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# A real-time X-ray melting study of partly drawn UHMW-polyethylene

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A real-time X-ray study was made of the constrained melting of partly drawn, solution-crystallized ultra-high molecular weight polyethylene. Using the benefits of synchrotron X-ray techniques, it was possible to obtain direct evidence for the presence of the hexagonal structure as an intermediate phase prior to complete melting. The lifetime of the hexagonal phase in a system drawn to approximately 25% of its maximum attainable draw ratio was determined to be less than 30 s.

(Keywords: UHMW-PE; WAXS; synchrotron; melting; ultra-drawing; hexagonal phase; real-time; d.s.c.)

## Introduction

Ultra-high molecular weight polyethylene (UHMW-PE) spun or cast from (semi)dilute solutions can be drawn to high draw ratios to produce PE structures possessing extreme mechanical properties<sup>1-6</sup>.

One of the techniques used to characterize the morphology of such drawn materials is differential scanning calorimetry (d.s.c.). Undrawn material usually shows only one rather broad endothermic peak due to direct melting of the lamellar (single) crystals, as reported in the literature<sup>4-10</sup>. Fully drawn material shows a more complex melting behaviour. If free melting is allowed, a single endothermic peak at 140–145°C, depending on the drawing conditions, is detectable. This peak can be assigned to direct melting of the orthorhombic phase. Upon constrained melting, e.g. the sample is heated whilst embedded in a matrix, distinct endotherms can be observed at 153°C and approximately 175°C<sup>11</sup>. The position of the latter peak depends on the constraining efficiency. Both endotherms have been characterized via wide angle X-ray scattering (WAXS) and can unambiguously be assigned to the solid–solid orthorhombic to hexagonal phase transition and the hexagonal phase to melt transition, respectively.

Apart from these ultimate morphologies, i.e. undrawn lamellar crystals and fully ultra-drawn fibrous UHMW-PE, little is known about thermal transitions in partly drawn material. Upon (constrained) melting, partly drawn ultra-drawable UHMW-PE sometimes shows several endothermic peaks<sup>4-9,12-18</sup>. In the literature, discussions about the origin of these peaks are rather confusing. Several authors have associated the endothermic peak at approximately 150°C with a crystal–crystal phase transition from the common orthorhombic to the hexagonal structure, although they could not confirm this with direct X-ray results<sup>16,17</sup>. Others have hesitated to associate one of the endothermic peaks with such a phase transition because of the absence of a distinct melting peak of the hexagonal phase<sup>7,12</sup>. In some cases the presence of several endothermic maxima at approximately 150°C was attributed to the coexistence of different morphological components<sup>7-9,12,13</sup>. For draw ratios below approximately 50% of the maximum attainable value, the coexistence of different morphologies can be understood in terms of the deformation mechanism derived for ultra-drawable,

solution-crystallized UHMW-PE<sup>19</sup>. However, at higher draw ratios the presence of two or more distinct morphologies, giving rise to clearly resolved endothermic peaks, is rather unlikely.

Up to now direct X-ray evidence for the presence of a hexagonal structure in uncrosslinked linear PE has been found only under rather special conditions. PE under high hydrostatic pressure<sup>20</sup>, stirrer-induced UHMW-PE fibres under constraint<sup>21</sup> and ultra-drawn, solution-crystallized UHMW-PE fibres/tapes embedded in an epoxy matrix<sup>11</sup> exhibit a solid–solid orthorhombic to hexagonal phase transition upon heating.

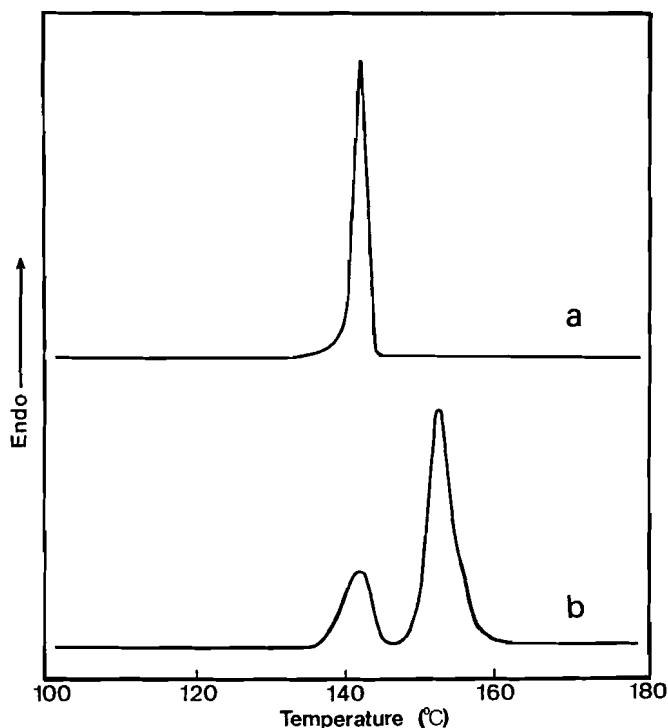
For a better understanding of the melting behaviour of partly drawn PE, a real-time X-ray melting study was performed. Reduction of the X-ray exposure times from approximately 30 min in the case of conventional X-ray techniques to a few seconds, could be achieved by using synchrotron facilities. By constrained heating of a solution-crystallized UHMW-PE, drawn to about 25% of its maximum draw ratio, the presence of the hexagonal structure prior to complete melting could be detected.

## Experimental

UHMW-PE Hostalen Gur 412 (Hoechst/Ruhrchemie) was used as starting material,  $M_w \approx 1500 \text{ kg mol}^{-1}$ ;  $M_n \approx 200 \text{ kg mol}^{-1}$ . Films were cast from a 2 wt% solution in xylene as described in the literature<sup>22</sup>. After complete removal of the solvent, the cast films were pressed at room temperature in order to obtain flat samples. The samples were drawn at approximately 125°C to a draw ratio of 25, which is approximately 25% of the maximum attainable value under these conditions.

Melting endotherms were recorded using a Perkin–Elmer DSC-7 differential scanning calorimeter. Free melting endotherms were obtained by heating chopped tapes in a sample pan with a drop of silicon oil. For the constrained melting experiments, the samples were embedded in an epoxy resin as described in the literature<sup>11</sup>. Indium was used for temperature calibration ( $T_m = 156.6^\circ\text{C}$ ). A standard heating rate of  $10^\circ\text{C min}^{-1}$  was used.

Conventional WAXS patterns were recorded with a Statton camera, using Ni-filtered Cu K $\alpha$ -radiation generated by a conventional X-ray generator at 50 kV and 40 mA. The real-time WAXS patterns were recorded using the synchrotron facilities at DESY-Hamburg. The



**Figure 1** D.s.c. melting endotherms of a 2 wt% UHMW-PE tape, drawn to a draw ratio of 25. (a) Unconstrained melting, (b) constrained melting

X-rays, generated at 5.260 GeV and 33 mA, were monochromatized to a wavelength of  $1.61 \pm 0.02$  Å. By combining the intense synchrotron radiation with a two-dimensional Westinghouse Vidicon X-ray detector, the exposure time could be reduced to 10 s per WAXS pattern. The resulting iso-intensity contourplots were obtained in a straightforward manner, i.e. without any special background corrections.

For the real-time melting study the PE sample was drawn at 125°C using a special heatable stretching device<sup>23</sup>. As a draw ratio of approximately 25 was reached, drawing was stopped, without relieving the applied stretching force. At this point the oven temperature of the stretching device was increased under synchronous monitoring of the WAXS characteristics, the oven temperature and the relative stress decay. The difference between the oven temperature and the actual sample temperature ranged within approximately 2°C. Due to the oven construction, the real-time measurements could only be performed with the X-ray beam directed perpendicular to the tape surface<sup>23</sup>.

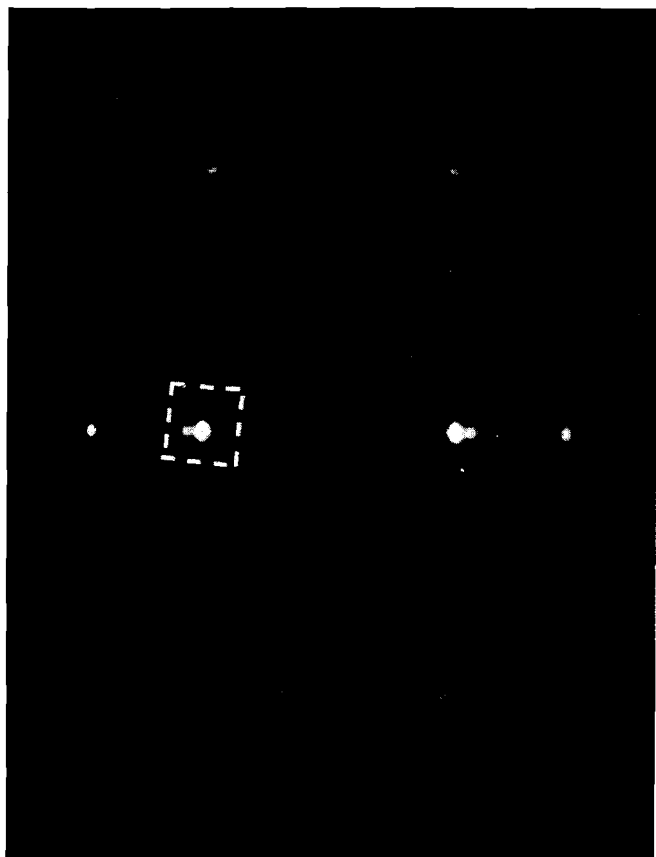
### Results and Discussion

**D.s.c.** In Figure 1 the d.s.c. thermograms of an unconstrained (a) and a constrained (via embedding in an epoxy matrix) PE tape (b) are shown, drawn to approximately 25% of its maximum draw ratio. As can be seen, the unconstrained tape exhibits only one endothermic maximum, i.e. at 142°C, which can be assigned unambiguously to the melting of the common orthorhombic structure. The absence of further endothermic peaks, strongly points to the absence of two or more distinct morphological structures in this partly drawn tape. Upon constraining however, the d.s.c. thermogram shows two distinct endothermic peaks, at 142 and 152°C, respectively. Comparison with the unconstrained melting thermogram shows that the former peak can be attributed to melting of the common

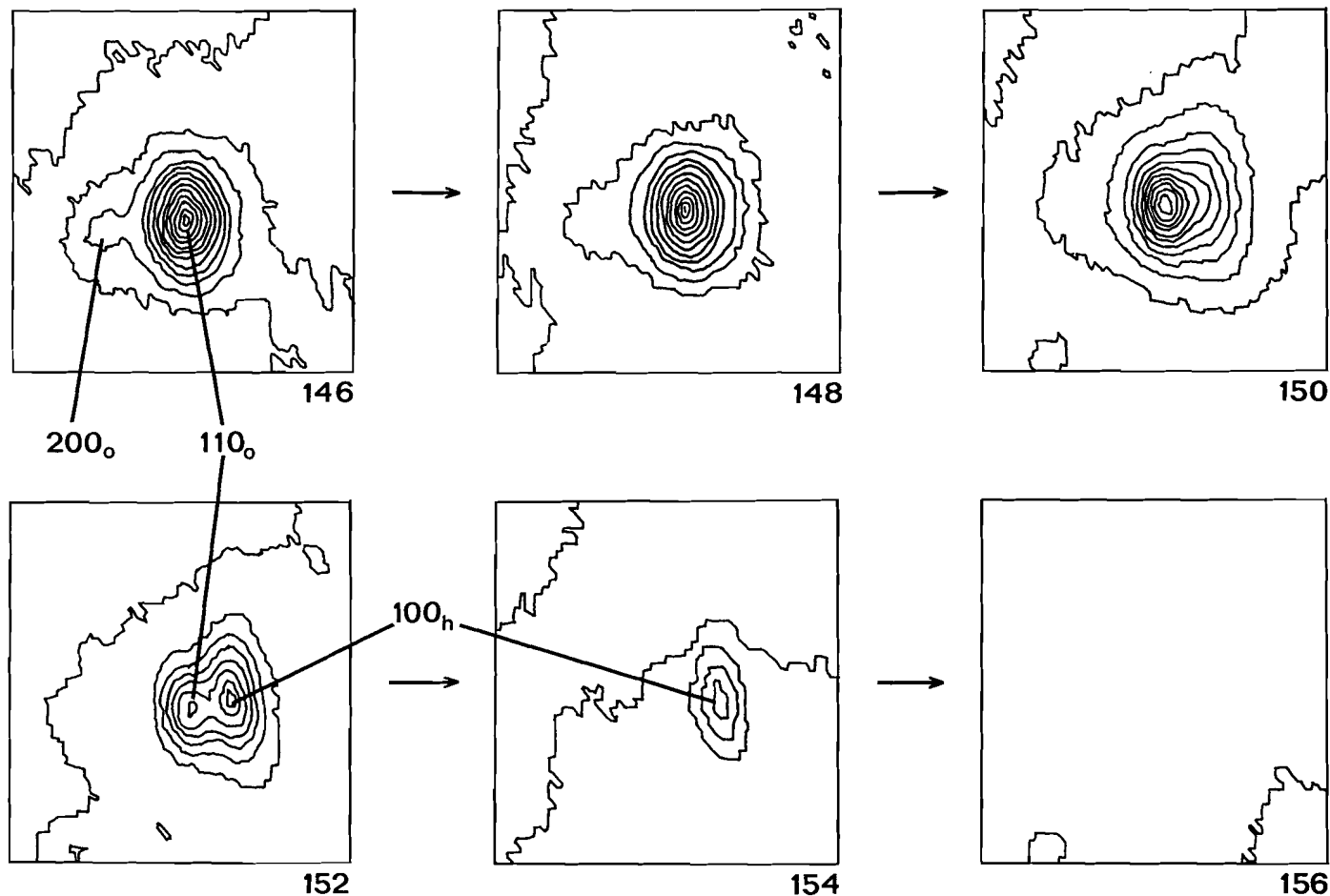
orthorhombic crystal structure. This endotherm arises from a fraction of the embedded PE tape, which was not constrained effectively enough. As will be shown further on, the endothermic peak at 152°C can be assigned to the crystal-crystal phase transition from the orthorhombic to the hexagonal structure. Close inspection of this latter endotherm reveals the presence of a rather poorly resolved third peak on the high temperature side. This endothermic fraction very probably arises from melting of the hexagonal structure. However, it should be noted that the constraining procedure for partly drawn tapes via epoxy embedding is not extremely reproducible. The constraining efficiency depends on the dimensions of the embedded tape, the resin used, any surface treatments, curing procedure, etc.

**WAXS.** For a partly drawn, solution-crystallized UHMW-PE sample the presence of a hexagonal structure prior to complete melting has never yet been confirmed via WAXS. Therefore, the melting behaviour was studied under constraint, using conventional X-ray equipment. It was found to be impossible to detect the hexagonal structure upon heating.

Due to an increased molecular mobility in the hexagonal crystal structure, the constraining capabilities will decrease within the tape<sup>16,20</sup>. This effect will reduce the lifetime of any hexagonal structure existing beyond the conventional X-ray detection limits. Therefore, reduction of the detection time seemed to be necessary for determining the possible existence of the hexagonal structure prior to complete melting. Reduction could be realized by combined use of a very bright synchrotron X-



**Figure 2** Wide angle X-ray pattern of a 2 wt% UHMW-PE tape, with a corresponding draw ratio of 25. The drawing direction is vertical. The dashed box indicates the area that was detected during the real-time experiments



**Figure 3** Series of WAXS patterns as a function of temperature for a constrained 2wt% UHMW-PE tape, drawn to a draw ratio of 25. The corresponding temperature is indicated (in °C) in the lower right corner of each pattern

ray source and a two-dimensional detector, thus enabling a melting study in real-time. In *Figure 2* a conventional WAXS pattern of the partly drawn sample is given. Due to the limited size of the two-dimensional X-ray detector, only a small part of the WAXS pattern could be detected in the real-time study. The corresponding area for the real-time measurements is indicated in *Figure 2* by a dashed box.

*Figure 3* shows a series of real-time WAXS patterns as a function of the temperature. Unfortunately, due to the presence of biaxial orientation in the drawn UHMW-PE sample, the equatorial 200 reflection spot is relatively weak compared with the equatorial 110 reflection. Upon heating, the intensity of both the orthorhombic 110 and 200 reflection (indicated in *Figure 3* as 110<sub>o</sub> and 200<sub>o</sub>, respectively) decrease gradually. At a temperature of 152°C an additional, clearly distinct reflection becomes detectable with a corresponding *d*-spacing of 4.35 Å. This spacing corresponds to the 100 reflection of the hexagonal modification of PE (indicated in *Figure 3* as 100<sub>h</sub>). Upon further heating the orthorhombic reflections disappear completely and the hexagonal reflection is still detectable for a short time. After about 25 s, however, this latter reflection has also disappeared, indicating the melting of the material.

Synchronous detection of the stress revealed a steadily increasing stress decay upon heating from 125°C (the initial drawing temperature). As the temperature reaches the phase transition temperature of 152°C, the stress falls off very rapidly to zero. These results are completely in line with the findings reported in literature<sup>16,21</sup> and can

be explained by an increased molecular mobility in the hexagonal phase. Apparently, the considerable volume expansion of the crystal lattice due to the phase transition accelerates the relaxation of the more or less chain-extended PE segments, thus leading to a dramatic increase in stress decay. As soon as the constraining power within the sample is lost, the tape melts.

To our knowledge this is the first time that the hexagonal structure could directly be detected via WAXS for an uncrosslinked, constrained PE sample, drawn to approximately 25% of its maximum draw ratio. It shows that upon constrained heating an oriented PE system transforms into the hexagonal phase before it melts completely. Since the lifetime of the hexagonal phase under constraint was found to be < 30 s, the impossibility to detect this phase with conventional X-ray techniques is quite obvious. Additionally, the results show the strong power of synchrotron facilities to study phase transitions and crystal phases with very short lifetimes.

#### Conclusions

From the results presented it may be concluded in general that the presence of several endothermic peaks due to the (constrained) melting of solid state drawn, solution-crystallized UHMW-PE materials, can be attributed as follows:

(1) endothermic peaks below approximately 150°C arise from direct melting of common orthorhombic PE, which is not constrained effectively enough. The presence of more than one endothermic peak below 150°C can be attributed to the coexistence of different morphologies

and/or the presence of material which is superheated to some degree;

(2) endotherms at approximately 150°C most probably arise from a crystal-crystal phase transition from the orthorhombic to the hexagonal structure;

(3) endotherms above 155°C point to the melting of the hexagonal phase. In some cases the constraining efficiency for the hexagonal structure is too poor to give rise to a distinctly resolved melting endotherm for this structure. As soon as some material has been transformed into the mobile hexagonal structure, the constraining power is reduced to such an extent that almost immediate melting of this phase occurs. This latter process may be that fast, that it is not easily detectable via d.s.c. (cf. Figure 1b).

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## Straightening of pleated sheet structure in fibres of poly(*p*-phenyleneterephthalamide)—Kevlar 149

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Structural differences between two commercial poly(*p*-phenyleneterephthalamide) (Kevlar) fibres were studied with scanning electron microscopy and wide angle X-ray scattering. Compared with Kevlar 49, fibres of Kevlar 149 had higher crystallite orientation, larger crystallite size and/or reduced crystalline disorder, and did not display the 300–500 nm axially periodic, pleated sheet structure of Kevlar 49. The high tensile modulus of Kevlar 149 (179 GPa), which is 80–90% of the theoretically predicted value, is attributed to the permanent 'straightening' of the pleated sheet structure associated with increased orientation and improved crystallite ordering.

(Keywords: poly(*p*-phenyleneterephthalamide); scanning electron microscopy; wide angle X-ray scattering; modulus of elasticity)

#### Introduction

Recently, an improved version of commercial PPTA (poly(*p*-phenyleneterephthalamide)) fibre, Du Pont's Kevlar 149, has been announced<sup>1</sup>. The tensile strength of 3.5 GPa of Kevlar 149 is similar to an earlier version of PPTA, Kevlar 49, but the tensile modulus of Kevlar 149 is 179 GPa, 35% higher than Kevlar 49. This represents an unusually high value of 80–90% of the theoretically

predicted modulus, which ranges between 200 GPa and 232 GPa<sup>2–4</sup>. In this communication we are reporting structural differences between Kevlar 49 and Kevlar 149 observed in scanning electron microscopy (SEM) and wide angle X-ray scattering (WAXS), which we believe primarily account for the improved modulus of Kevlar 149.