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Liquid Crystalline Main Chain Polymers with a Poly(p-Phenyleneterephthalate) Backbone. 2. Fiber Spinning and Mechanical Properties of Polyesters with Alkoxy Side Chains

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SYNOPSIS

Fiber spinning and mechanical properties of four rigid polyesters with alkoxy substituents of different length and placement were evaluated. Properties of oriented fibers from the polymer with dodecyloxy substituents on the terephthalate moiety, PTA12HQ, were significantly affected by the crystal modification. At room temperature the following properties (tensile modulus $E$, tensile strength $\sigma_b$, and strain at break $\varepsilon_b$) could be obtained: $E = 9.5$ GPa, $\sigma_b = 85$ MPa and $\varepsilon_b = 1.1\%$ for phase $L_c$ (the “frozen in layered mesophase”); $E = 10.4$ GPa, $\sigma_b = 59$ MPa and $\varepsilon_b = 0.6\%$ for modification A; $E = 17.3$ GPa, $\sigma_b = 158$ MPa and $\varepsilon_b = 1.2\%$ for modification B. Because of the higher amount of main chains per cross-sectional area the polymer with hexyloxy side chains, PTAGHQ, showed better properties at a comparable degree of molecular orientation: $E = 24$ GPa, $\sigma_b = 270$ MPa, $\varepsilon_b = 1.4\%$. Fibers obtained from the polyester with dodecyloxy substituents on the hydroquinone moiety, PTAHQ12, were too brittle to handle. The polyester with dodecyloxy substituents on both moieties, PTA12HQ12, was spun from the isotropic melt. Because of the obtained low degree of orientation, properties ($E = 1$ GPa, $\sigma_b = 40$ MPa, and $\varepsilon_b = 6.3\%$) were governed by interactions between the chains (the main chains are not load-bearing).

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Keywords: rigid rod polymer • thermotropic • aromatic polyester • fiber • modulus • crystal structure

INTRODUCTION

Rigid backbone polymers with the ability to form liquid crystalline structures in the melt have received a great deal of attention in the past years. From a technological point of view the main interest arises because of the low melt-viscosity of (preferentially nematic) mesophases. This will allow the production of for example thin-walled precision products by injection moulding. Another important feature associated with liquid crystalline behavior is the relative ease with which molecular orientation can be obtained. From theory as well as practice it is well known that orientation is an important factor for achieving high modulus materials.

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These and similar polymers were characterized by DSC and x-ray diffraction by others as well.\textsuperscript{5-9}

For PTA\textsubscript{12}HQ the phase behavior was shown\textsuperscript{4} to be as depicted in Figure 1. At room temperature two different solid phases A and B can exist. In both room temperature phases the main chains are aligned parallel in layers, which are separated by the alkoxy side chains at a distance $d$ (Fig. 2). When heating these modifications above the side-chain disordering temperature $T_\text{s}$ an intermediate phase $A'$ is formed. At the melting temperature of the main chains $T_m$ a layered mesophase is formed. The ordering present in this phase disappears at the transition to the isotropic melt $T_i$.

For a polymer with shorter side chains, PTA\textsubscript{6}HQ, it was shown that a nematic mesophase can exist when the inherent viscosity is sufficiently high.\textsuperscript{4,9} The phase behavior of this polymer is shown schematically in Figure 3. By rheological measurements it was shown that the layered mesophase $L_m$ behaves like a solid rather than a liquid.\textsuperscript{4} The nematic mesophase $N$ was shown to have the very low melt viscosity typical of liquid crystalline polymers.\textsuperscript{4}

The influence of molecular structure (placement and amount of side chains) on the phase behavior was investigated by including two related polymers with dodecyloxy side chains, PTAHQ\textsubscript{12} and PTA\textsubscript{12}HQ\textsubscript{12}. Though both polymers do not show liquid-crystalline behavior on heating, PTAHQ\textsubscript{12} shows a layered mesophase on cooling (monotropic behavior).\textsuperscript{4,8} The phase behavior of both polymers is shown schematically in Figures 4 and 5.

The first objective of this report is to relate the feasibility of obtaining oriented fibers from these polymers to their rheological behavior described earlier.\textsuperscript{4} The second objective is to investigate whether the high chain modulus of the rigid backbone is reflected in the mechanical properties of such 'diluted' polymers. The third objective is to illustrate the influence of molecular structure on the physical properties.

Subsequent communications will deal in more detail with the tensile modulus of PTA\textsubscript{12}HQ films\textsuperscript{10} (as a function of temperature and draw-ratio) and the crystal structures\textsuperscript{11} of PTA\textsubscript{12}HQ.

**EXPERIMENTAL**

The polymers used in this study were prepared by solution polycondensation as described earlier.\textsuperscript{4}

All DSC measurements were performed on a DuPont 9900 DSC with a heating rate of 20°C/min in a nitrogen atmosphere. The peak of the melting endotherm was taken as the melting point.

Inherent viscosities were determined at 25°C with solutions of the polymer in CHCl\textsubscript{3} (2 g/L) using an Ubbelohde capillary viscosimeter. As PTAHQ\textsubscript{12} was insoluble in chloroform its inherent viscosity was determined in $p$-chlorophenol at 50°C.

Fibers were spun using a home built capillary rheometer (die diameter 0.5 mm, $L/D = 50$, diameter of the reservoir 1 cm) equipped with a winding unit. The shear rate was 326 s\textsuperscript{-1} and spinning velocity 1.22 m/min. Drawing of fibers was performed by hand on a hot shoe. For PTA\textsubscript{12}HQ a typical draw-ratio of 7 resulted in a fiber diameter of about 0.2 mm (24 tex). Only PTA\textsubscript{6}HQ was oriented by draw-down during fiber spinning. More details with regard to fiber spinning are given in Results and Discussion.

Mechanical measurements were performed on an Instron tensile testing machine, according to ASTM D3379. Crosshead speed was 5 mm/min and the gauge length 50 mm. At least five measurements were taken for each sample.

Flat-plate fiber diffractograms were recorded in transmission using Ni-filtered CuK\textsubscript{α} radiation. Orientation of the fibers is given as the half-width at half-height of equatorial reflections (azimuthal scan). The reflections used are the first, second, and third order of the characteristic layer distance $d$ of the layered structure.

High temperature x-ray diffraction measurements were made using a Guinier-Lenne camera equipped

![Diagram](image)

Figure 1. Scheme of the phase behavior in PTA\textsubscript{12}HQ powders.\textsuperscript{4} The two room temperature modifications A and B can transfer to the intermediate phase $A'$ at the side chain disordering temperature $T_s$. At the main chain melting temperature $T_m$ the layered mesophase $L_m$ is formed and the isotropic melt I is reached at the clearing temperature $T_i$. Note that modification B is only available in the as-made powders.
Figure 2. Schematic representation of the layered modifications A (a) and B (b) in PTAnHQ. The layer spacing $d$ and tilt angle $\beta$ are typical for the different phases. For ease of drawing the tilt angle in modification B is taken in the xy-plane. It should be noted that the same layer distance can also be obtained by tilting the side chains with respect to the main chains in the xz-plane.

RESULTS AND DISCUSSION

Fiber Spinning

For PTAl2HQ an attempt was made to spin fibers from the highly viscous\textsuperscript{4} layered mesophase $L_m$ in the temperature region between 200 and 240°C. The fibers that were obtained in this way were very irregular. Similar to melt fracture of isotropic polymers the number of irregularities increased at an increasing shear rate. The only way to obtain smooth fibers from PTAl2HQ was spinning from the isotropic melt at 260°C. Oriented fibers could be obtained by drawing during spinning or by drawing as spun, unoriented, fibers in the layered mesophase ($\approx 200$°C) on a hot shoe. Because the drawing temperature is better defined by drawing on a hot shoe this technique was used in the course of this study. Draw ratios up to $\lambda \approx 7$ could only be reached if the polymer had an inherent viscosity well above 2 dL/g.

Figure 3. Scheme of the phase behavior in PTA6HQ powders,\textsuperscript{4} showing the subsequent transitions to the layered mesophase $L_m$, the nematic mesophase $N$, and the isotropic phase I.

Figure 4. Scheme of the phase behavior in PTAHQ12 powders.\textsuperscript{4} At the side-chain disordering temperature $T_s$ (B) the intermediate phase B' is obtained, which transforms to the isotropic melt I at the clearing temperature $T_i$. On cooling from the isotropic melt the layered mesophase $L_m$ is passed (monotropic behavior).
Figure 5. Scheme of the phase behavior in PTA12HQ12 powders. Above the side-chain disordering temperature $T_s$, an intermediate phase is formed, which transforms to the isotropic melt at the clearing temperature $T_i$.

PTA6HQ could be spun from the nematic melt at 240°C and oriented fibers were obtained by draw-down ($\lambda \approx 20$).

Fibers of PTA12HQ12 were too brittle to handle. As a consequence mechanical properties could not be measured. The polymer with the double amount of side chains, PTA12HQ12, could only be spun into smooth fibers at a temperature of 230°C, well above the DSC endotherm at 188°C. They could be oriented to a moderate degree ($\lambda = 1.8$) at 155°C on a hot shoe. The fiber mechanical properties and molecular orientations of PTA6HQ, PTA12HQ, and PTA12HQ12 are listed in Table I.

### Fiber Characterization by DSC and X-Ray Diffraction

**PTA12HQ**

The DSC thermogram of a PTA12HQ fiber spun at 260°C and stretched on a hot shoe at 200°C to $\lambda = 7$ is shown in Figure 6, curve a. Two transitions at, respectively, 170 and 240°C, can be seen which correspond to $T_m$ and $T_i$ (see Fig. 1). A transition which can be associated with a side chain disordering (at $T_s$) is not found. The x-ray diffraction pattern of this fiber (Fig. 7) shows a low amount of three-

![Figure 6](image-url)

**Figure 6.** DSC thermograms of PTA12HQ fibers in (a) phase $L_f$, (b) mixture of phase $L_f$ and modification B, obtained after "annealing" of phase $L_f$ for 26 days at room temperature, (c) modification B, obtained after "annealing" of phase $L_f$ for about 300 days at room temperature, (d) modification A.

### Table I. Fibre Properties of PTA6HQ, PTA12HQ, and PTA12HQ12

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Crystal Modification</th>
<th>$\lambda^*$</th>
<th>$\varphi$ (deg)$^b$</th>
<th>$E$ (GPa)$^c$</th>
<th>$\sigma_0$ (MPa)$^d$</th>
<th>$\varepsilon_0$ (%)$^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTA6HQ</td>
<td>A</td>
<td>20</td>
<td>5.8</td>
<td>24</td>
<td>270</td>
<td>1.4</td>
</tr>
<tr>
<td>(2.3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PTA12HQ</td>
<td>$L_f$</td>
<td>1.9</td>
<td>12</td>
<td>1.1</td>
<td>52</td>
<td>16</td>
</tr>
<tr>
<td>(2.3)</td>
<td>$L_f$</td>
<td>7.0</td>
<td>6</td>
<td>9.5</td>
<td>85</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>7.0</td>
<td>6</td>
<td>10.4</td>
<td>59</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>7.0</td>
<td>6</td>
<td>17.3</td>
<td>158</td>
<td>1.2</td>
</tr>
<tr>
<td>PTA12HQ12</td>
<td>$L_f$</td>
<td>1.8</td>
<td>&gt; 10</td>
<td>0.5</td>
<td>21</td>
<td>24</td>
</tr>
<tr>
<td>(1.4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Draw-ratio. For PTA6HQ draw-down during spinning, all other polymers were drawn on a hot shoe (see text).

$^b$ Orientation angle, from half-width at half-maximum.

$^c$ Tensile modulus.

$^d$ Tensile strength.

$^e$ Strain at break.

$^f$ Not oriented.

$^g$ Non-interdigitated layered structure, see Rodriguez-Parada. 

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dimensional ordering (streak like meridional reflections, no off-axis reflections). This leads to the conclusion that by fast cooling from the layered mesophase a 'frozen in phase' is found at room temperature. Obviously the cooling rate after orienting a fiber on a hot shoe is much larger than the cooling rate used in the DSC experiments earlier. This 'frozen in layered mesophase' structure will be referred to as phase $L_f$. It can be added to the initial scheme of the phase behavior of PTA12HQ shown in Figure 1, which was based on DSC measurements of powders. This leads to the more extensive scheme of the phase behavior of PTA12HQ. As indicated in Figure 8, phase $L_f$ is not stable at room temperature; it transforms slowly to a modification in which a much higher amount of ordering is present. The x-ray diffractogram of such a fiber after 'annealing' for about 300 days at room temperature is shown in Figure 9. A highly crystalline structure is found with a layer spacing $d$ of 15.2 Å, corresponding to modification B. This structure can also be induced within a week by immersing as spun fibers (phase $L_f$) in methanol, which agrees well with the fact that as-made PTA12HQ powders, made by solution polycondensation followed by precipitation in methanol, are also in phase B.

The rate of the transformation from phase $L_f$ to modification B can be followed by DSC measurements as the side-chain disordering endotherm at $T_s$ (B) gradually increases (Fig. 6, curves b and c). By plotting the heat of fusion of this endotherm ($\Delta H_s$) against time the low rate of this process becomes visible (Fig. 10). It is interesting to note that during this process $T_m$ as well as $\Delta H_m$ do not change. This indicates that, regardless of prior history, all fibers are in phase A' below the main chain melting temperature, as was already indicated in Figure 8.

By heating an as-spun PTA12HQ fiber (phase $L_f$) to 140°C (phase A'), followed by cooling to room temperature, a fiber in modification A can be obtained. The DSC thermogram of such a fiber (Fig. 6 curve d) shows the characteristic side-chain disordering endotherm at 40°C of modification A.

![Figure 7](image7.png)

**Figure 7.** Flat-plate x-ray diffractogram of a PTA12HQ fiber quenched from the layered mesophase (phase $L_f$, $\lambda = 7$). Fiber axis is vertical, sample to film distance 6 cm.

![Figure 8](image8.png)

**Figure 8.** Scheme of the phase behavior in PTA12HQ fibers. Compared with the scheme for PTA12HQ powders (Figure 1) an extra phase $L_f$ ('frozen-in layered mesophase') is found.

![Figure 9](image9.png)

**Figure 9.** Flat-plate x-ray diffractogram of a PTA12HQ fiber in modification B ($\lambda = 7$). Fiber axis is vertical, sample to film distance 6 cm.
ther evidence for the presence of modification A is found by x-ray diffraction (Figure 11), from which the characteristic layer distance of 21 Å of PTA12HQ in modification A can be deduced. In table II the characteristic distances as derived from the x-ray reflections of PTA12HQ in the different structures are summarized. Fiber densities are also reported in this table. As expected the density of PTA12HQ increases when going from the less crystalline structures (phase $L_I$ and modification A) to the highly crystalline modification B. A similar increase in density has been reported by Stern for poly(3-n-alkyl-4-hydroxybenzoate)s. More details on the crystal structure of PTA12HQ as well as high temperature x-ray diffraction will be published separately.

**Figure 11.** Flat-plate x-ray diffractogram of a PTA12HQ fiber in modification A ($\lambda = 7$). Fiber axis is vertical, sample to film distance 6 cm.

**PTA6HQ**

In Figure 12a the x-ray diffractogram at room temperature of an oriented PTA6HQ fiber is shown. This fiber was made by spinning from the nematic mesophase, followed by draw-down. The streak-like meridional reflections indicate that a low amount of three-dimensional order is present. By annealing the quenched fiber for one hour at 160°C sharp Bragg reflections develop, pointing to an ordered three-dimensional structure (Fig. 12b). From the equatorial reflection at $\approx 14$ Å and its higher order at

<table>
<thead>
<tr>
<th>Table II. Densities and Characteristic Distances of the Fibres</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
</tr>
<tr>
<td>------------------</td>
</tr>
<tr>
<td>PTA6HQ</td>
</tr>
<tr>
<td>PTA12HQ</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>PTAHQ12$^f$</td>
</tr>
<tr>
<td>PTA12HQ12$^f$</td>
</tr>
</tbody>
</table>

$^a$ Characteristic layer distance $d$.
$^b$ Characteristic equatorial reflection, associated with the $y$-direction.
$^c$ Fibre repeat distance.
$^d$ Obtained by fast cooling after drawing in the layered mesophase.
$^e$ Not determined.
$^f$ Compression moulded sample.
$^g$ Non-interdigitated layered structure, see Rodriguez-Parada.®
Figure 12. (a) Flat-plate x-ray diffractogram of an oriented PTA6HQ fiber spun from the nematic mesophase ($\lambda = 20$). (b) The same fiber after annealing one hour at 160°C. Fiber axis is vertical, sample to film distance 6 cm.

7.05 Å it is concluded that a considerable amount of polymer in the annealed fiber is in a layered structure with a layer distance of approximately 14.1 Å (resembling modification A).\(^7\) If we index the strong reflection at 11.4 Å on the first layer line as the (001) reflection and assume a monoclinic unit cell, a tentative unit cell with $a = 15.6$ Å, $b = 7.26$ Å, $c = 12.6$ Å and $\beta = 115.2^\circ$ is proposed. All observed reflections can be indexed using this unit cell (Table III), but it should be noted that the amount of reflections is not very high. The density of this unit cell (containing two repeat units) amounts to 1.132 g/cm\(^3\) and compares fairly well with the measured density of 1.14 g/cm\(^3\). If we compare the density with results obtained by Stern\(^12\) on poly(3-n-alkyl-4-hydroxybenzoate) a similar increase of the density with decreasing side chain length is observed (compare PTA12HQ, Table II).

**PTAHQ12**

Though no oriented fibers could be obtained from PTAHQ12 we thought it useful to characterize some melt-pressed samples by x-ray diffraction and density measurements. By x-ray diffraction a layer distance $d$ of 15.6 Å was measured for the room temperature structure, which compares well with a distance of 15.5 Å reported by Rodriguez-Parada et al.\(^8\) Based on this distance these authors proposed that PTAHQ12 is in structure B at room temperature. This is supported by our density measurements. For PTAHQ12 we measure a density of 1.078 g/cm\(^3\) which compares well with the density of 1.084 g/cm\(^3\) of PTA12HQ in modification B. By high temperature x-ray diffraction we measure that the temperature dependence of this reflection is fairly low. This makes the earlier made assumption\(^4\) that modification B transforms to phase B′ (Fig. 4), which has a similar layer spacing, more plausible.

**Table III.** Comparison of Calculated and Observed $d$-Spacings for an Annealed PTA6HQ Fibre*

<table>
<thead>
<tr>
<th>Reflection Index (hkl)</th>
<th>Calculated Spacing (Å)</th>
<th>Observed Spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>14.1</td>
<td>≈ 14 (vs)</td>
</tr>
<tr>
<td>001</td>
<td>11.4</td>
<td>11.4 (vs)</td>
</tr>
<tr>
<td>200</td>
<td>7.06</td>
<td>7.05 (s)</td>
</tr>
<tr>
<td>110</td>
<td>6.46</td>
<td>6.49 (w)</td>
</tr>
<tr>
<td>102</td>
<td>6.30</td>
<td>6.25 (vw)</td>
</tr>
<tr>
<td>002</td>
<td>5.70</td>
<td>5.69 (vw)</td>
</tr>
<tr>
<td>210</td>
<td>5.06</td>
<td>5.06 (m)</td>
</tr>
<tr>
<td>300</td>
<td>4.71</td>
<td>4.70 (w)</td>
</tr>
<tr>
<td>102</td>
<td>4.64</td>
<td>4.63 (w)</td>
</tr>
<tr>
<td>301</td>
<td>3.81</td>
<td>3.83 (w)</td>
</tr>
<tr>
<td>202</td>
<td>3.73</td>
<td>3.76 (w)</td>
</tr>
<tr>
<td>020</td>
<td>3.63</td>
<td>3.63 (s)</td>
</tr>
<tr>
<td>120</td>
<td>3.52</td>
<td>3.54 (m)</td>
</tr>
<tr>
<td>412</td>
<td>3.38</td>
<td>3.36 (w)</td>
</tr>
</tbody>
</table>

*Monoclinic unit cell, $a = 15.6$ Å, $b = 7.26$ Å, $c = 12.6$ Å, $\beta = 115.2^\circ$. 
PTA12HQ12

The x-ray fiber-diffractogram of PTA12HQ12, stretched to $\lambda = 1.8$, is shown in Figure 13. The equatorial reflection at approximately 26 Å and its higher orders can be explained by the noninterdigitated layered structure proposed by Rodriguez-Parada for PTA16HQ16. As they measured a layer spacing of 32.5 Å for PTA16HQ16, a layer spacing increment of 1.6 Å for each added CH$_2$ unit can be calculated. In a noninterdigitated structure this means that a tilt angle of approximately 41° can be derived. This corresponds well with the suggestion of Rodriguez-Parada that the tilt angle of PTA16HQ16 is similar to that found in PTAHQ16 in modification B. Apparently such a tilt angle allows a more efficient packing of the side chains.

Relation Between Structure, Orientation, and Fiber Properties

The mechanical properties (especially Young’s modulus) of unoriented PTA12HQ12 and PTA12HQ fibers were almost the same (see Table I). This is not surprising, since the properties of both unoriented polymers will be governed by intermolecular interactions between the polymer chains, especially between the aliphatic side chains. Stretching these two polymers two times their original length ($\lambda = 1.8$–1.9) increased the molecular orientation slightly. Fiber properties are still governed by intermolecular interactions ($E \approx 1$ GPa).

PTA12HQ could be stretched up to $\lambda = 7$ and had a molecular orientation, determined from the half-width at half height of the major equatorial reflections, $\varphi$, of approximately 6 degrees. At this degree of orientation the main chains become load bearing and start to govern the fiber properties. The high degree of orientation is reflected in the fibrillar structure of the fibers which is obvious from the electron microscopy photograph shown in Figure 14. The light microscopy photograph with crossed polarizers shown in Figure 15 shows that upon bending (or loading) these fibers, kink-bands typical

Figure 13. Flat-plate x-ray diffractograms of a PTA12HQ12 fiber spun from the isotropic phase and drawn to $\lambda = 1.8$ on a hot shoe. Fiber axis is vertical, sample to film distance 6 cm.

Figure 14. Electron microscopy photograph (crossed polarizers) of the tip of a broken PTA12HQ fiber in modification B.

Figure 15. Light microscopy photograph showing the kink bands upon bending an oriented PTA12HQ fiber (modification A).
of oriented systems occur. With regard to the mechanical properties of PTA12HQ fibers it was found that, depending on the crystal form, moduli of 9 to 17 GPa were readily obtained (Table I). Tensile strength increased from 15 MPa in the unoriented fiber to 158 MPa in the oriented fiber in crystal form B, while the strain at break decreased from 92 to 1%. A comparison between the moduli of the three crystal modifications (Table I) shows that the more ordered structure also has the highest modulus. With the present degrees of orientation a detailed quantitative interpretation and comparison with theory is not possible. In our next publication (dealing with films of an even higher degree of orientation) the dependence of the modulus of PTA12HQ upon the crystal form, molecular orientation and temperature will be addressed in great detail.

For the polymer with shorter side chains, PTA6HQ, the molecular orientation that could be obtained was comparable to the one found for PTA12HQ. As the number of main chains per cross-sectional area is about 50% higher for PTA6HQ compared with PTA12HQ it was anticipated that the modulus of PTA6HQ should be higher. This was confirmed by the mechanical measurements (Table I), which also showed that the strength at break was considerably higher in PTA6HQ at a comparable inherent viscosity.

If we compare the moduli obtained for PTA6HQ and PTA12HQ with the modulus of 4 GPa obtained by Postema et al. for poly(n-hexyl isocyanate)\(^4\) with an even higher degree of molecular orientation (\(\varphi \approx 4.6^\circ\)) the difference is striking. It was however pointed out by these authors that the lack of strong interactions between the main chains (that are surrounded by the side chains) is the main factor determining the experimental modulus of poly(n-hexyl isocyanate). To obtain higher moduli in the systems under discussion they suggested two options. The first one is to increase the number of interactions (per main chain) between the main chains by increasing the molecular weight (like in polyethylene). The second possibility is to increase the strength of the interactions between the main chains (as in aramids). Obviously we obtained the second possibility (in our case a layered structure) which indeed results in enhanced mechanical properties.

**CONCLUSIONS**

Fiber spinning from the layered mesophase is impossible due to the high viscosity of this phase.

The elastic modulus of PTA12HQ and PTA12-HQ12 fibers with a very low degree of orientation is governed by the interactions between the side chains and does not exceed 1 GPa. Fibers spun from PTAHQ12 are too brittle to handle.

Oriented fibers with a high degree of orientation can be obtained from PTA6HQ and PTA12HQ and the presence of the stiff backbone is reflected in the modulus of these fibers. The Young’s modulus of oriented PTA12HQ depends significantly upon the crystal modification and ranges from 9 to 17 GPa. PTA6HQ fibers with a molecular orientation comparable to that of the PTA12HQ fibers have a higher modulus (24 GPa) due to the higher amount of main chains per cross-sectional area.

We are indebted to Dr. Ir. J. A. H. M. Buijs, Dr. G. J. Vroege, and Prof. Dr. M. Ballauff for stimulating discussions and carefully reading the manuscript. The performance of the x-ray diffraction measurements by E. J. Sonneveld is greatly appreciated. Financial support from the Dutch Ministry of Economic Affairs (IOP-PCBP 302) and DSM is gratefully acknowledged.

**REFERENCES AND NOTES**

4. S. B. Damman, F. P. M. Merx, and C. M. Kootwijk-Damman, article 1 in this series, *Polymer* (accepted for publication).
10. S. B. Damman, F. P. M. Merx, and P. J. Lemstra, Article 3 in this series, *Polymer* (accepted for publ.).
11. S. B. Damman and G. J. Vroege, article 4 in this series, *Polymer* (accepted for publication).

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