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A new study of glass transition of polymers by high pressure DSC

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The glass transition temperatures of polycarbonate (PC) were measured by means of high pressure DSC in He, N_2, and CO_2 atmospheres. It was found that the glass transition temperature (T_g) of PC was independent in He with pressure up to 70 atm, whereas the T_g of PC shifted by 6° towards the lower temperature end in N_2 atmosphere when the pressure was 70 atm. The depression in T_g by high pressure CO_2 was found to be even more remarkable due to a stronger plasticization effect. It was also found that the glass transition for PC/CO_2 system exhibited an endothermic peak. It was believed that the endothermic behaviour resulted from the excessive desorption of the absorbed gas at T_g due to the increase in chain mobility. This conclusion was further confirmed by examining the glass transition behaviour of poly(vinyl benzoate) in CO_2 at 2 atm. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: glass transition temperatures; high pressure DSC)

INTRODUCTION

It has been reported that the glass transition temperature (T_g) of polymers can be affected by the gas molecules absorbed in the polymer matrix, and the depression in T_g by absorbed gas is explained by the plasticization effect[1–3]. Kamiya *et al.* reported, based on their study of the solubility isotherms for CO_2 in poly(vinyl benzoate) (PVB), that the glass transition temperature of PVB was depressed from 65° to 45°C at CO_2 pressure of 17 atm, to 35°C at CO_2 pressure of 26 atm, and to 25°C at CO_2 pressure of 34 atm, respectively[3]. However, the direct measurement of T_g at a specific CO_2 pressure was not offered. Recently, Handa *et al.* reported the effect of pressure on the glass transition temperatures by a high pressure calorimeter, which is, however, not a highly sensitive DSC apparatus that enables one to examine subtle chain motions and thermal behaviour of polymers[1]. The method of using DSC for evaluating the effect of absorbed gas molecules on the glass transition temperature of polymers was described by Chiou *et al.* in which the polymer specimen was first enclosed in a high pressure CO_2 chamber for a period of time to reach the sorption equilibrium, and then the specimen was taken out of the chamber for DSC measurement after the pressure was released[2]. The shortcoming of such an operation is that the number of gas molecules in the polymer specimen can never be accurately known since the desorption occurs soon after the specimen is taken out of the pressure chamber. Secondly, additional noise could be shown in the DSC traces because the pressure cannot be held constant during the DSC measurement, since desorption will be continuously taking place during scanning. However, for the consideration of both application and academic interest it is necessary to determine the glass transition temperature of polymer/small molecule systems and to understand its mechanism[1,4].

In this study we offer the results of DSC measurements for polymer gas systems with an on-line high pressure DSC cell mounted on the DSC apparatus so that the pressure could be monitored and maintained constant during the measurement.

EXPERIMENTAL

The DSC measurements were done with a TA 2910 differential scanning calorimeter. A special accessory—a high pressure DSC cell—was ordered from TA Instruments Inc., Delaware, USA, which enables one to run DSC measurements under different gases at pressures up to 75 atm. The polycarbonate ($M_n = 120\,000$) was ordered from Dow Chemical Co., USA. The gases used in this study are high purity ultra-dry He, N_2, and CO_2 purchased from Hong Kong Town Gas Company.

The polycarbonate pellets were first dissolved in chloroform and then precipitated in methanol. The PC precipitate was then dried in a vacuum oven for one week to remove the volatile residuals, and then ground into a fine powder. The fine PC powder was used in order to shorten the time required for sorption and desorption equilibrium, because the gas diffusion coefficient is inversely proportional to the square of the sample thickness.

To start the pressure DSC measurement the PC powder was enclosed in the sample pan and a small hole was made on the top of the pan to allow gas into contact with the polymer enclosed in the sample pan during the measurement. The sample was first heated to 200°C to eliminate the thermal history. The temperature was controlled below 200°C in order to prevent possible sintering from taking place at higher temperatures under pressure, so that sorption and desorption equilibrium can be kept in a fast fashion. However, due to the strong plasticization effect, we still found sintering had occurred at high CO_2 pressures. Consequently, longer sorption equilibrium time was given for such measurements. The sorption equilibrium time was set to 12 h for N_2, 12 h for CO_2, and 10 h for He before

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the DSC measurement at each pressure. The DSC measurements were carried out at the heating rate of 10°C min^{-1}.

The advantage of using on-line high pressure DSC cell is that the high pressure chamber will keep the pressure of the working gas constant during the entire DSC measurement. Therefore, we are able to monitor the *in situ* glass transition behaviour at a given pressure.

RESULTS AND DISCUSSION

Figure 1 shows the DSC traces for PC at different pressures in N_2 atmosphere. The pressures indicated on the plot are the gauge pressure of the pressure DSC cell during the measurement. As the pressure in the DSC cell varied from 0 to 70 atm, the glass transition temperature of PC shifted from 156°C to 149°C, which is clearly indicated in *Figure 1* and listed in *Table 1*. It is also seen, in *Figure 1*, that the T_g of PC at N_2 pressure of 70 atm with the equilibrium time of 12 h and of 48 h remains unchanged, suggesting that the sorption equilibrium time of 12 h for N_2 in PC powders is sufficient. The depression in T_g for PC in N_2 atmosphere should be understood as a plasticization effect[1–3].

Figure 2 shows the DSC traces for PC at different pressures in He atmosphere. A noticeable difference from *Figure 1* is that the T_g of PC remains invariant as the pressure of He changes from 10 to 70 atm. A close examination of *Table 1* should lead one to realize that there seems to be a trend in T_g of first decreasing and then increasing. Nevertheless, the variation is within 2–3°C, so it can be taken as a constant T_g. However, it should be pointed out that another effect of high pressure gas on T_g is that the hydrostatic pressure tends to raise the T_g. Therefore, the invariant T_g of the PC/He system implies that the plasticization effect and hydrostatic pressure effect are cancelled out by each other.

Figure 3 shows the DSC traces for PC at different pressures in CO_2 atmosphere. It can be seen that a much stronger plasticization effect was observed in which a depression in T_g by about 20°C was found when CO_2 pressure was increased to 10 atm. More interestingly it was found that instead of being a step function, as observed in *Figures 1 and 2,* the T_g transition at 10 atm for the PC/CO_2 system becomes an endothermic peak. The endothermic peak area under the dashed line in *Figure 3* yields an enthalpy value of 5.40 J g^{-1}.

Our explanation of this phenomenon is that as the

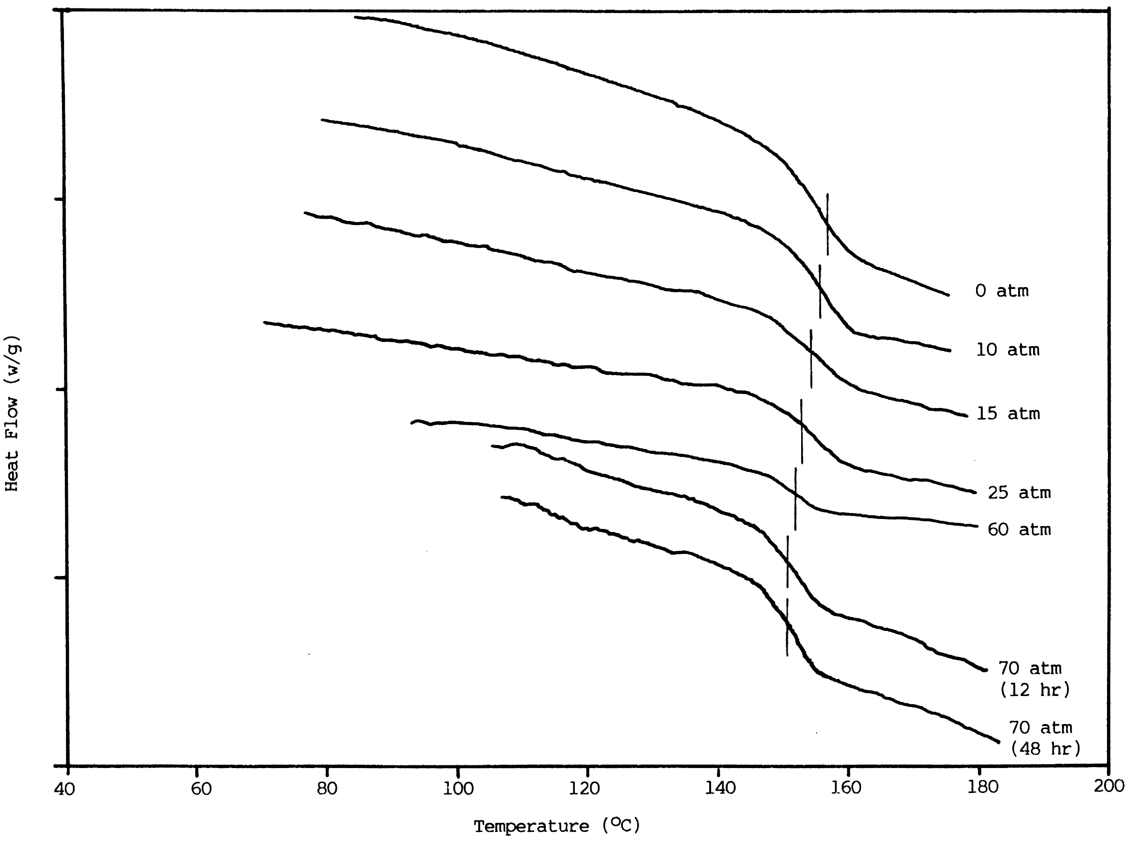

Figure 1 The dependence of glass transition temperature of polycarbonate on the pressure of N_2. (The pressures indicated in the figure are the gauge pressures of the high pressure DSC chamber)

Table 1 The glass transition temperatures of polycarbonate at different pressures of N_2, He and CO_2

N_2 pressure (atm)	0	10	15	25	40	60	70	—
T_g (°C)	157	156	156	153	153	152	151	—
He pressure (atm)	0	10	20	30	40	50	60	70
T_g (°C)	157	153	155	154	155	155	155	157
CO_2 pressure (atm)	0	1	2	5	10	—	—	—
T_g (°C)	156	153	158	146	138	—	—	—

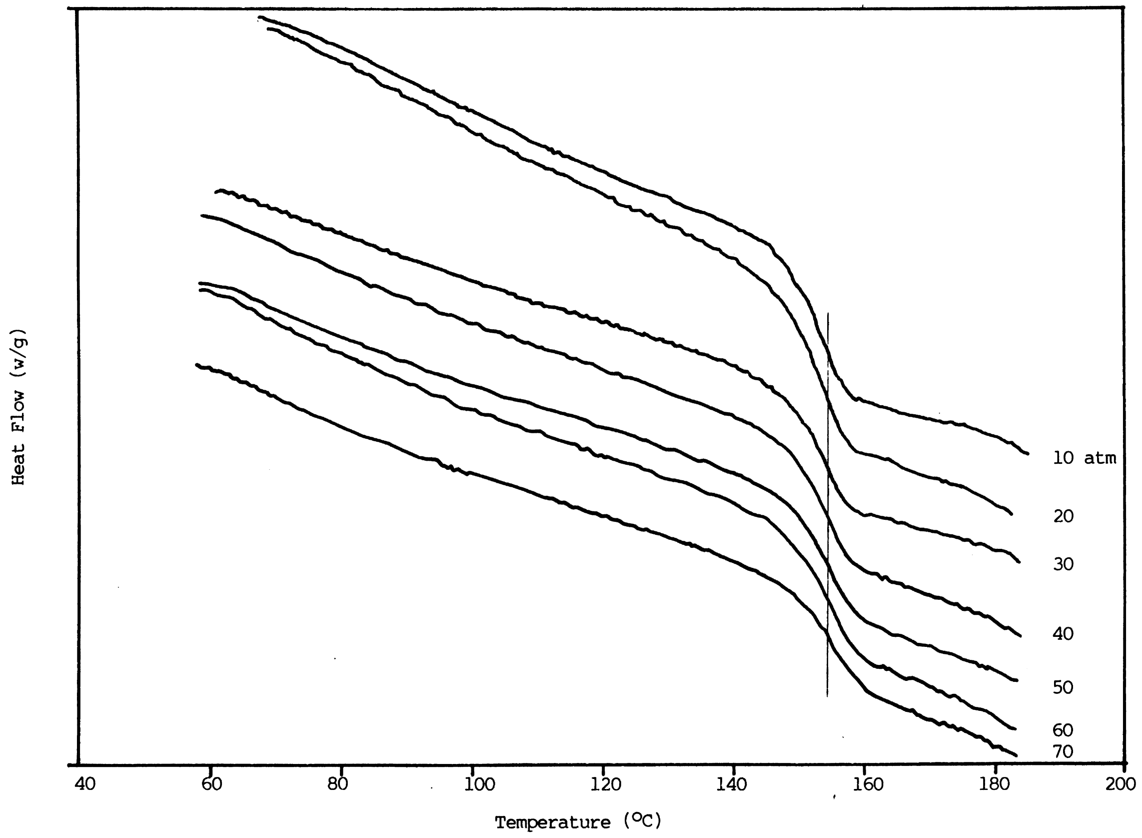

Figure 2 The dependence of glass transition temperature of polycarbonate on the pressures of He. (The pressures indicated in the figure are the gauge pressures of the high pressure DSC chamber)

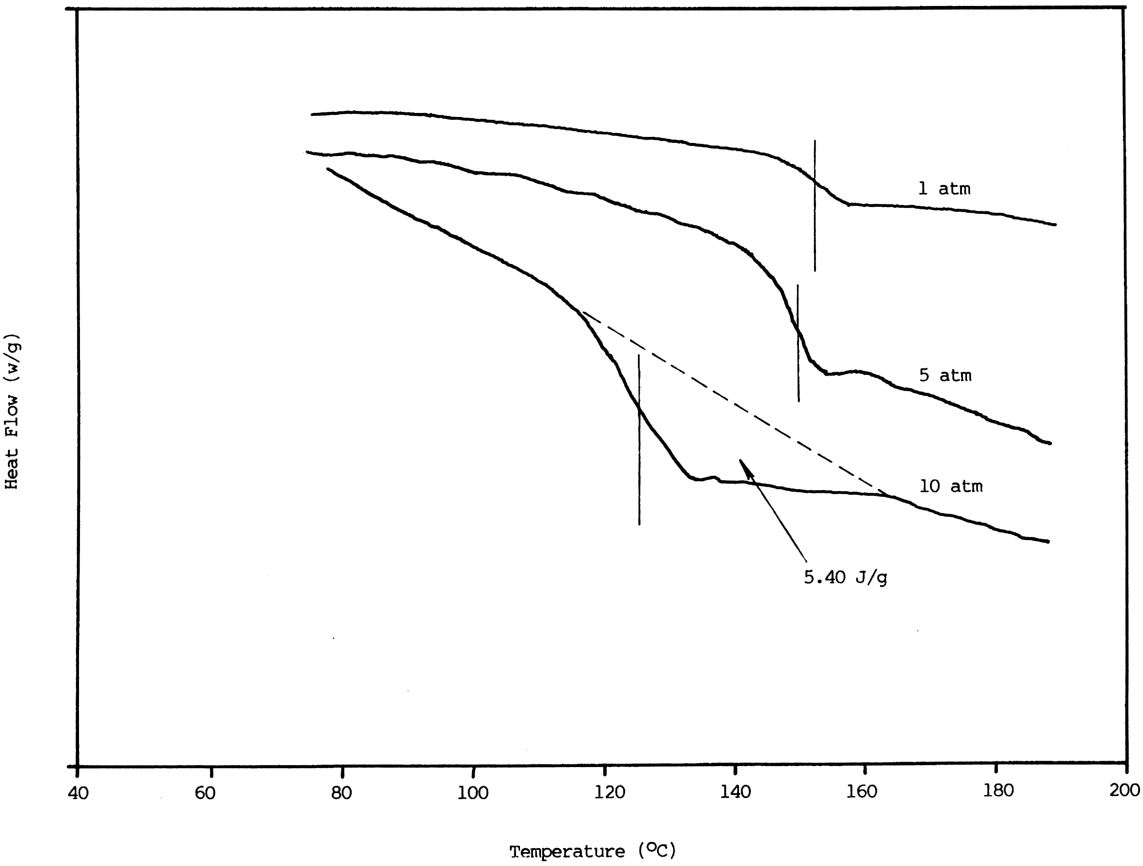

Figure 3 The dependence of glass transition temperature of polycarbonate on the pressures of CO_2. (The pressures indicated in the figure are the gauge pressures of the high pressure DSC chamber)

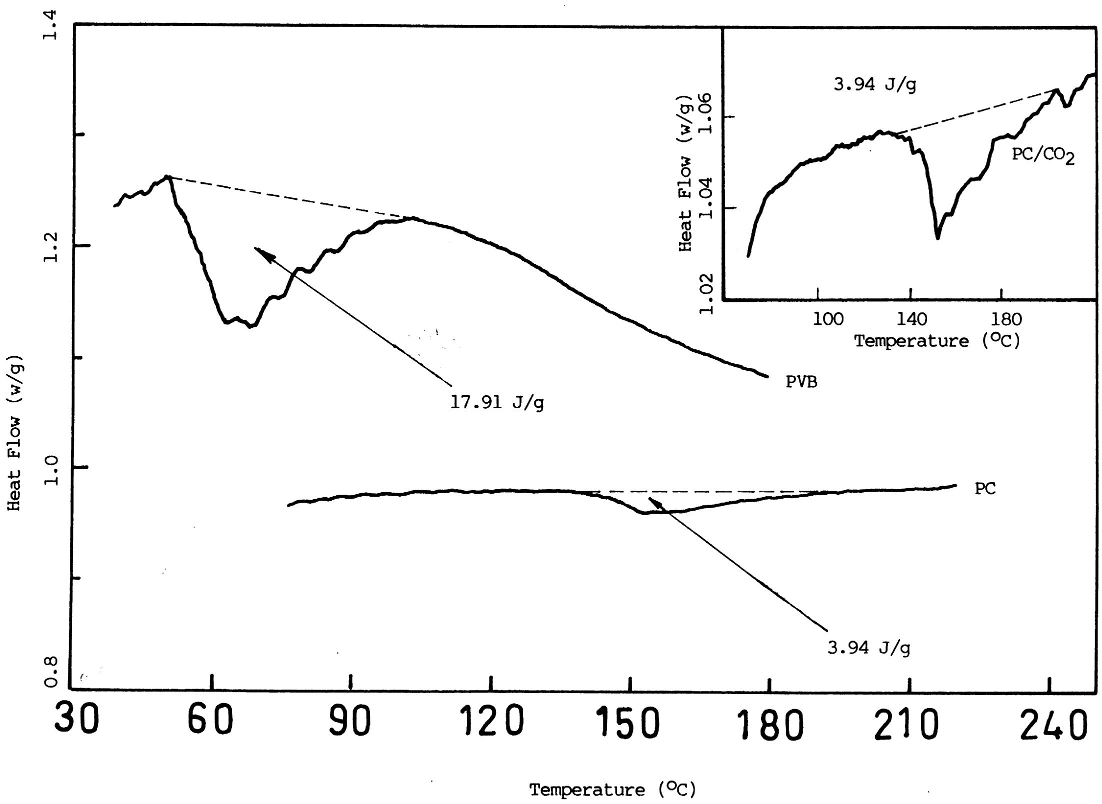

Figure 4 The DSC curves of poly(vinyl benzoate) and polycarbonate in CO_2 at 2 atm

specimen in the pressure DSC chamber is heated from low to high temperature the polymer specimen will continuously release gas since the desorption process is endothermic. However, at the glass-to-rubber transition temperature the desorption rate may suddenly be accelerated since the chain mobility of the polymer suddenly becomes higher. This phenomenon can be best illustrated by the shaken champagne bottle at the ceremony of car racing. Because of the sudden release of an excessive amount of gas molecules an endothermic peak is observed.

Refering to *Figure 3* one finds that the glass transition of the PC/CO_2 system becomes a noticeable endothermic peak at relatively higher pressure, whereas at lower pressures it is not too obvious. This is because the amount of gas absorbed in polymers is greater at higher pressures[5,6]. Consequently, at higher pressures the relatively larger amount of gas would be desorbed at T_g transition and a significant heat effect can be detected by DSC. For PC/N_2 and PC/He systems, cf. *Figures 1 and 2*, the shape of step function in all DSC curves was preserved even to a pressure as high as 70 atm, which can be reasoned as the solubility of N_2 in polymers being much lower than that of CO_2 and the solubility of He being even lower[5]. Therefore, for PC/N_2 and PC/He systems the main heat effect at glass transition is accounted for by the higher chain mobility.

In order to verify the above argument we chose poly(vinyl benzoate) PVB to study its glass transition behaviour in the CO_2 environment. The reason for choosing PVB is that it has a T_g of about 65°C[3]. The gas solubility in polymers is known to be a strong function of temperature, being lower at elevated temperatures[6]. Therefore, it is expected that the heat effect of the desorption endothermic peak, which happens at the glass transition, would be stronger for the PVB/CO_2 system.

Figure 4 shows a the DSC curve for PVB/CO_2 in comparison with the DSC trace of PC/CO_2 at 2 atm. It clearly shows that the glass transition exhibits a stronger endothermic peak with an enthalpy value of 17.91 J g^{-1}. In the top right corner of *Figure 4* a magnified glass transition peak of PC/CO_2 is shown, which indicates that PC/CO_2 also endorses an endothermic peak with the total area yielding an enthalpy value of 3.94 J g^{-1}.

CONCLUSIONS

The effect of absorbed gas on the glass transition temperature was studied. It is believed that the endothermic behaviour of the glass transition of the PC/CO_2 and PVB/CO_2 systems is due to the heat effect concurrent to the desorption of CO_2 out of the polymer matrix owing to the sudden enhancement in chain mobility at the onset of the glass transition.

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