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Temperature of Melting of the Mesophase of Isotactic Polypropylene

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Structure and Formation of the Mesophase of Isotactic Polypropylene. Mesophase formation in isotactic polypropylene (iPP) has first been reported in the late 1950s,^{1–3} shortly after the successful introduction of stereospecific synthesis of this polymer. It is recognized in the wide-angle X-ray scattering (WAXS) pattern by the presence of two characteristic halos at spacings of about 0.59 nm, which is related to the average distance between parallel aligned chains in the mesophase, and 0.41 nm, which has been assigned to the repeating period within the 3₁ helix of an isotactic sequence of the macromolecule.^{3–5} The mesophase develops upon quenching the quiescent liquid to ambient temperature and coexists at this temperature with amorphous structure within an arrested metastable thermodynamic state.

Initially, the structure of the quenched form of iPP has been described as a paracrystalline smectic arrangement of molecular stems. It was suggested that parallel aligned helices of different handedness are randomly arranged within a pseudo-hexagonal lattice.^{1–3} Alternative interpretations of the WAXS data of quenched iPP include the suggestion of a higher degree of local order than in a smectic phase, that is, the presence of fine crystallites of hexagonal structure^{6–8} or of small and disordered monoclinic microcrystals.⁹ In a more recent study it was confirmed that the mesophase contains bundles of parallel aligned chains with a 3-fold helix conformation, being terminated in direction of the chain axis by helix reversals or other conformational defects. In particular, the observation of broad peaks on well-defined layer lines in the fiber diffraction pattern of the stretched mesophase indicated an ordered conformation of chain segments and only short-range correlations between atoms of neighbored chain segments. The lateral correlation between different chain segments was described to be closer to a monoclinic rather than a hexagonal lattice, though the structure cannot be described by one type of unit cell, even at local scale.^{10–12}

The morphology of the mesophase is nodular as has been proven by several studies employing different imaging techniques, including scanning electron microscopy,¹³ transmission electron microscopy,^{8,14–16} or atomic force microscopy.^{17,18} The size of the mesomorphic domains is of the order of 5–20 nm, and a higher order organization within a superstructure is not observed.^{19,20} The maximum fraction of mesophase at ambient temperature has not unequivocally been evaluated yet and is of the order of 25–50%.^{7,21,22}

The exact conditions of formation of mesophase with respect to cooling rate and temperature/supercooling were established recently.^{17,19,21,23–25} In short, the mesophase develops at temperatures between about 300 K and the glass transition temperature of the unstrained amorphous phase at around 250 K.^{13,26,27} A further prerequisite for mesophase formation in this temperature range is prior suppression of development of monoclinic crystals at low supercooling, by rapid cooling of the liquid faster than about 100 K s^{–1}. Cooling to a temperature lower than the glass transition faster than 1000 K s^{–1} even inhibits mesophase formation, which, however, then forms by cold crystallization on subsequent heating of the amorphous glass.^{13,27}

Stability of the Mesophase of Isotactic Polypropylene. Former research about the stability of the mesophase of quenched iPP mainly included the analysis of the temperature dependence of structure by X-ray techniques, differential scanning calorimetry (DSC), and microscopy. The data available in the literature to date, however, do not lead to a unique figure about the temperature dependence of the various reorganization processes which occur on heating quenched iPP. Such reorganization processes include (a) a transformation of the mesophase into monoclinic structure, which occurs at local scale within existing nodules, (b) a change of the morphology of domains/crystals, and (c) cold crystallization of supercooled liquid. Unequivocal identification of these processes has not yet been achieved, as is demonstrated with Figure 1. It shows with the bold and thin lines a DSC heating scan of initially semi-mesomorphic iPP and heat capacities of fully liquid and solid iPP, respectively, with the latter serving for easy recognition of thermal events involving a change of latent heat. Data were taken from an earlier work of the authors²⁸ and replotted for illustration of the complexity of the reorganization behavior of quenched iPP. The DSC heating scan shows three transitions which are labeled by Roman numbers. The endothermic transition (I) is centered at around 325–330 K and has suggested to be a classical annealing peak.^{29–31} An alternative interpretation is that this peak reflects “some form of premelting transition that occurs prior to recrystallization”.¹³ The endotherm (I) is followed by a broad exothermic peak (II) centered at about 370 K. This exotherm has frequently been assigned to the mesophase–monoclinic phase transition,^{6,13,29,30,32} which, however, is not consistently confirmed by X-ray analyses. The horizontal bars/arrows in Figure 1 show selected results regarding the temperature range of the mesomorphic–monoclinic phase transformation, as were gained by X-ray measurements, available in the literature.^{7,15,22,29,32–34} The data suggest that the mesophase converts on heating in a rather broad temperature range into monoclinic crystals, with the start temperature, width, and end temperature of transition largely differing in the various studies. As such, it seems not fully agreed upon that the DSC exotherm (II) indeed is related to the phase transition. Regarding the general observation of a rather broad temperature range of the mesophase–monoclinic phase transformation, this may indicate (a) presence of mesomorphic regions of different stability, which convert at different temperature into monoclinic crystals, and/or (b) a distinct effect of time of analysis. Both probably are true since it is proven that mesophase formation on quenching does not necessarily

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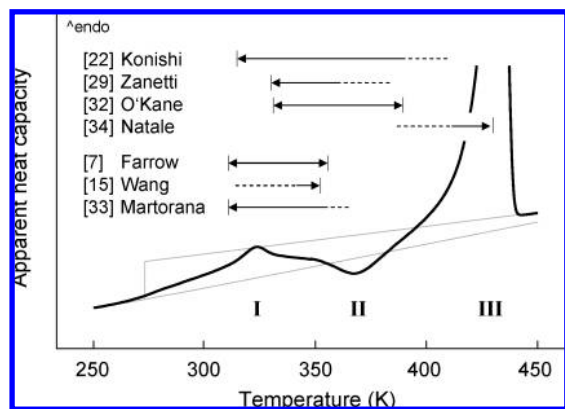


Figure 1. DSC heating scan of quenched iPP (thick line). The thin lines represent heat capacities of fully solid and liquid iPP and serve as reference for easy recognition of transitions connected with a change of latent heat. The horizontal bars/arrows indicate temperature ranges of the mesomorphic–monoclinic phase transformation, as are reported in the literature, based on WAXS data.

occur at a single temperature only, rather than in a temperature range,^{23–25} causing perhaps a size distribution and a nonuniform local distribution of lattice defects in the mesophase, leading to a stability distribution. Furthermore, it has been shown in numerous studies that the phase transformation obeys a distinct kinetics;^{29,30} that is, the temperature range of the phase transition depends on the exact condition of analysis. Nonetheless, the data of Figure 1 suggest that the exothermic event in DSC analysis may not necessarily be related to the mesomorphic–monoclinic phase transformation. Further reasons can be reorganization of the crystal morphology^{14–18} or cold crystallization of supercooled liquid, with the latter recognized by a decrease of the amorphous fraction on heating.^{33,34} Finally, the exothermic peak (II) is contiguously followed by melting of reorganized or cold-crystallized monoclinic crystals at about 430 K (III).

In this Communication we intend to contribute to the discussion of the thermodynamic stability of the mesophase in quenched iPP, which we believe is not fully investigated yet, as is demonstrated with Figure 1. We attempt to gain further information about the stability of the mesophase of quenched iPP by suppression of reorganization of initial structure by fast heating.³⁵ As such, it is a priori assumed that (a) the mesomorphic–monoclinic phase transition, (b) reorganization of the domain/crystal morphology, and (c) cold crystallization, which all occur at specific temperatures, depend on time and can be suppressed by passing the specific temperature window of the various transitions at sufficiently high rate of temperature change.

Experimental Results. For analysis of the reorganization behavior as a function of the heating rate in a wide range between 10^{-1} and 10^4 K s⁻¹ we employed both standard DSC and fast scanning chip calorimetry (FSC). Standard DSC experiments were performed on a Perkin-Elmer power-compensation DSC 7 and a Mettler-Toledo heat-flux DSC 820, using films of an iPP homopolymer of 100 μ m thickness. Formation of a semi-mesomorphic structure was in this case achieved by quenching the quiescent liquid into a mixture of dry ice and ethanol and subsequent aging at ambient temperature. The experimental setup of the FSC instrument has been described in detail elsewhere.³⁶ Semi-mesomorphic samples were directly prepared in the FSC instrument, using the high cooling capacity of the device.³⁷ The temperature–time profile used for preparation of semi-mesomorphic specimens in the FSC instrument is shown in Figure 2a.

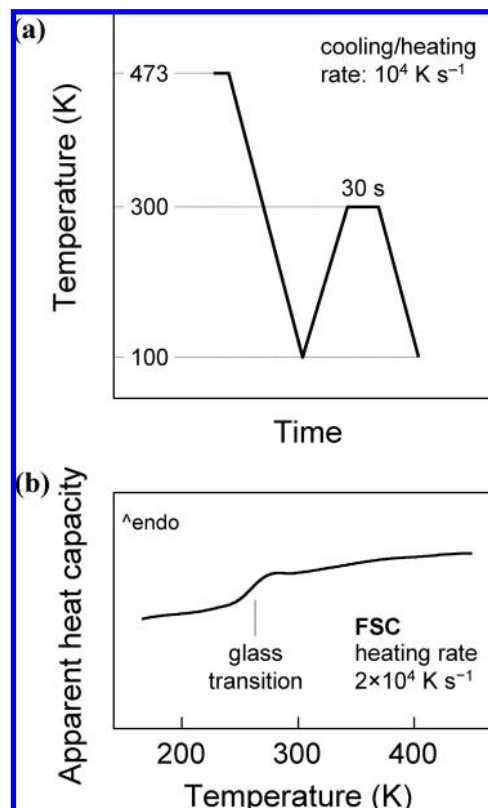


Figure 2. (a) Temperature–time profile used for preparation of semi-mesomorphic specimens for FSC analyses. (b) Apparent heat capacity as a function of temperature on heating fully amorphous iPP at a rate of 2×10^4 K s⁻¹. The data serve as evidence for complete suppression of formation of crystals and mesophase on prior cooling at a rate of 10^4 K s⁻¹.

Samples with an approximate mass of a few tens of nanograms were cooled at a rate of 10^4 K s⁻¹ from 473 to 100 K, which resulted in suppression of both development of monoclinic crystals and mesomorphic domains and formation of a glassy, fully amorphous structure.²³ Subsequently, the sample was heated at identical rate to 300 K and annealed for 30 s, leading to isothermal mesophase formation. Note that the approximate half-time of mesophase formation at 300 K is about 0.1 s;²⁴ that is, annealing for 30 s allowed completion of the liquid–mesophase transition. Figure 2b shows a FSC heating scan, starting at 100 K, after the sample has been cooled from 473 to 100 K at a rate of 10^4 K s⁻¹. It provides evidence that prior cooling did not allow formation of mesophase and/or crystals.

Figure 3 shows DSC scans obtained on heating semi-mesomorphic iPP at 2, 6, 20, 40, 60, and 100 K min⁻¹, which covers the range of rates typically assessed by standard DSC. The standard DSC heating scans are in accord with the observations shown and discussed with Figure 1. There is observed an endothermic event (I) at about 310–320 K, which is followed by an exothermic peak (II) at about 360–370 K and final melting at about 430 K (III). The temperatures of transitions I and II increase slightly with increasing heating rate, while the temperature of transition III decreases with increasing heating rate, supporting a melting–recrystallization–melting scheme.

Figure 4 is a plot of selected FSC scans obtained on heating semi-mesomorphic iPP at rates between 5×10^2 and 4×10^4 K s⁻¹. Analysis of the reorganization behavior of semi-mesomorphic iPP by FSC on variation the heating rate reveals similar systematic changes of the temperature of transitions I and III as were observed on

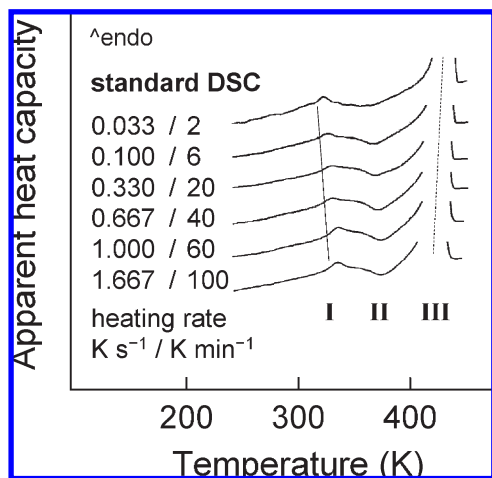


Figure 3. Apparent heat capacity as a function of temperature on heating semi-mesomorphic iPP at different rate. Data were collected using standard DSC.

using standard DSC. There is observed an increase of the onset temperature of transition I with increasing heating rate, as is illustrated with the solid vertical line, due to superheating of the melting transition of mesomorphic domains formed on isothermal annealing at 300 K.³⁸ While on heating at rather low rate the transition seems superimposed by a further, at higher temperature occurring thermal event, it appears as a well separated peak only on heating at rates faster than $1 \times 10^4 \text{ K s}^{-1}$. The observation of a single endothermic peak on fast heating of semi-mesomorphic iPP must be interpreted as melting of the non-reorganized mesophase, formed during isothermal annealing at 300 K for 30 s. Note that recording of only a single melting temperature requires continuation of the heating ramp to a temperature higher than the temperature range in which formation of monoclinic crystals may occur. In other words, we expect that disruption of the heating scan at e.g. 373 K will immediately allow formation of monoclinic crystals. Heating at rates lower than $2 \times 10^4 \text{ K s}^{-1}$ is connected with the observation of a second endothermic peak, which increases in intensity and temperature with decreasing heating rate, as is indicated in Figure 4 with the vertical dotted line. This endotherm likely is related to melting of reorganized crystals, as was labeled before as transition III in Figures 1 and 3. The amount and thermodynamic stability of reorganized crystals increase with decreasing heating rate since reorganization is a kinetically controlled process. In contrast to standard DSC, the FSC data do not reveal a separate exothermic peak. The minimum between the endothermic transitions I and III in FSC experiments, regardless of the exact heating rate, is always above the level of the heat capacity of the liquid, as is indicated in the FSC scan performed at a rate of $7 \times 10^3 \text{ K s}^{-1}$. This, however, must not necessarily be interpreted as the absence of exothermic reorganization, due to possible superposition with the endothermic transitions I and III.

Figure 5 is a plot of the onset temperature of transition I and peak temperature of transition III as a function of heating rate, as were extracted from both standard DSC and FSC experiments shown in Figures 3 and 4. The inset is a plot of the transition temperatures versus the logarithm of the heating rate. In this plot, additional literature data obtained by standard DSC were included to increase the database.^{13,15,28} For discussion of the temperature of transition I, we analyzed the onset temperature since the peak temperature may be an erroneous measure due to super-

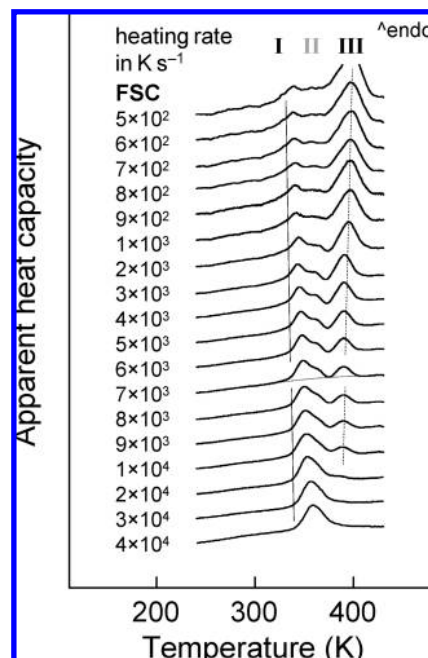


Figure 4. Apparent heat capacity as a function of temperature on heating semi-mesomorphic iPP at different rate. Data were collected using FSC.

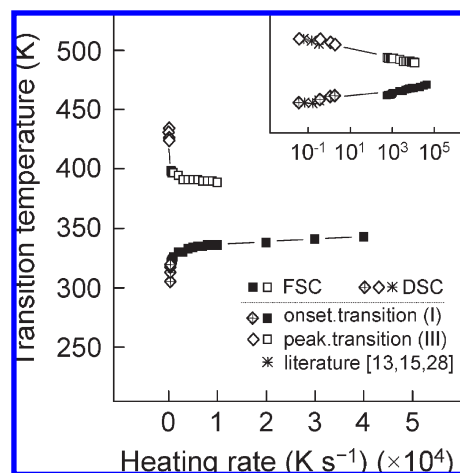


Figure 5. Onset temperature of the low-temperature endotherm I and peak temperature of the high-temperature endotherm III as a function of heating rate. The inset shows the transition temperatures plotted versus the logarithm of the heating rate.

position with exothermic heat flow on analysis at low heating rate. In contrast, in case of transition III we evaluated the peak temperature since the onset temperature cannot accurately be defined. Inspection of the data of Figure 5 leads to the important information that standard DSC and FSC results complement each other, that is, temperatures of both transitions I and III obtained by DSC and FSC fit single relationships, regardless of whether plotted linearly or logarithmically versus heating rate. Accordingly, the melting peak of the mesophase observed on heating semi-mesomorphic iPP at rates faster than $1 \times 10^4 \text{ K s}^{-1}$ must be related to the commonly as “annealing peak” in the literature denoted endothermic low-temperature event I. The onset temperature of this transition increases with heating rate, which we suggest is due to superheating of the particular phase transition.³⁸ In other words, it is assumed that the phase transition I obeys a specific kinetics and is delayed on

analysis at high heating rate. An explanation can be the presence of a rigid amorphous fraction which surrounds the mesomorphic domains.²⁶ Visual extrapolation of the transition temperature to zero heating rate yields a melting temperature of the mesophase of only 300–310 K, which is reasonable from the point of view that the mesophase was isothermally formed at 300 K.

The temperature of the phase transition III, in contrast, decreases with increasing heating rate, which is due to increasing imperfection of crystals reorganized on heating. This result is expected since it is a general observation in polymer crystallization that the melting temperature of reorganized crystals increases with both increasing annealing temperature/decreasing rate of heating.

Conclusions. Heating of semi-mesomorphic iPP to a temperature higher than the equilibrium melting point of monoclinic crystals at rates faster than $1 \times 10^4 \text{ K s}^{-1}$ inhibits reorganization of mesophase and cold crystallization of supercooled liquid phase. The absence of reorganization and cold crystallization on fast heating allows straightforward detection of an upper limit of the melting temperature of the mesophase. The observation of a melting temperature and an enthalpy of transition allows to classify the mesophase of iPP as a metastable partially ordered phase which transforms on fast heating thermodynamically irreversible at temperatures lower about 350–360 K into a supercooled liquid within a first-order phase transition. The mesophase can be superheated since the temperature of the mesophase–liquid phase transition increases with increasing heating rate. In standard DSC, the stability limit of the mesophase is indicated with the low-temperature endotherm or “annealing peak”, respectively. Accordingly, the exothermic event detected at 360–370 K in standard DSC analysis likely is caused by cold crystallization of supercooled liquid and/or classical crystal reorganization.

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