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Melt behaviour, crystallinity and morphology of poly(*p*-dioxanone)

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Abstract

The melt behaviour of poly(*p*-dioxanone) (PPD) has been studied by differential scanning calorimetry (DSC). Crystallinity and morphology were evaluated by modulated differential scanning calorimetry (MDSC) and polarizing optical microscopy. The melting curves showed two melting endotherms, a higher melting (HM) peak at a constant temperature of 105°C and a lower melting (LM) peak at temperatures depending on the crystallization temperature T_c. The corresponding peak temperature increased linearly with T_c, yielding an extrapolated value for the equilibrium melting temperature, $T_m°$, of 114°C. The occurrence of HM peak is a result of recrystallization. The optical micrographs showed a spherulitic morphology, with regular concentric rings, which might be caused by a periodical twisting of the lamellae during crystallization. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(*p*-dioxanone); Crystallinity; Morphology

1. Introduction

Poly(*p*-dioxanone) (PPD) is a crystalline polymer developed specifically for use in bioabsorbable sutures [1,2]. The polymer is synthesized by the polymerization of *para*-dioxanone in the presence of an organometallic catalyst, like diethylzinc or zirconium acetylacetone, to obtain a high molecular weight polymer suitable for melt extrusion into monofilament fibers [3]. Due to its high flexibility, good mechanical properties and high degradation rate, PPD is also useful for other applications in the medical field, for instance being an alternative for other bioabsorbable polyesters such as polyhydroxybutyrate (PHB) [4] and poly(L-lactic acid) (PLLA) [5] which are too brittle and have a low degradation rate. The purpose of this work is to investigate the melt behavior, the crystallinity and spherulitic morphology of PPD films.

2. Experimental

Violet polydioxanone sutures (PDS®) of size 2–0 used in this study were supplied by Johnson and Johnson. The dye was completely extracted with methylene chloride (Merck) prior to use. Hexafluoroisopropanol (HFIP) was purchased from Aldrich. Films were prepared by solvent casting at room temperature from a 10 w/v% solution of PPD in HFIP. The solution was prepared by mechanical mixing for 2 h at room temperature. The mixture was poured in a glass mold (50 × 30 × 5 mm) and placed in an evaporator system, consisting of a glass box with constant dried air flux (1 l/min), for 24 h at room temperature. The films were completely dried in a vacuum oven for 24 h at 60°C and stored in a desiccator.

Calorimetric measurements were performed with a Perkin Elmer DSC 7 apparatus. For determination of melting temperatures, T_m, samples of 4–5 mg, sealed in aluminium pans, were first heated up to 150°C annealed for 1 min, and subsequently, cooled to the desired temperature of crystallization, T_c, at a rate of 40°C/min. At T_c the samples were annealed for 30–60 min, later they were heated up to 150°C at a scan speed of 10°C/min.

For determining the recrystallization, a heat-only modulated differential scanning calorimetry (MDSC) experiment was performed with a TA-Instruments DSC 2920 in the modulated mode with an underlying heating rate of 2°C/min; a period of 60 s and an amplitude of +/−0.32°C of PPD crystallized at 75°C for 60 min.

For light microscopic investigations, films of about 40 μm thickness were obtained by melt pressing at 200°C for 1 min using a pressure of 30 000 pounds (lbs)/400 cm^2. Before crystallization, samples (sandwiched between two cover glasses) were first heated up to 200°C for 1 min

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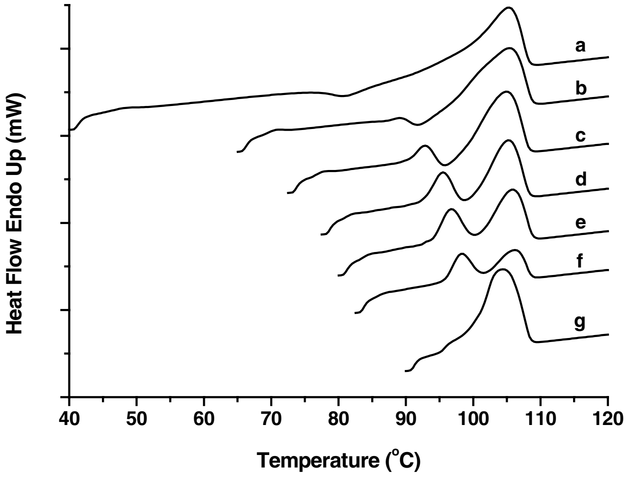


Fig. 1. DSC melting curves of PPD crystallized at different T_cs: (a) 40°, (b) 65°, (c) 72.5°, (d) 77.5°, (e) 80°, (f) 82.5°, (g) 90°C.

then they were cooled to $T_c = 65$°C. A Zeiss Axiophot polarizing microscope equipped with a hot stage (Mettler FP82) was used to visualize the morphology.

3. Results and discussion

From Hoffman and Weeks [6], the relation between the observed melting point, T_m, and the isothermal crystallization temperature, T_c, is given by the following equation:

$$T_m = T_m{}^\circ(1 - 1/\gamma) + T_c/\gamma \qquad (1)$$

where γ is the ratio of the initial to the final lamellar thickness and $T_m{}^\circ$ is the equilibrium melting point, obtained from a plot of T_m vs. T_c by extrapolating the linear data until intersection with the line $T_m = T_c$.

Typical DSC melting curves of PPD samples crystallized in the melt at various T_cs, are shown in Fig. 1. The melting points, T_m, are collected in a T_m vs. T_c diagram as shown in Fig. 2. These melting curves appear after crystallization at temperatures below 100°C. It can be seen that a lower melting (LM) peak appears at temperatures depending on T_c, and a higher melting (HM) peak at a constant temperature of 105°C. The temperature of the LM peak shifts to higher temperatures with increasing value of T_c. Extrapolating the T_{LM}-line with a slope of 0.52 to $T_m = T_c$ yields $T_m{}^\circ = 114$°C. Because of the extrapolation over a large distance this $T_m{}^\circ$ is only an approximation. Two melting peaks were observed at T_cs between 70 and 85°C. The same behavior was observed for other polymers like isotactic polystyrene [9] and isotactic poly(2-vinylpyridine)[10]. Above $T_c = 90$°C, the rate of crystallization is very low.

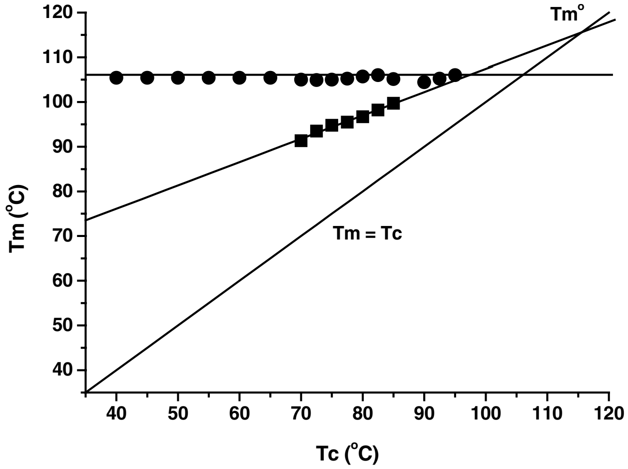


Fig. 2. Peak melting temperatures of PPD as a function of crystallization temperature. (●) HM endotherms; (■) LM endotherms. Heating rate: 10°C/min.

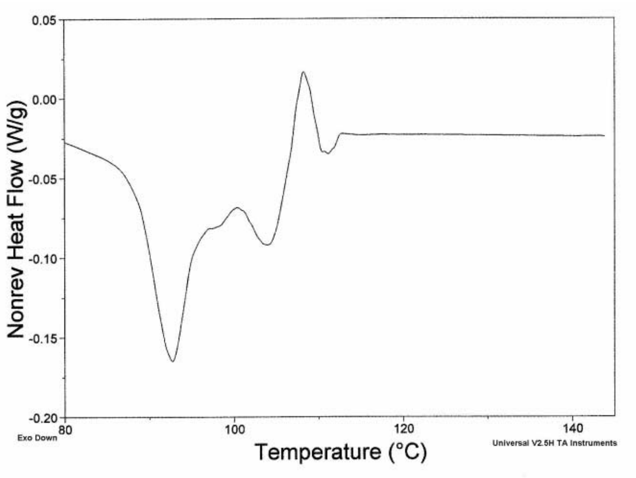
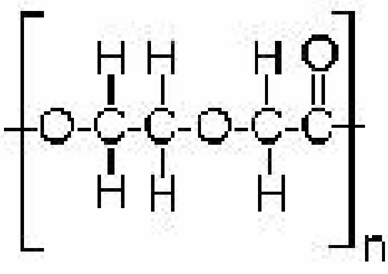


Fig. 3. MDSC non-reversing curve of PPD crystallized at 75°C for 60 min.

Two theories exist to explain the origin of multiple melting when crystalline polymers are heated in a DSC. Bell and Dumbleton [7] ascribed that the occurrence of two melting peaks is due to the melting of morphologically different crystal structures such as folded-chain crystals and crystals containing partially extended chains. Roberts [8], on the other hand, explained the occurrence of double melting in terms of recrystallization during melting, and consequently higher melting crystals. Further experimental evidence for this view was produced by Lemstra [9]. There are at least



$$\left[-O-CH_2-CH_2-O-CH_2-C(=O)-\right]_n$$

Fig. 4. Molecular structure of PPD.

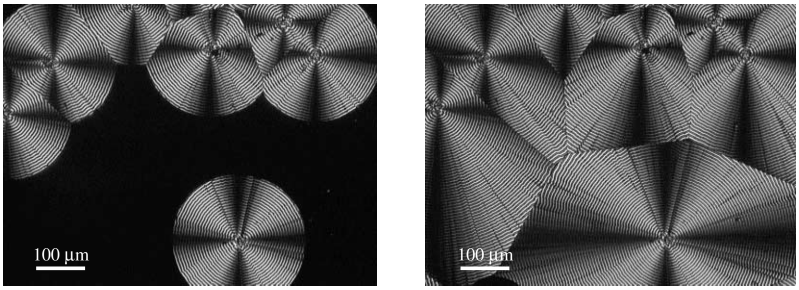


Fig. 5. Spherulitic morphology of PPD crystallized at 65°C. The magnification is 110 ×.

three ways to determine if the double melting behavior is due to recrystallization or melting of two different crystal structures. The first way is using different heating rates to determine if double melting behavior is for recrystallization. With increasing heating rate, the LM peak remains constant or increases a little at higher heating rates, but the HM peak decreases with increasing heating rate. The total heat of fusion remains approximately constant. The second way is by doing a partial scan. Comparing the two scans — the first one a full scan and the second one a scan recorded after the sample is heated beyond the LM peak and cooled down again — using exactly the same crystallization procedure, if the area of the HM peak of the second scan is equal to the sum of the areas of the LM and HM peak from the first one then there is recrystallization. The last method is a heat-only scan of a crystallized sample using the MDSC. If there is an exothermal effect in the non-reversing heat flow curve then recrystallization has occurred.

In this work, the last method was used to explain the origin of multiple melting, because MDSC is the latest and most simple method. The resulting non-reversing heat flow curve of a sample crystallized at 75°C for 60 min (Fig. 3), showed very strong multiple exothermic effects. The occurrence of double melting for PPD is the result of recrystallization. The constant temperature of the HM peak, 105°C is independent of T_c, can be explained as follows. When a crystal starts to melt, a continuous recrystallization and melting process takes place during the scan. At increasing temperatures, the rate of crystallization becomes low owing to a lower degree of supercooling, and the final result is a melting endotherm at a temperature independent of the original crystallization temperature of the sample.

The heat of fusion of 100% crystallized PPD was calculated using the additive group contribution method from van Krevelen [12]. This method is a very rough first approximation of how crystallinity strongly depends on the processing conditions. The value was calculated from the structure of PPD, described in Fig. 4, and the values of ΔH_m of each group are given in Table 1.

Table 1
Calculation of ΔH_m of PPD

Quantity	Group	ΔH_m of the group [12] (kJ/mol)	ΔH_m of PPD (kJ/mol)
3	$-CH_2-$	4	12
1	–O–	1	1
1	–COO–	−2.5	−2.5
			10.5

Since the base molecular mass of PPD is 102, this results in a value of 102.9 J/g for ΔH_m of PPD. The crystallinity for PPD was 69.1%. This value was calculated from the experimentally determined value for the heat of fusion (71.1 J/g) of the heat-only MDSC experiment (total heat flow curve) and divided by the van Krevelen value for 100% crystalline PPD (χ_cPPD = 102.9 J/g).

Fig. 5 shows some typical micrographs of spherulites of PPD crystallized at 65°C. The first picture shows the spherulites growing and the second one shows a space-filling crystallization, because the crystallization time was much higher. The real diameter of the spherulite at the bottom of Fig. 5a is 230 μm. The spherulites in both pictures show regular concentric rings. These bands might be caused by a periodical twisting of lamellae during crystallization [13].

4. Conclusion

The melting curves showed two melting endotherms, a HM peak at constant temperature of 105°C and a LM peak at temperatures depending on the crystallization temperature T_c. The LM peak temperature increased linearly with T_c, yielding an extrapolated value for the equilibrium melting temperature, $T_m^\circ$of 114°C. These two melting peaks were observed in the T_c range of 70–85°C. Above $T_c = 90$°C, the rate of crystallization is very low. The enthalpy of fusion of the crystalline phase of PPD, ΔH_{mPPD}, was 102.9 J/g and the crystallinity of the PPD, χ_c (PPD), was 69.1%. PPD presented a spherulitic morphology, with regular concentric rings, which might be caused by a periodical twisting of the lamellae during crystallization.

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