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Mechanical properties and structural transitions in the new rigid-rod polymer fibre PIPD ('M5') during the manufacturing process

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The polymer poly{2,6-diimidazo[4,5-b:4′,5′-e]pyridinylene-1,4(2,5-dihydroxy)phenylene} (PIPD) is spun from a liquid crystalline solution in polyphosphoric acid. The as-spun fibre is a crystal hydrate, which transforms into a bidirectional hydrogen-bonded structure during heat treatment. This transition results in an increase in crystalline modulus along the chain direction due to a decrease of the cross-sectional area per chain, and in an increase in shear modulus due to stronger interaction between the chains caused by the hydrogen bonds. Heat-treated PIPD has a tensile modulus up to 360 GPa, a tensile strength well above 4 GPa, an internal shear modulus of 7 GPa, and a compressive strength of 1.7 GPa. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: rigid-rod polymer fibre; PIPD; mechanical properties; shear modulus)

INTRODUCTION

In the last two decades research has been performed on new polymer fibres with improved tensile and compressive properties. A new class of polymers has been developed in the US Air Force Ordered Polymer Program[1]. Of these so-called rigid-rod polymers, the polymers investigated most are poly(*p*-phenylene benzobisthiazole) (PBT) and poly(*p*-phenylene benzobisoxazole) (PBO). The PBO and PBT fibres exhibit tensile moduli of approximately 300 GPa, which is about three times the modulus of poly(*p*-phenylene terephtalamide) (PPTA). In contrast to the excellent tensile properties the compressive properties of PBO and PBT are rather poor[2].

Whereas the tensile properties of a polymer fibre are governed by the covalent bonds in the polymer chain and by the interchain bonds, the compressive properties of a fibre are mainly determined by the interchain bonds. Due to the weak Van der Waals forces between the chains, the torsion modulus of PBO and PBT, which is a measure for the interchain interaction, is approximately 1 GPa[3]. In the crystal structure of PPTA the chains are hydrogen-bonded in a single direction, which results in a torsion modulus of 2 GPa[4].

Many investigations have focused on increasing the interaction between the chains of rigid-rod polymers. Most investigators tried to obtain a stronger bonding between the chains by crosslinking the polymer chains[5–8]. Only a minimal improvement in compressive strength was achieved, which in most cases was accompanied by a strong decrease in tensile properties. Another group of investigators introduced pendent hydroxyl groups aimed at introducing hydrogen bonds between chains[9–11]. However, instead of intermolecular hydrogen bonds resulting in higher interchain interaction, it is thought that intramolecular hydrogen bonds were formed.

Recently a new member of the rigid-rod polymer family was synthesized at Akzo Nobel Central Research. This new polymer poly{2,6-diimidazo[4,5-b:4′,5′-e]pyridinylene-1,4(2,5-dihydroxy)phenylene} (see *Figure 1*), abbreviated here as PIPD, and in the developing stage called M5, has the ability to form hydrogen bonds between adjacent chains[12].

In this study the mechanical properties and the structural transitions in the spinning and heat treatment of the PIPD fibre were investigated. The manufacturing process consists of four stages: cooling and orientation of the spinning solution in the air gap, coagulation of the solution using water, washing of the fibre, and finally heat treatment of the fibre.

The structural transitions were primarily investigated by X-ray diffraction techniques, supplemented by calorimetric and rheological measurements. The mechanical properties of the fibres were determined both in tensile mode and in compression.

EXPERIMENTAL

Fibre production

The PIPD fibres are spun using the air gap spinning method. An 18 wt% solution of PIPD in polyphosphoric acid (PPA) is extruded through a spinneret with holes ranging from 65 to 200 μm, depending on the experiment. Prior to coagulation the polymer solution is subjected to a draw ratio of between 6 and 70 depending on the diameter of the holes. After coagulation the remaining PPA is removed in a washing stage using hot water, and subsequently the fibre is dried at low temperatures. The diameter of the filaments is approximately 12 μm.

In order to improve its properties the as-spun fibre is heat treated at temperatures above 400°C by passing it through a tube oven under constant stress. The oven is slowly flushed with nitrogen gas. The residence time in the oven is approximately 20 s.

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X-ray diffraction

The polymer solution, the as-spun fibres and the heat-treated fibres were investigated using X-ray diffraction (XRD). The XRD patterns were recorded with a flat-plate Statton camera. Room temperature diffractograms were recorded using a Siemens D5000 transmission diffractometer, and high-temperature diffractograms using a D5000 reflection diffractometer equipped with an Anton Paar HTK oven.

The orientation of the fibres was determined by making azimuthal scans of the most intense equatorial reflection (110)[13]. The azimuthal orientation curve, which was used to calculate the orientation distribution $\langle \sin^2 \phi \rangle_E$ was fitted by a Pearson function.

Heat treatment

In order to improve the orientation and the modulus of as-spun fibres made by a wet-spinning process they are subjected to heat treatment under tension. In PIPD fibres this orientation effect was shown to be accompanied by a structural change causing an increase in shear modulus[14]. The influence of the heat treatment on the structure and the mechanical properties was investigated using a filament oven. A schematic drawing of the filament oven is shown in *Figure 2*.

The oven consists of a quartz tube which is heated by a glowing metal spiral and hot nitrogen gas. The temperature in the oven is measured at three points using micro-thermocouples. The oven is placed between the clamps of a Zwick tensile tester. This arrangement makes it possible to subject a filament to heat treatment under specified stress conditions and to measure its mechanical properties (gauge length 100 mm, testing rate 5%/min) after the heat treatment. The filament count was measured using a Mettler microbalance. The filaments were cut to a length of 150 mm, and the count was determined by weighing each filament at least two times. The filaments have also been used for the XRD investigation and for the measurement of the compressive strength.

Calorimetry

Heat effects in the polymer solution were investigated using a Setaram C80d calorimeter. As the PPA of the polymer solution is corrosive at high temperatures, a glass tube is used as sample container. The glass tube is placed in the measuring vessel and brought into the calorimeter. The sample is equilibrated at 30°C for 10^4 s. The solution is then heated to 200°C at a heating rate of 0.2°C/min. It is kept at this temperature for 10^4 s and subsequently cooled at the same rate of 0.2°C/min.

Rheology

The dynamical viscosity of the solution was measured with a Rheometrics dynamical mechanical spectrometer (RDS II). The solution is placed between two gold-plated discs. The sample is heated to 180°C under nitrogen. After equilibration the temperature is decreased in steps of 2°C, and the dynamical viscosity is measured. Each step takes 1 min, consisting of 20 s for the temperature change, 30 s for stabilization of the temperature, and 10 s for the actual measurement. The amplitude of the test is variable, because the large difference between the viscosity at high and at low temperature makes it impossible to use the same amplitude. This may affect the absolute value of the viscosity but does not change the transition temperature. After the solution was cooled down to 100°C, the measurement was repeated during heating to 180°C.

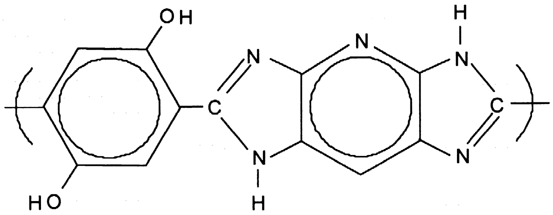

Figure 1 Structural formula of PIPD

Compressive strength

The compressive strength was measured using the elastica test[15]. The filament is wound into a single loop, which is then gradually contracted. During contraction the length of the short axis (a) and the long axis (c) are measured. As long as the deformation of the fibre is elastic, the c/a ratio has a constant value of 1.34. When compressive failure occurs, the c/a ratio increases. The compressive strength can now be calculated from the equation

$$\sigma_{\text{compression}} = 2.85 \times E \times \frac{r}{c_{\text{crit}}} \qquad (1)$$

where E is the modulus, r is the radius of the fibre and c_{crit} is the value of the c-axis at which the c/a ratio starts to deviate from 1.34. Equation (1) is based on the assumption that the modulus in compression equals the tensile modulus, and that it is linear-elastic up to compressive failure. Measurements of the tensile and compressive moduli of PIPD composites indicate that these assumptions are valid[16].

RESULTS

Structural transitions in non-coagulated fibres

Preliminary XRD observations suggested the existence of two different crystal solvate phases. At room temperature the polymer solution is in the crystal solvate 1 (XS_1) phase. At 85°C a transition to the crystal solvate 2 (XS_2) phase starts, which is completed at 115°C. Above 135°C the crystal solvate phases have disappeared, and a nematic phase can be observed. It should be mentioned here that the phases and phase transitions were observed starting at room temperature and using a heating rate of 10°C/h up to 700°C. During the spinning of the fibre the polymer solution is extruded at a temperature of 180–190°C and subsequently cooled to about 20°C in approximately 1 s. The solution is therefore expected to be far from thermodynamic

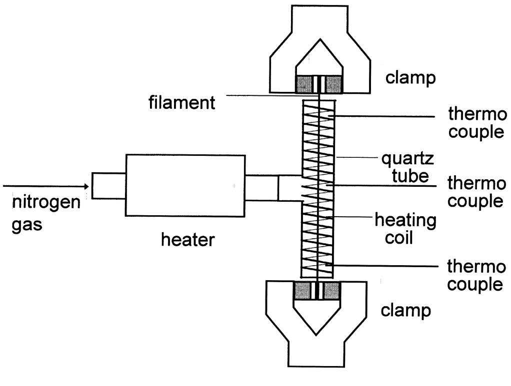

Figure 2 Schematic drawing of the fast filament oven

equilibrium. Hence, the transitions at this cooling rate can be different from those observed during slow heating in the XRD measurement.

For the investigation of the structure of the crystal solvates, a fibre was spun and prevented from coagulating by using paraffin oil. The draw ratio in the air gap was 6. A flat-plate XRD pattern of the non-coagulated fibre, showing a highly oriented and crystalline structure is displayed in *Figure 3*. The crystallinity of the pattern is higher than of the crystal solvates of other rigid-rod polymers such as PBO and PBT.

For further investigation of the transitions in the polymer solution a calorimetric scan was made from 30°C to 200°C and down again to 30°C at a heating and cooling rate of 0.2°C/min. This scan is shown in *Figure 4*, where the upscan and the downscan are plotted at the same scale by multiplying the downscan by -1. In the upscan an endothermic transition is observed at a temperature of 137°C. In the downscan the corresponding exothermic transition is observed at 108°C; in addition, a small peak is observed at 147°C. The shape of the peaks indicates a melt/crystallization transition and not a glass transition temperature. This crystallization peak can be associated with a transition from the nematic phase (at higher temperature) to a crystal solvate phase. The difference between the transition temperatures recorded in the upscan and in the downscan can be associated with undercooling of the sample during the downscan.

The rheological behaviour of the solutions can also provide information about structural transitions in the polymer solution. The result of a scan of an 18 wt% PIPD solution in PPA is shown in *Figure 5*. In the downscan (cooling down of the solution) a transition is observed at 120°C. During the upscan a similar transition is observed; however, this occurs at a temperature which is about 20°C higher. These temperatures are in excellent agreement with the transitions observed using calorimetry. The value of the viscosity before and after the transition shows that the phases can indeed be described as a nematic solution and a crystal solvate.

Structural transitions during coagulation and washing

The transition from the nematic phase to the crystal solvate, as described in the previous section, is caused by cooling of the solution. The cooling takes place in the air gap of the spinning process and, possibly, in the first part of the coagulation bath. After this cooling the solution is coagulated in a water bath. In order to investigate the coagulation of the crystal solvate, equatorial scans of the non-coagulated fibre were made using a X-ray transmission diffractometer. The fibre was mounted in the diffractometer in air to allow slow coagulation. During a period of 9 h the coagulation was monitored by making scans of 13 min from

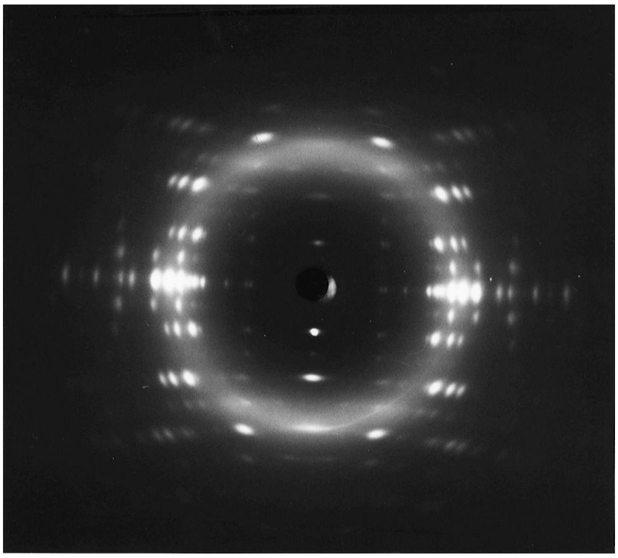

Figure 3 X-ray diffraction pattern of non-coagulated PIPD fibre

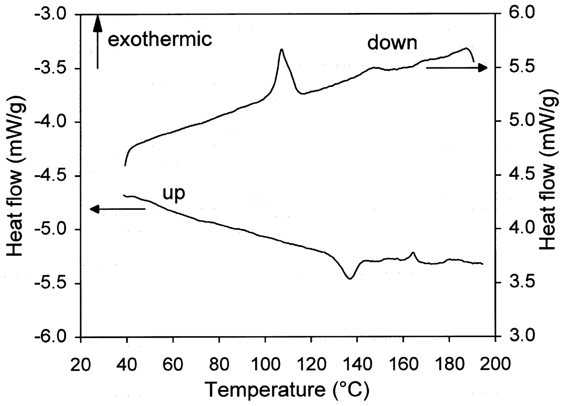

Figure 4 Calorimetric scan of PIPD/PPA solution, scan rate 0.2°C/min

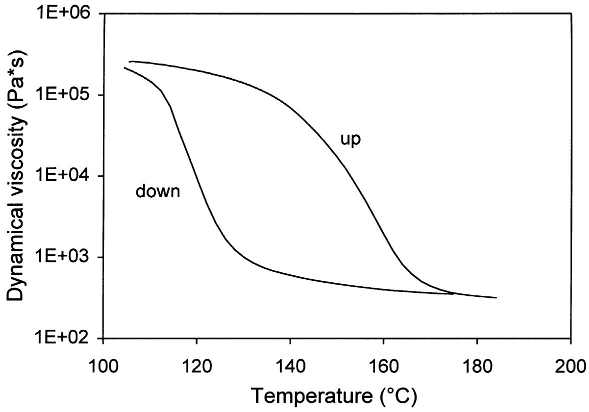

Figure 5 Dynamical viscosity as a function of temperature

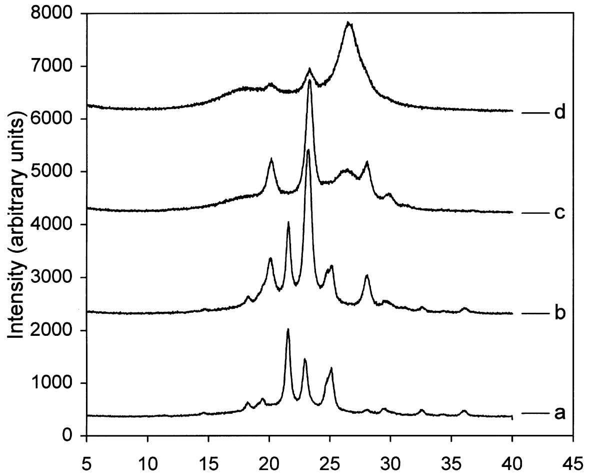

Figure 6 Equatorial X-ray diffractograms during coagulation of PIPD fibre: (a) $t = 0$; (b) $t = 10$ min; (c) $t = 4$ h; (d) $t = 8$ h

5 to 40 degrees 2θ, where θ is the Bragg angle (*Figure 6*). During this period the crystal solvate phase changes into another phase showing a diffraction pattern that resembles the polymer phase. In *Figure 7* this equatorial XRD pattern is compared with the pattern of a fibre which had passed the coagulation bath but had not been washed yet. The upper pattern is from the fibre coagulated in the process, and the bottom pattern is from the fibre coagulated in air. Except for the sharper peaks at 20 and 23 degrees 2θ, the two patterns are similar. This may be an indication that during the spinning process the fibre coagulates from the crystal solvate phase.

In the last stage of the spinning process the fibre is washed with water at 80°C after coagulation. Equatorial scans of fibres taken from different stages of the washing process are shown in *Figure 8*. The bottom curve is from a fibre taken after coagulation but before washing. The fibre contains 44% PPA. Further washing results in the decrease of the reflection at approximately 18 degrees and the development of a reflection at 10 degrees. The upper curve is from the fibre after the washing stage, i.e. from the as-spun fibre.

Structural transitions during heat treatment of fibres

After the fibre is washed and dried, it is subjected to a heat treatment. During this heat treatment two phenomena are observed. The first phenomenon is an improvement of the orientation of the fibre. The second phenomenon is a change in crystal structure, see *Figure 9*. During heat treatment of the as-spun fibre the first equatorial diffraction peak shows a considerable shift to larger 2θ-values, i.e. to smaller d-spacings. The other strong equatorial reflection shows a much less pronounced shift to smaller diffraction angles, i.e. larger d-spacings. The latter effect can be attributed to thermal expansion. An upward shift of the equatorial reflection at 10 degrees 2θ is also observed during drying of the fibre with dry nitrogen at room temperature, whereas the position of the other reflection remains unchanged[13]. If the fibre is subjected to ambient conditions, the shifted peak returns to its initial position. This indicates that the transition is caused by the removal of water from the crystal structure. The as-spun structure thus represents a crystal hydrate, which is transformed into the water-free polymer crystal during heat treatment. The fact that one of the peaks shifts to larger d-spacings, whereas the position of the other peak remains constant, implies that the unit cell of the as-spun crystal structure is expanded in just one direction due to the water molecules compared with the water-free crystal structure[13]. The projection of both the as-spun and the heat-treated structures is shown in *Figure 10*.

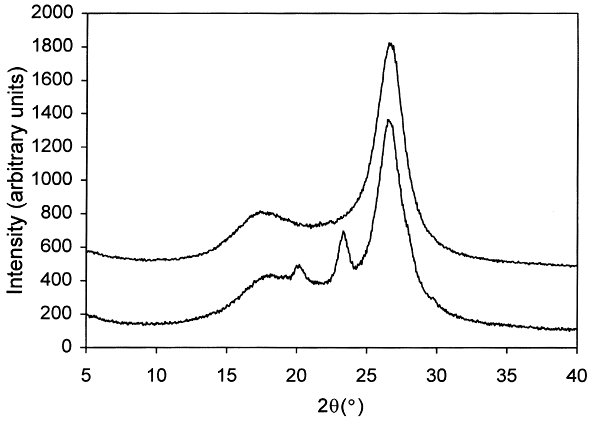

Figure 7 Equatorial X-ray diffractograms of coagulated (unwashed) PIPD fibre taken from the spinning process (upper curve) and PIPD fibre coagulated by exposure to air (lower curve)

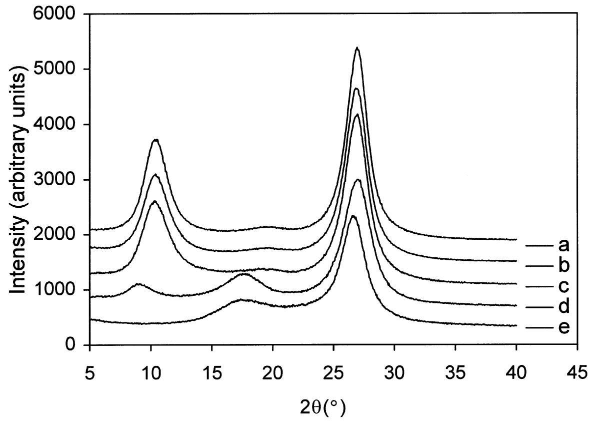

Figure 8 Equatorial X-ray diffractograms of fibres taken from different stages of the washing process: (a) PPA concentration < 0.06%; (b) 0.14%; (c) 4.4%; (d) 28%; (e) 44%

The heat-treated fibre has a crystal structure in which hydrogen bonds are possible in two directions[13]. This bidirectional hydrogen-bonded network causes a strong interaction between polymer chains and is therefore expected to result in a high shear modulus. In the as-spun state the water molecules between the polymer chains weaken the interchain interactions, suggesting a lower shear modulus. The cross-sectional area perpendicular to the chain direction decreases during the removal of water from 28.5 to 20.8 Å^2 (see ref [13]). This results in an increase of the crystalline modulus along the chain direction (expressed in GN/m^2 = GPa) by 37%.

Discussion of the structure development during the fibre fabrication process

In the preceding sections the structural transitions during the different stages of the fibre manufacturing process were described. In this section a summary of the structure development during the process is given and schematically shown in *Figure 11*.

In the first part of the spinning process the spinning dope is heated to about 180°C. At this temperature the solution is in the nematic phase (position 1 in *Figure 11*). In the

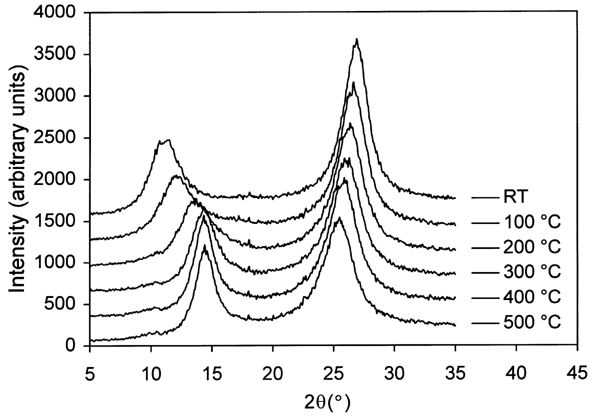

Figure 9 Equatorial X-ray diffractograms of as-spun PIPD fibre at different temperatures

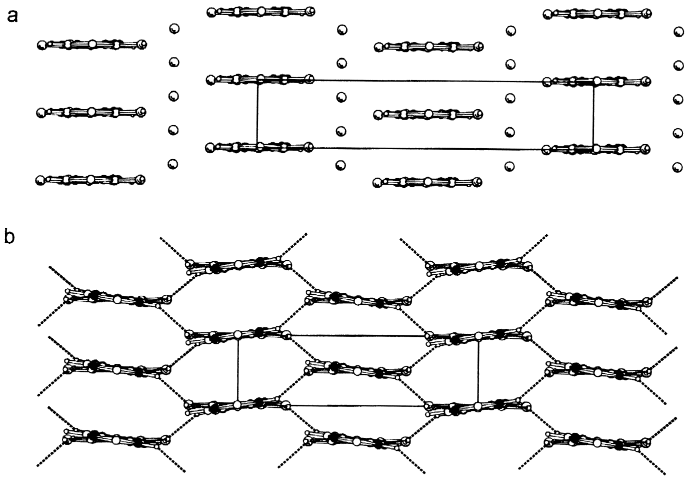

Figure 10 Projection of as-spun structure (a) and heat-treated structure (b)

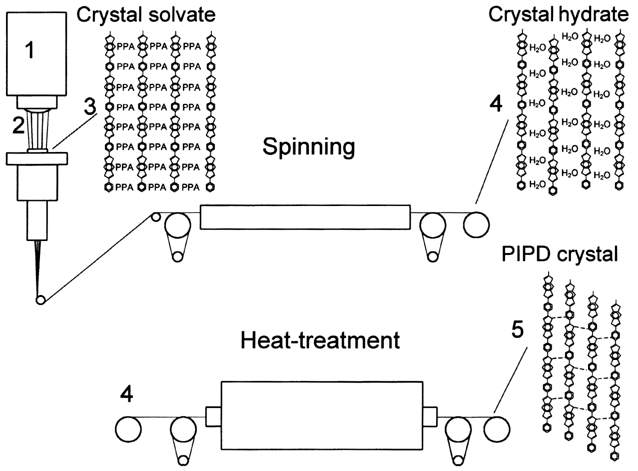

Figure 11 Structure development during the fibre fabrication process: 1, nematic phase; 2, oriented nematic phase; 3, crystal solvate; 4, crystal hydrate; 5, water-free structure

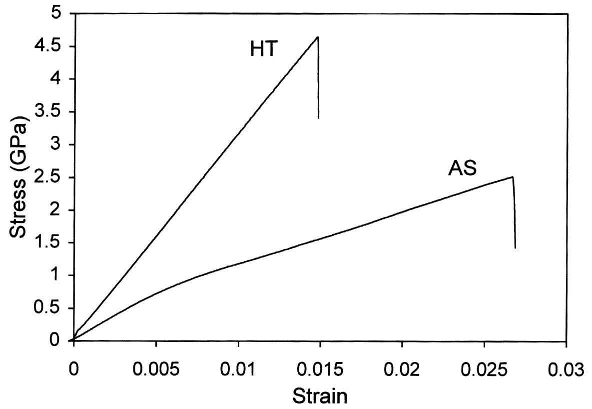

Figure 12 Stress–strain curves of as-spun (AS) and heat-treated (HT) filaments

spinneret and in the first part of the air gap the orientation of the nematic phase takes place[17] (position 2). After cooling of the solution the nematic phase transforms into a crystal solvate phase (position 3). The fibre is subsequently coagulated and washed. The PPA in the crystal solvate phase is replaced by water, and the structure is transformed into a crystal hydrate (position 4). After mild drying, the water is still present in the structure. At this stage the fibre is called as-spun. During heat treatment of the fibre the water is removed from the crystal structure and the water-free PIPD structure is formed (position 5). If the heat treatment temperature is too low or the residence time in the oven too short, the transition from crystal hydrate to PIPD crystal is reversible.

Mechanical properties

During heat treatment a phase transition from a crystal hydrate to a water-free structure is observed. The mechanical behaviour of the heat-treated fibre differs to a large extent from that of the as-spun fibre. Stress–strain curves of both as-spun and heat-treated filaments, measured with an Instron 1121 tensile tester using a test length of 100 mm and a strain rate of 10%/min, are shown in *Figure 12*. The initial modulus of the heat-treated fibre is about twice that of the as-spun fibre. Another striking difference is observed in the yielding behaviour of the two fibres. Whereas the slope of the tensile curve of the as-spun filaments decreases from approximately 150 GPa before yielding to 80 GPa after yielding, there is practically no yielding observed in the heat-treated filaments. Yielding occurs when the shear stress in a fibre reaches a critical value[18]. The shear stress acting on a polymer chain is given by $\sigma \sin\phi \cos\phi$, where σ is the tensile stress, and ϕ is the disorientation angle of the polymer chain with respect to the fibre axis. The critical value of the shear stress at which yielding occurs is thought to be a fraction of the shear modulus[19]. The absence of yielding in the heat-treated filaments can thus be explained by an increase in orientation (resulting in a decrease in shear stress) and/or by an increase in shear modulus (resulting in an increase in critical shear stress) during heat-treatment.

Determination of the shear modulus

The relation between the modulus and the chain orientation is given by[20]

$$\frac{1}{E}=\frac{1}{e_c}+\frac{\langle\sin^2\phi\rangle_E}{2g} \tag{2}$$

where E is the tensile modulus, e_c the crystalline or chain modulus, $\langle\sin^2\phi\rangle_E$ the second moment of the orientation distribution, and g is the shear modulus. This equation shows that in a graph of $1/E$ *versus* $\langle\sin^2\phi\rangle_E$ the datapoints of fibres having the same shear modulus g are positioned on a straight line with slope 1/2*g*. In a previous section it was shown that the crystal structure changes during heat treatment. This transformation is expected to yield an increase in shear modulus. This suggests that by plotting 1/*E versus* $\langle\sin^2\phi\rangle_E$ lines with different slopes for as-spun fibres and heat-treated fibres should be obtained. In order to test this hypothesis, as-spun filaments were selected from yarns with different moduli, which were obtained using different process conditions. The moduli of one half of the number of filaments were measured using a Zwick tensile tester. The filaments were only subjected to small strains to prevent failure. Subsequently, the orientation of the filaments was determined by means of X-ray diffraction using a filament holder, which makes it possible to determine the orientation of single filaments. The remaining filaments were heat-treated using the oven described in the experimental section. The heat treatment temperature was 400°C, and the stress was varied for the different filaments. The orientation of these fibres was measured using X-ray diffraction. The modulus of the as-spun filaments ranged from 80 to 150 GPa, and the modulus of the heat-treated filaments from 210 to 360 GPa. The results are shown in *Figure 13*. In this figure three effects can be observed, each resulting in an increase in tensile modulus. One effect is the increase in shear modulus, visualized by a change in slope of the line fitted through the experimental values after the heat treatment compared with that before the heat treatment. This increase in shear modulus is probably caused by the development of hydrogen bonds. A second effect is the increase in crystalline modulus along the chain direction. This originates from the decrease of the cross-sectional area per chain perpendicular to the chain direction during the removal of water. Finally, an increase in modulus is caused by the improved orientation after the heat treatment. The values of the crystalline modulus along the chain direction and the shear modulus were calculated by applying linear regression to the experimental values in *Figure 13*. The results are shown in *Table 1*. The increase in crystalline modulus by 55% is more than is suggested by the 27% decrease in cross-section per chain which results in a 37% increase of the crystalline modulus. If the large standard error shown in *Table 1* is taken into account, the two observations are in good agreement.

In *Figure 14* the three effects are shown in a schematic drawing. Step 1 presents the increase in tensile modulus caused by the increase in shear modulus, step 2 by the increase in crystalline modulus, step 3 by the orientation effect, and step 4 is the total effect of the heat treatment on the modulus.

Compressive strength

Experimentally, a relation between the compressive strength and the torsion modulus *G* was found for a number of fibres[21]

$$\sigma_c = 0.3G \tag{3}$$

For perfectly oriented fibres and random lateral texture the torsion modulus *G* equals the internal shear modulus *g*.

In the previous section it was shown that during heat treatment the shear modulus of PIPD fibres increases from 3.8 to 7.4 GPa. If equation (3) holds, the compressive strength of as-spun PIPD fibres should be equal to 1.1 GPa, and the compressive strength of heat-treated PIPD to 2.2 GPa. This was tested by measuring the compressive strength of as-spun filaments, and filaments heat-treated at either 200°C or 400°C. The tensile modulus necessary for the calculation of the compressive strength was measured using a Zwick tensile tester. The results are shown in *Table 2*. The compressive strength of the filaments heat-treated at 200°C is considerably higher than the compressive strength of the filaments heat-treated at 400°C. Investigation with polarizing microscopy showed that cracks were present in the filaments heat-treated at 400°C, which probably result in a decrease in compressive properties. The compressive strength of the filaments heat-treated at 200°C is 140% higher than the compressive strength of as-spun filaments, which is apparently an even higher increase than that predicted by equation (3).

Table 1 Elastic constants derived from linear regression of the data in Figure 13

		Regression value (GPa)	Standard error (GPa)
As-spun	e_c	320	56
	g	3.8	0.4
Heat-treated	e_c	500	60
	g	7.4	0.9

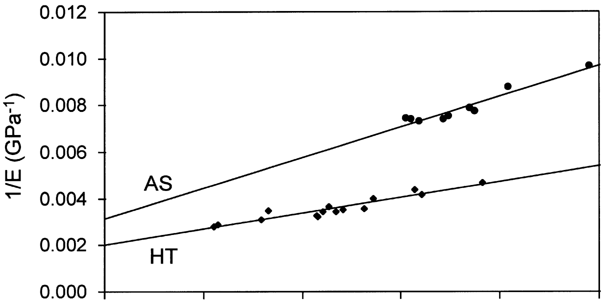

Figure 13 The relation of 1/*E* and $\langle\sin^2\phi\rangle_E$ for as-spun (AS) and heat-treated (HT) filaments

Table 2 Average tensile moduli and compressive strengths of as-spun filaments (AS), and filaments heat-treated (HT) at 200°C and 400°C

	Tensile modulus (GPa)	Compressive strength (GPa)
AS	195	0.7
HT 200°C	295	1.7
HT 400°C	320	1.1

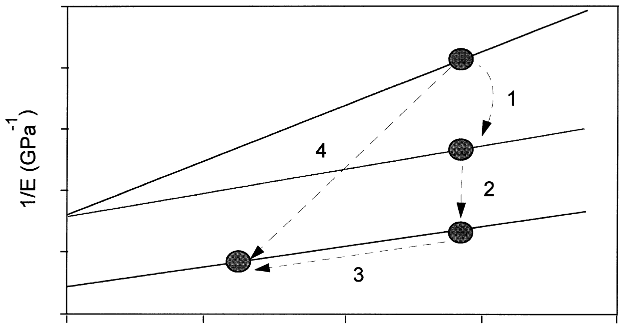

Figure 14 Schematic drawing of modulus increase during heat treatment: 1, increase in shear modulus; 2, increase in crystalline modulus; 3, increase in orientation; 4, total effect of heat treatment

CONCLUSIONS

During the fibre production process of PIPD different types of structural order have been observed, associated with a nematic solution, a crystal solvate, a crystal hydrate, and a bidirectional hydrogen-bonded structure. The structural transition from crystal hydrate to the bidirectional hydrogen-bonded structure is realized by a heat treatment at high temperature under stress. Together with this structural transition a large increase in tensile modulus is observed. This increase is caused by an increase in orientation, an increase in shear modulus, and an increase in crystalline modulus. These three effects combined result in an increase in modulus from about 150 GPa for as-spun fibres to about 350 GPa for heat-treated fibres.

The internal shear modulus of 7.4 GPa after the heat treatment results in a high compressive strength of the heat-treated fibre. Whereas other polymer fibres have compressive strengths between 0.2 and 0.6 GPa, the PIPD fibre has a compressive strength of 1.7 GPa.

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