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Notes

CO_2-Assisted Melting of Semicrystalline Polymers[†]

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Introduction

It is well-known by now that certain compressed gases above their critical temperatures can dissolve to considerable extents in polymers[1] causing depression of glass transition, T_g, and crystallization, T_c, temperatures. The gas-induced crystallization has been studied in a few polymers such as poly(vinylidene fluoride),[2] poly(ethylene terephthalate) (PET),[2−4] polycarbonate,[5] poly(ether ether ketone) (PEEK),[6] poly(*p*-phenylene sulfide) (PPS),[7] methyl-substituted PEEK (MePEEK),[8] and syndiotactic polystyrene (sPS).[9] Semicrystalline morphologies obtained in the presence of compressed gases may be different from those obtained by annealing under ambient pressure. For example, morphologies exhibiting rather sharp melting peaks and with increased melting temperatures were obtained when MePEEK was thermally annealed in the presence of supercritical mixtures of CO_2 with methanol or dichloromethane.[8] The activity of a compressed gas above its critical temperature can be changed continuously by simply changing its pressure. Such fluids provide a highly tunable technique to affect changes in polymer morphology by plasticizing the polymer matrix and by changing its crystallization kinetics and crystalline structure.[8,9] One of the advantages of using compressed gases is that, unlike liquid solvents, they can be easily removed by depressurizing the system once the desired morphology change has been brought about.

Whereas there have been numerous investigations of CO_2-induced depression in T_g of polymers,[10−12] the corresponding investigations for T_c have been reported only for PPS[7] and syndiotactic polystyrene (sPS).[9] In the latter study, it was shown that T_c decreased linearly with an increase in CO_2 pressure, in a fashion similar to the change in T_g with pressure. Furthermore, CO_2 was also found to crystallize glassy sPS into its various crystalline forms and also to induce solid−solid transitions between the various crystalline forms.[9] In particular, CO_2 was found to transform α-sPS into its β form at a temperature at which the α form was initially crystallized under ambient pressure. Such an apparent solid−solid transition below the melting temperature of the α form could be conjectured only if the α crystals somehow underwent melting at a depressed temperature and then transformed to the β form. This conjecture led us to undertake the present investigation on the effect of CO_2 on the melting behavior of semicrystalline polymers.

Experimental Section

The sPS sample used was the same as described before.[9] PET was purchased from Aldrich and had a specified M_w = 180 000. The sPS and PET samples were compressed at 300 °C and then quenched into ice water to obtain glassy films. The glass transition temperatures of completely amorphous sPS and PET were 97 and 79 °C, respectively. Semicrystalline films of the polymers were obtained by cooling the mold slowly from 300 °C. For sPS, semicrystalline films were also obtained by annealing the amorphous films at 240 °C for 1 h. The melting temperatures of sPS and PET were 277 and 257 °C, respectively. The crystallinities of the films, estimated by DSC and using 53.2 and 140 J g^{-1} for the heat of fusion of 100% crystalline sPS[13] and PET,[14] respectively, were found to be 38% for sPS and 35% for PET.

The melting behavior and glass transition temperatures of the polymer−CO_2 systems were characterized using Setaram DSC121 equipped with high-pressure vessels rated to 100 atm. The experimental details for conducting high-pressure measurements with the DSC121 are given elesewhere.[15] Briefly, after installing about a 50 mg sample, the system was evacuated for 1 h to degas the polymer film. Subsequently, both the reference and sample sides were pressurized with CO_2 to the desired value and held at 35 °C for 2 h for the semicrystalline films and 1 h for the amorphous films, respectively, to establish polymer−gas equilibrium. The samples were then scanned at 5 °C/min while still under the gas pressure.

Results and Discussion

Figure 1 shows the melting behavior of the α form of sPS. The first peak is associated with the melting and reorganization of the crystals into more perfect form, followed immediately by the main melting peak. In the presence of CO_2, both peaks are shifted to lower temperatures; the onset temperature of the first melting peak is, in fact, below 240 °C. It was previously[9] found that the α form of sPS, obtained by annealing the glassy sample at 240 °C, transformed into the β form at the same temperature in the presence of compressed CO_2. A possible reason for this transition was conjectured to be that the α form crystals melt in the presence of CO_2, allowing, thereby, the recrystallization of the sample into the β form. The results in Figure 1 clearly demonstrate the lowering of the melting temperature in the presence of dissolved CO_2.

In order to further investigate the effect of CO_2 on the melting behavior of sPS, samples in the α form but with a single melting peak were prepared by crystallizing sPS from the melt. Figure 2 shows the DSC scans on these samples under various conditions. The CO_2-induced shift of the melting peak is clearly seen. However, when CO_2 is replaced with compressed N_2 at almost the same pressure, there is no change in the melting behavior of sPS. Evidently, the melting temperature depression depends on the solubility of the gas in the polymer; the solubility of N_2 being negligible at the elevated temperatures under consideration. The melting point, T_m, expressed as the peak temperature,

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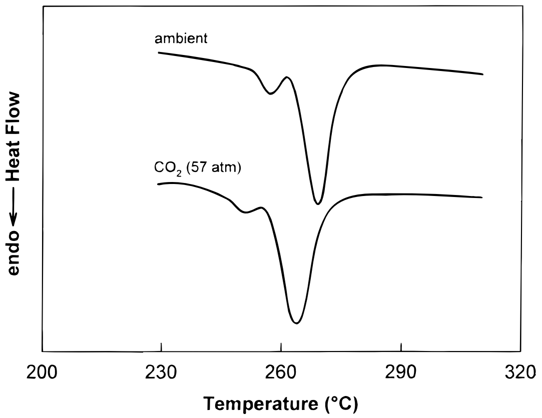

Figure 1. DSC scans under different gas pressures on sPS crystallized from the glassy state.

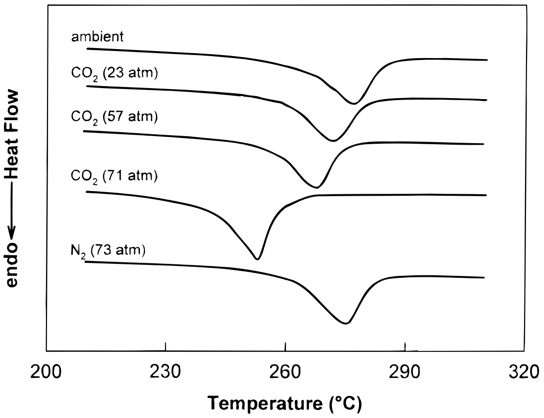

Figure 2. DSC scans under various gas pressures on sPS crystallized from the melt state.

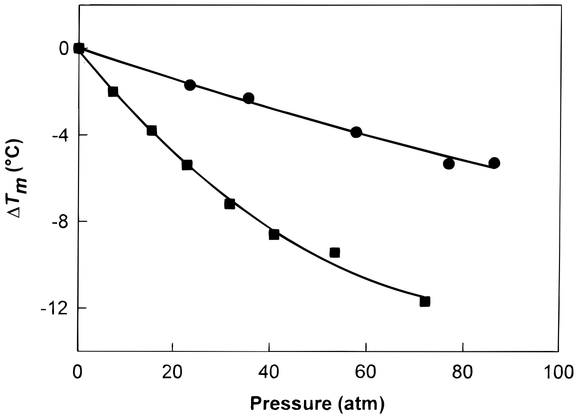

Figure 3. Depression in the melting temperatures of melt-crystallized sPS (■) and PET (●) as a function of CO$_2$ pressure.

is shown in Figure 3, as a function of CO$_2$ pressure, p. It shows a rapid decrease initially and then tends to level off at higher pressures. This leveling off effect has also been observed in the T_g–p behavior[10,12] and has been attributed to the antiplasticization effect caused by the hydrostatic pressure exerted by the gas at the elevated pressures. As seen in Figure 3, CO$_2$ was found to have a similar effect on the melting behavior of PET. The PET samples used were also characterized by a single melting peak. The depression in T_m follows a trend similar to that observed for sPS though the effect is not as large. Again, compressed N$_2$ under similar pressures was found to have no effect on the melting behavior of PET.

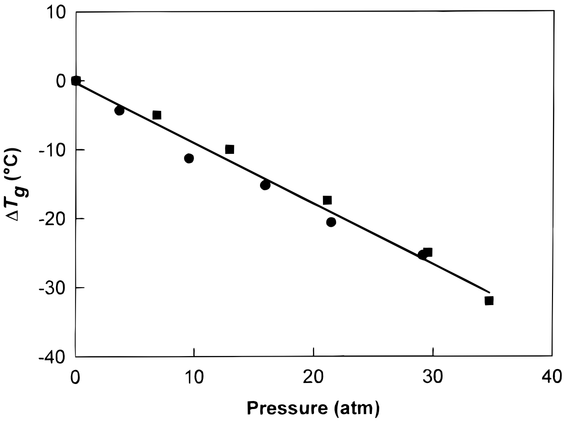

Figure 4. Depression in the glass transition temperatures of amorphous sPS (■) and PET (●) as a function of CO$_2$ pressure.

A comparison of the effects induced by CO$_2$ and N$_2$ suggests that the polymer–gas interactions (and the gas solubility) are responsible for the depression in T_m. The dissolved gas reduces the interchain interactions and, thus, elevates their enthalpic state. As a result, the glass transition temperature is lowered and the heat capacity change at the glass transition becomes smaller.[16] The plasticization effects of CO$_2$ on glassy sPS and PET are shown in Figure 4; the depression in T_g for both polymers is about −0.86 °C/atm. Since the gas dissolves in the amorphous region only and since the crystallinity in the sPS and PET samples used is about the same, similar plasticization effects will be expected to occur for the two polymers unless they have different levels of the rigid amorphous fraction.[14]

In terms of the Thomson–Gibbs equation, the shift in the melting temperature is given by[17]

$$T_m = T_m^\circ\left(1 - \frac{2\delta_e}{l\Delta h}\right) \qquad (1)$$

where T_m° is the melting point of an infinitely large crystal, δ_e is the specific surface free energy, l is the lamellar thickness, and Δh is the heat of fusion per unit volume. Since T_m, l, and Δh are generally constant for a given polymer, the decrease in T_m can be attributed to the increase in δ_e caused by the dissolved CO$_2$. Denoting $T_m(0)$ and $\delta_e(0)$ as the values under ambient conditions, and $T_m(p)$ and $\delta_e(p)$ the values at gas pressure p, eq 1 can be rearranged to give

$$\frac{T_m(0) - T(p)}{T_m(0)} = 2\frac{\delta_e(p) - \delta_e(0)}{l\Delta h} \qquad (2)$$

Accordingly, the depression in melting temeprature is dictated by both the polymer–gas interactions in the amorphous region and the intrinsic crystal characteristics, l and Δh. Thus, even though the crystallinity levels in the sPS and PET samples used are quite similar, the heats of fusion of the two polymers are significantly different. Consequently, for the present case, the denominator term in eq 2 will dominate the T_m–p behavior. This leads to the rather different T_m–p profiles for the two polymers although their T_g–p profiles are the same. It should be noted that CO$_2$ not only shifts the melting peak temperature but the melting onset temperature also, and the breadth of the peak is not altered. This suggests that, in terms of the layer-by-layer melting mechanism of polymer crystals,[17] as a layer melts, CO_2 is able to diffuse fast enough to raise the δ_e of the next layer and so on.

The melting behavior observed here for sPS−CO_2 and PET−CO_2 systems is expected to occur in other polymer−gas systems also whenever the gas sorption and the accompanying plasticization effect are much pronounced.

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