

Study of the Fine Crystalline Structure of Polyethylenes via Annealing and Thermal Fractionation

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ABSTRACT: The fine crystalline structures of two polyethylenes have been investigated with annealing and fractionation techniques via modulated differential scanning calorimetry. The molecular structure and polydispersity of both high-density polyethylene and low-density polyethylene have been characterized by multiple-step annealing and successive self-nucleation/annealing thermal fractionation methods. The effects of annealing on the crystallinity and mechanical properties and the possible mechanism of the

formation of the different fine crystalline structures related to the macromolecular chain motion for the two polyethylenes have also been studied and analyzed according to detailed annealing and fractionation processes. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2686–2691, 2003

Key words: annealing; fractionation of polymers; structure; polyethylene (PE); differential scanning calorimetry (DSC)

INTRODUCTION

This work presents a study of the influence of annealing at a high temperature (near the melting point) on the fine crystalline structure of two polyethylenes (PEs). According to modulated differential scanning calorimetry (MDSC) data, annealing high-density polyethylene (HDPE) and low-density polyethylene (LDPE) at a high temperature results in a gradual increase in the thermal stability compared with that of the original metastable crystals. It can change the crystalline structure and properties of PEs significantly because it cannot only eliminate the remnant inner stress of the polymer but also upgrade the perfection of the crystalline structure, including the crystallinity and related mechanical properties.^{1,2} The most important advantages of annealing are its simplicity and convenience. With annealing, the crystallinity and crystalline structure of a polymer can effectively be changed and controlled to a certain extent.

MDSC analysis can be used to study the mechanism of the melting and recrystallization of polymers.^{3–5} In this study, it has been used to investigate the possible mechanism of the formation of the different fine crystalline structures of two PEs during single-step annealing. Higher mechanical strengths and higher crystallinities for the annealed sample are always obtained

(with respect to the original properties). The macromolecular chain branching structure of HDPE and LDPE has been characterized with multiple-step annealing and successive self-nucleation/annealing thermal fractionation. The results indicate that annealing is, in fact, a fractionation process.

EXPERIMENTAL

Materials

The characteristics of the materials used in this study, commercial products available from Qilu Petroleum and Chemical Co. (China), are listed in Table I.

Measurements

Differential scanning calorimetry (DSC) measurements

All the DSC measurements were performed with a TA MDSC2910 instrument (New Castle, DE) equipped with a refrigerated cooling system. The temperature was always calibrated with indium (156.6°C), and the heat-flow rate was calibrated with the heat of fusion of indium (28.71 J/g). The heat capacity constant was calibrated with sapphire. The heating and cooling rates were 10°C/min. The furnace was purged with dry nitrogen at a flow rate of 50 mL/min. MDSC experiments were performed at a basic heating rate of 5°C/min with an amplitude of $\pm 0.5^\circ\text{C}$ and a period of 40 s.

Measurement of the crystallinity (X_c). The basic equation for the calculation of X_c for PE via DSC is as follows:⁶

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TABLE I
Characteristics of Different PEs

Sample	$M_n \times 10^4$	$M_w \times 10^4$	M_w/M_n	T_m (°C)	$X_{X\text{-ray}}$ (%) ^b	X_{DSC} (%)
PE-1 (HDPE) ^a	1.1	19.6	17.8	124.9	61	59
PE-2 (LDPE)	1.6	9.5	5.9	105.9	37	39

M_n = number-average molecular weight; M_w = weight-average molecular weight; T_m = melting temperature.

^a Comonomer: but-1-ene.

^b $X_{X\text{-ray}}$: crystallinity measured with X-ray diffractometer. X_{DSC} : crystallinity measured with DSC. Test temperature; 25°C.

$$X_c = \frac{\Delta H}{\Delta H_{100}} \quad (1)$$

where ΔH is the integrated melting enthalpy based on the chosen baseline shown in Figure 1(a) and ΔH_{100} is the melting enthalpy of 100% crystalline PE (287.3 J/g^{7,8} in this study). X_c was calculated with software from TA Instrument Co.

Single-step annealing. A PE sample of about 5 mg was crimped into an aluminum pan. The sample was heated to 170°C and kept isothermal for 3 min so that the thermal history would be eliminated. Then, the temperature was lowered to 30°C, and crystallinity X_1 was measured. After the elimination of the thermal history again and the heating of the sample to the annealing temperature (T_a) for 10 min, crystallinity X_2 was measured. The thermal programs are shown in Figure 1(b).

*Successive self-nucleation/annealing thermal fractionation*⁹. A PE sample of about 5 mg was crimped into an aluminum pan. The sample was first heated rapidly to 170°C and kept there for 3 min so that the thermal history would be eliminated. After that, the temperature was lowered to 30°C, and the sample was reheated to the first predetermined annealing temperature (T_{f1}) and kept there for 60 min. The annealing steps were repeated at five different temperatures

(PE-1, $T_{fj} = 132, 129, 124, 120,$ and 110°C , and PE-2, $T_{fj} = 115, 110, 105, 100, 95^\circ\text{C}$), as shown in Figure 1(b).

X-ray diffraction measurements

A Philips wide-angle X-ray diffractometer (Eindhoven, The Netherlands) was employed, equipped with a graphite monochromatic instrument and a Cu anticathode (40 kV, 40 mA, scanning rate = 2.5°/min, $2\theta = 5\text{--}50^\circ$). The ambient temperature was 25°C. The crystallinity was calculated with a computer peak dividing program.

Stress-strain tests

Uniaxial stress-strain tests were carried out (Chinese standard testing method GB/T-1040-92) with a ZMG-250 testing machine (Germany) at 25°C and 50% relative humidity. The dumbbell-shaped samples were 115 mm long and 2 mm thick, and a 100 mm min⁻¹ crosshead speed was used.

Determination of the molecular weight and molecular weight distribution

The molecular weights of two PEs were measured in 1,2,4-trichlorobenzene by size exclusion chromatogra-

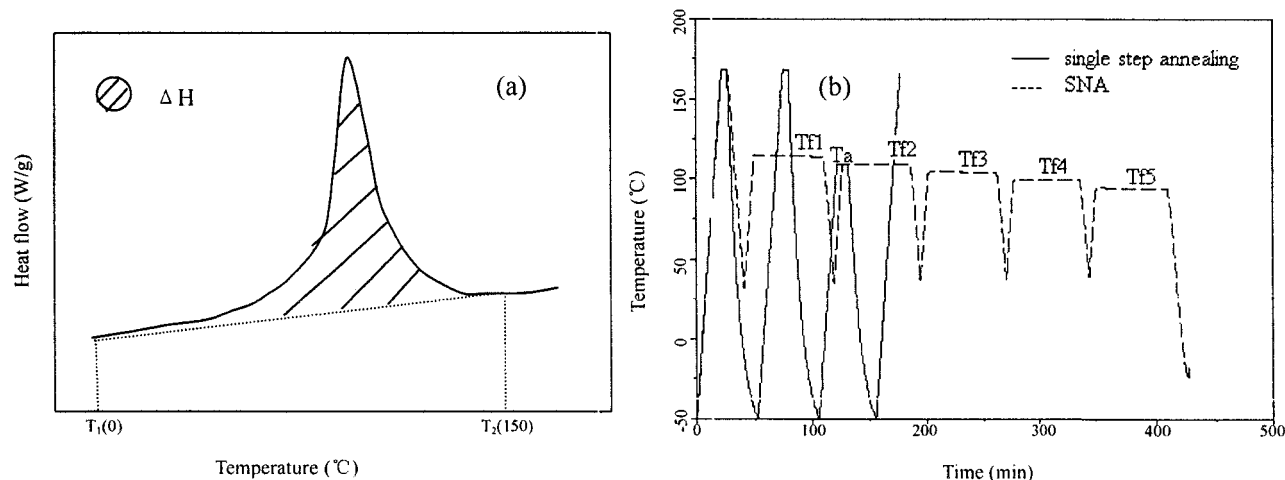


Figure 1 (a) Baseline connecting mode for crystallinity measurements and (b) schematic thermal programs for single-step annealing and self-nucleation/annealing (SNA) processes by DSC.

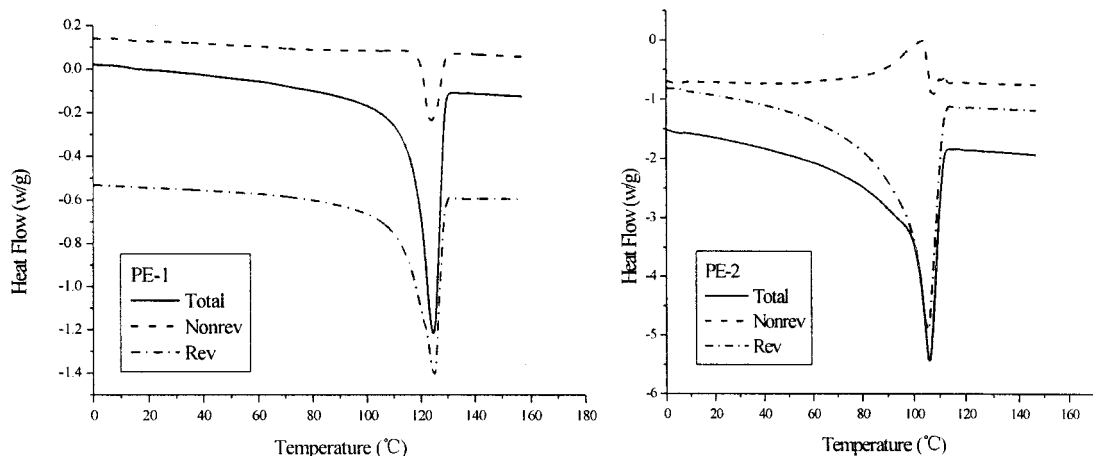


Figure 2 MDSC heating curves of original PE-1 and PE-2 samples.

phy (GPC-PL220, Shropshire, UK) calibrated with polystyrene standards. The flow rate was 1.0 mL/min at 160°C.

RESULTS AND DISCUSSION

Annealing mechanism studied by MDSC

Figure 2 shows the MDSC curves of original samples of PE-1 and PE-2. It shows marked differences in the reversing-, nonreversing-, and total-heat-flow curves for the two samples. For the PE-1 sample, the nonreversing-heat-flow curve presents a sharp endothermic melting peak, which indicates high crystallizability with a more perfect crystalline structure. For the PE-2 sample, the nonreversing-heat-flow curve shows a simultaneous crystallization process during melting, which may reflect low crystallinity with a less perfect crystalline structure.

Figure 3 shows the MDSC heating curves of PE-1 ($T_a = 120^\circ\text{C}$) and PE-2 ($T_a = 105^\circ\text{C}$) after single-step annealing for 10 min. Compared with the MDSC curves

of the originals in Figure 2, these total-heat-flow curves show new annealing melting peaks at about 118°C for PE-1 and at about 95°C for PE-2. From the nonreversing-heat-flow curves for both samples, we can see that there exist smaller exothermic peaks (1 and 2) after annealing, which is possibly a recrystallization process for samples during heating.¹⁰ Obviously, the thickness of these crystals, related to the annealed peaks, is less than that of other lamellar crystals related to the main melting peaks. Besides, compared with the temperatures from the original MDSC curves in Figure 2, the temperatures of the main melting peaks increase about 1°C after annealing; this result may imply that some smaller chain segments or defects have been excluded from the main lamellae during the melting and recrystallization and the isothermal thickening process.

During the melting of PE-2, there are two recrystallization peaks (2 and 3) in the nonreversing-heat-flow curve. These peaks may be related to the formation of differently sized crystals in the melting–recrystalliza-

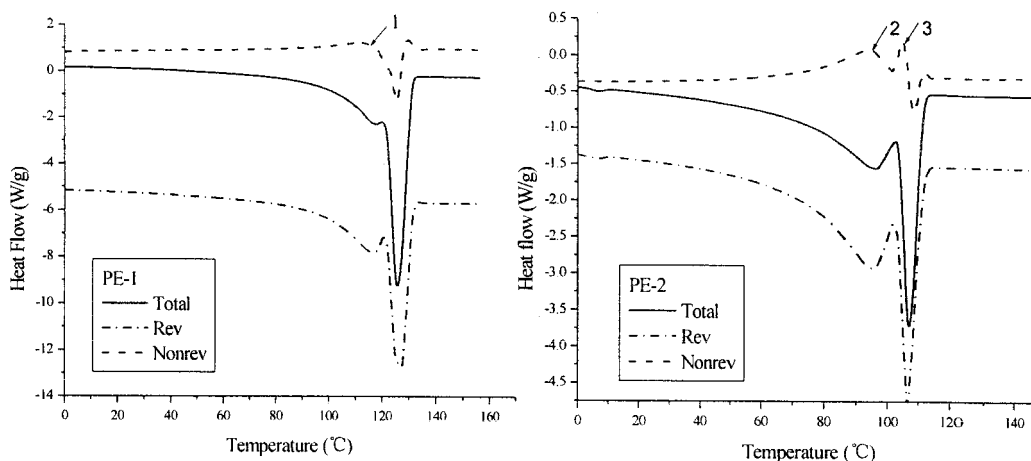


Figure 3 MDSC heating curves of PE-1 and PE-2 after annealing.

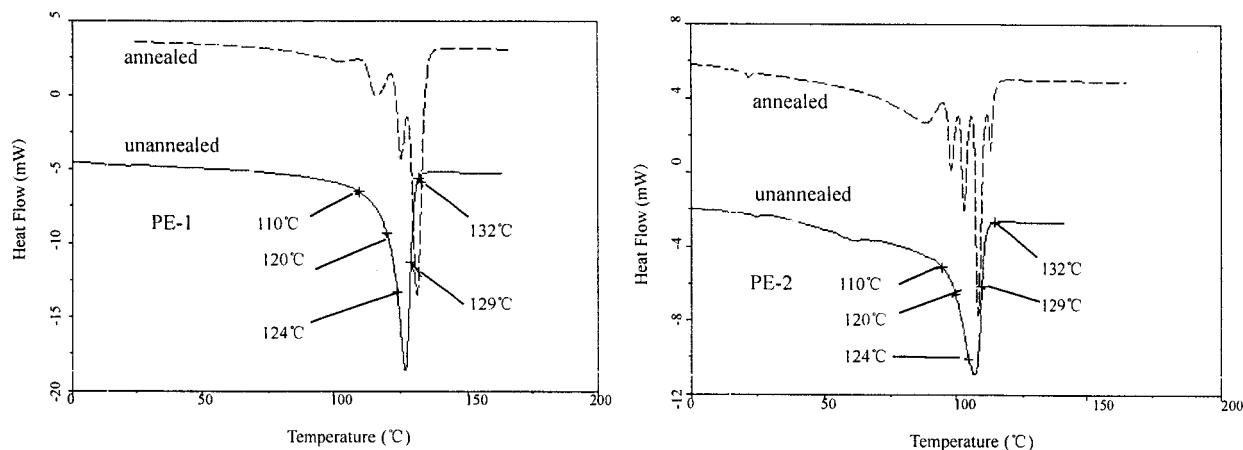


Figure 4 DSC heating curves of PE-1 and PE-2.

tion process and also indicate that there exist more irregular and branched molecules than found in PE-1. Usually, segregation, according to different chain segments, occurs with T_a and can form differently sized and perfect crystals during cooling. As some large irregular segments have long relaxation times and cannot or can only partially crystallize during cooling, the recrystallization occurs in another elevated temperature heating process. Therefore, the nonreversing-heat-flow curve for a PE-2 sample, representing recrystallization and melting, shows a less perfect crystalline structure feature with a relatively lower crystallinity.

Thermal fractionation behavior for two PEs

Successive self-nucleation/annealing thermal fractionation is a technique that can promote different structure units of PE to form a more stable equilibrium state during a crystallizing and melting process. After the segregation of samples based on different crystallizable ethylene sequence lengths (ESLs) via thermal fractions, relatively stable lamellar crystals are formed through the melting–recrystallization process according to T_a . Figure 4 presents the heating curves of PE-1 and PE-2 samples before and after annealing. Table II also shows the thicknesses of different lamellar crys-

tals calculated with the Thomson–Gibbs equation,¹¹ and the crystallinity percentage (W_f) for each fractionation peak related to the total crystallinity is also calculated and listed in Table II.

Evidently, multiple melting peaks of PE-1 and PE-2 can be observed after thermal fractionation. Because the highest T_a 's for PE-1 and PE-2 samples are close to their melting points, no annealing fractionation peaks occur under this temperature. The DSC curve for PE-2 shows five melting peaks related to their fractionation temperatures. For PE-1, there are only four, and no fractionation melting peak occurs between 120 and 124°C.¹² The crystallinity calculated with the lowest melting peak (88.7°C) for PE-2 accounts for 39.2% of its total crystallinity, whereas the crystallinity calculated with the highest melting peak (113.4°C) is only 7.4%. The results suggest the existence of a high concentration of irregular molecular structure units in the PE-2 sample; it may also be attributed to the greater amount of chain branching and shorter ESL unit in this sample. For PE-1, the crystallinity calculated with the peak of the highest melting point related to $T_a = 131.5^\circ\text{C}$ accounts for 49.6% of the total crystallinity, indicating to a good linear chain structure with a relatively large molecular weight.

TABLE II
Lamellar Thickness (L) Corresponding to Different Melting Peaks Calculated with the Thomson–Gibbs Equation

Sample	T_{mf} (°C)	102.85	116.15	—	125.26	131.52
PE-1	L (nm)	5.3	8.0	—	12.6	20.6
	W_f (%)	11.9	16.0	—	22.5	49.6
	T_{mf} (°C)	88.68	98.40	103.21	108.67	113.35
PE-2	L (nm)	3.8	4.7	5.3	6.2	7.2
	W_f (%)	39.2	12.1	15.7	25.6	7.4

Equilibrium melting point of PE crystal (T_m^0) = 141.4°C; $\Delta H = 287 \times 10^6 \text{ J/m}^3$; surface energy of PE crystal (σ) = $70 \times 10^{-3} \text{ J/m}^2$; density of PE crystal (ρ_c) = $1 \times 10^3 \text{ kg/m}^3$.

T_{mf} : melting point of fractionation peak.

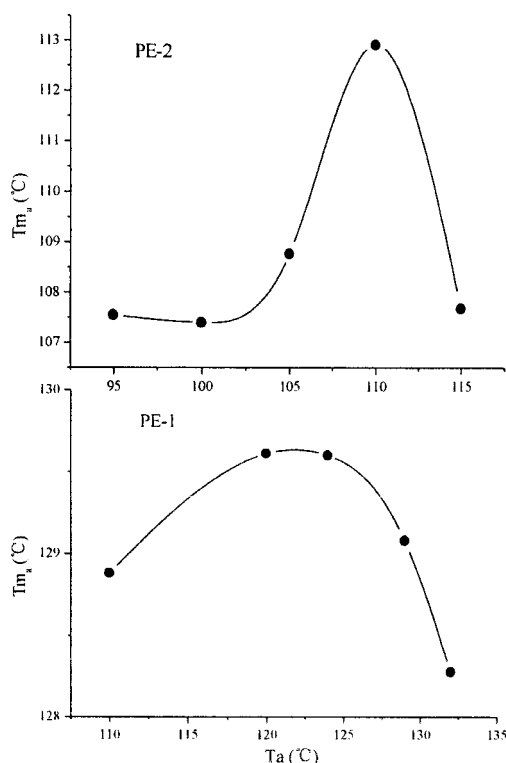


Figure 5 T_{ma} values of PEs after annealing at various T_a 's.

Effect of annealing on the crystallinity of PEs

Figure 5 shows the annealing melting point (T_{ma}) versus T_a of the main melting peak for samples of PE-1 and PE-2. Obviously, when samples are annealed in the temperature region slightly lower than the original melting point (called *domain I* in ref. 13), they show a slow increase in T_{ma} with an increase in T_a . The results may be involved in the melting and recrystallization and isothermal thickening for crystals due to incomplete melting.^{14–16} During annealing in the temperature region 3–5°C higher than the original melting point (called *domain II* in ref. 13), PE usually exists in a partially melting state; that is, the primary nuclei cannot be eliminated completely, and chain segments can crystallize on the surfaces of the remaining crystals. This is called the *self-nucleation effect*. On the basis of this effect, thinner lamellar crystals can be created, and so its T_{ma} can be lowered. Our data in Figure 5 also conform well with this conclusion.

Figure 6 presents the variation of the crystallinity of the two PEs before and after annealing. Usually for PE, a recrystallization process can be conducted during annealing, and the crystallinity can be increased.¹⁰ The results shown in Figure 6 indicate that the crystallinity of PE-1 increases up to 2% after annealing in the temperature range of 110–125°C for 10 min, and this suggests a fast recrystallization process in this temperature range. There is almost no alteration of the crystallinity for PE-1 annealed at about 3–5°C over its

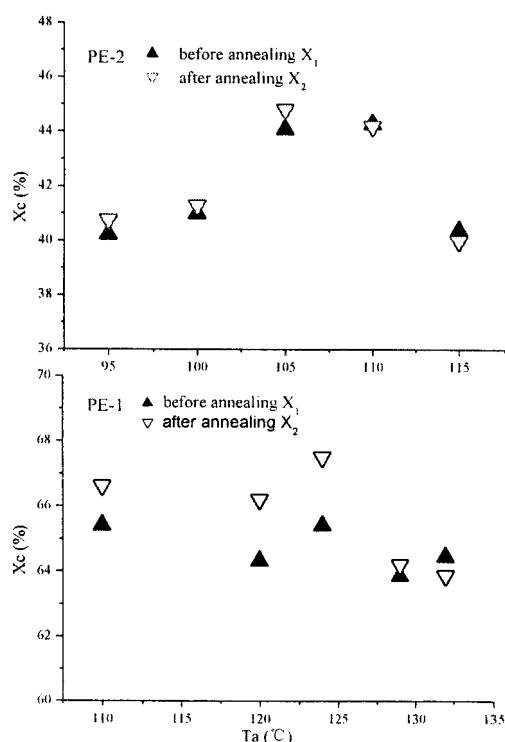


Figure 6 Changes in X_c values of PEs after annealing at various T_a 's for 10 min.

original melting point for 10 min because of the self-nucleation process. By contrast, the crystallinity of PE-2 increases by no more than 1% after annealing in the temperature range of 95–105°C for 10 min, and this indicates its relatively slow recrystallization character.

Effects of annealing on the tensile properties

Table III lists the values of the yield strength of PE-1 and PE-2 in accordance with the different T_a 's. The results indicate that the yield strength of PE can be improved effectively via annealing at about 2–10°C below the sample's melting point. It is well known that the physical properties of semicrystalline polymers are closely related to their crystalline structures; in particular, there exists an important relation between the yield strength of PE and its crystallinity.¹ As an annealing process can effectively reduce the mate-

TABLE III
Yield Strength (σ) of PEs After Annealing at Different Temperatures

PE-1 T_a (°C)	σ (MPa)	PE-2 T_a /(°C)	σ (MPa)
Raw	20.9	raw	9.0
110	22.5	95	9.3
120	24.1	100	9.9
124	22.9	105	9.4

Annealing time: 120 minutes.

rial's defects and increase the crystallinity, the yield strength of PE can be enhanced markedly.

CONCLUSIONS

An MDSC study indicates that annealing is a process that can cause molecular segregation in agreement with the different chain structures of PE, and so new annealing melting peaks occur during the successive heating of PE-1 and PE-2. The MDSC nonreversing-heat-flow curve clearly shows a PE-2 sample's double-recrystallization process after single-step annealing, and this suggests a more irregular and branching polydisperse molecular structure existing in this sample.

Annealing can affect the fine crystalline structure and crystallinity of PE significantly. Single-step annealing indicates that thicker lamellar crystals with more perfection, as well as higher melting points and higher crystallinities, can be obtained by annealing at a temperature 2–10°C lower than the sample's original melting point. For PE-1, after 10 min of annealing, the crystallinity can be increased markedly. However, PE-2 may not behave in the same way. The results of multiple-step annealing and thermal fractionation show that both samples have different chain sizes and branching contents. The yield strengths for both PE-1

and PE-2 can also be enhanced via an annealing process at a temperature near the melting point.

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