Chapter 3.

PREPARATION OF HIGH-STRENGTH POLYKETONE FIBERS

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3.1 Summary

High-strength fibers are prepared by spinning high-molecular-weight perfectly-alternating ethylene-carbon monoxide copolymer from phenolic solutions followed by solid-state drawing at elevated temperatures. The maximum tensile strength attained for highly oriented fibers is 3.8-3.9 GPa. The initial tensile modulus is strongly dependent on the drawing temperature, which can be explained by the semi-crystalline nature of the polyketone. Fibers with a high elongation at break are prepared by allowing some orientation relaxation within non-crystalline domains. Unrelaxed fully oriented high-strength fibers show an elongation at break of 4-5 % and an initial tensile modulus of 5055 GPa. As a result of relaxation the elongation at break can be increased to 7-8 %, at the expense of a lower modulus [40-45 GPa]. The maximum attainable draw ratio is limited to a value of 26, and above a draw ratio of 17 the formation of cracks in the material was encountered. The temperature has a pronounced positive effect on the drawability, but the maximum temperature for efficient draw is limited by the onset of melting. When crystals start to melt a deterioration in lateral stress transfer between the chains sets in, and as a result less effective orientation is observed due to slippage of chain ends through entanglements.

3.2 Introduction

Solid-state drawing is a common technique to induce molecular orientation in flexible polymer systems. It is well-known that the tensile modulus of polymer fibers is governed by the degree of molecular orientation in the direction of deformation.\textsuperscript{13} For
non-polar polymers (e.g., polyethylene) the orientability is strongly influenced by the amount of remnant topological defects in the material, which can be altered by rearrangement of macromolecules in solution. The latter is controlled by the initial polymer concentration, since by a dilution of these topological interactions the contour length between network nodes (e.g., entanglements) is increased. During fiber spinning a low entanglement density present in semi-dilute solutions can effectively be preserved in the solid-state by means of gelation crystallization.

In addition to the influence of the dissolution conditions, the maximum attainable draw ratio is also dependent on the nature of the lateral (polar) interactions between the chains. The deformation of polymers requires a certain mobility within the network to accomodate large strains. Because of the complexity of the molecular rearrangement upon large-scale deformation, we proposed recently that the polarity dominates the effectiveness of entanglement transport through and along the formed oriented fibrillar structures. A reduction in the effective number of topological interchain couplings will increase the contour length between network nodes, resulting in appreciably higher draw ratios. This process requires the dissociation of lateral bonds between the chains, which is more likely to occur in a less polar environment and/or at elevated temperatures. Hence, in this respect non-polar polymers are favored for achieving high degrees of orientation at the obvious expense of high-temperature performance, creep properties and compressive strength.

Polymers with intermediate polarity, like poly(vinyl alcohol), can also be drawn to satisfactory ratios ($\lambda_{\text{max}}>30$) and good tensile properties have been reported. An additional advantage of these materials is the relatively high melting temperature, which makes them more suited for advanced industrial applications.

In the present thesis, we have focussed our efforts on a new, moderately polar polymer (i.e., the perfectly alternating ethylene-carbon monoxide copolymer (polyketone-C$_2$; POK-C$_2$)). A first approximation for the theoretical chain modulus of this material gave a high value (360 GPa) compared to other moderately polar flexible polymers. Due to the strong electrostatic interactions between the carbonyl
groups, the packing of the chains in the crystal lattice is very dense, and the cross section of the polyketone (POK-a) crystal unit cell (35.2 Å²) is even smaller than that of the polyethylene unit cell (36.2 Å²). In addition to its high melting temperature (260 °C), this polymer exhibits some other favorable characteristics for fiber applications, viz. good adhesion properties and a satisfactory creep resistance. Due to the limited thermal stability of the 1,4-arrangement of carbonyls, high-melting polyketones seem to suffer from degradation during meltprocessing. Therefore, at present we restricted ourselves to solution spun fibers (i.e., high-molecular-weight fibers in which the entanglement density has been reduced). Oriented fibers were prepared from phenolic solutions followed by solid-state drawing at elevated temperatures. The aim of the present investigations is to gain insight into the mechanism of chain alignment in order to produce high strength polyketone fibers.

![Perfectly alternating ethylene-carbon monoxide copolymer](polyketone)

**3.3 Experimental**

-Spinning

Perfectly alternating copolymers can be synthesized from ethylene and carbon monoxide using a cis-fixed palladium bidentate catalyst system. Polyketones are not commercially available and the polymer was, therefore, produced according to the procedure given in ref. 10. Some variation in molecular weight occurred between different batches. The intrinsic viscosity (m-cresol, 25 °C) of the samples used ranges
from 4.6 to 6.1 \( \text{dL/g} \), corresponding to a molecular weight of 300,000 to 420,000 \( \text{kg/kmol} \). In the present work, we observed that this limited variation in molecular weight had no significant effect on the properties studied.

A representative description of the solution spinning method applied follows. Polyketone fibers were prepared from thoroughly homogenized semidilute (9-15 wt-%) solutions in phenol.\(^{12}\) A small amount of acetone was added in order to avoid the interference of solvent crystallization with the fiber formation process. These solutions were dry-jet-wet spun at 70 °C through capillaries of 250 \( \mu \text{m} \) into an acetone cooling/coagulation bath (-5 °C), and fibers were collected on a bobbin at a winding speed of 1 \( \text{m/min} \). Relaxation in both the air-gap as well as in the swollen state was allowed to avoid preferential molecular orientation in the as-spun material.

**-Drawing**

Thoroughly washed and dried fibers were subjected to tensile drawing at elevated temperatures. The elongation at break of unoriented material (\( \varepsilon_b \)) was determined at various temperatures and at an initial draw rate of 100 \%/min (0.017 \( \text{s}^{-1} \)) and 1000 \%/min (0.17 \( \text{s}^{-1} \)) using a horizontal tensile tester equipped with an oven. The maximum draw ratio (\( \lambda_{\text{max}} = \varepsilon_b + 1 \)) was derived from the average value for the elongation at break of at least 20 single filaments. The same tensile tester was applied to prepare short fiber samples at a draw rate of 100 \%/min. In this batchwise drawing process the stretching was stopped at the required draw ratio, and the sample was cooled to room temperature under tension. In some cases, the tension upon cooling was lowered, whereby some orientation relaxation was allowed.

Yarn samples were also continuously drawn to various ratios at a yarn feeding speed of 1 and 10 \text{mm/s} using hot plates, and the temperature of the plates was measured using a contact thermocouple. The drawing stress was measured on-line using a \text{Schmidt}™ Yarn Tension Meter (0-5 N). The maximum attainable draw ratio in our single stage continuous drawing procedure was limited to a value of 13. Therefore, a second stage was applied to achieve higher draw ratios (\( \lambda = \lambda_1 \cdot \lambda_2 \) with \( \lambda_1 = 9.5 \)). The deformation in the first drawing stage occurred in a high temperature trajectory of
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about 4 cm. In this case the draw rate was derived from the residence time of the yarn in the deformation zone assuming a linear velocity profile. Experiments were also carried out at a sufficiently high temperature that partial melting occurred (i.e., \( T_{\text{draw}} = 247 \, ^\circ\text{C} \)). In order to avoid premature sample failure due to melting, somewhat higher draw rates were applied (i.e., a feeding speed of 20 mm/s).

**Analysis**

Prior to testing, the oriented yarns were conditioned for at least 24 hours at 21 °C and 65 % relative humidity. The tensile tests were performed on single filament samples using an Instron Tensile Tester, equipped with pneumatic clamps (type 3A) covered with Arnitel™ faces. The gauge length was 500 mm and the cross-head speed 50 mm/min (10 %/min). All tensile measurements were repeated five times.

Differential scanning calorimetry was carried out in a nitrogen atmosphere at a scanning speed of 20 °C/min on about 1.5 mg of short pieces (5 mm) of fiber sample, using a Perkin Elmer™ DSC-7, equipped with a sample changer. The DSC was calibrated with indium (onset temperature 156.6 °C) and zinc (onset temperature 417.5 °C) test samples. Perkin Elmer™ software was used to derive the peak melting temperature and melting enthalpy from the recorded DSC trace.

A Kiessig camera and an x-ray tube with copper anode were employed to record the small angle x-ray diffraction pattern of highly oriented fibers. Long periods were calculated from the peak positions of the meridional reflection, using Bragg's formula.\(^\text{13}\) Also, confocal laser scanning microscopic images were taken from the center section of the fiber using a Leica™ CLSM.

### 3.4 Results and Discussion

**Spinning and High Temperature Drawing**

Semidilute solutions of polyketones (< 10 wt-%) in phenolic solvents do not crystallize at a rate sufficient for **thermo-reversible gelation** to occur on a time scale
corresponding to the residence time in the cooling trajectory of the spinning process. The diffusion of an appropriate non-solvent (e.g., a small polar organic molecule) enhances the crystallization rate and we succeeded in collecting fibers at practical winding speeds using acetone as the coagulation medium.

The maximum draw ratio $(\lambda_f)$ of these solution spun polyketone fibers is dependent on the temperature, as is shown in Figure 2. The perfectly alternating ethylene-carbon monoxide copolymer exhibits a solid-solid phase transition from the POK-a (orthorhombic) to the POK-β (orthorhombic) crystal structure at 110-130 °C (see Fig. 3). As is indicated in Figure 2, the change in packing of the chains affects the drawing behavior above the transition temperature $(T^1=0.0026 \, \text{K}^{-1})$.

![Figure 2. The maximum attainable draw ratio for polyketone fibers vs temperature $(M_w = 300,000 \, \text{kg/kmol}; \text{fibers drawn batchwise, initial draw rate: } 0.017 \, \text{s}^{-1} (\square) \text{ and } 0.17 \, \text{s}^{-1} (\square))$.](image)

At an initial deformation rate of 0.017 s$^{-1}$, a strong decline in drawability is observed above 225 °C $(T^1=0.002 \, \text{K}^{-1})$. This temperature is 20-25 °C lower than the peak
melting temperature of as-spun fiber and coincides with the onset temperature of melting. Hence, the decline in drawability is associated with first melting phenomena of poorly formed (POK-β) crystals in unoriented material. To demonstrate the effect of (partial) melting on the drawing behavior, DSC traces of oriented polyketone yarns were recorded. The yarns were produced by orienting as-spun fiber via a continuous drawing operation using a hot plate and two roller sets.

Figure 3. Thermograms of polyketone fibers continuously drawn to various ratios at 247 °C ($M_w = 340,000$ kg/kmol: feeding speed was kept constant and in this series the draw rate increases from approximately 2 $s^{-1}$ to 20 $s^{-1}$).
The drawing temperature in this particular case was 247 °C (i.e., significantly above the onset of the melting endotherm) and in this series the rate of deformation was increased from approximately 2 s\(^{-1}\) to 20 s\(^{-1}\). These deformation speeds allow the unoriented fibers to be processed under these conditions, as the onset of the decline in drawability is shifted toward higher temperatures at increasing draw rates (see Fig. 2). This shift can be attributed to a time-temperature superposition generally observed for macromolecular relaxation processes.\(^{16}\) At low draw ratios two melting endotherms are observed; the first one at about the same temperature as for the undrawn material; the second one at slightly higher temperatures. The latter peak can be ascribed to melting of oriented (fibrillar) material, which shifts toward higher temperatures with increasing draw ratio. The endotherm at lower temperatures is due to melting of less extended lamellar-like crystals. In this series the fraction of low-melting material steadily decreases implying that during the deformation process an increasing amount of chains become elongated in the direction of orientation.

As is demonstrated in Figure 4, fibers drawn at somewhat lower temperatures (i.e., below 230 °C) show a continuous increase in melting temperature, viz. from about 250 °C for unoriented material (\(\lambda=1\)) to 273 °C for drawn fibers (\(\lambda=11\)).\(^{17}\) For these oriented fibers no low-melting crystal population was observed in the thermograms. Generally, the increase in melting temperature upon stretching (i.e., orientation) can be explained by a reduction in surface free energy of the oblong-shaped crystals formed.\(^{18}\) The presence of two populations of crystals in fibers prepared under partially molten conditions implies that under these circumstances the polymer network breaks up into different morphological entities. In melts or solutions of flexible polymers this phenomenon has been described using Taylor's meniscus instabilities.\(^{19}\) When crystalline interactions diminish, stress transfer along the chains prevails. As a result, intermolecular stress transfer by means of topological interchain coupling (i.e., entanglements) becomes increasingly important.

High-strength polyethylene fibers are prepared from very high-molecular-weight polymer (\(\mathcal{M} = 4 \cdot 10^6\) kg/kmol; \(m = 28\) kg/kmol).\(^{4}\) In comparison, the number of chain ends in the polyketone sample used (\(\mathcal{M} = 3.4 \cdot 10^5\) kg/kmol; \(m = 56\) kg/kmol) is high.
Network imperfections in the unoriented polyketone fiber cause that slippage of chain ends through entanglements occurs under the applied temperature conditions. Disentangled (unloaded) chain segments will recoil to gain conformational entropy leading to less extended lamellar-like (low-melting) crystals upon cooling. The lower fraction of low-melting material in the more oriented fibers suggests that the time scale on which these flow-related events take place is dominated by the complexity of the required reptation process.

Figure 4. Melting temperature of polyketone fibers ($M_w = 420,000$ kg/kmol) continuously drawn to various ratios slightly below the critical drawing temperature (230 °C). In a one stage drawing process fibers show "overdrawing" characteristics at $\lambda > 11$.

The elongational "solid-state" flow field is regarded to nucleate the formation of fibrils between entanglements, which are still effective at the rate of deformation applied
to the transient network. The more extended chains between these entanglements will aggregate into the oblong-shaped fibrillar crystals, and, supposedly, the lamellar-like crystals will grow at somewhat lower temperatures epitaxially on the surface of these fibrils. As a consequence, the fibrillar crystals will predominantly provide the stress transfer in this composite material.

These so-called "shish-kebab" composite structures generally show a low tensile strength, due to the limited capacity for axial stress transfer. Also, a large amount of topological defects are incorporated into the polymer matrix surrounding the extended material, which contribute to local stress concentrations to occur upon loading.

**Tenacity Development**

To improve the tensile strength of polyketone fibers the influence of the drawing temperature on the mechanical properties was investigated. As expected, the tenacity development is less for fibers oriented in a partially molten stage than for fibers drawn below the onset of first melting phenomena (see Fig. 5). Furthermore, these fibers do not show a pronounced "shish-kebab" composite structure as is evidenced by a single melting endotherm observed during thermal analysis (see Fig. 4). These findings clearly indicate that to prepare high-strength fibers from relatively low-molecular-weight polymers the drawing temperature should be lower than the onset temperature of the decline in the lateral stress transfer mechanism.

Due to the limited drawability at lower temperatures, however, premature damage (e.g., cracks) can be caused. This process, here referred to as "overdrawing", results in a shiny white, non-transparent appearance of the oriented fiber. The onset of the formation of cracks, as indicated by the arrows in Figure 5, is shifted toward higher temperatures according to a similar relation (see Fig. 2). These phenomena are not uniquely related to polyketone fibers and have been observed for a number of other flexible polymers as well. Overdrawing is accompanied by a decreased tenacity development upon stretching, whereas the increase in initial tensile modulus remains in line with the improved molecular orientation. In some cases, a drop in melting
temperature can also be observed, as is shown in Figure 4.

Figure 5. Tensile strength of polyketone fibers drawn under different conditions at a feeding speed of 1 mm/s, the arrows indicate the onset of crack formation and for $\lambda > 17$ only the maximum values are presented ((A) fibers continuously drawn at $T < 230 \, ^\circ$C ($M_w = 340,000 \, \text{kg/kmol}$, fibers drawn according to a multistage procedure are not included); (O): fibers continuously drawn at $T = 234 \, ^\circ$C ($M_w = 340,000 \, \text{kg/kmol}$); (■): fibers drawn batchwise in two stages ($M_w = 420,000 \, \text{kg/kmol}$, initial draw rate $0.017 \, \text{s}^{-1}$, $T_1 = 225 \, ^\circ$C ($A, <10$) and $T_2 = 250 \, ^\circ$C)).

The introduction of morphological defects is reflected in a lower density of the material, due to the formation of voids. A confocal laser scanning microscopic image of an overdrawn polyketone sample is displayed in Figure 6. At low magnifications the cracks are visible as an irregular banded structure, where the bands are oriented perpendicular to the fiber axis. At higher magnifications, it becomes clear that the cracks have a similar appearance as crazes in glassy polymers. The first stage is the lateral isolation of fibrils, which is associated with the formation of relatively large oblong-shaped voids. The formation of these voids is related to a premature fracture
mechanism initiating catastrophic failure of the sample. At higher strains, a larger number of fibrils propagating through the growing crazelike regions start to fail and cracks are formed. Ultimately, the few intact fibrils can not sustain the fiber load and the sample breaks. Obviously, these irreversible flaws in the fiber should be avoided, as they give rise to local stress concentrations in the material, which result in a deterioration of its mechanical performance, especially under dynamic conditions.

The tensile strength of "crack-free" fibers oriented at different temperatures between 170 and 230 °C is uniquely related to the draw ratio, pointing to a single deformation mechanism in this temperature regime. After the first drawing stage, the melting temperature of the material increases significantly (see Fig. 44 allowing the fibers to be processed at higher temperatures in subsequent stages. Accordingly, in a multistage drawing procedure the onset of crack formation is shifted toward higher draw ratios as is indicated in Figures 2 and 5.

Figure 6. Confocal microscopic image of an "overdrawn" polyketone fiber (fiber direction vertical, filament diameter is about 10 µm).

In spite of the extensive work done to produce very high degrees of molecular alignment, like four-stage drawing or applying very low feeding speeds, we have not
been able to prepare crack-free fibers at draw ratios exceeding the value of 17 in a continuous fashion. Accordingly, the tensile strength of multi-filament yarns was limited to a value of 2.5-3 GPa. In order to investigate the development in mechanical properties at higher draw ratios, fibers were also prepared batchwise according to a two-stage procedure, and the results are included in Figure 5. In case of regularly drawn fibers (\( \lambda < 17 \)), the average values for the tensile strength of at least 5 independent single filament tests are presented. It should be noted, that we observed a broad distribution in tensile strength for fibers prepared at higher draw ratios (\( \lambda > 17 \)), due to the statistical nature of the fracture process. In order to rule out the effects of local stress concentrations due to formation of voids, only the maximum values for the tensile strength of selected single filaments are presented in this draw ratio regime. The maximum attainable draw ratio of solution spun polyketone fibers seemed to be limited to a value of 26. At higher draw ratios the probability of fracture has became so high that it was impossible to produce single filaments with a length of more than 500 mm at an initial draw rate of 0.017 s\(^{-1}\). The near to linear correlation between the tensile strength and the draw ratio indicates the effectiveness of the drawing procedure to induce molecular alignment at different temperatures below 230 °C. In the high draw ratio range the amount of load bearing molecules still gradually increases with the macroscopic degree of stretching; the large scatter in tensile strength data can be attributed to overdrawing.

The maximum attained tensile strength of 3.8 GPa for oriented polyketone is rather high, especially considering its low draw ratio (\( \lambda = 26 \)). For example, for poly(vinyl alcohol) with comparable molecular weight (DP = 5,000), a tensile strength of 2.8 GPa has been reported for a highly drawn fiber (\( \lambda > 30 \)). The superior tensile strength of polyketone is attributed to a higher capacity for stress transfer (i.e., covalent linkages per unit of cross sectional area).

**Modulus Development**

In contrast to the tensile strength of continuously drawn polyketone fibers, the initial tensile modulus [at room temperature] steadily decreases with the applied drawing temperature, as is shown in Figure 7.
Figure 7. The initial tensile modulus of polyketone fibers \( [M_w = 340,000 \text{ kg/kmol}] \) continuously drawn at a feeding speed of 1 mm/s (drawing temperatures are indicated, the dashed line represents the modulus development under optimized conditions (see Figure 10)).

Figure 8. True drawing tension vs the draw ratio; drawing temperatures are indicated. (As-spun fibers \( [M_w = 340,000 \text{ kg/kmol}] \) continuously drawn at a feeding speed of 1 mm/s).
This effect is related to the reduction in the drawing stress at higher temperatures (see Figure 8).

In Figure 9 a small angle x-ray (SAXS) pattern of an oriented polyketone fiber is displayed. The pronounced shaking at the equator can be attributed to longitudinal void scattering typical for highly drawn material. After prolonged exposure, the SAXS pattern also reveals a long period of about 190 Å, which is caused by density fluctuations within the material. The presence of a long period reflex implies that the material consists of a sequence of crystalline and less perfect or even non-crystalline (amorphous) domains in the axial direction of the fiber. This result demonstrates the semi-crystalline nature of the material and from a first approximation to the heat of fusion of perfectly crystalline material we estimate a crystallinity of 70-80 % for well-oriented polyketone fiber.9

Figure 9. *Small angle x-ray pattern of an "overdrawn" polyketone fiber (λ = 19.5)* showing longitudinal void scattering and a long period of about 190 Å. [Note the low intensity of the reflex on the meridian even after an exposure time of 1 day].
The modulus of amorphous material at elevated temperatures and accordingly the macroscopic shrinkage forces are proportional to the thermal energy at a given temperature, viz. RT. At high temperatures, the low tension acting on the fiber allows some orientation relaxation of chain segments in the amorphous rubber-like state resulting in a decrease in tensile modulus.

![Graph](image)

**Figure 10.** The initial tensile modulus of polyketone fibers prepared under optimized drawing conditions (○): feeding speed of 10 mm/s \(M_w = 340,000 \text{ kg/kmol}, T_1 < 230 \degree\text{C} (\lambda < 10) \text{ and } T_2 = 245 \degree\text{C}); (■): fibers drawn batchwise in two stages \(M_w = 420,000 \text{ kg/kmol}, \text{ initial draw rate } 0.017 \text{ s}^{-1}, T_1 = 225 \degree\text{C} (\lambda < 10) \text{ and } T_2 = 250 \degree\text{C}).

Loss of orientation of these chain segments can be avoided by cooling down to room temperature, whilst maintaining a high tension to the material. Room temperature is close to the glass transition temperature of unoriented polyketone \(T_g = 5-10 \degree\text{C}\), and the driving force to recoil is vanishingly small under these conditions. In the present work, the latter constraint cooling procedure is followed for the batchwise preparation of drawn fibers.

A more convenient and practical way to avoid molecular relaxation phenomena is to
carry out the drawing procedure at higher speeds. These conditions are accompanied by significantly higher drawing stresses. The tensile modulus of fibers produced according to the latter technique and those of batchwise drawn fibers are presented in Figure 10. Under these conditions, the modulus increases at a steeper slope with the applied draw ratio, implying that the molecular relaxation of chain segments in the non-crystalline state is noticeably suppressed. Fibers oriented to the maximum attainable draw ratio of 26 show an initial tensile modulus of 50-55 GPa. Another way to accomplish higher drawing stresses might be to increase the polymer concentration during fiber spinning. Although we have not investigated concentration effects extensively, the increase in the amount of topological defects (e.g., entanglements) will likely alter the drawing behavior, since these interchain interactions act as barriers for orienting dissipative flow.

-Orientation Development

The overall degree of molecular orientation or the Hermans' orientation factor relates to the molecular orientation distribution.

\[
<P_2> = \frac{3 \langle \cos^2 \phi \rangle - 1}{2}
\]

where \( \phi \) is the angle between the local director of a chain segment and the fiber axis and the parameter \( \langle \cos^2 \phi \rangle \) characterizes the orientation distribution. The orientation parameter \( <P_2> \) increases with the degree of stretching of an unoriented solid flexible polymer, viz. the ratio to which an as-spun fiber is drawn (1). The overall molecular orientation parameter \( <P_2> \) is proportional to the optical anisotropy, viz. the birefringence of the material \( (\Delta n) \).

\[
<P_2> = \frac{\Delta n}{\Delta n_{\text{max}}}
\]
where $\Delta$ is the birefringence of perfectly axially oriented fiber. In section we will derive a first approximation to this value.

In Figure 11 a comparison is made of the development of the birefringence of fibers prepared under different drawing conditions. As is obvious from the results described above, the development of the degree of molecular orientation in solution spun polyketone fibers is strongly improved under optimized drawing conditions.

In order to establish a first approximation to $\Delta$ we assume that the orientation development under optimized conditions has been accomplished according to an affine type of deformation.

Figure 11. The birefringence of polyketone fibers oriented under different circumstances ((○): unoptimized continuous drawing; (□): optimized continuous drawing; (■): optimized batch-wise drawing; solid line: eq. 3 with $A_{n,\text{opt}} = 710 \cdot 10^4$).
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The affine deformation scheme of Kuhn and Grun\(^{28}\) has been used to described the orientation development in flexible polymers\(^{2,29}\) as well as the domain orientation order in more worm-like liquid crystalline polymers, like \textit{para-aramids}.\(^{50}\) According to the Kuhn and Grun theory \(<P_2>\) relates to the macroscopic degree of extension (\(\lambda\)) via

\[
<P_2> = \frac{2}{2} \frac{\lambda^3 + 1}{(\lambda^3 - 1)} - \frac{3}{2} \frac{\lambda^3}{(\lambda^3 - 1)^{3/2}} \tan^{-1}((\lambda^3 - 1)^{1/2})
\]

Eq. (3) suggests a unique relation between the draw ratio and \(<P_2>\), but in this approach molecular relaxation and non-orienting deformation are not taken into consideration. Clearly, this relation is not generally applicable as is evidenced in Figure 11. On the other hand an equal development of both the birefringence and the tensile modulus of the two types of fibers prepared under optimized conditions is observed (see Figures 10 and 11, symbols represent comparable experiments). The latter result suggests that orientation relaxation phenomena are entirely or at least largely surpressed. Accordingly, equation (3) is used to describe the overall orientation parameter in these fibers and a value of \(710 \cdot 10^4\) for \(A_n\) gave a good match between the predicted and the observed values for the birefringence.

Summarizing our results on the optimization of the drawing process, we conclude that variations in processing conditions result in polyketone fibers with largely different mechanical properties. The tensile modulus and molecular orientation of oriented fibers strongly depends on the drawing stress, which is controlled by the process temperature and drawing rate. At lower temperatures, the modulus development in polyketone fibers is improved. However, overdriving should be avoided since this results in a deterioration of the tensile strength. In comparison to solution spun polyethylene fibers the modulus development with the draw ratio is less rapid.\(^{29}\) In view of the expected higher theoretical modulus of POK-fibers,\(^9\) the latter remarkable observation might be attributed to a lower average (macroscopic)shear modulus. Preliminary investigations indeed corroborated this idea, but still more work has to be done to provide a better understanding of this intriguing phenomenon.
To demonstrate the effect of orientation relaxation on the overall stress-strain behavior of polyketone fibers, some fibers were prepared batchwise at less constraint cooling conditions. The high elongation at break, which can be achieved this way, is advantageous for various industrial applications. As is demonstrated in the stress-strain curves in Figure 12, the elongation at break of an unrelaxed highly oriented polyketone fiber is typically between 4-5%.

![Stress-Strain Curves](image)

**Figure 12.** The stress-strain curves of highly oriented relaxed and of unrelaxed polyketone fiber ($M_w = 340,000$ kg/kmol).

In contrast, for a (partially) relaxed fiber with a comparable tensile strength (3.9 GPa), but a lower modulus (42 GPa), the elongation at break can be as high as 7-8%. Obviously, the increase in the elongation at break occurs at the expense of a lower modulus. We attempted to produce similar high elongation yarns by relaxing drawn fibers by means of a low tension aftertreatment at elevated temperatures. This route
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was, however, not successful, due to low hot air shrinkage (at 160 °C below 2 %). The latter result may indicate that additional stiffening and reorganisation occurs within the non-crystalline domains upon cooling and after the drawing procedure has been completed.

3.5 Conclusions

The drawability of polyketone increases with temperature. However, the temperature for effective drawing is limited by the onset of slippage of chain ends through entanglements. This non-orienting flow occurs under conditions when lateral stress transfer by means of crystalline interactions starts to vanish (T > 230 °C). The semi-crystalline nature of the material becomes very noticeable when orientation relaxation within non-crystalline domains is allowed. A marked improvement in the development of both the tensile modulus and the degree of molecular orientation is observed at lower drawing temperatures. Under these drawing conditions the induced degree of molecular orientation can be described using the affine deformation concept in combination with a value for the maximum birefringence of perfectly oriented fiber (An) of 710 \cdot 10^4. The development of the tensile strength at T_{draw} < 230 °C is independent of the drawing temperature and is solely governed by the draw ratio, provided that the material has not been overdrawn. Beyond a draw ratio of 17 the formation of local stress concentrations (i.e., voids and cracks) in solution spun multifilament yarns seems to be inevitable.

Although the drawability of solution spun fibers prepared from perfectly alternating ethylene-carbon monoxide copolymer (A_{pol} = 26) is significantly less than for the non-polar polyethylene, a high strength of about 4 GPa and a satisfactory modulus of about 50-55 GPa can be attained. The combination of a high strength, and a low initial tensile modulus/high elongation at break is an unique feature of relaxed polyketone fibers. This set of properties clearly demonstrates the possibility to prepare tough high-strength polyketone fibers with a relatively high energy absorption.
3.6 References and Notes


   The molecular weights were derived from size exclusion chromatography [SEC/GPC] measurements carried out by A. Buijtenhuijs and coworkers (to be published).


16. Highly oriented fibers (A - 20), prepared via a multi stage drawing process, can show a melting temperature as high as 282 °C.

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25. Similar overdrawing phenomena have been observed in meltspun poly(ethylene terephthalate), polyethylene and in solution spun poly(vinyl alcohol) fibers. J. Veurink, (private communications).