The Crystallization and Melting of Linear Polyethylene Studied by Temperature-Modulated SAXS and WAXD

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SUMMARY: Temperature-reversible and -irreversible morphological events could be separated in the case of linear polyethylene during quasi-isothermal crystallization by using simultaneous temperature-modulated synchrotron SAXS and WAXD. Crystallization and subsequent annealing was followed at 126 °C for 90 min while applying a temperature modulation with an amplitude of 1 °C and a period of 2 min. The crystal growth rate associated with the irreversible part of the crystallization decreases with increasing temperature in a cycle. The crystalline lamellae irreversibly thicken with time. The actual crystallite thickness, however, exhibits a superimposed modulation out of phase with that of the temperature modulation. Melting was studied during heating at 1 °C/min after cooling at 10 °C/min. A temperature modulation was superimposed with an amplitude of 2 °C and a period of 3 min. Once again temperature-reversible crystal thickness changes and irreversible crystal thickening could be observed.

Introduction

There is growing evidence for temperature-reversible melting and crystallization phenomena in semicrystalline polymers, based on temperature-modulated differential scanning calorimetry[1] (TM-DSC) experiments. The complex heat capacity (also referred to as the reversing heat capacity) measured by TM-DSC under quasi-isothermal conditions often displays an excess heat capacity superimposed to the baseline heat capacity[2-4]. This has been interpreted as being due to reversible melting and crystallization, which implies crystallization without the need for supercooling. This concept falls out of the realm of classic polymer crystallization theories which rely on nucleation concepts[5,6]. The mechanism of reversible melting and crystallization is not settled. The literature on the subject is rather speculative since the reversing excess heat capacity signal in TM-DSC does not provide any direct information about the morphological or molecular aspects of interest. The present paper sheds a light on this matter in the case of linear polyethylene (LPE). The structural changes during quasi-isothermal crystallization and during melting under typical TM-DSC conditions are reported. Temperature-reversible

morphological events are separated from irreversible ones. Simultaneous synchrotron wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) were used to meet this goal in conjunction with a high-brilliance synchrotron X-ray source (the X33 double focusing camera of the EMBL in HASYLAB, on the storage ring DORIS of the Deutsches Elektronen Synchrotron (DESY) at a wavelength of 1.5 Å[7]) to collect data at short sampling intervals during the rather fast-oscillating temperature programs.

Experimental

All measurements were performed on a linear polyethylene (DSM code JW1114), synthesized using a single-site vanadium-based catalyst, with a weight-average molar mass of 52 300 g/mol and a polydispersity (M_w/M_n) of 3.2.

The experimental conditions and the data processing procedures have been described earlier[8]. The WAXD data were analyzed to provide information on changes of the crystalline density, the crystalline fraction and the lateral dimensions of the crystals. SAXS data yielded values for the crystalline (T_c) and amorphous layer thickness (T_a), the long period (LP), the specific inner surface (O_s), the fraction of semicrystalline regions (α), the local (ϕ) and overall crystallinity. SAXS data processing involves the calculation and evaluation of the total scattering power or invariant (Q), of linear correlation functions ($CF(x)$)[9] and interface distribution functions ($IDF(x)$)[8], with x representing the distance in real space.

Crystallization and subsequent annealing was followed at 126 °C for 90 min while applying a temperature modulation with an amplitude of 1 °C and a period of 2 min. A Mettler FP82-HT controlled the temperature. Sets of successive frames of 20 s were recorded. One frame consisted of 14-s waiting time and 6-s acquisition time. A mini-shutter placed upstream from the sample was closed during the waiting periods. Melting was studied during heating at 1 °C/min between 80 °C and 140 °C after cooling at 10 °C/min from 200 °C down to 40 °C. A temperature modulation was superimposed with an amplitude of 2 °C and a period of 3 min. SAXS and WAXD patterns were collected consecutively every 6 s.

Results and Discussion

The findings associated with the quasi-isothermal crystallization experiment were discussed in detail in an earlier paper and can be summarized as follows[8]. Crystallization is mainly irreversible, i.e. the crystallinity progressively increases with time. The instantaneous crystallization rate, however, depends on the actual temperature: a decrease is observed with increasing temperature in a cycle. The lamellar crystals irreversibly thicken with time.

Superimposed to this overall thickening process, a small reversible change is observed out of phase with the temperature excursions, i.e. T_c slightly decreases with increasing temperature and vice versa. This activity at the fold surface of the lamellar crystals appears to be the key mechanism behind reversible melting and crystallization as observed by TM-DSC.

A similar observation can be reported for the TM-DSC-like melting experiment. Figure 1 displays the evolution of T_c and it also illustrates the used temperature program.
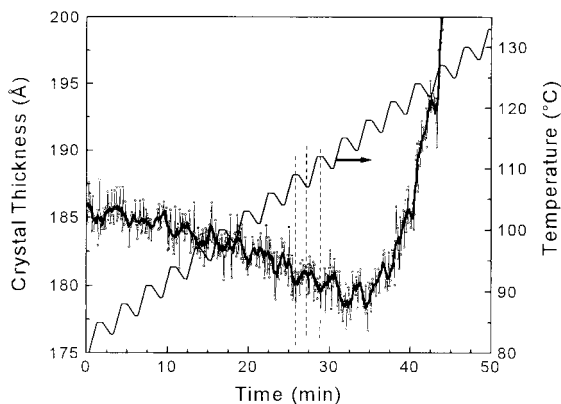

Figure 1: Evolution of T_c (small circles) during the melting of a linear polyethylene heated according to the temperature program illustrated by the oscillating full line. The thick full line represents a smoothing of T_c by a seven-point averaging. The dashed lines are guides to the eye.

An overall decrease in T_c of up to 35 min ($\pm$ 115 °C) can be observed with an additional small oscillation out of phase with that of temperature. This clearly illustrates the reversible character of fold surface melting and crystallization. At longer times (higher temperatures), the crystals start to thicken. This irreversible thickening is an annealing effect associated with the relatively long residence time at each temperature. After all, the underlying heating rate is only 1 °C/min. This thickening can be avoided by increasing the heating rate. Figure 2 shows the evolution of T_c as a function of temperature together with the evolution of T_c when heated at 10 °C/min without the application of a temperature modulation. In the latter case surface melting continues even beyond 115 °C and crystal thickening is not observed. Note that the irreversible thickening essentially occurs during the heating step of a temperature cycle. During subsequent cooling, T_c slightly decreases as expected for reversible fold surface activity.
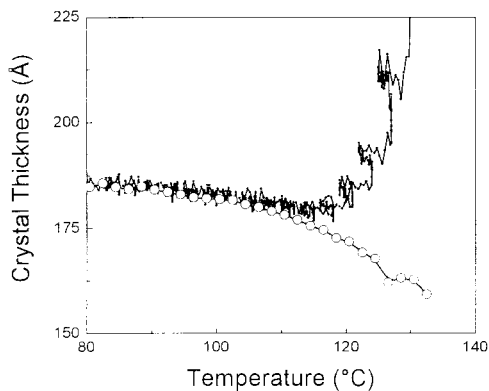
Figure 2: T_c data of Fig. 1 but plotted as a function of temperature (small connected closed circles). The large open circles represent the evolution of T_c when heated at a rate of 10 °C/min. Both samples where cooled to 10 °C prior to heating.

An analysis of the total scattering power reveals that when crystals start to thicken, there is some concomitant irreversible melting involved, which gains importance with increasing temperature.

Conclusions

The present data illustrate the metastable character of lamellar PE crystals. There is a tendency to gain stability by thickening during (quasi-)isothermal crystallization as well as during slow heating. This process takes time and competes with melting during heating. Because of this natural thickening tendency, complete (irreversible) melting cannot be the limit case of fold surface melting. In other words, a thinner crystal cannot be more stable than a thicker one. The limit temperature for stability of a lamellar crystal with a given thickness most likely follows the trend indicated by the well-known Gibbs-Thomson equation. Reversible fold surface activity (melting) in the case of linear polyethylene was recently associated with the temperature-dependent amount and distribution of gauche defects in the crystals[10].

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