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Melting parameters of poly(glycolic acid)

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Abstract

Equilibrium melting temperature T_m^0, heat of fusion ΔH_f, and entropy of fusion ΔS_f of poly(glycolic acid) (PGA) was determined by using Clapeyron–Clausius equation. Equilibrium melting temperature T_m^0 was 504.6 K which was determined by Hoffman–Weeks plots. The pressure dependence of T_m^0 was determined by high pressure DTA up to 150 MPa. Volume change ΔV_f at melting was determined by using dilatometer. Heat of fusion in PGA was 183.2 (J g^{-1}), which is very close to the value reported by Chujo et al. who determined it by using T_m depression in copolymer with poly(lactic acid). ΔS_f of PGA was 0.363 (J g^{-1} K^{-1}), which is about twice that of PLA, and the reason was discussed on the basis of the elastic modulus below T_m.

Keywords: Poly(glycolic acid); Heat of fusion; Clapeyron–clausius equation

1. Introduction

It is very important to determine thermodynamic parameters of polymers from the scientific and practical point of view. Heat of fusion ΔH_f and equilibrium melting temperature T_m^0 for polymer crystals are determined through various methods. ΔH_f is determined by the use of differential scanning calorimetry (DSC) or by calculating it from Clapeyron–Clausius equation using the data of pressure dependence of T_m.

Poly(glycolic acid) (PGA) is simplest aliphatic polyester and used as a biomedical material such as suture in the area of surgery. ΔH_f of PGA was reported by two groups but a discrepancy exists between these values. Chujo et al. determined it from calculation of melting point depression by co-polymerization using Flory's theory to be 2500 cal per repeating unit (180.4 J g^{-1}) from glycolide–lactide copolymerization and 2800 cal per repeating unit (202.1 J g^{-1}) from glycolide-1,3 dioxolane copolymerization [1]. Cohn et al. [2] reported 139.1 J g^{-1} for the heat of fusion of PGA crystal through the DSC melting of the high molecular weight sample of the crystallinity 52% to be 72.3 J g^{-1}. The value of ΔH_f of 180.4 and 202.1 J g^{-1} by Chujo et al. is much larger than the value reported by Cohn et al.

To determine the heat of fusion by using DSC is not so simple. In most polyester, multiple melting behaviors are observed and two or three endothermic peaks appear [3–5]. Furthermore, sometimes melting begins to occur far below the melting peak temperature in most polymers. In some polyester, crystallization peak appears just below the endothermic melting peak.

To determine ΔH_f through Clapeyron–Clausius equation is more direct, but pressure dependence of the melting temperature (dT_m/dp), the equilibrium melting temperature T_m^0 and the volume change at melting should be known. There is no report on determining ΔH_f of PGA by such a method.

In this report, heat of fusion ΔH_f and entropy of fusion ΔS_f of PGA is determined by using Clapeyron–Clausius equation. Equilibrium melting temperature, pressure dependence of T_m and the volume change of it in the crystal melting were measured to calculate ΔH_f and ΔS_f. These values are compared with the values of poly(L-lactic acid) (PLLA) [6] that are also aliphatic polyester and also used as a suture in microsurgery.

2. Experimental

Commercial grade PGA pellet sample purchased from Sigma-Aldrich Co. was used. The molecular weight according to supplier's data was between 100,000 and 125,000.

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Pressure dependence of T_m of PGA was determined by high pressure DTA. The apparatus was described elsewhere. PGA pellet sample as obtained with 1.8 mm in diameter was cut within 1.3 mm in length (about 8 mmg) and wrapped with aluminium foil tightly and attached to the thermocouple junction for high pressure DTA with epoxy resin. High pressure DTA was performed up to 150 MPa. The apparatus and the experimental method was described elsewhere [7].

The equilibrium melting temperature T_m^0 of PGA was determined by Hoffman–Weeks plots using crystallization temperature T_c and melting temperature. Rigaku DSC 8230D with TAS200 control system was used to determine T_m of the sample.

Volume change at melting (ΔV_f) of the sample was measured by conventional dilatometer made of Pyrex glass capillary. The sample part was heated in silicone oil bath. The top of the mercury height was measured by cathetometer.

Crystallinity of the PGA sample was determined by the density (ρ) measurement. A set of $ZnBr_2$ solution between 46.6% ($\rho = 1.575$) and 48.0% ($\rho = 1.600$) with 0.2% each was made. The crystalline density of PGA is 1.70 (g cm^{-3}) [8] and the amorphous density is 1.50 (g cm^{-3}) [6]. The PGA density in this measurement was 1.585. Therefore, the crystallinity of the sample was 53%.

3. Results and discussion

In high pressure DTA of PGA, a single endothermic peak of melting appeared at about 220 °C at 0.1 MPa. The peak shifted to the high temperature side with increasing pressure. Pressure dependence of T_m of PGA is shown in Fig. 1. Pressure dependence of PGA is fitted to the following quadratic equation,

$$T_m = 221.6 + 0.30p - 3.3 \times 10^{-4}p^2$$

Where p is the pressure. The correlation coefficient R was 0.997. Pressure dependence of T_m was determined to be 0.30 KMPa^{-1}. This value of dT_m/dp is larger than that of PLLA (0.21 KMPa^{-1}) but in average value among polymer crystals.

Fig. 2 shows T_m vs. crystallization temperature T_c (Hoffman–Weeks plots). T_m^0 was determined by extrapolating melting temperature to $T_m = T_c$ straight line. The value of T_m^0 in PGA was 231.6 °C.

On the evaluation of ΔH_f, we used the value of 0.32 KMPa^{-1} for the pressure dependence of the equilibrium melting temperature according to the following estimation. In the case of polyethylene, we studied the pressure change of T_m of the folded chain crystals (FCC) formed by melt-crystallization at 0.1 MPa and the extended chain crystals (ECC) formed by melt-crystallization under high pressure of 450 MPa. T_m of ECC is about 141 °C which is considered to be almost the same temperature as the value of the equilibrium melting temperature of PE. Pressure dependence of T_m^0 (ECC) in PE [9] is 0.30 KMPa^{-1} and that of T_m (FCC) [10] is 0.28 KMPa^{-1}. The temperature difference of T_m^0 and T_m is about 9 °C in PE. In the case of PGA, the temperature difference of T_m^0 and T_m is about 10 °C. Therefore, it is supposed that the pressure dependence of T_m^0 of PGA is 0.32 KMPa^{-1}.

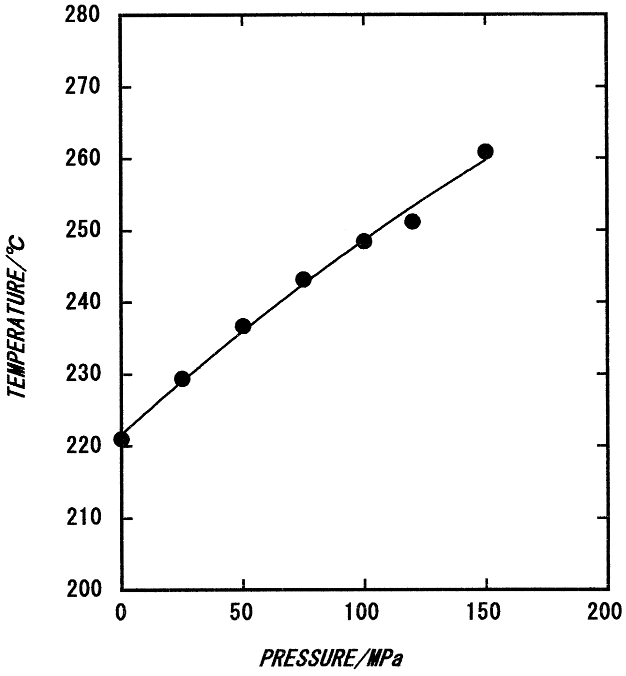

Fig. 1. Pressure dependence of T_m of PGA.

Fig. 3 shows volume change of PGA around melting region. The heating rate was 6 kmin^{-1}. The change of the mercury height during melting of PGA (($\Delta \ell$)) was 5.6 cm. The area of the inside glass capillary was 0.0015 cm^2, so

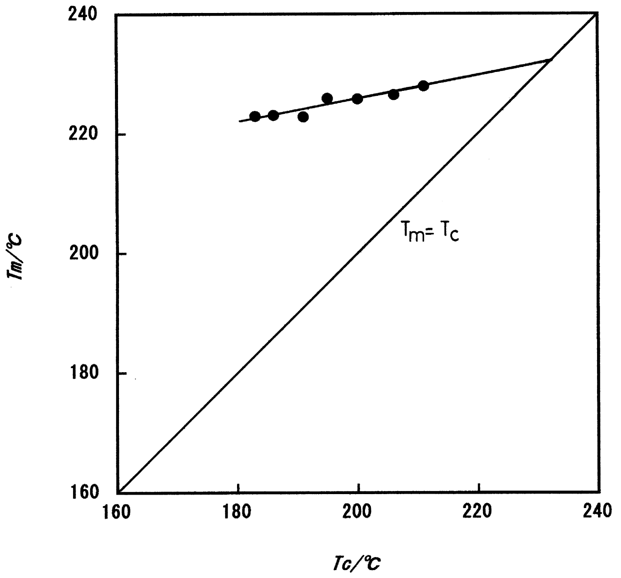

Fig. 2. Hoffman–Weeks plot of PGA.

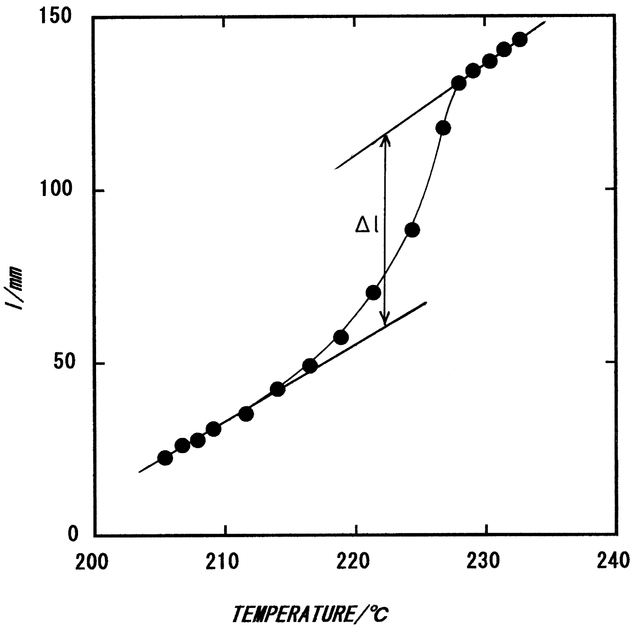

Fig. 3. Volume change vs. temperature of PGA around melting region.

that the volume change around melting region of PGA was 0.0092 $\text{cm}^3\ \text{g}^{-1}$. The crystallinity of the PGA sample in this experiment was 53% and the sample mass in the dilatometer was 150.5 mg. Therefore, ΔV_f is 0.1162 $\text{cm}^3\ \text{g}^{-1}$ if we take the sample crystallinity 100%.

The heat of fusion ΔH_f is determined by following Clapeyron–Clausius equation

$$\frac{\mathrm{d}T_\mathrm{m}}{\mathrm{d}p}=\frac{T_\mathrm{m}^0\Delta V_\mathrm{f}}{\Delta H_\mathrm{f}} \tag{1}$$

Heat of fusion ΔH_f obtained by calculating from Eq. (1) is 183.2 (J g^{-1}).

Table 1 lists the values of equilibrium melting temperature, ΔH_f and entropy of melting ΔS_f for PGA in this experiment and those reported by Cohn et al. The values for poly(L-lactic acid) in Ref. [6] are also listed. The value of ΔS_f was obtained by dividing ΔH_f by T_m^0.

The value of ΔH_f in this work is very close to the value obtained by Chujo et al. [1]. They reported that ΔH_f obtained by T_m depression in copolymer with PLA was 180.4 (J g^{-1}) and 202.1 (J g^{-1}) in copolymer with 1,3-dioxolane. As the value of T_m^0, 500.15 or 502.15 K that is close to the value obtained in this work (504.6 K) are used. The value of ΔH_f reported by Chujo et al. by T_m depression in copolymer with PLA corresponded to the value obtained in this work within experimental error.

The value obtained by Cohn et al. using DSC [2] is smaller than the values obtained in this work and by Chujo et al. Heat of fusion determined by DSC includes some ambiguity in determining peak area of melting. The smaller value reported by Cohn et al. may be ascribed to the method. The value of ΔS_f reported by Cohn et al. is also smaller than the values in this work and that reported by Chujo et al.

Table 1
Comparison of melting parameters of PGA in this work, by Cohn et al., by Chujo et al. and reference data of PLLA

	PGA	PLLA
T_m^0 (K)	504.6	480.15
$\mathrm{d}T_\mathrm{m}^0/\mathrm{d}p$ (KMPa^{-1})	0.32	0.21
ΔV ($\text{cm}^3\ \text{g}^{-1}$)	0.1162	–
ΔH_f (J g^{-1})	183.2 ± 6.0 (this work), 139.0 (by Cohn et al.), 180.4 (by Chujo et al.), 202.1 (by Chujo et al.)	88.8
ΔS_f ($\text{J g}^{-1}\ \text{K}^{-1}$)	0.363 ± 0.012 (this work), 0.275 (by Cohn et al.)	0.185

Both ΔH_f and ΔS_f values of PGA are larger than those values for PLLA. This difference of ΔS_f in PGA and PLLA should be reasonable if we consider the temperature change of the elastic modulus for both samples. Tensile modulus E of PGA slightly decreased from 2.55×10^9 Pa at 0 °C to 4.37×10^8 Pa at 130 °C [11]. If we extend the curve to higher temperature, the value of E at 220 °C is about 1.05×10^8 Pa. The value of E' at 220 °C obtained by dynamic mechanical measurement is also higher than 2.0×10^8 Pa. On the contrary, the tensile modulus of PLLA drastically decreased above glass transition temperature of about 55 °C. Below T_g, E of PLLA is 9×10^8 Pa at 0 °C but it becomes lower than 1×10^7 Pa even at 60 °C and decreased drastically at higher temperature. Modulus of crystalline region of PGA is hold just below the melting temperature but in PLLA it does not occur.

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