T_g$ (Figs. 3–6) can be treated by using Arrhenius equation. Activation energies of permeation $E_P(T_g)$ and diffusion $E_D(T_g)$ found in this way are in the range 3–7 kcal/mol (Table VIII). These values are similar to common activation energies of permeation and diffusion of gases in polymers⁴³; in addition, in most cases $E_D > E_P$. It is also worth recalling that apparent enthalpy of sorption of carbon dioxide $\Delta H_s(T_g)$

= $E_D - E_P$ also has a normal value (Fig. 9). Therefore, the second assumption also looks plausible.

To make a distinction between these two extremities, a method is needed that will allow an assessment of free volume directly at T_g . To pursue this goal, positron annihilation lifetime (PAL) spectroscopy can be used. This technique gives direct information on the microstructure of polymers.⁴⁴

After entering the polymer, a positron may exist as a free positron e^+ (lifetime 0.3–0.5 ns) or a form of bound state ($e - e^+$ pair or positronium atom, Ps). The triplet state of Ps, *ortho*-positronium (*o*-Ps), has a lifetime of 142 ns in vacuum. In amorphous polymers, *o*-Ps is trapped in regions of lower electronic density, which are usually interpreted as holes and microcavities. The observed *o*-Ps lifetime in the holes is reduced to several nanoseconds because annihilation is facilitated by the overlap of the positron wavefunction with molecular electrons. In such a way, the lifetime of *o*-Ps depends on the hole size,^{45,46} whereas its relative intensity is interpreted to be proportional to the *o*-Ps formation probability and, hence, the concentration of holes.^{47,48} The longer lifetime τ_{Ps} is due to *o*-Ps annihilation. According to refs. 45, 46, and 49, *o*-Ps lifetime enables one to obtain the mean free-volume hole radius R by the following semiempirical equation:

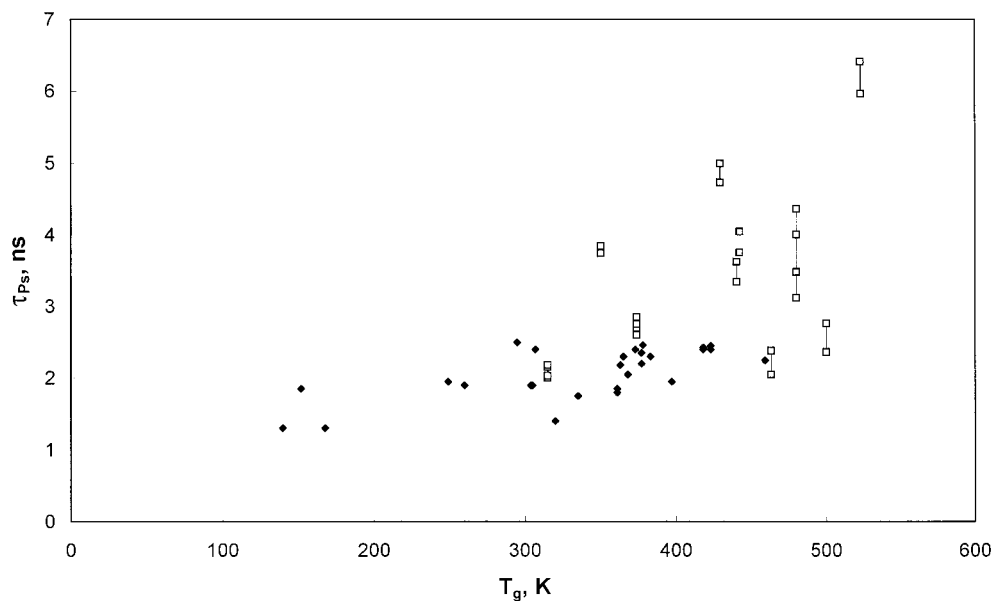
$$\tau_{Ps} = \frac{1}{2} [1 - (R/R_0) + (\frac{1}{2}\pi) \sin(2\pi R/R_0)]^{-1} \quad (13)$$

where R_0 is equal to $R + \Delta R$ and ΔR is the fitted empirical electron layer thickness equal to 1.66 Å. Assuming that the microcavities have the geometry of a sphere, one obtains the mean volume of microcavity $v_f = 4\pi R^3/3$, so the FFV(%) can be expressed by an empirically fitted equation⁵⁰

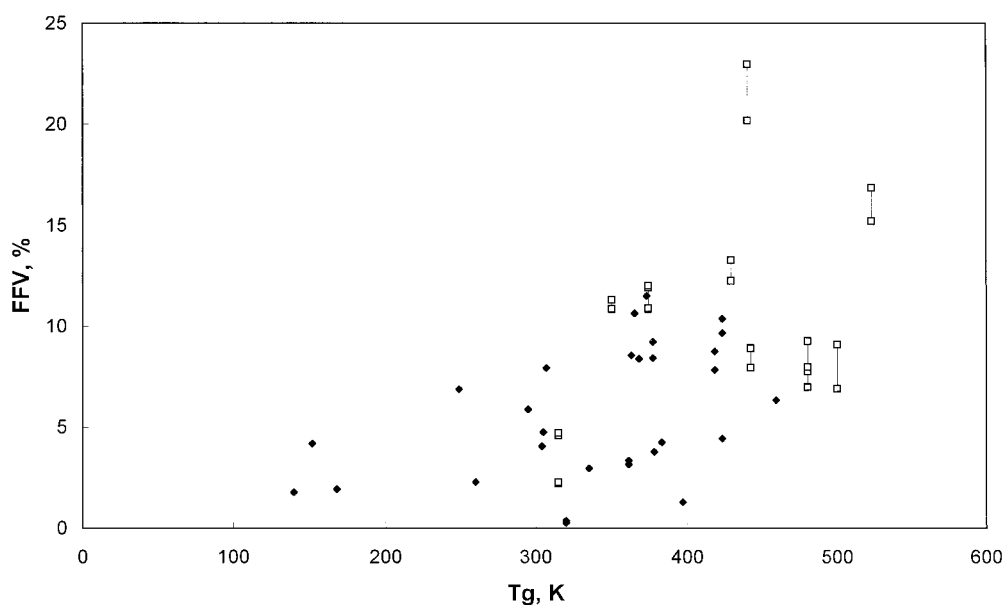
$$\text{FFV} = C v_f I_{Ps} \quad (14)$$

Table VIII Apparent Activation Energies of Permeation $E_P(T_g)$ and Diffusion $E_D(T_g)$ (kcal/mol)

Gas	$E_P(T_g)$	$E_D(T_g)$
He	5.7	5.0
O ₂	4.1	4.9
N ₂	6.0	6.5
CO ₂	3.6	6.0
CH ₄	6.5	6.9



(a)



(b)

Figure 10 Effects of the glass transition temperatures T_g on (a) *o*-Ps lifetime and (b) fractional free volume: filled points are the data based on direct measurements τ_{Ps} at T_g ; open points are the data based on extrapolation of τ_{Ps} from ambient temperature to T_g ; lower value correspond τ_{Ps} at ambient temperature, higher value is obtained by extrapolation.

where I_{Ps} (in percent) is the intensity of the exponential term associated with lifetime τ_{Ps} and C (in \AA^{-3}) is the constant empirically determined from the specific volume data. It should be noted that the assumption of spherical form of the microcavities in polymers might not be realistic;

more probably, the geometry of a cylinder or ellipsoid can be anticipated. The values of the parameter C in the range of 0.001–0.002 were reported for different polymers,⁵¹ which may reflect this variation of the microcavity geometry. On the other hand, there is no doubt that τ_{Ps} can be

considered as a measure of free-volume size, because rather good correlations of gas diffusion and permeability coefficients with τ_{Ps} were demonstrated.⁵²

PAL spectra were measured in a wide temperature range, including T_g , by many authors.⁵³⁻⁷⁰ These studies included both rubbers having glass transitions as low as 140–150 K and glassy polymers with $T_g > 400$ K. Hence the values τ_{Ps} at T_g and the FFV calculated therefrom can be examined in the range of T_g from 140 to 410 K. In addition, it was shown that the temperature dependencies $\tau_{Ps}(T)$ in most polymers correspond to $\alpha_{\text{holes}} \approx 2 \times 10^{-3} \text{ ns K}^{-1}$. So an extrapolation of the τ_{Ps} values measured at ambient temperatures to T_g can also be performed. I_{Ps} values also change with temperature; however, this dependence is rather weak and can be neglected in the first approximation. So if τ_{Ps} and I_{Ps} values were measured for some polymers only at ambient temperatures, an estimation of FFV at T_g can be made as well.

Figure 10 shows dependencies of (a) τ_{Ps} and (b) FFV on the T_g 's of different polymers. Both the results of direct measurements⁵³⁻⁶⁴ of τ_{Ps} and I_{Ps} and extrapolation along temperature⁶⁵⁻⁷⁰ were included. Some scatter in the graphs might imply that eqs. (13) and (14) are only approximately valid. Reasons for it, namely variations of microcavity geometry and of the C parameter, were discussed earlier. It can be assumed that τ_{Ps} , the radii of microcavities, and FFV depend on some other features of polymers and not only on T_g , otherwise significant scatter of the points cannot be explained. Nevertheless, it is obvious that an increase in T_g results in growth of τ_{Ps} , size of microcavity, and FFV at corresponding glass transitions independent on polymer structure.

A more detailed analysis in a recently published article⁶³ led to hole-volume fraction $F_h(\%)$ at T_g in different polymers (PMMA, PS, PC) having T_g in the range 105–150°C. The results of this work that are independent of arbitrary assumptions regarding the constant C show that F_h increases from 4.0 to 9.4% with increasing T_g . So PAL studies of free volume in polymers at T_g are in evident contradiction with the isofree volume concept.

Now having these results we can return to eq. (12) and answer why diffusion and permeability coefficients at T_g grow up when T_g increases. By using the parameters a_D from Table 3, one can find that an increase in T_g from 300 to 500 K leads to the increase in D values by a factor of

100–700 depending on the gas molecule. Meanwhile, the same increase in T_g , as is seen from Figure 10, is accompanied by a growth of FFV by a factor of 3–4. Therefore, the main reason for increases in $D(T_g)$ and $P(T_g)$ values with T_g is thermal activation of diffusion process at higher T_g as is characterized by the factor $\exp(-E/RT)$ in eq. (12).

CONCLUSIONS

This work aimed to shed light on following problems: what are the upper limits of gas permeability coefficients and diffusion coefficients, permselectivity of polymers in the glassy state, that is, what values can have these quantities at corresponding T_g ; how gas permeability, diffusion, and solubility coefficients at T_g vary, when T_g values are changed significantly; and does free volume at T_g , as manifested in the transport parameters, obey isofree volume concept.

Both direct measurements of P and D at different T_g and extrapolation to T_g of the P and D values measured at ambient temperature indicated that an increase in T_g leads to increases in $P(T_g)$ and $D(T_g)$ values for different gases and reduction of permselectivities of polymers at T_g with respect to commonly considered gas pairs. Direct measurements of solubility coefficients S at T_g in various polymers showed that a growth of the T_g values results in a decrease in the S values in quantitative agreement with indirect estimations of solubility coefficients via P and D values. Although free volume at T_g in polymers increases for higher T_g , this dependence cannot explain a marked growth of the P and D values with T_g . The main contribution into this dependence is provided by thermal activation of the diffusion process at higher T_g . In conclusion, it should be noted again that unified behavior of $P(T_g)$, $D(T_g)$, and $S(T_g)$ values as functions of T_g was observed for numerous polymers independently of their chemical structures.

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