Theories of Sorption and Transport in Polymer Membrane

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ABSTRACT: This paper reviews some phenomenological models which are employed in recent years to interpret and analyze permeation behavior of gases and gas mixtures through non-porous polymer membranes. The applicability and limitations of the models are discussed in light of recent experimental results of permeation of gas/vapor mixtures through a disubstituted polyacetylene, poly[1-(trimethylsilyl)-1-propyne], membrane.
KEY WORDS   Sorption / Permeation / Dual-Mode Transport Model / Free-Volume Model / Permeability Coefficient / Gas/Vapor Mixture / Poly[1-(trimethylsilyl)-1-propyne]/

The interest in sorption and transport behavior of gases and gas mixtures in nonporous polymer membranes is growing year by year with accelerating development of many important practical applications. These applications, which include packing materials, protective coatings, and separation membrane systems, depend wholly or largely on the behavior. Concerning the sorption and transport behavior of pure gases and vapors in polymer solids, extensive knowledge of the fundamental features of the behavior has been accumulated in the last four decades, and many reviews have been written by several authors.[1-14]

In comparison with the case of pure gases or vapors, still a little information, both theoretical and experimental, is available on characteristics of the sorption and transport behavior of mixtures of gases and vapors in nonporous polymer membranes.[1,5,10,13,15-18] If component gases exhibit very low solubilities in a polymer, each gas molecule can permeate independently through the polymer membrane. Sorption and transport characteristics of the gas mixture are predicted from those data of pure gases.[1,10,15] When a gas mixture contains more soluble components, however, the sorption and transport behavior of a component is affected by that of other component(s). Thus it is anticipated that the behavior of the gas mixture is not simply correlated with that of pure component gases.

The permeation of gases through a nonporous membrane is governed by the coupled solution-diffusion mechanism proposed by Graham many years ago.[19] First, solution (sorption) of gas molecules occurs in the surface layer on the upstream side of the membrane, then the molecules diffuse across the membrane in response to concentration gradient, and finally evaporate from the other surface on the downstream side.

According to the state of a penetrant-polymer system concerned,

the permeation behavior of gas mixture has been explained by either of the two different phenomenological models, the dual-mode transport, or mobility, model and the free-volume model. Both models stem from the solution-diffusion concept[19] mentioned above. If the system is in the glassy state, the dual-mode transport model is conveniently used to analyze permeation behavior of gas mixtures. On the other hand, permeation behavior of a system of gas mixture and rubbery polymer is usually considered by the free-volume model. One can find many articles in the literature, which show these models respectively explain well the permeation behavior of gas mixtures observed in the glassy and the rubbery regimes, both are far from the glass transition region of a given system.[13,18,21-26]

This paper reviews these phenomenological models developed to describe the permeation of gas mixtures. The applicability and limitations of the models will be discussed in light of recent experimental data. Extension of molecular models, like the model of Pace and Datyner,[27-29] to the transport of mixtures of gases and vapors in nonporous polymer membranes has not been attempted yet.

TRANSPORT MODELS AND RELATED CORRELATIONS

The Dual-Mode Transport Model

This model has been formulated based upon the dual-mode sorption model.[9-14,18,30-33] For systems of a gas and a glassy polymer, sorption isotherms are frequently concave to the pressure axis, approaching linearity at higher pressures. The sorption isotherm of this shape has been described by assuming that the penetrant dissolves by two component processes:

(1) Ordinary dissolution in continuous amorphous matrix, the concentration of this mode, C_D, is represented by Henry's law, and

(2) Sorption in a limited number of fixed preexisting microvoids, or at fixed sites, in the polymer, the concentration of this mode C_H is represented by the Langmuir equation.

The total concentration C of sorbed penetrant is then given by the dual-mode sorption model:

$$C = C_D + C_H = k_D p + C'_H bp / (1 + bp) \qquad (1),$$

where k_D is the Henry's law constant, p the equilibrium penetrant pressure, C_H' the Langmuir capacity constant, and b the Langmuir affinity constant.

The solubility of most gases and vapors in a polymer decreases with increasing temperature. This is reflected on the fact that the dual-mode parameters k_D, C_H', and b decrease as the temperature rises. For many systems, C_H' tends to decrease nearly linearly with increasing temperature and vanishes at a temperature very close to the glass transition temperature of the polymer. Equation (1) then reduces to Henry's law.

The diffusion of gases in glassy polymers is best represented by assuming that the two penetrant species, dissolved respectively in polymer matrix and microvoids, are both mobile. According to this partial immobilization hypothesis, the mobilities of the two penetrant populations, of concentrations C_D and C_H, are characterized by the diffusion coefficients D_D and D_H, respectively. Then the local penetrant flux, J, normal to a plane at any position coordinate x in a

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glassy polymer can be expressed in terms of a two part contribution[31,32,34,35]:

$$J = - D_D \left(\partial C_D / \partial x \right) - D_H \left(\partial C_H / \partial x \right) \qquad (2).$$

This expression can be written in terms of Fick's first law with an effective diffusion coefficient, $D_{eff}(C)$, which is dependent on local concentration, by the relation:

$$J = - D_{eff}(C) \left(\partial C / \partial x \right) \qquad (3).$$

$D_{eff}(C)$ is related to D_D and D_H by the expression:

$$D_{eff}(C) = D_D \left[\frac{1 + FK / (1 + \alpha C_D)2}{1 + K / (1 + \alpha C_D)^2} \right] \qquad (4)$$

where $F = D_H / D_D$, $K = C_H \cdot b / k_D$, $\alpha = b / k_D$, and also $\alpha C_D = bp$. Both D_D and D_H are assumed to be constant. Equation (4) shows that $D_{eff}(C)$ increases with increasing C_D, and hence with increasing pressure.

The steady-state permeability coefficient of a pure component in a glassy polymer, P, is given by Eq.(5) when the downstream receiving pressure is effectively zero and the upstream driving pressure is p, that is,

$$P = k_D D_D \left[1 + FK / (1 + bp) \right] \qquad (5).$$

According to Eq.(5), P decreases with increasing p from a maximum of $P = k_D D_D (1 + FK)$ at $p \to 0$ to a minimum of $P = k_D D_D$ at $p \to \infty$. In another derivation, the parameter F represents a fraction of the penetrant population dissolved in microvoids, i.e. the Langmuir domains, which has the same mobility as the population dissolved in polymer matrix, i.e. the Henry's domain. When D_D and D_H are constant, this formulation also gives the same expression for the pressure dependence of P as Eq.(5).[35]

The dual-mode transport model gives the expression for the time lag, θ, as [31,35]

$$\theta = (l^2 / 6D_D) \left[1 + f(K,F,b,p) \right] \qquad (6)$$

where $f(K,F,b,p)$ is a function of the parameters listed. At very large values of bp, θ reduces to $l^2 / 6D_D$. However, at very low values of bp, the following limiting form applies: $\theta = (l^2 / 6D_D)[(1 + F) / (1 + FK)]$.

For cases involving little penetrant-penetrant interaction, it may be expected that sorption of a binary gas mixture A/B in the polymer matrix in the absence of plasticizing effect will occur essentially additively, that is, the Henry-mode solubility of a given gas is independent of the existence of another component. In the Langmuir mode of sorption, on the other hand, there will be competition between A and B for the fixed number of sites. This effect may cause significant depression in sorption of both penetrants in the binary mixture. Extension of the dual-mode sorption model to the binary mixture then gives the following expression for the concentration of A as a function of the partial 0pressures, p_A and p_B, of the two components[36]:

$$C_A = k_{DA}p_A + C'_{HA}b_Ap_A / (1 + b_Ap_A + b_Bp_B) \qquad (7)$$

Compared with Eq.(1), an additional term appearing in the denominator of the second term of Eq.(7) reflects the competition of the mixture for the limited microvoid capacity. The dual-mode model thus predicts a reduction in sorption of any gas, at a fixed partial pressure, as the partial pressure of a second gas is increased.

With a negligible downstream partial pressure of components A and B, the permeability coefficient for component A in the binary-component feed A/B is given by the relation[37].

$$P_A = k_D D_{DA}[1 + F_A K_A / (1 + b_Ap_A + b_Bp_B)] \qquad (8).$$

Thus the reduction in sorption of gas A mentioned before, which results from the competition in the presence of a second gas B, suppresses the permeability of component A. The predicted dependence of permeability coefficient on pressure is shown schematically in Fig.1. This so-called competitive sorption mixed gas permeability model and a similar model first proposed by Petropoulos[34], which is based not on concentration gradient but on chemical potential gradient, assume that the diffusion coefficients characteristic of the Henry and the Langmuir populations of sorbed gas molecules are unaffected by the presence of nearby sorbed gas molecules[38]. These models predict that the presence of a second gas B lowers gas A permeability only by reducing the sorption level of gas A. A recently proposed permeability model[39], which considers direct competition between penetrant molecules for both sorption sites and diffusion pathways, has been extended to include gas mixtures[38]. This competitive sorption/diffusion model also predicts similar dependence on pressure of the permeability coefficient. As described before, the predicted depression of the permeability coefficient for one component by the other has been substantiated in permeation behavior of several systems of a binary gas mixture and a glassy polymer[10-14,17,18,21,23,24].
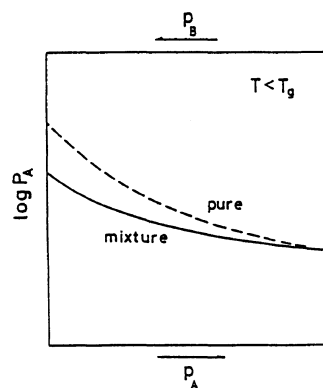

Figure 1. Schematic representation of pressure dependence, predicted by the dual-mode competitive sorption model, of permeability coefficient for component A in permeation of A/B mixture through a glassy polymer membrane. Total pressure is constant.

The formulations of the dual-mode sorption and transport models presented heretofore assume that the penetrant solubility in polymer matrix is very low, and that consequently the polymer is not plasticized to any extent by the penetrant. However, the plasticizing effects are known to be operative in a number of important practical applications such as membrane separation processes for mixtures of gases and vapors.

Extensions of the dual-mode sorption and transport models have been made by Stern and others in recent years. In the first success-

ful attempt, the dual-mode models have been extended to cases where the effective diffusion coefficient[40], or the mutual diffusion coefficients D_D and D_H[41], are dependent on concentration. This extension, which assumes Henry's law for the ordinary dissolution mode and is called the modified dual-mode transport model, has also examined the effects of antiplasticization or clustering of penetrant molecules[41]. Another extension of the dual-mode models assume that both solubility and diffusion coefficients are dependent on concentration and that some of the penetrant species sorbed in the Langmuir domains are partially immobilized[42]. This extended dual-mode transport model also explains well experimental data[43,44]. An attempt to extend the formulations to analyze permeation behavior of gas mixtures has not been made yet.

Although the dual-mode concept has provided a satisfactory representation of sorption and transport behavior in glassy polymers, it should be remembered that the concept is based on rather drastic assumptions and too simple physical picture of the complex system. Concerning the Langmuir domains, for instance, we know neither nature nor distribution of the microvoids, or holes. It is very difficult to imagine that circumstances in these microvoids are similar to those near the surface of a solid placed in gas phase of very low pressure, on which the adsorption behavior of penetrant molecules can be described on the basis of the kinetic theory of gases. Also, as has been noticed by Petropoulos[13], formal conformity to a Langmuir isotherm may be observed even when the isoenergetic site assumption is incorrect.

The transport processes of gases and vapors in glassy polymers, except for those of very small penetrant molecules, are controlled by the diffusion mechanism and concurrently by the relaxation mechanism of polymer chains. Under the circumstances, departures from normal Fickian diffusion behavior, non-Fickian anomalies, are usually observed. As described before, the expression of the transient time lag has also been given by the dual-mode transport model [Eq.(6)][35] and by its modified version[40]. However, time lags calculated by these expressions, on the basis of the relevant solubility and permeability data, do not agree with the corresponding experimental values when the non-Fickian kinetics is observed[13]. Also, no correlation has been found between parameter(s) and the relaxation characteristics of the polymer chains. Thus the dual-mode transport model is viewed by researchers in the field of materials science as a purely phenomenological treatment. Development of theoretical work on the molecular basis, which aims at analysis and interpretation of permeation behavior of gas mixtures, is hoped. Accumulation of experimental results which show clearly how the transport behavior correlates with microstructures of the glassy polymer membrane, for instance, with data of average intersegmental distance of polymer chains measured by WAXD[45-54], is considered to help much the theoreticians who will work on this subject. Also, results of measurements of dynamic viscoelastic behavior of the polymer membrane[55-57], which were performed to obtain knowledge of local molecular motions in the membrane, will be very helpful. Furthermore, the observation of the effects of physical aging on the dual-mode parameters[58,59] will give valuable information upon the development of the theoretical work.

The Free-Volume Model

The free-volume model, which has been developed by Stern et al. to represent permeation data of gas mixtures through membranes of rubbery polymer[21,59], is based on an earlier model proposed by Fujita and others[60,61]. The validity of Fujita's model has been demonstrated for a number of systems of organic vapor and amorphous polymer in the rubbery state, which exhibit rather strong dependence of the mutual diffusion coefficient on penetrant concentration, and also on temperature[1-3,5,12,14,61].

Fujita assumes that the mobility of a diffusing species, m_d, is a function of the average fractional free volume of the penetrant-polymer system, f, by the following equation:

$$m_d = A_d \exp(- B_d / f) \qquad (9)$$

where A_d and B_d are characteristic parameters which are assumed to be independent of penetrant concentration and temperature. A_d and B_d depend primarily on the size and shape of the penetrant molecule. The usual definition of m_d is

$$D_T = RTm_d \qquad (10)$$

where D_T is the thermodynamic diffusion coefficient for the penetrant-polymer system, R the gas constant, and T the absolute temperature of the system.

For relatively low penetrant concentrations, which are usually treated in permeation experiments, f at temperature T, pressure p, and volume fraction of penetrant v is represented by the relation[62]:

$$f (T,p,v) = f_s (T_s, p_s, 0) + \alpha (T - T_s) - \beta (p - p_s) + \gamma v \qquad (11).$$

Here f_s is the fractional free volume in the pure polymer at a reference temperature T_s and a reference pressure p_s, and the thermal coefficient α, the pressure coefficient β, and the concentration coefficient γ are characteristic parameters. γ represents the effectiveness of the penetrant component for the increase of free volume that is caused when it is dispersed in the given polymer. Equation (11) can be written in the form:

$$f = f_0 + \gamma v \qquad (12)$$

where

$$f_0 = f_s + \alpha (T - T_s) - \beta (p - p_s) \qquad (13).$$

Here f_0 is the fractional free volume of the pure polymer at T and p. If only pressure on the polymer membrane is that of the penetrant gas and the downstream pressure is negligibly smaller than the upstream one, then p in the above equation is equal to the latter pressure.

In the analysis of viscoelastic data of polymers by employing the WLF (Williams-Landel-Ferry) equation[63], which explains well the temperature dependence of the shift factor for the time-temperature superposition in terms of the free volume concept, T_s is usually taken as $T_g^0 + 50°C$, where T_g^0 is the glass transition temperature of a

given pure polymer. Also, Williams et al. have pointed out the fact that values of α for many polymers agree reasonably well with the difference between the thermal expansion coefficients above and below T_g[o].[83]

The extension of Eq.(12) and relevant equations to the case of permeation of binary gas mixtures is made based on the following assumptions[60,61]:

(1) The solubilities of both components in the polymer are sufficiently low to obey Henry's law,

(2) The effect of the two components on the free volume of the penetrant-polymer system is additive, i.e. the second term on the right hand side of Eq. (12) is represented by $\gamma_A v_A + \gamma_B v_B$, where v_A and v_B are respectively volume fractions of the components A and B, and γ_A and γ_B are the concentration coefficients, and

(3) The molecules of the two penetrants do not differ much in size and shape, which implies, in tern, that the diffusion coefficients for them are of the same magnitude.

The permeability coefficient for component A is then given by the following relation when the downstream pressure is negligibly small,

$$\ln P_A = C_A(T) + m_A(T)p_A + (B_{dA} / B_{dB}) m_B(T) \, p_B \qquad (14)$$

where $C_A(T)$, $m_A(T)$, $m_B(T)$, B_{dA}, and B_{dB} are parameters. The parameters $C_A(T)$ and $m_A(T)$, or $m_B(T)$, can be determined from the permeability measurements with pure component. The ratio B_{dA} / B_{dB} can be estimated approximately from the relation $B_{dA} / B_{dB} = (d_A / d_B)^2$ where d is the molecular diameter of the penetrant. Equation (14) predicts that P_A in permeation of a binary gas mixture A/B is greater than that in permeation of pure gas A, as shown in Fig.2. Thus, the extended free-volume model predicts opposite pressure dependence of the permeability coefficient to that predicted by the dual-mode transport model. It has been reported that Eq.(14) described satisfactorily the permeation behavior of several systems of binary gas mixture and rubbery polymer[18,21,22,59].

A new version of the free-volume model has been developed by Vrentas and Duda[64]. This model is based on the free-volume models of Cohen and Turnbull[65] and of Fujita[60,61] with the Bearman's relation[66] between the mutual diffusion coefficient and the friction coefficient. The model employs also the Flory-Huggins polymer solution theory[67] and the entanglement theory of Bueche[68]. Though this complex formulation explains well the concentration dependence of the mutual diffusion coefficient for the solvent-polymer systems[69,70], this model requires more parameters to be determined, which reduce the
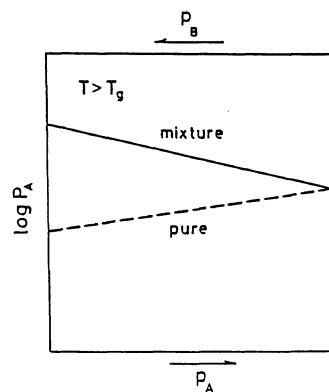

Figure 2. Schematic representation of pressure dependence, predicted by the free-volume model, of permeability coefficient for component A in permeation of A/B mixture through a rubbery polymer membrane. Total pressure is constant.

utility of the model. An extension of this model to the transport of gas/vapor mixtures has not been attempted yet.

Contrary to the case of the dual-mode transport model, the parameters of Fujita's model can be determined from either of transport and viscoelastic measurements of penetrant-polymer systems[1-3,5,14,60,61]. The value of f_0 at an atmospheric pressure can be calculated if $f(T_g^{\,0}, 1\ atm, 0)$, $T_g^{\,0}$, and α are known. For amorphous polymers the "universal" values, $f(T_g^{\,0}, 1\ atm, 0) = 0.025$ and $\alpha = 4.8 \times 10^{-4} K^{-1}$, suggested by Williams, Landel, and Ferry[63,71], offer a first estimate of f_0 at 1 atm when $T_g^{\,0}$ is known.

These situations allow membranologists to discuss problem concerned with transport (diffusion) in polymers from the same standpoint with researchers in other fields of materials science. To analyze the permeation behavior of gases and vapors, however, the free-volume model has no corresponding concept of sorption like the dual-mode model. For organic penetrant and rubbery polymer systems, the permeation behavior has often been discussed in terms of the free-volume concept[2,3,12,61,71] and the Flory-Huggins polymer solution theory[67].

PERMEATION OF GAS/VAPOR MIXTURES THROUGH A DISUBSTITUTED POLYACETYLENE

Nonporous membrane of a disubstituted polyacetylene, poly[1-(trimethylsilyl)-1-propyne] [P(TMSP)], which was prepared by solvent casting, shows extremely high permeability for gases, such as oxygen and nitrogen[72-76] For example, the permeability coefficient, P, for oxygen through the glassy P(TMSP) membrane at room temperature is about ten times as high as that through polydimethylsiloxane membrane, which has been known till then to show the highest value of P among nonporous polymer membranes. The high gas permeability exhibited by newly prepared membranes, however, decreased very much after keeping the membrane in vacuo for a certain period: for example, P for isobutane at 30°C decreased by about two orders of magnitude over the period of about 100 days under vacuum[74]. Similar decrease of the gas permeability with time or by thermal treatments has been reported by Takada and others[73] and also by Nakagawa and others[76]. Contrary to these results, Langsam and Robeson reported no change in either gas permeability or selectivity with solvent-cast membranes[77].

The very high gas permeability of the P(TMSP) membrane and the noticeable physical aging effect on it have been interpreted by taking into account of characteristic structures of the membrane. The scanning electron microscopic observations and adsorption experiments of nitrogen at liquid nitrogen temperature have revealed that the membrane has considerably rough surface of large total area, about 550 $m^2 g^{-1}$ [78]. Also, the existence of many holes of cylindrical shape was viewed in the scanning electron micrographs. These are consistent with the relatively low bulk density, less than 0.75 g cm^{-3}. All these observations indicate that the P(TMSP) membrane has very loose structures compared with membranes of other glassy polymers.

Extraordinarily high permeability of the P(TMSP) membrane is undoubtedly due to the characteristic structures mentioned above. Since the membrane has not shown appreciable changes in the feature of rough surface and in number and the size of the holes after keeping in a vacuum for long time, the physical aging process is considered as mostly due to slow coalescence of intersegmental gaps between main

chains. Slow narrowing of the wider intersegmental distances is probably caused by very high mobility of the side groups of P(TMSP) discussed later.
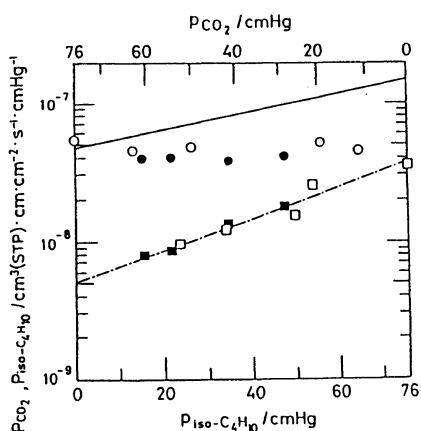
Permeability coefficients for gases through P(TMSP) membranes which have been aged physically for more than three months, however, still are on high levels comparable with those exhibited by membranes of rubbery polymers. Measurements of permeation of gas mixtures through the aged membrane were made by employing three binary gas mixtures comprised of carbon dioxide, isobutane, and acetone at total pressure of 1 atm.

In Fig.3, P for each component gas in the system of carbon dioxide/isobutane and P(TMSP) are plotted by filled symbols against the respective partial pressures in the mixture.[79,80] Permeability coefficients for pure components are also shown in the figure by unfilled symbols. Values of P for pure carbon dioxide are independent of pressure, while those for pure isobutane increase with increasing pressure. The $T_g{}^\circ$ of this polymer is thought to be above 200°C,[81] and the temperature of the experiments is far below $T_g{}^\circ$. Nevertheless, the observed dependence of P on p for both pure components does not conform to the predicted dependence of the dual-mode transport model, Eq.(5), but is partly in agreement with the prediction of the free-volume model.

In permeation of this gas mixture, plots of P for the respective components coincide well with those obtained in pure-component permeation; namely, no effect of one component on another was observed in mixed gas permeation. This implies that both components permeate through the P(TMSP) membrane independently.

Values of ln P for both components in mixed gas permeation have been calculated by the extended free-

Figure 3. Dependence of permeability coefficients for carbon dioxide and isobutane on their respective partial pressures at 30°C. Total pressure of the gas mixture is 1 atm. ○ : CO_2 (pure), ● : CO_2 (in mixture), □ : iso-C_4H_{10} (pure), ■ : iso-C_4H_{10} (in mixture). Calculated values, ——— : CO_2, ——·—— : iso-C_4H_{10}.

volume model, Eq.(14). As is seen in Fig.3, the P vs.p relation thus calculated is in good agreement with the observed relation for isobutane but not for that for carbon dioxide.

In permeation of the mixture of carbon dioxide and acetone vapor, P for carbon dioxide was influenced a little by the partner component acetone which showed positive dependence of P on pressure. The values of P for carbon dioxide calculated by Eq.(14) were 1.5 to 2.0 times as high as the observed values in the pressure region studied. On the other hand, the permeation of carbon dioxide did not interfere with that of acetone. This has been attributed to very low solubility of carbon dioxide in the P(TMSP) membrane[79].

The values of P for isobutane and those for acetone in permeation of the mixtures were higher than the respective pure-component values. The values of P for both components increased with increasing partial pressure of acetone in the mixture. This was explained by high solubility of acetone in P(TMSP)[78,80]. The agreement between the experimental and the calculated values, by employing Eq.(14), of P varied from 25% to a maximum of about 50%. By taking into consideration of the simplifying assumptions and also of the experimental error in the determination of P, it is concluded that the permeation behavior of the isobutane/acetone mixtures, and most behavior of other two gas mixtures also, are well explained in terms of the extended free-volume model.

It should be noticed here again that all the systems of gas mixture and P(TMSP) are not in the rubbery state but in the glassy state. Nevertheless most behavior observed conforms to the prediction based upon the free volume concept. This suggests that local environments in the P(TMSP) membrane, which govern the unit jump of the diffusing molecule in the transport processes, would resemble to a considerable extent those in membranes of rubbery polymers. The local molecular motions have been studied by high-resolution solid-state ^{13}C and ^{29}Si NMR spectroscopy[82,83]. The results of the NMR studies have revealed high mobility of the substituents of P(TMSP) at room temperature. The loose microstructures mentioned before may be another important factor to explain the local environments.

The results of observations and measurements with P(TMSP) membrane described above show clearly that permeation behavior of gases and gas mixtures through polymer membrane should be interpreted on the basis of information about local molecular motions and structures of the membrane. Formal application of either the dual-mode transport model or the free-volume model, which conforms to respectively whether the bulk penetrant-polymer system is in the glassy or the rubbery state, is sometimes possible to make wrong prediction of permeation behavior of penetrant(s). Detailed knowledge of structures and molecular motions in polymer membrane, which is obtained from various kinds of measurements, is considered indispensable for further development of theoretical work of transport in polymer membrane.

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