

Differential scanning calorimetry of polysulfone at high pressures of CO₂ and N₂O

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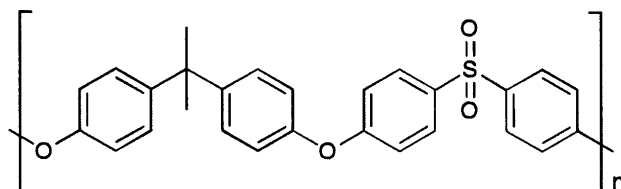
Summary

Polysulfone is less plasticized by compressed CO₂ than are amorphous vinyl polymers such as atactic polystyrene or poly(methyl methacrylate). N₂O, which is more polar than CO₂, is slightly more effective for plasticizing polysulfone than CO₂. Under the atmosphere of each gas, the depression in T_g is found to be linear with pressure. The dependence of T_g on pressure of CO₂ is $-0.52 \text{ K}\cdot\text{bar}^{-1}$, while that for N₂O is $-0.60 \text{ K}\cdot\text{bar}^{-1}$. Chow's thermodynamic model in combination with readily available gas solubility data does not describe well the pressure dependence of T_g in the polysulfone/CO₂ system.

Introduction

The thermodynamic behavior of glassy polymer/compressed gas systems at elevated pressure has received much attention in recent years as an important factor in several new applications such as the separation from gas mixture,^{1,2} the supercritical fluid extraction,³ and the impregnation of chemical compounds using supercritical fluids.⁴ In particular, the glass transition temperature (T_g) of polymers at high gas pressure is a principal factor that dominates the limiting temperature in practical use, and therefore, several reports have appeared which investigate the effect of compressed gases on the T_g of polymers using a high-pressure calorimeter.⁵⁻⁹

Polysulfone is used commercially as a membrane material for separating CO₂



polysulfone

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gas,¹⁰ and its gas transport properties have been extensively studied.^{1,2} Polysulfone shows a relatively high affinity for CO₂ or more polar media due to polar -SO₂- groups in its main chain. Such affinity promotes high gas sorption, which strongly correlates to the plasticization effect by the absorbed gas. However, to the best of our knowledge, no report has been published concerning the effect of these gases on the T_g of polysulfone. To know the CO₂ pressure dependence of polysulfone's T_g and to compare the result with those reported for a variety of polymers may help us to clarify the relationship between polymer structure and CO₂ pressure dependence.

Inspired by several preceding studies,^{5,9} in this work we examined the effect of compressed CO₂ (up to and above its critical pressure) or N₂O (up to 50 bar) on the T_g of polysulfone. CO₂ was used as a reference medium for several preceding studies on polymer/compressed CO₂ systems. N₂O has also been used as a more polar medium (μ 0.161 D at 20 °C)¹¹ than CO₂ (μ 0 D at 20 °C).¹¹

Experimental

Materials

Polysulfone ($M_n = 26\ 000$, melt index 3.5 g/10 min (343 °C/0.3 MPa (ASTM D 1238)) was purchased from Aldrich, and used as received. CO₂ (Ekika Tansan Co. Ltd., Kobe) and N₂O (Koike Medical, Tokyo) were used without further purification.

Procedures

The differential scanning calorimetry was performed on a Tian-Carvet type¹² SETARAM C80II calorimeter in combination with high-pressure cells. The calorimeter was calibrated by carrying out the measurement of the heat of fusion of tin (literature value: +7.03 KJ/mol¹³) under ambient and high pressures. The sample cell was charged with 150–200 mg of the polymer, and installed in the calorimeter. The entire system was then filled with an appropriate amount of either CO₂ or N₂O. CO₂ pressures higher than the gas cylinder pressure were achieved by pumping in the required amount of liquefied CO₂. N₂O was installed at gas cylinder pressure only. Once the whole

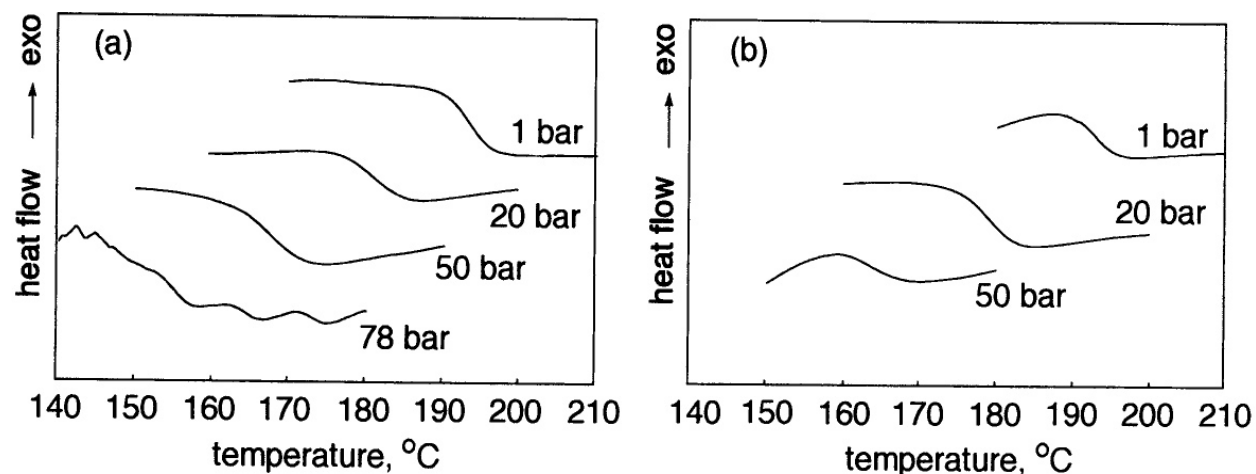


Figure 1. Representative DSC curves of (a) the polysulfone/CO₂ system and (b) the polysulfone/N₂O system.

Table 1. Glass transition temperature of polysulfone at elevated pressures of CO₂ or N₂O

pressure bar	T_g , °C	
	CO ₂	N ₂ O
1	194	193
11	188	187
20	181	179
35	174	170
50	167	164
78	155	
94	– ^a	

^a Glass transition was unclear.

system was pressurized, the sample was scanned at 2 K/min to a temperature about 60 K above the estimated T_g of the plasticized polymer, and the polymer was annealed at this temperature for at least 1 h. After annealing, the system was cooled at 1 K/min to a temperature about 50 K below the estimated T_g of the plasticized polymer and kept at the same temperature for at least 1 h. Then, the calorimeter was scanned again at 2 K/min to a temperature about 60 K above the estimated T_g of the plasticized polymer, and the T_g s described in this report were taken in this step. The pressure of the entire system rose by ca 5% during the heating. For measurements at different pressures, a fresh sample was used at each pressure.

X-ray diffraction analysis (XRD) was carried out on a Rigaku RINT-1200 X-ray diffractometer.

Results and Discussion

While CO₂-induced crystallization of poly(vinylidene fluoride)/poly(methyl methacrylate) blends,¹⁴ poly(ethylene terephthalate),¹⁵ polycarbonate,¹⁶ and syndiotactic polystyrene¹⁷ has been reported elsewhere, XRD analysis of our samples treated at each pressure of CO₂ or N₂O showed no noticeable peaks, indicating that the treatment with these gases did not induce crystallization of polysulfone. Some representative DSC outputs at various pressures of CO₂ and N₂O are shown in Figure 1. Under atmospheres of compressed CO₂ and N₂O, DSC traces clearly exhibit phase transition of polysulfone. In CO₂, a higher noise level was observed under its supercritical conditions (see Figure 1a). The T_g at 78 bar was barely estimated through a smoothing procedure using the spline function, while at 94 bar the T_g could no longer be estimated. T_g was taken as the temperature at the midpoint of the step. These T_g values were reproducible within the range of at least 1 degree. The results regarding the change in T_g of polysulfone as a function of the gas pressure are given in Table 1. The difference between the T_g at ambient pressure and the T_g at the pressure of interest, designated as ΔT_g , in each gas is plotted in Figure 2 against gas pressure. The ΔT_g decreased linearly with the increase in CO₂ pressure, and the slope ($d\Delta T_g/dp$) was $-0.52 \text{ K}\cdot\text{bar}^{-1}$. This $d\Delta T_g/dp$ value is lower than those for atactic polystyrene ($-0.9 \text{ K}\cdot\text{bar}^{-1}$),⁵ poly(methyl

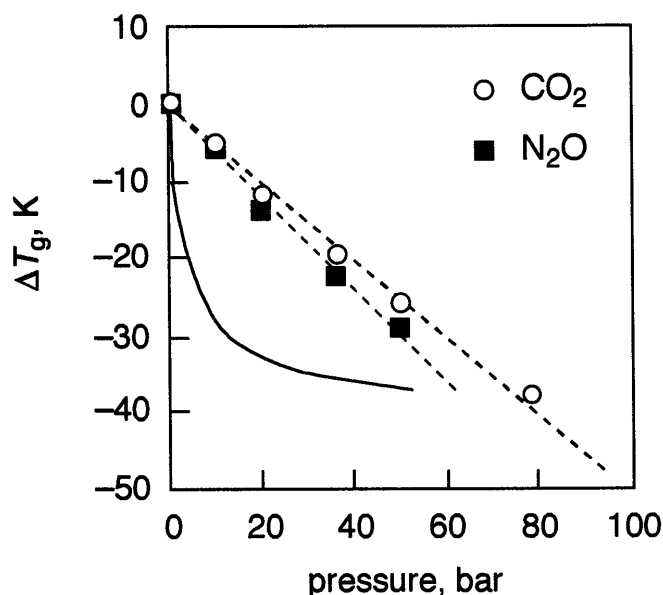


Figure 2. Dependence of T_g of polysulfone on the pressure of compressed CO_2 and N_2O . The solid line shows the predicted T_g values for the polysulfone/ CO_2 system based on the eqs. 1–3.

methacrylate) ($-1.2 \text{ K}\cdot\text{bar}^{-1}$),⁶ and syndiotactic polystyrene ($-0.86 \text{ K}\cdot\text{bar}^{-1}$).⁸ However, it is worth noting that the $d\Delta T_g/dp$ values for poly(2,6-dimethylphenylene oxide) ($-0.5 \text{ K}\cdot\text{bar}^{-1}$),⁷ poly(phenylene sulfide) ($-0.516 \text{ K}\cdot\text{bar}^{-1}$)⁹ and polysulfone, all of which have rigid aromatic rings along their main chain, are all close to $-0.5 \text{ K}\cdot\text{bar}^{-1}$.

In N_2O , the ΔT_g of polysulfone also decreased linearly with the increase in pressure, and $d\Delta T_g/dp$ of $-0.60 \text{ K}\cdot\text{bar}^{-1}$ was obtained, which is larger than that of the polysulfone/ CO_2 system. The larger pressure dependence of T_g in N_2O than in CO_2 means that the more polar N_2O interacts with and strongly plasticizes the polymer to a greater extent than does CO_2 . It was expected that at higher gas pressures, an antiplasticization effect due to the hydrostatic pressure¹⁸ would offset any decrease in T_g due to the plasticization effect of the dissolved gas, and lead to a deviation from the linear T_g - p relationship. However, no such effect was explicitly observed in the pressure range we examined for either CO_2 or N_2O .

Thus, it has been shown that the ability of compressed CO_2 and N_2O to plasticize "CO₂-philic" polysulfone is not so large. However, the more polar N_2O shows a slight dominance in the plasticization of polysulfone, suggesting that the polarity of gases has a large influence on the plasticization of polysulfone.

Chow derived a relationship to account for the change in T_g of polymers due to absorbed vapors or liquids on the basis of classical statistical thermodynamics (the Bragg-Williams approximation in the lattice model of small molecules).¹⁹ Later on, this relationship was shown by Chiou et al. to describe equally well polymer-gas systems.²⁰ Handa et al. discussed their experimental T_g values by using the same thermodynamic model.⁵⁻⁷ In this study, we also used this equation to estimate, albeit qualitatively, the strength of the interaction between the polymer chain and gas molecules. According to this model, T_g at pressures of interest is related to gas solubility by eqs. 1-3;

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

$$\beta = \frac{zR}{M_p \Delta C_p} \quad (2)$$

$$\theta = \frac{M_p}{zM_d} \frac{\omega}{1 - \omega} \quad (3)$$

where T_{g0} is the glass transition temperature at ambient pressure, M_p and M_d are the molar masses of the polymer repeat unit and the gas, respectively, R is the gas constant, ΔC_p is the heat capacity change associated with the glass transition of the pure polymer, ω is the gas solubility in the polymer, and z is the lattice coordination number that depends on the sizes of the gas molecule and the polymer repeat unit. Unfortunately, the solubility data of N_2O into polysulfone is not readily available in the literature, and we examined only for the polysulfone/ CO_2 system. The calculated T_g s using $\Delta C_p = 0.236 \text{ J K}^{-1} \text{ g}^{-1}$ and the gas solubilities measured by Chern et al. at 35°C ²¹ are shown by the solid line in Figure 2. Chiou et al. pointed out that for polymers with small repeat units, such as atactic polystyrene and poly(methyl methacrylate), a good fit for experimental results was obtained using $z = 1$ whereas for polymers with larger repeat units, such as polycarbonate, $z = 2$ gave a good fit.²⁰ In this comparison, we used $z = 2$. As seen in Figure 2, the ΔT_g values expected by Chow's model show an exponential decrease, and are constantly lower than our experimental ΔT_g values. This disparity may be ascribed to the following two factors. One is the uncertainty of the solubility at high temperatures and high pressures. Since accurate solubility data of CO_2 in polysulfone at higher temperatures and pressures are not available, we used the solubility data at 35°C and below 20 atm.¹⁷ In the DSC experiments the gas content of the polymer is likely to be slightly lower during the scan. Accordingly, the agreement between experimental and calculated values improves as T_g decreases. The other factor is the strong interaction between polymer main chains. Polysulfone has polar $-SO_2-$ groups and rigid aromatic rings in its main chain, making the polymer chain very rigid and coagulative. The strong polymer-polymer interaction may not satisfy the assumption for the model.

In summary, polysulfone is less plasticized by compressed CO_2 than are amorphous vinyl polymers such as atactic polystyrene or poly(methyl methacrylate). N_2O , which is more polar than CO_2 , is slightly more effective for plasticizing polysulfone. Under the atmosphere of each gas, the depression in T_g is found to be linear with pressure. The dependence of T_g on CO_2 pressure is $-0.52 \text{ K}\cdot\text{bar}^{-1}$, while that for N_2O is $-0.60 \text{ K}\cdot\text{bar}^{-1}$. Chow's thermodynamic model in combination with readily available gas solubility data does not describe well the pressure dependence of T_g in the polysulfone/ CO_2 system.

Acknowledgment

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