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Polymer Melting at an Equilibrium Temperature in a Zero Melting Range as well as Inter- and Intramolecular Stages of the Process

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SUMMARY

Our studies of ultra-highly oriented samples of polyethylene (PE) with a draw ratio up to 150 using the DSC technique have shown that polymer crystals likewise the crystals of other classes can melt at an equilibrium temperature within a zero melting range. The inter- and intramolecular stages of the melting process predicted theoretically by Flory have been confirmed experimentally.

INTRODUCTION

Melting of flexible-chain molecule crystals is believed to exhibit the following specific features (WUNDERLICH 1980, UBBELOHDE 1978):

1. A broad melting range ΔT_m amounting to several dozens of degrees;
2. Reduced melting temperatures $T_m < T_m^o$ where T_m^o is the equilibrium melting temperature corresponding to the zero entropy;
3. The predicted theoretically "two-stage" course of the melting process, i.e. the intermolecular disordering and the transition of the trans-conformation of the chain in the crystal into the molecular coil in the melt. This defines the inter- and intramolecular contributions to the enthalpy of fusion: $\Delta H_m = \Delta H'_m + \Delta H''_m$ (FLORY 1956). The temperature T_m^o has been experimentally achieved only for extended-chain crystals obtained by crystallization under pressure, for linear PE, in particular: $T_m = 413-414$ K at $T_m^o = 415 \pm 0.5$ K (WUNDERLICH 1980, SELIHOVA et al. 1977). However, melting of these crystals, as well as of highly oriented PE samples (SMITH and LEMSTRA 1980), occurred usually in the range of several degrees. As far as we know, the attempts to separate the melting process into the two stages mentioned above have failed; the multiplicity of melting peaks occasionally observed for polymer crystals was caused by their instability i.e. recrystallization and reorganization phenomena (WUNDERLICH and BAUR 1970).

We report in this paper that a clearly-fixed equilibrium melting temperature T_m^o at $\Delta T_m = 0$ can be registered and two stages of melting can be separately observed for polymer crystals using differential scanning calorimetry (DSC).

EXPERIMENTAL

Unique samples of ultra-highly oriented filaments of linear PE (SAVITSKY et al. 1983) with $M_w \approx 2 \cdot 10^6$ and a draw ratio λ up to 150 were used for experiments. The samples were prepared by spinning from a 2-wt.% solution of PE in decalin (SMITH and LEMSTRA 1980) with a subsequent drawing using the method that provided inhibition of the chain-degradation processes (ZHURKOV et al. 1969). At $\lambda = 150$, the filaments had the largest tensile strength and Young's modulus ($\sigma \approx 7$ GPa, $E \approx$ ≈ 144 GPa at 20°C, $\sigma \approx 9$ GPa and $E \approx 210$ GPa at -196°C), so far achieved for flexible-chain polymers, which did not differ much from the theoretical estimates for PE [$G_t \approx 12$-15 GPa (PEREPELKIN 1970), $E_t \approx 240$ GPa (SAKURADA et al. 1966) .

The experiments were carried out by means of a DSC-2 "Perkin- Elmer" calorimeter calibrated by the melting temperatures of indium (429.7 K) and water (273.1 K) and the heat capacity of sapphire. The values of T_m and $\Delta T_m = T_f - T_i$ (See Figs 1 and 2) obtained at a given heating rate v can be appreciably overestimated due to a thermal lag (at high v) or the structural instability of polymer samples (at small v), the error increasing in proportion to $v^{1/2}$ and sample mass m (ILLERS 1974). The true values of T_m and ΔT_m were, therefore, obtained from measurements at different scanning speeds $v = 0.3$-20 $K \cdot min^{-1}$ and m=const with a subsequent extrapolation of the obtained linear dependences of $T_m(v^{1/2})$ to $v = 0$. This method is known to give true values of T_m; for metals and paraffins, in particular, $\Delta T_m = 0$ (SELIHOVA et al. 1977, ILLERS 1974). The experimental error was ±0.2 K for T_m and ±0.5 cal/g for ΔH_m.

Measurements were carried out on isotropic PE obtained from a 2-wt.% solution in decalin or from the melt, and quenched from 430 to 290 K, as well as on PE filaments with a draw ratio $\lambda \approx 60$, 80, 100 and 150, which were 20–50 μm in diameter and 4 mm ($m_1 \approx 0.01$ mg) or 15 cm ($m_2 \approx 0.4$ mg) in length. Long filaments were studied both in a "free" (unconstrained) and restrained states including pressing into a capsule and reeling on an Al foil under a load of 10 g followed by ends restraint. In a number of experiments the filaments were placed into the Wood's alloy with $T_m = 346$ K to improve heat transfer.

RESULTS and DISCUSSION

The PE samples prepared from low-concentrated solutions have an improved ability to uniform crystallization and orientation. This is apparent from the draw ratio

λ = 150 obtained and from comparison of the melting parameters of the initial solution- and melt-prepared PE samples: while having the same $T_m \approx 402 \div 404$ K, the former melt in an appreciably more narrow temperature range $\Delta T_m = T_f - T_i$ (3K instead of 10K, see Figs. 1 and 2, curves 1 and 2) and their degree of crystallinity (70 ± 3%), as evidenced by DSC, is superior to that of the latter (40 ± 3%). Crystals in these isotropic samples are unstable; this is confirmed by strong T_m ($v^{1/2}$) deviations from linearity at low heating rates (Fig.2).

After drawing up to λ = 60 - 100 and 150 the degree of crystallinity increases from 70 to 80 and to 90 ± 3%, respectively. But the issue of major importance is that the melting behaviour of PE therewith becomes quite different. For instance, for a filament with λ = 150 a melting peak as narrow as 0.05K was observed for the first time, i.e. it was two orders of magnitude more narrow and two orders of magnitude higher than that normally obtained (Fig.1). The true melting parameters for this filament are (at v = 0): $T_m = 415 \pm 0.2\text{K} = T_m^0$ and $\Delta T_m = 0$, for a draw ratio of 60-100 $\Delta T_m = 0$ and $T_m = 414 \pm 0.2$K (Fig.2, curves 3 and 4).

We have found that at low heating rates v = 0.6 - - 2.5 K·min^{-1} the narrow melting endotherm of the filament (at $m_1 \approx 0.01$ mg) splits into two peaks, I and II, with 0.2 - 0.7° separation (Fig. 3, curves 1 and 2). For much greater mass of unconstrained samples or at higher heating rates, this splitting was not detected due to the peaks broadening (Fig.3, curve 3). At v→0 the two peaks coincide and, hence, the phenomena responsible for these peaks integrate into a single process.

The situation is different for heating long ($m_2 \approx 0.4$ mg) restrained filaments. If the sample is restrained non-uniformly (by pressing into a capsule) the DSC curve exhibits two additional peaks displaced towards high temperatures with respect to the initial one (Fig. 3, curves 4 and 5). If a filament with the restrained ends is used, there are only two latter melting peaks on the DSC curve (Fig.3, curve 6).

The occurrence of this doublet as well as of the melting doublet on the DSC curves for unconstrained filaments (Fig.3, curves 1 and 2) is not a result of the crystal instability. This is confirmed by a regular growth of T_m with the increasing heating rate (due to the thermal lag), a strictly linear behaviour of curves 3 - 6 in Fig.2, high T_m at v = 0 and a nearly constant relation between the peaks I and II areas for filaments with restrained ends, the heating rates being varied from 0.3 to 20 K·min^{-1}. It should also be emphasized that the restrained sample has two distinct true melting temperatures, i.e. 424.5 and 428 K, exceeding the equilibrium melting tempe-

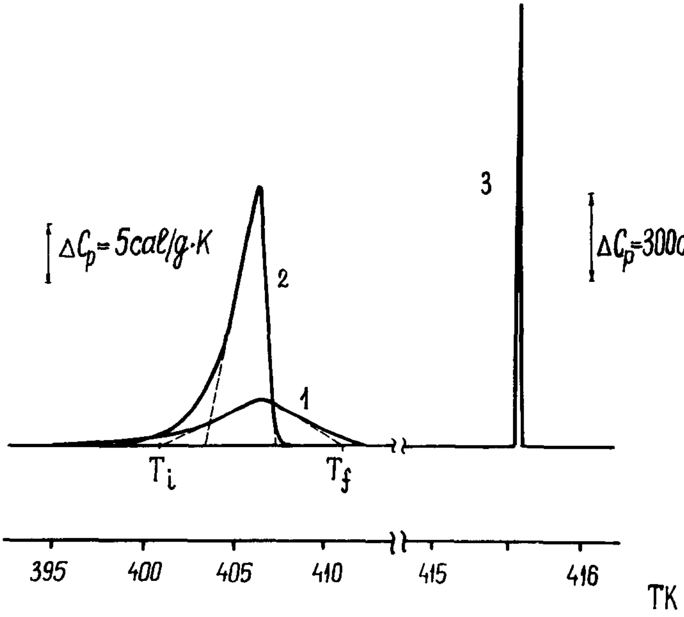

Fig.1. DSC-heating thermograms of linear PE prepared from the melt (1) or 2-wt% solution in decalin (2) and by drawing of the solution-spun filaments up to $\lambda \approx 150$ (3). Scanning speed is 0.3 K·min^{-1}.

rature T_m^o for PE crystals by 9.5 and 13K, respectively (see Fig.2, curves 5 and 6; at v = 0 $\Delta T_m = 0$).

The melting peaks I and II for short free and restrained filaments (Fig.3, curves 1, 2 and 6) turned out to be of the same physical nature. They correspond to two theoretically predicted (FLORY 1956) stages of melting, i.e. intermolecular disordering (with melting enthalpy $\Delta H_m'$) and transition of low-energy trans--chains into coils (with the intramolecular contribution to melting enthalpy due to T → G transitions $\Delta H_m''$).

Indeed, cessation of heating of free or restrained filaments after passing through peak I only (Fig.3) with their subsequent rapid cooling and visual examination indicates that, in spite of the fact that the major portion of the melting heat has been consumed ($\Delta H_m' > \Delta H_m''$), the filament retains its shape predetermined by the 60–150-fold drawing. After passing through melting peak II the molten filament contract by about its draw ratio, turning into a droplet. According to (WUNDERLICH 1980) the value expected for PE is $\Delta H_m'' < 0.25$ H_m. Indeed, for restrained filaments characterized by the most distinct separation of the two melting stages (by 3.5 K at v = 0, see

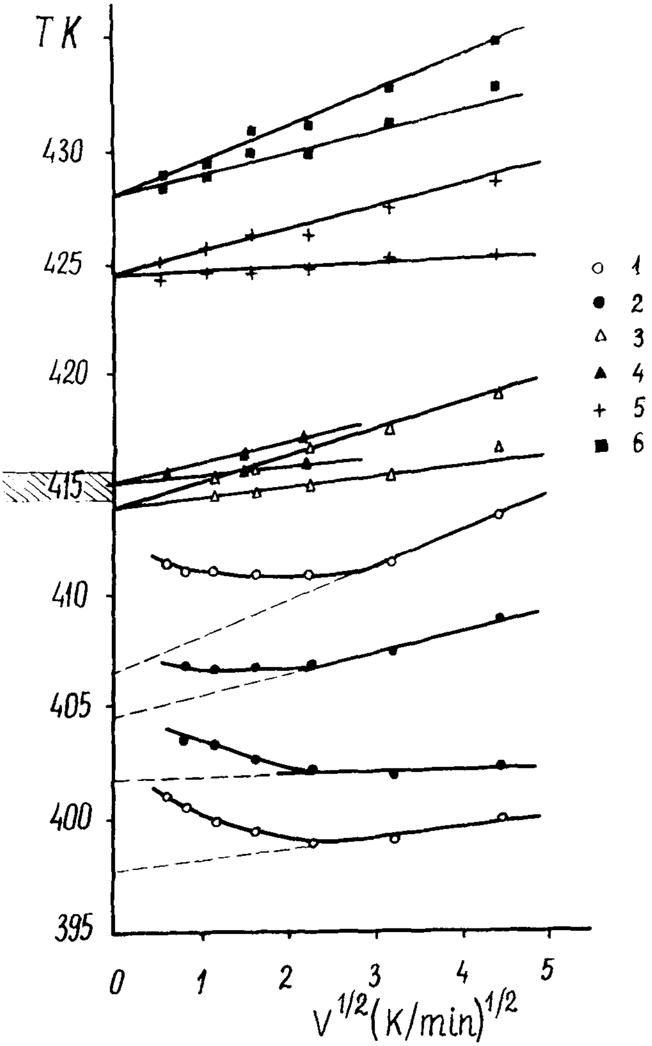

Fig.2. The initial and final melting temperatures (melting range $\Delta T_m = T_f - T_i$) of PE as functions of heating rate.
1 - quenching from the melt
2 - preparing from 2-wt% solution in decalin
3 - filament with a draw ratio $\lambda \approx 60 \div 100$
4 - ——..—— $\lambda \approx 150$
5,6 - ——..—— $\lambda \approx 80$, the filament ends are restrained, melting peaks I and II

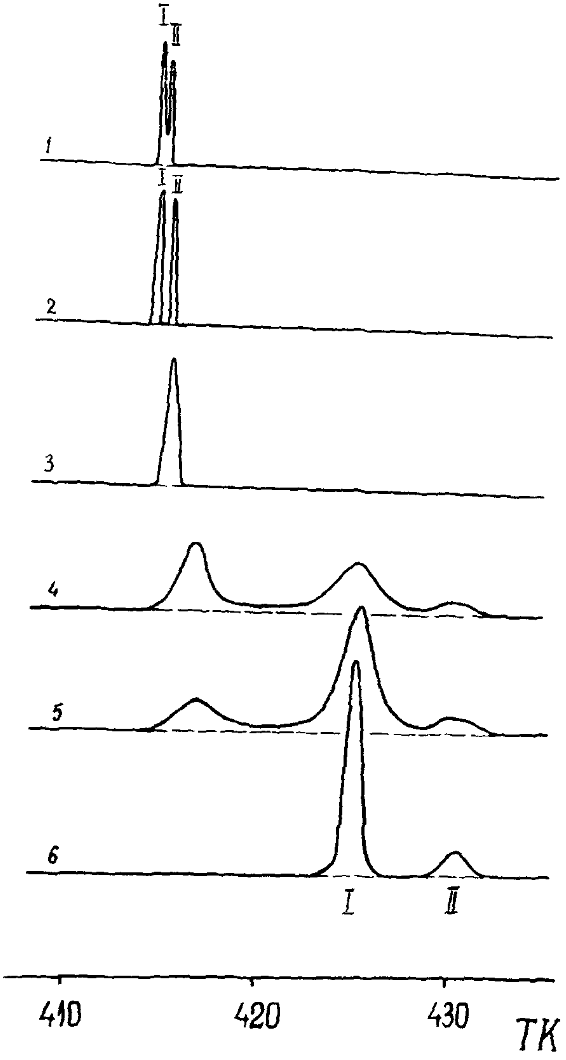

Fig.3. DSC-heating thermograms of linear PE filaments, $\lambda \approx 80$. Scanning speed is $1.25\ K \cdot min^{-1}$.
1,2 - unconstrained filaments of 4 mm in the length in nitrogen and Wood's alloy medium, respectively
3 - unconstrained filaments with a length of about 15 cm
4,5 - the filaments pressed into a capsule
6 - the filaments with the restrained ends

Fig.2), the peak II area related to $\Delta H_m''$ was $(0.15 \pm 0.03)\Delta H_m$.

The facts that the melting doublet for restrained filaments shifted towards higher temperatures* and the true T_m became higher than T_m^o are similar, in our opinion, to the T_m growth phenomenon in oriented polymers subjected to tensile loading (NOVAK et al. 1968, WUNDERLICH 1980). It is known that uniaxial extended-chain crystals (DADOBAEV and SLUTSKER 1981) and highly oriented PE samples (GODOVSKY 1982) are characterized by a negative thermal expansion coefficient along the macromolecular axis: $\beta_{\parallel} \approx -(1 + 3) \cdot 10^{-5} K^{-1}$. It is apparent that the heating of an ultra-high modulus restrained filament (E > 100 GPa) from 20°C to T_m without any noticeable stress relaxation should produce in the filament tensile stresses of the order of 100 MPa which significanty inhibit the melting of crystallites. It is obvious that the stress field has a more strong influence on the stage II of melting (See Fig.3).

Superheating of crystals up to temperatures $T > T_m^o$ is usually related either to the experimental technique (due to the thermal lag etc.) or to the reasons of physical origin; melting of free polymer samples is supposed to be inhibited by chains linking crystallites (WUNDERLICH 1980). However, it is evident from Fig.2 (curves 3 and 4) that the superheating effect does not exceed 2 + 5 K for ultraoriented PE samples with low mass $m \approx 0.01$ mg. Moreover, our experiments with PE samples of the same mass etched in nitric acid, the disordered component thus being removed (including tie chains), have shown that similar small superheatings take place in these samples too. This implies that the superheating effects for polymer crystals (unconstrained samples) at high heating rates have an experimental origin rather than a physical one.

The melting parameters obtained for the ultra-highly oriented filaments, their degree of crystallinity amounting to 90%, as well as the values of σ and E close to theoretical estimates permit to suggest that these filaments are characterized by a highly homogeneous crystalline structure and highly-oriented tie chains.

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[*] For a single (non-splitted) melting peak, the shift of T_m when restraining the ends of oriented polymer has been reported elsewhere (WUNDERLICH 1980, CLEMENTS and WARD 1982).

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