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Short Communication

REVERSIBLE AND IRREVERSIBLE CRYSTALLIZATION IN HIGH-DENSITY POLYETHYLENE AT LOW TEMPERATURE

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Abstract

Reversible and irreversible crystallization and melting of high-density polyethylene at low temperature has been re-evaluated and is discussed in terms of the concept of the specific reversibility of a crystal. The concept of the specific reversibility links reversible and irreversible melting of a specific crystal such that reversible melting occurs only at slightly lower temperature than irreversible melting. In this study evidence for irreversible crystallization at low temperature in high-density polyethylene is provided, non-avoidable by primary crystallization and extended annealing at high temperature. The simultaneously observed reversible crystallization and melting at low temperature can be attributed to lateral-crystal-surface activity in addition to the well-established reversible fold-surface melting, dominant at high temperature, and evidenced by small-angle X-ray data available in the literature.

Keywords: DSC, polyethylene, reversible and irreversible crystallization and melting, specific reversibility of crystals, temperature-modulated DSC

Introduction

Reversible crystallization and melting is a unique feature of polymer crystallization since it has been identified in a rather large number of structures involving both flexible and rigid macromolecules [1]. The detection of truly reversible crystallization

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and melting requires sensitive measuring techniques like temperature-modulated differential scanning calorimetry (TMDSC) in order to follow the symmetric response of the structure to temperature-modulation. Pre-requisite for the quantitative evaluation of the reversibility by TMDSC is the correct calibration of the instrument with respect to asymmetry, temperature, heat-flow rate, and frequency, and the proof of true reversibility by independence of the reversing heat capacity on time and frequency [2–5]. The reversing heat capacity serves for calculation of an excess heat capacity which is due to the reversibly exchanged latent heat, and which is the basic result for subsequent structural interpretation.

The investigation of the temperature-dependence of the thickness of well-ordered lamellae in high density polyethylene (HDPE) by small-angle X-ray scattering (SAXS) suggested to address the reversible transition to the fold-surface of crystals [6, 7]. Despite direct observation of the reversible change of structure by SAXS there are no consistent data about the specific heat of the reversible transition at the fold-surface, ranging from 50 [8] to 100% [9] of the specific heat of the irreversible transition, which obviously requires further efforts to examine the exact quantity and nature of the reversible transition in HDPE. Alternatively, there are indications that the reversible transition in polyethylene of low crystallinity and in polypropylene occurs at the lateral surface of existing crystals involving segments of molecules which remain part of the crystalline phase after reversible melting, avoiding repeated crystal and molecular nucleation in the subsequent crystallization step [10–12]. The model of lateral-surface activity requires that the crystal core has a slightly higher melting temperature than the reversibly melting surface layers, and that the reversible process occurs only on active crystals which are close to the full-strand melting temperature [13]. Reversible fold surface-melting of a particular crystal, in contrast, is observed also at temperatures far below the temperature of irreversible formation or melting, respectively, and together with the absence of irreversible crystallization it would be possible to exclude lateral-surface activity for HDPE at low temperatures.

With the present investigation we intend to show that irreversible low-temperature-crystallization and melting cannot be avoided by variation of the conditions of primary melt-crystallization as was recently proposed [9]. The proof of irreversible crystallization also at low temperature is suggested to have impact on the structural interpretation of the re-examined excess heat capacity of HDPE, such that lateral surface activity as option for reversible melting cannot be excluded a priori for HDPE.

Experimental section

High-density polyethylene Lupolen 6011L from BASF with a mass-average molecular mass and polydispersity of about 125 kg mol^{-1} and 9.8, respectively [14], was used for the measurement of the excess heat capacity as function of temperature and as function of the history of crystallization. Films of about 200 μm thickness were prepared by compression-molding in order to optimize the heat transfer in the aluminum pan in subsequent thermal analysis. For each crystallization experiment we used virgin samples since repeated long-term melt-crystallization of a single specimen caused non-reproducibility of the melting behavior.

Samples were isothermally melt-crystallized at 398 K (experiment I), isothermally melt-crystallized at 398 K and annealed at 403 K (experiment II), or melt-crystallized on continuous cooling (experiment III). The isothermal crystallization at 398 K and high-temperature annealing at 403 K were performed for a period of 12 h each. An extension of the isothermal segments has no effect on the subsequently recorded data, despite even after 24 h crystallization at 398 K, and annealing at 403 K the structure is still not in equilibrium. The crystallization on continuous cooling was performed at a cooling rate of 10 K min^{-1}. After completed primary crystallization the samples were stepwise cooled to pre-defined annealing temperatures of 378, 358, 338, 318, and 298 K for quasi-isothermal detection of the reversing heat capacity after 120 min annealing. The crystallization histories were designed according to recent investigations, for maximum comparability of results [9].

Calorimetric data were collected on the differential scanning calorimeters DSC 7 (Perkin Elmer) and DSC 820 (Mettler–Toledo), both operated in combination with the liquid nitrogen cooling accessory. The furnaces were purged with dry nitrogen. The temperature was calibrated by the onset melting temperatures of indium, tin and zinc, and the initial calibration of the heat-flow-rate was performed using the heat of fusion of indium. The heat-flow-rate raw data were corrected for instrumental asymmetry and subsequently calibrated using sapphire as standard before conversion into heat capacities. For the quasi-isothermal determination of the reversing specific heat capacity we used a saw-tooth modulation of the programmed temperature with an amplitude of 1 K and a frequency of $2\pi/120$ rad s^{-1} in case of the DSC 7 [15], or $2\pi/240$ rad s^{-1} in case of the DSC 820 [16], respectively.

Results and discussion

Figure 1 shows the reversing apparent specific heat capacity of HDPE of different history of crystallization as function of temperature (symbols), the true heat capacity of crystalline and liquid polyethylene as listed in the ATHAS data base [17] (dashed lines), and the heat-capacity baselines of the different semi-crystalline preparations (continuous lines). The heat-capacity baselines were calculated on basis of the temperature-dependence of the enthalpy-based crystallinity which was obtained from the subsequent heating scan. The difference between the heat-capacity baseline and the reversing heat capacity is the excess heat capacity due to reversible melting. Crystallization on continuous cooling and stepwise annealing (experiment III) leads to a crystallinity of about 90% at 298 K. Isothermal crystallization at 398 K and stepwise annealing on cooling (experiment I) results in slightly higher value of about 95% at 298 K. The additional high-temperature annealing step at 403 K in experiment II does not affect the crystallinity at low temperature. The reversing heat capacity of the isothermally crystallized preparations is about 0.1 J g^{-1} K^{-1} lower than the reversing heat capacity of the continuously crystallized sample. The excess heat capacity decreases with decreasing temperature, however, even at 298 K we still observed an ex-

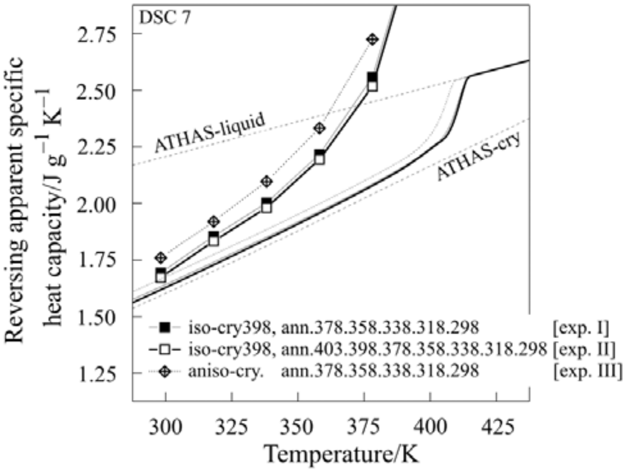

Fig. 1 Reversing apparent specific heat capacity of HDPE as function of temperature, obtained on stepwise cooling. Samples were crystallized isothermally at 398 K (filled squares), additionally annealed at 403 K (open squares), or crystallized on continuous cooling (crossed diamonds). The dashed lines are the heat capacities of liquid and crystalline polyethylene, and the solid and dotted lines are the heat-capacity-baselines of the semi-crystalline preparations

cess of about 0.06 and 0.1 J g^{-1} K^{-1} for the samples which were crystallized isothermally and continuously, respectively, before low-temperature annealing.

Figure 2 compares the reversing apparent specific heat capacity of experiments II and III of Fig. 1 with the subsequently detected total apparent specific heat capacity on heating at 20 K min^{-1} (lines without symbols). The apparent specific heat capacity obtained on heating is at all temperatures higher than was observed after annealing in the preceding cooling experiments. This is clear evidence that irreversible processes occur in the entire analyzed temperature range, i.e., even after extended isothermal crystallization at 398 K and subsequent perfection at 403 K, as performed with experiment II, occurs at low temperature secondary crystallization on cooling and irreversible melting/reorganization on subsequent heating. Further evidence for irreversible processes occurring at low temperature, regardless of the regime of primary crystallization, is given by the shallow annealing peaks which can be recognized after careful inspection of the temperature-dependence of the total heat capacity obtained on heating, or by direct monitoring of the annealing process in the time-domain.

Figure 3 shows the reversing apparent specific heat capacity during isothermal annealing at 318 and 298 K. The sample was isothermally crystallized and annealed at 398, 403 and 398 K, in the given sequence, with each step lasting 6 h, and further annealed on stepwise cooling at 378, 358 and 338 K for 2 h at each temperature. Data were recorded during all isothermal crystallization or annealing steps, respectively, however are in Fig. 3 only shown for the two lowest annealing temperatures. At all annealing temperatures we observed a clearly recognizable decay of the reversing

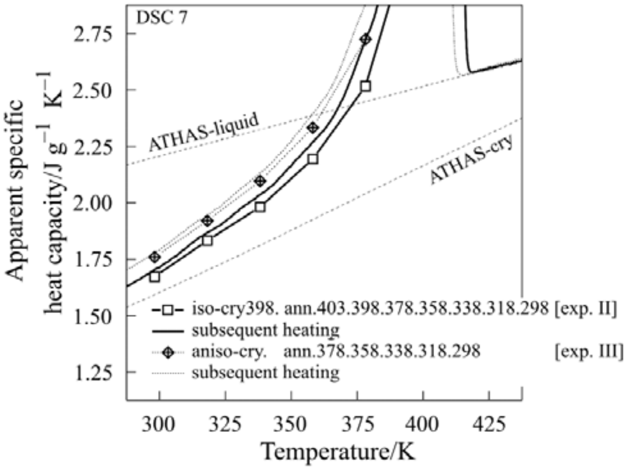

Fig. 2 Reversing apparent specific heat capacity of HDPE as function of temperature, obtained on stepwise cooling. Samples were crystallized isothermally at 398 K and additionally annealed at 403 K (open squares), and crystallized on continuous cooling (crossed diamonds). The continuous dotted and solid lines are the apparent specific heat capacity obtained on subsequent heating

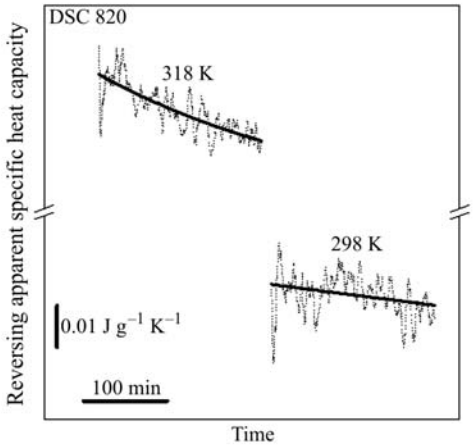

Fig. 3 Reversing apparent specific heat capacity of HDPE as function of time, obtained on isothermal annealing at 318 and 298 K. The sample was crystallized isothermally at 398 K for 6 h and annealed for 6 h at 403 and 398 K, respectively, and for 2 h at 378, 358 and 338 K, respectively

heat capacity *vs*. time which is further evidence for distinct irreversible secondary crystallization at low temperature. The annealing tendency gets weaker with decreasing temperature, however, is still evident at 318 and 298 K, respectively.

Conclusions

The regime of primary melt-crystallization of HDPE does not affect the crystallization behavior at low temperature, i.e., irreversible secondary crystallization at low temperature cannot be avoided by crystallization and perfection at high temperature. The irreversible low-temperature-crystallization is measured (a) by non-coincidence of the apparent heat capacity obtained on cooling and subsequent heating (Fig. 2), and (b) by non-constancy of the reversing heat capacity *vs*. time during isothermal annealing (Fig. 3).

Irreversible crystallization and melting in HDPE at temperatures lower than the primary crystallization temperature, in contrast, is not detected by SAXS, which was employed to classify the reversible process in HDPE as being solely due to fold-surface melting. Despite it is beyond the scope of the present study we may speculate that either fold-surface melting is only partially reversible, or that additional reversible processes occur in HDPE. Such an additional process could be reversible lateral-surface melting which was recently suggested as being the preliminary and inseparable stage of irreversible melting of polymer crystals [13], depending on the crystal morphology including the coupling of core and shell. The application of the concept of the specific reversibility of a crystal [13] suggests that a selected crystal may reversibly reduce its size by perhaps 2/3 before irreversible disappearance.

A comparison of the above presented data with the earlier data in the literature [9] shows reasonable agreement. The conclusions reached in the present research should apply, thus, also to the earlier work. Both data sets should be considered in generating a quantitative basis of further discussion of irreversible polymer crystallization and reversible melting.

References

1 B. Wunderlich, Progr. Polym. Sci., 28 (2003) 383.
2 B. Wunderlich, Thermal Analysis, Academic Press, Boston 1990.
3 M. Merzlyakov and C. Schick, Thermochim. Acta, 330 (1999) 55.
4 B. Wunderlich, Y. Jin and A. Boller, Thermochim. Acta, 238 (1994) 277.
5 A. Boller, Y. Jin and B. Wunderlich, J. Thermal Anal., 42 (1994) 307.
6 J. M. Schultz, E. W. Fischer, O. Schaumburg and H. A. Zachmann, J. Polym. Sci., Polym. Phys., 18 (1980) 239.
7 Y. Tanabe, G. R. Strobl and E. W. Fischer, Polymer, 27 (1986) 1147.
8 B. Goderis, H. Reynaers, R. Scherrenberg, V. B. F. Mathot and M. H. J. Koch, Macromolecules, 34 (2001) 1779.
9 T. Albrecht, S. Armbruster, S. Keller and G. Strobl, Macromolecules, 34 (2001) 8456.
10 R. Androsch and B. Wunderlich, Macromolecules, 33 (2000) 9076.
11 R. Androsch and B. Wunderlich, Macromolecules, 34 (2001) 5950.
12 B. Wunderlich, Macromolecular Physics. Crystal Nucleation, Growth, Annealing, Vol. 2, Academic Press, New York 1976.
13 R. Androsch and B. Wunderlich, J. Polym. Sci., Polym. Phys., 41 (2003) 2157.

14 Private communication, T. Schweizer, ETH Zürich, 2003.

15 R. Androsch, I. Moon, S. Kreitmeier and B. Wunderlich, Thermochim. Acta, 357–358 (2000) 267.

16 R. Androsch, J. Therm. Anal. Cal., 61 (2000) 75.

17 Advanced Thermal Analysis System; B. Wunderlich, Pure and Appl. Chem., 67 (1995) 1919; see also B. Wunderlich, Heat Capacity of Polymers, in S. Z. D. Cheng, Ed., Handbook of Thermal Analysis and Calorimetry, Vol. III, Elsevier Publ., New York 2002.