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MECHANISMS OF GAS PERMEATION THROUGH POLYMER MEMBRANES

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SUMMARY TECHNICAL REPORT

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MECHANISMS OF GAS PERMEATION THROUGH POLYMER MEMBRANES

SUMMARY

The main objective of this study is to provide the basic knowledge required for the development of new, energy-efficient membrane processes for the separation of gas mixtures. Considerable progress has been made in the following research projects concerned with the solution and transport of gases in glassy polymer membranes:

1. It has been found that the mechanism of gas solution and tranport in some poly(alkyl methacrylates) does not undergo the change observed with many other gas/polymer systems when the temperature is lowered through Tg, the glass-transition temperature of the polymers. This change is reflected in the dependence of the gas permeability, diffusion, and solubility coefficients ($\bar{P}$, D, and S, respectively, on the penetrant gas presure (p) or concentration (c) in the polymer. $\bar{P}$, D, and S become strongly nonlinear functions of p or c below Tg. In addition, plots of log $\bar{P}$, log D, and log S versus 1/T, the reciprocal absolute temperature, exhibit changes in slope at Tg. This behavior which can be represented quantitatively by a "dual-mode sorption" model. Such a behavior has been reported for many penetrant in a variety of glassy polymers, but, was not observed with the poly(alkyl methacrylates) studied even at temperatures 30-40°C below Tg.

2. The absence of dual-mode sorption behavior described above was attributed to the fact that the "excess" free volume in some glassy poly(alkyl methacrylates) is smaller than in other glass polymers. We predicted accordingly that the onset of dual-mode sorption behavior should be observed with the gas/poly(alkyl methacrylate) systems of this study at temperatures considerably below Tg, for the reasons discussed in this report. Our prediction was

confirmed by suitable gas solubility measurements at elevated pressures. These phenomena have not been reported previously in the literature.

3. The internal consistency of the dual-mode sorption model was tested and confirmed by a theoretical study of gas absorption/desorption kinetics in glassy polymers. The theoretical results were found to be in good agreement with pertinent experimental data from the literature.

4. The in-plane diffusion of small fluorophore molecules in glassy poly-(1-trimethylsylil-1-propyne) membranes has been studied by means of a new technique known as laser fluorescence photobleaching recovery. It was found that the penetrant molecules had two different mean mobilities. These mobilities were characterized by two diffusion coefficients which differed by two orders of magnitude. Such a behavior is consistent with the dual-mode sorption model of gas transport in glassy polymers, although it could be caused also by other factors.

5. The solubility of H_2 in a glassy polymer poly(vinyl acetate), (PVAc), was measured for the first time at elevated pressures, in order to determine whether very small molecules also exhibit dual-mode sorption behavior. The solubility of H_2 in PVAc was found to exhibit the type of dependence on pressure described by the model. The possible effects of penetrant size on the solubility and transport of gases in glassy polymers is discussed in light of these results.

PUBLICATIONS

It is expected that the above studies will result in the eight publications listed at the end of this report.

I. GENERAL CONSIDERATIONS

A. Phenomenology of Gas Permeation

The permeation, or transport, of gases through nonporous polymer membranes generally occurs by a "solution-diffusion" mechanism (1-6), which is controlled by the molecular diffusion of the penetrant gas in the polymer matrix. Solution equilibrium is established between the penetrant in the gas phases at the membrane interfaces and the penetrant dissolved in the membrane at these interfaces. The steady-state rate of gas permeation, J_s, through unit area of a homogeneous, isotropic, and planar (sheet) membrane of thickness, δ, when the pressures p_h and p_ℓ ($<p_h$) are maintained at the membrane interfaces, is given by the realtion:

$$J_s = \bar{P}\,(p_h - p_\ell)/\delta, \tag{1}$$

where $\bar{P}$ is a permeability coefficient which depends on the nature of the penetrant/polymer system, the temperature and, in the most general case, on both p_h and p_ℓ. It can be shown that (1-6):

$$\bar{P} = \bar{D}\cdot S, \tag{2}$$

where $\bar{D}$ is a mean diffusion coefficient defined by the relation:

$$\bar{D} = \int_{c_\ell}^{c_h} D(c)dc/(c_h - c_\ell) \tag{3}$$

and, when $p_h >> p_\ell$, S is a solubility coefficient defined by:

$$S = c/p|_h \quad ; \tag{4}$$

D(c) is the local mutual diffusion coefficient for the penetrant/polymer system; c is the penetrant concentration in the polymer at pressure p; and subscripts h and ℓ denote the high-pressure ("upstream") and low-pressure ("downstream")

membrane interfaces. D(c) is a kinetic factor which depends on the size and shape of the penetrant molecules, the relative motions of the penetrant molecules and of the surrounding polymer chain segments, and the pertinent intermolecular forces. S is a thermodynamic factor which depends mainly on the intermolecular forces and, in the case of glassy polymers, on the "excess" free volume of the polymers (which is discussed later).

Consequently, in order to elucidate the mechanisms of gas transport in and through polymers it is necessary to determine $\bar{P}$, D, and S for selected penetrant/polymer systems as a function of penetrant pressure (or concentration) and temperature. These measurements must then be related to the chemical and physicochemical properties of these systems.

B. The Dual-Mode Sorption Model

The mechanisms of gas transport in polymers (by solution and diffusion) and across polymer membranes (by permeation) are known to be very different at temperatures above and below the glass transition temperature, T_g, of the polymers (6-11). The difference in these mechanisms is reflected in the significant differences observed in the dependence of $\bar{P}$, D, and S on the pressure (or concentration) of the penetrant gases and on the temperature.

For example, the solubility of light gases (such as N_2, CH_4, and CO_2) in "rubbery" polymers, i.e., at temperatures above T_g, is often sufficiently low to be within the Henry's law limit. Therefore, the solubility coefficients, S, for such penetrant/polymers systems are independent of pressure, in some cases, over a wide range of temperatures and pressures. $\bar{P}$ and D for such systems also are independent of pressure (or concentration) or increase linearly with these variables. By contrast, $\bar{P}$, D, and S for light gases in many "glassy" polymers, i.e., at temperatures below T_g, are highly nonlinear functions of the

penetrant pressure (or concentration). Here D is the effective (measured) diffusion coefficient.

The nonlinear dependence of $\bar{P}$, D, and S on penetrant pressure (or concentration) can be described satisfactorily in terms of a "dual-mode sorption" model (2,3,6,8-11). This model postulates that a gas dissolved in a glassy polymer consists of two distinct molecular populations. The concentration of one population is related to the total gas pressure by Henry's law, while the concentration of the other population is related to the pressure by the Langmuir isotherm. Local equilibrium is assumed to exist between the two molecular populations. Moreover, it is assumed that the two populations may have different mean mobilities. The quantitative formulation of the dual-mode sorption model is presented in the attached Renewal Proposal. The environments of the molecular populations dissolved by the Henry's law and Langmuir modes are referred hereafter for expediency as "domains", even though the Langmuir domains may be of near molecular size (see Renewal Proposal).

Glassy polymers contain an "excess" free volume, compared to the free volume the polymers would have under conditions of thermodynamic equilibrium [see the shaded area in Figure 1(a)]. This excess free volume is a consequence of the non-equilibrium nature of the glassy polymer state.

II. SUMMARY OF RESULTS

Several problems related to the solution and transport of light gases in glassy polymers have been investigated in the framework of the dual-mode sorption mechanism. The results of these investigations are summarized below.

A. Effect of Glass Transition on Gas Solution and Transport in Polymers

The objective of this study was to examine the changes that occur in the mechanisms of gas solution and transport in polymers in their glass transition region. These changes are reflected in the type of dependence of $\bar{P}$, D, and S on penetrant gas pressure (or concentration in the polymer) and on temperature. As mentioned above, $\bar{P}$, D, and S for many penetrant/polymer systems have been found to become strongly nonlinear functions of the pressure (or concentration) at temperatures below T_g (4,6-11). Additionally, plots of ℓn D and ℓn S versus 1/T, the reciprocal absolute temperature, exhibit "breaks" (discontinuities) at or near T_g of some systems at constant pressure. This behavior indicates a change in the energy of activation for diffusion and of the enthalpy of solution in the glass transition region.

The dual-mode sorption model requires that $\bar{P}$ and S should decrease, and D (effective) should increase, as the penetrant pressure (or concentration) is increased. At sufficiently high pressures, $\bar{P}$ and D tend toward well defined limiting values (2,3,6,8-10). The dual-mode sorption model also predicts that $\bar{P}$, D, and S should reach constant values at sufficiently low pressures. A change in the slopes of plots of ℓn D and ℓn S versus 1/T should then be observed in the glass transition region (14).

In order to test the above behavior, $\bar{P}$, D, and S for CH_4, C_2H_6, and n-C_4H_{10} in poly(*n*-butyl methacrylate) (P*n*BMA) and poly(ethyl methacrylate) (PEMA) have been determined at subatmospheric pressures by either "time-lag" or absorption-desorption measurements, or both, as well as by steady-state permeability measurements at elevated pressures. All measurements were made over a temperature range that encompassed the glass transition region of the polymers. Additionally, the solubility of CH_4, C_2H_6, Ar, and CO_2 in P*n*BMA (T_g=22-35°C), PEMA (T_g=65°C) and poly(*n*-propyl methacrylate) (P*n*PMA, T_g=35°C)

was determined at pressures up to 30 atm. and temperatures between 30 and -25°C.

Examples of the many experimental results obtained are shown in Figures 2-9 [refs. (12-15)]. It should be noted that D in these figures is the effective diffusion coefficient. $\bar{P}$, D, and S for CH_4 and C_2H_6 in the poly(alkyl-methacrylates) studied were found to be independent of penetrant pressure (or concentration in the polymer), at least within the experimental error. This behavior, which is typical for rubbery polymers (i.e., at temperatures above T_g), was exhibited by the above-mentioned penetrant/polymer systems both above and below T_g. Contrary to previous experience, the nonlinear dependence of $\bar{P}$, D, and S on pressure (or concentration) predicted by the dual-mode sorption model was not observed even at temperatures 25-30°C below T_g. Nor were discontinuities observed in the plots of ℓn D and ℓn S versus 1/T in the experimental temperature range. The onset of dual-mode sorption behavior is commonly observed with other penetrant/polymer systems at temperatures closely below the glass transition [e.g., refs. (6,10,17)].

The absence of dual-mode sorption behavior in the poly(alkyl methacrylates) studied may be due to the fact that no significant Langmuir domains are formed or, in other words, that the "excess" free volume in these polymers is very small under the conditions of these studies. The extent of this excess free volume is related to $\Delta\alpha$, the difference between the coefficients of thermal expansion of a polymer in the rubber state, α_r, and in the glassy state, α_g. Polymers with a large $\Delta\alpha$ tend to have a larger excess free volume than polymers with a small $\Delta\alpha$, as is illustrated by the shaded areas in Figures 1(a) and 1(b). Table I shows that the poly(alkyl methacrylates) studied have smaller $\Delta\alpha$'s than other glassy polymers which are known to exhibit dual-mode sorption behavior.

Figure 1(b) indicates that the excess free volume increases as the temperature is lowered, which suggests that dual-mode sorption behavior might occur

at a sufficiently low temperature below T_g. This hypothesis appears to be confirmed by the high-pressure solubility measurements with CH_4 and Ar in P*n*BMA, PEMA, and PPMA. For example, Figures 10-13 show solubility isotherms for some of these penetrant/polymer systems at temperatures both above and below T_g. The isotherms are seen to be linear even at temperatures well below T_g, indicating that Henry's law is obeyed under these conditions. Only at -25°C do the solubility isotherms exhibit a slight concavity relative to the pressure axis, as predicted by the dual-mode sorption model; this temperature is over 40°C below the T_g of P*n*BMA and 90°C below the T_g of PEMA. Similar measurements with C_2H_6 and CO_2 showed that these penetrants plasticized the poly(alkyl methacrylates) at the lower temperatures, while *n*-C_4H_{10} had a plasticizing effect at all temperatures studied. This was due to the higher solubility of the penetrant.

B. Effect of Plasticization on the Transport of Gases through Polymers

Membrane separation plants sometimes process gas mixtures containing one or more gases which plasticize (swell) the polymer membranes used. Such gases, e.g., CO_2 and organic vapors, often exhibit a high solubility in polymers, compared to that of lighter, less condensable gases. The effect of plasticization is to modify the permeability of the polymer membranes to the other components of the gas mixture being separated. The permeability of the membranes is usually increasedaat higher penetrant pressures, but their gas selectivity may be reduced.

In the present study, the effects of plasticization on the transport of gases and vapors in and through glassy polymers was examined from the viewpoint of the dual-mode sorption model with partial immobilization (3,6,9-11,12). This model assumes the existence of two penetrant populations with different mobilities in the Henry's law and Langmuir domains of the glassy polymers (see

previous section). The penetrant mobilities are characterized by their respective mutual diffusion coefficients D_D and D_H. In the original version of the model, D_D and D_H were assumed to be constant (4,7,8). In order to describe the plasticization of a glassy polymer by penetrant gases, D_D and D_H have been taken to be exponential functions of the penetrant concentration in the two domains (17):

$$D_D = D_D(0) \exp (\beta_D c_D) \tag{5}$$

and

$$D_H = D_H(0) \exp (\beta_H c_H), \tag{6}$$

where c_D and c_H are the concentrations of the penetrant in the Henry's law and Langmuir domains, respectively; $D_D(0)$ and $D_H(0)$ are the mutual diffusion coefficients in the limits $c_D \to 0$ and $c_H \to 0$, respectively; β_D and β_H are empirical constants that characterize the magnitude of the plasticization effects. Plasticization is negligible when $\beta_D = \beta_H = 0$

Equations (5) and (6) lead to the following expressions for the effective (measured) diffusion coefficient, D:

$$D = D_D(0) \exp (\beta_D c_D) \left[\frac{1+FK/(1+\rho_2)^2}{1+K/(1+\rho_2)^2} \right], \tag{7}$$

and the effective permeability coefficient, $\mathcal{P}_{eff}$ (in dimensionless form):

$$\mathcal{P} = \frac{1}{\rho_2} \int_0^{\rho_2} \exp \left(\frac{\beta_D y}{\alpha} \right) \left[1 + \frac{FK}{(1+y)^2} \right] dy, \tag{8}$$

where K and α are parameters determined from solubility measurements; $F = D_H/D_D$; y is a "dummy" integration variable; ρ_2 is adimensionless "upstream" pressure, ($\rho_2 = \alpha c_D = b p_2$, where b is a parameter also obtained from solubility measurements), and p_2 is the penetrant pressure on the "upstream" side of the

membrane.

A plot of D versus the dimensionless pressure ρ_2 according to eqn. (7) is shown in Figure 14 for selected values of $F(0)\left[= D_D(0)/D_H(0)\right]$, K, α, and β_H, and for different values of β_D. Plasticization ($\beta_{H>0}$, $\beta_{D>0}$) causes an increase in D with increasing ρ_2. D can also decrease with increasing ρ_2, e.g., for $\beta_{D<0}$, due to antiplasticization or clustering of penetrant molecules. Both these effects can occur simultaneously, each effect predominating in a different pressure range.

A plot of $\mathcal{P}$ versus ρ_2 according to eqn. (8) for selected parameter values is shown in Figure 14. $\mathcal{P}$ first decreases with increasing dimensionless pressure, ρ_2, as predicted by the dual-mode sorption model, then increases due to the plasticization of the polymer by the penetrant.

This study provides information on the effects of plasticization on the penetrant transport in the Henry's law and Langmuir domains separately.

C. Dual-Mode Sorption Kinetics of Gases in Glassy Polymers

It has been mentioned earlier that the transport of gases in many glassy polymers by diffusion, and through glassy polymer membranes by permeation, can be described by means of the "dual-mode" sorption model (2,3,8-11). The dependence of diffusion and permeability coefficients on penetrant gas pressure, or concentration in a polymer, can be characterized by the model parameters. These parameters can be determined from solubility measurements in conjunction with absorption/desorption or "time-lag" measurements (see previous section).

The present study has addressed the inverse problem, namely, the prediction of the absorption/desorption behavior of a gas in a glassy polymer from a specified set of dual-mode sorption parameters (18). As is shown in Figures 16 and 17, satisfactory agreement is obtained between reported absorption rates of sul-

fur dioxide in glassy polycarbonate (19), as well as of water vapor in KAPTON* polyimide (20), and the rates predicted by the dual-mode sorption model. The present study also confirms the consistency of the dual-mode sorption model (18).

D. **Study of Dual-Mode Transport by Fluorescence Photobleaching Recovery**

The dual-mode sorption model discussed earlier describes satisfactorily the solution and transport behavior of many gases in a variety of glassy polymers. The model has been found to be useful for the correlation and comparison of solubility, diffusivity, and permeability data. However, the model has been challenged by some investigators [e.g., refs. (21-24)] because almost all evidence for the postulated existence of penetrant populations with two different mean mobilities has been obtained by measurements of an indirect nature (see previous sections).

Several investigators have attempted to use nuclear magnetic resonance to ascertain the validity of the dual-mobility hypothesis (21,22,25,26). The results of these studies are ambiguous or contradictory. Consequently, a new and promising experimental technique known as "laser fluorescence photobleaching recovery" (27,28) has been employed at Syracuse University, in collaboration with Prof. B. Ware, in order to test the above hypothesis.

The principle of fluorescence photobleaching recovery (FPR) is straightforward. At the start of a measurement, a fluorophore (a fluorescent dye) is uniformely dispersed in the glassy polymer membrane of interest. A burst of light from a laser is initially used to destroy the dye molecules in selected regions of the sample. The diffusion of remaining dye molecules into the "bleached" regions is then monitored by means of a low-intensity laser. The

*Trade name of E.I. du Pont de Nemours & Co.

time scale over which the bleaching dissipates is a function of the size of the bleached region and the rate of diffusion of the fluorescent dye.

It should be noted that the (net) direction of diffusion in FPR is parallel to the membrane interfaces, rather than perpendicular to these interfaces as is the case in gas or liquid permeation measurements. If glassy polymers contain two different types of morphological domains, as postulated by the dual-mode sorption model, the fluorescent dye molecules in these domains should have different mobilities. In other words, the dye molecules should diffuse throuh the two domains at different rates characterized by two different diffusion coefficients.

The polymer used in the present study was glassy poly (1-trimethylsilyl-1-propyne)(PMSP) because its very large free volume (29) permits the diffusion of bulky dye molecules. The fluorescent dye was 4-[N-(iodoacetoxy) ethyl-N-methyl] amino-7-nitrobenz-2-oxa-1,3-diazole (IANBD). FPR measurements with this dye/ polymer system at 40, 60, and 80°C. consistently indicated the presence of two IANBD populations diffusing in PMSP on different time scales. The diffusion coefficients of these populations differed by about two orders of magnitude. Thus, the values of the diffusion coefficients for the "slow" dye population increased from 9.0×10^{-13} cm^2/s at ~ 40°C to ~ 3.9×10^{-11} cm^2/s at 80°C, whereas the values of these coefficients for the "fast" dye population were 2.0×10^{-10} and 2.7×10^{-9} cm^2/s, respectively. The energies of activation for diffusion were found to be 23 and 14 kcal/mol for the "slow" and "fast" IANBD populations, respectively.

The above results indicate that IANDB dye dispersed in a PMSP membrane consists of two main penetrant populations with greatly different mean mobilities. These results are consistent with the dual-mode sorption model of gas solution and transport in glassy polymers.

E. Solubility of Hydrogen in Glassy Poly(Vinyl Acetate) at Elevated Pressures

The solubility of H_2 in poly(vinyl acetate)(PVAc, $T_g \approx 23°C$) was measured gravimetrically at 5.0 and -5.0°C at pressures up to 20 atm. This study had the following objectives:

1) The dual-mode sorption model of gas solution and transport in glassy polymers (2,3,6,8-11) predicts that the onset of dual-mode sorption behavior should be accompanied by a change in the slopes of plots of ℓn S and ℓn D versus 1/T at or near the T_g of the polymers. Dual-mode sorption behavior is characterized by a strongly nonlinear dependence of the solubility coefficients, S, and diffusion coefficients, D, on penetrant gas pressure or concentration in the polymers.

Meares (31) has reported that log S and ℓn D versus 1/T plots for H_2 and other light gases in PVAc exhibited discontinuities at 15-18°C (near T_g). These measurements were made at pressures which were too low to show dual-mode sorption behavior (12). However, the discontinuities in the ℓn S and ℓn D versus 1/T plots observed by Meares suggested that the H_2/PVAc system should exhibit dual-mode sorption behavior at higher pressures.

2) Some investigators have hypothesized that a change in the slope of a ℓn S or ℓn D versus 1/T plot at the T_g of a penetrant/polymer system will occur only if the size of the penetrant molecules exceeds a certain critical size which depends on the mean free volume of the polymer (31-34). If this hypothesis is correct, the penetrant size should also be a factor in the appearance of dual-mode sorption behavior at or near T_g. Dual-mode sorption behavior has been observed with CO_2 in PVAc (35), and consequently it was interesting to determine whether it would be observed also with a smaller molecule, such as H_2.

3) No solubility data appear to have been reported for H_2 in any type

of glassy polymer at elevated pressures.

The results of the present study are shown in Figure 22 in the form of isothermal plots of the H_2 concentration in PVAc, c, versus the H_2 pressure, p. The plots have the shape predicted by the dual-mode sorption model, and can be represented accordingly by the relation:

$$c = k_D\, p + c'_H bp/(1+bp), \qquad (9)$$

where k_D is a solubility coefficient in Henry's law limit; c'_H is a "Langmuirsaturation" constant; and b is a "Langmuir affinity" constant. Values of the parameters k_D, c'_H, and b are listed in Table II. The very low values of k_D and c'_H compared to those of other penetrant/polymer systems reflect the low solubility of H_2 in the Henry's law and Langmuir domans of PVAc. Hence, the relationship between the change in slope in the ℓn S versus 1/T plot and the onset of dual-mode sorption behavior, as the temperature is lowered through T_g is again confirmed. It should be noted that the solubility coefficient S (≡ c/p) can be calculated from eqn. (9).

PUBLICATIONS BASED ON THIS STUDY

In Print:

1. Stern, S. A., Vakil, U. M., and Mauze, G. R., "Solution and Transport of Light Gases in Poly(*n*-Butyl Methacrylate) in the Glass Transition Region. I. Absorption-Desorption Measurements", J. Polym. Sci.: Part B: Polym. Phys., 27(2), 405-429 (1989).

2. Zhou, S. and Stern, S. A., "The Effect of Plasticization on the Transport of Gases in and through Glassy Polymers", J. Polym. Sci.: Part B: Polym. Phys., 27 205-222 (1989).

Accepted for Publication:

3. Subramanian, S. and Stern, S. A., "Dual-Mode Sorption Kinetics of Gases in Glassy Polymers", Accepted for publication in J. Polym. Sci.: Part B: Polym. Phys.

4. Stern, S. A., Zhou, S., Arauz-Lara, J. L., and Ware, B. R., "Evidence of Dual-Mode Diffusion of Small Molecules in Poly(1-Trimethylsilyl-1-Propyne) from Fluorescence Photobleaching Recovery", Accepted for publication in Polym. Letters.

Submitted for Publication:

5. Zhou, S. and Stern, S. A., "Solubility of H_2 in Glassy Poly(Vinyl acetate) at Elevated Pressures", Submitted for publication in J. Polym. Sci.: Part B: Polym. Phys.

In Preparation:

6. Itoh, K. and Stern, S. A., "Solution and Transport of Light Gases in Poly (*n*-Butyl Methacrylate) in the Glass Transition Region. II. Time-Lag Measurements".

7. Stern, S. A. and R. Vaidyanathan, "Solution and Transport of Light Gases in Poly(Ethyl Methacrylate). Absorption-Desorption Measurements".

8. Zhou, S. and Stern, S. A., "The Solution of Gases in Poly(Alkyl Methacrylates) at Elevated Pressures."

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14. S. A. Stern and R. Vaidyanathan, "Solution and Transport of Light Gases in Poly(Ethyl Methacrylate) in the Glass Transition Region. Absorption-Desorption Measurements", in preparation.

15. S. Zhou and S. A. Stern, "Solubility of CH_4, C_2H_6, Ar, and CO_2 in Glassy Poly(Alkyl Methacrylates) at Elevated Pressures", in preparation.

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TABLE I

VARIATION IN THE COEFFICIENT OF THERMAL EXPANSION AT Tg FOR VARIOUS POLYMERS

Polymer	Tg (°C)	α_r	α_g	$\Delta\alpha$	$\frac{\Delta\alpha}{\alpha_g}$
		$(cm^3/g°K) \times 10^4$			
Poly(methyl acrylate)	3	5.13	1.74	3.39	1.948
Poly(vinyl acetate)	32	6.9	2.4	4.5	1.875
Poly(ethylene terephthalate)	67	9.87	1.87	8.0	4.278
Polycarbonate	150	5.16	1.53	4.34	2.837
Poly(*n*-butyl methacrylate)	27	6.26	3.85	2.41	0.626
Poly(ethyl methacrylate)	65	3.45	2.11	1.34	0.635

TABLE II

DUAL-MODE SORPTION PARAMETERS FOR H_2 IN POLY(VINYL ACETATE).

Temperature, t (°C)	Dual-Mode Sorption Parameters, k_D $\left[\frac{cm^3(STP)}{cm^3 polym.\cdot atm}\right]$	C'_H $\left[\frac{cm^3(STP)}{cm^3 polym.}\right]$	b $(atm)^{-1}$
5.0	0.0173	0.027	1.84
-5.0	0.0146	0.096	1.88

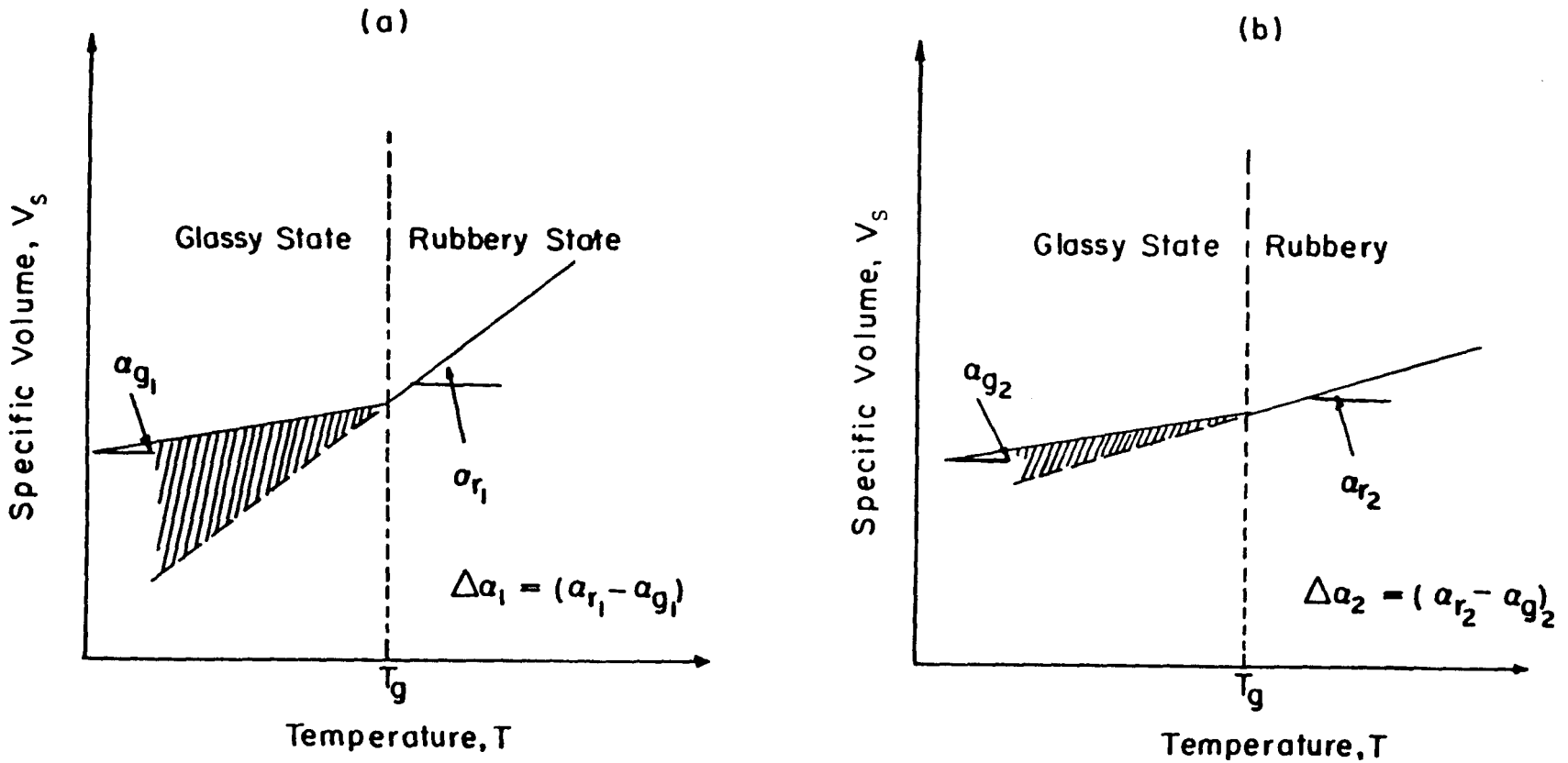

Figure 1. Typical Temperature Dependence of the Specific Volume of Two Polymer Samples Having Different Coefficients of Thermal Expansion ($\alpha 1 > \alpha 2$).

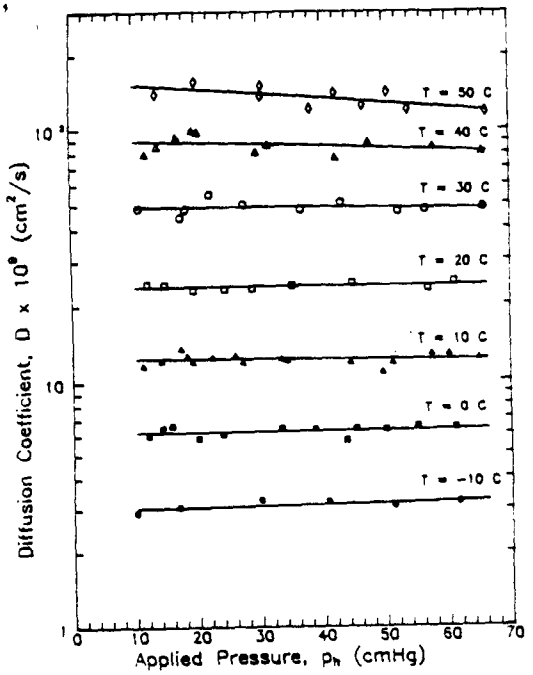

Figure 2. Diffusion Coefficients for Ethane in Poly(n-Butyl Methacrylate) from Time-Lag Measurement.

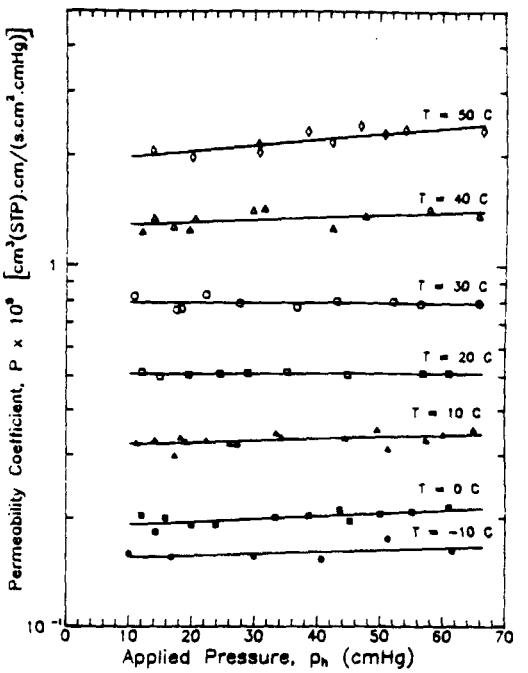

Figure 3. Permeability Coefficients for Ethane in Poly(n-Butyl Methacrylate) from Time-Lag Measurement.

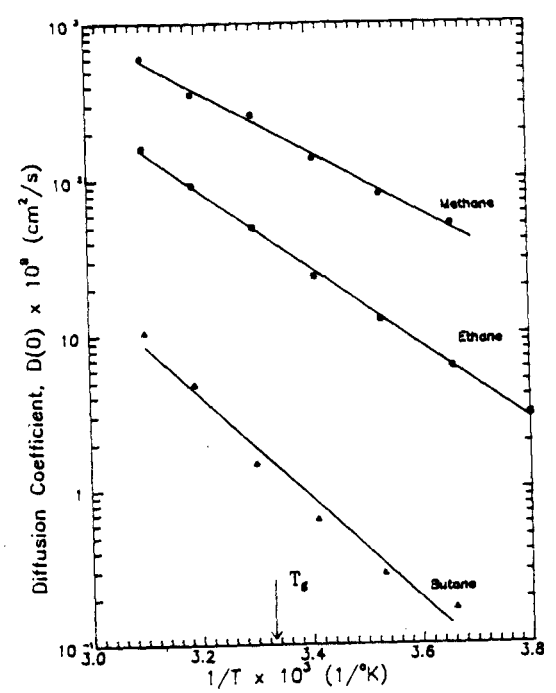

Figure 4. Temperature Dependence of Diffusion Coefficients for Methane, Ethane, and n-Butane in Poly(n-Butyl Methacrylate).

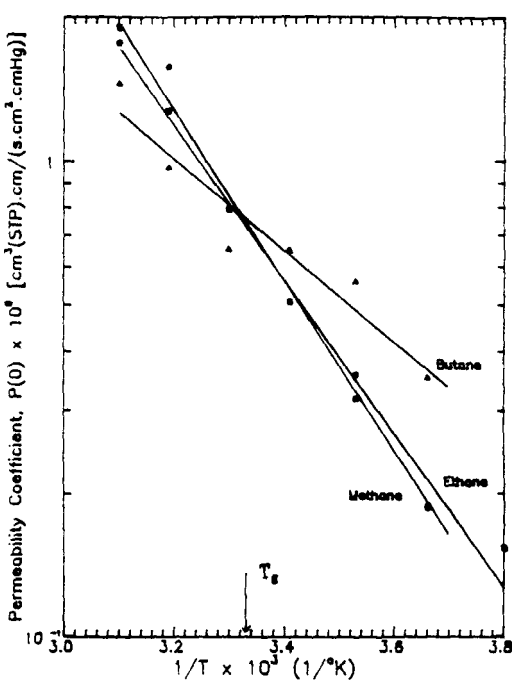

Figure 5. Temperature Dependence of Permeability Coefficients for Methane, Ethane, and n-Butane in Poly(n-Butyl Methacrylate).

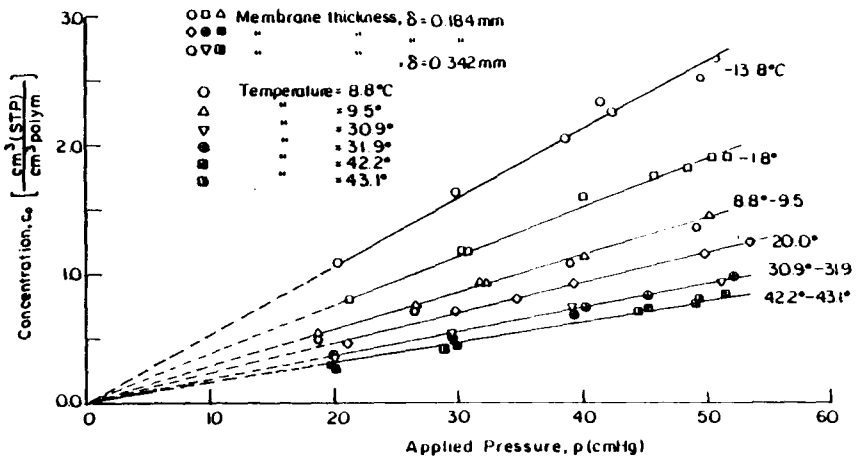

Figure 6. Solubility of Ethane in Poly(n-Butyl Methacrylate) as a Function of Pressure.

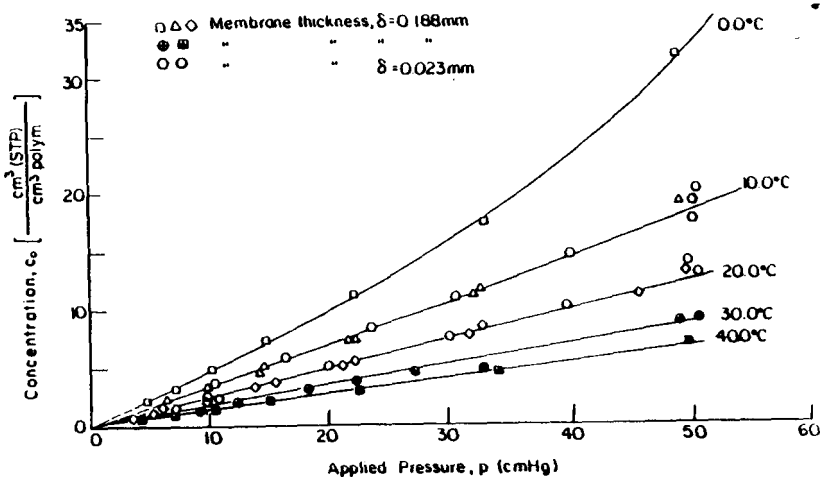

Figure 7. Solubility of n-Butane in Poly(n-Butyl Methacrylate) as a Function of Pressure.

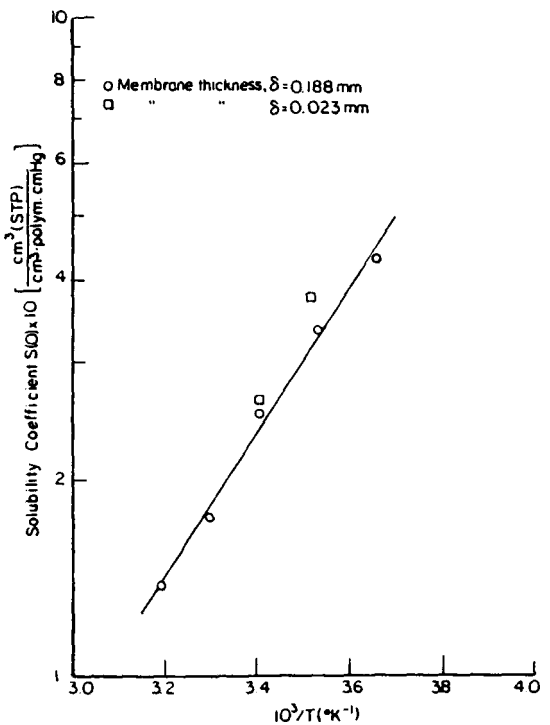

Figure 8. Temperature Dependence of Solubility Coefficients for n-Butane in Poly(n-Butyl Methacrylate).

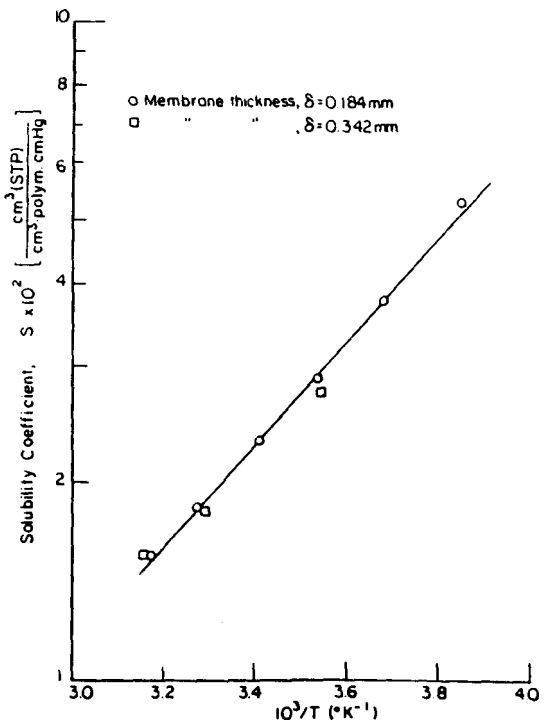

Figure 9. Temperature Dependence of Solubility Coefficients for Ethane in Poly(n-Butyl Methacrylate).

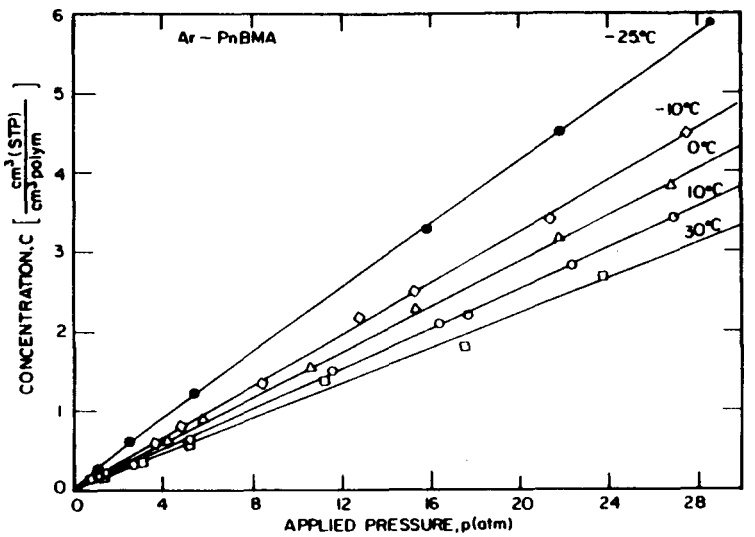

Figure 10. Solubility of Argon in Poly(n-Butyl Methacrylate) as a Function of Pressure.

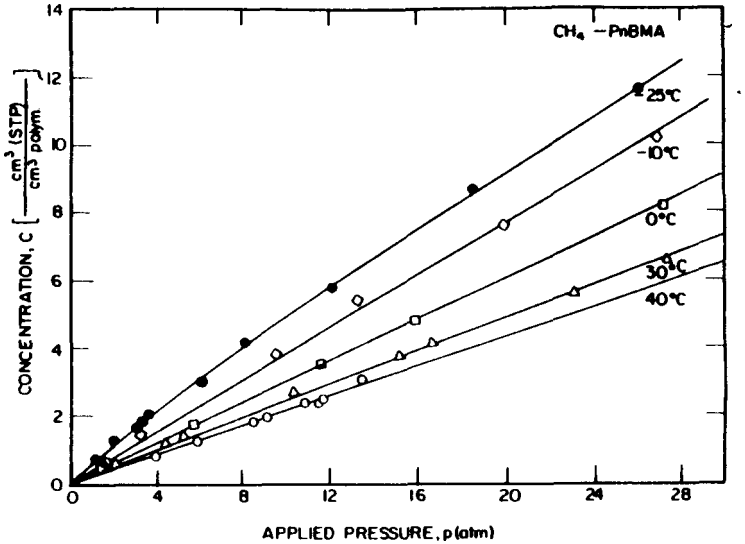

Figure 11. Solubility of Methane in Poly(n-Butyl Methacrylate) as a Function of Pressure.

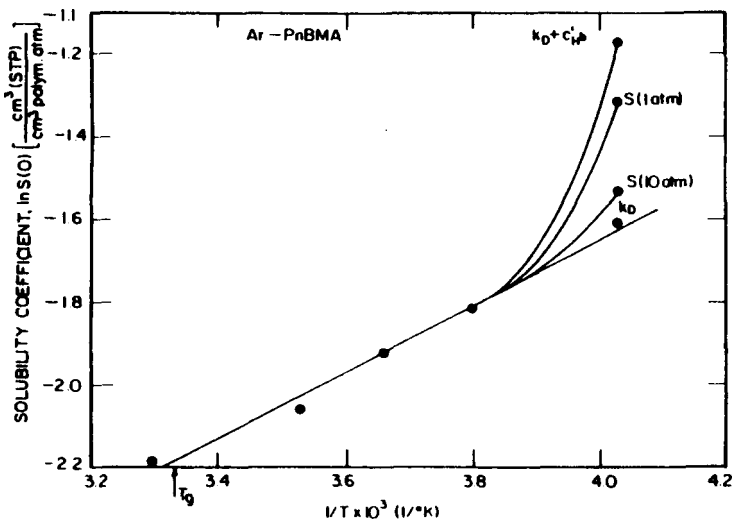

Figure 12. Temperature Dependence of Solubility Coefficients for Argon in Poly(n-Butyl Methacrylate).

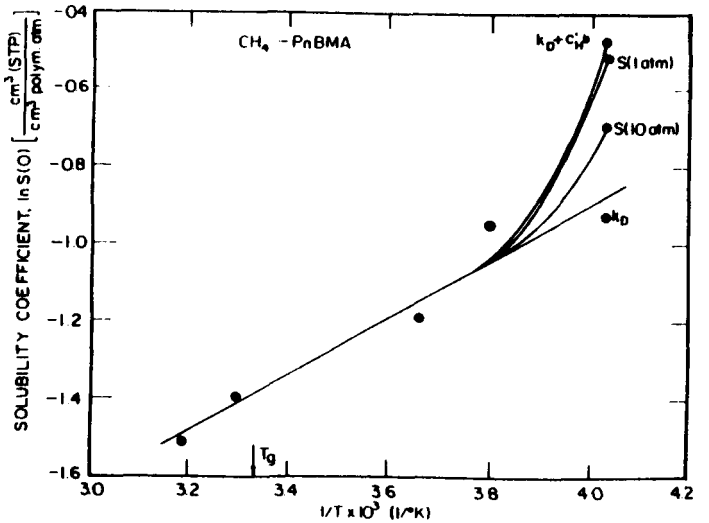

Figure 13. Temperature Dependence of Solubility Coefficients for Methane in Poly(n-Butyl Methacrylate)

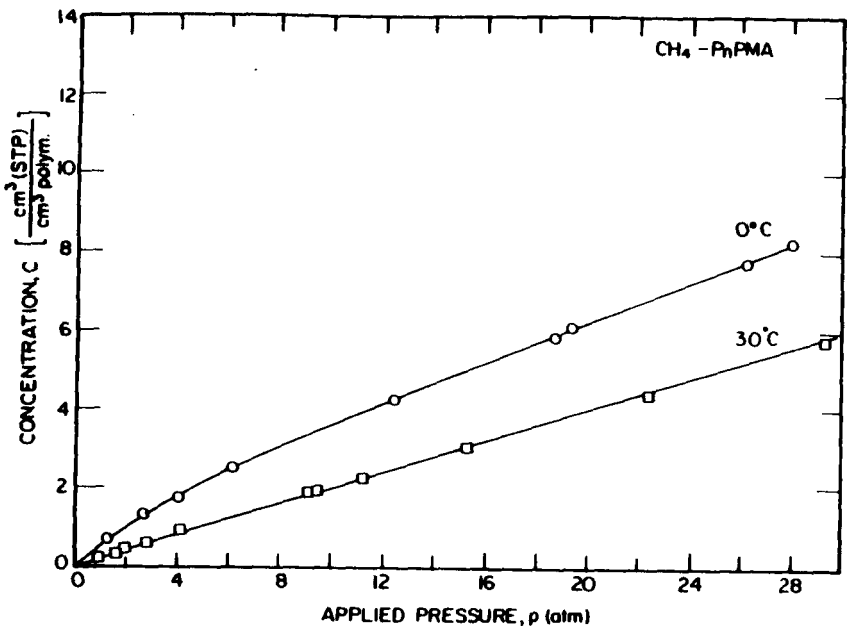

Figure 14. Solubility of Methane in Poly(n-Propyl Methacrylate) as a Function of Pressure.

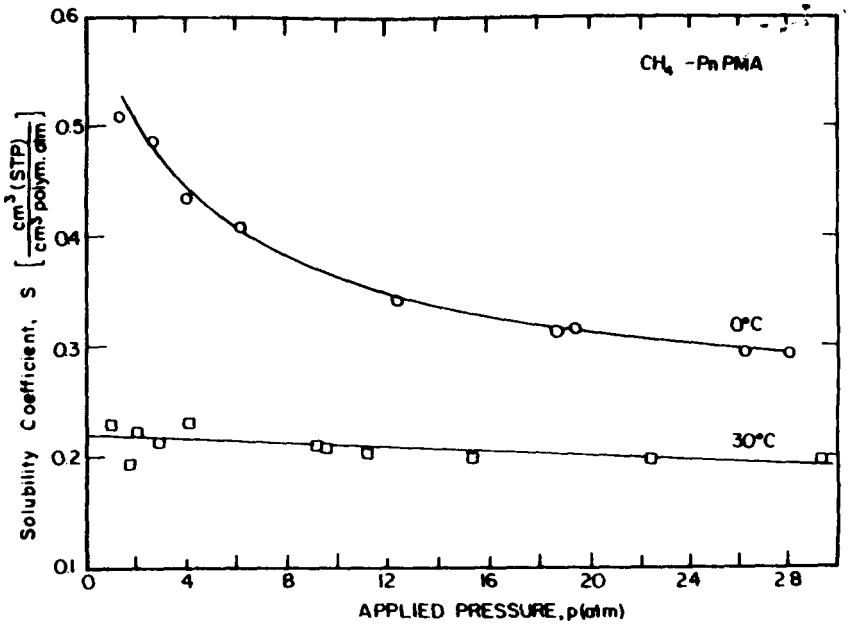

Figure 15. Solubility Coefficients of Methane in Poly(n-Propyl Methacrylate) as a Function of Pressure

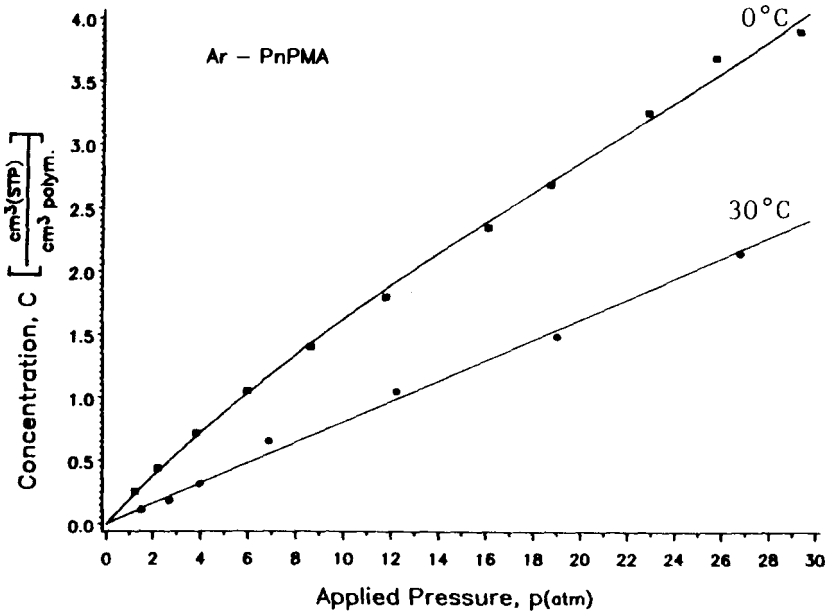

Figure 16. Solubility of Argon in Poly(n-Propyl Methacrylate) as a Function of Pressure.

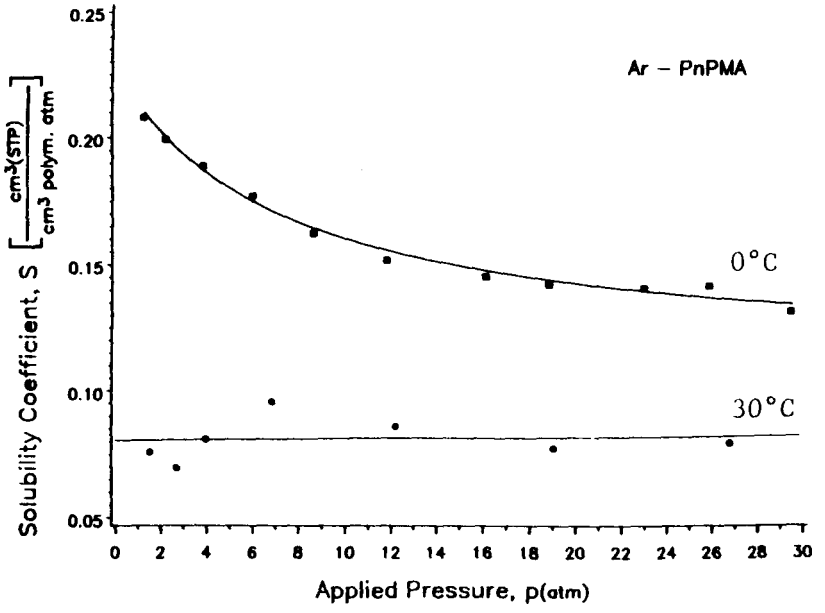

Figure 17. Solubility Coefficients of Argon in Poly(n-Propyl Methacrylate) as a Function of Pressure.

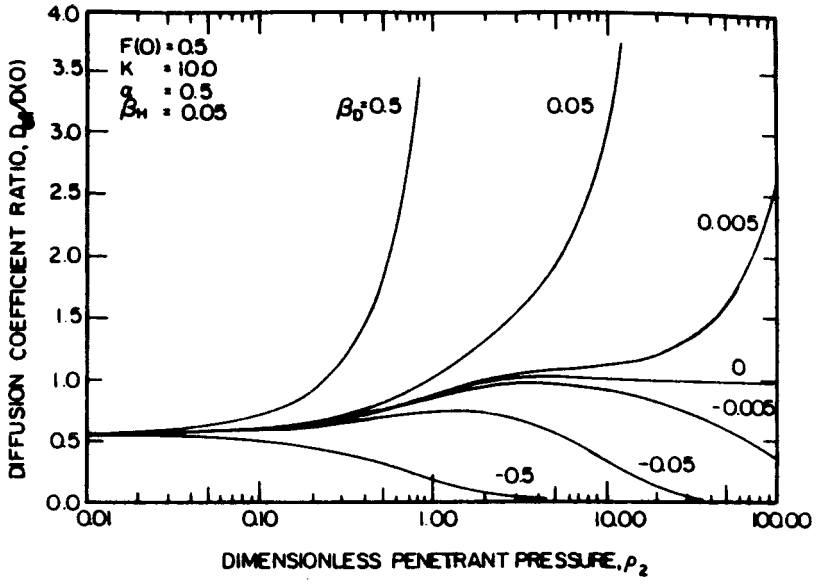

Figure 18. Ratio of diffusion coefficient $D_{eff}/D(0)$ as a function of dimensionless penetrant pressure ρ_2 according to eq. (7) for different values of β_D. Equation (7) assumes two penetrant populations with different mobilities.

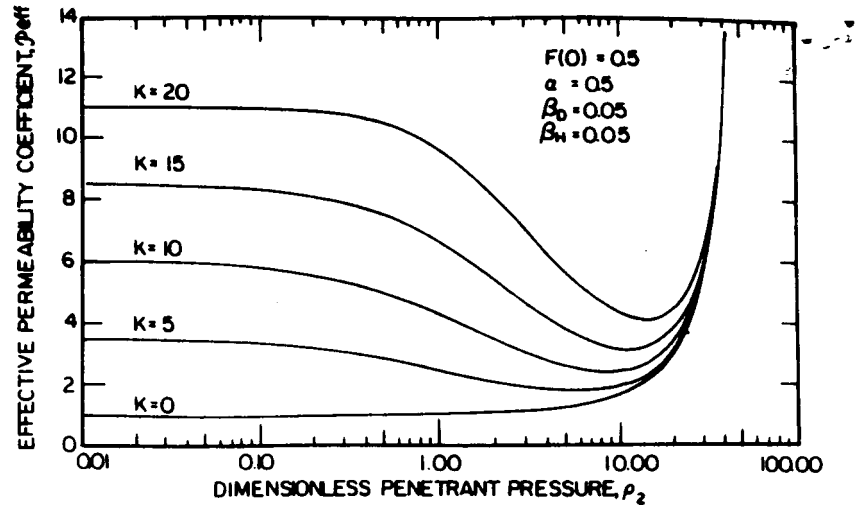

Figure 19. Effective permeability coefficient $\mathcal{P}_{eff}$ as a function of dimensionless penetrant pressure ρ_2 according to eq. (8), which assumes two penetrant populations with different mobilities.

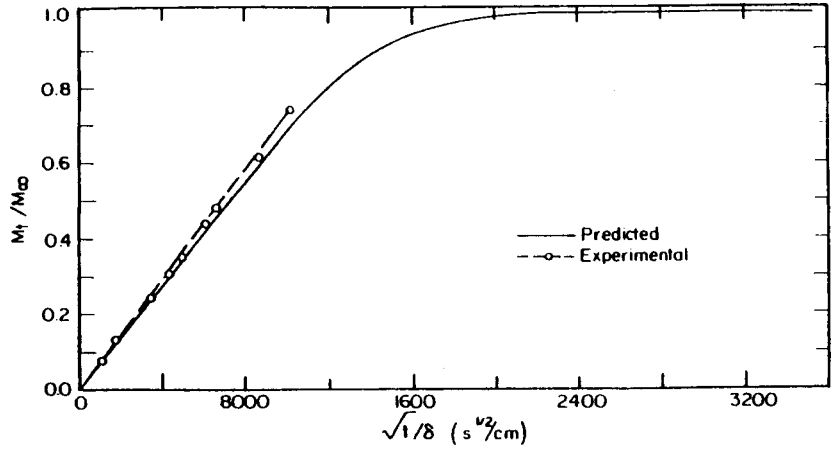

Figure 20. Fractional Absorption of Sulfur Dioxide in Polycarbonate at 25°C.

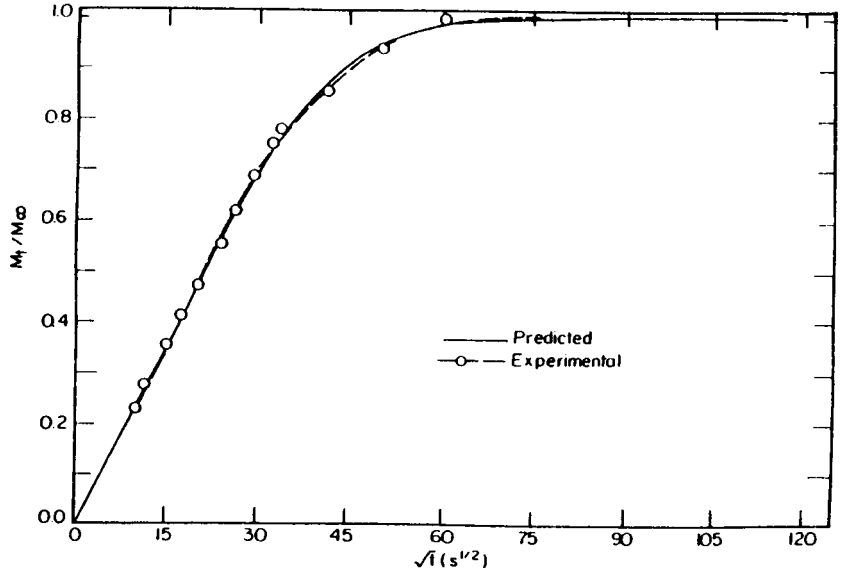

Figure 21. Fractional Absorption of Water Vapor in KAPTON Polyimide at 30°C.

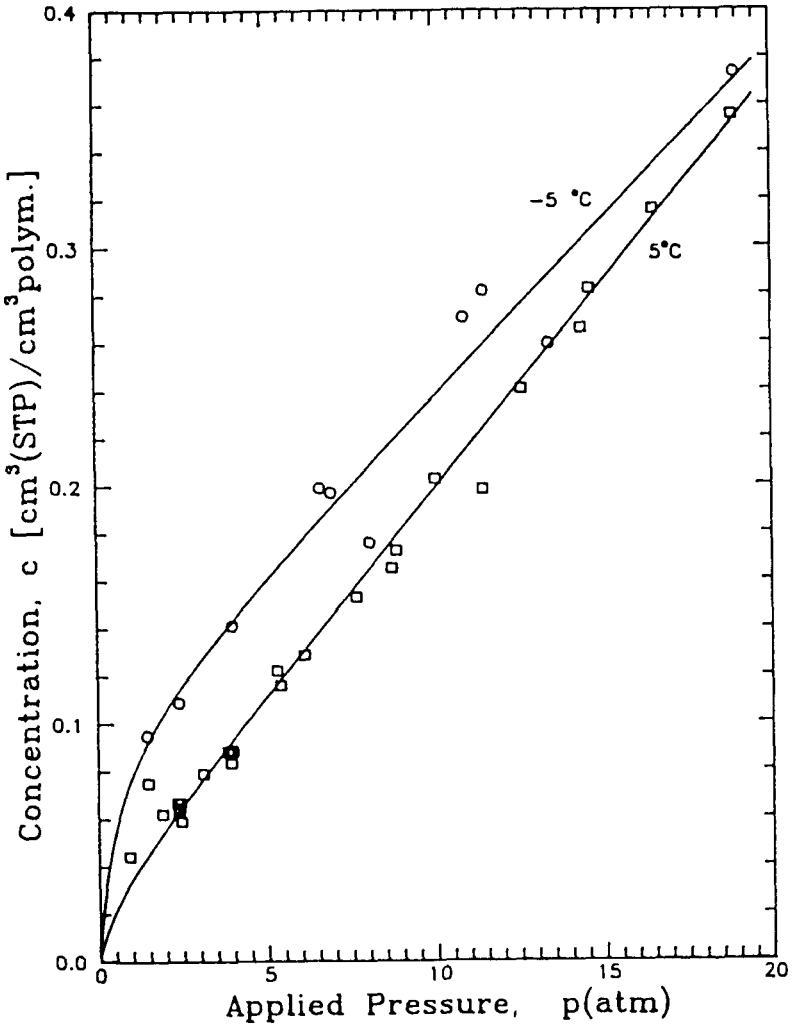

Figure 22. Solubility of Hydrogen in Poly(Vinyl Acetate) as a Function of Pressure.

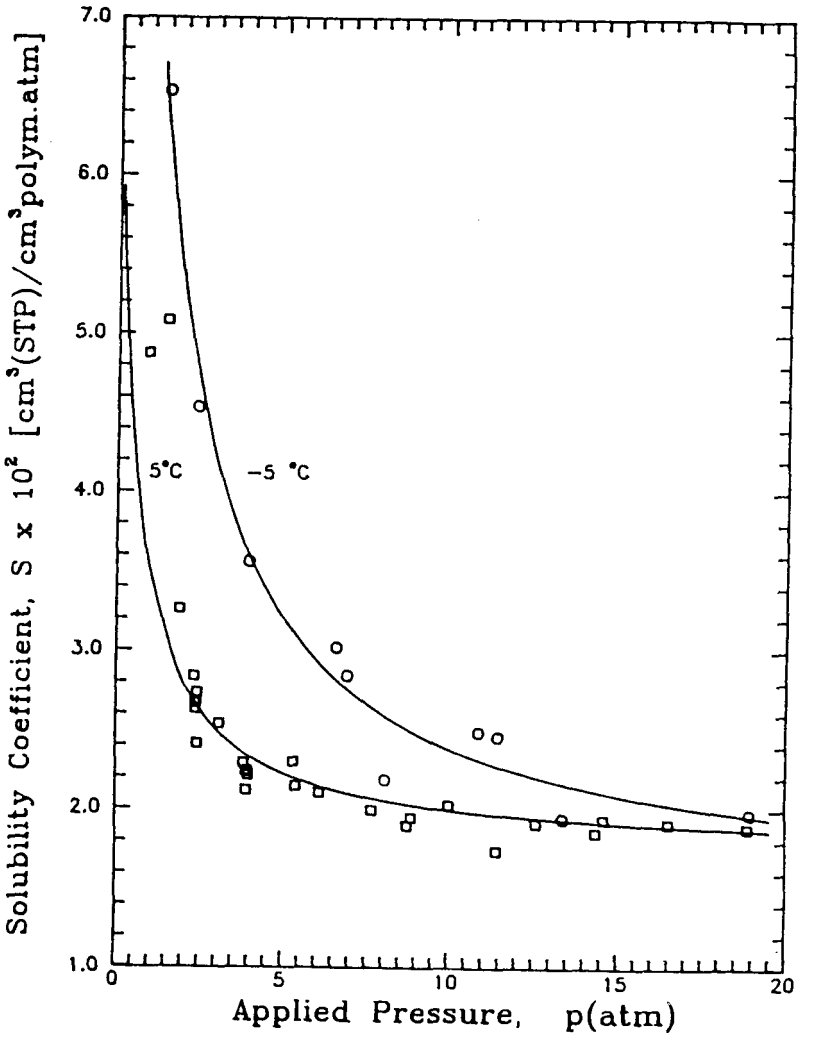

Figure 23. Solubility Coefficients of Hydrogen in Poly(Vinyl Acetate) as a Function of Pressure.