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High-Pressure Calorimetric Study of Plasticization of Poly(methyl methacrylate) by Methane, Ethylene, and Carbon Dioxide*

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SYNOPSIS

Glass transition in the system poly(methyl methacrylate)/compressed gas was studied as a function of the gas pressure *p* using a high-pressure Tian–Calvet heat flow calorimeter. Measurements were made on PMMA-CH_4, ;-C_2H_4, and ;-CO_2 at pressures to 200 atm. All three gases plasticize the polymer leading to depression of the glass transition temperature T_g. Trends in the T_g depression were the same as those reported for the solubility of these gases in PMMA; the higher the solubility the larger the depression in T_g. CO_2 was found to be the most effective plasticizer producing a depression of about 40°C at a pressure of about 37 atm. In the low-pressure limit, the pressure coefficient of the glass transition temperature (dT_g/dp) was found to be about -0.2°C atm^{-1} for PMMA-CH_4, the same as that observed for polystyrene-CH_4. For PMMA-C_2H_4, the pressure coefficient was -0.7°C atm^{-1}, which is lower than the value of -0.9°C atm^{-1} observed for PS-C_2H_4. The pressure coefficient for PMMA-CO_2 was found to be about -1.2°C atm^{-1}, which is larger than the value of -0.9°C atm^{-1} observed for PS-CO_2. © 1996 John Wiley & Sons, Inc.

Keywords: poly(methyl methacrylate) • compressed gases • glass transition • plasticization

INTRODUCTION

The solubilities and rates of diffusion of high-pressure gases and supercritical fluids in polymers have been studied for a variety of reasons. These stem from environmental and industrial impetus, ranging from the degassing of chemical species in manufactured plastics[1,2] and foams[3] to the characterization of polymer membranes for gas separations[4] or gas barrier properties for packaging materials.[5] Polymers can also be modified through extraction[1] or impregnation by supercritical fluids.[6] Polymer morphology[7-9] and phase behavior[10,11] can be deliberately changed by high-pressure gases, and there are now several reports on conducting polymerization in supercritical fluids.[12-14] A common aspect among most of these applications is that the polymer is plasticized by the high-pressure gas, plasticization being a desirable or an undesirable feature depending on the application. As a result, there is great interest in understanding the interactions between these two vastly different phases and in developing theoretical models for predicting the plasticization behavior in polymer/gas systems.[8] In spite of this, there are reported in the literature only a few experimental studies on the gas-induced plasticization of polymers.

Recently, we developed a high-pressure calorimetric technique for measuring directly the changes in the glass transition temperature T_g of a polymer while in equilibrium with a high-pressure gas. This technique was applied to polystyrene (PS) and a detailed study on the changes in T_g of PS induced by CH_4, C_2H_4, and CO_2 at various gas pressures was reported.[15] It was found that at moderate pressures, approximately 60 atm, gases like C_2H_4 and CO_2 could depress the T_g by about 60°C and that the depression in T_g was largely dependent on the amount of gas

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dissolved in the polymer. In this article, we report a similar calorimetric study on the plasticization of PMMA by CH_4, C_2H_4, and CO_2. During the course of our investigation, a few studies on T_g measurements in PMMA/CO_2 system by noncalorimetric techniques appeared in the literature. Results from these studies are also summarized.

EXPERIMENTAL

Methane, ethylene, and carbon dioxide with specified minimum purities of 99.9% were supplied by Matheson. PMMA used was a clean commercial sample (i.e., containing no additives) in the form of 2×3 mm cylindrical pellets with an $M_w \approx 200{,}000$ and $M_w/M_n \approx 2.0$. The polymer sample was generously provided by Rohm and Haas, USA.

A Tian–Calvet heat flow calorimeter (Setaram, model BT) was modified to allow for *in situ* measurements of the glass transition in the polymer/gas systems at gas pressures p up to 400 atm. Calorimeric cells, made from 316SS, with a pressure rating of 100 atm were purchased from Setaram. Higher pressure cells, rated to 700 atm, with the same dimensions as the Setaram cells were machined from 410SS. Initially, an O-ring seal design similar to the one used by Setaram was used. In this design, a nut is torqued into the body of the cell that houses the O-ring just under the female threads. The nut provides a protruded lip that serves as the seat for the O-ring. As the nut is torqued down, the pressure seal is made by the compressed O-ring. However, this seal design did not always work, especially at higher pressures. As the nut is torqued, the O-ring tends to rotate in its housing, leading, ultimately, to scoring of the ring or the cell body and, thus, failure of the seal. To overcome this problem, a new seal was designed, and is shown in Figure 1. The split design allows the nut to turn freely, imparting the torque to the O-ring without causing it to rotate. The O-ring is compressed leak-tight between the seat and the housing without using any excessive torque on the nut. This design provided the pressure seal every time at pressures to 700 atm, and the same O-ring could be used several times. Both Al and Cu O-rings were used in the present work.

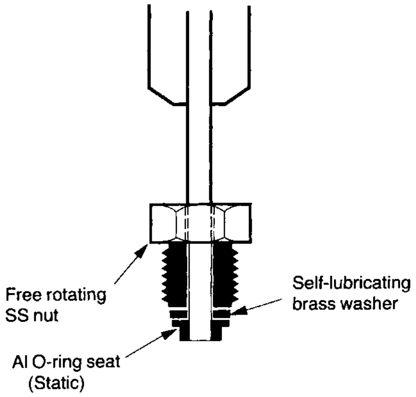

Figure 1. High-pressure seal design for the calorimetric cells used in this work.

A detailed description of the apparatus and the procedure is reported elsewhere.[15] The polymer samples were used in pellet form for all calorimetric measurements. Previous studies have shown our experimental set-up and the procedure developed to be superior to other calorimetric techniques for establishing the $T_g - p$ profiles to rather high pressures.[15] Briefly, about 2 g of polymer was placed in the calorimeter's sample cell, both sample and reference sides pressurized with the gas, and the calorimeter scanned at 7 or 10°C h^{-1} from a temperature about 2°C above the critical temperature of the gas to about 20°C above the T_g of the polymer/gas system. During the temperature scan, the pressure in the system remained almost constant as the pressure manifold contained a 500-mL buffer volume to dampen out any pressure fluctuations. Furthermore, the temperature of the manifold was held constant at a temperature slightly above the critical temperature of the gas. This ensured that during the scan no condensed phase of the gas was encountered anywhere in the entire apparatus.

A rather sluggish transition was observed during the first heating scan. This was primarily because the plasticization started at the surface of the pellet and progressed inwards as the temperature was raised. At the end of the first scan, the entire pellet was fully plasticized and equilibrated with the gas. The system was then cooled back at almost the same rate as the heating rate and then scanned again. A much sharper glass transition was observed during the second scan, and the T_g of the system was taken as the midpoint of the transition.

RESULTS AND DISCUSSION

The glass transition temperatures of PMMA with CH_4, C_2H_4, and CO_2 are given in Table I. The results are plotted in Figure 2 as ΔT_g against the gas pressure where $\Delta T_g = T_g^o - T_g$, T_g^o and T_g being the glass transition temperatures of the pure polymer and the polymer/gas mixture, respectively. The gas affects

Table I. T_g Values for the PMMA–Gas Systems at Various Gas Pressures

PMMA-CH_4		PMMA-C_2H_4		PMMA-CO_2	
p (atm)	T_g (°C)	p (atm)	T_g (°C)	p (atm)	T_g (°C)
0.0	90.7	0.0	90.7	0.0	90.7
11.4	88.0	11.0	80.2	8.8	80.5
24.5	87.2	21.8	74.7	18.2	69.2
48.4	84.3	21.8	73.7	22.3	63.7
97.0	80.8	36.3	66.8	29.5	59.7
152	75.5	54.5	57.3	37.2	50.8
218	73.5				

the T_g of the polymer in two ways: the dissolved gas tends to lower the T_g and the hydrostatic pressure exerted by the gas tends to raise the T_g. For PMMA,[16] the change in T_g due to hydrostatic pressure is 0.02°C atm^{-1}. At low pressures, correction for the hydrostatic effect is quite small. However, at pressures higher than 50 atm this correction becomes significant. Thus, the actual depression in T_g due to CH_4 is slightly larger than that shown in Figure 2 and reported in Table I.

The results for the PMMA/CO_2 system are compared with the literature values[17-19] in Figure 3; no literature data are available for the other systems. The DSC measurements[17] were made by saturating the polymer sample with CO_2, transferring it to the DSC cell, and then scanning it under ambient conditions. Chiou et al.[17] took the onset of the glass transition step as T_g. For comparison purposes, their results were recalculated by taking T_g as the midpoint of the transition, as done with the present measurements. The present results are in reasonable agreement with those obtained by DSC[17] and creep compliance[18,19] measurements.

The results shown in Figure 2 are very similar to those observed for PS with the same gases.[15] For both polymers PS and PMMA with CH_4, (dT_g/dp) values observed in the low-pressure limit are identical, −0.2°C atm^{-1}. With C_2H_4, (dT_g/dp) is −0.9°C atm^{-1} for PS and −0.7°C atm^{-1} for PMMA. For PS/CO_2, (dT_g/dp) is −0.9°C atm^{-1}, the same as that observed with C_2H_4. However, CO_2 induces a much stronger plasticization effect in PMMA with (dT_g/dp) of −1.2°C atm^{-1}. The trends in T_g depression observed for PS and PMMA are the same as those observed for the solubility of these gases in the two polymers.[20,21] This is in accordance with the statistical thermodynamic model of Chow[22] and with previous observations.[15,17,23] The increased solubility of CO_2 in PMMA over that in PS has been attributed to the preferred interactions of the gas with the ester moieties in PMMA.[24,25]

Recently, an interesting phenomenon of plasticization has been reported[8,18,19] for polymer/gas systems in which the gas dissolves to appreciable levels and the solubility shows a complex dependence on temperature and pressure. This occurs for systems, such as PS/CO_2 and PMMA/CO_2, where the gas is easily condensible and the critical temperature T_c of the gas, 31.1°C for CO_2, is not far removed from the T_g of the polymer. For such systems, it has been shown by creep compliance measurements[18,19] that up to four types of plasticization behavior can be observed. Of these, two types of plasticization are relevant for the present case. The first type is as shown in Figure 3, where the polymer is in the glassy state below the $T_g - p$ curve. Now, if at a constant pressure the system is cooled to lower temperatures then so much gas dissolves in the polymer that the polymer goes though a glass → liquid transition on *cooling*. The latter transition has been termed retrograde vitrification by Condo et al.[26] Thus, at a given pressure below the critical pressure of the gas, 72.8 atm for CO_2, two T_gs have been observed in creep compliance measurements. Accordingly, in a calorimetric heating scan, two transitions would be expected to be observed: an exothermic event for the liquid → glass transition and then an endothermic step for the glass → liquid transition.

In the present work, as well as in our previous work,[15] care was taken while scanning the systems through the retrograde regions. In some experiments, an exothermic step was observed but it could

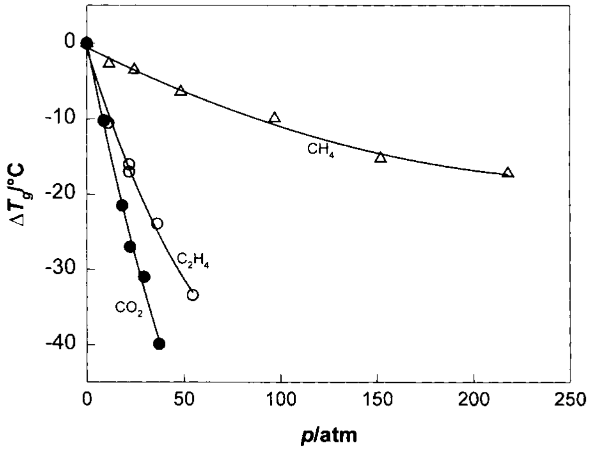

Figure 2. Depression in the glass temperature of PMMA due to sorbed gas plotted against the gas pressure. Solid curves are drawn to aid the eye.

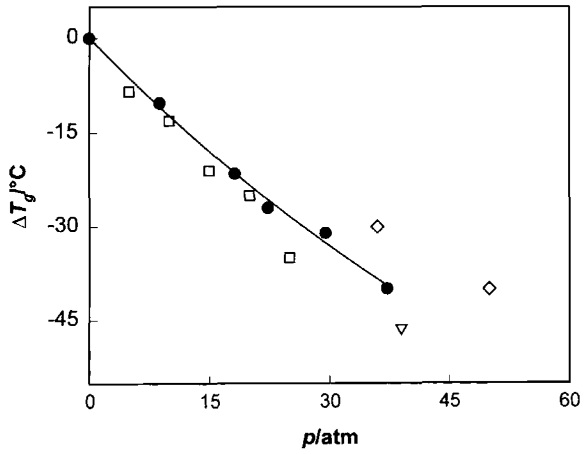

Figure 3. Depression in the glass temperature of PMMA due to sorbed CO_2 plotted against the gas pressure. (●) This work; (□) DSC results of Chiou et al.[17]; creep compliance results by Wissinger and Paulaitis[18] (▽) and by Condo and Johnston[19] (◇).

not be established unambiguously. This is perhaps due to the limitations of our calorimeter. The lowest temperature from which a scan could be started was about 2°C above the T_c of the gas so that no condensed phase of the gas was encountered during the scan. Furthermore, the calorimeter used had a large time constant and allowed only slow scan rates of 7-10°C h^{-1}. A high-pressure DSC is now being set up with the intention to explore the retrograde region with better resolution.

The plasticization of polymers by high-pressure gases has been inferred from a variety of techniques including NMR,[27] dielectric relaxation,[28,29] gas solubility and permeation,[30] DSC,[17,23] high-pressure calorimetry,[15] creep compliance,[18] dynamic mechanical response,[31,32] and X-ray diffraction.[33] Depending on the probe being used, the term plasticization refers either to the sub-T_g intrachain localized motions activated at T_γ or the large scale main chain motions activated at T_g. Permeability is defined as the product of diffusion and solubility coefficients. In the characterization of gas separation membranes, an upturn in permeability with pressure is usually taken as the onset of plasticization.[30,34] The plasticization effect observed during permeability measurements is either due to an increase in diffusivity resulting from an increase in the intrachain motions[35] or due to the increased solubility leading to the glass → rubber transition.[30,34] However, if an upturn in permeability is not observed, it does not mean that the polymer has not been plasticized under the T, p conditions of measurement. In fact, the polymer is always plasticized as soon as a foreign component enters its matrix, e.g. inert gases like N_2 and Ar have been shown to induce plasticization.[27,28] Once plasticized, the gas separation membranes suffer a drastic loss in performance, and thus an understanding of the plasticization phenomenon in such systems is of great practical interest.[36]

For PMMA, it has been reported[34] from permeability measurements that CO_2 shows plasticized transport behavior even at pressures below 1 atm whereas C_2H_4 does not show such a behavior at pressures up to 16 atm. This conclusion is based on the observation that the permeability of CO_2 shows anomalous behavior, that is, the permeability increases with pressure. On the other hand, the permeability of C_2H_4 first drops sharply[34] by about 95% as the pressure increases from 1 atm to 3 atm, after which the permeability decreases slightly with pressure in accordance with the dual mode theory.[37] The anomalous behavior exhibited by CO_2 has been explained as due to the activation of the sub-T_g segmental motion induced by the sorbed gas.[35] It has also been suggested[34] that the sorbed CO_2 disrupts the ester–ester interactions in PMMA, thereby providing additional diffusional pathways for CO_2. The solubility[20] of C_2H_4 in PMMA is about half that of CO_2. It has been shown[15,17] that plasticization depends mainly on the amount of penetrant in the polymer and thus C_2H_4 would be expected to plasticize PMMA as effectively as CO_2, albeit at slightly higher pressures. This indeed is observed in Figure 2. So, if CO_2 starts to plasticize PMMA at subatmospheric pressures then C_2H_4 would be expected to do the same at slightly higher pressures. But this is not observed in the permeability measurements. In this context, both CO_2 and C_2H_4 show anomalous transport behaviors. As noted above, permeability measurements give a rather complex picture of the plasticization effects. Clearly, the best way to account for these effects would be to determine directly the $T_\gamma - p$ behavior, in addition to the $T_g - p$ profiles reported here.

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