Transport of Gases in Miscible Polymer Blends Above and Below the Glass Transition Region

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The study of diffusion and permeation of methane, nitrogen, and helium in miscible blends of poly(styrene-stat-acrylonitrile) (PSAN) and poly(methyl methacrylate) (PMMA) at 35-140°C shows that permeation coefficients (P) of helium followed the linear logarithmic mixing rule. Positive deviations from the linear logarithmic mixing rule were observed for permeation and diffusion coefficients (D) of methane and nitrogen below the glass transition temperature (T_g). The deviations decreased with increasing temperature and disappeared above T_g. The experimental results were analyzed by free volume and activated state theories. The Arrhenius plots of log D or log P vs. the reciprocal of temperature exhibited discontinuities in the glass transition region for all gases and blend compositions. The discontinuities are caused by large thermal expansion coefficient differences between the rubbery and glassy states of PSAN and PMMA. The sorption of methane in 50/50 PSAN/PMMA has dual-mode characteristics below T_g.

Introduction

There is a growing body of literature on experimental studies of penetrant permeation in polymer blends and related copolymers. Hopfenberg and Paul (1978) reviewed the literature on gas transport in polymer blends and found that the following simple mixing rule for the permeation coefficient (P) was useful in the analysis of transport data in blends and copolymers:

$$\ln P = \phi_A \ln P_A + \phi_B \ln P_B \tag{1}$$

where ϕ_x is the volume fraction of component x, and P_x is the permeation coefficient. Paul (1982a,b, 1987) studied gas transport in blends of polycarbonate (PC) with a copolyester, polystyrene (PS) with poly(phenylene oxide) (PPO), and poly(methyl methacrylate) (PMMA) with poly(styrene-*stat*-acrylonitrile) (PSAN). While the experimental data for PC/copolyester and PS/PPO blends had negative deviations from the prediction of Eq. 1, the data for PMMA/PSAN blends had a positive deviation. Paul and his coworkers discussed the deviation of the experimental results from the linear logarithmic mixing rule in the context of both the activated state and free volume theories (Paul, 1982; Kumins and Kwei, 1968). In this study, the diffusivities and permeabilities of gases in PSAN/PMMA blends were measured at temperatures ranging from $T_g - 60°C$ to $T_g + 45°C$. The wide temperature range used for the acquisition of experimental data enabled us to carry out a more detailed analysis of the transport properties in terms of the activated state and free volume theories. PSAN and PMMA were selected because they were known to be miscible through earlier work (Suess et al., 1987; Pfennig et al., 1985) and were totally amorphous and their T_g's were approximately the same (near 100°C).

Experimental Studies

Materials

Poly(styrene-*stat*-acrylonitrile) (PSAN), containing 30 wt. % of acrylonitrile and poly(methyl methacrylate) (PMMA) were obtained from Scientific Polymer Products. The weight-average molecular weight of PSAN is 185,000 as supplied by the manufacturer. The weight-average molecular weight of PMMA is 93,000 and the number-average molecular weight 46,000.

The glass transition temperatures (T_g) of the polymers were measured by the use of a Perkin Elmer 7 Series differential scanning calorimeter (DSC). DSC experiments were carried

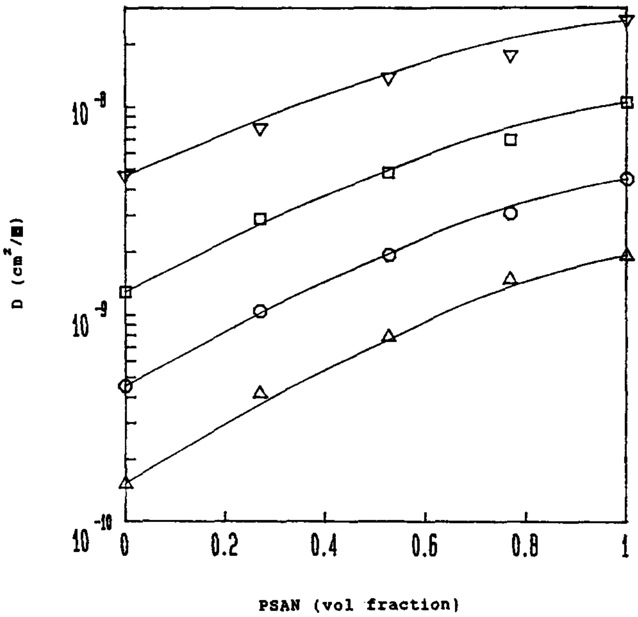

Figure 1. Diffusion coefficients of methane in PSAN/PMMA blends vs. blend composition.

△ at 35°C; ○ at 50°C; □ at 75°C; and ▽ at 90°C.

out in a nitrogen atmosphere at a heating rate of 10°C/min. The T_g of PSAN was found to be 95°C and that of PMMA 97°C.

Film preparation

Films of PSAN/PMMA blends were prepared by solution casting. For this purpose, PMMA and PSAN pellets in the desired weight ratio were dissolved in tetrahydrofuran (THF) to form homogeneous solutions containing about 10 wt. % of the total polymer. The solutions were then poured onto glass plates to cast films by allowing the solvent to evaporate slowly. The films were dried in an air-circulating oven by raising the temperature gradually (about 15°C each day) until the oven temperature reached 75°C and then maintained at that temperature for one week. Subsequently, the oven temperature was raised 10°C/d under vacuum until it reached 130°C. The oven temperature was kept at 130°C for another week. The films were then cooled from 130°C to ambient temperature in four hours and peeled off from the glass plates. The thickness of the film was measured with a Mitutoyo 227 low force micrometer. The accuracy of the micrometer is ±0.1 mil (1 in. = 1,000 mil).

Gas permeation experiments

A permeation apparatus (Koros et al., 1976) was used to measure the permeation and diffusion coefficients of gases through polymer films. A Neslab Tamson bath circulator was used to control the temperature of the silicon oil in the bath. The entire apparatus, except for the pressure transducer and the control valves, was immersed in the oil bath. The sensitivity of the MKS 128A pressure transducer was 10^{-3} torr. The upstream pressures were 40 psia (280 kPa) for helium and 100 psia (690 kPa) for methane and nitrogen. Since the polymer becomes rubbery when the temperature is above its T_g, it was possible that the film could have deformed under pressure during the permeation experiment. To avoid large errors arising from film deformation, we have developed a special procedure. All experiments at temperatures above T_g were preceded by an experiment at 70°C, which was below the T_g's of both component polymers and their blends. After experiments above T_g were completed, the temperature was lowered to 70°C and the experiment was repeated. If the permeation and diffusion coefficients measured from the two experiments at 70°C before and after the high-temperature experiments were within 10%, the measurements above T_g were deemed correct.

Gas sorption experiments

A sorption apparatus (Koros and Paul, 1976) was used to measure the solubility of gases in polymers. The temperature bath used was the same as that of the permeation apparatus. Two Setra 204 pressure transducers were used to measure the pressure. The pressure range and sensitivity of the pressure transducer were 0-500 psia (0-3.5 MPa) and 0.1 psia (0.7 kPa), respectively. For both the sorption and permeation apparatuses, the pressure transducers were connected to an Omega WB-31 A/D converter, which was in turn connected to an IBM personal computer. The pressure readings on different channels were monitored and recorded on the computer for further analysis.

Results and Discussions

Transport properties vs. blend composition

The permeability and diffusion coefficients of methane, nitrogen, and helium in PSAN, PMMA and 75/25, 50/50, 25/75 blends were measured at temperatures ranging from 35 to 140°C. The diffusion coefficients of methane and nitrogen are plotted against the volume fractions of PSAN at different temperatures (Figures 1-4). The data below and above the T_g

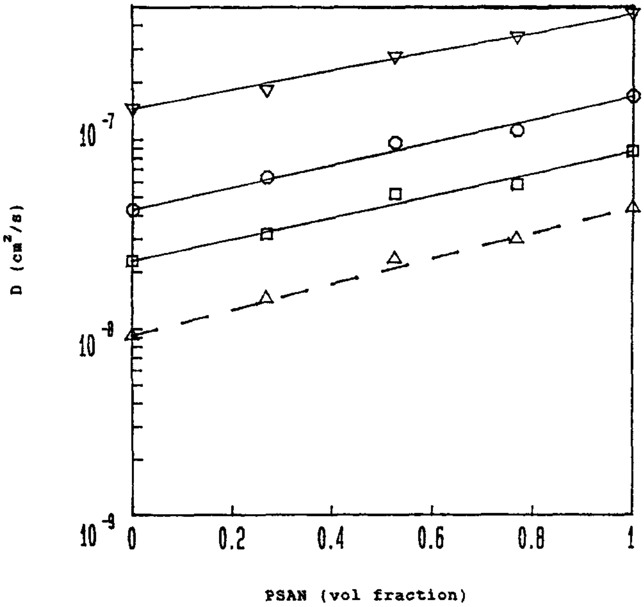

Figure 2. Diffusion coefficients of methane in PSAN/PMMA blends vs. blend composition.

△ at 100°C; □ at 110°C; ○ at 120°C; and ▽ at 140°C.

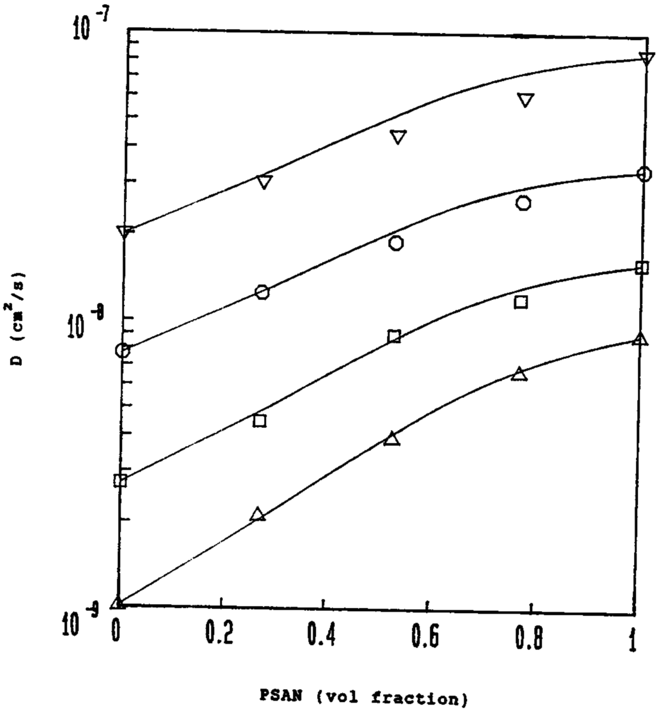

Figure 3. Diffusion coefficients of nitrogen in PSAN/PMMA blends vs. blend composition.

△ at 35°C; ▣ at 50°C; ○ at 75°C; and ▽ at 90°C.

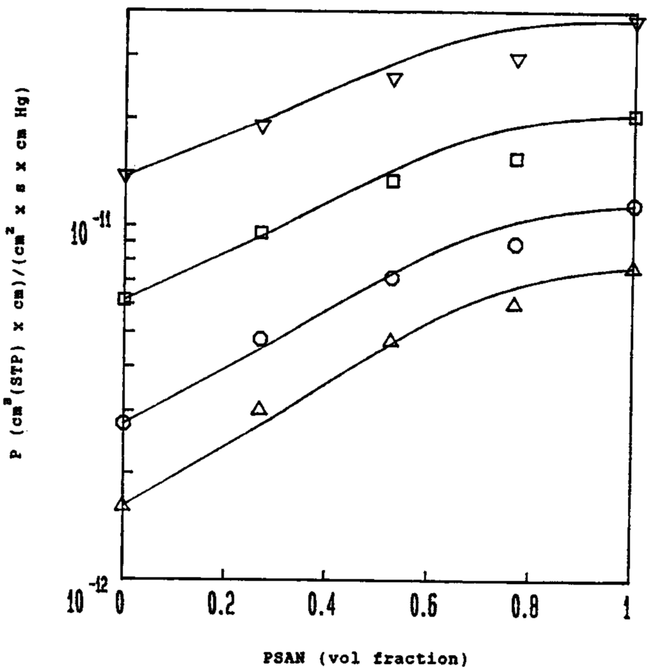

Figure 5. Permeation coefficients of nitrogen in PSAN/PMMA blends vs. blend composition.

△ at 35°C; ○ at 50°C; ▣ at 75°C; and ▽ at 90°C.

are plotted separately to maintain clarity of the presentation and to highlight the different composition dependencies in the two regions. It is obvious that the diffusion coefficients of N_2 and CH_4 in PSAN/PMMA blends show positive deviations from the linear logarithmic mixing rule at temperatures below T_g. The deviations decrease as the temperatures increase and become relatively minor when the T_g of the polymer is approached (near 90°C). At temperatures above T_g, the diffusion coefficients of nitrogen and methane follow the linear logarithmic mixing rule. Plots of the permeation coefficients of nitrogen, methane, and helium in PSAN/PMMA blends vs. the volume fraction of PSAN are given in Figures 5–10. Again, positive deviations from the linear logarithmic mixing rule

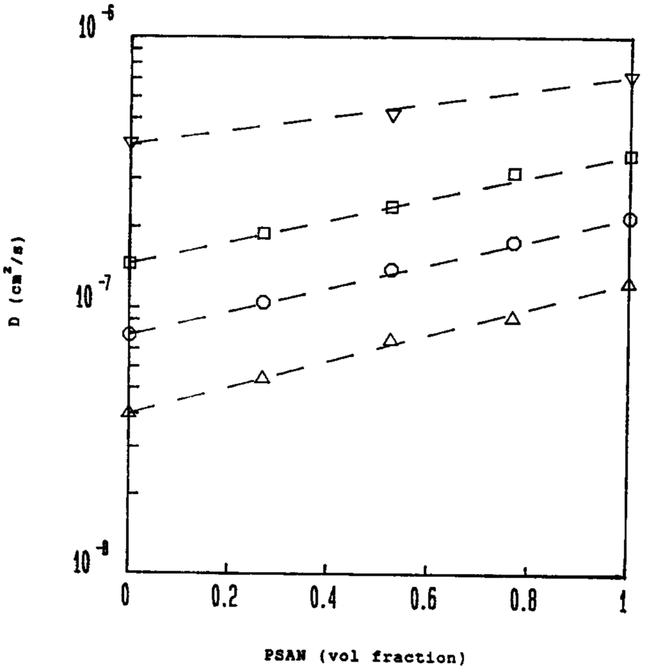

Figure 4. Diffusion coefficients of nitrogen in PSAN/PMMA blends vs. blend composition.

△ at 100°C; ○ at 110°C; □ at 120°C; and ▽ at 140°C.

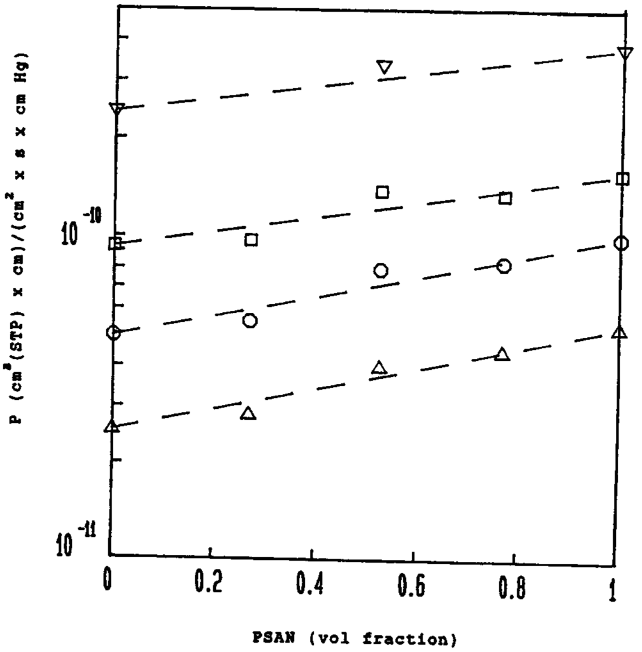

Figure 6. Permeation coefficients of nitrogen in PSAN/PMMA blends vs. blend composition.

△ at 100°C; ○ at 110°C; □ at 120°C; and ▽ at 140°C.

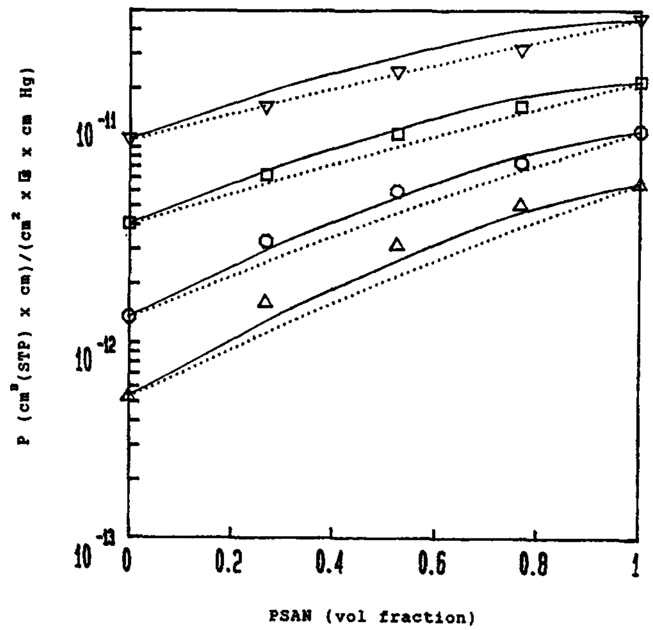

Figure 7. Permeation coefficients of methane in PSAN/PMMA blends vs. blend composition.
△ at 35°C; ○ at 50°C; □ at 75°C; and ▽ at 90°C.

represented by Eq. 1 were observed for nitrogen and methane, and the deviations decrease as the temperature increases. In contrast to the observations of nitrogen and methane, the permeation coefficients of helium follow the prediction of Eq. 1 very well for the entire temperature range. These phenomena and experimental data will be discussed using the free volume and the activated state theories.

Activated state theory

The transport of small molecules in polymers is often discussed in terms of an activated process of the Arrhenius type (Kumins and Kwei, 1968):

$$D = D_o \exp(-E_D/RT) \tag{2}$$

where T is the absolute temperature, E_D is the activation energy for diffusion, and D_o is a preexponential factor. Based on the "universal" correlation between ln D_o and E_D/T for a large number of gas-rubbery polymer combinations, Paul (1984) derived a rule of mixing on the basis of Eq. 2 for a polymer-containing components A and B as follows:

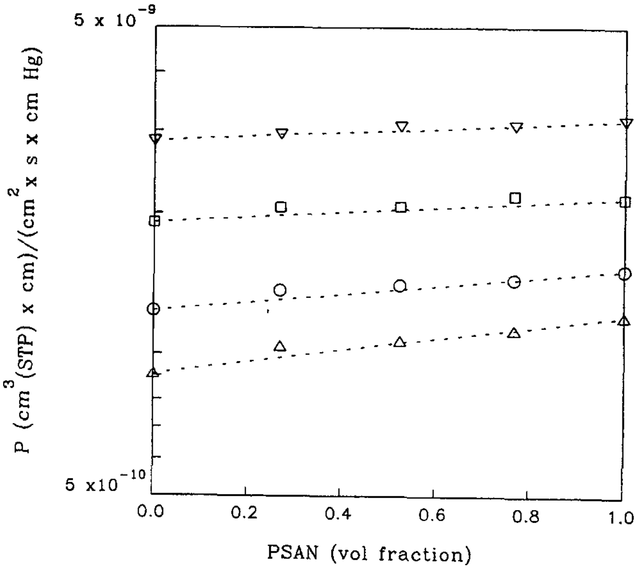

Figure 9. Permeation coefficients of helium in PSAN/PMMA blends vs. blend composition.
△ at 35°C; ○ at 50°C; □ at 75°C; and ▽ at 90°C.

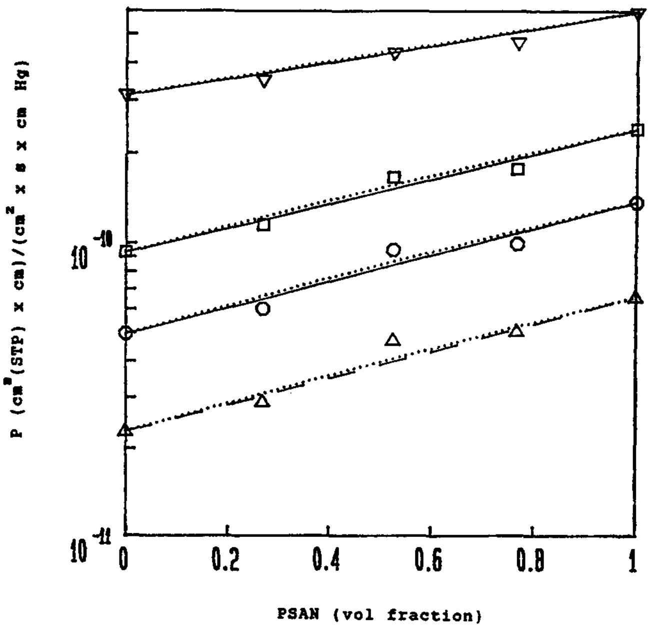

Figure 8. Permeation coefficients of methane in PSAN/PMMA blends vs. blend composition.
△ at 100°C; ○ at 110°C; □ at 120°C; and ▽ at 140°C.

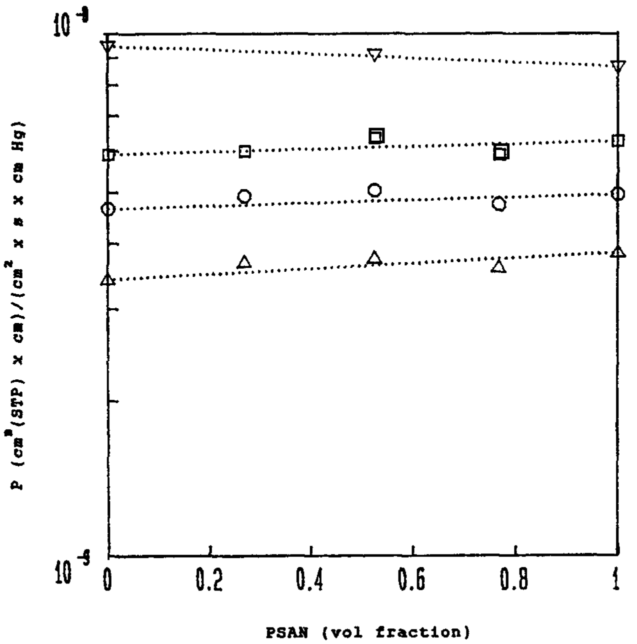

Figure 10. Permeation coefficients of helium in PSAN/PMMA blends vs. blend composition.
△ at 100°C; ○ at 110°C; □ at 120°C; and ▽ at 140°C.

Table 1. Activation Energies and Preexponential Factors of Diffusion and Permeation Coefficients of Methane in PSAN/PMMA Blends

CH_4	100% PSAN	75/25 PSAN/PMMA	50/50 PSAN/PMMA	25/75 PSAN/PMMA	100% PMMA
		Below Tg			
$D_o \times 10^2$ (cm²/s)	3.46	1.46	8.82	9.27	57.2
E_d (Kcal/mol)	10.20	9.88	10.85	11.77	13.50
ΔE_{AB} (Kcal/mol)	0.00	−1.09	−0.92	−0.85	0.00
$P_o \times 10^6$ (cm³×cm)/(cm²·s·cm Hg)	1.65	0.79	1.92	5.62	244.0
ΔE_p (Kcal/mol)	7.62	7.33	8.16	9.23	12.22
		Above Tg			
D_o (cm²/s)	478.40	330.97	417.00	490.80	1,369.2
E_d (Kcal/mol)	17.05	16.98	17.36	17.83	18.86
ΔE_{AB} (Kcal/mol)	0.00	−0.49	−0.55	−0.54	0.00
P_o (cm³×cm)/(m²·s·cm Hg)	0.054	0.138	0.425	1.509	3.770
ΔE_p (Kcal/mol)	15.05	16.02	17.00	18.29	19.08

$$\ln D - \phi_A \ln D_A - \phi_B \ln D_B = (bR-1)\Delta E_{AB}/RT \qquad (3)$$

where b is a constant derived from the universal correlation and ΔE_{AB} is related to the components and mixture by:

$$\Delta E_{AB} = E_D - \phi_A E_{DA} - \phi_B E_{DB} \qquad (4)$$

The quantity of $(bR-1)$ in Eq. 3 is negative (Paul, 1984) because bR is smaller than unity. Therefore, a positive ΔE_{AB} results in a lower diffusion coefficient than predicted by the linear logarithmic mixing rule, and a negative ΔE_{AB} results in a higher than predicted value. In analyzing our data by Eq. 3, we first calculated the D_o and E_D values below and above T_g by the regression analysis. The calculated values of D_o and E_D of methane and nitrogen are given in Tables 1 and 2, respectively. It was observed that the ΔE_{AB} values for the three blends were all negative at temperatures below T_g. According to Eq. 3, a negative ΔE_{AB} value would have a positive deviation of D from the linear logarithmic mixing rule. Our experimental results indeed agree with the prediction. Since $(bR-1)\Delta E_{AB}$ is a constant, the absolute values of $(bR-1)\Delta E_{AB}/RT$ decrease as temperatures increase. The decrease of $(bR-1)\Delta E_{AB}/RT$ contributes to the decrease of $\ln D - \phi_A \ln D_A - \phi_B \ln D_B$ as temperatures increase. This agrees qualitatively with the trend of our experimental observation.

Tables 1 and 2 show that the magnitude of ΔE_{AB} for methane or nitrogen diffusion in the blends at temperatures above T_g was about 1/2 of the respective value below T_g. Again, the smaller ΔE_{AB} above T_g should go with the small deviation from the linear logarithmic mixing rule. This agrees qualitatively with our experimental results as well.

It was also desired to check whether the predictions of Eq. 3 agreed quantitatively with our experimental results. A plot of log D_o vs. E_D for all of the data gathered in this study is given in Figure 11. A linear regression analysis of the ln D_o, E_D data below T_g gives the following expression:

$$\ln D_o = 0.414 E_D/T - 11.57 \qquad (5)$$

The same regression for the data above T_g gives:

$$\ln D_o = 0.506 E_D/T - 11.44 \qquad (6)$$

In Figures 1 to 4, the solid curves represent diffusivities calculated from Eq. 3 using E_D values from this study and experimentally determined b values of 0.414 and 0.506 for temperatures below and above T_g, respectively. The agreement between the predictions of Eq. 3 and the experimental diffusivities of N_2 and CH_4 in PSAN/PMMA blends is good. It is interesting to note that at temperatures above T_g, the magnitude of $(bR-1)$ in these gas/polymer systems is close to zero. Therefore, the relation of gas diffusivities between the two components and their blends in Eq. 3 was reduced to the linear logarithmic mixing rule at temperatures above T_g.

Table 2. Activation Energies and Preexponential Factors of Diffusion and Permeation Coefficients of Nitrogen in PSAN/PMMA Blends

N_2	100% PSAN	75/25 PSAN/PMMA	50/50 PSAN/PMMA	25/75 PSAN/PMMA	100% PMMA
		Below Tg			
$D_o \times 10^2$ (cm²/s)	3.55	1.26	2.59	9.55	25.3
E_d (Kcal/mol)	9.35	8.87	9.60	10.84	11.80
ΔE_{AB} (Kcal/mol)	0.00	−1.05	−0.91	−0.30	0.00
$P_o \times 10^7$ (cm³×cm)/(cm²·s·cm Hg)	2.70	1.97	3.32	5.57	21.9
E_p (Kcal/mol)	6.44	6.40	6.87	7.46	8.69
		Above Tg			
D_o (cm²/s)	2.04	—	9.90	—	171.43
E_d (Kcal/mol)	12.21	—	13.75	—	16.32
ΔE_{AB} (Kcal/mol)	0.00	—	−0.41	—	0.00
$P_o \times 10^3$ (cm³×cm)/(cm²·s·cm Hg)	1.72	—	18.5	—	135.0
E_p (Kcal/mol)	12.64	—	14.63	—	16.54

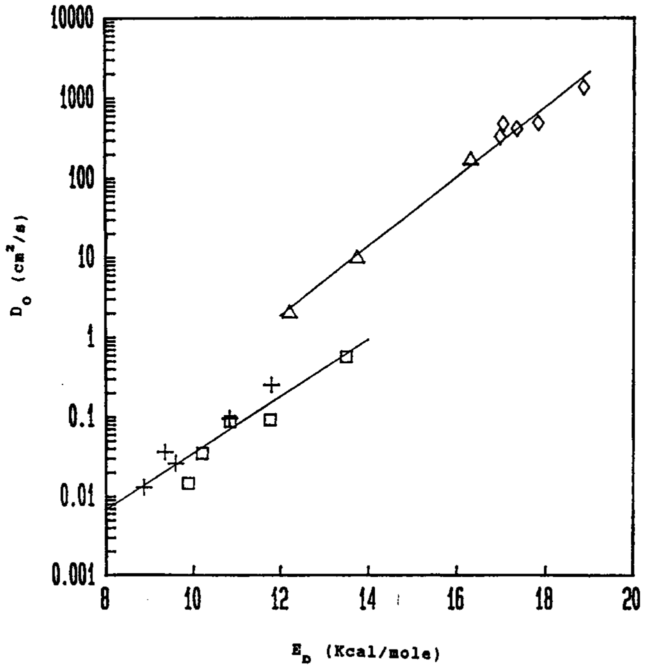

Figure 11. Plots of D_o against activation energy of diffusion.

□ for methane and + for nitrogen at temperatures below T_g; △ for methane and ◇ for nitrogen at temperatures above T_g.

The solubility coefficient, S, for a polymer blend is related to that of its components by:

$$\ln S = \phi_A \ln S_A + \phi_B \ln S_B + \frac{BV_s}{RT}\phi_A\phi_B \qquad (7)$$

where B is the binary interaction density (Flory, 1953) for the two-component polymers, and V_i is the molar volume of the small molecule penetrant (component i).

All the evidence to date including experimental measurement of densities, heat capacities, infrared spectra, dielectric relaxation, and calorimetry suggest that the net interaction force between PMMA and PSAN is weak (Pfennig et al., 1985; Naito et al., 1978; McBrierty et al., 1978) even as the AN content is varied from the edge of the miscibility window to the optimum value (Fowler et al., 1987). Since the net interaction force between PSAN and PMMA is weak, the value of B is small. Therefore, the solubility in the blend in Eq. 7 can be approximated as:

$$\ln S = \phi_A \ln S_A + \phi_B \ln S_B \qquad (8)$$

If Henry's law is obeyed, the permeability coefficient is related to the solubility and diffusion coefficients by:

$$P = DS \qquad (9)$$

Combination of Eqs. 3, 8 and 9 yields an equation similar to Eq. 3:

$$\ln P = \phi_A \ln P_A + \phi_B \ln P_B + (bR - 1)\Delta E_{AB}/RT \qquad (10)$$

The qualitative explanation to the deviation of permeabilities of methane and nitrogen from Eq. 1 will be the same as that of the diffusion coefficients. In Figures 5 to 8, the solid curves represent permeabilities calculated from Eq. 10. It can be seen that the permeabilities of N_2 and CH_4 in PSAN/PMMA blends can be described by Eq. 10. Due to the small time lag of helium at high temperatures, accurate measurements of the diffusion coefficients of helium for the determination of ΔE_{AB} were difficult. However, within the limit of accuracy of our experiments, we have seen only small or no permeability deviations from the linear logarithmic mixing rule in the entire temperature range. Hence, we arrive at the conclusion that the ΔE_{AB} values of helium are small both above and below the glass transition temperature.

Free volume theory

Kumins and Kwei (1968) discussed the application of the free volume theory of Cohen and Turnbull (1959) to the gas/polymer systems. The diffusion coefficient of gases through a polymer membrane can be expressed as:

$$D = A \exp(-v^*/v_f) \qquad (11)$$

where A is a characteristic constant of gas, v^* is the critical free volume required for a diffusional jump, and v_f is the free volume of the polymer. Although the Cohen-Turnbull theory was derived for liquids, the use of Eq. 11 for glassy state may be justified on the ground of Matsuoka's reformulation (Matsuoka, 1992) of Adam-Gibbs treatment (Adam and Gibbs, 1965) to allow for both equilibrium and nonequilibrium states. According to Matsuoka, the characteristic relaxation time λ_c is related to the fractional free volume f by Eq. 12:

$$\lambda_c = \lambda_r \exp\left(\frac{1}{f} - \frac{1}{f_r}\right) \qquad (12)$$

where the subscript r refers to a reference state of the observer's choosing. Clearly, the format of Eq. 11 is consistent with Matsuoka's treatment.

We now express the free volume of the blend as follows:

$$v_{fm} = \phi_A v_{fA} + \phi_B v_{fB} + \Delta v_f \qquad (13)$$

where v_{fA}, v_{fB}, and v_{fm} are the free volumes of component A, component B, and the blend, respectively. And Δv_f is the excess free volume. Combining Eqs. 11 and 13 yields the following mixing rule for the diffusion coefficient of a gas in a polymer blend:

$$\ln D - \phi_A \ln D_A - \phi_B \ln D_B = \frac{v^*}{v_{fm} v_{fA} v_{fB}} (\phi_A\phi_B(v_{fA} - v_{fB})^2 + \Delta v_f(\phi_A v_{fA} + \phi_B v_{fB})) \qquad (14)$$

Since $\phi_A\phi_B(v_{fA} - v_{fB})^2$ and $v^*/v_{fm}v_{fA}v_{fB}$ are always positive (ln $D - \phi_A \ln D_A - \phi_B \ln D_B$) is positive if $\Delta v_f \geq 0$. Even when $\Delta v_f < 0$, the deviation still can be positive if $\phi_A\phi_B(v_{fA} - v_{fB})^2 > |\Delta v_f(\phi_A v_{fA} + \phi_B v_{fB})|$. Equality between ln D and ϕ_A ln $D_A + \phi_B$ ln D_B occurs when

Table 3. Volumetric Parameters for PSAN/PMMA Blend at 23°C*

	100% PSAN	75/25 PSAN/PMMA	50/50 PSAN/PMMA	25/75 PSAN/PMMA	100% PMMA
M (g/mol)	80.7	84.8	89.3	94.4	100.0
V_{sp} (23°C) (cm^3/g)	0.9275	0.9124	0.8857	0.8613	0.8389
1.3 V_w (cm^3/mol)	63.1	65.1	67.5	70.0	72.9
SFV (cm^3/g)	0.145	0.144	0.130	0.120	0.109
Δv_f (cm^3/g)	—	0.0074	0.0021	0.0014	—

* V_{sp} is the specific volume, 1.3 V_w is the occupied volume, M is the molecular weight of the monomer, and SFV is the specific free volume.

$$\Delta v_f = 0 \quad \text{and} \quad \phi_A\phi_B(v_{fA} - v_{fB})^2 = 0 \tag{15}$$

or $\Delta v_f < 0$,

$$\phi_A\phi_B(v_{fA} - v_{fB})^2 = |\Delta v_f(\phi_A v_{fA} + \phi_B v_{fB})| \tag{16}$$

The condition for $\ln D < \phi_A \ln D_A + \phi_B \ln D_B$ to occur is when $\Delta v_f < 0$ and $\phi_A\phi_B(v_{fA} - v_{fB})^2 < |\Delta v_f(\phi_A v_{fA} + \phi_B v_{fB})|$.

The magnitude of v_f can be estimated as the difference between the specific volume of the polymer at temperature T and the occupied volume at 0 K. The latter is often approximated as 1.3 times the van der Waals volume, according to Bondi (1964). The specific volumes of PSAN, PMMA and their blends at 23°C were measured by Gsell (1990). The calculated specific free volumes of PSAN, PMMA and their blends at 23°C are in Table 3. The specific free volumes of the blends fall between those of the components, and Δv_f is positive for all the blend compositions, as shown in Table 3. From the free volume theory discussed above, positive Δv_f results in positive deviation from the linear logarithmic mixing rule. In Figures 1 and 3, the diffusion coefficients of nitrogen and methane vs. the volume fraction of PSAN at temperatures below T_g agree qualitatively with the prediction. Since the v^* value was not known, we were unable to engage in a quantitative comparison between experimental diffusion coefficients and calculated values.

As the temperature increases and approaches T_g, v_{fm}, v_{fA}, and v_{fB} increase but Δv_f decreases. The volume thermal expansion coefficient of PSAN ($=1.86\times10^{-4}$ cm^3/g·°C), which is calculated from those of polystyrene (PS) and polyacrylonitrile (PAN), is smaller than that of PMMA ($=2.36\times10^{-4}$ cm^3/g·°C) (Brandrup and Immergut, 1989) below T_g; therefore, $(v_{fA} - v_{fB})^2$ decreases with increasing temperature. The above-mentioned specific free volume changes with temperature contribute to the decrease of $(\ln D - \phi_A \ln D_A + \phi_B \ln D_B)$. The smaller deviations of the diffusion coefficients of the polymer blends from the linear logarithmic mixing rule, as the temperatures increase, agree with the predicted trend of the free volume theory. If this trend is to be followed, the deviations may become too small to be detected as the temperature approaches the glass transition region of PSAN/PMMA.

Since the gas permeability P is related to the diffusivity D by Eq. 9, P can be assumed to depend on free volume in the same way as D. This holds true as long as S is relatively insensitive to molecular structure changes when compared to D. The gas diffusivity in most polymers covers about six orders of magnitude, while gas solubility varies within two orders of magnitude. Thus, as a first approximation, it is not unreasonable to expect P to vary primarily with the free volume. Lee (1980) has shown impressive correlations for gas permeation through a wide range of polymers using the equation:

$$P = A\exp(-B'/v_f) \tag{17}$$

where A is a characteristic constant of gas, and B' is the constant for a particular gas which concerns only with the smallest volume of a hole for a jump to occur. By combining Eq. 13 with Eq. 17, an equation similar to Eq. 14 is derived:

$$\ln P - \phi_A \ln P_A - \phi_B \ln P_B$$

$$= \frac{B'}{v_{fm}v_{fA}v_{fB}}\left[\phi_A\phi_B(v_{fA} - v_{fB})^2 + \Delta v_f(\phi_A v_{fA} + \phi_B v_{fB})\right] \tag{18}$$

If follows that the underlying reason for the deviation of permeability of nitrogen and methane from Eq. 1 in PSAN/PMMA blends is the same as that for the deviation of the diffusion coefficients.

Methane and nitrogen molecules are much larger in size than helium; accordingly, they need larger holes for jumps to occur. As a result of this, the B' values of nitrogen and methane are much larger than that of helium. Equation 18 shows that a smaller value of B' results in a smaller deviation from the linear logarithmic mixing rule. Experimentally, there were very small or no deviations from the linear logarithmic mixing rule for helium permeation. It is concluded that the small deviation from the linear logarithmic mixing rule for the helium molecule is due to its small size.

Paul (1984) applied Eq. 17 to multicomponent polymer systems by assuming that the free volume of the mixture is given by additive contributions from each component:

$$\Delta v_f = 0 \tag{19}$$

Inserting Eqs. 13 and 19 into Eq. 17 and rearranging yield the following mixing rule for permeability (Paul, 1984):

$$\ln(P/A) = \left(\frac{\phi_A}{\ln(P_A/A)} + \frac{\phi_B}{\ln(P_B/A)}\right)^{-1} \tag{20}$$

In Figures 7 to 10, the dotted curves represent permeabilities calculated from Eq. 20 using A values of 2.2×10^{-6} and 3.86×10^{-6} for CH_4 and He, respectively (Maeda, 1986). The A value for nitrogen is unavailable. The permeability predictions from Eq. 20 quantitatively describe the permeabilities of methane at high temperatures (>90°C). However, agreement between the experimental permeabilities of methane and the predictions at low temperatures (<90°C) is not as good as shown in Figure 7. The permeation coefficients of helium in the two-component polymers are very close [P(PSAN) = 1.33 P(PMMA) at 35°C and P(PSAN) = 1.11 P(PMMA) at 90°C]. Therefore, Eq. 20 is not a critical test of the helium permeability data; nonetheless, the predictions agree well with experimental results over the entire temperature range.

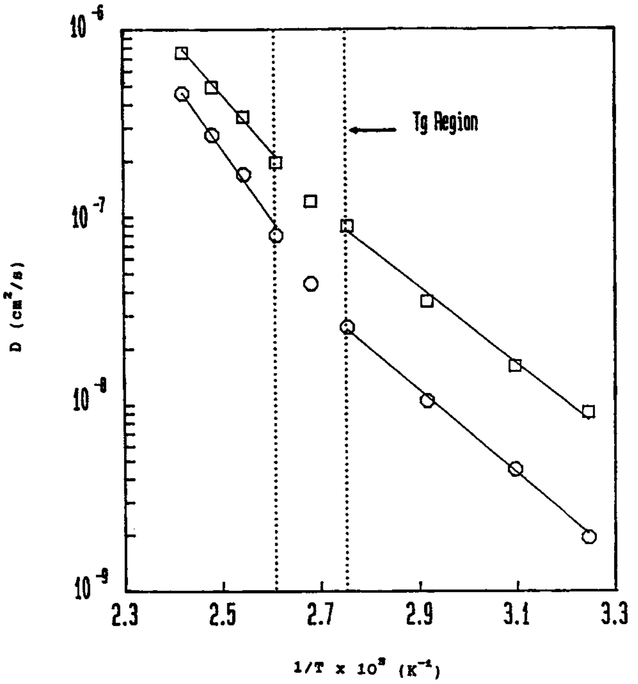

Figure 12. Diffusion coefficients of nitrogen and methane in PSAN vs. temperature.
o methane; □ nitrogen.

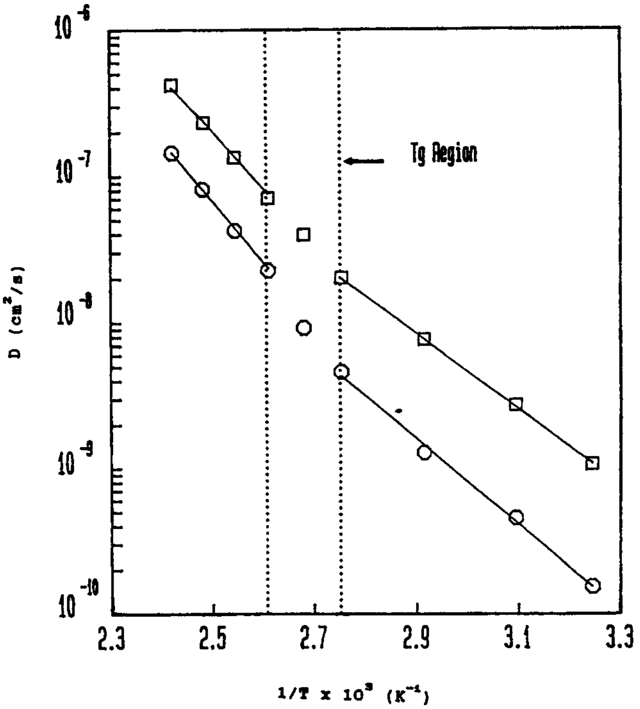

Figure 13. Diffusion coefficients of nitrogen and methane in PMMA vs. temperature.
o methane; □ nitrogen.

Discontinuities of transport properties in the glass transition region

The calculated values of D_o, ΔE_D, P_o, and ΔE_P from Arrhenius plots in Figures 12–14 are in Tables 1, 2 and 4. Due to the different values of E_D and E_P at temperatures above and below T_g, the plots of log D vs. $1/T$ and log P vs. $1/T$ show discontinuities in the glass transition region for nitrogen, helium, and methane.

The dependence of D on temperature for various gas/polymer systems has been studied in the T_g region of the polymers by a number of investigators (Meares, 1954, 1957; Toi et al., 1983; Kumins and Roteman, 1961; Stannett and Williams, 1965; Koros and Paul, 1978; Stern et al., 1989). Some investigators have reported discontinuities in plots of log D vs. $1/T$ for some gases in a number of polymers in the glass transition regions. However, such discontinuities were not observed for other gases in the same polymer or for the same gases in different polymers. Explanations of the dichotomy have been put forth by Stannett and Williams (1965), Kumins and Roteman (1961), and Frisch (1965). These authors pointed out the importance of penetrant size and the change in the thermal expansion coefficient of the polymer to the observed discontinuities and concluded that the discontinuities were linked to high $\Delta\alpha/\alpha_g$ values where α_g is the thermal expansion coefficient at the glassy state and $\Delta\alpha$ is the change of thermal expansion coefficient at T_g. It was the goal of this research to determine to what extent $\Delta\alpha/\alpha_g$ is related to the slope changes in the temperature dependence of D at T_g.

Table 5 shows the thermal expansion coefficients of the polymers and the gas diffusion results in the glass transition regions for some of the amorphous polymers as well as PSAN and PMMA. It is clear that considerably greater values of $\Delta\alpha/\alpha_g$ (>1.8) are shown by poly(vinyl acetate) (PVAc) (Meares, 1954, 1957) and poly(ethylene terephthalate) (PET) (Michaels et al., 1963; Koros and Paul, 1978) for which discontinuities in the glass transition regions are observed. In contrast,

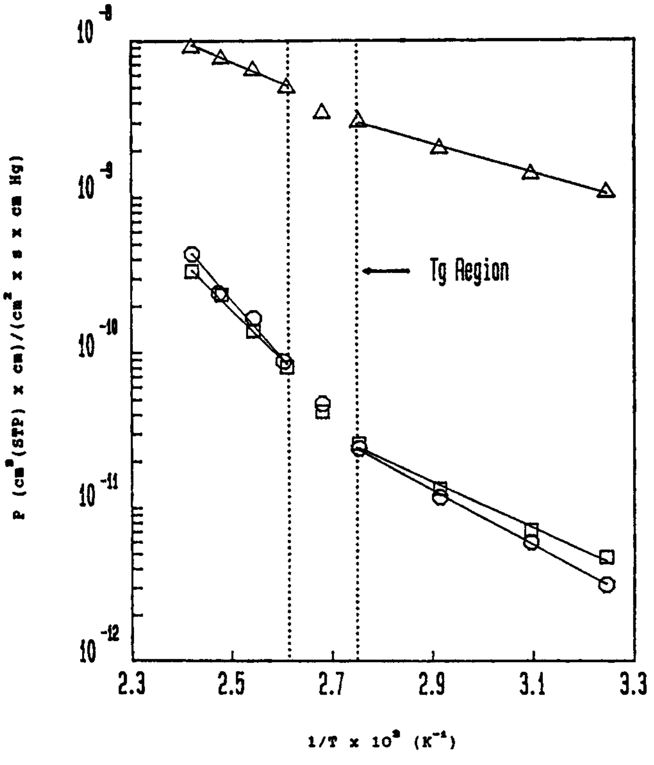

Figure 14. Permeation coefficients of gases in 50/50 PSAN/PMMA blend vs. temperature.
o methane; □ nitrogen; △ helium.

Table 4. Activation Energy and Preexponential Factor of Permeation Coefficients of Helium in PSAN/PMMA Blend

He	100% PSAN	75/25 PSAN/ PMMA	50/50 PSAN/ PMMA	25/75 PSAN/ PMMA	100% PMMA
			Below Tg		
$P_o \times 10^7$ ($cm^3 \times cm$)/($cm^2 \cdot s \cdot cm$ Hg)	7.78	9.29	11.0	10.5	17.5
ΔE_p (Kcal/mol)	3.90	4.13	4.26	4.25	4.64
			Above Tg		
$P_o \times 10^6$ ($cm^3 \times cm$)/($cm^2 \cdot s \cdot cm$ Hg)	9.55	—	21.9	—	77.2
ΔE_p (Kcal/mol)	5.74	—	6.37	—	7.40

poly(ethyl methacrylate) (Stannett and Williams, 1965) and poly(*n*-butyl methacrylate) (Aharoni, 1973; Stern et al., 1989), which have much lower values of $\Delta\alpha/\alpha_g$ (near 0.6), show no discontinuities. There was insufficient information to pass judgment on whether a discontinuity would manifest itself in a polymer with a $\Delta\alpha/\alpha_g$ value between 1.8 and 0.6. Our PSAN and PMMA samples were amorphous and had $\Delta\alpha/\alpha_g$ values between 1 and 1.8. We therefore speculate that the lower bound of the $\Delta\alpha/\alpha_g$ values for discontinuities to be observed is close to unity for amorphous polymers.

A different explanation was proposed by Stern (1989) to explain the discontinuity effect in the glass transition region. The discontinuity was thought to be the result of the transition from Henry's law to dual-mode sorption when T_g was transversed. It was suggested that for gas-polymer systems in which dual-mode sorption behaviors were observed, the plots of log D vs. $1/T$ exhibited discontinuity and vice versa. To check this possibility, we carried out methane sorption experiments for the 50/50 PSAN/PMMA blend at 66.8°C at pressures up to 22 atm. The experimental results are shown in Figure 15. The small curvature of the isotherm is consistent with dual-mode sorption, though it is much less pronounced than literature reports for CH_4-PMMA (Raymond and Paul, 1990) at 35°C, probably because the experimental temperature is closer to T_g than in Paul's studies.

Table 5. Effect of Glass Transition on Temperature Dependence of Diffusion Coefficients for Selected Gas/Polymer Systems and the Variation in the Thermal Expansion Coefficient at T_g for the Polymer

Polymer	T_g (°C)	α_g ($cm^3/g \cdot {}^\circ C \times 10^4$)	$\Delta\alpha$ ($cm^3/g \cdot {}^\circ C \times 10^4$)	$\Delta\alpha/\alpha_g$	Phenomena in Transition Region
Poly(vinyl acetate)	32	2.40	4.50	1.88	Double breaks for He, Ar, H_2, and O_2
Poly(ethylene terephthalate)	67	1.87	8.00	4.28	Single break for He, O_2, CO_2, CH_4, etc.
Poly(ethyl methacrylate)	65	2.11	1.34	0.64	No break for He, Ar, Kr, SF_6, Xe, etc.
Poly(*n*-butyl methacrylate)	27	3.85	2.41	0.63	No break for ethane
PSAN	95	1.86	3.02	1.62	Breaks for He, N_2 and CH_4
PMMA	97	2.36	2.68	1.14	Breaks for He, N_2 and CH_4

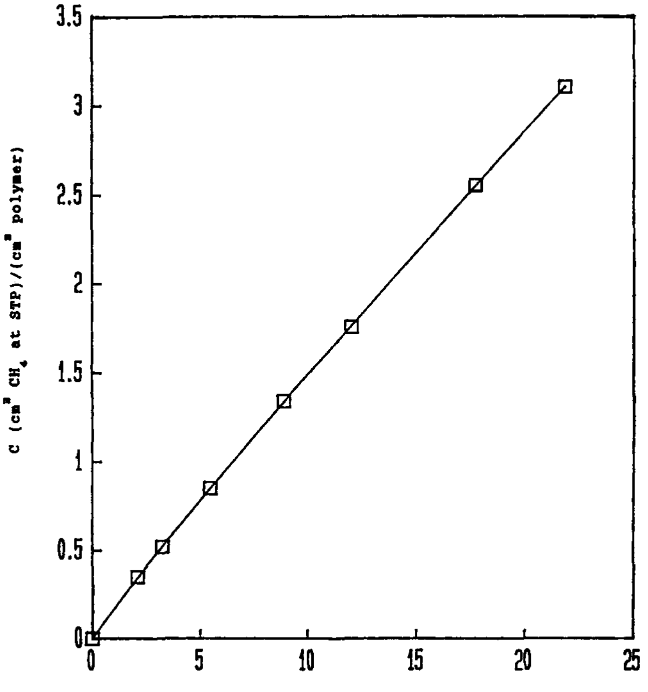

Figure 15. Methane sorption in 50/50 PSAN/PMMA blend at 66.8°C.

Conclusions

Permeabilities and diffusivities of nitrogen, methane and helium in the PSAN, PMMA, and PSAN/PMMA blends were studied from 35 to 140°C. It was observed that the permeation coefficients of helium followed the linear logarithmic mixing rule. Positive deviations from the linear logarithmic mixing were observed, however, for permeation and diffusion coefficients of methane and nitrogen at temperatures below T_g. The deviations decreased with increasing temperature and disappeared at temperatures above T_g. The observed phenomena were discussed in terms of the activated state and free volume theories. Both theories describe qualitatively the trend of the observed phenomena. The activated state theory predicts quantitatively the experimental data in the entire temperature range. Paul's mixing rule for P predicts accurately the experimental data at temperatures above T_g, but less perfectly at temperatures below T_g.

The Arrhenius plots of log D and log P vs. $1/T$ exhibited discontinuities in the glass transition region for all three gases and all blend compositions. There appears to be a correlation between high $\Delta\alpha/\alpha_g$ values and the discontinuities, as other researchers have proposed. On the other hand, Stern related the discontinuities in the gas-polymer systems to the dual-mode sorption at temperatures below T_g. We confirmed in this study that dual-mode sorption was operative in the diffusion of methane in a PSAN/PMMA (50/50) blend at temperatures below T_g.

Notation

A = characteristic constant of gas
b = universal correlation constant
B = binary interaction density for the two-component polymers
B' = constant for a particular gas
D = diffusion coefficient
D_A = diffusion coefficient of component A (in polymer blend of A and B)
D_B = diffusion coefficient of component B (in polymer blend of A and B)
D_o = preexponential factor
E_D = activation energy for diffusion
E_{DA} = activation energy for diffusion in component A
E_{DB} = activation energy for diffusion in component B
ΔE_{AB} = deviation of activation energy from the sum of additive contributions for components A and B
f = fraction free volume
f_r = fraction free volume (refers to a reference state of the observer's choosing)
P = permeation coefficient
P_A = permeation coefficient of component A (in polymer blend of A and B)
P_B = permeation coefficient of component B (in polymer blend of A and B)
R = ideal gas constant
S = solubility coefficient
S_A = solubility coefficient of component A
S_B = solubility coefficient of component B
T = absolute temperature
V_s = molar volume of the small molecule penetrant (component S)
V^* = critical free volume required for a diffusional jump
V_f = free volume of the polymer
V_{fA} = free volume of component A
V_{fB} = free volume of component B
V_{fm} = free volume of the blend
ΔV_f = excess free volume from the sum of additive contributions for components A and B

Greek letters

λ_c = characteristic relaxation time
λ_r = characteristic relaxation time (refers to a reference state of the observer's choosing)
ϕ_A = volume fraction of component A (in polymer blend of A and B)
ϕ_B = volume fraction of component B (in polymer blend of A and B)

Literature Cited

Adam, G., and J. H. Gibbs, "On the Temperature Dependence of Cooperative Relaxation Properties in Glass-Forming Liquids," *J. Chem. Phys.*, **43**, 139 (1965).

Aharoni, S. M., "A New Characteristic Temperature for Thermoplastic Polymers," *J. Polym. Sci., C*, **42**, 795 (1973).

Bondi, A., "van der Waals Volumes and Radii," *J. Phys. Chemistry*, **68**, 441 (1964).

Brandrup, J., and E. H. Immergut, eds., *Polymer Handbook*, Wiley Interscience, New York (1989).

Cohen, M. H., and D. Turnbull, "Molecular Transport in Liquids and Glasses," *J. Chem. Phys.*, **31**, 1164 (1959).

Flory, P. J., *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY (1953).

Fowler, M. E., J. W. Barlow, and D. R. Paul, "Effect of Copolymer Composition on the Miscibility of Blends of Styrene-Acrylonitrile Copolymers with Poly(methyl methacrylate)," *Polymer*, **28**, 1177 (1987).

Frisch, H. L., "Mechanism for Fickean Diffusion of Penetrants in Polymers," *J. Polym. Sci. B*, **3**, 13 (1965).

Gsell, T. C., E. M. Pearce, and T. K. Kwei, "Miscibility and Segment Mobility in Hydrogen Bonded Polymer Blends," *Polymer*, **32**, 1663 (1991).

Hopfenberg, H. B., and D. R. Paul, "Polymer Blends," D. R. Paul and S. Newman, eds., Vol. I, Academic Press, New York (1978).

Koros, W. J., and D. R. Paul, "Transition and Steady-State Permeation in Poly(ethyl Terephthalate) Above and Below the Glass Transition," *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 2171 (1978).

Koros, W. J., D. R. Paul, and A. A. Rocha, "Carbon Dioxide Sorption and Transport in Polycarbonate," *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 687 (1976).

Koros, W. J., and D. R. Paul, "Design Considerations for Measurement of Gas Sorption in Polymers by Pressure Decay," *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 1903 (1976).

Kumins, C. A., and T. K. Kwei, "Diffusion in Polymers," J. Crank and G. S. Park, eds., Academic Press, London (1968).

Kumins, C., and J. Roteman, "Diffusion of Gases and Vapors Through Polyvinyl Chloride-Polyvinyl Acetate Copolymer Films: 1. Glass Transition Effect," *J. Polym. Sci.*, **55**, 683 (1961).

Lee, W. M., "Selection of Barrier Materials for Molecular Structure," *Polym. Eng. Sci.*, **20**, 65 (1980).

Maeda, Y., "Homogeneous, Multicomponent Glassy Polymers as Membranes for Gas Separations," PhD Diss., University of Texas at Austin (1986).

Matsuoka, S., "Relaxation Phenomena in Polymers," Chap. 3, Hanser Publication, New York (1992).

McBrierty, V. J., D. C. Douglass, and T. K. Kwei, "Compatibility in Blends of Poly(methyl methacrylate) and Poly(styrene-co-acrylonitrile): 2. An NMR Study," *Macromolec.*, **11**, 1265 (1978).

Meares, P., "The Diffusion of Gases through Polyvinyl Acetate," *J. Amer. Chem. Soc.*, **76**, 3415 (1954).

Meares, P., "Diffusion of Gases in Poly(vinyl acetate) in Relation to the Second-Order Transition," *Trans. Farad. Soc.*, **53**, 101 (1957).

Michaels, A. S., W. R. Vieth, and J. A. Barrie, "Solution of Gases in Polyethylene Terephthalate," *J. Appl. Phys.*, **34**, 1 (1963).

Naito, K., G. E. Johnson, D. L. Allara, and T. K. Kwei, "Compatibility in Blends of Poly(methyl methacrylate) and Poly(styrene-co-acrylonitrile): 1. Physical Properties," *Macromolec.*, **11**, 1260 (1978).

Paul, D. R., and J. S. Chiou, "Gas Permeation in Miscible Homopolymer-copolymer Blends," *J. Appl. Polym. Sci.*, **34**, 1037 (1987).

Paul, D. R., P. Masi, and J. W. Barlow, "Gas Sorption and Transport in a Copolyester and Its Blend with Polycarbonate," *J. Polym. Sci.: Polym. Phys. Ed.*, **20**, 15 (1982a).

Paul, D. R., and G. Morel, "Carbon Dioxide Sorption and Transport in Miscible Poly(phenyl oxide)/Polystyrene Blends," *J. Membr. Sci.*, **10**, 273 (1982b).

Paul, D. R., "Gas Transport in Homogeneous Multicomponent Polymers," *J. Membr. Sci.*, **18**, 75 (1984).

Pfennig, J. L. G., H. Keskkula, J. W. Barlow, and D. R. Paul, "Experimental Simulation of the Effect of Intramolecular Repulsion on the Heat of Mixing for Polymer Blends," *Macromolec.*, **18**, 1937 (1985).

Raymond, P. C., and D. R. Paul, "Sorption and Transport of Pure CO_2 and CH_4 in Miscible Bisphenol Chloral Polycarbonate/Poly(methyl methacrylate) Blends," *J. Polym. Sci., Polym. Phys.*, **28**, 2103 (1990).

Stannett, V. T., and J. L. Williams, "The Permeability of Poly(ethyl methacrylate) to Gases and Water Vapors," *J. Polym. Sci. C*, **10**, 45 (1965).

Stern, S. A., U. M. Vakil, and G. R. Mauze, "The Solution and Transport of Gases in Poly(*n*-butyl methacrylate) in the Glass Transition Region: I. Absorption-Desorption Measurements," *J. Polym. Sci., Polym. Phys. Ed.*, **27**, 405 (1989).

Suess, M., J. Kressler, and H. W. Kammer, "The Miscibility Window of Poly(methyl methacrylate)/Poly(styrene-co-acrylonitrile)," *Polymer*, **28**, 956 (1987).

Toi, K., Y. Maeda, and T. Tokuda, "Mechanism of Diffusion and Sorption of Carbon Dioxide in Poly(vinyl acetate) Above and Below the Glass Transition Temperature," *J. Membr. Sci.*, **13**, 15 (1983).

Manuscript received Oct. 13, 1992, and revision received Mar. 2, 1993.