Chapter 6.

POLYMORPHISM IN ALTERNATING POLYOLEFIN KETONES

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6.1 Summary

The perfectly alternating ethylene-carbon monoxide copolymer shows a reversible phase transition between 110-130 °C from the dense POK-a (orthorhombic) to the POK-β (orthorhombic) crystal structure with a 10% change in crystalline density. Although the packing density of the β-structure is significantly smaller, the heat effect associated with the transition is relatively small. The occurrence of the POK-a structure at room temperature is strongly influenced by the amount of chain defects randomly incorporated into the polymer backbone. The effect of the incorporation of propylene-carbon monoxide segments on the α/β-transition is studied on oriented fiber samples. With more than 5 mole-% of defects, polyketone terpolymers are not capable of forming the POK-a structure in oriented fibers prepared from semi-dilute or concentrated solutions. The polymerization conditions have a pronounced effect on the occurrence of the α-structure in aspolymerized samples. The a-phase content in isotropic samples can be enriched by recrystallization from solution, which indicates that a certain (segmental) mobility is required to accomplish the formation of the dense α-modification.

6.2 Introduction

Already since the early '50's olefins and carbon monoxide were recognized as a potential cheap feedstock for new polymer materials (polyketones). Initially, these polyketones were prepared from ethylene and carbon monoxide via a radically
induced polymerization process. But polymers with a ethylene/CO ratio close to 1 could only be synthesized under extreme conditions. Chatani et al. determined the crystal structure of such a polyketone with an ethylene/CO ratio of 1.05. The latter structure is designated here as the POK-β modification.

Sen and coworkers at Penn. State university have studied the polymerization of polyolefin ketones using organometallic catalyst systems. Their palladium (Pd(II)) phosphine complexes were capable of forming alternating ethylene-carbon monoxide copolymer. A significant improvement in the rate of polymerization has been established by Drent et al., who developed the group of cis-fixed palladium bidentate catalyst compounds. In contrast to the radically induced copolymerization this special class of catalyst systems enables the manufacturing of high-molecular-weight polymers, whereas no defects, like non-alternating sequences, could be detected. Hence, the mechanism of polymerization seems to prohibit the incorporation of chain defects into the polymer backbone during chain growth.

At the beginning of this decade the field of homogeneous catalysis for the production of polyketones has rapidly emerged and at present a number of groups have become active. Their work is primarily focused on an understanding of the polymerization mechanism, and on the application of this class of catalyst systems for the production of novel polymers. Within our laboratories, we have focused our efforts on the application of these new polymers in fiber materials. The perfectly alternating ethylene-carbon monoxide copolymer (POK-C₂) seems to be the most promising one in this respect as this material shows a high melting temperature (260 °C). The crystal structure of this perfectly alternating material (i.e., the POK-a structure) turned out to be different from the POK-β structure observed in imperfectly alternating ethylene-carbon monoxide copolymers. The chain conformation in both structures is all-trans but the crystalline density of the POK-β structure is significantly lower than that of the POK-a structure.

In the present investigations, we study a structural transition in the POK-C₂ copolymer in order to gain insight into the high-temperature performance of polyketone fibers. At
present melt processing of high melting polyketones seems to be impossible. The poor thermal stability of the 1,4-arrangement of carbonyls gives rise to both intra- and intermolecular condensation reactions at high temperatures. For example, the well-known Paal-Knorr cyclization reaction\(^\text{19}\) results in the formation of furan structures (see Figure 1) and water is formed as the condensation product. To avoid thermal degradation the melting temperature of POK-C\(_2\) can be lowered via the random incorporation of a certain amount of propylene-carbon monoxide segments into the polymer backbone.\(^\text{17}\)

![Figure 1. Paal-Knorr type of cyclization reaction in 1,4-diketones.](image)

The melting point depression of these so-called POK-C\(_2/C_3\) terpolymers has been described in detail in Chapter 2. In this Chapter the influence of the fraction of chain defects on the room temperature crystal structure together with a structural transition in perfectly alternating ethylene-carbon monoxide copolymers will be reported.

### 6.3 Experimental

**-Materials**

POK-C\(_2\) copolymers were prepared from ethylene and carbon monoxide according to the description given in refs. 20 and 21, using the 1,3-bis(diphenyl-phosphino) propane palladium bidentate complex as the catalyst system. For the preparation of
low-molecular-weight polymers the so-called methanol slurry polymerization process is applied. The catalyst is dissolved in methanol and during polymerization the polymer precipitates from solution. After drying, a low bulk density powder is obtained. For the preparation of high-molecular-weight polymer the catalyst is coated on a small amount of low-molecular-weight polymer and the reaction is carried out in the polymer/gas interphase. Since methanol causes chain transfer reactions the absence of a large amount of solvent results in appreciably higher molecular weights. For the preparation of the POK-C2/C3 terpolymers via the methanol slurry process a small amount of propylene is added to the autoclave prior to pressurizing with a 1:1 mixture of ethylene and carbon monoxide.

The molecular weight of the polymer formed is strongly influenced by the temperature and pressure conditions in the autoclave. We conducted our polymerization experiments typically at a temperature between 40-60 °C and at a pressure between 60-80 bar. The intrinsic viscosity (m-cresol, 25 °C) of polymers obtained under these conditions via the methanol slurry process ranges from 0.4-2 dL/g, whereas the gas-phase process yields polymer with an intrinsic viscosity between 3-10 dL/g. For the terpolymers the amount of propylene randomly incorporated was measured using 1H-NMR in d6-phenol. The same correlation between the melting temperature and the fraction of chain defects was obtained as the one presented in Chapter 2. This correlation was based on the melting point depression of both perfectly alternating polyketone terpolymers and imperfectly alternating copolymers.

-Yarn samples
Polyketone fibers were prepared by solution spinning from phenol/acetone mixtures (9:1 weight ratio). Since melt spinning of high melting polyketones is seriously hampered by polymer degradation, the former spinning technique allows significantly lower processing temperatures, whereby the formation of chain defects via (thermal) degradation is completely avoided. The intrinsic viscosity ([η]), propylene content (mole %-C3) and melting temperature (Tm) of the various as-polymerized co- and terpolymers are given in Table I. Also the dissolution and spinning conditions are included (xpol is the polymer concentration). The solutions were spun into a (cold)
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acetone bath by application of an air-gap and using a piston-cylinder apparatus. The winding speed was slightly less than the extrusion speed (1 m/min). Hence, some relaxation and shrinkage of the swollen fiber were allowed. The fibers were washed with acetone, dried in air and subsequently drawn continuously at elevated temperatures using hot plates. The difference between the drawing temperature and the melting temperature was comparable in all cases.

Table I. Spinning and Drawing Conditions Applied for the Preparation of Polyketone Fibers with Different Propylene Content

<table>
<thead>
<tr>
<th>Sample</th>
<th>[η] [dL/g]</th>
<th>%-C₃ [mole/mole]</th>
<th>Tm [°C]</th>
<th>xpol</th>
<th>'spin [°C]</th>
<th>t'bath [°C]</th>
<th>t'draw [°C]</th>
<th>λ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>POK-C₂</td>
<td>9.0</td>
<td>0</td>
<td>258</td>
<td>5.1</td>
<td>80</td>
<td>-6</td>
<td>220-257ª</td>
<td>10-20ª</td>
</tr>
<tr>
<td>POK-C₂/C₃</td>
<td>1.9</td>
<td>3</td>
<td>238</td>
<td>22.0</td>
<td>68</td>
<td>20</td>
<td>210</td>
<td>10.3</td>
</tr>
<tr>
<td>POK-C₂/C₃</td>
<td>1.0</td>
<td>5</td>
<td>231</td>
<td>24.2</td>
<td>65</td>
<td>23</td>
<td>200</td>
<td>10.0</td>
</tr>
<tr>
<td>POK-C₂/C₃</td>
<td>1.5</td>
<td>12</td>
<td>206</td>
<td>20.0</td>
<td>30</td>
<td>25ª</td>
<td>179</td>
<td>10.5</td>
</tr>
<tr>
<td>POK-C₂/C₃</td>
<td>0.8</td>
<td>15</td>
<td>196</td>
<td>31.0</td>
<td>25</td>
<td>25</td>
<td>171</td>
<td>10.5</td>
</tr>
</tbody>
</table>

ª Fibers were drawn according to a multi-stage procedure; λ₁ = 5.6, λ₂ = 2.3 and λ=λ₁λ₂λ₃, where 1 is the draw ratio.
b No air-gap was applied.

-Analysis

DSC measurements were carried out using a Perkin Elmer DSC-7 thermal analyzer at a scanning speed of 20 °C/min. X-ray diffraction patterns were recorded using several techniques. A detailed description of the applied x-ray diffraction techniques is given in ref. 22.
6.4 Results and Discussion

-Solid-Solid Phase Transformation in Oriented POK-C₂ Fibers

Thermal analysis on oriented POK-C₂ fibers revealed a small endothermic effect in the temperature range between 110-130 °C (see Figure 2).

Figure 2. DSC scans of perfectly alternating POK-C₂ fiber. (a) heating to 300 °C; (b) heating to 150 °C (top curve) followed by cooling down (bottom curve)
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Upon cooling, an exotherm (with undercooling) is observed with a corresponding heat effect as the endotherm upon heating [see Figure 2b; endotherm: 14.4 J/g; exotherm: 13.8 J/g]. This result clearly indicates a reversible phase transition in oriented POK-C₂ polymers at about 110 °C. Initially, this was a point of concern to us, because some linear, less polar, flexible polymers with an all-trans conformation of the chains in the crystal lattice, like polyethylene (PE), poly tetrafluoroethylene (PTFE), poly-p-xylylene (PPX) or trans-1,4-polybutadiene, exhibit a solid-solid phase transition at elevated temperatures. Such a phase transition results in an increase in conformational disorder, allowing a liquid-like motion in the direction of the c-axis of the crystal. Therefore, these so-called condiscrystals are rather pliable and the mechanical properties rapidly deteriorate, when the transition temperature is approached.

In order to investigate the structural transformation in polyketone-C₂ fibers at 110-130 °C various x-ray diffraction techniques were employed. An equatorial Guinier-Lenné photograph of an oriented POK-C₂ fiber is shown in Figure 3. At low temperatures the equatorial diffraction pattern corresponds to the POK-a (orthorhombic) structure. At about 110 °C a structural transition becomes noticeable, which causes a significant change in the equatorial diffraction pattern. Upon cooling, the low-temperature POK-a modification is formed again and almost no remnants of the high-temperature modification are visible. Clearly, the reversible nature of the found structural transformation in oriented POK-C₂ copolymers is in line with the thermal analysis experiments (see Figure 2). The high-temperature modification of oriented POK-C₂ copolymers was studied by recording flat-plate x-ray diffraction photographs (see Figure 4) at 20 °C and slightly above the transition temperature (i.e., at 140 °C). The fiber under investigation was drawn to a ratio of 20 and the low degree of arcing of the reflections points to a high degree of crystalline orientation in this material. The high-temperature modification [right diffraction pattern: Figure 4b] matches the crystal structure reported by Chatani et al. (i.e., the POK-β (orthorhombic) structure found in oriented imperfectly alternating ethylene-carbon monoxide copolymers). The latter structure can be indexed with an orthorhombic unit cell with dimensions 8.24(2), 4.74(2) and 7.58(2) Å and spacegroup Pnam.
Figure 3. Guinier-Lenné photograph of perfectly alternating POK-C₃ fiber. Starting at the bottom of the photograph the applied temperature program was as follows: fixed temperature of 20 °C; heating from 20 to 130 °C at a rate of 2 °C/hr; fixed temperature of 130 °C; fast (uncontrolled) cooling from 130 to 20 °C; fixed temperature of 20 °C.
The crystal unit cell dimensions and crystalline density of the modifications found in polyketones and those of polyethylene are compiled in Table II. Only small differences are observed between the crystal structure in oriented POK-C₂ copolymers at 140 °C and the POK-β structure of Chatani et al. at room temperature, keeping in mind that part of the differences may be due to thermal expansion. In view of the similarities between the two structures, we have designated both structures as the POK-β modification.

Views of both the POK-α and the POK-β structure were presented in Chapter 2. The all-trans conformation of the polymer backbone remains unaffected when POK-α is transformed into the POK-β structure. Apart from the change in cell dimensions, the differences between the two structures can be described by an increase in the angle between the bc-plane and the planes of the polymer chains from 26° to 40°.
accompanied by a rotation of the center chain over 180° or equivalently by a shift $\frac{1}{2}c$ of the center chain in the direction of the fiber axis. The structural transformation results in a 10% increase in volume of the crystal unit cell. This is a significant change in crystal packing density, but the heat effect associated with the change in the orientation of the carbonyls is relatively small and amounts to roughly 5-10% of the heat of fusion ($\Delta H_f=140-200 \text{ J/g}$ for oriented fibers). This result suggests that the long-range dipolar interactions between adjacent chains are not strongly affected by the structural transformation. The latter is substantiated by the arrangement of the carbonyl dipoles in the POK-β crystal lattice.

Table II.  
*Unit Cell Dimensions and Crystalline Density of Alternating Polyketone Copolymers and Polyethylene (PE).*

<table>
<thead>
<tr>
<th>Sample</th>
<th>modification</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>$\rho_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>POK-C$_2$ (20°C)</td>
<td>a</td>
<td>6.87(2)</td>
<td>5.12(2)</td>
<td>7.60(2)</td>
<td>1.39</td>
</tr>
<tr>
<td>POK-C$_2$ (140 °C)</td>
<td>β</td>
<td>8.24(2)</td>
<td>4.74(2)</td>
<td>7.58(4)</td>
<td>1.26</td>
</tr>
<tr>
<td>POK-C$_2$ (Chatani et al.)</td>
<td>β</td>
<td>7.97</td>
<td>4.76</td>
<td>7.57</td>
<td>1.30</td>
</tr>
<tr>
<td>PE</td>
<td></td>
<td>7.40</td>
<td>4.93</td>
<td>2.534</td>
<td>1.00</td>
</tr>
</tbody>
</table>

In the dense POK-a structure the carbonyl groups are more directed along the $bc$ plane in the crystal unit cell (see Chapter 2), which gives rise to limited dipolar
interactions perpendicular to the bc plane. The overall thermal expansion of the POK-a unit cell with temperatures increasing from 22 °C to 100 °C amounts to 1.5 %. The expansion occurs mainly in the direction of the a-axis. In the POK-β structure the electrostatic interactions perpendicular to the bc plane are probably more effective relative to the POK-a structure due to the different arrangement of the dipolar interactions in the POK-β structure. Based on these results, we presume that the α/β-phase transition is not accompanied by a significant decrease in tensile properties of oriented POK-C fibers. This is in contrast to the less polar polymers, which exhibit a condens-phase transition at elevated temperatures. Since the c-axis of the crystalline unit cell is not affected by the solid-solid phase transition the volume change will only have a minor effect on the length of an oriented fiber. In fact the measured shrinkage of an oriented fiber at an applied load of 7 MPa was below 0.1 % at the transition temperature. However, for isotropic crystallized samples, which show the POK-a structure at room temperature, the volume change might be an important aspect. Assuming a crystallinity of 50 % in isotropic material, the net volume change will be 5 %. For various end-uses this may be a point of concern as 110-130 °C is below the maximum end-use temperature for a number of engineering plastic applications. The effect of the α/β-transition on the tensile modulus and tensile strength of polyketone fibers will be described in more detail in the next Chapter.

-Parameters Influencing The α/β-Transition
The α/β-transition temperature and melting point of POK-C fibers, drawn to different ratios, are presented in Figure 5. These particular fibers are drawn at a feeding speed of 1 mm/s between two roller sets over a hot plate (T_draw=228 °C). Hence, after the fiber is oriented, it is cooled from 228 °C to room temperature under the drawing tension. The melting temperature of high-molecular-weight POK-C fiber increases with the degree of orientation, which can be attributed to a reduction in surface free energy of the oblong-shaped crystals formed. In contrast to the melting temperature, the α/β-transition temperature decreases slightly with the draw ratio. It should be noted that the drawing of as-spun material is carried out at temperatures exceeding the α/β-transition temperature (i.e., at temperatures where the β modification is the most stable one). Hence, after the drawing procedure is completed the crystal
structure transforms from the $\beta$- to the a-structure. The increase in melting temperature indicates that the degree of perfection of the $\beta$-crystals formed is significantly improved by the orientation procedure. The drawing stress increases substantially with the draw ratio. The higher tension at higher draw ratios affects the degree of perfection of the a-modification formed upon cooling. This result points to a limited ability to form perfect POK-a crystals under more constraint conditions.

Figure 5. *Melting point and a/-transition temperature of polyketone-C$_2$ fibers, drawn to different ratios at 228 °C ([O]: data point taken from Fig. 3).*

To gain further insight into the kinetics of the transition process, we looked into the crystalline modifications in two as-synthesized (virgin) polymers, viz. a low-molecular-weight polymer prepared according to the methanol-slurry process and a high-molecular-weight polymer prepared according to the gas-phase process. Diffraction
patterns of these materials, measured with a reflection diffractometer, are displayed in Figure 6 together with the calculated powder patterns of POK-a and POK-β, respectively. The patterns were calculated from the crystal structure reported in ref. 17, and that of Chatani et al. for CuKα radiation and assuming an overall isotropic temperature parameter of 5.0 Å². The high-molecular-weight powder crystallizes almost completely in the POK-β modification, as can be concluded from Figure 6.

Figure 6. (a) Diffraction patterns of perfectly alternating POK-C₂ powder, upper curve: high-molecular-weight powder; lower curve: low-molecular-weight powder. (b) Calculated powder diffraction pattern of POK-a. (c) Calculated powder diffraction pattern of POK-β.
The low-molecular-weight material consists of a mixture of both POK-a and POK-β and its crystalline perfection is considerably larger than for the high-molecular weight polymer, as is indicated by the differences in the width of the intensity peaks. After recrystallization from a poor solvent, viz. propylene carbonate \( (T_c = 140 \, ^\circ C) \), the POK-β to POK-a transformation is almost complete, as can be deduced from Figure 7.

![Figure 7. High-temperature x-ray diffraction scans of lowmolecular-weight POK-C2, recrystallized from propylene carbonate.](image)

In the x-ray diffraction temperature scan the \( \alpha/\beta \)-transition takes place in a temperature range between 120-140 \( ^\circ C \). Upon cooling, the \( \beta \)-structure is not completely transformed into the \( \alpha \)-structure, since still remnants of the \( \beta \)-modification are present at room temperature. When the sample is subjected to another
temperature cycle (20 °C-180 °C-20 °C) the β-modification is again partly transformed into the α-modification. Hence, crystallization from solution enables the formation of the dense α-structure in isotropic samples, and when no solvent is present a certain amount of the β-modification remains untransformed.

Recrystallization of high-molecular-weight POK-C₂ from a good solvent system, viz. a phenol/acetone mixture (9:1 weight ratio), results also in an enriched α-content at room temperature. Since after drawing the fiber consists exclusively of POK-α [at room temperature] it can be concluded that the process of dissolution, spinning and drawing leads a transformation of unoriented β-rich material into oriented POK-α structures.

The results may be summarized by concluding that low-molecular-weight as-polymerized (virgin) material crystallizes at least partly in the α-modification, whereas (virgin) high-molecular-weight POK-C₂ crystallizes almost completely in the β-modification with a lower degree of crystalline perfection. These particular differences in crystallization behavior can be attributed to the kinetics of the crystallization process. For as-polymerized sample the latter process is predominantly determined by the polymerization conditions, viz. temperature, solvent, etc., yielding differences in molecular weight and morphology of the polyketone powders formed. Since our primary goal is to establish insight into crystal transition phenomena during fiber spinning and into the high-temperature performance of polyketone fibers, we will not discuss the influence of these parameters extensively. Recrystallization from solution results in an increase in α-content compared with as-polymerized material, indicating that a certain segmental mobility is required to facilitate the formation of the α-structure. During drawing the α/β-transition temperature decreases with the draw ratio, implying that the chain mobility under tension is noticeably reduced relative to unconstraint conditions, and as a result less perfect a-crystals are formed. In unoriented materials the nucleation of the β/α-transition is significantly hampered by the low degree of molecular alignment. In view of the relatively small heat effect associated with the α/β-transition, topological defects incorporated during crystallization can easily prevent the formation of the dense α-structure. The influence of these defects is less noticeable for oriented fibers, since during drawing lamellar
crystals are transformed into fibrillar structures. In the next section, we will describe the influence of other defects, viz. chain defects, in the form of small methylene side-groups on the occurrence of the $\alpha/\beta$-transition in oriented polyketones.

**Polyketone Terpolymers**

Fiber samples of polyketone (POK-$C_2/C_3$) terpolymers were prepared in essentially the same way as the POK-C, fibers. These polymers differ from the perfectly alternating POK-C, polymers by the presence of CH$_2$-groups randomly located along the polymer backbone.

![DSC scans](image)

**Figure 8.** DSC scans (20 °C/min) of alternating polyketones with varying propylene content.

In Figure 8, the DSC scans (20 °C/min) of terpolymer fibers, drawn to about the same ratio, are displayed and in Table III the results of the thermal analysis investigations are summarized. For oriented fiber samples with a propylene content above 5-mole % the endothermal peak associated with the $\alpha/\beta$-transition is not observed.
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Table III. DSC Data of Perfectly Alternating Polyketones with Varying Propylene Content.

<table>
<thead>
<tr>
<th>Sample</th>
<th>%C$_3$</th>
<th>$\lambda$</th>
<th>$T_{\alpha-\beta}$</th>
<th>$\Delta H_{\alpha-\beta}$</th>
<th>$T_m$</th>
<th>$\Delta H_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[mole/mole]</td>
<td>[-]</td>
<td>[°C]</td>
<td>[J/g]</td>
<td>[°C]</td>
<td>[J/g]</td>
</tr>
<tr>
<td>POK-C$_2$</td>
<td>0</td>
<td>10.0</td>
<td>112</td>
<td>16</td>
<td>269</td>
<td>157</td>
</tr>
<tr>
<td>POK-C$_2$/C$_3$</td>
<td>3</td>
<td>10.3</td>
<td>101</td>
<td>9</td>
<td>247</td>
<td>129</td>
</tr>
<tr>
<td>POK-C$_2$/C$_3$</td>
<td>5</td>
<td>10.0</td>
<td></td>
<td></td>
<td>232</td>
<td>123</td>
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<tr>
<td>POK-C$_2$/C$_3$</td>
<td>12</td>
<td>10.5</td>
<td></td>
<td></td>
<td>206</td>
<td>122</td>
</tr>
<tr>
<td>POK-C$_2$/C$_3$</td>
<td>15</td>
<td>10.5</td>
<td></td>
<td></td>
<td>194/199</td>
<td>98</td>
</tr>
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</table>

A precession photograph of POK-C$_2$/C$_3$ fiber with 12 mole% propylene is presented in Figure 9. The diffraction pattern matches the POK-β structure found in imperfectly alternating copolymers and in perfectly alternating POK-C$_2$ copolymer above 100-130 °C. This result indicates that the POK-β lattice is better suited to accommodate chain defects or thermal effects. It should be noted that we observed no trace of the POK-a structure in the oriented fiber sample with 12 mole-% of propylene. As will be demonstrated in forthcoming contributions$^{29,30}$ epitaxially grown crystals of the same sample on a hydroquinone substrate can indeed show the POK-a structure at room temperature. Since the hydroquinone substrate solely nucleates crystallization of the POK-a modification some segregation between defect-rich and defect-poor chain segments might take place prior to crystallization. Although the occurrence of POK-a structure in these epitaxially crystallized terpolymers remains to be investigated further, the nucleation of the β/α-transition in oriented fiber samples prepared from semi-dilute or concentrated solutions is inhibited by the incorporation of chemical defects.
Figure 9. A precession x-ray diffraction photograph of perfectly alternating POK-C₂/C₃ terpolymer with a fraction of 12 mole-% propylene-carbon monoxide chain defects.

6.5 Conclusions

Alternating polyolefin ketones exhibit polymorphism, and depending on temperature, composition, applied stress or kinetic factors, the POK-α or the POK-β crystal structure or a mixture of the two are observed. Oriented defect-free polyketones show the POK-α structure at room temperature, which reversibly transforms into the POK-β structure at 110-130 °C. This solid-solid phase transition is accompanied by a
decrease in crystalline density of 10%, whereas the heat effect associated with the transition is small (5-10% of the heat of fusion). The formation of the POK-a structure in crystallized samples prepared from semi-dilute or concentrated solutions is inhibited by the random incorporation of more than 5 mole-% of chain defects. This result explains the occurrence of the POK-b structure, as observed in previous investigations for oriented imperfectly alternating copolymers. The larger volume of the POK-b unit cell makes that this structure is better suited to accommodate temperature effects or chemical defects. In as-polymerized POK-C2 samples both structures are observed, depending on the conditions during polymerization, which yield differences in molecular weight and morphology of the powders formed.

6.6 References and Notes

J.C. Wittmann and coworkers. (in preparation).