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ANALYSIS OF REVERSIBLE MELTING IN POLYTETRAFLUOROETHYLENE

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The reversibility of crystallization and melting of polytetrafluoroethylene (PTFE) has been investigated as function of crystallization conditions and temperature by temperature-modulated differential scanning calorimetry (TMDSC). The total and average specific reversibility of the melt-crystallized PTFE is considerably larger than in case of as-polymerized powder. This experimental observation must be attributed to different coupling between crystallized sequences of the molecules within the globally semi-crystalline superstructure. The crystallinity of as-polymerized PTFE is close to 100%, and the crystals melt in a narrow temperature interval close to the equilibrium melting temperature. Melt-crystallized PTFE, in turn, shows a crystallinity of about only 40% and melts at lower temperatures. The morphology of the melt-crystallized PTFE allows molecule segments to melt and crystallize reversibly as a function of temperature. The extended-chain conformation, evident in as-polymerized powder, inhibits reversible melting due to required molecular nucleation after complete melting of a molecule. The experimental findings are discussed within the framework of a similar investigation on polyethylene of different crystal morphology and support both the concepts of lateral-surface activity and molecular nucleation.

Keywords: *DSC, polytetrafluoroethylene, reversible and irreversible crystallization and melting, specific reversibility of crystals, TMDSC*

Introduction

Reversible crystallization and melting of polymers

Crystallization of polymers from the nuclei-free melt is an irreversible process and can be recognized by the need for super-cooling the melt for formation of a stable crystal, i.e., crystal nucleation is required [1–3]. Furthermore, it was shown by specially designed experiments on polyethylene that the existence of a stable interface between crystal and liquid may not be the only pre-requisite for the crystallization of macromolecules. Macromolecules need to be in a state of a lower local entropy before an attachment of molecule segments to an existing surface is possible, in contrast to e.g. metals or small molecules. The local decrease of the entropy of a molecule before crystallization is synonymous to molecular nucleation, which, however, is not quantified yet, i.e., the required super-cooling for overcoming the energy-barrier is unknown [4–6].

Reversible crystallization of polymers requires absence of any nucleation steps within the framework of possible experimental registration, and must therefore reflect a local equilibrium within the overall, global semi-crystalline structure. Several local equilibria were suggested to explain experimentally observed reversible crystallization and melting: (a) insertion–crystallization at the growth front of lamellae, which are located between at higher temperature formed and curved lamellae in low-density polyethylene, controlled by temperature and the distribution of defects in the melt at the growth front [7, 8], (b) crystallization of short sequences of molecules in the restraint melt between lamellae, to form fringed micelles [9, 10], (c) fold-surface melting of lamellae in high-density polyethylene as consequence of a force-balance between the recovery tendency of loops on heating and thickening tendency of lamellae on cooling, adjusted by chain-sliding diffusion [11, 12], and (d) reversible lateral-surface melting as preliminary and in-

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separable step of irreversible melting due to a gradient of the local morphology of a crystal, i.e., different coupling of the outer and inner regions of a crystal to the surrounding liquid [13, 14]. For polytetrafluoroethylene (PTFE) only the latter two models, i.e., fold-surface melting of lamellae, and lateral-surface melting, need to be considered since the insertion–crystallization and formation of small bundle-crystals from the restraint melt can be excluded as mechanisms of reversible melting due to the non-existence of defects/branch-points along the chain. Reversible fold-surface melting and lateral-surface melting are not contradictory alternatives for explanation temperature-reversible changes of the structure of polymers, rather than parallel occurring mechanisms. Reversible fold-surface melting is a process which mainly is evident in polymers with ability of molecules for chain-sliding diffusion through the crystal, and was proven for linear polyethylene [15–19], and poly(ethylene oxide) [19, 20] by small-angle X-ray scattering. Lateral-surface melting we consider as general mechanism of reversible melting, and as being the preliminary part of irreversible melting, largely depending on the crystal morphology, in particular the structure of the fold-surface/basal plane [21]. Despite direct evidence for lateral-surface melting by microscopy or X-ray scattering is not available yet, a large number of experimental indications for supporting this concept were collected. Most striking is the huge fraction/amount of reversible melting in short-chain branched ethylene-copolymers without capability for chain-sliding diffusion due to non-existence of the required specific fold-surface structure [22–24]. Recent work on polyethylene of different molar mass, including paraffins, lead to a consistent model about the effect of chain length and crystal morphology on reversible melting, employing the concept of molecular nucleation [25–27]. In the presence of nuclei is crystallization and melting completely reversible if the all-*trans* chain length is less than about 100 Å. Crystallization and melting is then similarly nucleation controlled as in the case of metals [28]. At these chain lengths below 100 Å extended-chain crystals are evident, which, however, are short enough that molecular nucleation is not necessary to reverse the phase transition on temperature oscillation. If the molecule is longer than 100 Å, super-cooling is required to reverse the melting process, even in presence of primary crystal nuclei. This experimental finding is attributed to the need for molecular nucleation. The reversibility of melting is zero as long as extended-chain crystals are the dominant crystal morphology. Melting of an extended-chain molecule occurs always complete, i.e., once the molecule is detached from the crystal, molecular nucleation is required to permit recrystallization [27]. At a chain length longer 380 Å, the extended-chain crystal morphology is usually replaced by a folded-chain crystal morphology [29–32]. Supercooling and molecular nucleation are still necessary to revert the process of complete melting of a molecule. At the same time the reversibility of melting increases due to the largely increased probability of simultaneous existence of the macromolecule in the crystalline and amorphous phases. In other words, if a stem at the lateral surface of a crystal is melted, other parts of this particular macromolecule may remain in the crystal and are, even if partially melted, in a state of lower local entropy, minimizing the energy barrier for subsequent crystallization on lowering the temperature.

In the present work we attempt to strengthen the experimental results about the influence of the crystal morphology, i.e., of the coupling of the crystalline and amorphous phases on the reversible fraction of the melting process. An appropriate polymer for such an analysis is PTFE which contains extended-chain crystals after synthesis, and folded-chain lamellae after melt-crystallization. Furthermore, PTFE is not explored intensively as other semi-crystalline thermoplastics with respect to reversible melting [33]. We intend therefore also to widen the pool of reversibility-data as basis for a profound interpretation of the phenomenon of reversible melting.

Reversible melting of PTFE

PTFE shows low-temperature phase transitions at about 292 and 303 K at atmospheric pressure. The crystal structure at temperatures below 292 K is triclinic with the molecules exhibiting a 1·13/6 helix. At 292 K is the crystal structure changes from triclinic to hexagonal which is connected with a partial untwisting of the molecule to a 1·15/7 helix. The three-dimensional register of chains in the crystalline phase gets lost at 303 K, caused by a dynamic interchange of the left- and right-handed twist of the two *trans*-conformations of the molecule. The crystal symmetry above 303 K can best be described as pseudo-hexagonal [34–37]. The phase transitions at 292 and 303 K can be considered as part of the total melting process and were characterized with respect to the kinetics/reversibility in previous studies [38–40].

Final melting of the pseudo-hexagonal crystals, which is the focus of the present work, occurs at temperatures lower than the equilibrium melting point of about 600 and 607 K [36, 41, 42], depending on the condition of crystallization, i.e., the crystal morphology. PTFE, crystallized during polymerization, exhibits an extended-chain crystal morphology with the molecules aligned within fibrous crystals [37], or folded ribbons forming lamellae [43, 44]. The melting temperature is close to the equilibrium melting point, and the crystallinity is almost 100%. Melt-crystallization of PTFE results in the formation of lamellae with the molecules aligned perpendicular to the long dimension, and with a thickness less than the length of the molecule [37, 45, 46]. It is not unequivocally discussed whether the molecules fold back on themselves [45, 46], as is evidenced for the majority of semi-crystalline polymers on melt-crystallization, or enter the amorphous structure due to conformational restrictions and therefore limiting the lateral size of these crystals [43, 44]. Furthermore, melt-crystallization results in a lower melting temperature, and considerably lower degree of crystallization [47–49]. The reversibility of the pseudo-hexagonal crystal–melt transition of native and melt-crystallized PTFE was recently investigated using TMDSC [50]. The data revealed reversible melting in the temperature-range of irreversible melting, and being dependent on the history of crystallization. Despite the results indicate to some degree an increased reversibility in the melt-crystallized preparation, we believe that further investigations are necessary since these data cannot be considered quantitative. Furthermore, the authors did not work out the effect of the crystal morphology on reversible melting, which we attempt in the present study.

Experimental

Materials

The material used in this study is as-polymerized PTFE powder with a particle size of 35 μm, obtained from Polysciences, Inc., USA (Cat #08816, Lot #465784). The number-average molecular mass was estimated from the heat of crystallization and is about $1–2\cdot10^6$ g mol^{-1} [51].

Instrumentation

Thermal analysis was performed using a heat-flux differential scanning calorimeter DSC 820 (Mettler-Toledo GmbH), and a power-compensating differential scanning calorimeter DSC 7 (Perkin Elmer).

The DSC 820 was equipped with the ceramic sensor FRS 5 and operated in combination with the liquid nitrogen accessory. The furnace was purged with nitrogen at a flow rate of 80 mL min^{-1}. The temperature was calibrated using the onset temperatures of melting of indium and zinc, and the heat-flow rate was calibrated with the heat of fusion of indium. Samples with a mass of about 4.5±0.5 mg were placed in 20 μL aluminum pans. Quasi-isothermal TMDSC was performed using a sawtooth modulation of the program temperature with an amplitude and period of modulation of 1 K and 240 s, respectively [52]. In non-isothermal TMDSC experiments we used an underlying heating ate of 0.1 K min^{-1}, and an amplitude and period of modulation of 0.5 K and 240 s, respectively. The experimental, apparent heat capacity was internally calibrated by comparison with the vibrational heat capacity of the solid and the heat capacity of the liquid available in the ATHAS data base [53].

The DSC 7 was operated in combination with the cryogenic cooling accessory CCA 7 for adjustment of the heat-sink temperature to 223 K. The sample and reference furnaces were purged with nitrogen at a flow rate of 40 mL min^{-1}. The sensor temperature of the sample furnace was calibrated using the onset temperatures of melting of indium, tin, zinc and lead, and the initial calibration of the heat-flow rate was done using the heat of fusion of indium. The 20 μL aluminum pans of the DSC 820 were also used for the measurements on the DSC 7. The sample mass was about 6.5±0.5 mg. The raw data of the heat-flow-rate from the sample run were corrected for the instrumental asymmetry by subtraction of a baseline which was measured under identical conditions, including matching of the mass of the aluminum pans, before converting the data to the apparent specific heat capacities. Final calibration of the heat capacity was done using sapphire as standard, and subsequent additive internal calibration by comparison the measured heat capacity of the liquid with the expected value, as is listed in the ATHAS data base. The TMDSC was performed quasi-isothermally with a sawtooth-type temperature modulation, and a programmed amplitude and period of modulation of 1 K and 120 s, respectively [54, 55]. The calculation of the apparent reversing specific heat capacity from the modulated heat-flow-rate-raw data and modulated sample temperature is described elsewhere [56, 57]. Further processing of the apparent specific heat capacity is required before reversible melting is quantified for structural interpretation. This includes (a) the subtraction of the crystallinity dependent thermodynamic heat capacity from the equilibrium apparent specific heat capacity, in order to obtain an excess heat capacity due to reversibly exchanged latent heat, and (b) conversion of the excess heat capacity to a reversible change of the crystalline fraction by normalization with the bulk heat of fusion, to yield a total reversibility of melting, or additionally with the actual crystallinity, to yield an averaged specific reversibility of melting [14].

Results and discussion

In Fig. 1 standard-DSC heat-flow-rate data are shown as function of temperature, obtained on heating as-polymerized PTFE at a rate of 20 K min^{-1} (bold line), subsequent cooling at a rate of 10 K min^{-1} (dotted line), and second heating at 20 K min^{-1} (thin line). The data confirm the well-explored differences between native

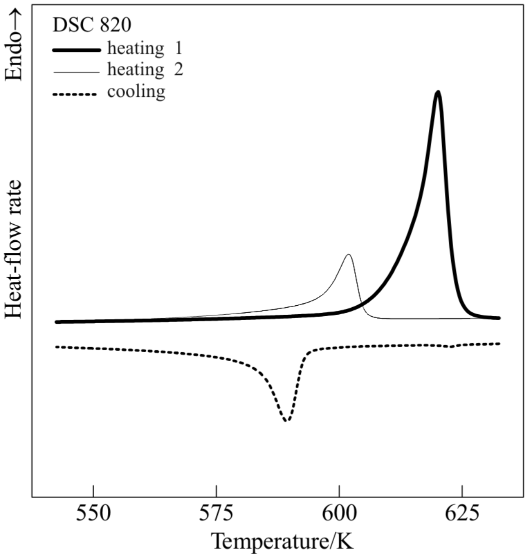

Fig. 1 Heat-flow rate as function of temperature, obtained on heating as-polymerized PTFE (bold line), subsequent cooling (dotted line) and reheating (thin line). The heating and cooling rates are 20 and 10 K min^{-1}, respectively

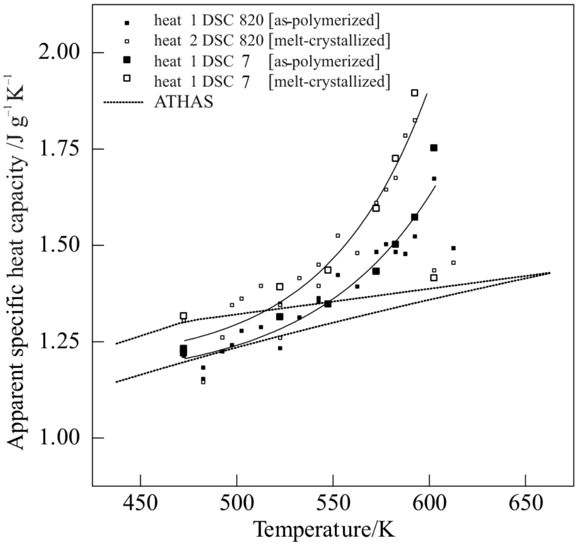

Fig. 2 Reversing apparent specific heat-capacity of as-polymerized (filled squares) and melt-crystallized (open squares) PTFE as function of temperature. Samples were heated to the temperature of quasi-isothermal analysis and subsequently melted. The dashed lines are thermodynamic heat-capacity data of amorphous and crystalline PTFE, respectively

and recrystallized PTFE with respect to both crystallinity and melting temperature. The estimated heat of fusion of as-polymerized and melt-crystallized PTFE is about 69 and 28 J g^{-1}, respectively. The enthalpy-based crystallinity was calculated using a specific heat of fusion of 82 J g^{-1} as reference [42], and is about 84 and 34% for as-polymerized and melt-crystallized PTFE, respectively. Since melting of extended-chain crystals is subjected to superheating [48, 58], we performed a separate series of experiments in order to evaluate the effect of heating rate. The onset temperature of melting in case of as-polymerized powder is 603 K at a heating rate of 2 K min^{-1} and increases to 613 K when using a heating rate of 100 K min^{-1}. The latter value is considerably higher than the equilibrium melting temperature, and must be explained by superheating. In melt-crystallized samples, in contrast, we did not observe an influence of the heating rate on the melting temperature of 594 K.

Figure 2 shows the reversing apparent specific heat capacity of as-polymerized (filled squares) and melt-crystallized (open squares) PTFE as function of temperature. Small symbols represent data, which were collected with the heat flux DSC 820, and large symbols represent data which were collected with the power-compensating DSC 7. Note that each data point is obtained in a separate experiment using a new sample since immediately after quasi-isothermal annealing the subsequent melting is measured. The analysis of subsequent melting without performing additional heat treatment is necessary for correct interpretation of the reversing heat capacity, representing the actual state of structure. The scattering of data is believed to be caused by preparation of powdered samples, however, is within the typical limit of about 3%. The dashed lines are thermodynamic-heat-capacity data of amorphous and crystalline PTFE, respectively. The data reveal an excess heat capacity at a temperature above about 500 K, which continuously increases until final melting occurs. At all temperatures the excess heat capacity of the melt-crystallized samples is higher than for as-polymerized PTFE. Since the excess heat capacity is caused by reversible melting at the surface of the crystals, the data can only be discussed with knowledge of the amount of crystals at the temperature of analysis. Therefore the crystallinity was estimated after each experiment by the heat of fusion.

Figure 3 shows with the closed and open symbols the heat of fusion (left axis) and crystallinity (right axis) of as-polymerized and melt-crystallized PTFE, respectively, which was measured after quasi-isothermal analysis of the apparent specific heat capacity, plotted in Fig. 2. The data confirm the results of Fig. 1, *i.e.*, the temperature of melting and heat of fusion of melt-crystallized PTFE are considerably lower than in case of as-polymerized PTFE. Furthermore, we observed constancy of the heat of fusion at temperatures lower than 575 and 545 K in as-polymerized and melt-crystallized PTFE, respectively, which is contrary to experimental findings in polyethylene. The importance of the temperature-dependence of the crystallinity can be illustrated as follows: an excess heat capacity of 0.11 J g^{-1} K^{-1} obtained on melt-crystallized PTFE at a temperature of 545 K is caused by a crystalline fraction of 34%, and an

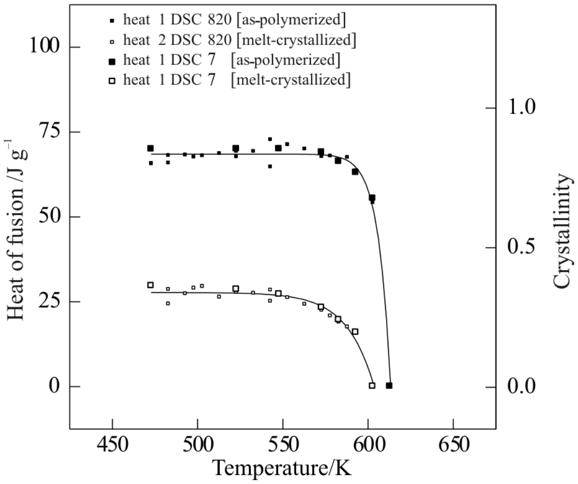

Fig. 3 Heat of fusion (left axis) and crystallinity (right axis) of as-polymerized (filled squares) and melt-crystallized (open squares) PTFE as function of temperature. Data were obtained by melting the quasi-isothermally annealed samples for determination the reversing apparent specific heat capacity shown in Fig. 2

excess heat capacity of 0.35 J g^{-1} K^{-1} at 585 K is caused by a crystalline fraction of only 22%. This rather simple relation justifies the need for further processing of the excess-heat-capacity data before further interpretation which was not considered in previous studies on PTFE [50].

In Fig. 4 is shown with the left axis the excess specific heat capacity and with the right axis the total reversibility of melting of as-polymerized (bold line) and melt-crystallized (thin line) PTFE, both as function of temperature. The data were calculated from the fit of the temperature-dependence of the apparent reversing specific heat capacity, shown by the solid lines in Fig. 2. The total reversibility is obtained by normalizing the excess specific heat capacity with the specific heat of fusion of PTFE of 82 J g^{-1} and is the total reversible change of crystallinity on temperature modulation in % K^{-1}. The excess specific heat capacity and total reversibility of melting is in case of melt-crystallized PTFE approximately twice the values of as-polymerized PTFE, despite the crystallinity is considerably lower. Further normalization by the actual crystallinity shown in Fig. 3 reveals the average specific reversibility of melting plotted in Fig. 5 for as-polymerized and melt-crystallized PTFE as function of temperature. The data are averages since the reversibility of melting is related to all crystals which melt at higher temperature without further assignment to a specific crystal population. The average specific reversibility of melting is still at all temperatures higher in melt-crystallized PTFE (thin line) than in as-polymerized PTFE (bold line). The physically more reasonable approach of the calculation of an average specific reversibility of melting, however, reveals in this case a difference of more than one magnitude of order between the two investigated crystal preparations, pointing to qualitatively different mechanisms of reversible melting.

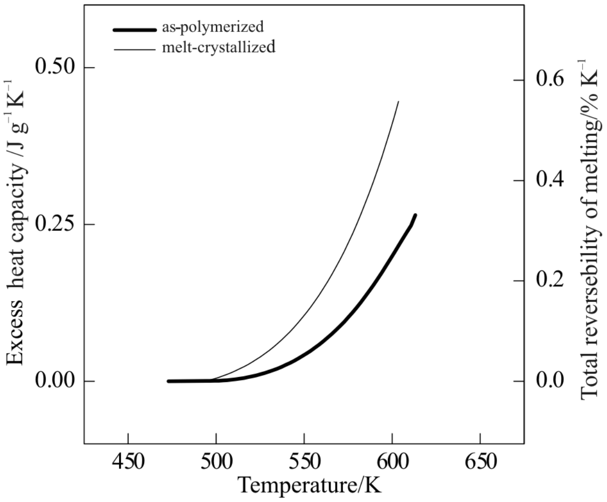

Fig. 4 Excess heat capacity (left axis) and total reversibility of melting (right axis) of as-polymerized (bold line) and melt-crystallized (thin line) PTFE as function of temperature

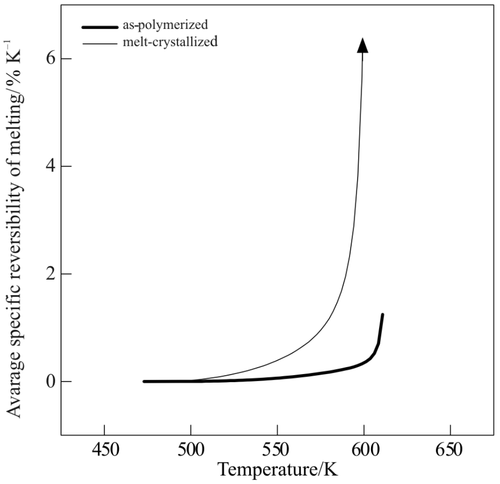

Fig. 5 Average specific reversibility of melting of as-polymerized (bold line) and melt-crystallized (thin line) PTFE as function of temperature

Final discussion and conclusions

The scope of the present study is the evaluation of the effect of the crystal morphology on reversible crystallization and melting, when keeping a constant chemical structure of the investigated species. Previous studies on flexible macromolecules indicated that an increased decoupling of segments of a molecule results in an increase of the reversible fraction of the melting process. Decoupling means that differently crystallized segments are dislocated from each other and melt therefore on heating at different tempera-

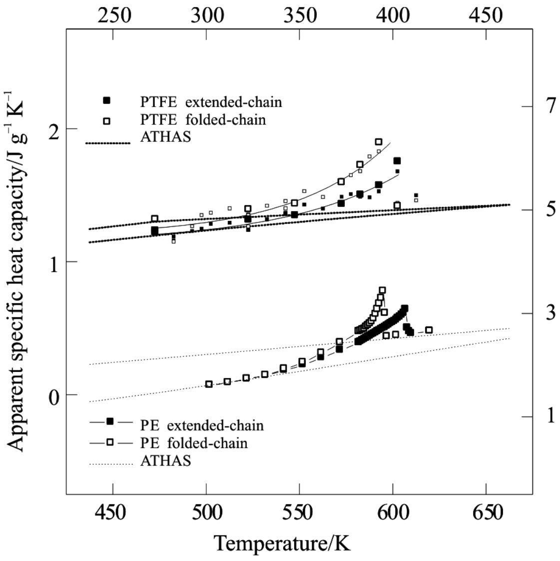

Fig. 6 Apparent specific heat capacity of extended-chain crystals (filled squares) and folded-chain crystals (open squares) of PTFE (left and bottom axes) and PE (right and top axes) as function of temperature. Data of PE were taken [27]

tures. For this reason it is expected, and evidenced for the case of polyethylene, that extended-chain crystals exhibit distinctively less reversible melting than folded-chain crystals, if the molecular weight is identical. Macromolecules in extended-chain crystals are not simultaneously part of several crystals which requires repeated nucleation after its complete removal from the crystal. In semi-crystalline, folded-chain crystals, the macromolecules usually are part of both the crystalline phase and the amorphous phase and may even traverse several times through the same or different crystals. In this case the total and local entropy of the macromolecule may remain lower after partial melting of a limited number of molecule segments or stems, respectively, which permits a nucleation-free and therefore reversible crystallization on subsequent lowering the temperature. The experimental data of the present study on PTFE confirm qualitatively similar results which recently were obtained on polyethylene. Figure 6 is a direct comparison of the apparent specific heat capacity of extended-chain crystals and folded-chain crystals of PTFE (upper two curves, left and bottom axis) and of polyethylene (lower two curves, right and top axis). The excess specific heat capacity obtained on re-crystallized and folded-chain crystals is in both cases about twice the excess specific heat capacity of the extended-chain crystals. The larger difference of absolute values in case of polyethylene can be attributed to the more than threefold specific heat of fusion of polyethylene.

Reversible melting of extended-chain crystals and folded-chain crystals occurs in a temperature range starting about 50 K below the final melting temperature. In case of PTFE the temperature-dependence of reversible melting parallels that of irreversible melting which is evidenced by the crystallinity-data of Fig. 3. We conclude therefore in accordance with the recently established concept of the specific reversibility of melting that reversible melting of a particular crystal occurs only close to the temperature of its irreversible formation or disappearance [21]. In other words, reversible melting is absent at temperatures considerably lower than the temperature of formation. Even if this conclusion lacks direct evidence, e.g. by scattering methods or microscopic techniques, we can at least with the present study narrow down the temperature range of reversible melting of a single crystal to 50 K or less, which was not possible with our previous experiments on polyethylene or polypropylene. Polyethylene and isotactic polypropylene show a continuous and an at least partially irreversible increase of the crystallinity on cooling even at ambient and sub-ambient temperature which is caused by the molecular weight distribution and/or distribution of defects along the chain [59]. The application of the concept of the specific reversibility of melting, *i.e.*, normalization of the specific equilibrium excess heat capacity by the actual crystalline fraction of the specimen amplifies the difference of the reversible fraction of melting between extended-chain crystals and folded-chain crystals, as is shown by the data of Fig. 5. The truly reversible fraction of total melting likely exceeds 10–20% if one would consider that not all crystals, which are existent at the temperature of analysis, exhibit reversible melting to the same degree at this temperature. This result confirms quantitatively our previous observation on polyethylenes of different crystallinity that the true reversible fraction of total melting is 1/3 to 1/2 of the total [60].

We cannot see a difference in the temperature-dependence of reversible melting between extended-chain crystals and folded-chain crystals. Both preparations show absence of reversible melting at temperatures about 50 K less than the final melting point, which was not observed before on other polymers, in particular polyolefins. This behavior strongly contrasts the temperature-dependence of reversible fold-surface melting in case of folded-chain crystals. Previous studies on high-density polyethylene suggested that lamellae, which were formed by isothermal melt-crystallization, and which were stabilized by high-temperature annealing, reversibly increase in thickness in a temperature-range exceeding 100 K. Reversible fold-surface melting in polyethylene is possible by diffusion of molecule segments through the crystal and is evidenced by small-angle X-ray scattering (SAXS) [15–20]. Direct evidence for longitudinal partial fusion of crystals in PTFE by SAXS is not available, however, was suggested to be the valid mechanism of reversible melting, mainly justified by the high chain-sliding ability above the partial disordering transition at 303 K [50]. Our data clearly point to absence of reversible melting at temperatures less than about 500 K, independent of the crystal morphology. We cannot unequivocally support the model of reversible fold-surface melting of folded-chain crystals in PTFE since defect-motion in the disordered crystalline phase sets in already at about 400 K [61] and since reversible melting is completely absent at this temperature. The striking correspondence between irreversible and reversible melting rather points to identical mechanisms, occurring at the lateral surface.

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