Gas and Vapor Sorption in Polymers Just Below T_g

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Synopsis

Generally, sorption isotherms for gases like CO_2 in glassy polymers are concave to the pressure axis, whereas in the rubbery state these isotherms are linear for gases or sometimes convex to the pressure axis for more condensable vapors. Examples of CO_2 isotherms are reported here that show at low pressure the curvature characteristic of glasses and then become linear at higher pressures. This is observed when the glass transition temperature T_g is not much greater than the observation temperature T, and plasticization of the polymer by sorbed CO_2 causes T_g to become equal to T within the range of pressures employed in the isotherm measurement. For the sorption of vapors in glassy polymers, this can lead to sigmoidal isotherms, as discussed using an illustration from the literature.

INTRODUCTION

Knowledge about the equilibrium sorption of gases or vapors in polymers is important in a variety of areas and especially for understanding the process of permeation. Thus, considerable effort has been devoted to measuring and interpreting the sorption isotherms for small molecules in rubbery, glassy, and semicrystalline polymers.[1-6] The limiting cases described below have proven particularly useful.

Application of the simple Flory-Huggins theory[7] to the equilibrium sorption of vapors in rubbery polymers leads to a form commonly observed. As seen in Figure 1, this model predicts the amount of the small molecule sorbed, expressed here as a volume fraction, to be concave upward when plotted versus partial pressure, or activity. The degree of curvature increases with the extent of sorption or as the interaction parameter χ_1 decreases or becomes more favorable. The shape of the isotherm will be altered somewhat if the interaction parameter is dependent on the amount of vapor sorbed, but the upward curvature remains a generally expected shape for simple systems where sorption can be modeled as a nearly random mixing process.

In the limit of low activities or small extents of sorption, a linear approximation to the sorption isotherm provides an adequate description; that is, Henry's law applies. This limiting case of the Flory-Huggins type of isotherm is normally used to analyze the behavior of gases in polymers above their glass transition temperatures. Figure 2 shows that sorption of CO_2 gas at 35°C in cross-linked butyl rubber[8] is well described by Henry's law up to at least 20 atm. Since the critical temperature of CO_2 is about 31°C, it is not possible to define an activity relative to the liquid state, but simple extrapolation of the vapor pressure curve to 35°C allows one to see that CO_2 at 20 atm has an effective activity of less than 0.3. If the mea-
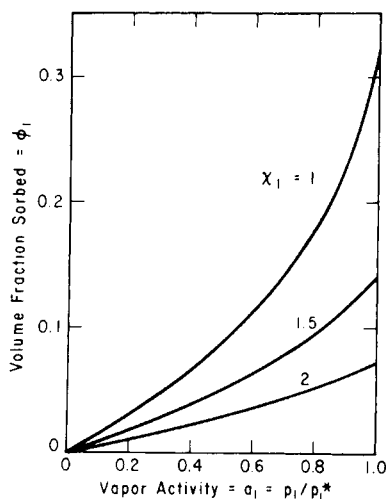
Fig. 1.   Prediction of sorption isotherm shape by the Flory-Huggins theory for a vapor in an amorphous, rubbery polymer using the interaction parameters indicated.

surements in Figure 2 were extended to pressures two to three times this level, curvature similar to that in Figure 1 would probably be seen. For less soluble gases, like O_2, N_2, and argon Henry's law behavior is assured over a very wide range of pressures. Consequently, it may be said that linear isotherms are characteristic of gas sorption in polymers in their rubbery state.

It is now well established that the shape of gas sorption isotherms in glassy polymers stands in marked contrast to that described above. The results shown in Figure 3 for CO_2 and polysulfone are typical.[9] The isotherms are far from linear, and the curvature has the opposite sense to that seen in Figure 1. Generally, gases are also more soluble in glassy polymers than in rubbery polymers.[6] These facts are commonly agreed to result from the nonequilibrium character of polymers below their glass transition temperatures. The so-called dual-sorption model[3-6,9,10] considers the curvature and higher solubility to result from an additional sorption mechanism associated
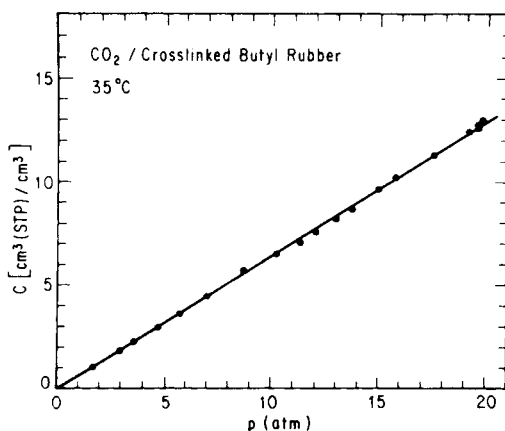

Fig. 2.   Sorption isotherm for CO_2 in a lightly cross-linked butyl rubber at 35°C.
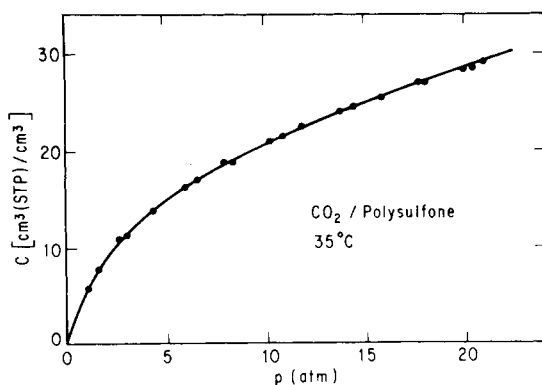
Fig. 3. Sorption isotherm for CO_2 in glassy polysulfone at 35°C.

with unrelaxed volume in the glass and provides an excellent description of measured isotherms. This model does not envision sorption of gases in glasses to be a simple random mixing process. Other points of view have been developed;[11,12] however, the downward curvature seen in Figure 3 is now well known to be another limiting shape for the sorption isotherm applicable when the polymer is in the glassy state.

The purpose of this paper is to demonstrate that the sorption isotherm under certain conditions may exhibit the characteristic glassy-type shape (Figure 3) at low pressures and then revert to the characteristic rubbery-type shape (Figure 2 or Figure 1) at higher pressures. This is seen for glassy systems whose T_g are not much higher than the temperature of sorption and whose T_g are lowered by plasticization[13-16] as gas or vapor is sorbed such that the original glass becomes a rubber within the range of pressures over which the isotherm is measured.

EXPERIMENTAL

Sorption isotherms for CO_2 in the various polymer systems described in this paper were determined using a dual-volume dual-transducer cell design based on the pressure decay principle. Details on the construction and use of this equipment have been described previously.[17,18] Samples were fully conditioned at the highest CO_2 pressure before measuring the isotherm. Pertinent information about the various polymers employed is listed in Table I.

EXPERIMENTAL RESULTS AND DISCUSSION

During the course of several studies in our laboratory on the sorption and transport of gases in a variety of polymers, we observed that sometimes the isotherms for CO_2 have the form of Figure 3 at low pressure but become linear, like Figure 2, at higher pressures. A number of examples of this behavior have been selected for presentation here to demonstrate the generality of this type of behavior and to call attention to the conditions and reasons for its occurrence.

The first example involves a completely amorphous and miscible blend containing 65% by weight of poly(methyl methacrylate) (PMMA) and 35%

TABLE I
Polymer Systems Used for CO_2 Sorption Isotherm Measurement

Polymer system	Glass transition temperature (°C)	Comments
Cross-linked butyl rubber	−76[a]	98% Isobutylene
Polysulfone	182[b]	—
Blend of 65% PMMA and 35% PVF_2	62[b]	Completely amorphous and miscible
Poly(ethyl methacrylate)	69[b]	—
Polystyrene + 3% mineral oil	87[b]	Commercial PS with average $M_n =$ 90,000 and average $M_w/M_n = 2.8$
Polystyrene + 10% tricresyl phosphate	70[b]	Commercial PS with average $M_n =$ 90,000 and average $M_w/M_n = 2.8$

[a] Literature value.[6]
[b] Measured by DSC at 20°C/min.

of poly(vinylidene fluoride). As seen in Figure 4, the CO_2 isotherm at 35°C initially curves downward as expected for a glassy polymer; however, at about 15 atm of CO_2 pressure this curvature ceases and the remaining portion of the isotherm is linear and extrapolates to the origin. The T_g of this blend in the absence of CO_2 is 62°C; however, sorption of CO_2 decreases this value continuously as the amount of CO_2 sorbed increases. This was demonstrated by a technique developed recently[13] based on differential scanning calorimetry (DSC), which allows the direct measurement of the glass transition for a polymer containing a fixed amount of sorbed gas. Results from this method show that the T_g for this system approaches the sorption temperature, 35°C, when equilibrated with about 16 atm of CO_2. At 25 atm of CO_2 the T_g is estimated to be several degrees below 35°C. Thus, the continual lowering of the T_g as CO_2 is sorbed results in T_g being equal to the sorption temperature at some pressure and the polymer becomes rubbery as further CO_2 is sorbed at higher pressures. Since the polymer-CO_2
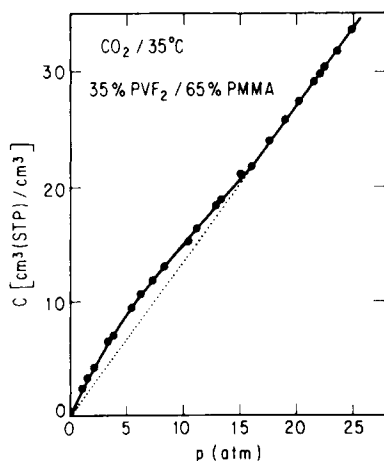

Fig. 4. Sorption isotherm for CO_2 in an amorphous blend containing 65% PMMA and 35% PVF_2 at 35°C.

mixture is a glass at pressures lower than about 16 atm, the isotherm in this region has the characteristic curvature seen in Figure 3 but the isotherm becomes linear at higher pressures since the polymer is in its rubbery state. Owing to the rate aspects of glass transition phenomena, T_g determined by DSC are higher than those applicable to the equilibrium sorption experiment, as discussed later.

It is interesting to note that pure PMMA does not show this shift in mechanism[19] since its T_g is sufficiently high that CO_2 sorption over the pressure range used will not depress its T_g to below 35°C. On the other hand, this can happen for poly(ethyl methacrylate), whose T_g is 69°C. As seen in Figure 5, the initially curved isotherm becomes linear at about 19 atm of CO_2 for this polymer.

This sorption isotherm anomaly has not been observed for CO_2 and polystyrene since evidently the T_g of about 100°C for this polymer is too high to be depressed to 35°C within the usual range of pressures used to measure sorption isotherms. However, by reducing the T_g via liquid plasticizers and raising the sorption temperature, we do see this behavior for polystyrene systems. The first example is for a commercial-grade polystyrene containing 3% by weight of mineral oil—its T_g is 87°C as measured by DSC at 20°C/min. Breaks in the sorption isotherms like those described above are seen in Figure 6 at sorption temperatures of 45, 55, and 65°C. The break occurs at lower pressures, or CO_2 concentrations, the higher the temperature consistent with the explanation given earlier since less plasticization by CO_2 is needed to reduce T_g to the higher sorption temperature. Similar findings are shown in Figure 7 for the same polystyrene containing 10% by weight of tricresyl phosphate.

Based on the interpretation given above, the break in the sorption isotherm defines the concentration of CO_2 at which the glass transition temperature for the system becomes equal to the temperature at which the isotherm is determined. Figure 8 is a plot of T_g versus CO_2 concentration
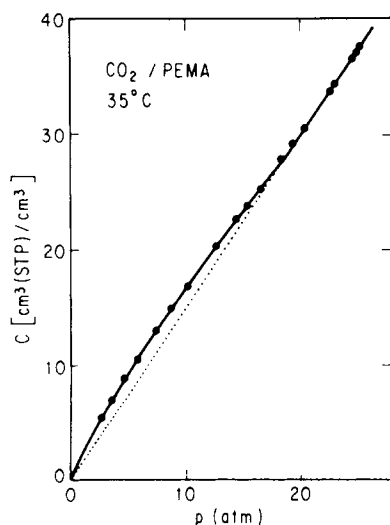

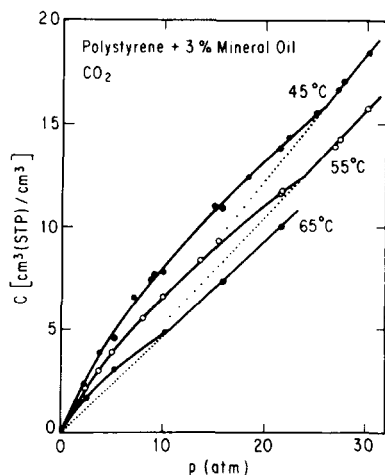Fig. 5. Sorption isotherm for CO_2 in poly(ethyl methacrylate) at 35°C.

Fig. 6. Effect of temperature on sorption isotherms for CO_2 in polystyrene containing 3% mineral oil.

for the commercial polystyrene containing the plasticizers indicated (see Table I). The points were determined from the breaks in the isotherms shown in Figures 6 and 7, whereas the lines drawn were computed using a recently published theoretical relation as described next. Chow[20] has developed the following equation for predicting the glass transition temperature T_g of a polymer-diluent mixture:

$$\ln\frac{T_g}{T_{g0}} = \beta[(1 - \theta) \ln (1 - \theta) + \theta \ln \theta] \tag{1}$$
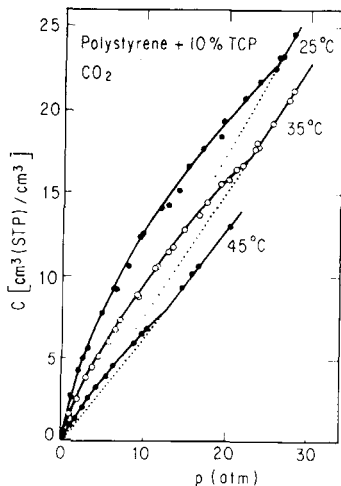

Fig. 7. Effect of temperature on sorption isotherms for CO_2 in polystyrene containing 10% tricresyl phosphate.
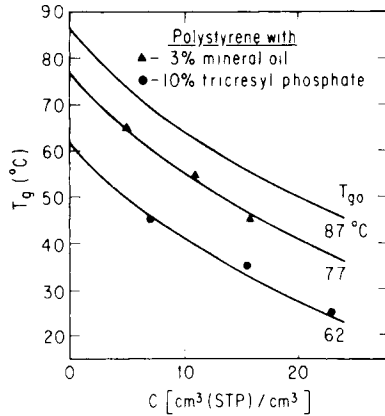
Fig. 8. Effect of the concentration of sorbed CO_2 on the glass transition of a commercial polystyrene containing the plasticizers indicated. Solid points taken from the break points in Figures 6 and 7. Lines were calculated from eq. (1) using $\Delta C_p = 0.062$ cal/g-°C and T_{g0} values as described in the text.

where T_{g0} is the glass transition at zero dilutent concentration, β is a physical constant, and θ is a measure of diluent concentration. The latter two quantities are defined as

$$\beta = \frac{zR}{M_P} \Delta C_P \qquad (2)$$

$$\theta = \frac{M_p}{zM_d} \frac{\omega}{1 - \omega} \qquad (3)$$

where z is the lattice coordination number, R is the gas constant, ΔC_P is the increase in the specific heat at the glass transition, ω is the mass fraction of diluent, and M_p and M_d are the molecular weights of the repeat units of the polymer (or monomer) and the diluent, respectively. Following Chow's suggestion a value of $z = 2$ is used here. The top curve in Figure 8 was computed for polystyrene plus 3% mineral oil by Chow's method using $T_{g0} = 87°C$ as determined by DSC. As seen, the calculated result is somewhat higher than the points obtained from the breaks in the sorption isotherms. A plausible cause for this is the effect of the experimental time scale on the T_g observed. That is, that T_g measured by an experiment with a time scale of seconds or minutes, as by DSC, will be higher than that measured by an experiment with a time scale of hours or days, such as sorption. For example, a change in heating rate in the DSC by an order of magnitude will shift T_g by about 7°C for polystyrene. Thus, we constructed the second curve from the top using a T_{g0} 10 degrees lower, and the points agree quite well with this calculated line. Similar agreement is seen for the polystyrene containing 10% tricresyl phosphate when an adjusted T_{g0} is used in the calculation. The exercise, although approximate in nature, demonstrates in another way that plasticization of the polymer by CO_2 is a reasonable explanation for the change in shape of the isotherms reported here. Direct

evidence for the T_g depression by CO_2 and comparison of this with predictions by Chow's equation are given elsewhere.[13]

The useful feature of the Chow equation for these calculations is that it does not require a T_g value for the diluent, which is not available in the case of CO_2. Obviously, the Chow equation is only an approximation limited to small concentrations of diluent. A mixing rule for T_g of multicomponent systems must employ a T_g for the diluent in order to be broadly applicable. Another limitation is that the lattice model used by Chow to develop this equation requires polymeric repeat units similar in size to that of the diluent, which is clearly not met for polymers like poly(ethylene terephthalate) and polycarbonate.

EXTENSION TO MORE CONDENSABLE VAPORS

For the effect demonstrated here, CO_2 is somewhat unique among the gases since it is soluble enough in polymers to cause significant plasticization but not soluble enough, within the pressure range used here, to cause departures from Henry's law when the polymer is in the rubbery state. Thus, the isotherms shown here become linear after enough CO_2 is sorbed to convert the glass into a rubber at the sorption temperature. Gases like O_2, N_2, or CH_4 are not soluble enough in polymers at these pressures to have any readily noticeable effects on T_g. Vapors more condensable than CO_2 are generally sufficiently soluble in polymers that in the rubbery state the isotherms are not linear but curve upward, as predicted by the Flory-Huggins form (Figure 1). One can expect vapors to cause a similar sorption anomaly like that seen here for CO_2 except after the break point the isotherm would curve upward.

Berens[21] has reported sigmoidally shaped isotherms for the sorption of vinyl chloride monomer in poly(vinyl chloride) at temperatures below the glass transition of pure PVC. We believe the inflection in such isotherms is the consequence of plasticization by the vapor, which depresses the T_g of the polymer to and below the observation temperature. The solid lines in Figure 9 are a reproduction of the isotherms reported by Berens.[21] Figure
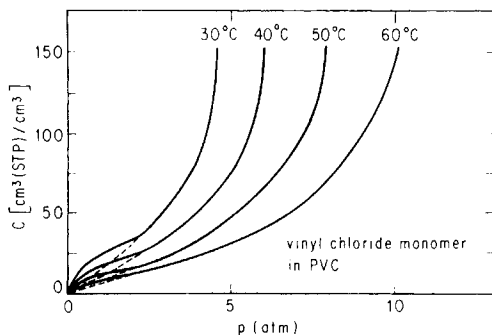

Fig. 9. Effect of temperature on sorption isotherms for vinyl chloride monomer in PVC as reported by Berens (solid curve). Dashed curve is extension of upwardly curved portion of isotherm to the origin. Intersection of dashed and solid lines occurs at concentration, which causes T_g (see Figure 10) to approach T.
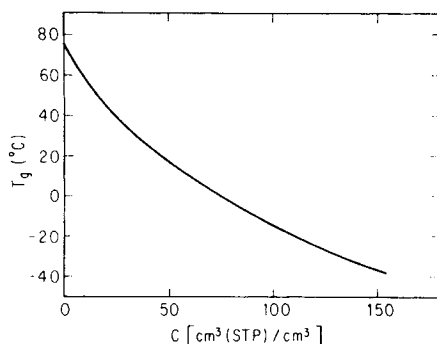
Fig. 10.   Influence of sorbed vinyl chloride monomer concentration on the glass transition temperature of poly(vinyl chloride) as predicted by eq. (1) using $\Delta C_p = 0.0693$ cal/g-°C.

10 is an estimation of the glass transition versus vinyl chloride monomer concentration relation for this system calculated from the Chow equation. According to this estimate, 35 cm³/(STP)/cm³ of vinyl chloride will drop the T_g of PVC to 30°C, demonstrating significant plasticization. The inflections in the isotherms occur very near the concentration in Figure 10 that corresponds to a T_g equal to the temperature at which each isotherm was determined. The dotted lines in Figure 9 were drawn as simple extensions to the origin of the upwardly curved portion of each isotherm, generating a shape over the entire pressure range like that in Figure 1, which would be expected if the polymer were not glassy originally. The dotted lines join the observed isotherms just at the point at which T_g has been depressed to the observation temperature. That the actual solubility lies above the dotted line is a consequence of the additional sorption mechanism operative in the glassy state, which disappears when the polymer is no longer glassy. These general issues have been recognized by others,[21,22] but the direct connection between the inflection point in these isotherms and the depression of T_g to the observation temperature does not seem to have been explicitly stated before. The results and interpretations given in Figures 9 and 10 make an appealing generalization of the observations reported here for CO_2.

SUMMARY

The shape of the sorption isotherm for gases or vapors in polymers depends on whether the polymer is in the glassy or rubbery state. Since the sorption of some gases and most vapors can cause appreciable reduction in the glass transition temperature within the range of pressures commonly encountered, the polymer may be in the glassy state at low sorption pressures and in the rubbery state at higher sorption pressures if its glass transition temperature is not too much greater than the temperature at which the isotherm is measured. This situation leads to a complex isotherm with a shape characteristic of glasses at low pressures and a shape characteristic of rubbers at higher pressures. The break or inflection in the isotherm occurs when the system's T_g equals the observation temperature; however, owing to the kinetic aspects of the glass transition, the T_g relevant to the sorption process is somewhat less than that measured by conventional techniques like thermal analysis.

Mathematical models for the complex isotherms described here can be constructed, at least conceptually, by appropriate modification of existing models. The dual sorption model defined by

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

(where k_D, C'_H, and b are model parameters) gives a good description for the sorption of gases in glassy polymers. It has been suggested[22] that the linear Henry's law term in eq. 4 should be replaced by an exponential Flory-Huggins term when the penetrant is a more highly soluble vapor, like the case shown in Figure 10. Extensive data for CO_2 sorption in polymers[5,23,24] with rather high glass transition temperatures reveal that the hole saturation term in eq. (4), C'_H, is directly proportional to the difference between the glass transition and observation temperatures, that is, $T_g - T$. When this difference is large, changes in T_g caused by sorption have little effect on $T_g - T$ or C'_H. However, for cases where T_g is only modestly higher than T the effect of the plasticization on C'_H must be accounted for. Based on the observed connection between C'_H and $T_g - T$ already established, it seems reasonable that a more general form for eq. (4) is one in which C'_H is replaced by the function

$$C'_H = C'_{H0} \frac{T_g - T}{T_{g0} - T} \qquad (5)$$

where C'_{H0} and T_{g0} are the Langmuir capacity term and the polymer glass transition temperature (with appropriate rate effects considered), respectively, in the absence of any plasticization; that is, $C = 0$, and T_g is the glass transition for the polymer-diluent mixture at pressure p or concentration C. Thus, when $T_g = T$ the second term in eq. (4) becomes zero and the isotherm becomes linear as seen in Figures 4–7 or exponential as seen in Figure 9. When $T_g > T$, isotherm curvature is caused by both the explicit pressure dependence of the second term in eq. (4) and the implicit pressure dependence of C'_H in that term, as seen in eq. (5). For cases when T_g is considerably larger than T, the latter effect is of relatively little importance; however, when T_g is only slightly larger than T, this effect is significant. For the CO_2 systems described here one can obtain the k_D parameter by simply noting the slope of the isotherm after it has become linear. The quantitative analysis of isotherms like those in Figures 4–8 using eqs. (4) and (5) is at present being pursued.

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