High-Pressure Sorption of Carbon Dioxide in Solvent-Cast Poly(methyl Methacrylate) and Poly(ethyl Methacrylate) Films

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Synopsis

Carbon dioxide sorption isotherms in poly(methyl methacrylate) (PMMA) and poly(ethyl methacrylate) (PEMA) are reported for pressures up to 20 atm. Temperatures between 35 and 80°C were studied for PMMA and temperatures between 30 and 55°C were studied for PEMA. Typical dual mode sorption isotherms concave to the pressure axis were observed in all cases. The measured Langmuir sorption capacities of both polymers extrapolated to zero at the glass transition (T_g) consistent with the behavior of other glassy polymer/gas systems. Sorption enthalpies for CO_2 in the Henry's law mode for PMMA and PEMA are in the same range (−2 to −4 kcal/mole) as has been reported for a variety of other glassy polymers such as poly(ethylene terephthalate), polycarbonate, and polyacrylonitrile. Some of the data suggest that postcasting treatment of the PEMA films left a small amount of residual solvent in the film. The presence of the trace residual solvent during quenching from the rubbery to the glassy state after annealing appears to cause a dilation of the Langmuir capacity and an alteration in the apparent Langmuir affinity constant of the PEMA film. These results suggest the possibility of tailoring physical properties of glassy polymers such as sorptivity, permeability, impact strength, and craze resistance by doping small amounts of selected residuals into polymers prior to quenching to the glassy state from the rubbery state.

INTRODUCTION

High-pressure sorption isotherms for gases in glassy polymers are well known to have a characteristic shape, concave to the pressure axis.[1] Such negative deviations from a linear relationship between sorbed concentration and the surrounding penetrant pressure are usually related to the presence of unrelaxed volume distributed discretely throughout glassy polymers. In the absence of penetrant-induced swelling, the sum of these packets of volume comprises a finite "excess" capacity for sorption which can be saturated at sufficiently high pressures. This unrelaxed volume presumably exists as molecular-scale "gaps" between chain segments and can be considered as analogous to the Langmuir capacity of microporous zeolites and charcoals. The amount and distribution of this excess volume can be altered by thermal treatment[2] as well as by penetrant sorption and degassing procedures.[3,4]

The void fraction in a glass is a constantly, although very slowly, changing function of time at a fixed temperature since large-scale chain relaxations take place extremely slowly below T_g. As the temperature is increased and the glass transition is approached, the frozen void fraction in the polymer decreases. Presumably, chain segments bordering on unrelaxed "gaps" are most likely to

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begin moving first.   As these boundary chain segments execute continually larger amplitude vibrations and eventually convolutions, they encroach on the previously frozen gap territory represented schematically as $V_g - V_l$ in Figure 1.   This encroachment no longer permits a sorbed molecule to experience a Langmuir (microvoid) environment.   Presumably the smallest gaps are eliminated first, and the Langmuir capacity is continually reduced since $V_g - V_l$ is reduced as T_g is approached.   Finally, above T_g all chains have sufficient mobility to preclude the existence of any permanently fixed gaps.[5]

The preceding description of the glassy state has important implications for many of the properties of a glassy polymer sample.   The modulus and impact strength of glassy polymers are related to the degree of segmental mobility of the component molecules which are, in turn, related to the amount of excess volume frozen into the glass.   Also, the tendency to initiate crazes is likely to be highest at points of lower mass density, i.e., the gaps or microvoids can serve as nuclei for craze formation.[6]   It is also anticipated that almost undetectable amounts of residuals remaining in solvent cast films or melt cast films that are studied without removal of residual monomers can significantly alter the apparent gas/polymer sorption equilibria.[7]   Competition by the penetrant gas and the residual for the fixed Langmuir capacity in the polymer would be expected to be controlled largely by the affinity constants of the two sorbates in the polymer.[7]   Such considerations are, of course, highly pertinent to the important problem of stripping residual monomers and solvents from glassy polymers using steam in postproduction processing.

Exposure of glassy polymers to high pressures of CO_2 is known to cause increased sorption levels subsequently measured at lower pressures.[5]   It is believed that such conditioning causes local rearrangements of the packets of unrelaxed volume and may in some cases actually cause an additional swelling of the whole glassy matrix which can give rise to an increased Langmuir capacity apparent in subsequent runs if the penetrant is withdrawn more quickly than the chains can relax.[2,8]

The notion of local rearrangements of unrelaxed volume at constant bulk
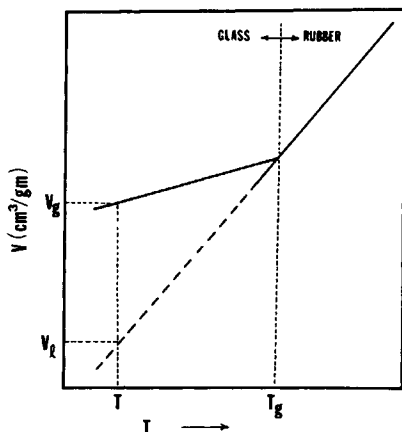

Fig. 1. Schematic representation of the unrelaxed volume $V_g - V_l$, which presumably is the locus of the Langmuir capacity of glassy polymers for gases.   Note that $V_g - V_l$ decreases as T approaches T_g and is zero in the rubbery region.

density is interesting since the implication is that if two identical glassy samples are exposed to high pressures of two different gases (such as CO_2 and CH_4) with different molecular diameters and then evacuated, even if the bulk density of the two samples is unchanged (no change in macroscopic dimensions) the internal distribution of unrelaxed volume might be different in the two cases. One might say that the two membranes had been internally "templated" by small-scale segmental readjustments to accommodate the two different types of molecules to a maximum extent in the existing unrelaxed volume. It is therefore possible that the transport of a third gas, say, helium or hydrogen, could be quite different in the two different samples after the conditioning gases have been removed. Any conditioning effects introduced might be very short-lived or semipermanent depending on whether the polymer is maintained far enough below T_g to greatly retard chain movement over extended time periods.

In a previous article,[5] an expression was developed to quantitatively predict the magnitude of the Langmuir capacity for CO_2 in terms of a polymer's dilatometric expansion coefficients above and below T_g. It is an objective of this study to extend such analyses to a series of polymers which lack the complications of crystallinity. This article presents the results of our work with PMMA and PEMA, the first two members of the interesting totally amorphous homologous series of methacrylates. Transport data derived from sorption kinetic measurements for CO_2 in these two polymers will be reported in part II of this series.

EXPERIMENTAL

Materials

The polymers used in this study were obtained from Aldrich Chemical Co., Milwaukee, WI. The molecular weights of the samples, determined by solution viscosity in butanone, were found to be 599,000 g/mole for PMMA and 309,000 g/mole for PEMA.

The CO_2 used for sorption experiments was obtained from Air Products, Inc., Bethlehem, PA. The CO_2 was >99.9% pure and was used as received.

Film Preparation

A sample of the polymer powder which was to be cast was first dried in a vacuum oven at 40°C for 24 hr. Seven percent (wt) solutions of the desired polymer were prepared using Fisher reagent grade acetone. Thin films (2.5 ± 0.1 mil final dry thickness) were cast on mercury and allowed to air dry for 12 hr in a humidity free environment. The films were then placed in a vacuum oven and slowly evacuated. After 1 hr, the temperature was raised 10°C/hr to 20°C above T_g. After 12 hr, the membranes were allowed to cool slowly at 10°C/hr under vacuum to room temperature.

Sorption Procedures

Because it was known that exposure to high-pressure CO_2 tends to cause conditioning of glassy polymers which is semipermanent at room temperature,[5,9,10] each of the polymer samples was equilibrated with CO_2 at 20 atm and

kept under pressure for 6 hr after all apparent changes in sorption had ceased. The sorption isotherms measured after such pretreatment were reproducible as long as the maximum sorption pressures never exceeded 20 atm.   In one case, the measurement pressure was overrun to 21 atm and it was found that a small but measurable increase in sorption level resulted at lower pressures compared to the earlier case where a maximum pressure of 20 atm was used.   While such effects are small [e.g., 32.07 vs. 31.88 cm^3 (STP)/(cm^3 polymer) for the overrun case versus the standard case at 20 atm], they can be responsible for introducing unnecessary scatter into the data and were minimized in the present study.

Sorption experiments were carried out in an "interval" fashion.   After pre-conditioning at 20 atm at the lowest temperature to be studied, the film was thoroughly evacuated for 24 hr and then equilibrated at increasing pressures (e.g., 3, 8, 12, 16 atm as a typical sequence) and then thoroughly reevacuated for another run sequence at different pressures.   After the first sorption isotherm was completed, the temperature was raised to the next test temperature and the preceding measurement procedure was repeated.   The detailed design and operating procedures for the dual volume, dual transducer cell used in this study are discussed in an earlier article.[9,11]   The cell design offers the important advantage of permitting one to perform a perfect material balance on all gas introduced to the cell, so very accurate isotherms can be measured.

RESULTS AND DISCUSSION

Sorption Isotherms

Carbon dioxide sorption isotherms at 35, 55, and 80°C are shown in Figure 2 for PMMA.   Similar isotherms for PEMA are presented in Figure 3 at 30, 40, and 55°C.   The isotherm shapes for both polymers are typical of those observed for gases in many other glassy polymers and can be described well by eq. (1), the standard dual mode sorption expression

$$C = k_D p + C'_H bp/(1 + bp) \tag{1}$$

where $k_D[= $ cm^3(STP)/(cm^3 polymer atm)] is the Henry's law constant, $b(=$
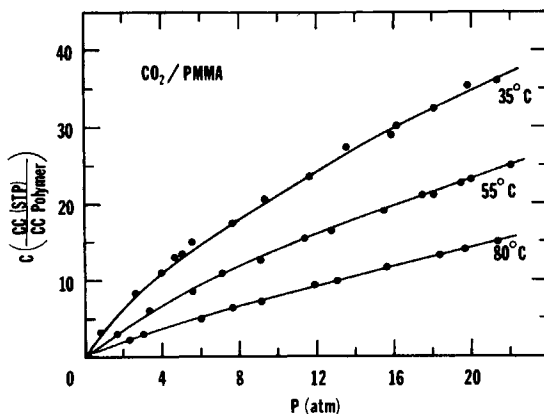

Fig. 2. Sorption isotherms for CO$_2$ in PMMA at 35, 55, and 80°C.   Note the reduction in curvature as the temperature increases.
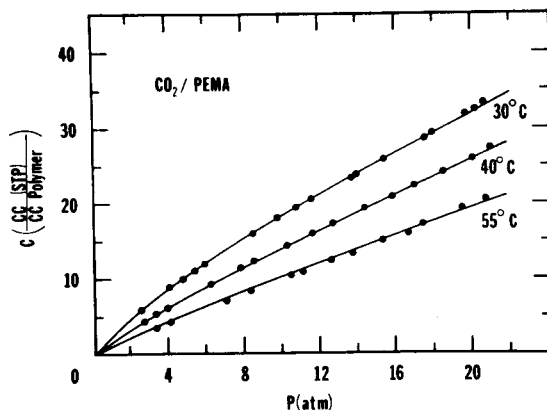
Fig. 3. Sorption isotherms for CO_2 in PEMA at 30, 40, and 55°C.

atm^{-1}) is the Langmuir affinity constant and C'_H [= cm^3(STP)/(cm^3 polymer)] is the Langmuir capacity constant of the polymer for the gas. The physical interpretations of the various parameters have been discussed in detail earlier.[5,9,12,13]

The values of the dual mode parameters at each temperature were fitted to eq. (1) using a nonlinear least-squares program,[9,12] and the values obtained are reported in Table I for both polymers at the various temperatures studied. The lines drawn through the points in Figures 2 and 3 were calculated from eq. (1) using the appropriate dual mode parameters reported in Table I. The data are clearly represented well by the model.

Interpretation of Parameters

It has been noted that k_D and b are amenable to a standard van't Hoff analysis.[5,13] The slopes of semilog plots of these parameters versus $1/T$ permits determination of the enthalpy change of sorption for transferring one mole of gas molecules from the gas phase into the Henry's law (ΔH_D) and the Langmuir (ΔH_b) environments, respectively. The apparent Henry's law constant k^*_D, equal to the low-pressure limiting slope of the C vs. p plot, is equal to $k_D + C'_H b$ and is also often represented by a van't Hoff expression. The apparent sorption enthalpy derived from such an analysis ΔH^*_D does not have a simple physical meaning analogous to ΔH_D and ΔH_b since the temperature dependency of C'_H

TABLE I
Dual Mode Parameters for PMMA and PEMA

Polymer	T (°C)	$k_D \left(\dfrac{\text{cm}^3(\text{STP})}{\text{cm}^3 \text{ polymer atm}} \right)$	$C'_H \left(\dfrac{\text{cm}^3(\text{STP})}{\text{cm}^3 \text{ polymer}} \right)$	b (atm^{-1})
PMMA	35	1.14	14.9	0.218
	55	0.74	12.0	0.116
	80	0.505	7.13	0.0683
PEMA	30	1.28	8.14	0.193
	40	1.14	3.78	0.204
	55	0.932	0.996	0.246

enters into ΔH_D^* as an apparent enthalpy.[14]   As discussed earlier, the primary reason for reduced Langmuir capacities as temperature is raised is the mobilization of "gap" regions rather than reduced energetic interactions with the sorbing gas, which would truly alter the difference in enthalpy of a gas molecule in the sorbed state.

van't Hoff plots for k_D and b are presented in Figures 4 and 5 for PMMA. Analogous plots are presented for PEMA in Figures 6 and 7.   The sorption enthalpies ΔH_D and ΔH_b are presented in Table II for the two polymers.

Henry's Law Constants and Affinity Constants

The enthalpic results for CO_2 sorption in PMMA are reasonably characteristic of many glassy polymers.   The absolute value of $\Delta H_D = -3900$ cal/g mole for CO_2 in PMMA is slightly lower than the corresponding value (-4000 cal/g mole) in polycarbonate,[2] but is considerably greater than the -2900 cal/g mole and -1700 cal/g mole values reported for CO_2 in poly(acrylonitrile)[16] and semicrystalline poly(ethylene terephthalate).[5]   The tendency for relatively strong interaction between PMMA and carbon dioxide is also signaled by the large value of $\Delta H_b = -5600$ cal/g mole for PMMA, which is even larger than the corresponding value of -4600 cal/g mole for the enthalpy of sorption of CO_2 in the Langmuir mode in polycarbonate.[2]   It is interesting that $\Delta H_D - \Delta H_b = 1700$ cal/g mole is the same magnitude as the corresponding difference in enthalpies between the dissolved and Langmuir modes observed for CO_2 in poly(ethylene terephthalate)[5] even though the respective values $\Delta H_D = -1700$ cal/mole and $\Delta H_b = -3000$ cal/mole were quite a bit lower for this polymer.
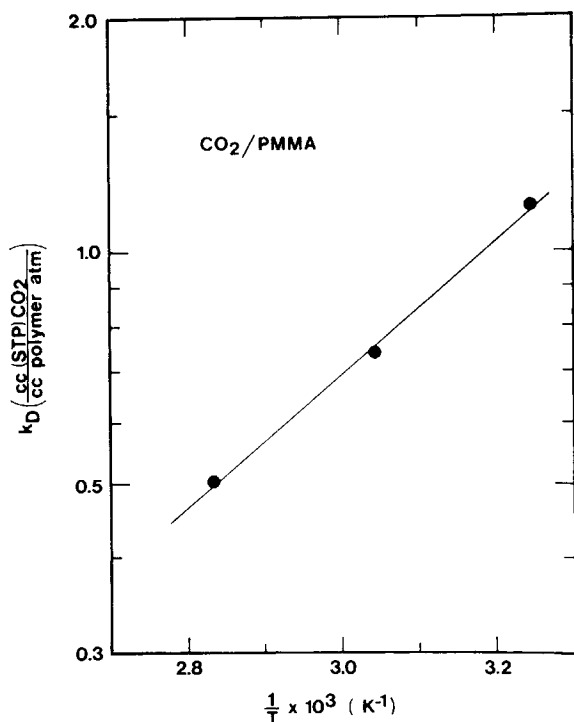

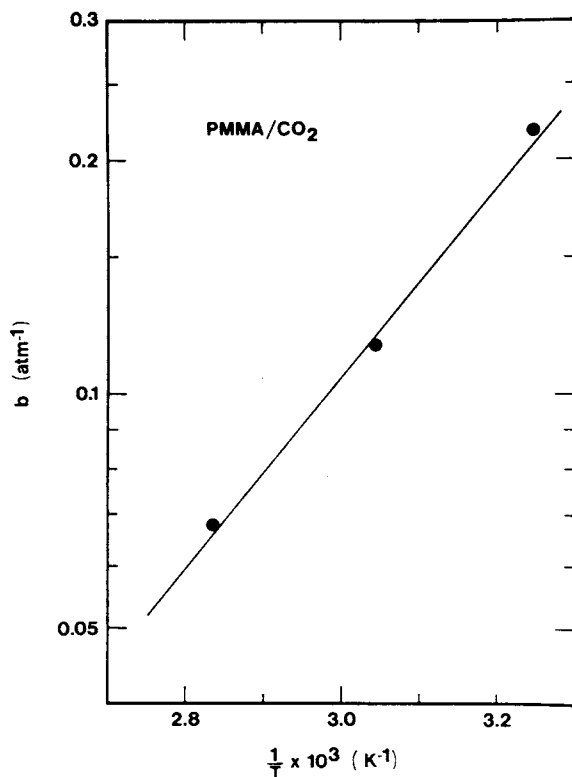Fig. 4. van't Hoff plot of the Henry's law constant for CO_2 in PMMA at 35, 55, and 80°C.

Fig. 5. van't Hoff plot of the Langmuir affinity constant for CO$_2$ in PMMA at 35, 55, and 80°C.

TABLE II
Sorption Enthalpies for CO$_2$ in PMMA and PEMA

Polymer	ΔH_D (cal/g mole K)	ΔH_b (cal/g mole K)
PMMA	−3900	−5600
PEMA	−2600	+2000

The enthalpic results for Henry's law mode sorption of CO$_2$ in PEMA are similar to those for PMMA but suggest slightly weaker specific interactions between this polymer and CO$_2$ compared to PMMA. The positive 2000 cal/mole enthalpy of sorption for CO$_2$ in the Langmuir mode in the PEMA sample is very nonstandard for sorption of gases in glassy polymers. In an earlier study with poly(acrylonitrile)[16] a similar positive value was found when a small amount of residual solvent was present. After removal of the residual, a negative value of −2800 cal/g mole was observed. This phenomenon clearly merits more detailed discussion.

In the discussion of the preparation of the two films, it was noted that both films were annealed for 12 hr at 20°C above their *respective* T_g's to remove residual acetone. In the case of PMMA, the films were annealed at 140°C, while PEMA annealing was carried out at only 90°C.

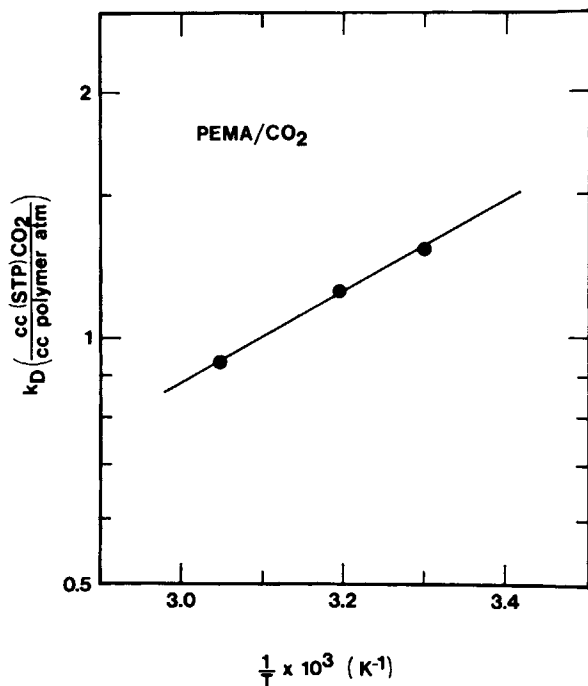Thermal analysis of the cast, annealed films and the dried as-received powders

Fig. 6. van't Hoff plot of the Henry's law constant for CO_2 in PEMA at 30, 40, and 55°C.

of both polymers was performed using a Perkin–Elmer DSC II at a scan rate of 20°C/min between 30 and 150°C. The first and second cycle glass-transition temperatures measured for PMMA were 120 and 119°C, respectively. The T_g measured for the as-received high-molecular-weight PMMA powder after 24 hr of drying at 40°C was also equal to 119°C. These data, therefore, indicate that essentially no residual acetone remained in the PMMA films after the casting
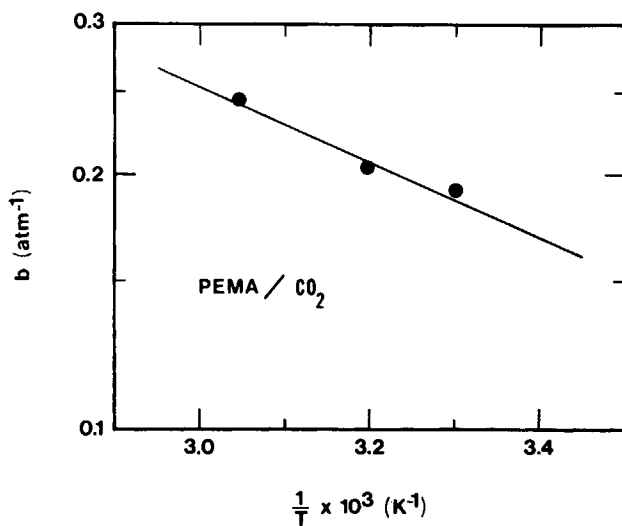

Fig. 7. van't Hoff plot of the Langmuir affinity constant for CO_2 in PEMA at 30, 40, and 55°C.

and annealing process. On the other hand, the dried as-received PEMA powder had a T_g of 71°C, while the first heat T_g of the cast, annealed film removed from the cell was only 57°C. After the first heat cycle to 150°C, the second heat T_g was 69°C and the third heat T_g was 71°C. Annealing at or above 140°C is therefore advisable to guarantee rapid and complete removal of acetone from such solution cast polymers.

An earlier theroetical treatment of the effects on the apparent enthalpy of sorption caused by the presence of a trace residual solvent with a high affinity constant and highly negative enthalpy of sorption (as would be expected for acetone in PEMA) demonstrated that an apparent *positive* enthalpy of sorption in the Langmuir mode would be expected for the penetrant gas. The apparent enthalpy of sorption for the Henry's law mode was also predicted to be only slightly affected by trace residual solvent.[7] Both of the preceding predictions are consistent with the current results for PEMA and with an earlier study with poly(acrylonitrile).[16] A confirmatory study with PEMA which has been annealed at 140°C for 12 hr must be performed to absolutely prove the hypothesized explanation of the positive ΔH_b for this polymer. Such studies are lengthy and tedious but are planned and will be reported in the future.

Langmuir Capacity Constants

The Langmuir capacity constants C'_H, for PMMA and PEMA are plotted as functions to $T_g - T$ in Figures 8 and 9. The T_g's used in developing the plots were the values determined by DSC for the actual polymers used in the sorption study ($T_g = 120°C$ for PMMA and $T_g = 57°C$ for PEMA). The PMMA value is higher than the values normally reported in the literature presumably due to the very high molecular weight of the sample used. Consistent with the earlier discussion of the tendency for gaps to be eliminated steadily and finally disappear at T_g, the Langmuir capacity of both of the polymers for carbon dioxide extrapolates to zero at T_g. This behavior has now been observed for a number of quite different glassy polymers.[2,5,17]

A more rigorous test of the hypothesis that C'_H is associated with the unrelaxed volume in a glassy polymer can be performed using eq. (2) (ref. 5):

$$C'_H = \rho^*(V_g - V_l)/V_g \qquad (2)$$

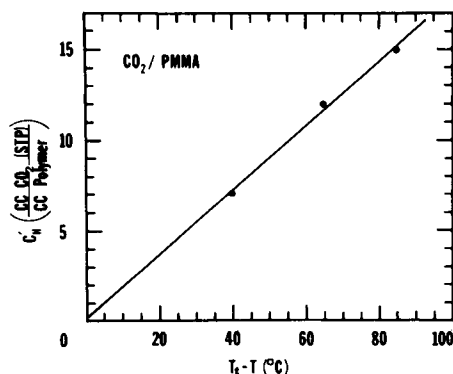where ρ^* is the molar density of a penetrant (CO$_2$) at saturation of the Langmuir

Fig. 8. Plot of the Langmuir capacity of PMMA at 35, 55, and 80°C demonstrating that C'_H extrapolates smoothly to zero at the polymer's $T_g = 120°C$.
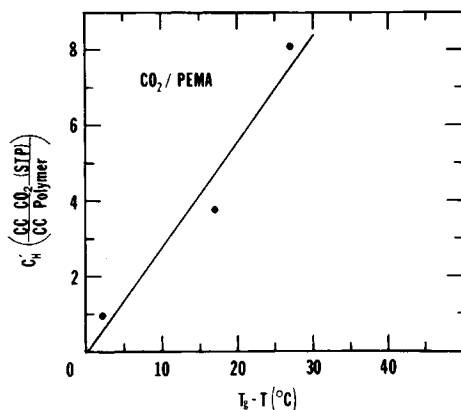
Fig. 9. Plot of the Langmuir capacity of PEMA at 30°C, 40, and 55°C demonstrating that C'_H extrapolates smoothly to zero at the polymer's $T_g = 57°C$.

capacity in the polymer, V_g is the actual specific volume of the sample at the temperature of interest (the solid line below T_g in Fig. 1), and V_l is the hypothetical specific volume of the sample at the temperature of interest if all gaps were isothermally annealed out (the dotted line below T_g in Fig. 1). The expression presented in eq. (2) is clearly consistent with the data in Figures 8 and 9, since as $T_g - T$ goes to zero, $V_g - V_l$ goes to zero and C'_H disappears. The value of ρ^* used in eq. (2) can be estimated from consideration of the Langmuir capacities of zeolites for CO_2 over the same temperature range. Alternatively, ρ^* can be approximated by the density of pure liquid CO_2 below its critical temperature (0.85 g/cm^3). Either of the above approximations gives results for ρ^* which suggest that the molar volume of CO_2 in the Langmuir mode is similar to that of CO_2 in a molecularly dissolved state in a variety of simple liquid solvents.[18] If one uses the density of pure CO_2 as a liquid in eq. (2) with values for dilatometric expansion coefficients for PMMA and PEMA from the literature[19] and the values for T_g from the DSC analysis, the agreement between measured and predicted Langmuir capacities can be seen from the plot in Figure 10. A variety of other polymers are also represented on this plot and the agreement is pleasing. If one considers the PEMA points by themselves, however, it is clear that they are somewhat aberrant. The exact reason for this behavior is not perfectly clear, but it is likely to be related to the trace residual acetone in the polymer. There are interesting data by Enscore et al.,[3] which suggest that very minor amounts of residual n-hexane in polystyrene quenches relaxation of preswollen polymer chains in some manner. The implication of the present data are that a very minor amount of residual acetone similarly prevents the normal relaxation of chains during cooling after the annealing step above T_g. The Langmuir capacity is therefore inflated above the value expected for the truly solvent-free sample, i.e., $V_g - V_l$ is larger for the present sample than for the solvent-free sample for which the dilatometric coefficients are reported in the literature. The presence of a residual during the quenching operation may, therefore, be capable of significantly increasing the Langmuir nature of the sample.
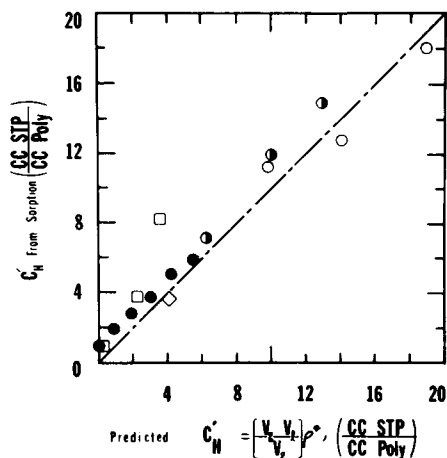
Fig. 10. Comparison of the C'_H for CO$_2$ measured by sorption with the Langmuir capacity predicted from eq. (2) using a value of $\rho^* = 0.85$ g/cm^3 for CO$_2$ and values of $V_g - V_l$ for the various polymers from the literature (ref. 18). The most significant difference between measured and predicted values occurs for PEMA at 30°C. The deviation in this case may be related in some fashion to the presence of residual acetone which was incompletely removed following the film casting. (O) Polycarbonate (ref. 2), ($\diamond$) poly(acrylonitrile) (ref. 15), (●) poly(ethylene terephthalate) (ref. 5), and (◑) PMMA, (□) PEMA (present study) at various temperatures.

CONCLUSIONS

The dual mode sorption model describes the data well for CO$_2$ in PMMA and PEMA. The Henry's law sorption enthalpies for CO$_2$ in both polymers are typical of values observed in other glassy polymers and suggest some specific polymer/penetrant interactions, especially in the case of PMMA.

The difference between ΔH_D and ΔH_b for PMMA is similar to the value of this difference observed for CO$_2$ in poly(ethylene terephthalate) in which case the CO$_2$ in the Langmuir mode had a much lower diffusional mobility than the Henry's law species.[20] Such an effect might be anticipated in the present case also.

The temperature dependence of the Langmuir capacity C'_H of both polymers for CO$_2$ is qualitatively consistent with an interpretation of C'_H in terms of un-relaxed gaps present in the polymer below T_g. These gaps become mobilized above T_g and C'_H disappears in the rubber. A simple quantitative model for prediction of C'_H was quite effective for PMMA, but measured capacities for PEMA were higher than predicted values using dilatometric expansion coefficients from the literature. Further, it was noted that the apparent positive sorption enthalpy for CO$_2$ in the Langmuir mode for PEMA strongly suggests that minute traces of acetone remained in the polymer even after annealing under vacuum 20°C above T_g for 12 hr (at 90°C). The PMMA films were annealed at 140°C for the same period of time and appeared to be free of solvent. The complete removal of casting solvent or residual monomer is therefore difficult, particularly when there is a tendency for strong polymer/solvent interaction as in the case with acetone and the methacrylates. This rather mundane and obvious conclusion is, nevertheless, of great importance to processing of polymers for contacting with foodstuffs. On the positive side, the results of this study related to C'_H have exciting potentials for formulating and understanding opti-

mum postreactor processing of glassy polymers to tailor the transport, impact and craze-related properties of the resultant materials.

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