Selective gas transport in miscible PPO–PS blends

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The permeation rates of He, CO_2 and CH_4 though miscible blends of polystyrene and poly(phenylene oxide) at 35°C are reported as a function of pressure. Sorption isotherms for CO_2 and CH_4 are also presented. By using ratios of the permeabilities of the pure gases the separation factors for the gas pairs He–CH_4 and CO_2–CH_4 can be estimated. For both pairs the estimated separation factor goes through a prominent maximum, thus indicating that these blends are more permselective than expected from the behaviour of polystyrene and poly(phenylene oxide). This stems from mobility considerations rather than solubility effects and a qualitative free volume argument is proposed as an explanation. The sorption and transport data have been interpreted and correlated using the dual sorption–mobility models developed previously for glassy polymers. Since the commercial polystyrene used contained a small amount of mineral oil to improve flow behaviour, the effect of this additive on polystyrene properties was explored in some detail.

(Keywords: blends; permeation; gas transport; polystyrene; poly(phenylene oxide))

In a previous paper[1] the sorption and transport behaviour of CO_2 gas in miscible, homogeneous blends of polystyrene, PS, and poly(phenylene oxide), PPO, were reported. This paper extends that work by reporting on measurements for the additional gases, helium and methane, for the purposes of assessing the potential of polymer blends generally, and the PS–PPO system specifically, as selective membrane materials for separation processes. Because of the history-dependent nature of the properties of glassy polymers, measurements for CO_2 have been repeated so that comparisons among the behaviour of the various gases would be more meaningful. The polystyrene used in this study differed slightly from that used in the previous work in that it contained a small amount of mineral oil, which is commonly added to commercial polystyrenes to improve flow behaviour. A detailed examination of the effects resulting from the presence of mineral oil is given.

The results reported here for CO_2 agree rather well with those reported previously; however, some minor differences have been noted, which may be attributed in part to the presence of mineral oil in the polystyrene and in part to improved preparation and measurement techniques incorporated into this work.

MATERIALS AND EXPERIMENTAL PROCEDURES

The PPO used was supplied by the General Electric Co. and was from the same lot employed in the previous study[1]. The polystyrene was a commercial product, Cosden Polystyrene 525, which was identical with the previous material, Cosden Polystyrene 550, except for the inclusion of 3% mineral oil to improve flow behaviour.

Films containing different proportions of these polymers were prepared by a spin casting method. Trichloroethylene solutions containing approximately 10% total polymer were prepared at room temperature by agitation for 3 days. These solutions were introduced into an aluminium cylinder which rotated at high speeds, thus uniformly distributing the solution onto the vertical walls of the cylinder. The temperature and pressure inside the cylinder can be adjusted to control the evaporation of solvent. After rotation was begun, the solvent was allowed to evaporate naturally at 80°C for 1 h and then under reduced pressure for 2 h. After cooling, the films were removed from the cylinder wall and placed in a vacuum oven at 70°C for one week to remove the remainder of the solvent. The glass transition temperatures and the densities of the cast film were measured by differential scanning calorimetry (d.s.c.) and by a density gradient column, respectively. The results are shown in *Figures 1* and *2*, along with comparison data from the literature. The dashed line in *Figure 1* is typical of T_g values for blends which do not contain mineral oil[2], whereas the present results reflect a slight T_g depression caused by the mineral oil, which gradually diminishes as the PPO content increases. *Figure 2* shows density data from three other sources[3–5]. All of the data show densification on mixing PPO and PS; however, the extent of this effect and the absolute density vary somewhat among the four sets of data. These differences most likely represent variations in history for these glassy materials and the varying content of mineral oil for the present results.

The equipment and procedures for measuring gas sorption and permeation were the same as those used in the earlier work[1]. Each film specimen was exposed to 20 atm of CO_2 for one day uniformly to condition[6] the glassy material prior to sorption or permeation measurements, which were made at 35°C.

SORPTION AND TRANSPORT RESULTS FOR BLENDS

Figures 3 and *4* display the sorption isotherms for CO_2 and CH_4, respectively, at 35°C in the various blends. The

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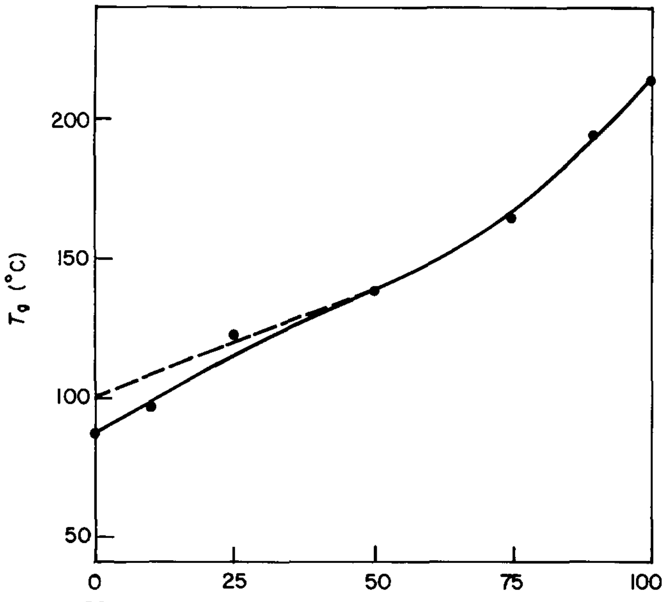

Figure 1 Glass transition behaviour by d.s.c. for PPO–PS 525 blends (solid points). (-----): PS without mineral oil[2]

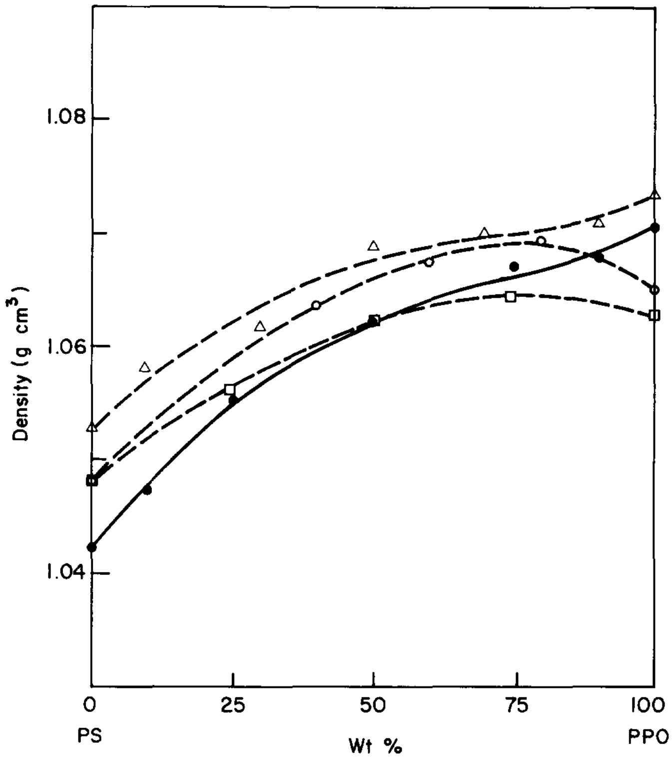

Figure 2 Density of PPO–PS blends. (●): from this work using PS 525. (△): Yee[3]; (○): Kleiner *et al.*[4]; (□): Jaques and Hopfenberg[5]

isotherm curvature is characteristic of that expected for glassy polymers[7,8]. For both gases, solubility in PPO is considerably higher than that in PS, which may be primarily attributable to the higher glass-transition temperature of the former[9]. There is a steady progression of the isotherms between these limits as blend composition is varied, consistent with expectations for miscible blends. Methane is less soluble in these polymers than is carbon dioxide by a factor of slightly more than two. Isotherms for helium sorption were not determined since the solubility of this gas is so low that such measurements are not practicable.

Permeability coefficients for He, CO_2 and CH_4 at 35°C for the various blends are given as a function of upstream driving pressure, p_2, in *Figures 5, 6* and *7*. For He, the permeability coefficients are quite independent of pressure for all polymer compositions, whereas CO_2 and

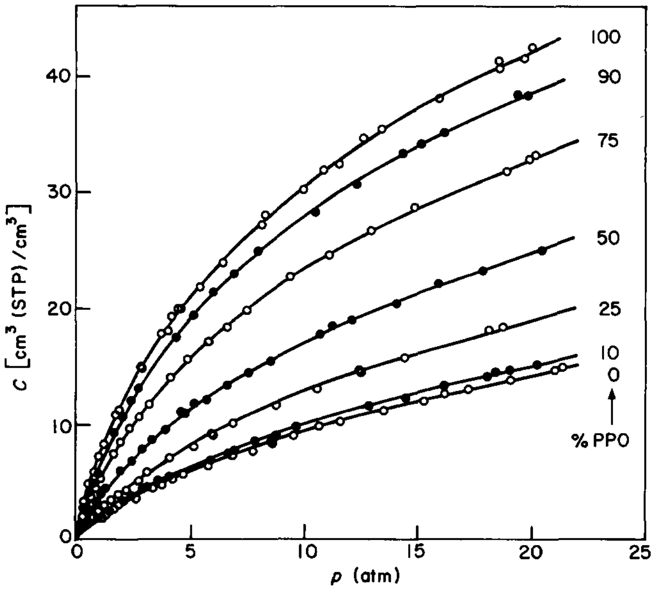

Figure 3 CO_2 sorption isotherms for PPO–PS blends at 35°C

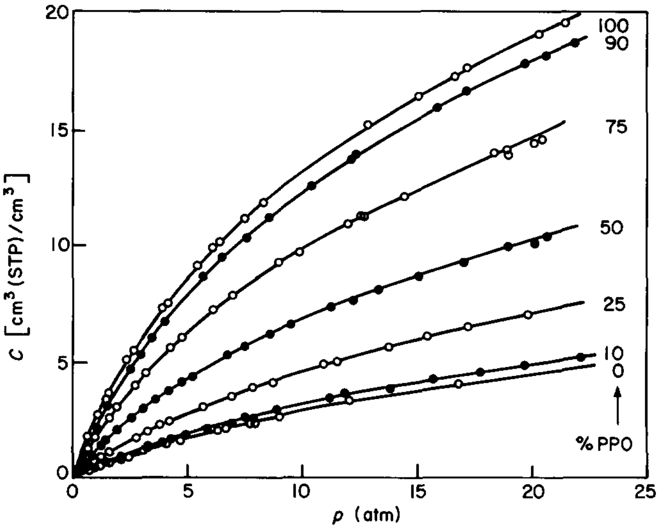

Figure 4 CH_4 sorption isotherms for PPO–PS blends at 35°C

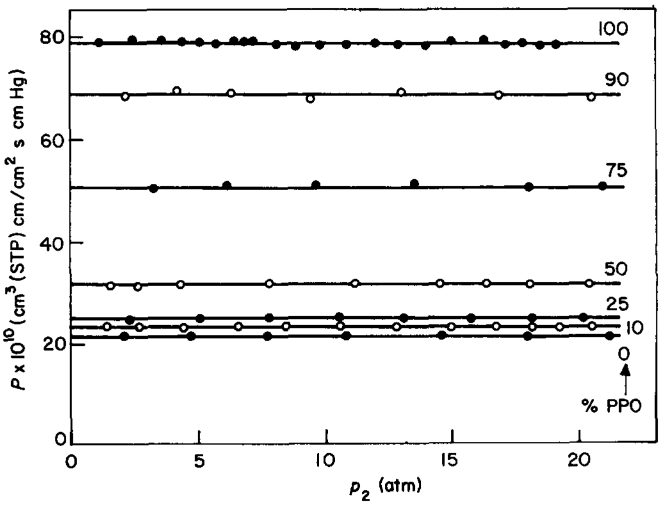

Figure 5 Helium permeability in blends at 35°C

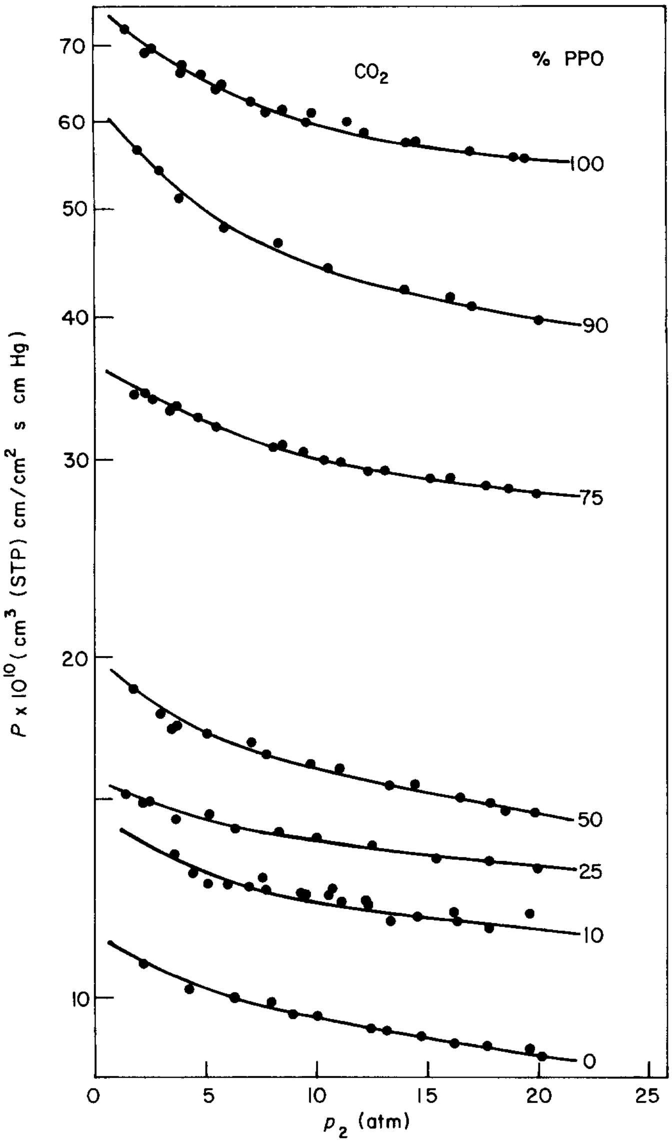

Figure 6 CO$_2$ permeability in blends at 35°C

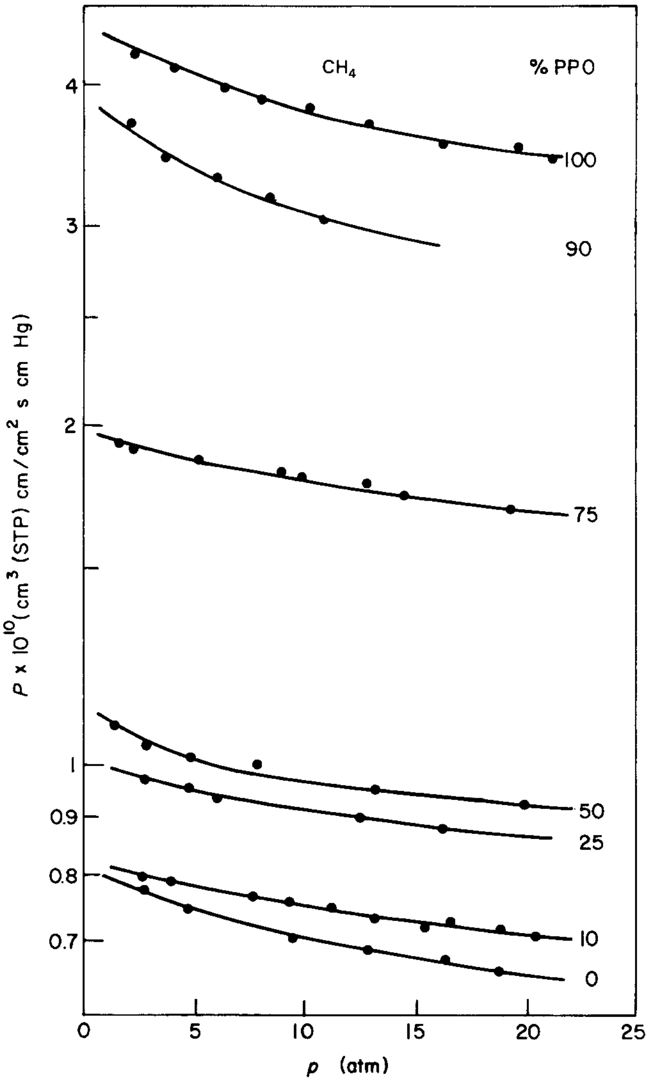

Figure 7 CH$_4$ permeability in blends at 35 C

CH$_4$ show permeabilities which decrease as the driving pressure increases for each polymer composition.

Various analyses and comments about these results will be given in subsequent sections.

EFFECT OF MINERAL OIL ON POLYSTYRENE PROPERTIES

As stated earlier, the commercial polystyrene used to prepare the blends for this study contained 3% mineral oil. In order to assess the effect of the presence of this additive mineral oil was added in various amounts to Cosden Polystyrene 550, which contains no mineral oil, and various properties were measured.

Figure 8 shows the extent to which mineral oil depresses the glass transition temperature of polystyrene. Addition of 3% mineral oil to Polystyrene 550 gives a T_g which exactly matches that of Polystyrene 525, as expected. Addition of this amount of mineral oil decreases the density of polystyrene by about 0.006 g cm^{-3}, which matches the amount by which the current data in *Figure 2* fall below other published results. Thus, without mineral oil the results given here for blends would agree well with the other data shown in *Figure 2*.

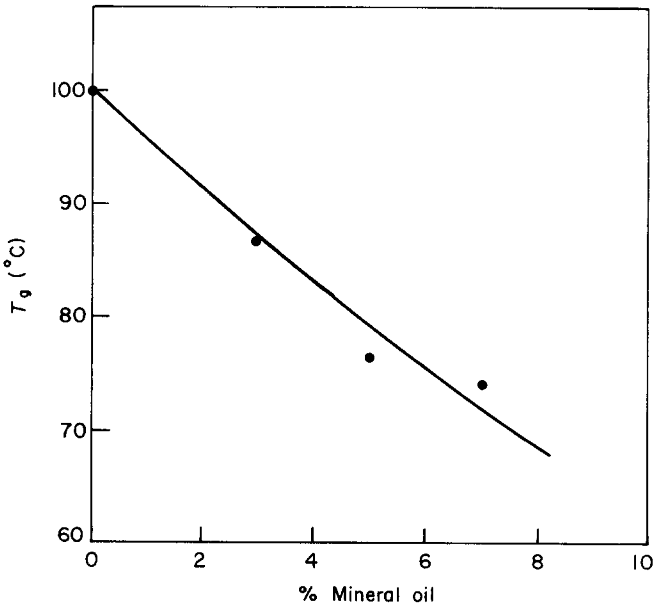

Figure 8 T_g depression of PS caused by mineral oil as determined by d.s.c.

Figure 9 shows CO_2 sorption isotherms for PS 525, PS 550, and mixtures of the latter with various amounts of mineral oil. The material containing 7% mineral oil has a noticeably lower sorption uptake of CO_2 but the others, including PS 525, are not distinguishably different, within experimental uncertainty, in this regard. On the other hand, a continuous reduction in permeability to gases occurs, as noted in *Figures 10* and *11*, upon addition of mineral oil to polystyrene. This is evidently the result of a slight antiplasticization effect[10-12], which causes a reduction in the diffusion coefficient that results from restrictions in molecular motions attending addition of small amounts of miscible diluents. There is a tendency to decrease the pressure dependence of the CO_2 permeability coefficient, as seen in *Figure 10*. The reduction in the permeability coefficient for He is slightly greater than for CO_2, as shown in *Figure 11*.

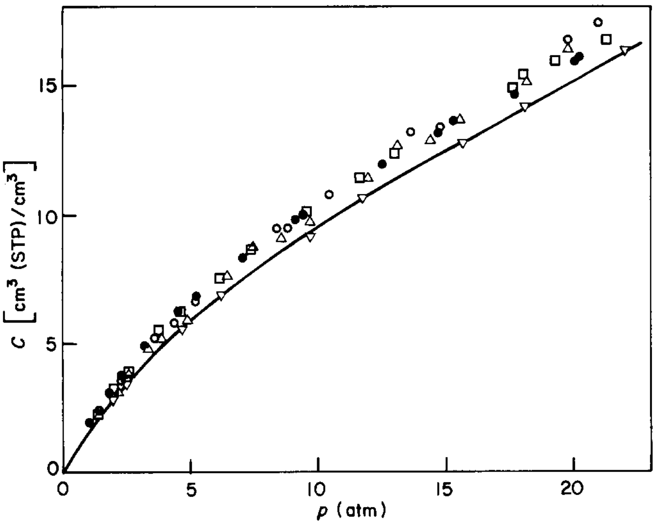

Figure 9 Effect of mineral oil in polystyrene on CO_2 sorption at 35°C. (○): PS 550; (△): +3% mineral oil; (□): +5% mineral oil; (▽): +7% mineral oil; (●): PS 525

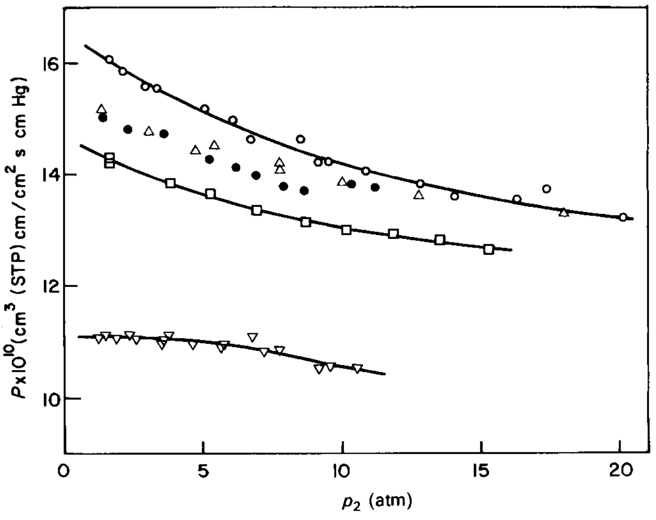

Figure 10 Effect of mineral oil and pressure on CO_2 permeability in PS at 35°C. (○): PS 550; (△): +3% mineral oil; (□): +5% mineral oil; (▽) +7% mineral oil; (●): PS 525

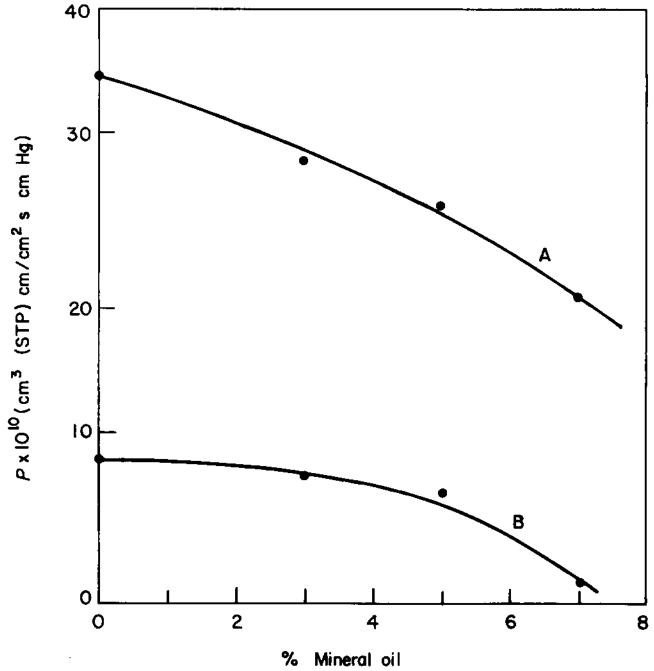

Figure 11 Effect of mineral oil in PS on He (curve A) and CO_2 (curve B) permeability at 10 atm and 35°C

ESTIMATION OF SEPARATION FACTORS FOR GAS PAIRS

One of the primary motivations for the present study was to assess how blending of miscible polymer pairs affects the rate of permeation of one gas relative to that of another gas, since this is a central issue in the selection of membrane materials for separation processes. An estimate of the permselectivity characteristics can be made by examining the ratio of the permeability coefficients for the two pure gases of interest; however, it must be pointed out that separation factors evaluated from permeation measurements on mixtures of these gases may differ somewhat from this estimate if the gases permeate not truly independently of each other. The latter would occur if the two gases compete for sorption sites[13,14] or diffusion pathways or if either gas plasticizes the polymer, causing changes in sorption and diffusion coefficients for the other gas. For present purposes, the pure gas permeabilities presented earlier will be used; however, before discussion these estimates, it is helpful to review some background on gas permeation in blend systems.

Simple mixture rules for gas permeation in miscible blends[15] suggest for weakly interacting components that the permeability, P, of a particular gas through a blend will be related to the permeabilities of that gas in the component polymers, i.e. P_1 and P_2, by

$$\ln P = \phi_1 \ln P_1 + \phi_2 \ln P_2 \tag{1}$$

where ϕ_i is the volume fraction of component i. For more strongly interacting components, the permeability is expected to fall below this additive value to an extent related to the degree of interaction[15]. A recent study on gas permeation through miscible blends of weakly interacting components[16] showed that equation (1) described the results for several different gases. Thus, the ideal separation factor for gas A relative to gas B defined as

$$\alpha_B^A \equiv \frac{P_A}{P_B} \tag{2}$$

may be shown to follow a similar mixing rule, i.e.

$$\ln \alpha_B^A = \phi_1 \ln(\alpha_B^A)_1 + \phi_2 \ln(\alpha_B^A)_2 \tag{3}$$

In this case, α_B^A for blends lies on a simple monotonic curve connecting the values of the separation factor for the pure component polymers. A response of exactly this type was observed for miscible blends of polycarbonate with a copolyester[17] even though the permeabilities for individual gases[17,18] deviated slightly below those predicted by equation (1). A larger departure from equation (1) was observed earlier[1,15] for CO_2 and PPO–PS blends. This fact combined with other information suggests that PPO–PS is a more strongly interacting system than the others mentioned. It was this fact which led us to explore the selectivity of gas transport in the PPO–PS system.

Figure 12 shows permeability coefficients, at an arbitrary p_2 of 10 atm, for the three gases as a function of blend composition. For polystyrene, two points are shown for each gas. The solid points [(●); (▲); (■)] in all cases correspond to samples prepared as described earlier, which included heat treatment at 70 and 80°C to remove solvent from the cast film. This necessary step also causes some sub-T_g annealing or relaxation that alters properties. These changes are the most pronounced for polystyrene owing to the closeness of its T_g to the drying temperatures compared with the higher glass transition temperatures of the blends. Ti eliminate this effect, a polystyrene film was heated above its T_g and quenched to room temperature. Permeabilities obtained for this sample are shown by the open points. These points form a more consistent relationship with data for the other compositions, evidently because the latter were less affected by the drying protocol since their higher glass transition temperatures allowed less sub-T_g relaxation during drying. In all cases, the plots of *Figure 12* deviate significantly from the relation suggested by equation (1) with the departure being greater in the order: He, CO_2, CH_4. This implies that the volume contraction on mixing seen in *Figure 2* does not result in a uniform decrease in free volume. Instead it would appear that there is a disproportionate loss in the larger elements of free volume available for permeation of the larger gas molecules. This is the proposed basis for the enhanced selectivity of transport by blends described next.

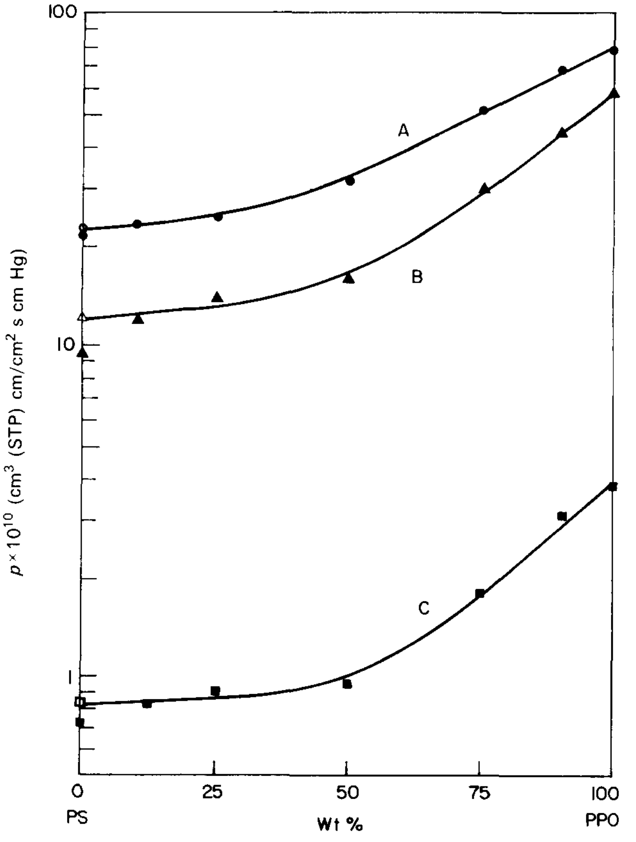

Figure 12 Effect of blend composition on permeability of He (curveA), CO_2 (curve B) and CH_4) curve C at 35°C

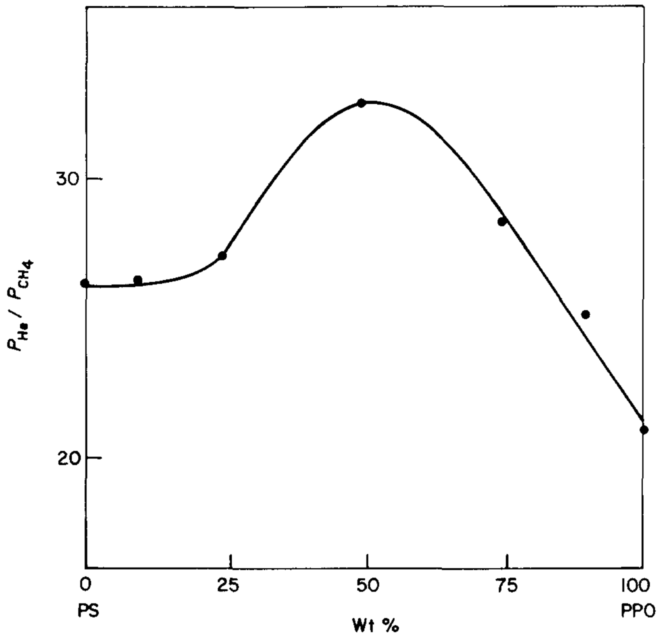

Figure 13 Estimate of separation factor for He–CH_4 pair at 10 atm and 35°C for blends

Figures 13 and *14* show the separation factors estimated from ratios of the pure gas permeability coefficients at 10 atm for the pairs He–CH_4 and CO_2–CH_4. The trends are qualitatively the same for other values of p_2. For both pairs, the estimated separation factors lie well above the prediction by equation (3), and, in fact, maxima occur with the most extreme case being for He–CH_4. Based on the argument advanced above this is not surprising since there is a larger difference in molecular diameters of He and CH_4 than CO_2 and CH_4. The enhancement in selectivity caused by blending is quite significant for the He–CH_4 pair. Since permeability is the product of solubility and mobility terms, one might wonder how the observed results partition between these two factors[19]. It is possible to separate the two effects for the CO_2–CH_4 pair since sorption isotherms are available for each of these gases (see *Figures 3* and *4*). Curve C in *Figure 14* (labelled 'solubility') was determind by using the ratios of the concentrations of CO_2 and CH_4 at 10 atm for each polymer composition. The resulting curve reveals the part of the permeability ratio stemming from solubility differences. A simple monotonic trend is seen. While both PS and PPO favour permeation of CO_2 over CH_4 on this basis, PS is slightly more solubility selective than is PPO. By dividing the solubility ratio into the permeability ratio for each material, that part of permselectivity stemming from mobility, or the average diffusion coefficients, considerations can be found and this is the curve labelled 'mobility' in *Figure 14*. Clearly, mobility issues are responsible for the major part of the permselectivity between CO_2 and CH_4 observed in these materials. PPO is a much more effective 'mobility' selector

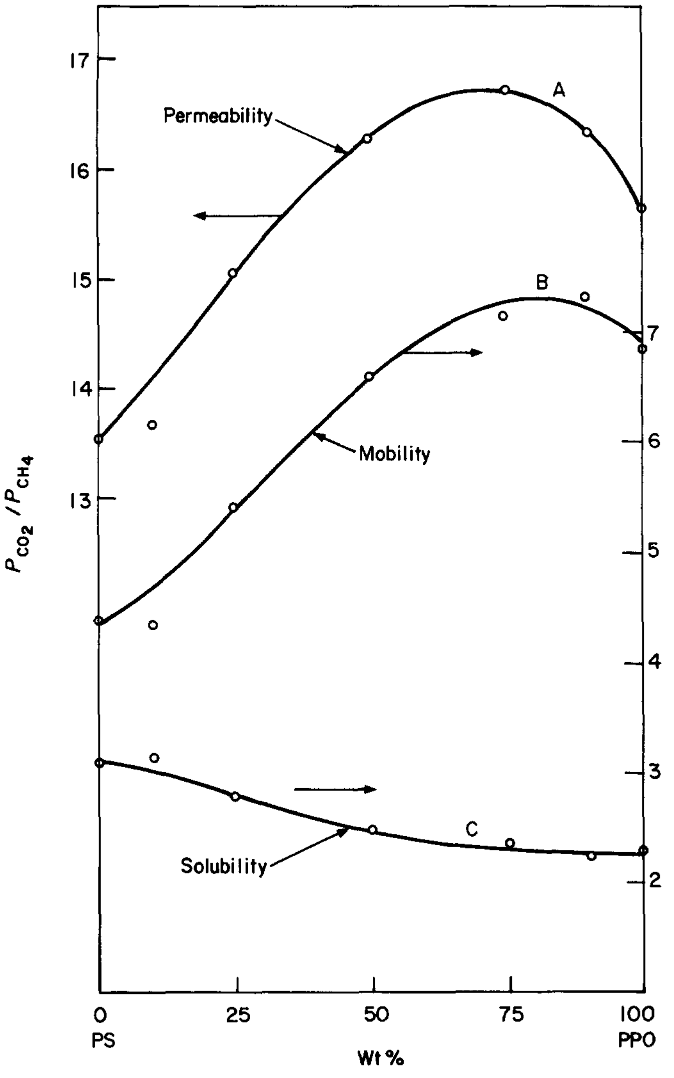

Figure 14 Estimate of separation factor for CO_2–CH_4 pair at 10 atm and 35°C and the individual contributions of solubility and mobility factors

than is PS. Interestingly, the mobility term goes through a maximum and is responsible for the maximum in the permeability ratio. This is reasonable based on the free volume argument proposed earlier. Similar trends are expected for the He–CH_4 pair, but unfortunately similar calculations cannot be made in this case since sorption isotherms for He could not be measured.

Figures 13 and *14* represent interesting examples of property synergism in miscible blends. Similar responses have been seen for certain mechanical properties of miscible blends[3,20,21].

MODEL INTERPRETATION OF SORPTION AND TRANSPORT RESULTS

The sorption of gases in glassy polymers has been successfully interpreted in terms of a dual sorption mechanism model[1,6–9,11,13,14,18,22,23], although other types of models have been suggested[24]. The dual sorption model envisages two modes of sorption following Henry's law and a Langmuir form, i.e.

$$C = k_D p + \frac{C'_H b p}{1 + bp} \qquad (4)$$

where k_D, C'_H and b are model parameters, which have obvious physical interpretations. Alternately, equation (4) can be expressed in terms of fugacity, f, rather than gas phase pressure, p. The various parameters for CO_2 and CH_4 were extracted from the sorption data shown in *Figure 3* and *4* using regression techniques described previously[23,24] and are plotted versus blend composition in *Figures 15–19*.

The Langmuir capacity terms for CO_2 and CH_4 are given in *Figure 15*. This quantity is several fold larger for both gases in PPO than in PS. This is the result of the much higher T_g of PPO than of PS, based on previous correlations for a large number of glassy polymers[1,7,9,18]. Values for the blends fall in between these limits owing to their intermediate glass transition temperatures. The values for CH_4 are approximately one-half those for CO_2, and the reason for this is of interest. We have found previously[1,6,7,9,18,22,23] that C'_H appears to be correlated with the unrelaxed volume of the glass relative to the equilibrium liquid state, i.e. $(V_g - V_l)$. Based on considerable experimental data for CO_2, it has been suggested that gases pack in the excess or unrelaxed volume with a liquid-like density. The molar volume of CO_2 in such a

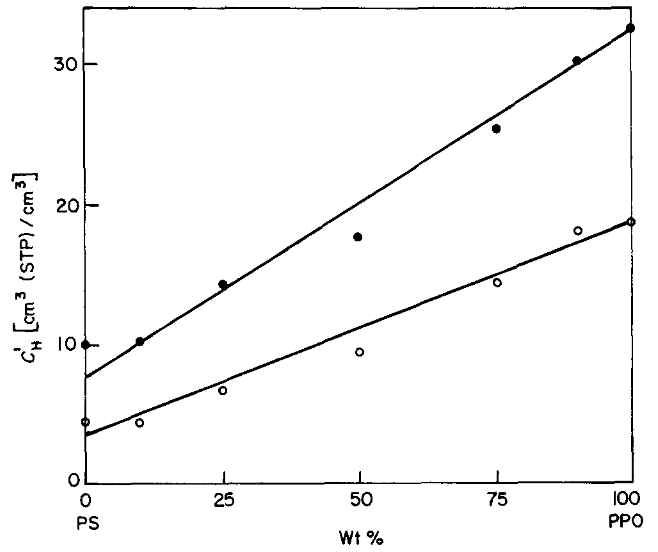

Figure 15 Langmuir sorption capacity parameter for CO_2: (●); and CH_4: (○)

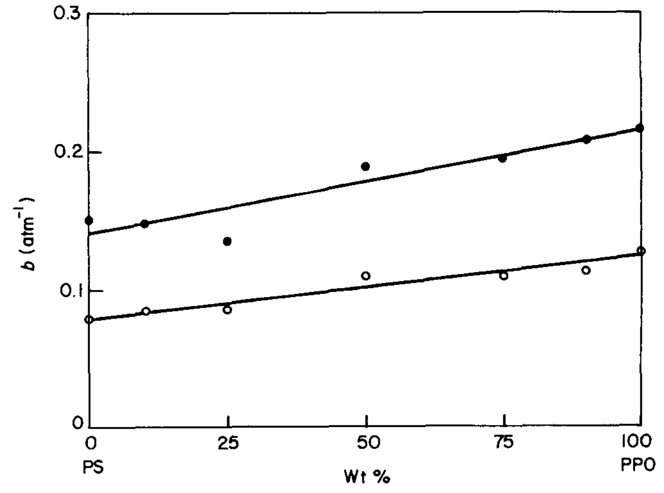

Figure 16 Langmuir affinity parameter for CO_2: (●); and CH_4: (○)

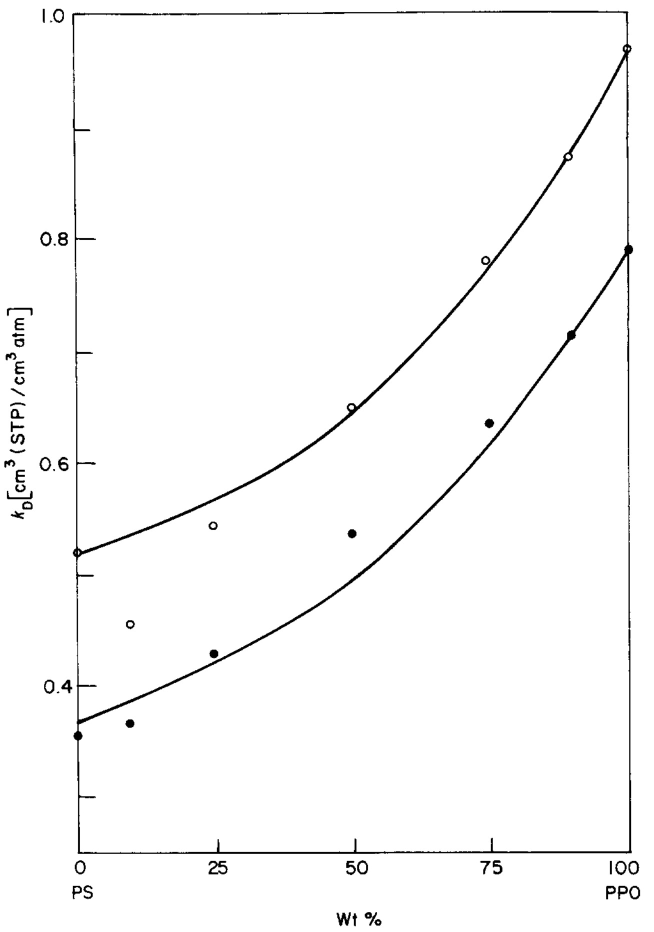

Figure 17 Henry's law sorption parameter for CO_2 based on use of pressure: (●) and of fugacity: (○) in equation (4). Solid curves calculated from equation (6) as described in text

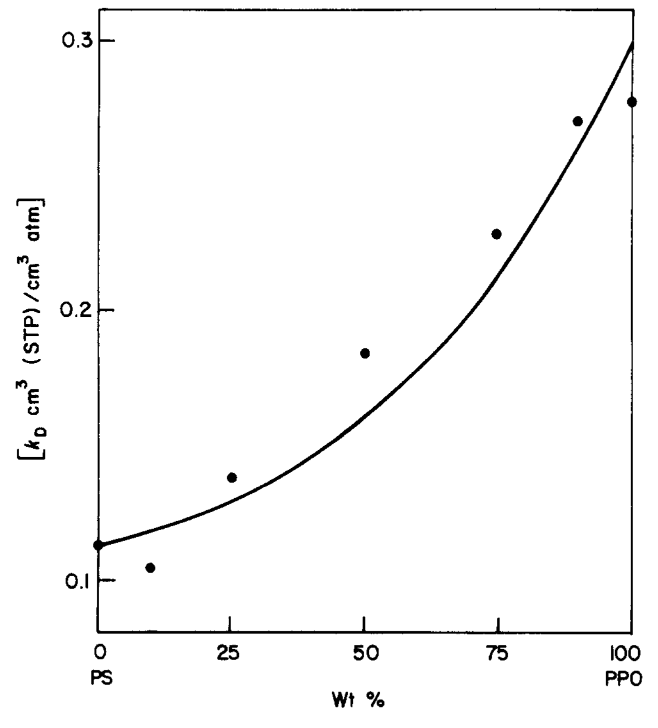

Figure 18 Henry's law sorption parameter for CH_4 (pressure based). Solid curve calculated as in *Figure 17*

state has been estimated to be 55 cm^3 mol^{-1}, using results from various sources including sorption in zeolite cavities. Estimates of the latter type[26] give a molar volume for CH_4 in this state of 78 cm^3 mol^{-1}. Based on these ideas and estimates of $(V_g - V_l)$ from thermal expansion coefficients above (α_l) and below (α_g) T_g, C'_H should be given by

$$C'_H \simeq 22\,414(\alpha_l - \alpha_g)(T_g - 35)/\tilde{V} \qquad (5)$$

at a measurement temperature of 35°C, where $\tilde{V}$ is the liquid-like molar volume of the gas. By appropriate rearrangement of equation (5) one can see that the coordinates used in *Figure 19* should permit evaluation of this approach for unifying the data in *Figure 15*. The thermal expansion coefficient data described previously[1] were employed here and the T_g data were taken from *Figure 1*. The perfect correlation line drawn in *Figure 19* agrees rather well but not perfectly with the points for both CO_2 and CH_4. The agreement is regarded as satisfactory in view of the many sources of data employed and the various approximations involved.

The Langmuir affinity parameter, b, is shown in *Figure 16* for CO_2 and CH_4 in the various blends. This quantity depends rather more on the nature of the gas than it does on the environment provided by the polymer. Little else can be said about this quantity in the present context.

Based on the points of view expressed above, the Henry's law parameter, k_D, should be closely related to the equilibrium polymer-gas interactions, and an analysis based on ternary solution theory has been suggested for use with polymer blends[1,15,18]. Use of the Flory–Huggins model in the limit of low penetrant, component 3, concentrations gives the mixture rule for k_D in blends as

$$\ln k_D = \phi_1 \ln k_{D1} + \phi_2 \ln k_{D2} + \frac{B\tilde{V}}{RT}\phi_1\phi_2 \qquad (6)$$

where B is the binary interaction parameter for mixing of components 1 and 2 and $\tilde{V}$ is the molar volume of the penetrant[15]. Weeks, Karasz and MacKnight[27] have

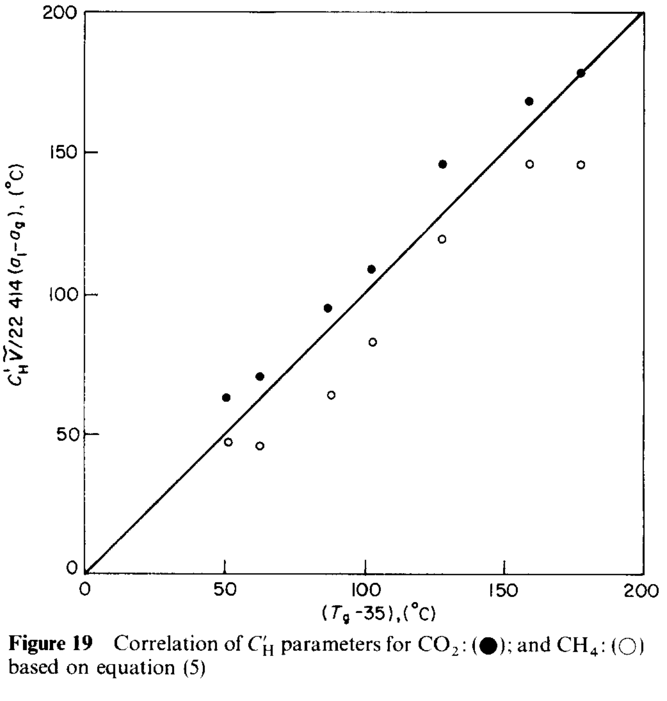

Figure 19 Correlation of C'_H parameters for CO_2: (●); and CH_4: (○) based on equation (5)

estimated the heat of mixing of PS and PPO using an indirect calorimetric approach, and their data suggest a value of $B = -4.4\ \mathrm{cal\ cm^{-3}}$ for this system.

Plots of k_D *versus* blend composition are shown in *Figure 17* for CO_2 (using both pressure and fugacity in equation (4)) and in *Figure 18* for CH_4 (pressure based only). The lines drawn were computed from equation (6) using the values of B and $\tilde{V}$ mentioned earlier. The CO_2 results in *Figure 17* are clearly consistent with this interpretation. The agreement for CH_4 is not quite as good and, in part, reflects the greater uncertainty in the CH_4 sorption data. As described previously[22], sorption parameters for CH_4 are more difficult to obtain accurately than is the case for CO_2. In contrast to our earlier paper[1], we feel it is preferable to say that the sorption data are consistent with this interpretation rather than using this approach to estimate the interaction parameter. The procedures used in the previous work[1] based the fitting very heavily on the value for pure polystyrene, and the current data are believed to be more correct. The interaction parameter obtained in the previous paper[1] is unreasonably large because of this.

We conclude that the dual sorption parameters for CO_2 and CH_4 in the PPO–PS blends are amenable to physical interpretation and can be rationalized with other physical information about the gases and the blends. This approach has obvious merit for interpolating and extrapolating this information to other situations.

A dual mobility model[28] has been proposed as an extension of the dual sorption model for interpreting transport behaviour of gases in glassy polymers. This approach leads to the following result for permeability

$$P = k_D D\left[1 + \frac{FK}{1 + bp_2}\right] \qquad (7)$$

where p_2 is the upstream driving pressure, K is $C'_H b/k_D$, D is the diffusion coefficient based on concentration gradients for gas sorbed in the Henry's law mode, and F is the ratio of the diffusion coefficient of gas sorbed by the Langmuir mode to D. An alternative formulation based on activity gradients gives

$$\bar{P}_T = k_D D_T\left[1 + KR\frac{\ln(1 + bf_2)}{bf_2}\right] \qquad (8)$$

where $\bar{P}_T$ is the permeability based on fugacity rather than pressure, f_2 is the fugacity of the gas corresponding to pressure p_2, and D_T and R are the activity based analogues of D and F. For consistency, equation (4) is expressed in terms of f rather than p which leads to somewhat different sorption parameters (see, for example, *Figure 17*).

Figures 20 and *21* show permeability data for CH_4 and CO_2 in PPO plotted as suggested by both equations (7) and (8). The fugacity based formulation seems to give better straight lines than does the pressure based formulation. As a result, the former was used to extract transport coefficients, i.e. D_T and R. In many other cases the pressure based approach works just as well. *Figure 22* shows plots of D_T versus blend composition for both CO_2 and CH_4. As expected, the values for CO_2 are nearly one order of magnitude larger than those for CH_4. In both cases, there appears to be a minimum at about 50% PPO. This apparently is a result of the loss in free volume on blending PPO and PS (see *Figure 2*). The corresponding values of R lie in the range of 0.05–0.08 for CO_2 and 0.04–0.13 for CH_4. No consistent trend with blend composition is evident for these results. Owing to the pressure independence of permeability noted for He, it is concluded that R is zero for this gas. In general, this model provides an adequate description of the data; however, other models might be equally adequate for curve fitting purposes.

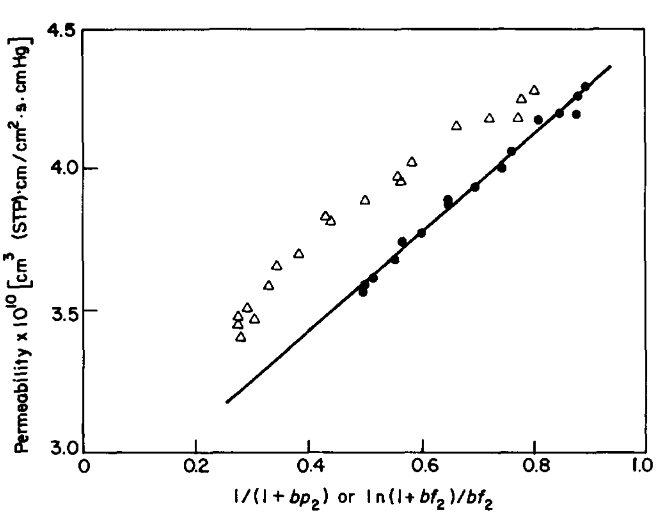

Figure 20 Permeability plotted according to two versions of dual mobility model for CH_4 in PPO. (●): P_T vs. $\ln(1+bf_2$; (△): P vs. $1/(1+bp_2)$

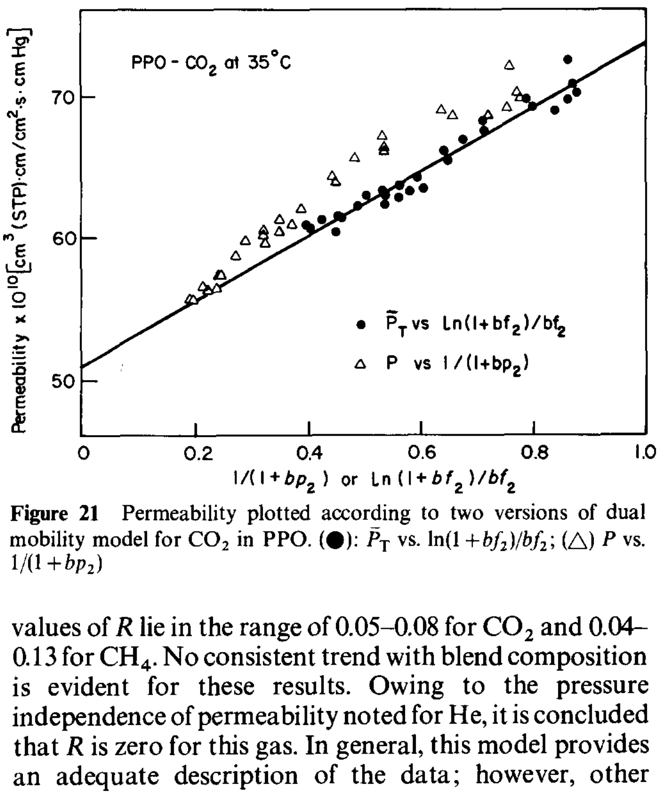

Figure 21 Permeability plotted according to two versions of dual mobility model for CO_2 in PPO. (●): $\bar{P}_T$ vs. $\ln(1+bf_2)/bf_2$; (△) P vs. $1/(1+bp_2)$

SUMMARY

Prior work on gas sorption and transport in miscible polymer blends has been extended to gases other than CO_2 to determine whether such systems offer any unique selectivity characteristics which might make this a useful approach for tailoring membranes for separation processes. For some PPO–PS mixtures, the estimated separation factors for He–CH_4 and CO_2–CH_4 are larger than those for either pure component polymer. This is in contrast to results for some other blend systems recently reported[16,17], where the separation factors vary monotonically between the values for the pure component polymers. This appears to be the result of stronger polymer–polymer interactions for the PPO–PS system.

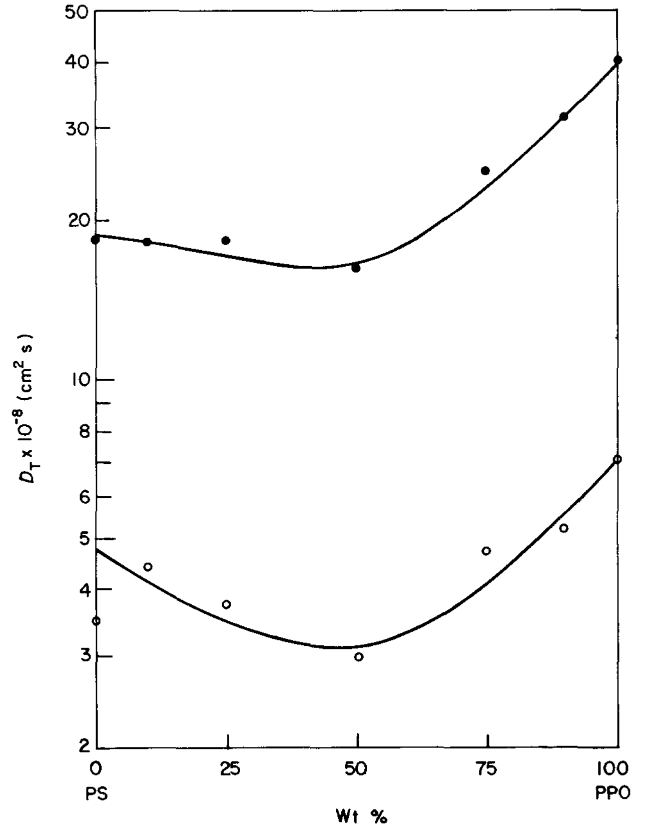

Figure 22 Thermodynamic (activity based) diffusion coefficients for Henry's law mode for CO_2: (●); and CH_4: (○)

There is a significant volume contraction on mixing these two polymers, which corresponds to a loss in free volume. One may conclude that there is also a change in distribution of free volume favouring transport of smaller molecules over larger ones. No formalism to quantify this idea is available at the present time.

The sorption and transport data are adequately described by the previously used dual sorption and mobility models for glassy polymers. The Langmuir capacity term in the model correlates well with the postulate that this mode is associated with the non-equilibrium character of the glassy state. The composition dependence of the Henry's law parameter is reasonably consistent with other estimates of the interaction energy between PPO and PS.

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