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STUDIES OF NON-ISOTHERMAL CRYSTALLIZATION AND MELTING OF ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE

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Abstract

The non-isothermal crystallization and melting of ultra high molecular weight polyethylene (UHMWPE) were observed by means of differential scanning calorimetry and compared with those of ordinary high-density polyethylene (HDPE). The crystallization temperature (T_c) and melting point (T_m) of UHMWPE were found to be higher than T_c and T_m of HDPE, and the latent heat of crystallization (ΔH_c) and fusion (ΔH_m) of UHMWPE are smaller than ΔH_c and ΔH_m of HDPE. The results were explained in terms of the theory of polymer crystallization and the structure characteristics of UHMWPE. The relationships between the parameters (T_c, T_m, ΔH_c and ΔH_m) and the molecular weight (M) of UHMWPE are discussed. Processing of the experimental data led to the establishment of four expressions describing the above relationships.

Keywords: crystallization, DSC, melting, ultra high molecular weight polyethylene

Introduction

Polyethylene (PE) with molecular weights over 700,000 is called ultra high molecular weight polyethylene (UHMWPE). As UHMWPE is similar to polytetrafluoroethylene (PTFE) in many ways, it is being increasingly used in various fields of material science and engineering. There is no basic difference between UHMWPE and PE in chemical composition; the M of UHMWPE is simply much higher than that of PE. In other words, the molecular weight is the main reason for differences between UHMWPE and PE. The relationships between the M of UHMWPE and its macroscopic properties are therefore very important. Because the melt viscosity of UHMWPE is so high, it does not possess a viscous state; UHMWPE is also insoluble. It is difficult to determine the M of UHMWPE by ordinary methods.

Polymer physics theory points out that the crystallization and melting of polymers are related to their M [1]. Suwa reported an expression describing the relationship between T_c and M of PTFE [2]. We have applied DSC in order to study the effects of M on the parameters of the phase transition of UHMWPE,

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and on the non-isothermal crystallization and melting of a series of UHMWPE samples with various *M*.

Experimental

The parameters of phase transition were measured on a Perkin-Elmer DSC-2C differential scanning calorimeter made in the U.S.A. A sample of 10 mg was heated from 300 to 450 K at a heating rate of 20 deg·min^{-1}. In order to eliminate the thermal history, each sample was annealed at 450 K for 20 min. It was then cooled to 300 K at a cooling rate of 10 deg·min^{-1}. The sample was next again heated up to 450 K at a heating rate of 10 deg·min^{-1}. The crystallization and melting curves were recorded with a TADS-3600 thermal analysis data station. Operations were carried out under anhydrous nitrogen.

Results and discussion

The curves of non-isothermal crystallization and melting of UHMWPE (M=1,500,000) and HDPE (M=216,000) are shown in Fig. 1.

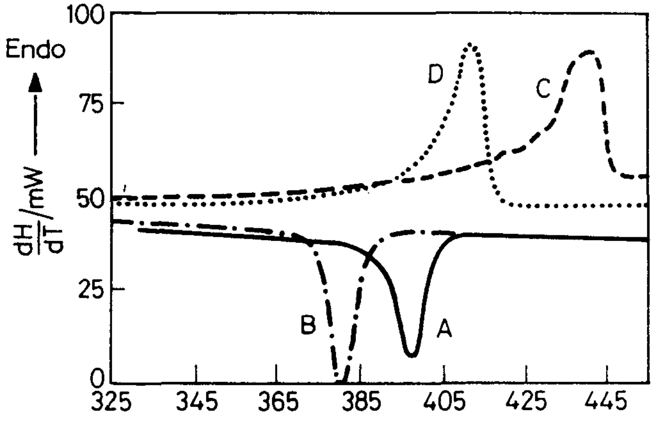

Fig. 1 DSC curves of non-isothermal crystallization and melting of UHMWPE and HDPE. A: crystallization curve of UHMWPE; B: crysatllization curve of HDPE; C: melting curve of UHMWPE; D: melting curve of HDPE

Figure 1 shows that the crystallization of UHMWPE exhibits the following characteristics: (1) the crystallization temperature is higher than that of HDPE; (2) the peak of crystallization is asymmetric. The crystallization of a polymer is a combination of "nucleation" and "growth" [3]. Since long chains of UHMWPE are apt to entangle, the chains can "freeze" and form crystal nuclei even at higher temperature, which leads to an increase in T_c. On the other hand, the crystal growth rate depends on the rate of chain movement. The longer the chain, the lower the moving rate. The asymmetry of the peak is due to the higher rate of nucleation and the lower rate of crystal growth. The results of studies on the crystal morphology of PE show that there is heteromorphism in PE [4]. The process of forming spherulites, dendrites and shish-kebab is called "secondary crystallization", which occurs subsequently and likewise causes asymmetry of the peak.

Figure 1 also reveals that the T_m of UHMWPE is higher and its melting peak is wider than those of HDPE. Melting is the reverse process of crystallization. It is necessary to supply more energy in order to destroy the complicated supermolecular structure of UHMWPE.

The crystallization and melting parameters (T_c, T_m, ΔH_c, ΔH_m and supercooling degree ΔT) are given in Table 1.

Table 1 Crystallization and melting parameters of UHMWPE samples

No.	1	2	3	4	5
$M\times10^{-4}$	58.2	86.7	105.3	125.8	150.1
T_c /K	386.1	393.9	397.2	400.6	402.5
T_m /K	410.7	412.3	413.4	413.8	414.6
ΔT /deg	24.6	18.4	16.2	13.2	12.1
ΔH_c /J·g^{-1}	106.8	97.1	90.5	85.9	83.4
ΔH_m /J·g^{-1}	119.5	103.6	96.4	91.5	88.3

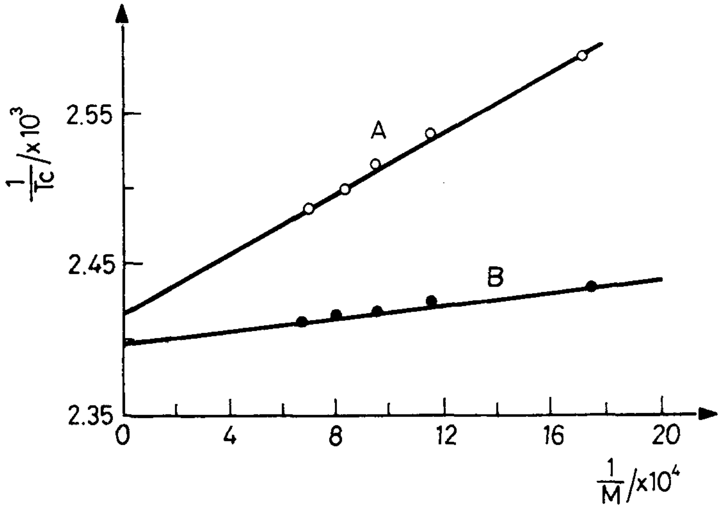

Fig. 2 Relationships between (1/*T*) and (1/*M*) for UHMWPE. A: (1/T_c) *vs.* (1/*M*); B: (1/T_m) *vs.* (1/*M*)

The data in Table 1 show that both T_c and T_m increase with increase of the M of the samples. Elias reported that the relationship between $(1/T_m)$ and $(1/M)$ for a homogeneous polymer is linear [5]. The relationships $(1/T_c)$ *vs.* $(1/M)$ and $(1/T_m)$ *vs.* $(1/M)$ for UHMWPE are plotted in Fig. 2.

Processing of the data in Table 1 yielded the following expressions describing the relationships between $(1/T_c)$, $(1/T_m)$ and $(1/M)$:

$$1/T_c \cdot 1000 = 2.419 + 10.08 \cdot 1/M \tag{1}$$

$$1/T_m \cdot 1000 = 2.399 + 2.14 \cdot 1/M \tag{2}$$

With Eqs (1) and (2), the T_c, T_m and ΔT of UHMWPE with infinite M can be calculated: they are 413.4 K, 416.8 K and 3.4 deg, respectively. It has been reported [5] that the equilibrium melting point of PE with infinite M and 100% crystallinity is 419.5 K. Figure 2 also shows that lines A and B are not parallel: the slope of A is nearly 5 times that of B. This means that the T_c of PE is more sensitive than T_m to M. The higher the molecular weight, the smaller the supercooling decrease in temperature.

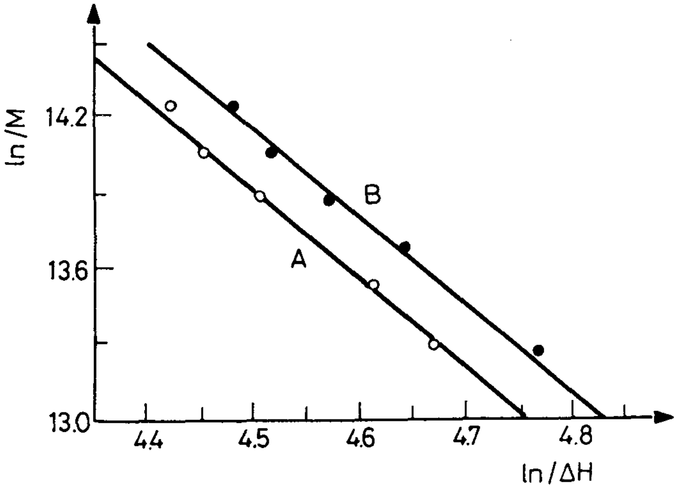

Fig. 3 Relationships between ln(Δ*H*) and ln(*M*) for UHMWPE. A: ln(ΔH_c) *vs.* ln(*M*); B: ln(ΔH_m) *vs.* ln(*M*)

The data in Table 1 show that both ΔH_c and ΔH_m decrease with increase of M. There are amorphous regions and crystal defects in the solid crystalline polymer, which lead to a decrease in the crystallinity degree. The longer the chain, the more evident this phenomenon. Suwa reported that the relationship between ln(ΔH_c) and ln(M) for PTFE [2] is linear. Processing of the data in Table 1 gave the plots for the relationships between ln(ΔH_c), ln(ΔH_m) and ln(M) (Fig. 3).

The expressions are represented by Eqs (3) and (4):

$$\ln(M) = 30.14 - 3.61\ln(\Delta H_c) \tag{3}$$

$$\ln(M) = 30.71 - 3.68\ln(\Delta H_m) \tag{4}$$

The four equations established in this paper permit measurement of the molecular weight of UHMWPE by means of thermal analysis.

* * *

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References

1 K. Kamide and K. Yamaguchi, Macromol. Chem., 162 (1972) 205.
2 T. Suwa and S. Machi, J. Appl. Polym. Sci., 17 (1973) 3253.
3 D. W. Van Krevelen, Properties of Polymers, Third, completely revised edition, Elsevier Science Publishing Company Inc., New York 1990, p. 129.
4 J. W. S. Hearle, Polymers and Their Properties, Vol. 1., Ellis Horwood Ltd., New York 1982, p. 234.
5 Hans-Georg Elias, Macromolecules I, Structure and Properties, Plenum Press Inc., 1977, p. 213.

Zusammenfassung — Mittels DSC wurde die nichtisotherme Kristallisation und das Schmelzen von Polyethylen mit ultrahohem Molekulargewicht (UHMWPE) beobachtet und mit der/dem von gewöhnlichem Polyethylen mit hoher Dichte (HDPE) verglichen. Für die Kristallisationstemperatur (T_c) und den Schmelzpunkt (T_m) von UHMWPE fand man höhere Werte als für T_c und T_m von HDPE und die Kristallisationswärme (ΔH_c) und Schmelzwärme (ΔH_m) von UHMWPE sind kleiner als die ΔH_c- und ΔH_m-Werte für HDPE. Die Ergebnisse wurden im Hinblick auf die Theorie der Polymerkristallisation und der Strukturmerkmale von UHMWPE gedeutet. Die Beziehungen zwischen den Parametern T_c, T_m, ΔH_c und ΔH_m sowie dem Molekulargewicht M von UHMWPE wurden diskutiert. Eine Auswertung der Versuchsdaten führte zur Erstellung von vier Ausdrücken, welche obige Beziehungen beschreiben.