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Citation for published version (APA):

Aerle, van, N. A. J. M., & Lemstra, P. J. (1988). Drawing of ultrahigh-molecular-weight polyethylene in the melt. Influence of crystallization history. *Makromolekulare Chemie*, 189(6), 1253-1266.
<https://doi.org/10.1002/macp.1988.021890603>

DOI:

[10.1002/macp.1988.021890603](https://doi.org/10.1002/macp.1988.021890603)

Document status and date:

Published: 01/01/1988

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Drawing of ultra-high-molecular-weight polyethylene in the melt. Influence of crystallization history

Dedicated to Prof. *H.-J. Cantow* on the occasion of his 65th birthday

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(Date of receipt: January 15, 1988)

SUMMARY:

Ultra-high-molecular-weight polyethylene (UHMW-PE) can be drawn in the melt in a limited temperature range between the melting point of lamellar crystals, appr. 135°C, and the orthorhombic → hexagonal phase transition temperature, at appr. 155°C. In this particular temperature range, referred to as region 2, drawing results in the formation of a composite structure composed of fibrous crystals as a result of strain-induced crystallization of the high molecular weight fraction, embedded in a melt of lower molecular weight material. After cooling to room temperature, this latter fraction crystallizes using the fibrous crystals as crystallization nuclei. The resulting structure exhibits a shish-kebab morphology. Solution-crystallized as well as melt-crystallized UHMW-PE samples were studied with respect to draw efficiency and structure formation during deformation in the melt.

Introduction

In the past two decades, various routes have been found to produce fibrous structures based on flexible macromolecules, possessing superior mechanical properties. Ward et al. developed processes at Leeds University for the production of high-modulus flexible polymers by tensile drawing, hydrostatic extrusion and die-drawing⁽¹⁾. A process which proved to be rather versatile and successful in producing high-strength polyethylene structures, such as fibres and tapes, is the so-called gelspinning process invented in the late seventies at DSM-Research^(2,3). In this process, solution-spun/cast ultra-high-molecular-weight polyethylene (UHMW-PE) is drawn in a temperature range close to but below the melting temperature.

A detailed study on the isothermal drawing behaviour of UHMW-PE has been published recently^(4,5). Three temperature regions could be discerned in the case of *isothermal* drawing:

- *Region 1* is the temperature region below 135°C (the melting temperature of lamellar crystals) in which ultra-drawing can be performed in the solid state, starting from solution-spun/cast samples. A detailed morphological study on the ultra-drawing of solution-cast UHMW-PE in this region will be published elsewhere⁽⁶⁾.
- *Region 2* is a narrow temperature domain between 135°C and 155°C in which isothermal drawing starts from the melt. Depending on the strain rate and the molecular weight, strain-induced crystallization can take place upon drawing. The

upper limit of appr. 155°C corresponds to the orthorhombic-hexagonal solid-solid phase transition in polyethylene (PE)⁷⁾.

— *Region 3* is above 155°C, drawing is impossible due to necking and failure of the sample at low strains.

The most important difference between (isothermal) drawing in region 1 and region 2 was found in the efficiency of draw on the mechanical properties. E.g., the linear relationship between Young's modulus and the draw ratio was found to be more than 3 times steeper in case of drawing a solution-cast film in region 1 compared to region 2^{4,5)}. This difference was explained in terms of conformational relaxation effects during isothermal drawing in region 2.

In this paper, a detailed structural study of isothermal drawing of both melt-crystallized and initially solution-crystallized UHMW-PE in temperature region 2 is presented. The molecular topology and orientation in the resulting crystalline textures was studied via different X-ray diffraction techniques and transmission electron microscopy. Furthermore, the melting behaviour of the drawn tapes was studied and related to the efficiency of the drawing process in region 2.

Experimental part

Materials

UHMW-PE Hostalen-GUR 412 (Hoechst/Ruhr Chemie) was used, $\bar{M}_w \approx 1700$ kg/mol. Solution-cast films were obtained by casting PE/xylene solutions of 1,5% w/v, as described in detail elsewhere⁵⁾. After complete removal of the solvent, the cast films were pressed at approximately 90–100°C at 2–10 MPa in order to remove voids in the samples. Melt-crystallized UHMW-PE films were prepared by compression moulding of as-received powder at 200°C for 20 min and subsequent quenching to room temperature.

Drawing

Isothermal drawing was performed in a Göttfert-Rheostrain using silicon oil with matched density to PE as heating medium. Dumb-bell shaped samples were kept at the drawing temperature of 150°C for about 5 min to allow for thermal equilibrium, subsequently drawn at a constant strain rate $\dot{\epsilon}$ of 0,1 s⁻¹, and finally cooled at fixed sample length below the crystallization temperature within less than one minute.

In order to exclude differences in thermal history, even the undrawn samples were kept at 150°C for about 5 min and cooled to room temperature prior to X-ray and DSC studies.

Under the drawing conditions given above, the maximum achievable draw ratio was found to be approximately 14 and 35 for the melt-crystallized and solution-crystallized UHMW-PE samples, respectively.

X-ray diffraction

Wide-angle X-ray scattering data (WAXS), monitored at room temperature, were obtained using a flat-film camera in combination with Ni-filtered Cu K α -radiation ($\lambda_x = 1,54$ Å), generated by a Philips PW1009 Generator operating at 40 kV and 25 mA. Some small-angle X-ray measurements (SAXS) were obtained with a Kiessig camera, using Ni-filtered Cu K α -radiation generated by a Nonius Diffractis Generator, operating at 40 kV and 26 mA. For more detailed and quantitative SAXS results, a Kratky camera with a line focus of 0,1 × 20 mm² was used with Ni-filtered Cu K α -radiation generated by a Philips PW1130 Generator, operating at

45 kV and 35 mA. In all cases, the samples covered the whole line-focussed X-ray beam of the Kratky camera. The scattering intensities were recorded photographically (D7 Agfa Gevaert film) and densitometerized with an Enraf Nonius micro-densitometer model 1⁸⁾. The data were processed with the programme FFSAXS⁹⁾. The SAXS patterns were corrected for liquid scattering, sample thickness and fluctuations in the intensity of the primary beam. All SAXS data were obtained at room temperature. Synchronous recording of SAXS and WAXS patterns at elevated temperatures was performed using a Kiessig camera equipped with an oven.

Transmission electron microscopy (TEM)

TEM was performed using a Philips EM 420T microscope, operating at 100 kV. Samples were treated with chlorosulphonic acid according to Kanig¹⁰⁾ at 60 °C for 16 h and embedded in a matrix. Subsequently, thin sections were obtained by ultramicrotomy at room temperature using a Reichert Ultracut E. Finally, the cut sections were stained with uranyl acetate.

Differential scanning calorimetry (DSC)

Melting endotherms were recorded using a Perkin-Elmer DSC-7 differential scanning calorimeter. To eliminate constraining effects during melting, the studied samples were chopped to pieces of about 2 mm length³⁾. Furthermore, a droplet of silicon oil was added to ensure a good thermal conduction. A standard heating rate of 10 K/min was chosen. Indium was used for temperature calibration ($T_m = 156,6^\circ\text{C}$). The temperatures at which the endotherms show a maximum were taken as the melting temperatures.

Results and discussion

Under the experimental conditions adopted for our studies, isothermal drawing of UHMW-PE at 150 °C starts from an isotropic melt (see below). During drawing strain-induced crystallization occurs, as can be observed visually, the samples transform from transparent into opaque, and from the stress-strain behaviour^{4,5)}.

WAXS at room temperature

Solution-cast UHMW-PE samples

Fig. 1 shows a series of drawn, initially solution-crystallized samples. The WAXS patterns, as examined at room temperature, show radial symmetry along the drawing direction (fibre symmetry), as is expected for drawing of an isotropic melt. This is quite different from the biaxial orientation effects, observed by solid-state drawing of solution-cast films^{5,6,11)}, i. e. drawing in region 1.

The WAXS patterns clearly show that the *b*-axis of the crystallites almost immediately tends to align perpendicular to the drawing direction, as can be concluded from the presence of only equatorial 020 reflection arcs in the drawn samples (the 020 arc may be not clear in the reproduction of Fig. 1 for $\lambda = 3$, but can be seen in the original). At higher draw ratios, the *b*-axis orientation increases. The 200 reflection arcs show a different orientation behaviour as a function of the draw ratio. Two different sets of 200-arcs can be distinguished:

a) The presence of 200 reflection intensity on the equator, combined with the equatorial 020 reflections, arise from crystallites in which the *c*-axis is preferentially

Fig. 1. WAXS patterns of solution-crystallized UHMW-PE drawn at 150°C, monitored at room temperature. The corresponding draw ratios are indicated in the upper right corner. The drawing direction was vertical

oriented parallel to the drawing direction (to be referred to as type I-crystallites analogous to the nomenclature of Hill et al.¹²⁻¹⁴). An equatorial 200 reflection signal remains observable at all draw ratios of 10 and higher.

b) A second class of 200 reflections shows a completely different orientation behaviour. This kind starts from meridional 200 reflection maxima at low draw ratios. The meridional 200 reflection arc splits into two arcs on either side of the meridian as the draw ratio reaches 17. Probably the broad meridional 200-arc observed for draw ratios 10 and 17 results from the overlap of two split arcs, as observed for draw ratios 22 and 35. Combining this second kind of 200 reflection arcs, tending to move towards the equator, with the equatorial 020 reflections, definitely indicate the presence of a second kind of crystallites (in this paper referred to as type II-crystallites¹²⁻¹⁴). Also, in this latter kind of crystallites, the *b*-axis is always directed perpendicular to the drawing direction, and the *a*-axis tends to orient more and more away from the drawing direction as the drawing proceeds.

These results are quite different from the X-ray patterns obtained for similar solution-crystallized samples, but drawn in the solid state (region 1)^{5,6}.

Using conventional bright-field transmission electron microscopy (TEM), it is possible to visualize the two types of crystallites described above. In Fig. 2, TEM micrographs obtained for solution-cast PE drawn at 150°C to draw ratios of 10 and 29, respectively, show the presence of the well-known shish-kebab morphology¹⁵. The type I-crystallites form a core of more or less chain-extended molecules (the shish-part), whereas the type II-crystallites are observable as lamellar overgrowth.

The shish component (type I-crystallites), with the *c*-axis oriented parallel towards the drawing direction, probably originates from strain-induced crystallization of the high molecular weight part of the material. The lower molecular weight part and the dangling ends of the oriented ultra-high molecular weight chains of the oriented sample relax during the drawing process and give rise to the formation of type II-crystallites after cooling to room temperature. This is in line with earlier work of Kitamaru et al.^{16,17}. By performing birefringence experiments on the gel fraction of cross-linked oriented PE, they concluded that the cross-linked chains participate in the *c*-axis oriented crystallites, whereas the free chains crystallize into structures like type II-crystallites. The presence of the two stated textures (type I and type II) is also consistent with the findings for cross-linked lower molecular weight PE, deformed in the melt^{12-14,18}.

Type II-crystallites arise from crystallization of molten material, using the fibrous type I-crystallites as crystallization nuclei. At low draw ratios, the fraction of fibrous type I-crystallites is limited, and consequently the amount of crystallization nuclei is low. In this case, lamellar overgrowth of molten material can extend far enough to twist around the *b*-axis, as is well known for spherulitic crystallized PE (cf. $\lambda = 10$ in Fig. 2). This results in a row structure for the lamellar overgrowth, as was originally described by Keller¹⁹. However, as the draw ratio increases, a higher fraction of type I-crystallites will be formed. In this case, a more dense array of crystallization nuclei is present and the lamellae impinge before growing far enough to twist several times (cf. $\lambda = 29$ in Fig. 2). This results in type II-crystallites with an incomplete row orientation, as was originally described by Keller and Machin¹⁸ and later considered more fundamentally by Nagasawa et al.²⁰.

Fig. 2. Conventional bright-field transmission electron micrographs of solution-crystallized UHMW-PE, drawn at 150°C to a draw ratio of 10 (a) and 29 (b), respectively. The drawing direction is indicated by an arrow

Melt-crystallized UHMW-PE samples

In Fig. 3 some characteristic WAXS patterns of melt-crystallized samples are shown, obtained under similar conditions as the solution-cast samples discussed above. Under these drawing conditions, the maximum achievable draw ratio was found to be approximately 14. Initially, melt-crystallized samples exhibit features similar to the drawn solution-cast samples, i.e. the presence of two different textures. However, a significant difference can be observed in a more efficient generation of the fibrous material (type I-crystallites) in case of melt-crystallized UHMW-PE.

SAXS at room temperature

In order to get more information about the influence of drawing in region 2 on changes in the texture on a scale 50–600 Å, SAXS measurements were performed. In Fig. 4 typical SAXS patterns are presented, obtained for the same samples as in Fig. 1. In the undrawn sample, no preferentially oriented long-range ordering can be

Fig. 3. WAXS patterns of melt-crystallized UHMW-PE drawn at 150 °C, monitored at room temperature. The corresponding draw ratios are indicated in the upper right corner. The drawing direction is vertical

Fig. 4. SAXS patterns at room temperature, obtained for the same samples as shown in Fig. 1. The drawing direction is vertical. The corresponding draw ratios are indicated below each pattern

Fig. 5. Meridional (a) and equatorial (b) SAXS intensity curves as a function of s , recorded with a Kratky camera at room temperature for solution-crystallized UHMW-PE, drawn at 150°C to various draw ratios indicated.
 $s = 2 \cdot \sin \theta / \lambda_x$

observed. For a draw ratio of 3, however, some SAXS intensity can be detected parallel to the drawing direction. At higher draw ratios, also SAXS intensity perpendicular to the drawing is observable. For more information, a high resolution Kratky camera was used. The orientation in the SAXS region, as can be seen in

Fig. 4, implies that the scattering curves obtained with a linefocus camera and the samples with their drawing direction exactly parallel or perpendicular to the slits of the camera are implicitly desmeared.

Fig. 5(a) shows the resulting meridional SAXS intensity vs. s plots for different samples. These curves are comparable to a vertical densitometer scan of the SAXS patterns in Fig. 4. The curves, especially for draw ratio 22 and 35, indicate the presence of an alternating array of crystalline and amorphous phases with a long-range ordering of 475–490 Å, parallel to the drawing direction. In the curves for draw ratios 10 and 17, the presence of such a kind of long-range ordering is less pronounced, possibly because of a large spread in the long-range ordering, as could also be deduced from the TEM micrographs shown in Fig. 2.

Fig. 5(b) represents the equatorial SAXS intensity vs. s plots, comparable to a horizontal densitometer scan of patterns in Fig. 4. These curves do not show any long-range ordering of the kind as could be seen in Fig. 5(a). The small intensity differences between the equatorial and meridional SAXS signals exclude the possibility of a high concentration of elongated voids, responsible for the detected equatorial SAXS intensity. Both the meridional and equatorial SAXS intensity results can be easily interpreted in terms of shish-kebab structures, as shown in Fig. 2.

Fig. 6. DSC melting endotherms recorded on solution-crystallized UHMW-PE, drawn at 150°C to the various draw ratios indicated

*Differential scanning calorimetry (DSC)***Solution-crystallized UHMW-PE samples**

Additional proof for the coexistence of two textures, fibrillar (type I) and lamellar (type II), was obtained via DSC. Fig. 6 shows the melting endotherms for PE tapes drawn at 150°C up to various draw ratios.

The undrawn tape (after holding at the drawing temperature of 150°C to obtain a similar thermal history for all samples) shows a single melting peak with a maximum at about 131°C, characteristic for the melting of lamellar crystals obtained by (re)crystallization from the melt. With increasing draw ratio, an additional melting endotherm is observable with a corresponding melting temperature of $140 \pm 1^\circ\text{C}$. Similar melting endotherms have been described for cross-linked, stress-crystallized PE^{18, 21, 22}, extruded PE²³ and melt-crystallized UHMW-PE drawn at temperatures between 135 and 150°C^{24, 25}. However, in the case of melt-drawn, initially solution-crystallized UHMW-PE, the endotherms are much better resolved.

The assignment of the two observed melting endotherms, at 131°C and 141°C, can be obtained via X-ray studies at elevated temperatures. In Fig. 7 two sets of WAXS and SAXS patterns are presented, monitored at room temperature and at 137°C, for samples with draw ratios of 10 and 29. At 137°C the non-equatorial 110 and 200 reflection arcs, as well as the meridional SAXS intensity, both characteristics ascribed to the lamella-like type II-crystallites, have disappeared. Consequently, the melting

Fig. 7. Influence of monitoring temperature on the WAXS and SAXS patterns of solution-crystallized UHMW-PE, drawn at 150°C to a draw ratio of 10 (a) and 29 (b), respectively. The patterns on the left are monitored at room temperature, whereas the patterns on the right are monitored at 137°C

point at $140 \pm 1^\circ\text{C}$ is related to the type-I crystallites. This is consistent with wide-angle X-ray results of cross-linked lower molecular weight PE, deformed in the melt^{12, 13, 26}.

The peak melting temperatures of both endotherms exhibit only a very small increase (at most $1 - 2^\circ\text{C}$) when the draw ratio increases from 10 to 35. This effect is quite different for PE drawn below the melting point. In the latter case, a strong melting point dependence on the draw ratio is observed²⁷⁻³¹. Yet, despite the very small change in melting temperature, drastic changes in the contribution of both endotherms can be seen when the draw ratio increases (see Fig. 6). The constancy of the melting point of the type II-crystallites is not surprising, since they are created by chain-folded crystallization of the molten, low molecular weight part material and dangling ends of the high molecular weight material. On the other hand, the very small increase of the melting point of the type I-crystallites is less obvious and will be commented upon in a following section.

Melt-crystallized UHMW-PE samples

Similar DSC results are found for melt-crystallized UHMW-PE (Fig. 8), drawn under identical conditions. However, the melt-crystallized and drawn UHMW-PE

Fig. 8. DSC melting endotherms recorded for melt-crystallized UHMW-PE, drawn at 150°C to the various draw ratios indicated

samples do not show distinct resolved endotherms. Furthermore, the formation of the fibrous type I-crystallite fraction is found to be more efficient in case of originally melt-crystallized material. This can be deduced from a stronger increase of the fibrous fraction as a function of the draw ratio compared to initially solution-crystallized UHMW-PE (cf. Fig. 6 versus Fig. 8), and is consistent with the X-ray results discussed.

Mechanical properties related to structural parameters

The drawability of molten UHMW-PE in a limited time-temperature window is obviously related to strain-induced crystallization. During draw, chain-extension of the high molecular weight part of the sample occurs to some extent, giving rise to fibrous subunits. The resulting composite-like structure of partly chain-extended fibrillar crystals embedded in (relaxed) molten material, possesses sufficient strength to prevent premature failure during drawing in the melt. Standard linear PE grades cannot be drawn isothermally in the melt due to the absence of strain-induced crystallization as a consequence of the overall lower molecular weight and hence relatively fast relaxation processes. The upper temperature limit for drawing in the melt is approximately 155°C, the orthorhombic $\rightarrow$ hexagonal phase transition temperature of PE. In the hexagonal phase, the fibrillar crystals cannot withstand any load, due to a high degree of chain mobility along the *c*-axis⁷⁾.

Under the experimental conditions adopted for our studies, i.e. isothermal drawing in the melt and subsequent cooling at fixed sample length, some relaxation occurs within the fibrous units during the cooling/crystallization step. This can be observed from the immediate stress decay during cooling and from the melting behaviour of the drawn specimens. During the actual drawing process, the melting point of the type-I material can be as high as 155°C as a consequence of the applied stress (constrained melting of PE). In the absence of stress or imposed constraints, the melting point of chain-extended UHMW-PE is 145°C⁷⁾. In the case of drawing in region 2, however, the somewhat lower melting point of 141°C is very probably related to relaxation during cooling/crystallization within the fibrous subunits.

Consequently, drawing in region 2 is inherently less efficient compared to the ultra-drawing of solution-cast UHMW-PE in region 1 due to relaxation. Nevertheless, drawing in region 2 results in chain-extension, and with increasing draw ratio the fraction of type-I crystals increases linearly, as shown in Fig. 9. Combining this result with the observed linear dependence of Young's modulus vs. draw ratio^{4,5)}, strongly suggests that the melt-strength and modulus of the drawn specimen are directly related to the fraction of type-I crystals.

It is of interest to note the difference in drawability and draw efficiency in region 2 between melt-crystallized and initially solution-crystallized UHMW-PE. A crystallization memory effect can be observed in the melt related to a difference in topological constraints during the deformation step. Solution-crystallized samples are ultra-drawable in contrast to melt-crystallized UHMW-PE if drawing is performed in region 1, i.e. in the solid state. These differences with respect to drawability remain to some extent if the samples are heated above the melting point and subjected to large

Fig. 9. Influence of drawing on R , defined as the fraction of type I-crystallites observed as the contribution of the melting endotherm at appr. 140°C, for solution-crystallized UHMW-PE drawn at 150°C

deformations. However, if measured in shear at small deformations, no noticeable difference in rheological properties is observed in the melt between melt-crystallized and initially solution-crystallized samples. These crystallization memory effects will be discussed in detail elsewhere³²⁾.

Concluding remarks

Strain-induced crystallization occurs if UHMW-PE is drawn in the melt in a limited temperature range between the melting point of lamellar crystals and the orthorhombic $\rightarrow$ hexagonal transition temperature of appr. 155°C. As a consequence of strain-induced crystallization, fibrillar crystals are formed which provide sufficient melt-strength by acting as load-bearing parts during deformation.

A significant difference with respect to draw efficiency and draw ratio exists between initially solution-cast samples and UHMW-PE samples which were obtained via direct compression-moulding of as-received reactor powder. These differences could be explained in terms of a reduced intermolecular connectivity and hence less topological constraints during drawing of solution-crystallized samples. Compared to drawing in the solid state, melt-drawing in the so-called region 2 is rather inefficient with respect to the formation of high-strength/high-modulus structures.

Finally, the results explain the reported "processing-gap" of UHMW-PE in region 2³³⁾. UHMW-PE is well known as a rather intractable material for processing due to the high viscosity in the melt. At processing temperatures of 160–250°C, the high viscosity is prohibitive for conventional processing of UHMW-PE and usually compression moulding is employed, after which finished products are made by machining. However, in region 2, UHMW-PE is remarkably ductile and can be processed and shaped at low stresses rather easily³³⁾. This phenomenon is clearly related to the formation of the composite structure discussed above during deformation in the limited temperature range referred to as region 2 in this paper.

The authors are indebted to Prof. A. Keller (University of Bristol, UK), Prof. H. Meijer, Dr. A. Braam, Dr. C. Vonk, and Mr. C. Bastiaansen for stimulating discussions and valuable comments during the preparation of this manuscript. Furthermore, they wish to thank Mr. A. Pijpers for performing the TEM experiments and Mr. W. Ramaekers for his technical support in performing the X-ray experiments at elevated temperatures. This work was performed at DSM-Research.

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