Gas solubility in glassy polymers—a correlation with excess enthalpy

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Solubility coefficients for CO_2, Ar and CH_4 in polystyrene (PS) films with glass transition temperatures (T_g) of 52 to 107°C were measured in a pressure-decay sorption apparatus at 1 atm over a temperature range of 20 to 90°C. The gas solubility at 30°C increased as the T_g of the PS increased; the heat of solution was largest for the PS with the highest T_g. This observed dependence of gas solubility on T_g was analysed in terms of enthalpy–temperature relationships for glassy polymers. The solubilities for PS samples with different glass transition temperatures converged when comparisons were made on the basis of states of equal enthalpy instead of the temperature of measurement.

(Keywords: glassy polymers; gas solubility; excess enthalpy)

INTRODUCTION

A unique value for the solubility of a gas in a glassy polymer is difficult to determine, owing to the complexity of specifying the state of a glass at a given temperature. Because the volume or enthalpy of a glass is strongly dependent on its thermal history, it is reasonable to expect multiple values for the gas solubility at a given measurement temperature. Although the various enthalpy or volume states are always relaxing towards a unique equilibrium state for the measurement temperature, any given non-equilibrium state may be essentially frozen-in, because the relaxation rates of a glass are slow relative to experimental time-scales.

To quantify gas transport measurements in glassy polymers, recent workers[1–4] have been careful to specify the thermal history of the material. Sub-T_g annealing has been shown to have a measurable effect on the enthalpy and volume of the polymer and on the gas solubility[1–3]. Lower solubilities were measured in glassy polymers which had been aged longer and were therefore closer to the equilibrium state of volume or enthalpy[1–4]. The dual-mode sorption model[5] has been used to attribute the decreased solubility to the shrinkage of Langmuir sorption sites upon ageing. This paper presents an explanation for the dependence of the gas solubility on the state of the glass, based on temperature–enthalpy relationships for glassy polymers.

THEORY

This section provides a theoretical framework which allows the experimental observations to be anticipated. Use is made of the non-equilibrium nature of amorphous polymers below the glass transition temperature and the fact that at a specified cooling rate the amount of undercooling below T_g determines the initial amount of departure from equilibrium at any given observation temperature T_o. Therefore if a given polymeric material of fixed chemical composition can be manipulated (see below) at the molecular level to give a series of specimens with significantly different T_g values, it becomes possible to conduct a set of experiments at a single temperature T_o but at significantly different values of undercooling ($T_g - T_o$). In the case of gas sorption experiments this is a particularly useful idea, since the measurements are carried out with the gas always at the measurement temperature T_o but with the absorbing substrate (glassy polymer) at a variable effective temperature (to be defined below). It is therefore possible to separate the effect of temperature of the substrate from that of the gas in the temperature dependence of the sorption process, something not achievable when both the gas and the substrate are heated or cooled together.

Enthalpy–temperature relationships

Figure 1 is a schematic of the enthalpy–temperature profile for two glassy polymers of the same chemical composition, P1 and P2, but with different glass transition temperatures T_{g1} and T_{g2} ($T_{g1} < T_{g2}$). Both materials follow the same liquid temperature–enthalpy equilibrium line above the glass transition temperatures where $\partial H/\partial T = C_{pL}$. As P2 becomes a glass upon cooling below T_{g2}, the temperature–enthalpy behaviour departs from the equilibrium line and follows the non-equilibrium glassy line described by $\partial H/\partial T = C_{pg}$. P2 would follow the equilibrium line below T_{g2} if the cooling rate were sufficiently slow, but such a rate is not experimentally achievable; an amount of excess enthalpy is frozen into the glassy material.

P1 becomes a glass at T_{g1}, at which point it also deviates from the equilibrium liquid curve and follows the glassy curve given by $\partial H/\partial T = C_{pg}$. At a given

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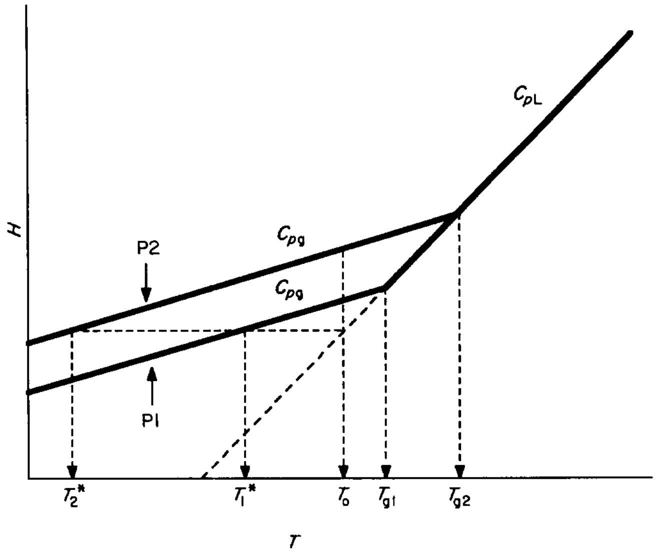

Figure 1 Temperature–enthalpy curve for polymers PS1 and PS2 with glass transition temperatures at T_{g1} and T_{g2}, respectively. T^* is defined as the temperature which the polymer would have to assume to obtain the equilibrium value of enthalpy at temperature T_0

temperature T_o below T_{g1}, P1 and P2 are in two different enthalpy states. The excess enthalpy in P1 is equal to $(C_{pL} - C_{pg})(T_{g1} - T_o)$, and the excess enthalpy in P2 is equal to $(C_{pL} - C_{pg})(T_{g2} - T_o)$. At T_o, the difference between the enthalpy of P1 and P2 is equal to $(T_{g1} - T_{g2})(C_{pL} - C_{pg})$ (a negative quantity). A sorption experiment conducted at a temperature T_o below T_{g1} would therefore compare the solubility of a gas at a given temperature in a material of common chemical structure (i.e. polystyrene) but in different enthalpy states. It is the purpose of this paper to correlate this difference in enthalpy states with measured differences in the solubilities in the two glassy polymers.

Since both enthalpy and volume are known to be influenced similarly by sub-T_g annealing of glassy polymers, there is reason to believe that a correlation of excess volume, instead of enthalpy, with gas solubility could be equally well constructed. Here it is preferred to use the frozen-in enthalpy, because by definition ($H = U + PV$) it accounts for the volumetric state of the material and its internal energy. The latter reflects the molecular motions of the material into which gas is sorbing. Although large-scale thermal motion of chain molecules is frozen for glassy polymers, it is reasonable to expect that some short-range motions persist and that these motions are diminished as T drops further below T_g. To the extent that these short-range thermal agitations reduce the equilibrium amount of gas that can be sorbed into a glassy substrate at sorption equilibrium, a correlation based on H, rather than V, should be superior. If thermal motions in all the substrates are identical or if they have no influence on the gas solubility at sorption equilibrium, then volume or enthalpy correlations can be used equally well to explain the gas sorption behaviour in glassy polymers.

Development of T^*

An adjusted temperature scale will be useful to compare the solubilities of samples with different T_gs so that the comparisons are made at equal polymer enthalpy states. Here a temperature T^* is defined as the temperature which a glass must assume in order to reach the enthalpy equal to that at the equilibrium state at T_o, the temperature of measurement. Above T_g, T^* is equal to the measurement temperature, since the liquid or rubber is in an equilibrium state. Below T_g, T^* is equal to the temperature necessary to reduce the enthalpy by an amount equal to the excess enthalpy defined above. T^* is defined as

$$T^* = T_o - [(T_g - T_o)(C_{pL} - C_{pg})]/C_{pg} \qquad (1)$$

Thus for a given value of T_o, the value of T^* depends on the T_g and the difference in heat capacities between the glassy and rubbery states. *Figure 1* shows schematically the calculation of T^* at a given temperature T_o for P1 and P2. P2 has a higher T_g than P1 and therefore contains more excess enthalpy at T_o. A greater reduction in temperature (lower T^*) is necessary for P2 to attain the equilibrium enthalpy associated with temperature T_o. Thus P2 is considered to exist at a lower effective temperature; it is 'colder' than P1 in the solubility measurements at T_o.

Gas solubility and T^*

The gas solubility is expected to be higher in P2 than in P1 at temperatures below T_{g2}, since P2 has a lower effective temperature T^*. (It is commonly observed that the solubility coefficient S increases as measurement temperature decreases; generally this trend has been attributed[6] to the increased condensability of the gas rather than the state of the material into which the gas is sorbing.) At a fixed temperature, measuring the gas solubility in a series of glasses with increasing T_gs is equivalent to lowering the temperature of the polymer, thereby explaining the observed result of increasing solubility with increasing T_g.

The temperature scale T^* can also be used to analyse the temperature dependence of the gas solubility in a glass compared with the behaviour in the corresponding rubber. The temperature dependence of the gas solubility in a polymer sample above its T_g would follow the temperature of the measurement, since $T^* = T_o$ above T_g. In the glassy state, the temperature of the measurement changes directly with T_o, while the state of enthalpy of the polymer changes with T^*. Since

$$T^* = T_o(1 + [(C_{pL} - C_{pg})] - T_g(C_{pL} - C_{pg})/C_{pg} \qquad (2)$$

$$\partial T^* = \partial T_o(1 + [(C_{pL} - C_{pg})/C_{pg})] \qquad (3)$$

Thus T^* changes more rapidly than T_o. Plotted against T_o, the temperature dependence of S in the glassy state should be stronger (more exothermic) than in the rubbery state.

These thermodynamic arguments regarding solubility and its temperature dependence were used to analyse the measured solubility of CO_2, CH_4 and Ar in a model set of polystyrene (PS) samples with different T_gs.

EXPERIMENTAL

The CO_2 and Ar had purities in excess of 99.99%, and the CH_4 had a purity specified as 99.0%. Two PS homopolymers were obtained from Polysciences, Inc. with nominal molecular weights of 250000 (PS4) and 20000 (PS1). Two additional PS samples were prepared by fractionating PS1. Methanol was slowly dripped into a 10% PS1–toluene solution until a significant amount

Table 1 Characterization of PS samples

Polymer	T_g (°C)	M_w	M_n
PS1	52	25600	2100
PS2	72	26000	3000
PS3	91	34000	5700
PS4	107	250000	200000

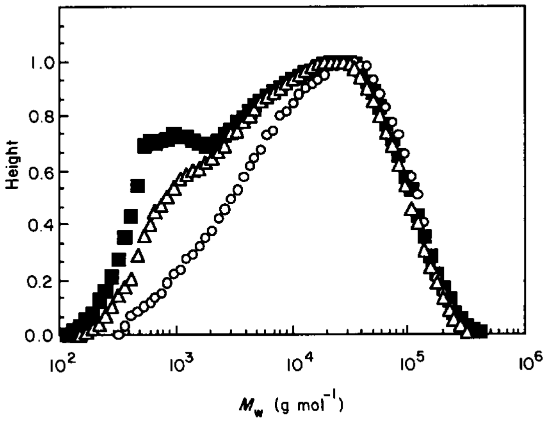

Figure 2 G.p.c. chromatograms of PS1 (■), PS2 (△) (PS1 fractionated once), and PS3 (○) (PS1 fractionated twice)

of polymer had precipitated. This filtered precipitate (PS2) was fractionated again to yield PS3. All four PS samples were annealed in vacuum just below T_g for 4 days to remove residual solvent.

Gel permeation chromatography (g.p.c.), differential scanning calorimetry (d.s.c., 10 K min^{-1}) and proton n.m.r. were used to characterize the polymer samples. The gas solubility (S) and diffusion (D) coefficients were measured at 1 atmosphere pressure in a pressure-decay sorption apparatus described in detail elsewhere[7]. The D and S values for CO_2, Ar and CH_4 in PS1, PS2, PS3 and PS4 were determined over the temperature range 20–90°C.

RESULTS AND DISCUSSION

Polystyrene fractionation

Table 1 summarizes the d.s.c. and g.p.c. results for the four PS samples. The glass transition temperature (T_g) for PS varied from 52 to 107°C as M_n varied from 2100 to 200000 g mol^{-1}. None of the measured T_g values was influenced by the presence of any sorbed gases at the pressures and temperatures used in this study. The n.m.r. spectra of the four samples were all identical and indistinguishable from PS spectra in the literature, precluding the presence of externally added plasticizers or other significant impurities. The g.p.c. chromatograms for PS1, PS2 and PS3 are shown in *Figure 2*. Low-molecular-weight oligomers of styrene appear in large concentrations in PS1. Evidently the presence of these oligomers is responsible for the depression of the T_g of PS1 to 52°C. The fractionation steps used to prepare PS2 and PS3 successfully removed the low-molecular-weight oligomers and increased the proportion of the longer chains. Removal of the oligomers increased T_g of PS2 to 72°C and T_g of PS3 to 90°C. The g.p.c. results for PS4 indicated a broad distribution of long chains with no low-molecular-weight species.

Solubility coefficient

The behaviour of the solubility coefficients (measured at 1 atm) for CO_2, Ar and CH_4 as a function of temperature for PS1 and PS4 is shown in *Figure 3(a–c)*. The heats of solution (E_s, kJ mol^{-1}) obtained from these plots for PS1 ($T_g = 52$°C) were −12.4, −4.6 and −6.2 for CO_2, CH_4 and Ar, respectively; the heats of solution (kJ mol^{-1}) for PS4 ($T_g = 107$°C) were larger in magnitude, at −22.0, −15.7 and −11.3, respectively. The observed order of increasing gas solubilities (Ar < CH_4 < CO_2) reflects the trend of increasing gas boiling temperatures and increasing Lennard–Jones gas

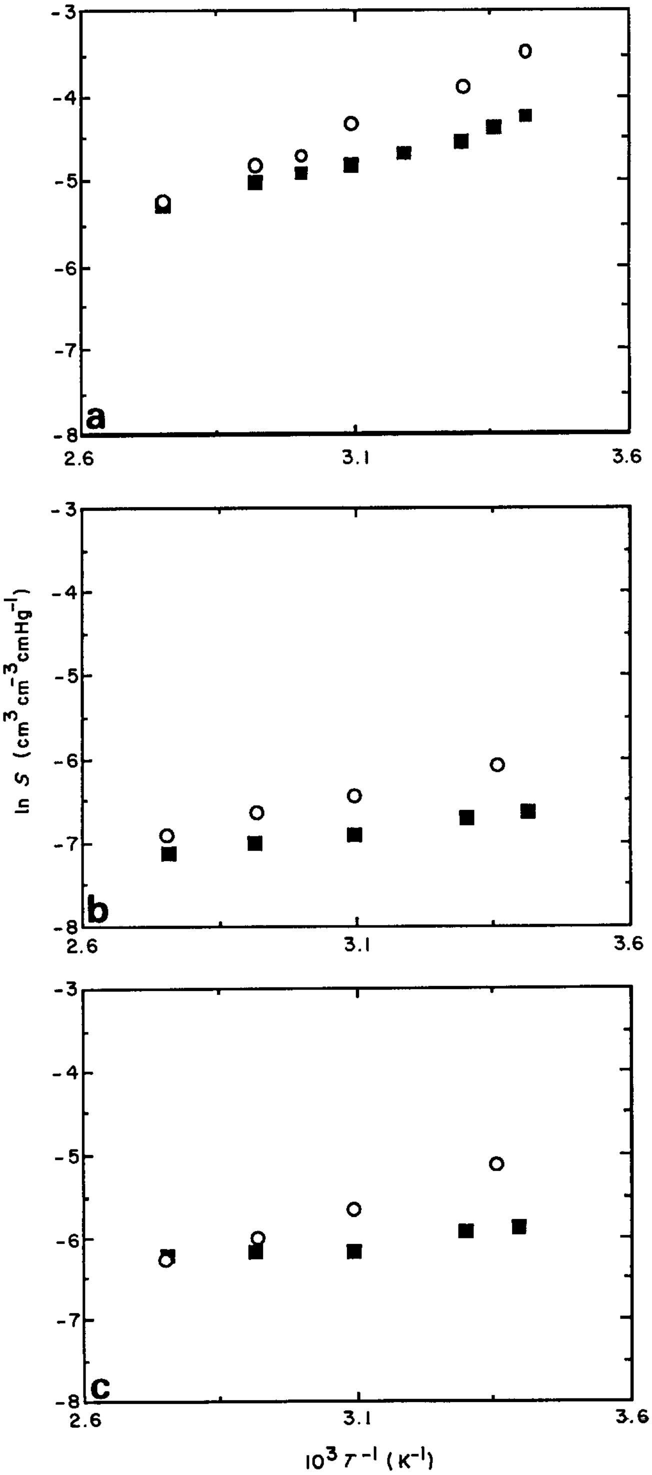

Figure 3 Temperature dependence of the equilibrium solubility coefficients for PS1 (■) and PS4 (○): (a) CO_2; (b) Ar; (c) CH_4

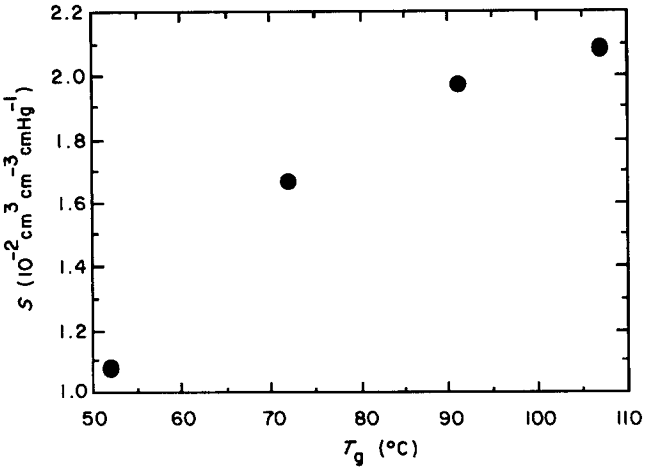

Figure 4 Effect of polystyrene T_g on CO_2 solubility at 30°C

potentials. This is consistent with reported correlations of increasing gas solubility with increasing ease of gas condensability[5].

For all three gases used, the heats of solution for the PS with the highest T_g (PS4) were more exothermic than those for the PS with the lowest T_g (PS1). This behaviour can be understood by considering the enthalpy of PS1 and PS4 at the measurement temperatures. Over the temperature range 20–90°C, PS1 was primarily in the melt (liquid state) and the glass transition zone, while PS4 was in the glassy state. The enthalpy of PS1 was therefore either equal to or close to the equilibrium-state enthalpy, whereas PS4 always contained an amount of excess enthalpy. Comparison of the gas solubilities on a temperature scale based on the measurement temperature T_0 instead of T^* predicts a stronger temperature dependence (more exothermic) for the solubility in a glass than in the corresponding rubber, which is what was observed.

The CO_2 solubility in PS at 30°C decreased as the T_g of the PS sample decreased (see *Figure 4*). This dependence of the solubility on T_g was less pronounced at higher test temperatures, and disappeared when all the materials became rubbery (see *Figure 3(a–c)*). Again the solubility behaviour is consistent with the different enthalpy states that the PS samples assume at 30°C. At 30°C PS4 has the largest excess enthalpy since it has the highest T_g, and PS1 has the smallest amount of excess enthalpy. Using the adjusted temperature scale T^* to compare the polymer gas solubilities on an equal-enthalpy basis, PS4 reaches a lower temperature T^* than PS1 in order to attain the enthalpy equal to the equilibrium enthalpy at 30°C. Since CO_2 solubility increases as the temperature decreases, the polymer at the lower temperature T^* (PS4) should have a higher solubility, as observed. Assuming that the differences in solubities among polymer samples depend on the amount of excess enthalpy, all observed differences in gas solubilities should disappear as the highest T_g of the samples is approached. This is observed in *Figure 3(a–c)*.

The effect of excess enthalpy on the gas solubility and the heat of solution can be quantified using equation (3) with an estimate of the value of $(C_{pL} - C_{pg})/C_{pg}$. For PS, a value of 0.6 was chosen based on ref. 8. According to the proposal outlined above, solubilities of gases in PS with equal states of enthalpy should be identical. This comparison is possible by plotting the gas solubilities in PS as a function of T^*. *Figure 5(a–c)* displays the CO_2, Ar and CH_4 solubility coefficients for PS1 and PS4 as a function of $1/T^*$. The heats of solution (kJ mol^{-1}) for CO_2, CH_4 and Ar in PS calculated from *Figures 5a–c* lie in the range −12.1 to −9.1, −7.0 to −3.5, and −6.3 to −4.7, respectively. The range of E_s is larger for CH_4 and Ar owing to the increased uncertainty in the measurement.

Table 2 summarizes the heats of solution for CO_2, CH_4 and Ar in PS1 and PS4 calculated from solubilities plotted against the measurement temperature (E_s) and against the adjusted temperature scale T^* (E^*). The E^*

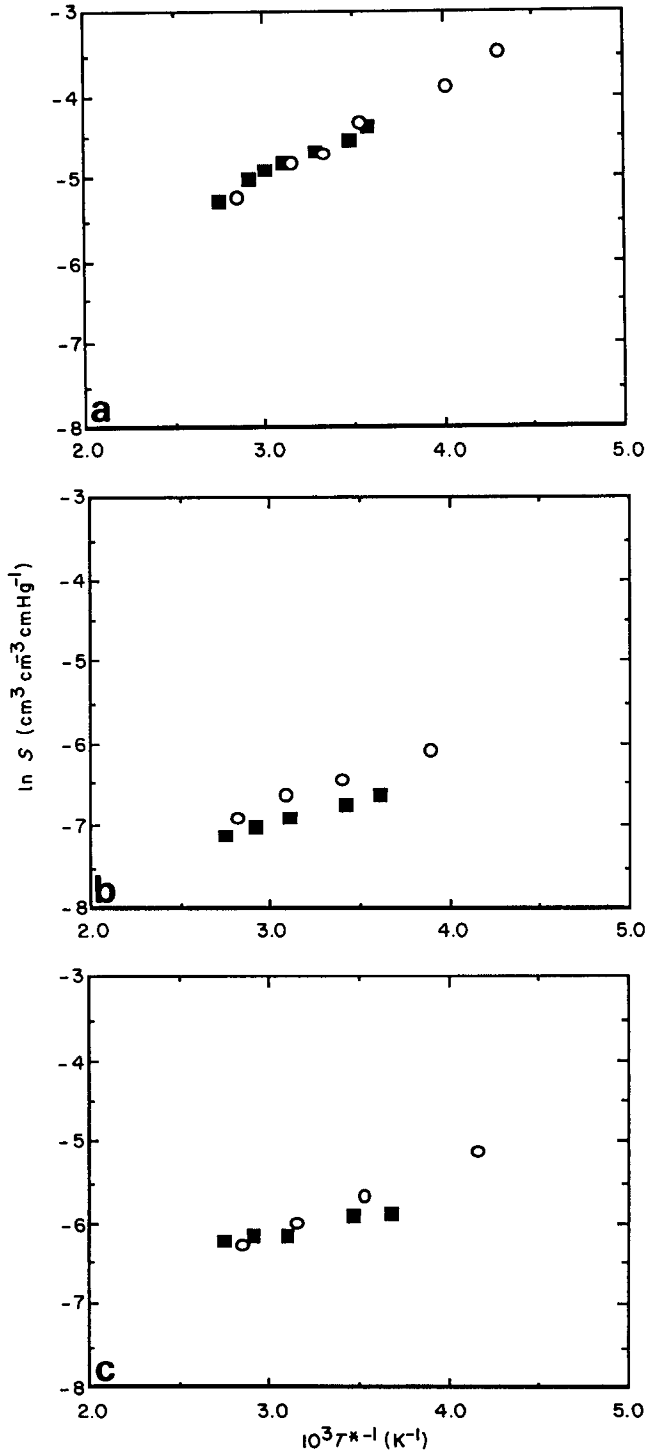

Figure 5 Measured solubility in PS1 (■) and PS4 (○) compared at equal enthalpy states using the temperature scale T^* and $(C_{pL} - C_{pg})/C_{pg} = 0.6$: (a) CO_2; (b) Ar; (c) CH_4

Table 2 Heats of solution in PS1 and PS4 (kJ mol^{-1})

	E_s		
Gas	PS4	PS1	E^{*a}
CO_2	−22.0	−12.1	−10.5
CH_4	−15.7	−4.6	−5.2
Ar	−11.3	−6.2	−5.5

[a] E^* is the heat of solution for all the PS samples based on the T^* temperature scale

values in *Table 2* are the midpoint of the range of values calculated from *Figure 5(a–c)*. The E^* values are close to those of E_s for PS1, since PS1 is in the rubbery state and the early glass transition region over the temperature range explored. The use of equal-enthalpy states to compare solubilities in glasses instead of the measurement temperature results in convergence of the solubility and heat-of-solution values for PS samples with different glass transition temperatures. This convergence is most clearly seen for the CO_2 data.

CONCLUSIONS

Solubility of gases in polymers depends on the chemical nature of the gas and polymer and on the state of enthalpy of the polymer. Above T_g the polymer is always in a state of equilibrium enthalpy, so S depends only on the test temperature T_o, and generally increases as T_o decreases. However, in the glassy state, excess enthalpy exists at a given test temperature and the amount of this excess enthalpy depends primarily on the value of T_g for the material. (T_g can vary widely for a given polymer, depending upon molecular weight and its distribution.) Therefore glassy polymers must be considered to exist at an effective temperature, T^*, which is less than T_o, the measurement temperature; the value of T^* is lower for samples with higher T_gs. This qualitative analysis explains the trends in experimental data on the solubility of gases in a series of PSs of different T_g. The most notable trend is the large increase, by as much as a factor of 1.9 in S (measured at 30°C) with increasing substrate T_g.

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