

## Compressed-gas-induced plasticization of polymers<sup>1,2</sup>

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### Abstract

The glass transition in polystyrene–ethylene at pressures up to 78 atm has been studied using a Tian–Calvet heat-flow calorimeter. The glass transition temperature  $T_g$  decreases with an increase in ethylene pressure, the largest depression being 67°C at 78 atm. The plasticization effect of ethylene is found to be almost the same as that of CO<sub>2</sub>, and is predicted well by the statistical thermodynamical formulation of the glass transition in polymer–diluent systems. The plasticization of amorphous poly(aryl ether ether ketone), PEEK, with CO<sub>2</sub> at 100°C and 100 atm results in induction of about 17% crystallinity in a high molecular weight sample. Overall crystallinity values as high as 44% are observed in the case of a low molecular weight PEEK sample.

### INTRODUCTION

The changes in morphological characteristics of polymers due to sorption of polar or polarizable organic fluids is well established. The effect of the sorbed material is to lower the glass transition temperature  $T_g$  of the polymer due to an increase in the free volume fraction or the mobility of the chains. This can lead to considerable swelling in the case of amorphous polymers and to induction of crystallinity or growth of the already nucleated crystalline phase in the case of crystallizable or semi-crystalline polymers. Recently a number of studies [1–8] have shown that similar morphological changes can be affected by contacting the polymer with supercritical fluids or compressed gases. A distinct advantage associated with the use of compressed gas is that after bringing about the desired morphological change, the gas is removed from the polymer matrix on depressurization, leaving behind the modified polymer.

Polystyrene (PS) is an amorphous polymer whose  $T_g$  is lowered by several tens of degrees on plasticization by organic fluids [9]. Wang et al. [1] reported that depression in  $T_g$  by as much as 65°C can be caused by

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sorption of CO<sub>2</sub> in PS at a pressure of about 100 atm. Similar results have been reported by Chiou and coworkers [2, 3, 5] and by Wissinger and Paulaitis [4] for PS–CO<sub>2</sub> and other systems. However, in all these studies, the  $T_g$  for the polymer–gas system was derived from non-thermodynamic or from ambient-pressure DSC measurements on a sample which had previously been treated with the high pressure gas. No direct calorimetric measurements of the polymer–gas system have been reported in the literature. In this paper, we report high pressure calorimetric measurements on the system polystyrene–ethylene, PS–C<sub>2</sub>H<sub>4</sub>.

The induction of crystallinity in polymers due to sorption of high pressure gas was first reported by Chiou et al. [5]. This technique was subsequently used by a few other investigators [6–8] for studying the crystallinity induced in poly(ethylene terephthalate) by CO<sub>2</sub>. Poly(aryl ether ether ketone) (PEEK) is a semi-crystalline polymer in which crystallinities as high as 40%–50% have been induced by sorption of solvents [10] or by thermal relaxation [11–13] at various temperatures between  $T_g$  and the melting point. In this paper, we report on the high-pressure CO<sub>2</sub>-induced crystallinity in low and high molecular weight PEEK.

## EXPERIMENTAL

Research grade C<sub>2</sub>H<sub>4</sub> and CO<sub>2</sub> were obtained from Matheson and Scott Specialty Gases, respectively. Polystyrene (Styron 680) was generously provided to us by Dr. Morris Rogers, Dow Chemical, Canada. The sample was in the form of 2 mm × 3 mm cylindrical pellets, contained no additives, and had  $M_w = 193700$  and  $M_w/M_n = 2.45$ . Two amorphous PEEK samples were investigated: a Stabar K200 0.2-mm-thick film from ICI, and a low molecular weight sample ( $M_w = 18000$ ,  $M_w/M_n = 1.24$ ) in the form of a fine powder prepared at NRC. The thermal and crystallization behavior of the latter sample has been reported elsewhere [13].

A Tian–Calvet heat-flow calorimeter (Setaram, model BT) was modified for measuring the glass transition in the system PS–C<sub>2</sub>H<sub>4</sub> at various gas pressures. The details of the calorimeter have been given previously [14]. Briefly, the sample and reference cells are connected via a manifold to vacuum, a pressure transducer (Setra, model 204), and a gas reservoir. The total volume of the gas space is 550 cm<sup>3</sup> of which about 50 cm<sup>3</sup> is associated with the manifold and the cells. The internal volume of the calorimeter cell is 8 cm<sup>3</sup>. About 2 g of PS was placed in the sample cell and the entire system evacuated. An appropriate amount of C<sub>2</sub>H<sub>4</sub> was then transferred to the gas reservoir such that when opened to the manifold and the cells it generated the desired pressure. The calorimeter was then scanned from a temperature about 2°C above the critical temperature  $T_c$  of C<sub>2</sub>H<sub>4</sub> to a temperature 10–20°C above  $T_g$ . The scan rate used was 7 or 10°C h<sup>-1</sup>. At the end of the scan, the calorimeter was cooled back to the starting temperature at a rate slower than that scan rate, and the sample was

scanned again. The first scan simply served to fully plasticize the PS pellet and to establish the polymer–gas equilibrium. The  $T_g$  was determined from the second scan. During the scans, the manifold and the gas reservoir were thermostatted at a temperature 10–15°C above the  $T_c$  of the gas, and the temperature of the gas phase inside the calorimeter was always kept above  $T_c$ . This avoided any condensation of the gas phase. Because the volume associated with the cells was quite small compared to the total volume of the system, the pressure during a scan changed by 5–10%, and remained almost constant during the transition event.

PEEK samples were plasticized with CO<sub>2</sub> at various temperatures in the range 100–200°C and pressures in the range 100–400 atm using a Suprex MPS/225 system. The sample size was 10–15 mg and the contact time with the gas was 60 min. After plasticization, the samples were cooled back to room temperature and depressurized. Crystallinity measurements were made using a DSC 2910–TA 2100 system (TA Instruments). The samples were scanned from ambient temperature to 400°C at 10°C min<sup>-1</sup> under a dry N<sub>2</sub> gas flow of 50 ml min<sup>-1</sup>. X-ray diffraction measurements at room temperature were made using a Scintag diffractometer (model XDS 2000) equipped with a graphite monochromator and Cu K $\alpha$  radiation source.

## RESULTS AND DISCUSSION

### PS–C<sub>2</sub>H<sub>4</sub> system

The calorimeter scans at selected pressures are shown in Fig. 1. It should be noted that a fresh sample of PS was used for each different pressure

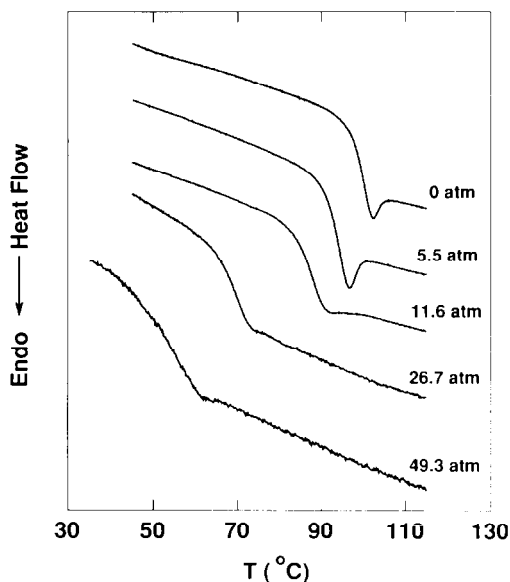


Fig. 1. Calorimetric scans for the system polystyrene–ethylene at various gas-pressures.

investigated. The glass transition of PS in the presence of about 0.1 atm helium gas, labelled as 0 atm, shows the usual sharp step in heat capacity. The transition observed during the first heating of the sample under the gas pressure was found to be quite sluggish and was spread over a temperature range of about 50°C. However, when the sample was cooled back and scanned again, the transition became much sharper. Thus, it appears that the plasticization starts at the surface of the polystyrene pellet and progresses towards the interior of the pellet during the first heat. The pellet is almost fully plasticized by the end of the first scan, thereby making the glass transition much sharper during the second scan. Accordingly, as mentioned above, the samples were scanned at least twice at each of the pressures and the results from the second scan are shown in Fig. 1. The glass transition under the gas pressure is still not as sharp as that observed for the pure polymer. Some sluggishness in the transition is to be expected because even though the measurements were made under almost isobaric conditions, the solubility of  $C_2H_4$  in PS is constantly changing during the scan.

The glass transition temperature is usually determined as the temperature corresponding to 50% conversion of the glass to the rubber state. We have chosen to take the onset temperature of the transition as  $T_g$  because, owing to the somewhat sluggish nature of the transition, the uncertainty associated with  $T_g$  determined this way is smaller than when determined the conventional way. Furthermore, because we are interested in the relative

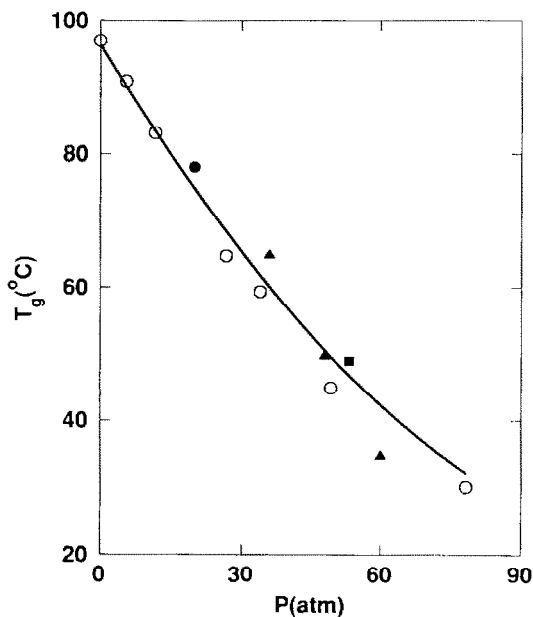


Fig. 2. The glass transition temperature  $T_g$  plotted against the gas pressure  $P$ : ○, polystyrene-ethylene system (this work); and the polystyrene- $CO_2$  system: ■ [1], ● [2], ▲ [4].

shift of  $T_g$  due to the gas pressure, this method of assigning  $T_g$  seems justified.

The  $T_g$  values are plotted against the ethylene gas pressure  $P$  in Fig. 2 and given in Table 1. Also shown in Fig. 2 are the results for the PS–CO<sub>2</sub> system taken from the literature. The literature values are shown by the solid symbols. The value at 20 atm was determined by DSC scanning of a PS sample pretreated with CO<sub>2</sub> under the given pressure [2]; the rest of the literature values shown were derived from measurements of Young's modulus and static creep compliance [1, 4]. The agreement among our results and those reported in the literature [1, 2, 4] is quite reasonable, considering the different techniques used to establish the glass transition temperatures.

Chow [15] has proposed a relation to account for the change in  $T_g$  due to the sorbed component

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

where

$$\theta = \frac{M_p \omega}{zM_d(1 - \omega)} \quad (2)$$

and

$$\beta = \frac{zR}{M_p \Delta C_p} \quad (3)$$

In eqns. (1)–(3),  $T_g$  and  $T_g^0$  are the glass transition temperatures for the polymer–gas system and the pure polymer, respectively,  $M_p$  is the molar mass of the polymer repeat unit,  $M_d$  is the molar mass of the gas,  $R$  is the gas constant,  $\omega$  is the gas solubility in the polymer,  $\Delta C_p$  is the heat capacity change associated with the glass transition of the pure polymer, and  $z$  is the lattice coordination number. Chow [15] suggested a value of  $z = 2$  for PS. However, Chiou et al. found that values of  $T_g$  calculated using  $z = 1$  gave

TABLE 1

$T_g$  values of the polystyrene–ethylene system at various gas pressures

$P/\text{atm}$	$T_g/^\circ\text{C}$	$P/\text{atm}$	$T_g/^\circ\text{C}$
0.0	96.9	34.0	59.4
5.5	90.8	49.3	44.9
11.6	83.1	78.3	30.1
26.7	64.7		

better agreement with the experimental results. The solubility of  $C_2H_4$  in PS is not known. However, as seen in Fig. 2, the  $T_g$ s for the systems PS- $C_2H_4$  and PS- $CO_2$  are almost the same and, therefore, the solubility of  $C_2H_4$  in PS can be assumed to be the same as that of  $CO_2$ . Wissinger and Paulaitis [16] have reported the solubility of  $CO_2$  in PS at various temperatures and pressures. These were used to estimate the solubility of  $C_2H_4$  in PS at the temperatures and pressures reported in Table 1. The calculated values of  $T_g$ s using  $z = 1$ ,  $M_p = 104.2 \text{ g mol}^{-1}$ , and  $\Delta C_p = 0.259 \text{ J K}^{-1} \text{ g}^{-1}$  are shown by the solid line in Fig. 2. The agreement with the experimental values is quite satisfactory.

As seen in Fig. 2, there is a rather sharp decrease in  $T_g$  due to the plasticization effect of the gas, the largest decrease observed in our work being  $67^\circ\text{C}$  at 78 atm. However, the  $T_g$  of polystyrene increases under hydrostatic pressure and limiting values for  $dT_g/dP$  in the range  $0.034\text{--}0.046^\circ\text{C atm}^{-1}$  have been reported in the literature [17, 18]. The hydrostatic correction for the pressures in Fig. 2 is quite small and, thus, the decrease in  $T_g$  can be assumed to be entirely due to the plasticization effect. The critical temperature of  $C_2H_4$  is  $9.2^\circ\text{C}$ . It takes about one hour for the calorimeter to settle to a steady heat-flow state, and at the scan rate of  $10^\circ\text{C h}^{-1}$  the lowest  $T_g$  which can be detected for the PS- $C_2H_4$  system is around  $25^\circ\text{C}$ , allowing for establishment of the initial baseline after the initial transient signal. In terms of the results shown in Fig. 2, the highest pressure at which the glass transition will be observed for the present system is about 95 atm. This, indeed, was found to be the case. At 90 atm, the calorimeter scan showed only the latter part of the glass transition; the initial baseline and the onset of the transition could not be established unambiguously.

### *PEEK- $CO_2$ system*

A scan of amorphous PEEK (Stabar K200) is shown in Fig. 3, curve 1. A glass transition is observed at  $150^\circ\text{C}$  followed by spontaneous crystallization at about  $170^\circ\text{C}$ . It has been suggested [12, 13] that a gradual growth in overall crystallinity continues all the way to the melting point and, thus, for the purpose of integrating the melting peak, the signal in the range  $155\text{--}170^\circ\text{C}$ , pertaining to the supercooled liquid, should be chosen as the initial baseline. The melting peak is then integrated with respect to a linear extrapolation of the initial baseline and the post-melting baseline [12, 19]. However, if after the initial scan to about  $200^\circ\text{C}$  the sample is cooled back to room temperature and then scanned again no well-defined glass transition is observed (curve 2) even though the sample is still mostly amorphous. In such a case, the best way to integrate the melting peak is to use the conventional sigmoidal extrapolation of the pre- and post-melting baselines. It was found that the crystallinities calculated by these two methods of integration differed by 1%–3%. In the present work, all

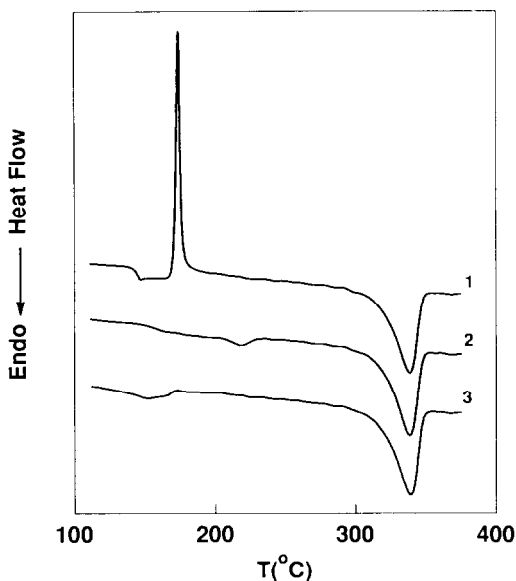


Fig. 3. DSC scans of amorphous PEEK: curve 1, normal scan; curve 2, after annealing at 200°C; curve 3, after treatment with CO<sub>2</sub> at 100°C and 300 atm.

crystallinity calculations were made by performing *sigmoidal* integration and using a value of 130 J g<sup>-1</sup> for the heat of melting of fully crystalline PEEK [11].

On simply heating Stabar K200 to 400°C at 10°C min<sup>-1</sup>, a crystallinity of about 17% was obtained from the crystallization peak at 170°C and of about 32% from the melting peak at 320°C. A sample annealed at 100°C for 60 min, cooled back to room temperature and then scanned in the usual manner gave a thermogram exactly the same as curve 1 in Fig. 3, and the crystallinity value obtained was 32%. However, a sample which had been contacted with CO<sub>2</sub> at 100°C and 300 atm for 60 min behaved quite differently. Its scan is shown by curve 3 in Fig. 3. The total crystallinity obtained in this case was still 32% but the disappearance of the crystallization peak in this scan indicates that at least about 17% of the crystallinity was induced at 100°C, about 70°C below the normal crystallization temperature. The induction of crystallinity is also confirmed by the X-ray diffraction patterns for the amorphous sample (curve 1) and the CO<sub>2</sub>-treated sample (curve 2) shown in Fig. 4. The extra peaks in curve 2 are due to the PEEK crystallites [11].

The Stabar sample was plasticized at different temperatures in the range 100–190°C and at pressures in the range 100–400 atm. The time of contact with the gas was 60 min. The maximum crystallinity was always found to be around 32%. The plasticization depends on the amount of material dissolved in the polymer. The solubility of the gas decreases at higher temperatures and further decreases as the crystallinity of the polymer

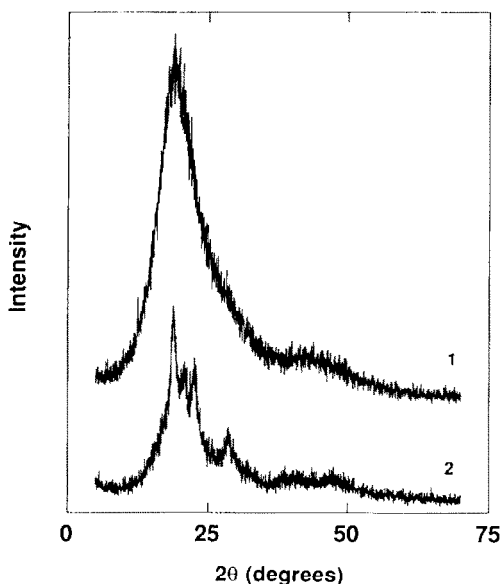


Fig. 4. X-ray diffraction patterns for amorphous PEEK (curve 1) and amorphous PEEK treated with CO<sub>2</sub> at 100°C and 300 atm (curve 2).

increases. The fact that the crystallinity value is always the same indicates that under the conditions investigated, CO<sub>2</sub> induces only a part of the overall crystallinity and the rest is induced by the dynamic enthalpy relaxation as the sample is heated to its melting point during the DSC scan.

For the low molecular weight PEEK sample ( $T_g = 143^\circ\text{C}$ ), a crystallinity of 44% was obtained after treatment with CO<sub>2</sub> at 175°C and 400 atm for 60 min. This is significantly higher than the value of 34% obtained on simply heating the amorphous sample. The higher crystallinity obtained in this case is most likely due to the lower molecular weight of the sample but also may be due to the fact that this sample was in the form of a fine powder which allowed for better polymer–CO<sub>2</sub> interactions.

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