Gas Permeation in Miscible Homopolymer-Copolymer Blends: II. Tetramethyl Bisphenol-A Polycarbonate and a Styrene/Acrylonitrile Copolymer

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Synopsis

Gas sorption and transport properties for He, H_2, O_2, N_2, Ar, CH_4, and CO_2 at 35°C near atmospheric pressure have been obtained for miscible blends of tetramethyl bisphenol-A polycarbonate (TMPC) and a random copolymer of styrene with acrylonitrile (SAN) containing 9.5% by weight of acrylonitrile. All gas permeability, diffusion, and solubility coefficients obtained are lower than that calculated from the semilogarithmic additivity rule. These results are qualitatively interpreted by ternary solution theory and activated state theory which have been proposed to describe gas sorption and diffusion in miscible blends. The negative deviation of gas permeabilities for the blends from this rule can be explained semiquantitatively by free volume theory which takes volume contraction on mixing into account. The negative deviation increases with gas molecular size which results in larger ideal gas separation factors than that calculated from the additivity rule. For He/CH_4 and H_2/CH_4 pairs, the permselectivities for the blends are higher than that for either pure TMPC or SAN. The deviation from additivity for gas transport properties of TMPC/SAN blends is the opposite of that observed in the first paper of this series for PMMA/SAN blends. This can be attributed to the stronger interactions in TMPC/SAN blends than in PMMA/SAN blends.

INTRODUCTION

Several recent papers from our laboratory[1-9] have examined the relationship between composition and gas transport properties for several miscible polymer blends. One motivation for these studies has been the premise that the polymer–polymer interactions responsible for miscibility play an influential role in the nature of this relationship. This idea is supported by simple models developed[4] from both the activated state and the free volume theories for the transport process. The free volume treatment considers that polymer–polymer interactions are manifested solely in terms of volume changes on mixing which can be readily measured; whereas, in the activated state approach these interactions are manifested as energy terms that are not so easily determined by separate experiments.

In special cases where the polymer–polymer interactions are quite weak, both theoretical approaches predict that the gas permeability coefficient for blends on a semilogarithmic scale is a simple function of composition that linearly connects the values for the two component polymers. Blends of poly(epichlorohydrin)/poly(methyl acrylate), which form a weakly interacting system, show exactly this type of response.[6] When stronger attractive poly-

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mer–polymer interactions exist, both model approaches predict negative departures from this simple semilogarithmic mixture rule. Numerous examples of this kind of behavior have been reported recently.[2-5,7-9] For the case of zero volume change on mixing, the free volume approach can predict positive deviations from this simple logarithmic mixture rule when the permeability coefficients for the two component polymers are significantly different in value.[1,4,8] Recent experimental work has shown that blends of poly(methyl methacrylate) (PMMA) and random styrene/acrylonitrile copolymers (SANs) interact very weakly and exhibit zero volume change on mixing.[10-12] The first paper in this two part series[1] showed that PMMA/SAN blends give gas permeability coefficients which deviate positively from the semilogarithmic mixing rule and agree very well quantitatively with the predictions of the free volume model made for the case of no volume change on mixing. Other studies in our laboratory have shown that the same copolymer, SAN, is miscible with tetramethyl bisphenol-A polycarbonate (TMPC) and that this blend system has a significant volume contraction on mixing.[16] The purpose of this paper is to contrast the gas transport behavior for the very weakly interacting PMMA/SAN system with the much more strongly interacting TMPC/SAN system. It will be shown that the deviations from the semilogarithmic mixing rule are exactly reversed in these two cases which lends support to the notion that the relationship between transport properties and composition in miscible blends is indeed related to the strength of the polymer–polymer interactions.

EXPERIMENTAL

The TMPC used in this work was obtained from Bayer AG. This polymer has the chemical repeat unit shown below:
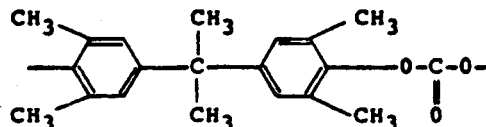
and is totally amorphous with a glass transition temperature (T_g) of 193°C measured by differential scanning calorimetry (DSC). The SAN used was obtained from Asahi Chemical Industry Co., Ltd. and it has an acrylonitrile (AN) content of 9.5% by weight. This copolymer is also totally amorphous and has a T_g of 103°C.

Films of the two polymers and their blends were prepared by solution casting. TMPC and SAN in the desired ratio were dissolved in methylene chloride at a concentration of about 5 g of total polymer per 100 cm³ of the solvent and then cast onto glass plates. The solvent was allowed to evaporate slowly at room temperature and the films formed were dried in a vacuum oven at temperatures about 30°C higher than their T_g's. After drying, the films were quenched to ambient temperature.

The T_g's of TMPC/SAN blends were measured using a Perkin-Elmer DSC-2 differential scanning calorimeter equipped with a Thermal Analysis Data Station. The heating rate was 20°C/min and the onset of the change in

heat capacity was defined as the T_g. The densities of the blends were measured at 30°C by a density gradient column using aqueous solutions of calcium nitrate. The gas permeability coefficients for He, H_2, O_2, N_2, Ar, CH_4, and CO_2 at 35°C were measured by a high pressure permeation cell whose design and operation have been described elsewhere.[13,14] The upstream pressure was kept at 1 to 2 atm, while the downstream pressure was effectively zero.

RESULTS AND DISCUSSION

Glass Transition Temperatures and Specific Volumes

TMPC has been known for some time to be miscible with polystyrene;[15] however, recently it has been shown to be also miscible with copolymers of styrene and acrylonitrile when the AN content of the copolymer is about 11% by weight or less.[16] The interactions between TMPC and SANs seem to vary significantly with the AN content of the SAN as revealed by density measurements. Specific volumes of the blends show maximum deviation from additivity when the AN content is about 9 to 11% by weight. This suggests that the net interaction between TMPC and SAN may have a maximum strength when the AN content is within this range. Because the purpose of this study is to contrast the gas transport behavior in TMPC/SAN blends to that in PMMA/SAN blends by virtue of the stronger interactions in the former, an SAN with 9.5% AN content was selected.
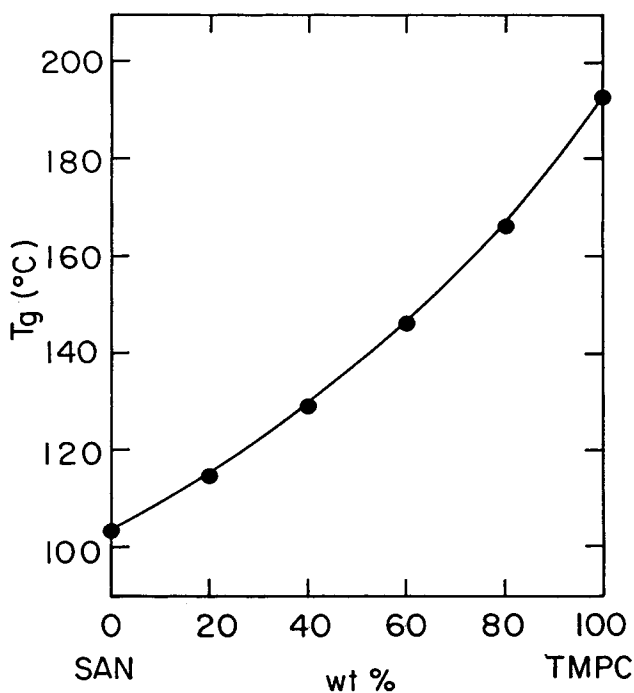

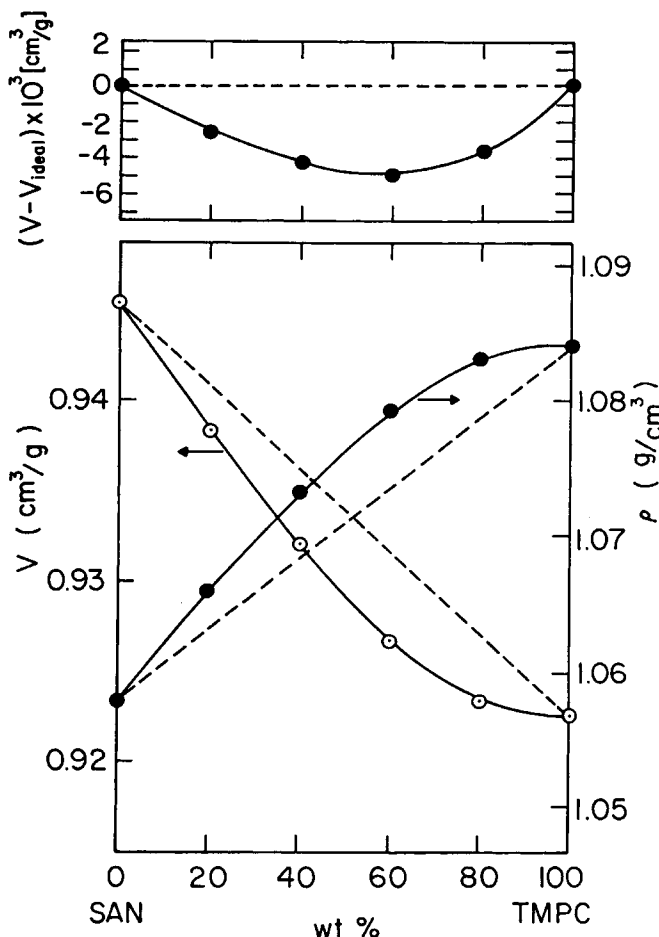Fig. 1. Glass transition temperatures by DSC for TMPC/SAN blends.

Fig. 2.   Density and specific volume data for TMPC/SAN blends at 30°C. The upper part shows the excess specific volume.

Miscibility between TMPC and this SAN is demonstrated by the single composition-dependent T_g for their blends shown in Figure 1. Density and specific volume data for the blends are shown in Figure 2. As can be seen, the specific volume, V, is lower than that calculated from the simple additivity rule, i.e.

$$V_{ideal} = V_1 W_1 + V_2 W_2 \tag{1}$$

where W is the weight fraction and subscripts 1 and 2 denote TMPC and SAN, respectively. The excess volumes of the blends defined as $(V - V_{ideal})$, which are qualitatively an indication of the extent of blend interaction, are also shown in the upper part of Figure 2. The significant contraction in volume when TMPC and SAN are mixed is an indication of the strong interaction between these two polymers.
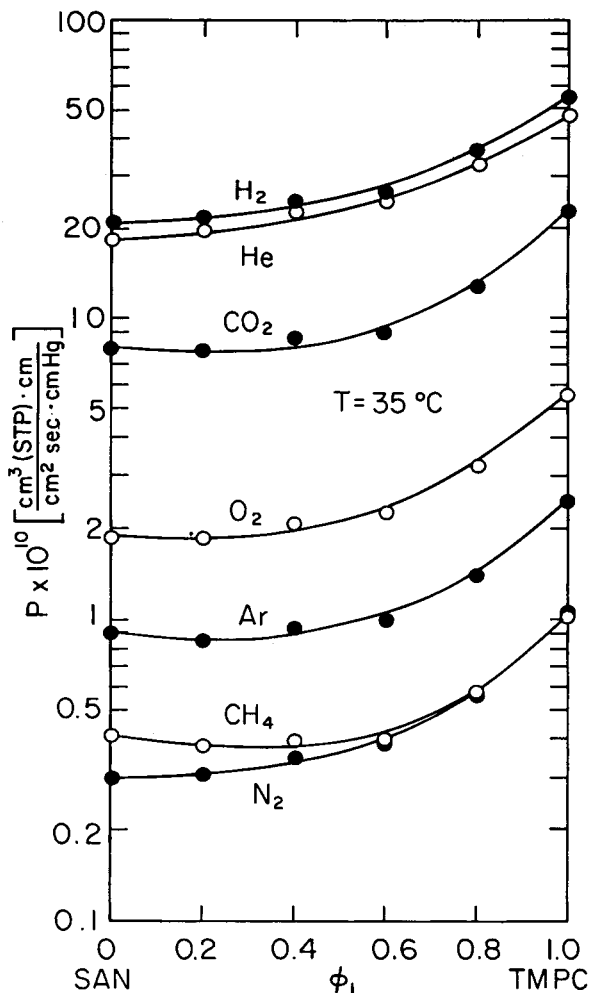
Fig. 3. Semilogarithmic plots of gas permeability coefficients vs. volume fraction of TMPC in the blend. T = 35°C

Gas Permeation

The permeability coefficients for TMPC/SAN blends for all gases studied here are plotted semilogarithmically versus the volume fraction of TMPC of the blend, ϕ_1, in Figure 3. Obviously, gas permeabilities for the blends are lower than that calculated from the semilogarithmic additivity rule, i.e.

$$\ln P = \phi_1 \ln P_1 + \phi_2 \ln P_2 \qquad (2)$$

In Figures 4 to 8, the apparent diffusion coefficients, D_a, and solubility coefficients, S_a, for O_2, N_2, Ar, CH_4, and CO_2 are also plotted semilogarithmically versus ϕ_1. Here, D_a is defined as
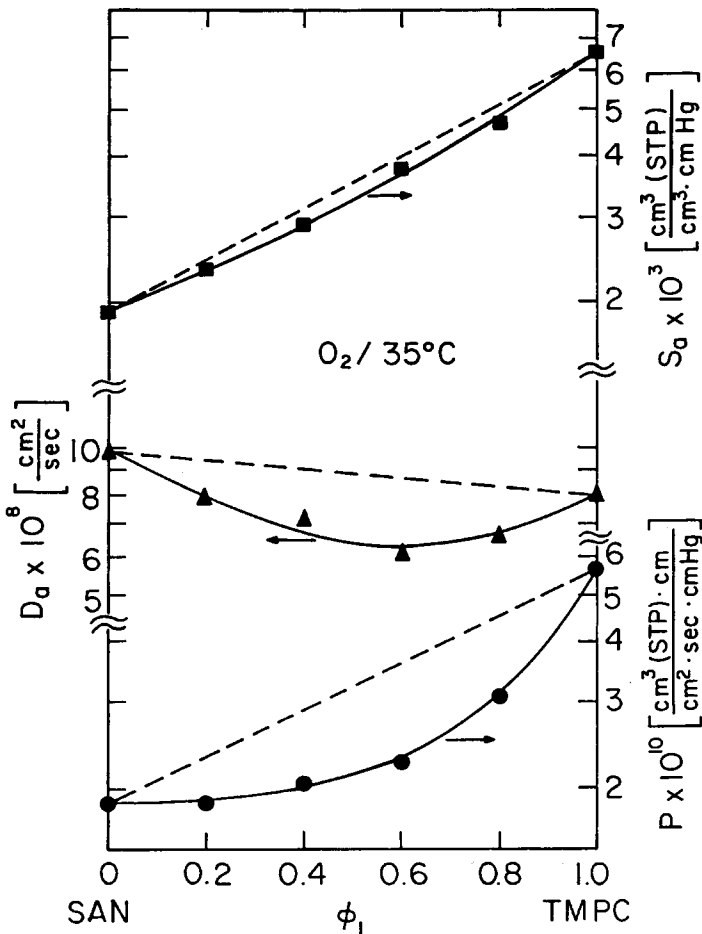
$$D_a = l^2/6\theta \qquad (3)$$

Fig. 4. Semilogarithmic plots of O_2 permeability at 35°C, apparent diffusion and solubility coefficients vs. volume fraction of TMPC in the blend.

and S_a is defined as

$$S_a = P/D_a \tag{4}$$

where l is the film thickness and θ is the diffusion time lag. In all cases, the gas permeability, diffusion, and solubility coefficients for TMPC/SAN blends are lower than that calculated from the semilogarithmic additivity rule. These results are opposite to those observed for PMMA/SAN blends but are similar to many other blend systems reported previously.[2-5,7-9]

The negative deviations of the solubility and diffusion coefficients seen in Figures 4 to 8 for TMPC/SAN blends can be explained by mixture rules based on various approaches[2-4,17] developed recently to describe gas sorption and transport properties in miscible blends. From ternary solution theory, the solubility coefficient, S, for a blend can be related to that of the component polymers by

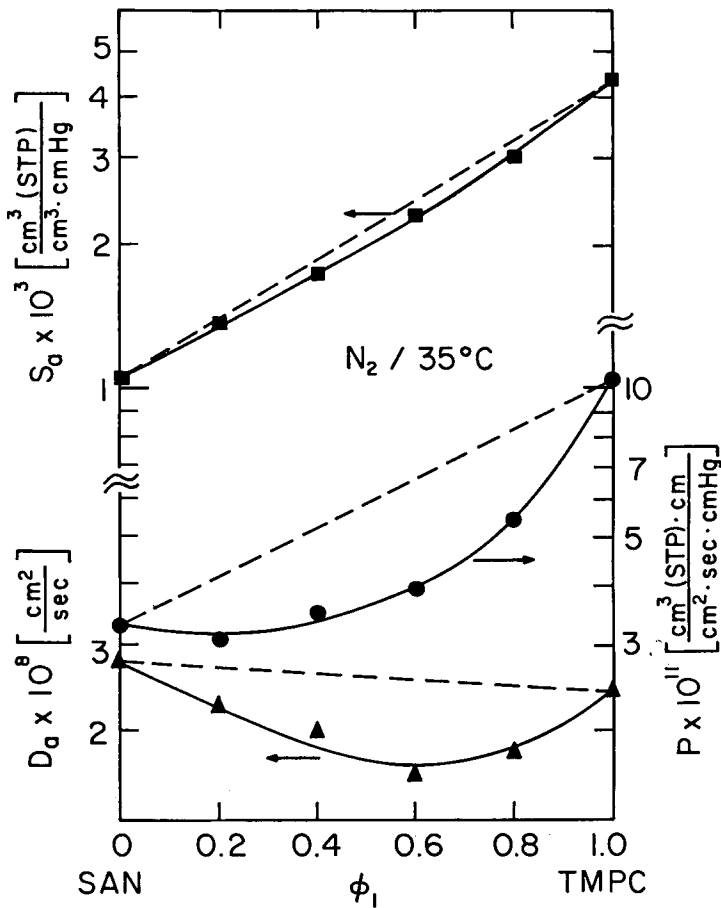$$\ln S = \phi_1 \ln S_1 + \phi_2 \ln S_2 + (BV_3/RT)\phi_1\phi_2 \tag{5}$$

Fig. 5. Semilogarithmic plots of N_2 permeability at 35°C, apparent diffusion and solubility coefficients vs. volume fraction of TMPC in the blend.

where B is the binary interaction parameter for the blend and V_3 is the molar volume of the penetrant in the sorbed state. Since B is negative for miscible blends, the solubility coefficients for blends are expected to be smaller than that calculated from the semilogarithmic additivity relation given by Eq. (5) when the last term is omitted. For most miscible blend systems with mild to strong interactions, the value of B is typically less than -5 cal/cm^3. The molar volume for simple gases in the sorbed state is usually on the order of 50 cm^3/mole; for example, $V_3 = 55$ cm^3/mole for CO_2.[18] Based on these parameters, it can be seen that the maximum deviation for the solubility coefficient at T = 35°C is only about 10% when $\phi_1 = \phi_2 = 0.5$. This is about the extent of deviation observed in Figures 4 to 8 for TMPC/SAN blends.

On the other hand, the much larger negative deviations for the diffusion coefficients can be understood in terms of the activated state theory result for blends[4]

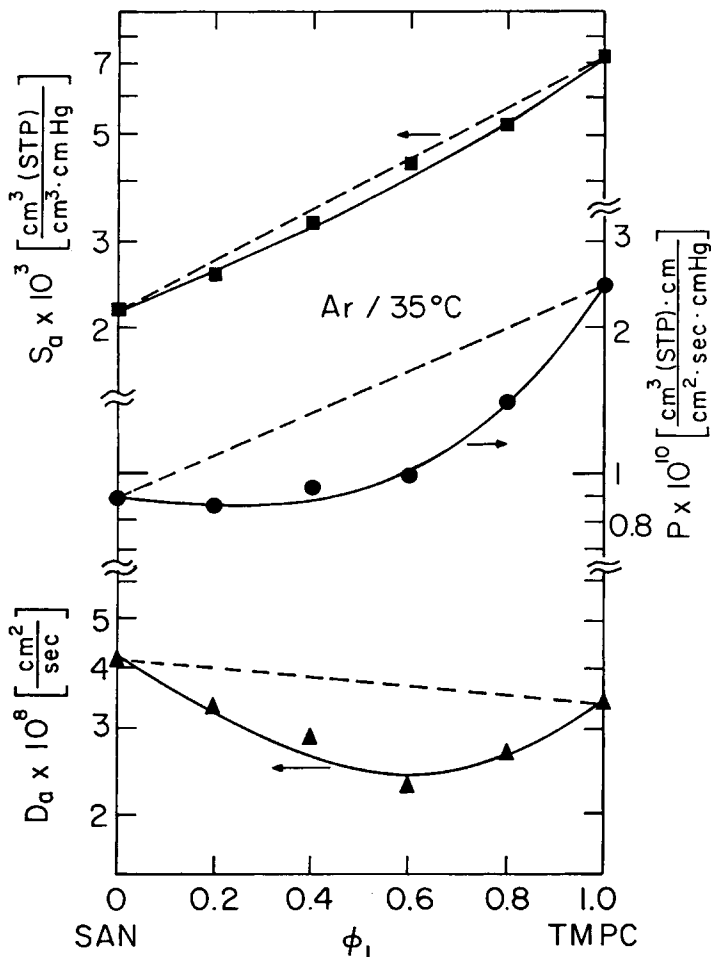$$\ln D = \phi_1 \ln D_1 + \phi_2 \ln D_2 + (\alpha RT - 1)\Delta E_{12}/RT \qquad (6)$$

Fig. 6. Semilogarithmic plots of Ar permeability at 35°C, apparent diffusion and solubility coefficients vs. volume fraction of TMPC in the blend.

where α is a constant which gives $(\alpha RT - 1)$ a negative value of approximately -0.5, R is the gas constant, T is the temperature, and ΔE_{12} is the deviation term for the activation energy, E_D, defined as

$$E_D = \phi_1 E_{D1} + \phi_2 E_{D2} + \Delta E_{12} \qquad (7)$$

The negative deviations of gas diffusion coefficients from the semilogarithmic additivity rule [omitting the last term in Eq. (6)] imply a positive value of ΔE_{12}, i.e., gas diffusion in the blends requires a higher activation energy than that predicted from the simple additivity. For the TMPC/SAN blends studied here, the maximum negative deviation of the diffusion coefficient, which occurs at about 60% TMPC, is 30 to 35%. This corresponds to a ΔE_{12} of about 500 cal/mole.
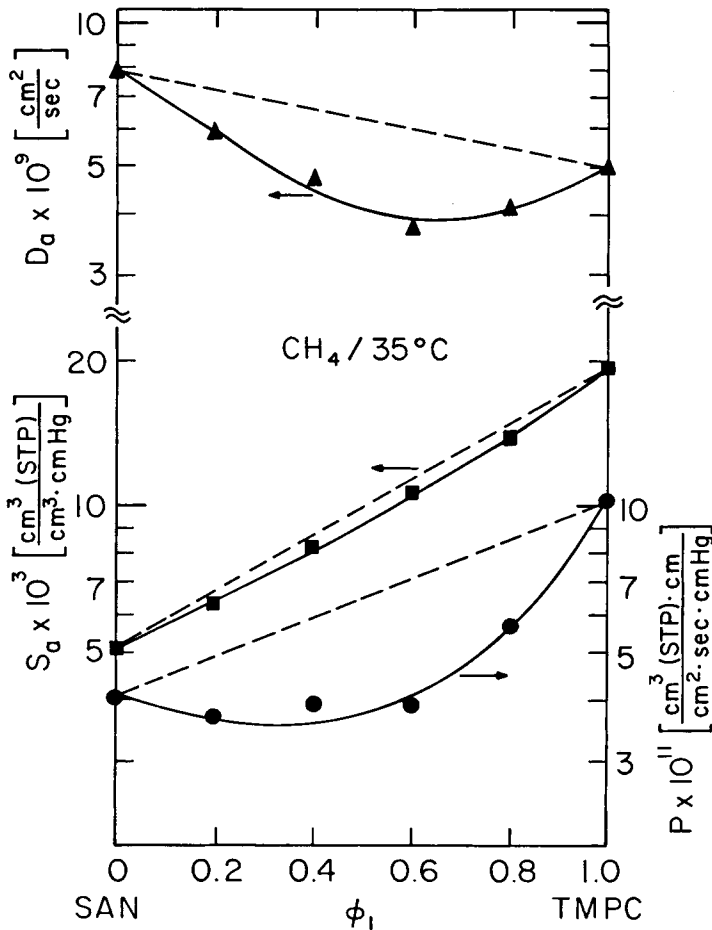
Fig. 7. Semilogarithmic plots of CH_4 permeability at 35°C, apparent diffusion, and solubility coefficients vs. volume fraction of TMPC in the blend.

The permeability coefficient is the product of the diffusion and solubility coefficients, i.e.

$$P = DS \qquad (8)$$

Combining eqs. 5, 6 and 8 yields

$$\ln P = \phi_1 \ln P_1 + \phi_2 \ln P_2 + (BV_3/RT)\phi_1\phi_2$$

$$+ (\alpha RT - 1)\Delta E_{12}/RT \qquad (9)$$

The even larger negative deviations of the gas permeability coefficients from the semilogarithmic additivity rule (see Figs. 4 to 8) are simply the combined result of the last two terms in Eq. (9).

The dependence of gas permeability coefficients on blend composition has also been explained by a free volume approach. Lee[19] has shown that gas
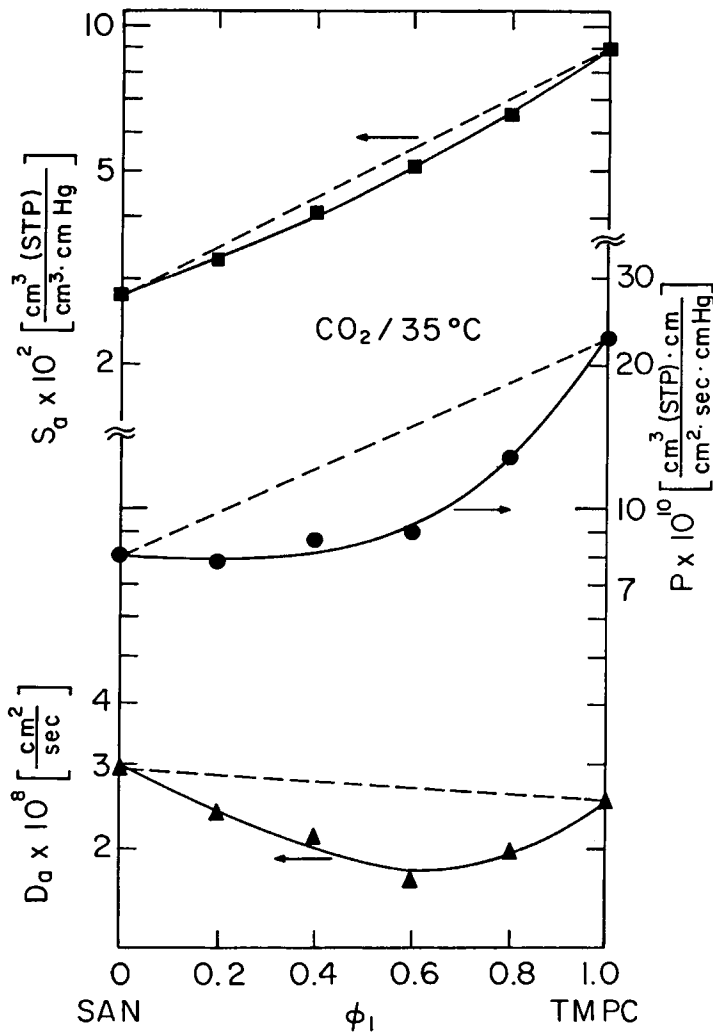
Fig. 8. Semilogarithmic plots of CO_2 permeability at 35°C, apparent diffusion, and solubility coefficients vs. volume fraction of TMPC in the blend.

permeability coefficients for a wide range of polymers can be well correlated to their free volumes using

$$P = A \exp[-B/(V - V_0)] \tag{10}$$

where A and B are constants for a specific gas and V_0 is the volume occupied by polymer chains. By assuming that the free volumes of the polymer mixtures are additive, i.e.

$$(V - V_0) = W_1(V - V_0)_1 + W_2(V - V_0)_2 \tag{11}$$

the gas permeability for a miscible blend can be related to that of the two

component polymers by[4]

$$\ln(P/A) = [W_1/\ln(P_1/A) + W_2/\ln(P_2/A)]^{-1} \tag{12}$$

Since the densities of most polymers are rather similar, the weight fractions in Eqs. (11) and (12) can be replaced by volume fractions with minimal difference. This replacement is convenient for comparison with other relationships [e.g., Eq. (5)] and following past practice,[4] volume fractions will be used in the graphical presentations which follow.

When there is a relatively strong attraction between the two component polymers, there is often a volume contraction on mixing and the assumption of Eq. (11) is no longer correct. In this case, the gas permeability will be lower than that calculated from Eq. (12) by a factor of ξ

$$\xi = \exp\left[B\Delta V_{\text{mix}}/(V - V_0)^2 \right] \tag{13}$$
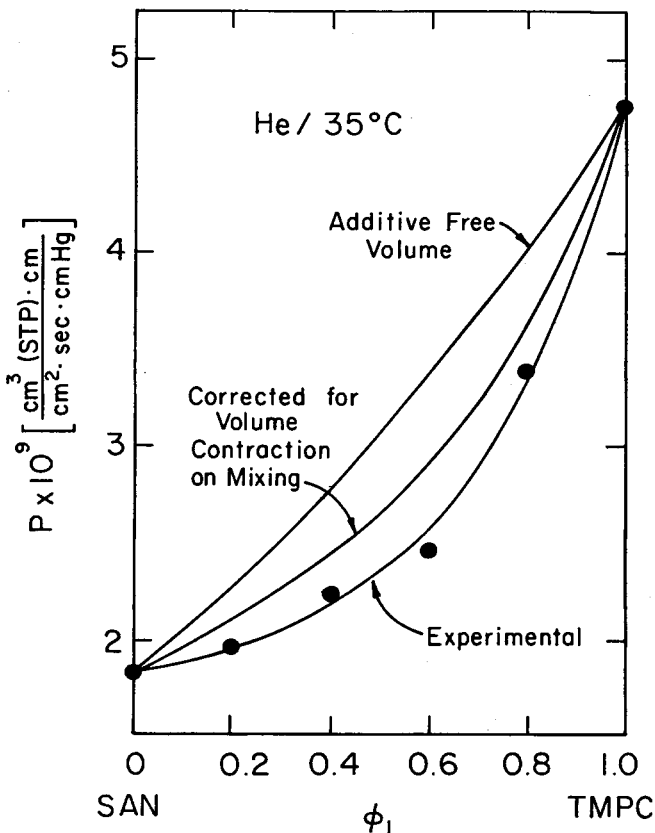

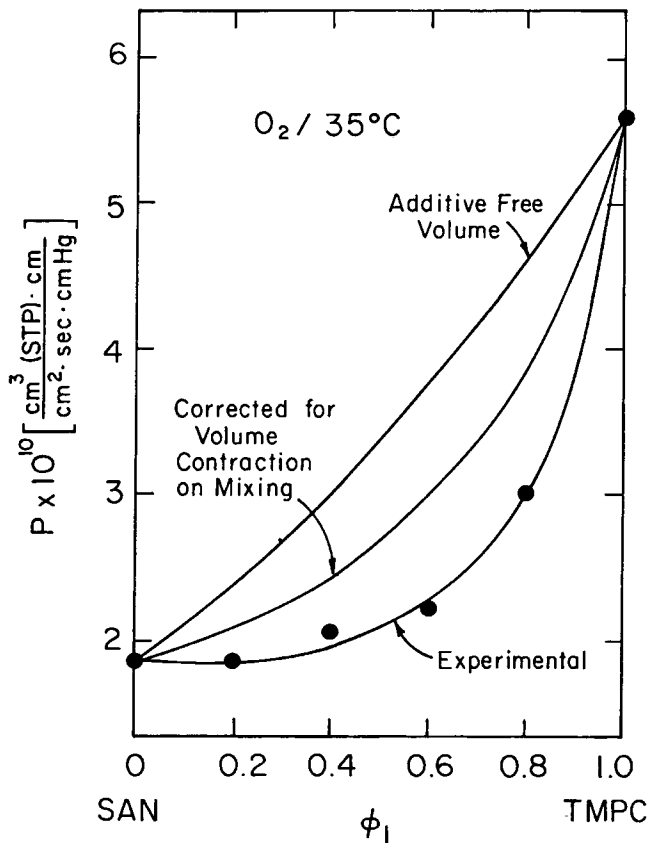Fig. 9. Comparison of measured He permeabilities at 35°C with calculated values from free volume theory.

Fig. 10. Comparison of measured O_2 permeabilities at 35°C with calculated values from free volume theory.

where ΔV_{mix} is the contraction in free volume defined as

$$(V - V_0) = W_1(V - V_0)_1 + W_2(V - V_0)_2 + \Delta V_{mix} \qquad (14)$$

The gas permeabilities for TMPC/SAN blends to He, O_2, CH_4, and CO_2 calculated from Eq. (12) assuming no volume contraction and those corrected using Eq. (13) to take volume contraction into account are plotted versus blend composition in Figures 9 to 12 for comparison with the experimental data. The characteristic constants A and B used in these calculations for each gas are listed in Table I. The volume contraction ΔV_{mix} for each blend composition was taken from Figure 2 (i.e., $\Delta V_{mix} = V - V_{ideal}$). The occupied volumes V_0 were estimated using Bondi's method[20] by

$$V_0 = 1.3V_w \qquad (15)$$

where V_w is the van der Waals volume for the polymer repeat unit whose value can be calculated by a group contribution method.[21] As seen in Figures 9 to 13, the measured permeabilities for the blends are somewhat lower than
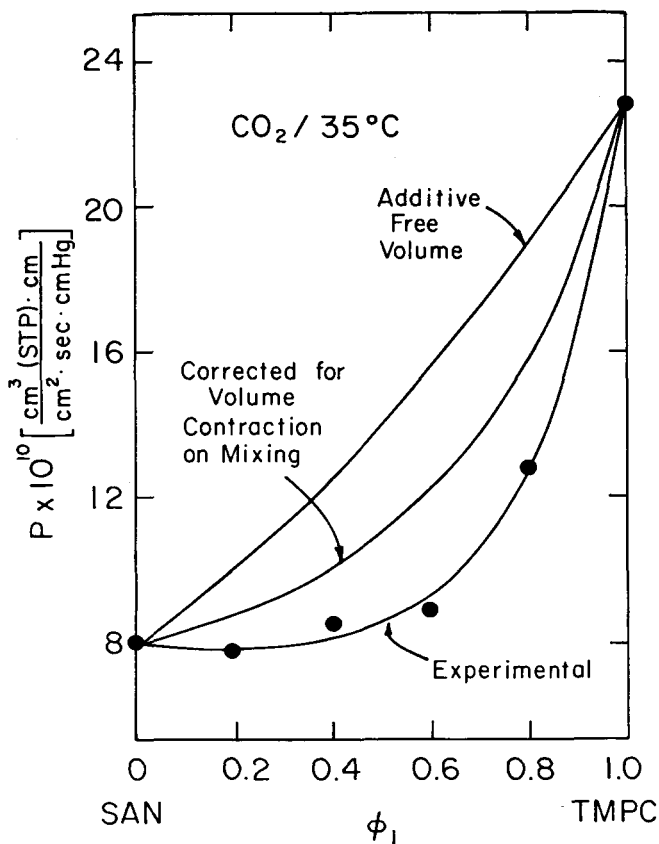
Fig. 11. Comparison of measured CH_4 permeabilities at 35°C with calculated values from free volume theory.

that calculated by taking volume contractions into account. However, the calculated volume contraction effect semiquantitatively accounts for the negative deviation of gas permeabilities for the blends. Figures 9–13 employ an arithmetic coordinate for the permeability axis. When plotted semilogarithmically, the upper curves in Figures 9 to 13 would show slightly positive deviations from the linear tie line while those corrected for volume contraction and those experimentally measured would fall below the tie line.

Ideal Gas Separation Factor

Several recent studies on gas transport in miscible polymer blends have shown that while gas permeabilities for the blends are often lower than that calculated from the semilogarithmic additivity rule, the gas permselectivities behave in the opposite manner. That is, on semilogarithmic coordinates, the ideal separation factors for gas A relative to gas B, i.e.
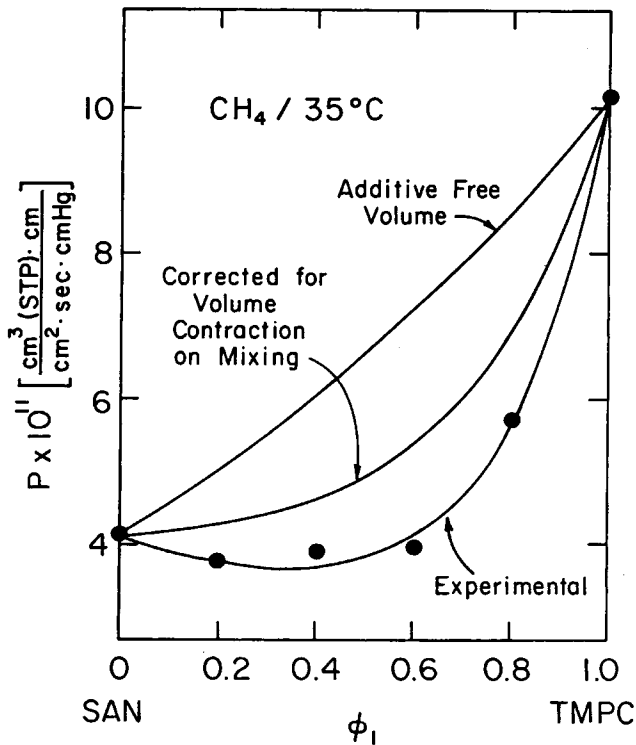
$$\alpha_B^A = P_A/P_B \qquad (16)$$

Fig. 12. Comparison of measured CO_2 permeabilities at 35°C with calculated values from free volume theory.

TABLE I
Parameters A and B in Eq. (10)

Gas	A $\left[\dfrac{cm^3 \ (STP) \ cm}{cm^2 \ sec \ cm \ Hg} \right]$	B $[cm^3/g]$
He[a]	3.86×10^{-6}	0.780
O_2[b]	7.9×10^{-7}	1.335
CH_4[a]	2.17×10^{-6}	1.589
CO_2[a]	6.56×10^{-6}	1.333

[a] Data from ref. 22 at 35°C.
[b] Data from ref. 4 at 25°C.

show positive deviations from the tie line for the blends. The ideal separation factors for four gas pairs, namely He/CH_4, H_2/CH_4, O_2/N_2, and CO_2/CH_4, are shown in Figures 13 to 15 for TMPC/SAN blends. Here, arithmetic coordinates are used in order to magnify the deviations since TMPC and SAN have very similar gas separation factors. As seen in Figure 13, the permselectivities for He/CH_4 and H_2/CH_4 gas pairs are even higher for the blends than for the two components. On the other hand, the permselectivities for the O_2/N_2 pair follow linear additivity within the experimental errors, and
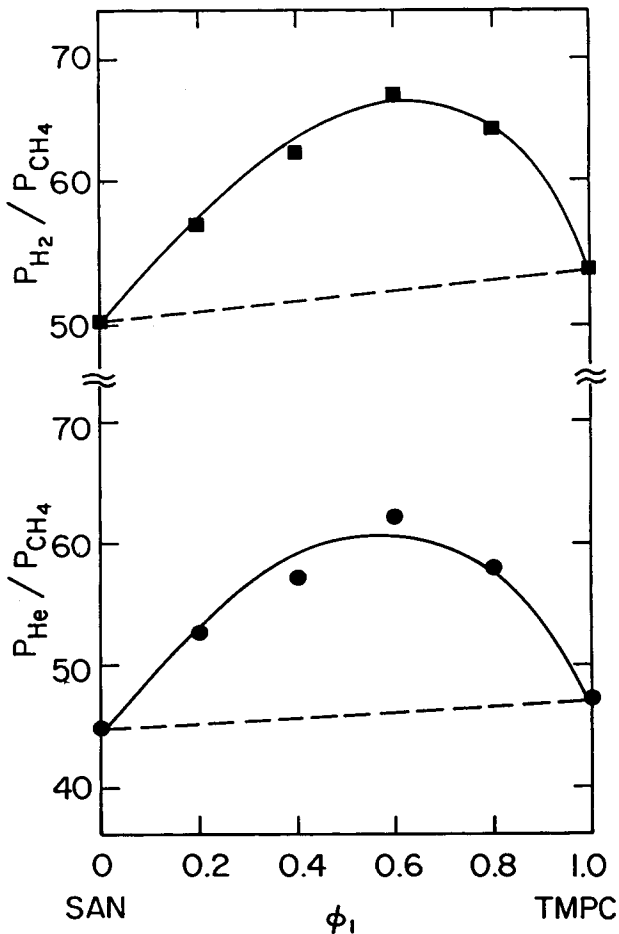
Fig. 13. Ideal gas separation factors for He/CH_4 and H_2/CH_4 pairs plotted vs. volume fraction of TMPC in blend.

the permselectivities for the CO_2/CH_4 pair are only slightly higher than the linear tie line.

The different permselectivity behavior for the four gas pairs mentioned above stems from molecular size differences for the various gas pairs. From Figures 3 to 12, it can be seen that the larger the molecular size of the gas, the larger the negative deviation of gas permeability from any additivity rule. This observation is generally true as seen from other studies[5,7-9] and is believed to result from a greater contraction on mixing of the larger elements of the free volume distribution which contribute to transport of the larger gas molecules. Since He and H_2 have the smallest molecular sizes and CH_4 the largest, the ideal separation factors for He/CH_4 and H_2/CH_4 pairs exhibit the largest positive deviations from additivity. On the other hand, for the O_2/N_2 and CO_2/CH_4 pairs, the molecular sizes are relatively close and, therefore, smaller deviations can be expected.

Since the gas permeability coefficient is a product of diffusion and solubility coefficients, the gas permselectivity can be separated into two contributions,
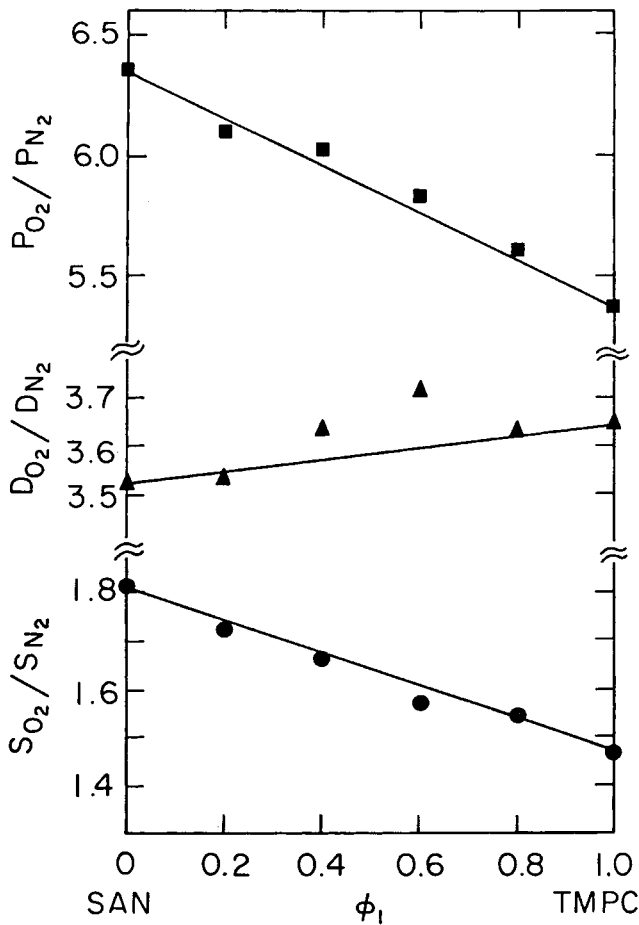
Fig. 14. Ideal gas separation factors for O_2/N_2 pair and the individual contributions from diffusion and solubility factors.

one from the ratio of diffusion coefficients and the other from the ratio of gas solubility coefficients for the two gases. Figures 14 and 15 break the total permselectivity into these two contributions for the O_2/N_2 and CO_2/CH_4 pairs. While the mobility or diffusion factors behave similar to the overall permselectivity, the thermodynamic or solubility factors show no significant deviations from linear additivity within experimental error. The latter is understandable since as noted before the deviations of gas solubilities for the blends are small in magnitude regardless of the gas species.

SUMMARY

This study has shown that, in terms of the relationship between gas transport properties and blend composition, TMPC/SAN blends behave like most other miscible blend systems which exhibit mild to strong polymer–polymer interactions. The permeability, diffusion, and solubility coefficients for TMPC/SAN blends for various gases are all lower than that calculated from
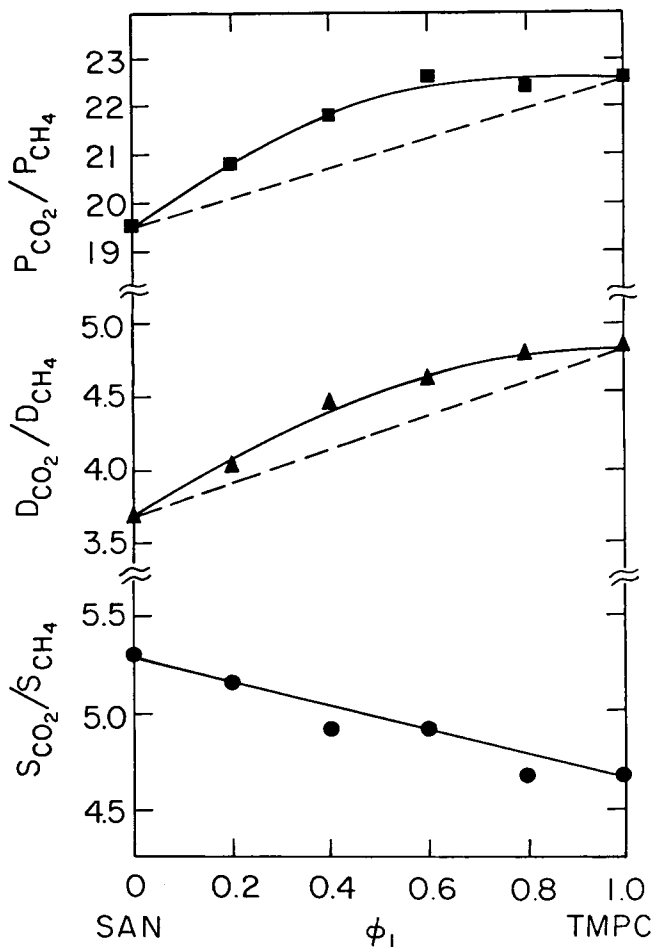
Fig. 15. Ideal gas separation factors for CO_2/CH_4 pair and the individual contributions from diffusion and solubility factors.

semilogarithmic additivity rules. These results may be interpreted qualitatively by the activated state theory for gas diffusion and the ternary solution theory for gas solubility in miscible polymer blends. The negative deviations of gas permeabilities from this rule can also be explained semiquantitatively by a free volume theory by taking volume contractions for the blends into account. These negative deviations increase with the gas molecular size. As a result, the ideal gas separation factors for He/CH_4 and H_2/CH_4 pairs can be even larger for blends than for either component polymer because TMPC and SAN have rather similar permselectivities.

The gas transport behavior observed for TMPC/SAN blends as mentioned above is opposite to that observed for PMMA/SAN blends as reported in the first part of this series. This is attributed to the different magnitude of interactions in the two blend systems. For TMPC/SAN blends, such interactions may be relatively strong as indicated by the large volume contraction when TMPC and SAN are mixed. To the contrary, no contraction was

observed for PMMA/SAN blends, which suggests weaker interactions for this pair. This contrast demonstrates that the interactions in blends play an important role in gas transport behavior for miscible blends.

We have used two approaches to interpret transport behavior in blends for this and previous studies. The one based on separate analysis of the sorption and diffusion terms via thermodynamic and activated state theories generally suffers from not having information about the interaction terms B or ΔE_{12}; although, in principle both can be measured. The one based on free volume fails to properly separate mobility and solubility issues, but it offers the advantage of only requiring information about the volume change on mixing for the blend. It seems to do a very good job of describing the behavior of weakly interacting systems like PMMA/SAN. However, for more strongly interacting systems such as TMPC/SAN and several others[4,5,7-9] it predicts departures from additivity which are somewhat less than those observed experimentally. The reason for this deficiency is more fundamental than simply not explicitly accounting for solubility effects since these are at most no greater than about 10%.

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