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Melting Kinetics in Polymers

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In polymers, it is possible to obtain single chain forming single crystals. It is feasible to melt these crystals by simple consecutive detachment of chain segments from the crystalline substrate and its diffusion into the melt. However, complication in the melting process occurs when the chain in the process of detachment from the surface is shared between different crystals. Experimentally, a clear distinction in different melting processes is observed, by the differences in the activation energies required for the consecutive detachment of chain segments or of segments having topological constraints. The consecutive detachment of free chain segments starts at the melting temperature predicted from the Gibbs-Thomson equation, whereas higher temperature or time is required if the chain has to overcome the constraints.

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Melting of solids can be described using a thermodynamic approach, where the melting temperature is defined as a first-order transition at the intersection of the Gibbs free energy of the solid and liquid state. The thermodynamic approach starts from equilibrium conditions and infinite sizes of both phases. For polymers these conditions are not fulfilled; there is no equilibrium, crystallization is not complete, and the crystal size is finite. Many semicrystalline polymers form lamellae crystals, which are 10–30 nm thick and at least 1 order of magnitude larger in the lateral direction [1,2]. The melting transition is not sharp, but covers a certain temperature range that is correlated to the thickness distribution of the lamellae, which has been quantitatively described by using the Gibbs-Thomson equation [3].

Melting in semicrystalline polymers can be highly complicated. Depending on the reorganization process of the amorphous and crystalline regions, which are connected by chains, the heating rate dependence on the melting temperature can be either positive or negative. For polymers where crystal thickening and/or crystal perfectioning is feasible, the measured melting temperature increases with decreasing heating rate [4]. On the other hand, in polymers where no such reorganization occurs (e.g., extended chain crystals), the measured melting temperature decreases with decreasing heating rate. The increase of the melting temperature with increasing heating rate is attributed to superheating [5], as well as thermal lag.

In this Letter, linear polyethylene, having number average molar mass greater than 1×10^6 is used [ultrahigh molecular weight polyethylene (UHMW-PE)]. The material as synthesized (nascent UHMW-PE) crystallizes during polymerization at lower temperatures into small crystallites, which thicken on annealing below the melting temperature to a maximum value of $l = 25$ nm [6,7]. The melting temperature predicted from the Gibbs-Thomson

equation [4] [$T_m = 414.2 - 259.7/l$] for that lamellae thickness is 131 °C [8]. These crystals melt, however, at 141 °C; such a high melting temperature is normally found for “chain-extended” polyethylene crystals which are extremely thick ($>1 \mu\text{m}$). Furthermore, the high melting temperature of 141 °C is lost on second heating where a melting temperature of 135 °C is measured [6]. These melting aspects involved in this polymer cannot be explained by existing thermodynamic concepts alone. Investigation of this unique melting behavior of nascent UHMW-PE leads to the presence of a new time dependent melting process. The findings are that if the sample is given sufficient time melting occurs at much lower temperatures, this cannot be explained by superheating [5] effects alone.

By controlled synthesis it is possible to vary the chain topology. For example, with high catalyst activity at high polymerization temperature an *entangled* UHMW-PE is obtained where the crystalline lamellae and the adjacent amorphous regions are composed of several *different* PE chains. On the other hand, with a single site catalyst at low polymerization temperature, it is possible to obtain *disentangled* chains, ultimately a single crystal formed from a *single* chain [9]. Independent of the polymerization conditions the nascent UHMW-PE crystals show a melting temperature of 141 °C. These materials, when crystallized from the melt, form crystals where a larger number of chains are shared between different crystallites, thus having a lower melting temperature of 135 °C [10]. To avoid the complexity of the melt crystallized material in this Letter, we address the nascent UHMW-PE only.

The difference in the entangled and disentangled material, having similar molar masses ($\sim 4.0 \times 10^6$ g/mol), is observed by solid-state deformation above the alpha relaxation temperature [11]. For example, at 125 °C, the disentangled sample presented in this Letter can be drawn more than 150 times, whereas the entangled sample only

7 times. Other methods to realize the entanglements in such samples are described elsewhere [9]. In the heating rate region of 20 to 0.1 K/min, a nonlinear relationship between the peak temperature and the heating rate of entangled and disentangled nascent UHMW-PE polymer is observed. The melting temperature, when plotted against the heating rate to the power 0.2, shows a linear relationship (Fig. 1). Similar observations are reported by Toda *et al.* [5]. The true melting temperature is determined by extrapolation to the zero heating rate. The shift in the observed melting temperature at nonzero heating rates is attributed to “superheating.” This superheating is caused (i) by thermal inertia (the transport of heat from the heater to the sample) and (ii) by time dependence of the melting process. Adopting this existing knowledge, the extrapolated, true melting temperature for these nascent polymers is 138.4 and 138.2 °C for our disentangled and entangled samples, respectively, (Fig. 1). Corresponding to the mentioned Gibbs-Thomson equation this melting temperature belongs to a crystal thickness of approximately 100 nm. The experimental observations are, however, that these crystals do not thicken more than 26 nm [7] even when the sample is left to anneal for several hours at 120 °C. Distinction between the entangled and disentangled polymers starts to feature with decreasing heating rates below 1 °C/min. At these low heating rates the disentangled sample shows two melting peaks whereas the entangled sample shows only one melting peak. This finding suggests an influence of the different chain topology on the melting behavior of the two polymers.

To get more insight in the melt mechanism, annealing experiments below the extrapolated, true melting temperature of 138.4 °C (Fig. 1) were performed with the disentangled nascent UHMW-PE. Using differential scanning

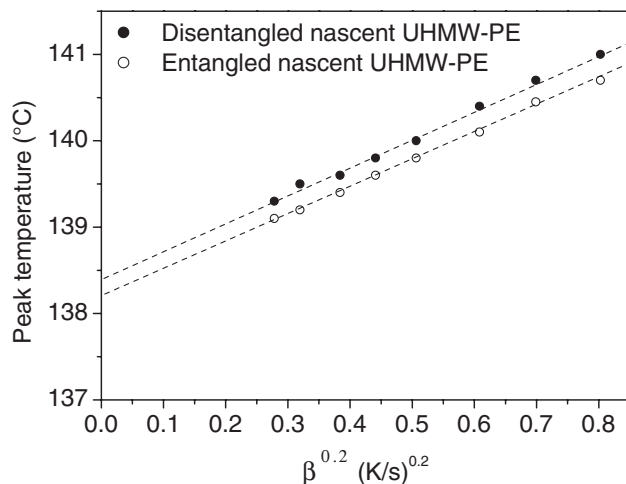


FIG. 1. The measured melting peak temperatures for entangled and disentangled nascent UHMW-PE at different heating rates β . The nonlinear abscissa allows extrapolation to zero heating rate. The extrapolation is needed to determine the true melting temperature.

calorimetry (DSC), the sample was kept for a certain time at annealing temperatures ranging from 132 to 138 °C. Next, the sample was cooled to room temperature and reheated (at 10 K/min) to 150 °C. Two melting peaks were observed at 135 and 141 °C, respectively, [Fig. 2(a), inset]. The peaks are associated with the melting of material recrystallized during cooling from the annealing temperature, and crystal domains in the initial state, respectively. The ratio between the areas of the two peaks changes with the annealing time at the given annealing temperature. In the annealing temperature region of 137.5–136.0 °C [Fig. 2(a)], an exponential decrease of the high temperature peak area, showing a first-order transition, is observed. Whereas Fig. 2(b) shows the existence of more than one time constant at annealing temperatures below

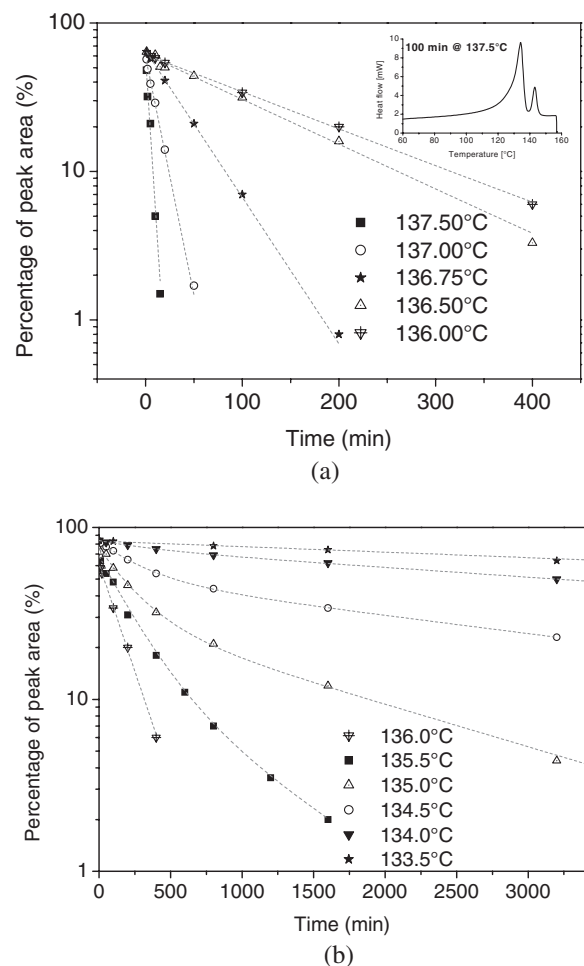


FIG. 2. The relative decrease in the area of the 141 °C melting peak of the disentangled nascent UHMW-PE with annealing time at different temperatures. (a) In the higher temperature region (136–135.5 °C) a first-order behavior with only one time constant for each annealing temperature is observed. Inset shows a DSC curve on heating a sample that was annealed for 100 min at 137.5 °C. (b) In the lower annealing temperature region (135.5–133.5 °C) for each annealing temperature at least two time constants exist.

136 °C, suggesting at least two different processes. Starting from a time law of Debye (Arrhenius) type for the fusion process in question, the enthalpy change reads $H(T, t) = H_0(T) \exp[t/\tau(T)]$, and the time constant (τ) can be related to an activation energy by $\tau = \tau_0 \exp(E_A/RT)$.

Figure 3 summarizes the relaxation times determined from Fig. 2 for the disentangled nascent UHMW-PE sample. Open symbols in the figure represent relaxation times for an entangled sample determined similar to the disentangled material shown in Fig. 2. For the disentangled sample only one single relaxation time exists above 135 °C, whereas below this temperature two relaxation times exist. Unlike in the disentangled sample, the entangled polymer shows only one relaxation time within the temperature range.

Three different slopes of the relaxation times are observed in the $\log \tau$ versus $1/T$ plot (Fig. 3), indicating involvement of three different activation energies in the two different temperature regions. The activation energies vary from 5000 ± 1000 kJ/mol [from (c)] for temperatures above 136 °C to 2100 ± 150 kJ/mol [from (b)] and 600 ± 50 kJ/mol [from (a)] for temperatures below 136 °C, respectively.

The presence of three activation energies suggests the involvement of three different melting processes in the disentangled nascent UHMW-PE. The measured activation energy can be assigned to detachment of the chain stem from the crystal surface, followed by the diffusion of the detached chain into the melt. The measured lowest activation energy of 600 ± 50 kJ/mol (a) can be assigned to the detachment of a chain segment of ~ 28 nm (this has been calculated considering the activation energy for detachment of a single CH_2 group and its diffusion into the melt, 2.7 kJ/mol and the C-C distance in the orthorhombic

lattice along the c axis 0.127 nm) [12]. This equals roughly one chain (stem) at the lateral surface of the lamellar crystal. The activation energy of 2100 ± 150 kJ/mol (b) then refers to the simultaneous detachment of three stems from the crystalline substrate and their cooperative diffusion and that of 5000 ± 1000 kJ/mol (c) refers to the breakdown of the crystal by simultaneous randomization of at least 7–8 stems. The low activation energies determined from the slopes (a) and (b) suggest the involvement of a new melting behavior, whereas the slope (c) refers to the conventional melting at higher temperatures.

Contrary to the disentangled polymer, the entangled polymer exhibits the absence of the process leading to slope of (a), suggesting the absence of melting with consecutive detachment of single chain stems from the crystalline substrate. The differences within the slopes of (b) and (c) of the entangled and disentangled samples are similar, which indicate that melting of the entangled sample occurs in clusters of several chain stems. For the entangled sample such melting [slope (b)] may arise because of the topological constraints.

The melting phenomenon similar to the disentangled nascent UHMW-PE can be obtained with the entangled nascent UHMW-PE on crystallization from solution (for example 1 wt. % of UHMW-PE in decalin). Crystals thus obtained are disentangled and have been investigated in detail [13]. Similar to the disentangled nascent UHMW-PE the solution crystallized sample can also be drawn more than 150 times in the solid state (at 120 °C), suggesting the presence of a disentangled amorphous region. Unlike the disentangled nascent UHMW-PE, the solution crystallized samples show regular stacking of crystals favoring crystal thickening [13]. To investigate the implications of these morphological differences on melting, experiments similar to those with the nascent UHMW-PE on the solution crystallized UHMW-PE are summarized in Fig. 4.

Figure 4 shows the enthalpic relaxation times for the solution cast films at different temperatures. In the explored temperature region, similar to Fig. 3, two distinct slopes (a) and (c) are observed. Slope (a) refers to the activation energy of 700 ± 50 kJ/mol (i.e., the energy required for the detachment and diffusion of chain stems of approximately 30 nm length) a value in accordance with the measured crystal thickness prior to the melt [13]. Slope (c) refers to the activation energy of 4200 ± 1000 kJ/mol, a value comparable to that of the nascent UHMW-PE. This large activation energy is again associated to the breakdown of the crystal lattice. The absence of the slope (b) in Fig. 4 suggests that within the temperature region of 128 to 130.5 °C the melting in these solution cast films mainly occurs by removal of single chain stems from the crystal substrate.

Since slopes (a) and (c) in Figs. 3 and 4 are similar and crystal thicknesses are comparable, this suggests that the activation energy required for the respective processes,

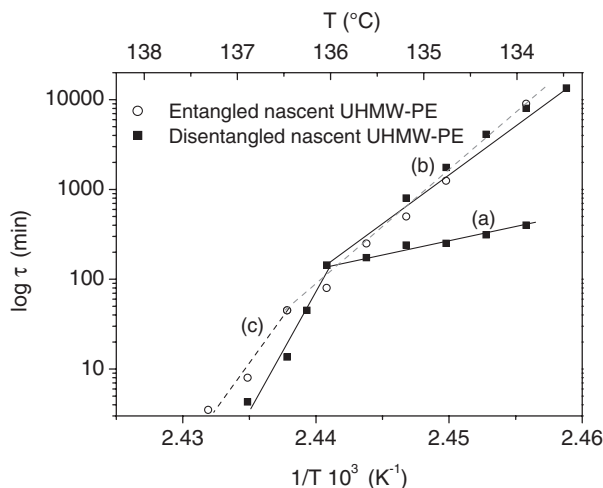


FIG. 3. Arrhenius plot of the time constants determined from the slopes of the curves in Fig. 2 for the entangled and disentangled nascent UHMW-PE. The activation energies of the involved processes follow from the different slopes of the plotted fit curves in the figure.

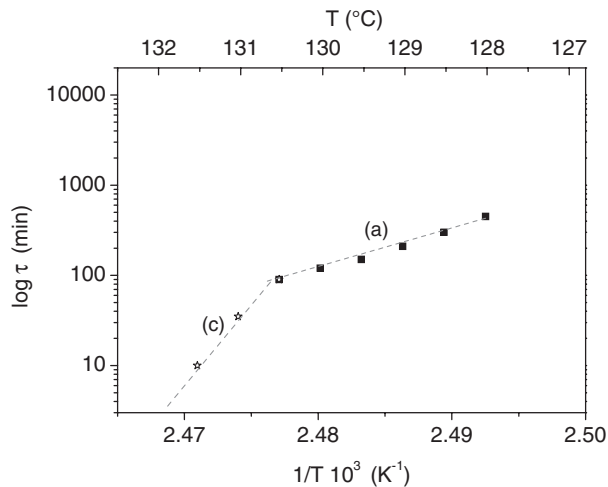


FIG. 4. Arrhenius plot for solution crystallized UHMW-PE samples. The different relaxation times at the given annealing temperatures (determined from a plot similar to Fig. 2) show two activated processes. The activation energy can be determined from the slopes.

namely, the removal of single chain stems from the surface followed by its diffusion in the melt [slope (a)] as well as the breakdown of larger parts of the crystal lattice [slope (c)], occurs independently of the morphological distinctions in the two samples.

However, the temperature regions where these melting processes occur in solution crystallized films are shifted parallel by nearly 5 K along the temperature axis, compared to the nascent material. To quote, a similar difference in the melting temperature of crystals of the same thickness is observed for alkanes and linear polyethylenes. For example, the melting temperature of alkanes of 25 nm thickness is 127 °C, whereas the melting temperature of linear polyethylene of similar thickness is 131 °C. This can be explained because of the differences in the topological constraints and the differences in the surface free energies. For example, in alkanes there are no entanglements, and the chains are always extended if the number of CH₂ units is less than 140.

From the series of experiments reported here it is evident that melting of the nascent and solution crystallized UHMW-PE samples shows distinction in the melting processes at the two different temperature regions, low and high. Melting in the low temperature region occurs by cooperative detachment of chain stems from the surface invoking a time dependent melting process, whereas melting in the high temperature region leads to a breakdown of larger parts of the lattice. The melts obtained from the two temperature regions show a remarkable distinction in the distribution of the topological constraints in the melt [9]. Reported observations in this Letter have implications in our understanding of the melting behavior of polymers in general and are not limited to UHMW-PE only. These

findings are further supported by solid-state NMR performed on the melting behavior of the entangled and disentangled nascent UHMW-PE, as described in the supplementary material [14]. To summarize, during melting the entangled polymer the amorphous phase can be described by a single relaxation time, whereas in the disentangled polymer two relaxation times are required, suggesting the involvement of two different melt processes. The resultant melt state lead to different rheological behavior as described elsewhere [9].

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