# Plasticization of Glassy Polymers by $CO_2$

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## Synopsis

A technique is described which uses differential scanning calorimetry to estimate the glass transition of polymers containing a dissolved gas. The technique is simple and appears to give reliable results. The effects of $CO_2$ sorption at pressures up to 25 atm were examined in detail for poly(methyl methacrylate) and its blends with poly(vinylidene fluoride). Less extensive results for polystyrene, polycarbonate, poly(vinyl chloride), and poly(ethylene terephthalate) are also given. Reductions in $T_g$ of up to 50°C are observed. A theoretical relation by Chow predicts results in reasonable agreement with the experimental data. These findings are relevant to various applications such as membrane separation processes for gases.

## INTRODUCTION

It is well known that sorption of vapors and liquids by polymers can cause significant plasticization resulting in substantial decreases in the glass transition temperature.[1-4] On the other hand, such effects are rarely considered important in the sorption of gases by polymers since the solubility levels are so low. For example, gases such as He, $N_2$, Ar, and $CH_4$ typically have solubility coefficients of the order of $10^{-4}$–$10^{-3}$ $cm^3$ (STP)/$cm^3$ cm Hg in polymers, and at a pressure of 20 atm the amount dissolved would be less than 1% on a weight basis which, for most purposes, would not cause a noticeable reduction in $T_g$. Of course, at extremely high pressures the situation is expected to be different as shown by Assink[5] using NMR measurements. He demonstrated noticeable plasticization of silicone rubber by argon in the pressure range of 500–2000 atm owing to the significant amounts of argon which are dissolved in the polymer under these conditions.

Gases like $CO_2$ with higher critical temperatures than those mentioned above are considerably more soluble, particularly in glassy polymers, as described in a number of recent publications.[6-17] This fact coupled with a report on an increase in creep rate for polycarbonate pipe pressurized by $CO_2$ gas[18] led to an interest in how much $T_g$ may be reduced by sorption of $CO_2$; however, as may be easily recognized, the experimental determination of this information is not straightforward. One experiment was reported[6] which merely demonstrated that $CO_2$ sorption can cause significant reduction in $T_g$. Using a special differential thermal analyzer, the glass transition of polycarbonate was measured while heating in the presence of 6.8 atm of $CO_2$ and was found to be 8–9°C lower than when no $CO_2$ was present. The obvious difficulties and limitations of this approach discouraged any further use of it. Since then, Wang, Kramer, and Sachse[19] have reported on another approach in which they estimated the $T_g$ from changes in the mechanical relaxation behavior of polystyrene when exposed to a $CO_2$ en-

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vironment. At 100 atm of $CO_2$, they estimate reductions in $T_g$ of the order of 60°C.

Here we report on a new aproach to the experimental problem of determining the effect of dissolved gas on the $T_g$ of a polymer which is relatively simple and appears to be quite reliable. It is based on heating sealed samples in a differential scanning calorimeter, DCS. The technique was developed during the course of studying $CO_2$ sorption and transport in miscible blends of poly(vinylidene fluoride), $PVF_2$, and poly(methyl methacrylate), PMMA; however, to demonstrate the general use of this procedure, some other polymers of interest to us were also examined and these results are included here. Two related papers dealing with crystallization of polymers induced by $CO_2$ sorption[20] and the change in shape of the sorption isotherm when $T_g$ is depressed to the measurement temperature[21] will appear.

The technique and results described here will be of considerable value for assessing the changes in properties and performance of polymers when exposed to high pressure gases, e.g., membrane modules for gas separations, gas storage systems, etc.

## EXPERIMENTAL PROCEDURE AND MATERIALS

The experimental procedure involved sealing a polymer sample, previously equilibrated with $CO_2$ gas at the desired pressure, into a sample pan followed by thermal analysis in a Perkin-Elmer DSC-2 differential scanning calorimeter equipped with a Thermal Analysis Data Station (TADS). A schematic of the procedure is shown in Figure 1. Relatively thick polymer specimens were used to minimize the fractional loss of $CO_2$ by diffusion prior to the determination of the glass transition temperature. To prepare a suitable sample from film specimens, several disks having the same diameter as the DSC sample pan were punched from the original polymer film and stacked into the pan. An aluminum lid was placed over the polymer, and this assembly was pressed slightly with a metal plunger of the same diameter and heated to 50–100°C above the polymer $T_g$ or 30°C above the $T_m$, whichever was higher, to form a laminate 20–30 mils thick. For film which tended to shrink on heating, a heating pretreatment was used to insure a snug fit of the sample in the pan. The thick sample was encapsulated in the pan by crimping, but not sealing, the rim of the pan. Next the assembly was placed in a stainless steel sorption chamber, immersed in a water bath set at 35°C, where $CO_2$ was introduced to the desired pressure after prior evacuation of air. The sample was exposed to this $CO_2$ environ-
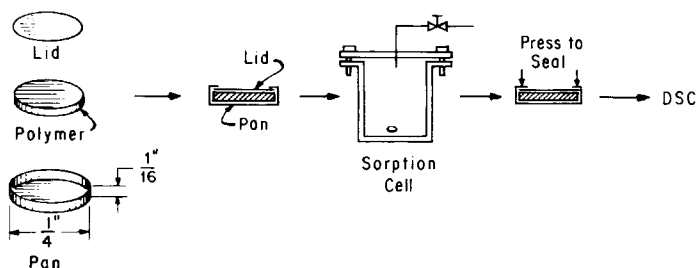


Fig. 1.   Schematic of experimental technique.

ment for an adequate time, usually 1–3 weeks, to insure sorption equilibrium was attained. Following this step, the CO$_2$ pressure was rapidly released, the chamber was opened, and the sample pan assembly was sealed by hammering a metal bar on the crimped pan. The total time for removing the CO$_2$ to sealing of the pan was about 2–3 min. To minimize any desorption of CO$_2$, the pan was placed on ice while transferring it to the DSC holder which had been cooled to −60°C. After the sample was properly placed in the DSC, heating at 20°C/min was commenced.

Most of the materials used were miscible blends of poly(vinylidene fluoride) and poly(methyl methacrylate). The PVF$_2$, Kynar 460N from Pennwalt Co., and the PMMA, Plexiglas V(811) from Rohm and Haas Co., were in pellet form as received by the suppliers and were converted into blend films by extrusion. Pellets of the two pure polymers were mixed in the desired proportions and dried for a few days at 80°C. The mixed pellets were fed to a Brabender extruder, barrel temperature = 210–220°C, to which a 6-in. slit die heated to 190–220°C was attached. The film was taken off using chilled rolls. The extrusion speed, takeup velocity, and die gap were set to obtain film having thicknesses in the range of 3–6 mils. The polystyrene used, Cosden 550, was cast into film from trichloroethylene solutions. The poly(vinyl chloride) (Pentaform 170 from Klockner-Pentaplast of America), polycarbonate (Lexan from General Electric Co.), and poly(ethylene terephthalate) (Kinmar) used were commercial products supplied in film form.

## EXPERIMENTAL RESULTS

Figures 2–5 show typical thermograms obtained by this procedure. Figure 2 contains a series of first heats for PMMA equilibrated with various pressures of CO$_2$. Two characteristics extraneous to the $T_g$ determination require comment. First, there is a small peak or hump prior to the $T_g$ for some of the samples which is caused by sub-$T_g$ enthalpy relaxation resulting from annealing of the polymer below its glass transition as is well known.[22-25] Second, erratic fluctuations are seen above the $T_g$ owing to CO$_2$ desorption from the rubbery polymer.
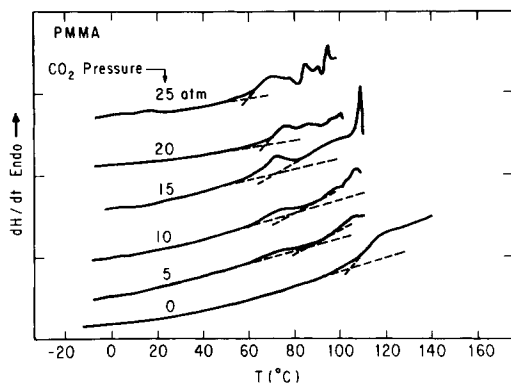


Fig. 2.  DSC scans for PMMA containing CO$_2$ corresponding to the sorption equilibration pressures shown.
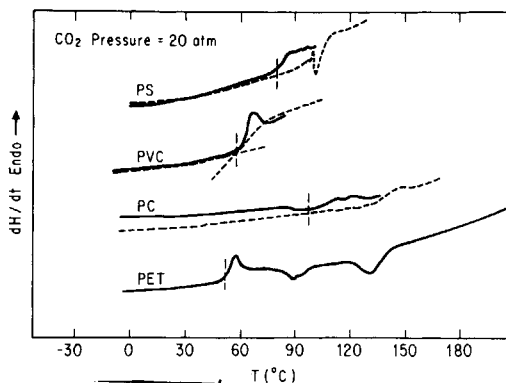
Fig. 3. DSC scans for various polymers after equilibration with $CO_2$ at 20 atm: (—) first scan; (- - -) second scan.
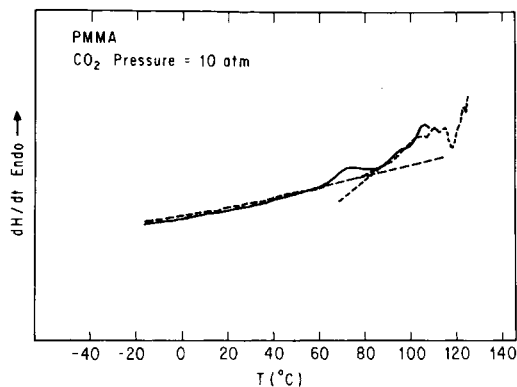


Fig. 4. First and second DSC scans for PMMA after equilibration with $CO_2$ at 10 atm: (—) first scan; (- - -) second scan.
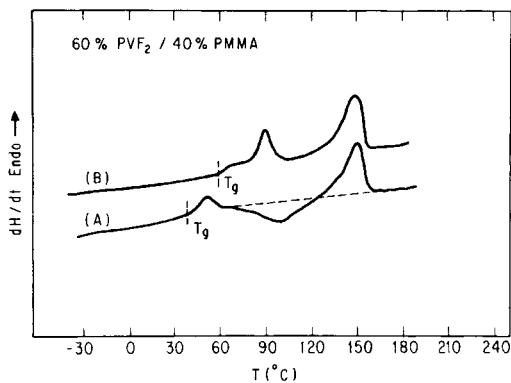


Fig. 5. DSC scans for 60% $PVF_2$ blends. Curve A is prior to $CO_2$ exposure. Curve B was run after sample was exposed to $CO_2$ at 20 atm and then degassed.

Sub-$T_g$ annealing effects naturally accompany the sorption of $CO_2$ into PMMA since the latter was done at 35°C which is lower than the $T_g$ of PMMA even after equilibration with 25 atm of $CO_2$. However, the nature of this relaxation effect is influenced by the $CO_2$ pressure used for reasons that are readily understood. As seen in Figure 2, The sub-$T_g$ relaxation peak increases in intensity and shifts to higher temperatures as the $CO_2$ equilibration pressure is increased. This occurs because of the steady reduction in the $T_g$ of the polymer as more $CO_2$ is dissolved at higher pressures and the nature of the kinetics of the relaxation process which is influenced by the difference in $T_g$ and the annealing temperature $T_a$. A similar effect would result from increasing $T_a$ for a pure polymer of fixed $T_g$.[24,25] At low $CO_2$ pressures, $T_g - T_a$ is large and the extent of relaxation is small. The peak occurs at a low temperature. For higher $CO_2$ pressures, $T_g - T_a$ is smaller and more relaxation occurs giving a larger peak which occurs at a higher temperature. At even higher pressures, the peak becomes smaller and is merged into the glass transition.

The determination of the $T_g$ can be confused by the presence of such relaxation effects. However, this confusion can be eliminated by careful use of a second heat as demonstrated in Figure 3. To do this, it is important on the first heat to go only slightly above $T_g$ followed by immediate quenching. The point is to erase the prior glassy state history without significant desorption of $CO_2$. This is nicely illustrated for PVC in Figure 3 and for PMMA in Figure 4. These polymers have low $CO_2$ diffusion coefficients such that the extent of desorption is minimal and $T_g$'s for the second heat agree well with those determined in the first heat using onset temperature constructions like those shown by the dotted lines in Figure 2. However, for polymers like polystyrene and polycarbonate which have significantly larger $CO_2$ diffusion coefficients, the $T_g$ observed in the second scan is noticeably higher than seen in the first scan owing to the loss of $CO_2$ from the sample during heating.

Rapid $CO_2$ desorption above the glass transition causes the erratic nature of the thermal scans seen in some cases. Loss of gas changes the enthalpy of the specimen, but, more importantly, perhaps is the motion and loss of good thermal contact of the sample this may cause. For specimens heated much beyond the $T_g$, the pan assembly was often found to be inflated by $CO_2$ which was desorbed from the polymer but which could not escape the pan. This fact indicates that the pans were, in fact, well sealed. At even higher temperatures, the pans often ruptured and exuded foamed polymer.

Glass transition temperatures for various $PVF_2$/PMMA blend compositions are listed in Table I as a function of the pressure of $CO_2$ at which these materials were equilibrated prior to sealing in the sample pans. Similar data are shown in Table II for PVC, polystyrene, polycarbonate, and PET at a single $CO_2$ pressure of 20 atm.

For blends containing 60% $PVF_2$, the depression of $T_g$ caused by $CO_2$ is relatively small owing to the low amount of $CO_2$ sorption. However, another factor is operative for this composition, viz., crystallization induced by $CO_2$ sorption which is discussed in detail elsewhere.[20] Figure 5 illustrates this phenomenon. Thermal scan A is for a sample which had no previous $CO_2$ exposure. This scan was obtained after quenching the sample from the melt,

| % PVF$_2$ | CO$_2$ sorption pressure (atm) | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 5 | 10 | 15 | 20 | 25 |
| 0 | 105°C | 88°C | 81°C | 70°C | 67°C | 60°C |
| 20 | 80 | 68 | 57 | 55 | 50 | 44 |
| 40 | 57 | 44 | 37 | 35 | 32 | 24 |
| 60 | 37 | 34 | 30 | 32 | 27 | 26 |

and on reheating it exhibits a $T_g$ at 37°C and a crystallization exotherm is noted above the $T_g$. Prior to heating, this sample was essentially not crystalline since the area of the crystallization exotherm is about the same as the area of the melting endotherm. However, curve B is a scan for the same material after exposure to 20 atm of CO$_2$ for 12 days and then thoroughly degassed. Two melting peaks are observed on the first heat in the DSC having heats of fusion of 1.44 and 4.21 cal/g which sum up to a crystallinity level of 25% based on a value of 22.3 cal/g for the heat of fusion for 100% crystalline PVF$_2$.[26] The amorphous phase in this case has a PVF$_2$ content of 47% by weight owing to the removal of the amount of PVF$_2$ to form this separate crystalline phase. This causes the $T_g$ to increase to 55°C. So in the presence of CO$_2$, there is an *increase* in $T_g$ caused by crystallization and a *decrease* caused by plasticization such that the observed value cannot be simply interpreted. Similar effects occur for the 40% PVF$_2$ blend and for PET; however, the extent of CO$_2$-induced crystallization in these cases is so small that it can be ignored for present purposes.

Measurements on the depression of $T_g$ by CO$_2$ in blends containing more than 60% PVF$_2$ are not reported since the changes in heat capacity are so small in these cases that accurate determination of $T_g$ is not possible.

| | PVC | polystyrene | polycarbonate | PET |
|---|---|---|---|---|
| $T_{g0}$ (°C) | 75 | 100 | 148 | 74[d] |
| $T_g$ (exptl) (°C) | 57 | 78 | 97 | 52 |
| $T_g$ (cald) (°C) | | | | |
|   $z = 1$ | 49.7 | 75.4 | 115.9 | 59.5 |
|   $z = 2$ | 45.6 | 70.6 | 104.8 | 56.3 |
| $C$ [cm$^3$(STP)/cm$^3$][b] | 19.0[8] | 17.6[9] | 29.5[7] | 16.2[e,7] |
| $M_p$ (g/mol) | 62.5 | 104 | 254 | 192 |
| $\Delta C_p$ (cal/g °C)[c] | 0.0693 | 0.0767 | 0.0585 | 0.0812 |
| $\rho$ (g/cm$^3$) | 1.36 | 1.05 | 1.20 | 1.33[e] |

  [a] Parameters used for calculations with eq. (1) are also listed.
  [b] Concentration of CO$_2$ in the polymers shown at 20 atm and 35°C as given by references indicated.
  [c] Average values in Ref. 29.
  [d] Based on quenched samples.
  [e] Based on amorphous phase.

## COMPARISON WITH CALCULATED $T_g$ DEPRESSIONS

The experimentally determined depressions of the glass transition temperature for all the materials considered are plotted in Figure 6 vs. the amount of $CO_2$ sorbed under the conditions of measurement. The latter were obtained from measured $CO_2$ sorption isotherms.[7-9,21] For crystalline samples, the $CO_2$ concentration has been adjusted to reflect that all of this $CO_2$ was present in the amorphous phase. Except for polycarbonate, the data are all described well by a single line.

Chow[27] has developed a useful theoretical relation for estimating the depression of $T_g$ caused by diluents. This relation does not require knowledge of the $T_g$ for the diluent, which in the case of $CO_2$ is not known, as may be seen

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

where

$$\theta = \frac{M_p}{zM_d}\frac{\omega}{1-\omega} \quad \text{and} \quad \beta = \frac{zR}{M_p\Delta C_p}$$

Here $T_{g0}$ is the glass transition temperature for the pure polymer, while $T_g$ is the value when the weight fraction of diluent is $\omega$. The other terms are: $M_d$ is the molecular weight of the diluent, $M_p$ is the molecular weight of the polymer repeat unit, $\Delta C_p$ is the change in specific heat of the polymer at its glass transition, $z$ is a coordination number, and $R$ is the gas constant. All of these parameters are known or can be directly measured except for $z$. Based on comparison with experimental data, Chow[27] suggests using $z = 2$; however, we find that this may not be appropriate for all cases. The various physical parameters for the polymers of interest here are tabulated in Tables II and III. The $\Delta C_p$ values shown were measured by DSC or taken from the literature. Calculated $T_g$'s using $z = 1$ and $z = 2$ are listed in
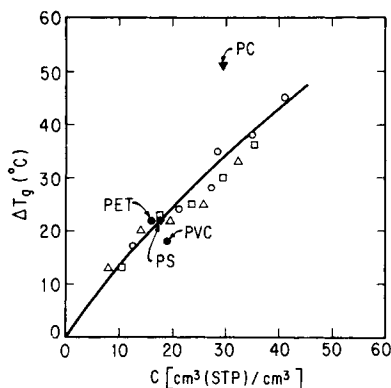


Fig. 6. Depression of the glass transition vs. amount of $CO_2$ sorbed for the materials indicated. $PVF_2$/PMMA: (○) 0/100; (□) 20/80; (△) 40/60; (◯) 60/40.

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TABLE III
Parameters for PVF$_2$/PMMA Blends Used in Calculations with Eq. (1)

|  | PMMA | 20% PVF$_2$/ 80% PMMA | 40% PVF$_2$/ 60% MMA |
|---|---|---|---|
| $M_p$ (g/mol) | 100 | 89.9[a] | 86.1[a,b] |
| $\Delta C_p$ (cal/g °C) | 0.0746 | 0.0664 | 0.0570 |
| $\rho$ (g/cm$^3$) | 1.18 | 1.26 | 1.34 |
| $T_{g0}$ (°C) | 105 | 80 | 57[b] |

[a] Molar average value.

[b] The effect of small amount of CO$_2$ induced crystallinity is neglected.

Table II at 20 atm of CO$_2$ for PVC, polystyrene, polycarbonate, and PET while Figure 7 shows them plotted vs. CO$_2$ concentration for various PVF$_2$/ PMMA blends. The points in Figure 7 are the experimental observations from Table I. A value of $z = 1$ seems to fit the experimental observations better than does $z = 2$ except in the case of polycarbonate. We believe that the polycarbonate is exceptional because the theory arbitrarily bases the lattice on the polymer repeat unit which is very large for polycarbonate. The point here is that the glass transition temperatures predicted by this approach are in relatively good accord with our experimental observations.

## ESTIMATES OF CO$_2$ DESORPTION LOSSES

One obvious difficulty with the technique described here is the possible desorption of CO$_2$ prior to sealing the sample pans. Some estimates for this loss are given here. For short times, the percent loss of sorbed CO$_2$ should be approximated by

$$\% \text{ loss} = \frac{4}{l}\left(\frac{Dt}{\pi}\right)^{1/2} \times 100 \qquad (2)$$

where $l$ is the sample thickness ($\sim$25 mil), $t$ is the length of time to install the sample (generously taken as 3 min), and D is an average diffusion
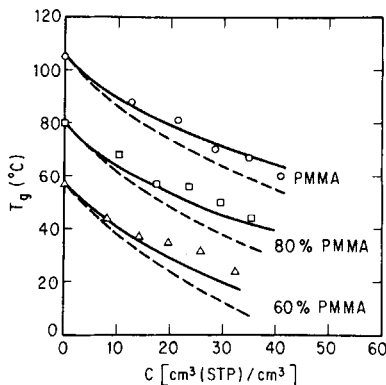


Fig. 7. Comparison of measured and calculated glass transition temperatures for various PVF$_2$/PMMA blends as a function of CO$_2$ content. $z$: (——) 1; (- - -) 2.

TABLE IV
Estimation of $CO_2$ Losses by Desorption

| | PMMA | 40% PVF$_2$/ 60% PMMA | PVC | polystyrene | polycarbonate | PET |
|---|---|---|---|---|---|---|
| $D \times 10^8$ (cm$^2$/s) | 0.10 | 0.36 | 0.18 | 7.5 | 2.6 | 0.16 |
| % loss | 1.5 | 2.8 | 2.0 | 13.1 | 7.6 | 1.9 |

coefficient for $CO_2$ in the polymer—Table IV lists experimental values.[7,8,28] As seen in Table IV, loss of $CO_2$ is only appreciable in the case of polystyrene and polycarbonate. We have assumed that desorption of $CO_2$ once the sample is sealed in the pan is negligible, i.e., the seal is perfect and there is no free space in the pan.

## SUMMARY

The technique described here provides a quick and simple method to estimate the glass transition of the polymer containing dissolved gas. With appropriate care and precautions the results appear to be reliable. Carbon dioxide at modest pressures can cause significant reductions in the glass transition temperature of glassy polymers which have high $CO_2$ solubility. This phenomenon may be quite important in certain applications such as in membrane separation processes where the membrane and other module components are exposed to $CO_2$ or other rather soluble gases at high partial pressures. Some novel consequences of $CO_2$ plasticization of polymers are described in companion papers.[20,21] The theoretical equation developed by Chow provides reasonable estimates of the extent of the $T_g$ reduction caused by gas sorption.

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