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Differential scanning calorimetry of isotactic polypropene at high CO_2 pressures

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Abstract

Compressed CO_2 gas (1–94 bar) depresses both the crystallisation temperature (T_c) and the melting temperature (T_m) of isotactic polypropene (iPP). The T_c of CO_2-treated iPP decreases linearly with a dT_c/dP value of -0.18 K/bar. Similar to T_c, the T_m of CO_2-treated iPP decreases linearly with a dT_m/dP value of -0.12 K/bar. Experimental ΔT_m ($= T_m - T'_m$) values, where T'_m is the melting temperature at a CO_2 pressure of 1 bar, coincide with those predicted on the basis of the Flory–Huggins theory. © 2000 Published by Elsevier Science Ltd. All rights reserved.

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1. Introduction

Considerable attention has been paid recently to the thermodynamic behaviour of polymers in contact with high pressure gases or supercritical fluids as an important factor in several new process applications (for example see Ref. [1]). It is important to study the pressure dependence of the glass-transition temperature, T_g, the melting temperature, T_m, and the crystallisation temperature, T_c, since these thermodynamic parameters are the main factors limiting temperatures in practical use. In fact, CO_2 has been shown to be a very effective plasticiser that can lower T_g [2–4] and, in some cases, can induce crystallisation of semicrystalline polymers at lower temperatures [5–7]. To the best of our knowledge, however, in situ studies on the CO_2-induced shift of T_m and T_c of semicrystalline polymers using a high pressure calorimeter have been limited to poly(phenylene sulfide) [8], poly(ethylene terephthalate) (PET) [9,10] and syndiotactic polystyrene (sPS) [9]. Here we investigated the effect of CO_2 pressure on the melting and crystallisation behaviours of isotactic polypropene (iPP) for the following reasons: (1) for iPP a variety of physicochemical data are readily available such as the solubility of CO_2 in bulk iPP at high pressures, the equilibrium melting temperature, and the equilibrium heat of fusion; (2) by utilising these data we can compare our experimental results with the thermodynamic model proposed by Flory [11,12].

2. Experimental

2.1. Materials

iPP ($M_w = 1.33 \times 10^5$, $M_w/M_n = 3.2$, $[mmmm] = 0.86$) was purchased from Aldrich. CO_2 gas (>99.99% purity) was obtained from Ekika Tansan Co. Ltd.

2.2. Procedure

Differential scanning calorimetry of iPP was carried out on a Tian–Calvet type SETARAM C80II calorimeter [13]. The calorimeter was calibrated by carrying out the measurement of the heat of fusion of tin (literature value: +7.03 kJ/mol [14]) under ambient and high pressures. About 170 mg of a polymer sample was heated to 250°C at a rate of 2 K/min, and was annealed at this temperature for 1 h. After the annealing, the system was cooled to 100°C at a rate of 1 K/min and kept at the same temperature for 1 h. The sample then was heated to 250°C again at 2 K/min. T_m and T_c were taken in the second heating process and the first cooling process, respectively. X-ray diffraction analysis (XRD) was performed on a Rigaku RINT-1200 X-ray diffractometer.

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Table 1
Effect of compressed CO_2 on the melting and crystallisation behaviours of isotactic polypropene

Pressure (bar)	Heating			Cooling		
	T_m (°C)	T_m(onset) (°C)	ΔH_m (J/g)	T_c (°C)	T_c(onset) (°C)	ΔH_c (J/g)
1	180	166	92	131	136	−97
10	179	163	89	130	135	−97
20	177	160	92	127	133	−97
36	175	155	90	125	131	−95
50	175	152	84	122	128	−91
78	171	149	81	117	124	−90
88	169	148	76	116	123	−86
94	169	145	88	115	122	−84

3. Results and discussion

Table 1 summarises the pressure dependence of T_m, the melting onset temperature, T_m(onset), T_c, and the crystallisation onset temperature, T_c(onset), as well as the heat of fusion and crystallisation for iPP. In our study, T_m and T_c are expressed as the minimum-endo- and maximum-exothermic temperatures reached during melting and crystallisation, respectively. Both T_c and T_m barely shifted in the subsequent heating–cooling cycles (up to four times). The shape of the exothermic peak due to crystallisation was independent of CO_2 pressure, but T_c decreased almost linearly with an increase in CO_2 pressure with a slope of -0.18 K/bar. The heat of crystallisation (ΔH_c) as well as the heat of melting (ΔH_m) showed a tendency to become smaller with increasing pressure, indicating a decrease in crystallinity of the CO_2-treated iPP. XRD analysis showed that treatment of the iPP sample with CO_2 (up to 94 bar) caused no significant change in the basic morphology of the crystalline phase (α form).

Table 1 also shows that the exposure to CO_2 brought about a shift of both T_m(onset) and T_m. The shift of T_m(onset) was larger than that of T_m, and therefore the melting endothermic peak broadened slightly as the CO_2 pressure increased. In Fig. 1, values for $\Delta T_m = T_m - T'_m$, where T'_m is the melting temperature at the CO_2 pressure of 1 bar, were plotted against the CO_2 pressure. It is worth noting that ΔT_m decreased linearly with an increase in the pressure of CO_2 gas. The linear dependence of ΔT_m on the pressure of CO_2 gas is in contrast to those of PET [9] and sPS [9].

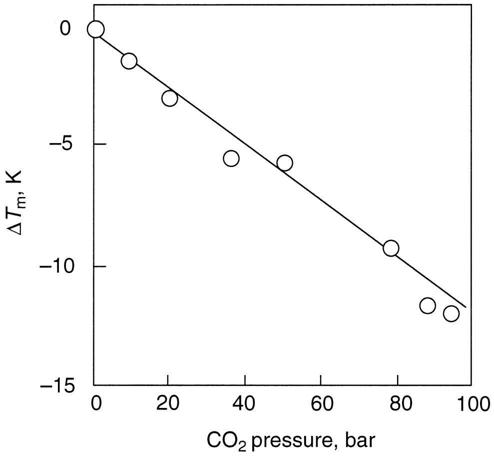

Fig. 1. Dependence of ΔT_m of isotactic polypropene on CO_2 pressure. The solid line indicates the values predicted from Eq. (5).

According to the Flory–Huggins theory, T_ms of plasticised semicrystalline polymers with sufficiently high molecular weights can be correlated to the volume fraction of the plasticiser (v_1), as shown in Eq. (1) [11,12]:

$$\left(\frac{1}{T_m} - \frac{1}{T_m^0}\right)\left(\frac{1}{v_1}\right) = \frac{R}{\Delta H_m^0}\left(\frac{V_{2u}}{V_1}\right)(1 - \chi v_1) \tag{1}$$

where T_m^0, V_1, V_{2u}, χ, ΔH_m^0, R are the equilibrium melting temperature of the polymer of interest, the molar volume of CO_2, the molar volume of the repeating unit of the polymer, the interaction parameter, the equilibrium heat of fusion, and the gas constant, respectively. From Eq. (1), T_m can be written as follows:

$$T_m = \frac{T_m^0}{1 + K(v_1 - \chi v_1^2)} \tag{2}$$

where $K = (RT_m^0/\Delta H_m^0)(V_{2u}/V_1)$. When v_1 values are much less than unity, the v_1^2 term is negligible. Thus, T_m is expressed by Eq. (3):

$$T_m \approx \frac{T_m^0}{1 + Kv_1} \approx T_m^0(1 - Kv_1) \tag{3}$$

We can calculate the volume fraction of CO_2 in the iPP sample from the solubility data. Fardi et al. have reported that the solubility of CO_2 in iPP obeys Henry's law over a CO_2 pressure range of 5–20 MPa, and Henry's constant (H) of the iPP/CO_2 system is found to be independent of temperature [15]. Thus, the v_1 at P (bar) is:

$$v_1 = \frac{wHP\dfrac{V_r}{V_{ig}}}{wHP\dfrac{V_r}{V_{ig}} + \left(\dfrac{w}{\rho}\right)} \approx \frac{wHP\dfrac{V_r}{V_{ig}}}{\left(\dfrac{w}{\rho}\right)} = \frac{V_r}{V_{ig}}\rho HP \tag{4}$$

where w, ρ, V_{ig} and V_r are the weight, the specific gravity of the polymer sample employed, the molar volume of the ideal gas ($=22{,}400$ cm^3) and the molar volume of the CO_2 dissolved in the polymer, respectively.

The iPP sample employed here had a number-average degree of polymerisation of ca. 2500, and under our condition v_1 values were found to be at most 0.07. Therefore, the Flory–Huggins equation (Eq. (1)) and Eq. (3), which is derived from Eq. (1), can be applied to this system. By substituting Eq. (4) for Eq. (3), ΔT_m can be written as follows:

$$\Delta T_\mathrm{m} = T_\mathrm{m} - T'_\mathrm{m} = -T^0_\mathrm{m}\frac{V_\mathrm{r}}{V_\mathrm{ig}}\left(\frac{\mathrm{R}T^0_\mathrm{m}}{\Delta H^0_\mathrm{m}}\right)\left(\frac{V_{2\mathrm{u}}}{V_1}\right)\rho HP + (T^0_\mathrm{m} - T'_\mathrm{m}) \qquad (5)$$

Thus, it should be noted that ΔT_m, or T_m, of this system is expected to decrease linearly with the increase in CO_2-pressure.

The solid line in Fig. 1 indicates the ΔT_m values predicted from Eq. (5) by using a V_1 value of 45 cm^3 [16], an H value of 0.4 cc(STP) g^{-1} bar^{-1} [15], a T_m^0 of 460.65 K [17] and ΔH_m^0 of 165.3 J/g [18]. The V_{2u} value can be estimated from the literature [17], and in this discussion, the V_r value of 45 cm^3 was used [19]. In the Flory–Huggins equation thermodynamic equilibrium T_ms are used, and the thermodynamic equilibrium T_ms are generally higher by several degrees than T_ms obtained at normal scanning rates (1–20K/min). Though our experimental T_ms are not thermodynamic equilibrium T_ms, we focused on the difference between two T_ms, both of which were measured under identical conditions, and the comparison of our experimental ΔT_m values with Eq. (5) is valid. As can be seen in Fig. 1, Eq. (5) agrees very well with the experimental ΔT_m values over the whole CO_2 pressure range examined. The slope of the ΔT_m-pressure plot was -0.12 K/bar. This result shows that Eq. (5) is applicable to the prediction of the T_m values of the iPP/CO_2 system and the interaction between iPP and CO_2 is weak.

Handa et al. attributed the levelling behaviour of T_m of the sPS/CO_2 and the PET/CO_2 systems to the antiplasticisation effect of the hydrostatic pressure of CO_2 [2,9]. In contrast, in our iPP/CO_2 system this was not the case and linear dependence of T_m on CO_2 pressure was shown. Consequently, the antiplasticisation effect of compressed CO_2 is expected to be much smaller in the iPP/CO_2 system than in the sPS/CO_2 and the PET/CO_2 systems.

In summary, compressed CO_2 gas (1–94 bar) depresses both the crystallisation temperature (T_c) and the melting temperature (T_m) of iPP. The T_c of CO_2-treated iPP decreases linearly with a dT_c/dP value of -0.18 K/bar. Similar to T_c, the T_m of CO_2-treated iPP decreases linearly with a dT_c/dP value of -0.12 K/bar. Experimental ΔT_m ($= T_m - T'_m$) values, where T'_m is the melting temperature at a CO_2 pressure of 1 bar, coincide quantitatively with those predicted on the basis of the Flory–Huggins theory.

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References

[1] McHugh MA, Krukonis VJ. Supercritical fluid extraction: principle and practice, 2. Butterworth–Heinemann: Boston, 1994.
[2] O'Neill ML, Handa YP. In: Seyler RJ, editor. Assignment of the glass transition, ASTM STP 1249Philadelphia: American Society for Testing and Materials, 1994. p. 165.
[3] Handa YP, Lampron S, O'Neill ML. J Polym Sci: Polym Phys Ed 1994;32:2549.
[4] Kishimoto Y, Ishii R. Polym Bull 1999; in press.
[5] Chiou JS, Barlow JW, Paul DR. J Appl Polym Sci 1985;30:3911.
[6] Handa YP, Roovers J, Wang F. Macromolecules 1994;27:5511.
[7] Handa YP, Zhang Z, Wong B. Macromolecules 1997;30:8499.
[8] Schultze JD, Engelmann IAD, Boehning M, Springer J. Polym Adv Technol 1991;2:123.
[9] Zhang Z, Handa YP. Macromolecules 1997;30:8505.
[10] Zhong Z, Zheng S, Mi Y. Polymer 1999;40:3829.
[11] Flory PJ. J Chem Phys 1949;17:223.
[12] Flory PJ. Principles of polymer chemistry, New York: Cornell University Press, 1953.
[13] Calvet E, Prat H. Microcalorimètrie, applications physiciochimiques et biologiques, Paris: Masson, 1956.
[14] Speros DM, Woodhouse RL. J Phys Chem 1964;67:2164.
[15] Fardi N, Dey SK, Chawda A. Soc Plast Eng 55th Annu Technol Conf 1997;2:2221.
[16] Kamiya Y, Naito Y, Mizoguchi K, Terada K, Moreau J. J Polym Sci: Polym Phys Ed 1997;35:1049.
[17] Kamide K, Toyama K. Sen-igakkaishi (Tokyo) 1969;25:49.
[18] Wunderlich B. Macromolecular physics, vol. 3: crystal melting, New York: Academic Press, 1980.
[19] Zoller P. J Appl Polym Sci 1979;23:1057.