Chapter 2.

STRUCTURE AND MELTING OF PERFECTLY ALTERNATING
ETHYLENE-CARBON MONOXIDE COPOLYMERS

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2.1 Abstract

The perfectly alternating ethylene-carbon monoxide copolymer (polyketone; POK) has
been studied by means of 'H-nuclear magnetic resonance and thermal analysis, and
the crystal structure, determined by wide angle x-ray scattering methods, is
presented. The crystal structure of this polymer in well-oriented fibers (POK-a) is as
follows: Space group Pbnm, \( a = 6.91(2) \ \text{Å} \), \( b = 5.12(2) \ \text{Å} \), \( c = 7.60(3) \ \text{Å} \) (fiber axis),
\( \rho_c = 1383 \ \text{kg/m}^3 \). This differs from the structure reported earlier by Chatani et al.
(POK-β). The very dense packing in the POK-a structure is a result of the arrangement
of the dipoles in the crystal lattice, giving rise to strong lateral forces between the
polymer chains. Owing to the all-trans conformation of the polymer chain in the crystal
lattice, high moduli can be achieved for well-oriented fibers. A first approximation
results in a value of 360 GPa for the theoretical modulus. From the melting data for a
series of low-molecular-weight polyketone homologs, a first, estimate is derived for the
heat of fusion (215-330 J/g) for crystals of infinite chain length. As a result of the
strong lateral forces, this polymer shows a high heat of fusion for perfectly
crystalline material, and the creep resistance and compressive strength of oriented
fibers are expected to be superior to those of high modulus polyethylene fibers.

2.2 Introduction

Since the development of the high-strength polyethylene fiber, solution spinning of
linear high-molecular-weight flexible-chain polymers has received considerable interest. Compared with polyethylene, copolymers of carbon monoxide and ethylene (polyketones) with a high carbon monoxide content show significantly higher melting temperatures\textsuperscript{4,5} as well as rather good adhesion properties.\textsuperscript{6} Therefore, these polyketones may be interesting starting materials for fibers, provided that good mechanical properties can be obtained.

![Solid-state C-NMR spectrum of photodegradable Budweiser "six-pack" yokes.](image)

A point of concern for fiber applications is the sensitivity of polyketones toward ultraviolet (UV) light, in particular when considering presently commercially available materials. Polyketones with a low carbon monoxide content are currently used as photodegradable plastics.\textsuperscript{7,8} A solid-state C\textsuperscript{13} nuclear magnetic resonance (NMR) trace of "six-pack" yokes\textsuperscript{9} made of such a polymer is shown in Figure 1, revealing that some carbonyl groups (< 1 wt %) are incorporated into the polyethylene chain.
Ultraviolet radiation can induce Norrish-I and Norrish-II [the latter is predominant at room temperature] types of reactions (see Fig. 2), causing chain cleavage. The molecular weights of the fragments formed correspond to the molecular weights of the parts of the chain between carbonyl groups.\textsuperscript{10-13}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{structure.png}
\caption{Schemes of Norrish-I and Norrish-II types of chain cleavage reactions (ref 10).}
\end{figure}

In the past, several techniques have been developed for synthesizing polyolefin ketones, viz. radical copolymerization at high pressure\textsuperscript{14-18} and transition-metal catalyzed copolymerization under moderate conditions.\textsuperscript{19-23} A review of the different techniques is given by Sen.\textsuperscript{24,25} Already in 1961 Chatani et al.\textsuperscript{26} reported the crystal structure of an alternating polyketone copolymer from oriented film samples. The polymer was prepared by \(\gamma\)-radiation-initiated copolymerization and a melting point of 175-185 °C was reported. We designate this structure as polyolefin(\(C_2\))-ketone \(\beta\) (POK-\(\beta\)).\textsuperscript{27} The \(ab\) projection of the orthorhombic unit cell of this structure is very similar to that of polyethylene. The conformation of the extended polymer chain is planar (zig-zag) and owing to a small chain cross-section, high moduli can be achieved for well-oriented crystalline material.

More recently, a catalytic polymerization method has been developed by Drent et al.\textsuperscript{28,29} of the Royal Dutch Shell laboratories, resulting in a perfectly alternating
copolymers with a melting point of 257 °C (Fig. 3). An interesting feature of this perfectly alternating copolymer is that Norrish-II reactions are inhibited owing to the absence of CH₂ groups at the y-position of the carbonyl groups, resulting in an improved UV stability. It has also been shown by Gooden et al.¹⁰ that for extended (crystalline) material the contribution of the Norrish-II type of chain scission to the total photodegradation is greatly decreased.

Figure 3.  Perfectly alternating ethylene carbon monoxide copolymer.

Taking these features into account, alternating polyketones thus seem to fulfill all preconditions for attractive high-performance material applications. We were indeed able to spin this alternating copolymer from a solution into a highly drawable fiber, resulting in well-oriented, highly crystalline material with good mechanical properties. The present Chapter describes the characterization of the copolymer by means of ¹H-NMR and thermal analysis. The crystal structure, as determined by wide-angle x-ray fiber diffraction, is presented. The differences between the latter structure, which will be designated as polyolefin(C₂)ₙ-ketone a (POK-a), and the POK-β structure are discussed. The melting points of a series of homologs and a series of copolymers are scrutinized. From these results, a first approximation for the theoretical modulus for the perfectly alternating polyketone is derived, and the crystallinity in oriented fibers has been estimated.
2.3 Experimental

- Materials

A lowmolecular-weight copolymer of ethylene and carbon monoxide was prepared according to the description given in ref. 31, using a solution of 10.5 mg palladium acetate, 19.5 mg 1,3-bis(diphenylphosphino)propane, and 18.1 mg p-toluene sulfonic acid in 1 L of methanol as the catalyst system. The following bidentate complex compound, displayed in Figure 4, is the active species in the reaction.\textsuperscript{28,29}

![Palladium complex](image)

Ph = Phenyl group

**Figure 4.** Palladium 1,3-bis(diphenylphosphino)propane complex (the weakly coordinating p-toluenesulfonate anion(s) are not depicted).

The solution was discharged into a 2 L stirred Hofer autoclave, which was subsequently pressurized at 60 bar at a temperature of 85 °C with a 1 : 1 mixture of carbon monoxide and ethylene. After pressurizing for 50 h, the resulting white powder was discharged and washed with methanol.

A high-molecular-weight sample was prepared by gas phase polymerization according to the description given in ref. 32. The catalyst system was prepared by adding a solution of 7.02 mg palladium acetate, 12.90 mg 1,3-bis(diphenylphosphino)propane and 12.04 mg p-toluene sulfonic acid in 20 mL of acetone to 10 g of the low molecular-weight polymer. This mixture was thoroughly homogenized and discharged into the Hofer autoclave. After the acetone had evaporated, the autoclave was pressurized at 50 bar and kept at a temperature of 65 °C with a 1:1 gas mixture of
carbon monoxide and ethylene. After a reaction time of 100 h, 180 g of a high-
molecular-weight polymer could be discharged from the autoclave. The limiting
viscosity numbers of the two polymer samples, determined in \textit{m-cresol} at 25 °C, are
0.52 and 6.1 dL/g.

As lowmolecular-weight polyketone \textit{homologs 3,6,9-undecanetrione,} \textit{2,5-}
hexanedione (Fluka) and \textit{3-pentanone} (Janssen) were used. The \textit{2,5-hexanedione} was
first purified by distillation under vacuum. For comparison with literature data, two
polyketone terpolymers (ethylene-CO/propylene-CO) were polymerized according to
the description given in ref. 36, using the same catalyst recipe as for the copolymer.

-\textit{Yarn Sample}

A 10 wt.-% solution of the \textit{high-molecular-weight} sample was prepared in a
\textit{phenol/acetone} mixture (9:1) at 110 °C. The solution was homogenized vigorously
under a nitrogen atmosphere for 5 h, using a glass stirrer in order to avoid corrosion
by the phenol. The solution was conditioned at 100 °C in a piston-cylinder apparatus
for 90 min. The fiber was extruded at a speed of 2 m/min. through one capillary (500
\mu m, L/d=20) into a cold acetone bath (-5 °C). An \textit{air gap} of 2 mm was used in order
to bridge the temperature difference. The yarn was collected almost tensionless on a
bobbin at a speed close to 2 m/min., thereby allowing some shrinkage of the yarn
during the evaporation of the residual acetone in the swollen fiber. The yarn was
washed, dried and subsequently drawn in three steps using hot plates to a total draw
ratio of 19 at temperatures of 217, 242 and 257 °C, respectively, resulting in a fiber
with a maximum modulus of 45 GPa and a tensile strength of 1.9 GPa.

-X-Ray Diffraction Analysis

X-ray diffraction patterns of the yarn were made using several techniques: flat-plate
fiber photographs, precession photographs and diffractometer scans (for intensity
measurements) using CuKa- and MoKa-radiation. A precession photograph is shown in
Figure 5. A model for the polymer chain assuming a planar \textit{zigzag} backbone was
generated with the aid of a local computer program.
Table 1. *Bond Lengths and Bond Angles Used for Constituting the Polymer Chain*

<table>
<thead>
<tr>
<th>Bond Length</th>
<th>Bond Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂CH₂</td>
<td>1.54 Å</td>
</tr>
<tr>
<td>CH₂CO</td>
<td>1.51 Å</td>
</tr>
<tr>
<td>C=O</td>
<td>1.23 Å</td>
</tr>
</tbody>
</table>

Figure 5. *Precession x-ray diffraction photograph of a perfectly alternating polyketone fiber, drawn in three stages to a total draw ratio of 19 at 217, 242 and 257 °C, respectively. The (110), (200), and (210) reflections are indicated.*
Table II. Comparison Between Observed and Calculated Intensities of Different Reflections

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>1 1 0</td>
<td>273</td>
<td>vs</td>
<td></td>
<td>0 0 2</td>
<td>1 0 0</td>
<td>vs</td>
<td></td>
</tr>
<tr>
<td>2 0 0</td>
<td>132</td>
<td>vs</td>
<td></td>
<td>1 1 2</td>
<td>&lt;1</td>
<td>w</td>
<td></td>
</tr>
<tr>
<td>2 1 0</td>
<td>40</td>
<td>s</td>
<td></td>
<td>2 0 2</td>
<td>1</td>
<td>w</td>
<td></td>
</tr>
<tr>
<td>0 2 0</td>
<td>&lt;1</td>
<td>-</td>
<td></td>
<td>2 1 2</td>
<td>9</td>
<td>w-m</td>
<td></td>
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<tr>
<td>3 1 0</td>
<td>15</td>
<td>m</td>
<td></td>
<td>0 2 2</td>
<td>3</td>
<td>w</td>
<td></td>
</tr>
<tr>
<td>2 2 0</td>
<td>3</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 0 0</td>
<td>&lt;1</td>
<td>vw</td>
<td></td>
<td>1 0 3</td>
<td>14</td>
<td>m-s</td>
<td></td>
</tr>
<tr>
<td>3 2 0</td>
<td>&lt;1</td>
<td>vw</td>
<td></td>
<td>1 1 3</td>
<td>40</td>
<td>s</td>
<td></td>
</tr>
<tr>
<td>1 3 0</td>
<td>&lt;1</td>
<td>w</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>1 0 1</td>
<td>28</td>
<td>w-m</td>
<td></td>
<td>0 0 4</td>
<td>95</td>
<td>vs</td>
<td></td>
</tr>
<tr>
<td>1 1 1</td>
<td>33</td>
<td>s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 1 1</td>
<td>&lt;1</td>
<td>w</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

The observed reflections are indicated as very weak (vw), weak (w), medium (m), strong (s), or very strong (vs) reflections.

Standard bond lengths and bond angles were used (listed in Table 1). Twice the calculated monomer length agreed well with the observed fiber-axis unit-cell length. Intensities were calculated using a local computer program. No H atoms were included in the intensity calculations. The intensities of the (1 1 0) and (2 0 0) reflections were measured accurately by recording radial and azimuthal scans, using a transmission diffractometer. The measured intensity ratio of these reflections was found to be
2.08. The angle between the molecular plane and the \textit{bc} plane was then adjusted until the calculated and the measured intensity ratios of the 110 and the 200 reflections were in agreement. The intensities of the other reflections, calculated by using the optimized angle between the molecular plane and the \textit{bc} plane, are also in qualitative agreement with the observed intensities (see Table II).

\textbf{-Analytical Methods}

\textbf{Thermograms} of the materials were recorded using a \textit{Perkin Elmer DSC 7} thermal analyzer at a scanning speed of 20 °C/min. The melting temperatures were taken as peak melting temperatures and the heats of fusion were calculated from the area of the melting peaks. \textit{'H-NMR} spectra of the as-synthesized polymers were recorded in d\textsuperscript{6}-phenol or in d\textsuperscript{6}-dimethyl sulfoxide (DMSO) on a Bruker \textit{AM 400} (400 MHz) spectrometer at a temperature of 100 °C.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{{\textit{'H-NMR} spectrum in d\textsuperscript{6}-phenol at 100 °C of the low-molecular-weight ethylene-carbon monoxide copolymer (LVN=0.52 dL/g).}}
\end{figure}
2.4 Results and Discussion

**1H-NMR Analysis**

The 'H-NMR spectrum of the low-molecular-weight ethylene- carbon monoxide copolymer in d<sub>6</sub>-phenol is given in Figure 6. No significant enolization is detected. Solvents with a strong hydrogen-bonding capacity can stabilize the keto form;<sup>37,38</sup> and in order to rule out possible solvent effects, also d<sup>6</sup>-dimethyl sulfoxide was used.

<table>
<thead>
<tr>
<th>1H-NMR&lt;sup&gt;a&lt;/sup&gt; (ppm)</th>
<th>Assignment</th>
<th>Integration&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.09</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;-CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.0047 (3)</td>
</tr>
<tr>
<td>2.36</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;-CH&lt;sub&gt;2&lt;/sub&gt;-C(O)</td>
<td>0.0050 (2)</td>
</tr>
<tr>
<td>2.53</td>
<td>O-C(O)-CH&lt;sub&gt;2&lt;/sub&gt;-CH&lt;sub&gt;2&lt;/sub&gt;-C(O)</td>
<td>0.0041 (2)</td>
</tr>
<tr>
<td>2.69</td>
<td>C(O)(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;-C(O)</td>
<td>1 (4)</td>
</tr>
<tr>
<td>2.85</td>
<td>O-C(O)-CH&lt;sub&gt;2&lt;/sub&gt;-CH&lt;sub&gt;2&lt;/sub&gt;-C(O)</td>
<td>0.0040 (2)</td>
</tr>
<tr>
<td>3.64</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;-O-C(O)</td>
<td>0.0032 (3)</td>
</tr>
<tr>
<td>3.40</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;-OH</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> d<sup>6</sup>-phenol (370 K) referenced to phenol (7.0 ppm) s–singlet, d–doublet, t–triplet, q–quartet. A small amount of methanol was added in order to ensure the methanol assignment.

<sup>b</sup> Integrated value per proton, numbers in parentheses indicate the number of protons.
Only a limited amount of polymer was soluble (10 wt% at 100 °C, quantified using dimethyl terephthalate as a standard), but again no enolization was observed in this aprotic solvent. Furthermore, end-groups of the low-molecular-weight polymer were investigated. The observed chemical shifts are listed in Table III. The end-groups observed are in agreement with the polymerization mechanism consisting of two interdependent reaction cycles as proposed by Drent et al.\textsuperscript{29} Initiation is probably accomplished by the formation of a palladium methoxy bond, and subsequently a carbon monoxide molecule is incorporated, forming ester end-groups. Chain growth occurs by incorporating alternately ethylene and carbon monoxide. Termination is accomplished by the insertion of methanol into the palladium alkyl bond, while forming a new active palladium methoxy catalyst species. The alcoholic solvent present during the reaction can therefore be regarded as a chain transfer agent. When the alcoholic solvent is incorporated into a palladium acyl bond, chain growth is terminated by the formation of a methyl ester end-group and an active palladium hydride catalyst species is formed. The latter can induce a new polymerization cycle, which is comparable to the reaction mechanism as proposed by Lai and Sen\textsuperscript{23} where initiation is accomplished by the formation of alkyl end-groups. It should be noted that no aldehyde or methyl ether end-groups are observed for our polymer samples.

The formation of ester end-groups is confirmed by other investigators.\textsuperscript{23,24,39,40} Chepaikin et al.\textsuperscript{40} used acetic acid as part of the solvent mixture for a palladium-based catalyst system and observed also ester end-groups. This result seems to support the proposed mechanism for initiation via the palladium methoxy (or palladium acetoxy) complex; otherwise, in the case of acetic acid as a solvent one would have expected anhydride (or acid) terminated end-groups to be present in the polymer. However, in strong acidic solvents protonolysis of palladium-alkyl bonds is more likely to occur. Owing to a stronger coordination ability of carbon monoxide, the net rate of insertion of carbon monoxide into the polymer backbone will be much faster than that of ethylene. Consequently the amount of palladium alkyl bonds is much lower than the amount of palladium acyl bonds. Because the formation of 1,2-diketone structures seems to be impossible under these conditions, the rate-determining step for the polymerization will be the coordination and/or the
incorporation of ethylene. Therefore, the observed end-groups do not present conclusive evidence for distinguishing between the two possible mechanisms of initiation.

-Crystal Structure
From the observed x-ray reflections, an orthorhombic unit cell was deduced with \( a=6.91(2) \) Å, \( b=5.12(2) \) Å, and \( c({\text{fiber axis}})=7.60(3) \) Å. The calculated density with four monomer units in the unit cell is 1383 kg/m\(^3\). From systematic extinctions, the space group Pbnm (a variant of space group Pnma-Nr. 62 in the International Tables\(^3\)) was determined. The symmetry of this space group fixes the position of the chain in the unit cell so that the chain must have its backbone at \( x=0, y=0 \) (corner chain) and \( x=0.5, y=0.5 \) (center chain), and the z-axis coordinates of the carbonyl groups must be 0.25 and 0.75, where \( x, y \) and \( z \) are fractional coordinates. As a result, the polymer chain is highly symmetric. This results in only one degree of freedom for the chain in the cell (i.e., the angle between the plane of the zig-zag chain and the bc plane of the unit cell). For a series of angles between the molecular plane and the bc plane, the intensities were calculated and compared with the observed ones. The best agreement was found for an angle of 26°. The estimated standard deviation is 2°. The atomic coordinates of this structure, designated as POK-a, are given in Table IV and the equivalent positions of the space group are listed in Table V.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>C</td>
<td>-0.032</td>
<td>0.087</td>
</tr>
<tr>
<td>C(0)</td>
<td>0.016</td>
<td>-0.045</td>
</tr>
<tr>
<td>O</td>
<td>0.095</td>
<td>-0.261</td>
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</tbody>
</table>
Table V. *Equivalent Positions of the Space Group Pbnm*\(^a\)

<table>
<thead>
<tr>
<th>(x,)</th>
<th>(y,)</th>
<th>(z,)</th>
<th>(-x,)</th>
<th>(-y,)</th>
<th>(-z,)</th>
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</thead>
<tbody>
<tr>
<td>(\frac{1}{2} + x,)</td>
<td>(\frac{1}{2} - y,)</td>
<td>(\frac{1}{2} + z,)</td>
<td>(\frac{1}{2} - x,)</td>
<td>(\frac{1}{2} + y,)</td>
<td>(\frac{1}{2} - z,)</td>
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<tr>
<td>(x,)</td>
<td>(y,)</td>
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<td>(-x,)</td>
<td>(-y,)</td>
<td>(\frac{1}{2} + z,)</td>
</tr>
<tr>
<td>(\frac{1}{2} + x,)</td>
<td>(\frac{1}{2} - y,)</td>
<td>(-z,)</td>
<td>(-x,)</td>
<td>(\frac{1}{2} + y,)</td>
<td>(z,)</td>
</tr>
</tbody>
</table>

\(^a\) All other atoms in the unit cell can be generated by applying the symmetry operations of this space group.

Plots of the POK-a structure are given in Figures 7 and 8. Also a plot of the structure of Chatani et al.42 (POK-f) is displayed (Fig. 9). Comparison of the structures reveals some interesting points. The calculated crystalline density of the POK-f structure is 1.297 g/cm\(^3\), whereas the density of the POK-a structure is 1.383 g/cm\(^3\). The conformation of the polymer backbone is identical for the two structures; however, the packing is rather different. This difference can be attributed to the different orientation of the carbonyl groups of the centre chain relative to the corner chains. The angle between the molecular plane and the bc plane is 26° for the POK-a structure and 40° for the POK-f structure. In POK-a the symmetry operation relating corner and centre chain is \(\frac{1}{2} - x, \frac{1}{2} + y, z\), whereas for the POK-f structure this operation is \(\frac{1}{2} + x, \frac{1}{2} - y, z\). Hence, the difference between the two structures can be described by a rotation of the centre chain through an angle of approximately 180° about the chain axis or equivalently by a translation of the centre chain over half the fiber-axis unit cell length. For the POK-a structure all carbonyl dipoles point in about the same direction at equal height \(z\), whereas in the POK-f structure the dipole of the carbonyl group of the corner and the centre chain point in different directions. Therefore, the packing in the POK-a structure is very effective. The cross-sectional area of the unit cell perpendicular to the fiber axis amounts to 35.2 Å\(^2\), which is even smaller than for the polyethylene unit cell\(^{43,44}\) (36.2 Å\(^2\)).
Figure 7.  View of crystal structure (POK-a) of perfectly alternating ethylene-carbon monoxide copolymer (fiber, c-axis is vertical).

Figure 8.  ab Projection of POK-a unit cell.
Figure 9. View of POK-β crystal structure of polyketone, as determined by Chatani et al. (fiber, c-axis vertical).

Table VI. Contact Distances (Å) Between Neighbouring Carbonyl Groups

<table>
<thead>
<tr>
<th>Contact</th>
<th>POK-a</th>
<th>POK-β</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–C</td>
<td>4.12</td>
<td>4.42</td>
</tr>
<tr>
<td>O–O</td>
<td>3.34</td>
<td>3.99</td>
</tr>
<tr>
<td>C–O</td>
<td>3.05</td>
<td>3.38</td>
</tr>
</tbody>
</table>
The occurrence of the POK-β structure, observed by Chatani et al.,\textsuperscript{26} may have been the result of molecular defects in the polymer chain. The POK-β packing is less dense than the POK-a packing, as is obvious from an increased cross-section of 37.9 Å\textsuperscript{2}. The intermolecular distances (see Table VI) in the POK-a structure are smaller than in the POK-β structure.

Melting

The melting point of ethylene-carbon monoxide copolymers has been a subject of discussion among three groups.\textsuperscript{4,5,26,45} Chatani et al.\textsuperscript{26} stated that the slight difference in the melting point of the copolymer they studied with respect to polyethylene can be attributed partly to a decrease in rotational freedom, due to the presence of the carbonyl group. Starkweather\textsuperscript{5} determined a heat of fusion of 134 J/g. (2.5 kJ/mol chain atoms) from a series of non-alternating ethylene-carbon monoxide copolymers by applying the Flory-Huggins copolymer melting point relation\textsuperscript{46}. On the basis of this result, he stated that the high melting point of the perfectly alternating copolymer (244 °C) is due to the low entropy of fusion, which was reported to be about 60 % of the value found for polyethylene per mol of chain atoms. Starkweather's results do not coincide with those of Wittwer et al.\textsuperscript{45} The latter authors have developed a rotational isomeric state scheme and concluded that on the basis of the results of their calculations, the unperturbed chain dimensions are of the same order of magnitude as those of a polyethylene chain. Hence, to a first approximation the entropy change upon melting can be taken equal to that for polyethylene and the high melting point must, accordingly, be attributed to a high packing energy in the crystal. According to their results, this high packing energy is also reflected in the low solubility of the perfectly alternating polyketone copolymer.

In order to gain a clear insight into the melting behaviour of the perfectly alternating copolymer we have scrutinized melting data for a series of low-molecular-weight polyketone homologs as given in Table VII. A rough approximation for the heat of fusion for crystals of infinite chain length can be obtained by following a procedure similar to that described by Garner et al.\textsuperscript{48} for polyethylene. The heats of fusion for the low-molecular-weight (symmetrical) homologs are extrapolated towards zero
defects, where the fraction of defects is given by

\[ x_{\text{defect}} = \frac{2}{N_{\text{C-atoms}}} \tag{1} \]

where \( N_{\text{C-atoms}} \) is the number of carbon atoms in the chain.

Table VII. *Enthalpy and Entropy of Fusion of Low-Molecular-Weight Polyethylene and (Symmetrical) Polyketone Homologs*

<table>
<thead>
<tr>
<th></th>
<th>( \Delta H_f )</th>
<th>( \Delta S_f )</th>
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<tbody>
<tr>
<td></td>
<td>( \text{kJ/mole Chain Atoms} )</td>
<td>( \text{J/mole Chain Atoms} \cdot K )</td>
</tr>
<tr>
<td>Olefins</td>
<td>Olefin Ketones</td>
<td>Olefins</td>
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</tr>
<tr>
<td>( C_5 )</td>
<td>1.2</td>
<td>1.9</td>
</tr>
<tr>
<td>( C_6 )</td>
<td>1.7</td>
<td>2.0</td>
</tr>
<tr>
<td>( C_7 )</td>
<td>2.2</td>
<td>2.9</td>
</tr>
<tr>
<td>( C_{10} )</td>
<td>2.9</td>
<td>-</td>
</tr>
<tr>
<td>( C_{11} )</td>
<td>2.0</td>
<td>3.1</td>
</tr>
<tr>
<td>( C_{12} )</td>
<td>3.0</td>
<td>-</td>
</tr>
<tr>
<td>( C_{=} )</td>
<td>4.1</td>
<td>4.6</td>
</tr>
</tbody>
</table>

Heats of fusion of the olefin ketones \( C_5 \text{-} C_{11} \) (3-pentanone, 2,5-hexanedione and 3,6,9-undecanetrione) are determined by thermal analysis (scanning speed 20 °C/min) and the melting point of 3,6,9-undecanetrione is taken from ref. 33. Other data are taken from ref. 47.
Fraction defects \( p_{\text{OK}} \) or \( (1 - \text{fraction defects}_{\text{PE}}) / [-] \)

Figure 10. Heats of fusion for low-molecular-weight polyketone and low-molecular-weight polyethylene homologs. (The shaded area indicates the range expected for higher molecular-weight polyketone homologs, solid line represents the heats of fusion for polyethylene homologs mainly with even number of chain atoms; [■] : Polyketone homologs (Table VII); [□] : Polyethylene homologs (ref 47 and 50)).

Though less pronounced, the effect observed for the heats of fusion is similar to the well-known odd-even effects for the heats of fusion of low-molecular-weight polyethylene homologs, as is shown in Figure 10. Although this effect can be attributed partly to the type of end-groups, viz. methyl or ethyl end-groups, crystal structure differences should also be considered. Therefore, the estimated value based on this rather small data set (i.e. 4 kJ/mol chain atoms) can be regarded as an underestimation. Because the end-group effect will diminish for higher molecular-weight compounds, the heat of fusion will converge to a higher and probably more
reliable value for crystals of infinite chain length (see Table VII).

In order to understand the significant discrepancy between the derived underestimated value and the value reported by Starkweather, an analysis based on the melting points of non-(perfectly) alternating polyolefin ketones (data set ref. 5) and terpolymers containing propylene-carbon monoxide and ethylene-carbon monoxide units (data set ref. 51) has also been carried out. The latter data set is verified by means of 'H-NMR-analysis in d6-phenol for two terpolymer samples and the data of both sets are plotted in Figure 11, where the fraction of defects in the terpolymers is calculated from the number of ethylene and propylene units,

\[ x_{\text{detect}} = \frac{N_{\text{propene}}}{N_{\text{ethene}} + N_{\text{propene}}} \quad (2) \]

whereas the fraction of defects in imperfectly alternating copolymers is given by

\[ x_{\text{detect}} = \frac{N_{\text{ethene}} - N_{\text{CO}}}{N_{\text{ethene}}} \quad (3) \]

A regression analysis has been conducted using both data sets by applying the Flory-Huggins copolymer melting point relation,\textsuperscript{46}

\[ \frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_f} \ln(1 - x_{\text{detect}}) \quad (4) \]

and this regression resulted again in too low a value \((2.23 \text{ kJ/mol chain atoms for } x_{\text{detect}} < 0.4, r^2 = 0.992)\) for the crystalline heat of fusion. This result gives rise to the conclusion that, notwithstanding the good correlation, Flory's lattice theory is not applicable for describing the melting point depression caused by the incorporation of molecular defects for polyketone polymers, at least for the examples evaluated.
According to Bunn and Peiser\textsuperscript{52} the carbonyl group can be incorporated in low concentrations into the crystal lattice of polyethylene without inducing structural changes and evidence for this is presented by Chatani et al.\textsuperscript{42} More elaborated models have been reported to describe the thermodynamics of the partial exclusion of molecular defects from the crystalline phase; \textsuperscript{55-56} \textbf{but} these models require extensive data on the crystallization kinetics of the copolymers and terpolymers in order to derive a value for the excess free energy for the different type of defects.

\textbf{Figure 11.} Melting points of imperfectly alternating \textit{ethylene-carbon monoxide} copolymers (solid line), \textit{ethylene-carbon monoxide/propylene-carbon monoxide} terpolymers, low-molecularweight [symmetrical] polyketone (\textit{C}_{18}) and polyethylene homologs (\textit{C}_{30}). ([■]) : Imperfectly alternating \textit{ethylene-carbon monoxide} copolymers (refs. 5 and 50); (○) : \textit{Ethylene-carbon monoxide/propylene-carbon monoxide} terpolymers (ref 51); (□) : thermal and \textit{'H-NMR} analysis; (□) : Polyketone low molecularweight homologs (refs. 28, 33 and 47); (0) : Polyethylene low-molecularweight homologs (refs. 47 and 50).
Wu and Ovenall\textsuperscript{57} have shown that chain branching can occur in non-alternating polyketones. However, branching does not seem to be an important aspect for the imperfectly alternating polyketones prepared by radical induced copolymerization, because the melting point depression is comparable with that of the unbranched ethylene-CO/propylene-CO terpolymers (see Figure 11).

Melting points of the low-molecular-weight polyketone homologs are depicted in Figure 11. Again a slight, though consistent, end-group effect on the melting point is observed. Flory and Vrij\textsuperscript{58} derived a thermodynamic expression, which relates the melting point to the number of atoms in the polymer chain. We will use the simplified expression \[ \text{eq.}(5) \], introduced by Hay\textsuperscript{59} to establish a heat of fusion for crystals of infinite chain length \( (\Delta H_f) \):

\[
T_m = T_m^0 (1 - \frac{2RT_m^0 \ln(N)}{\Delta H_f \cdot N})
\]  

The heat of fusion calculated by this method is sensitive to the value for the equilibrium melting temperature \( (T_m^0) \). For polyethylene it is known that the melting temperature for well-oriented crystalline material is a good approximation for the actual equilibrium melting temperature.\textsuperscript{60,61} Therefore, the maximum measured melting temperature for the highly drawn fiber, i.e. 278 °C, is substituted in eq. (5). It should be remarked that for most polymers a linear correlation is only obtained for \( \ln(N)/N < 0.2 \). For low- molecular-weight homologs of polyethylene and polyketone, the relation between \( T_m/2R(T_m^0) \) and \( \ln(N)/N \) can be well described with the help of a third-order polynomial \( r_{PE}^2 = 0.993 \) and \( r_{POK}^2 = 1.000 \). In the case of polyethylene, higher molecular-weight homologs (up to C\textsubscript{14}) were included in the regression analysis in order to diminish the discontinuities caused by strong odd-even effects (see Figure 12). From the initial slope at \( \ln(N)/N = 0 \) the heat of fusion is calculated, resulting in \( \Delta H_{POK} = 6.2 \) and \( \Delta H_{PE} = 4.7 \) kJ/mol chain atoms (330 and 340 J/g, respectively). Despite the broad extrapolation range, the latter value is in good agreement with the well-accepted value for the heat of fusion of polyethylene\textsuperscript{50} (i.e., 4.1 kJ/mol chain
atoms (293 J/g). Therefore, this procedure results in slightly overestimated values and taking the extrapolation based on the measured heats of fusion for the low-molecular-weight polyketone homologs into account, the true value for $\Delta H_{\text{f}(\text{POK})}$ is expected to be between 4 and 6.2 kJ/mol chain atoms (215-330 J/g).

![Graph](image)

**Figure 12.** Melting point analysis for low-molecular-weight (symmetrical) polyketone and polyethylene homologs ($T_m^0(\text{POK})=278 \, ^\circ\text{C}$ and $T_m^0(\text{PE})=141.4 \, ^\circ\text{C}$ for $N\to\infty$): (■) Polyketone homologs (refs. 28, 33 and 47); (□) Polyethylene homologs (refs. 47 and 50).

Both crystal structures POK-a and POK-β show a high packing fraction (i.e., the fraction of volume in the unit cell occupied by the atoms). The packing fraction for the POK-a structure (78 %, calculated using the method described by Wunderlich\textsuperscript{62}) is to our knowledge the highest ever observed for organic polymers. This remarkably high
packing fraction is a result of the arrangement of the dipoles of the carbonyl groups in
the crystal lattice (see Figure 7). Because of the strong electrostatic interactions the
packing energy for both structures will be high. However, not all dipole interactions
will disappear upon melting, but to what extend this will affect enthalpy of fusion and
the entropy of fusion is unclear.

Table VIII. Melting Data for Some Flexible Chain Polymers

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H_f$ [kJ/mole·Chain Atoms]</th>
<th>$T_m$ [K]</th>
<th>$\Delta S_f$ [J/mole·K]</th>
<th>Packing Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>POK-low</td>
<td>4</td>
<td>551</td>
<td>7.3</td>
<td>0.78 (a)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.73 (β)</td>
</tr>
<tr>
<td>PEO</td>
<td>2.9</td>
<td>342</td>
<td>8.4</td>
<td>0.65</td>
</tr>
<tr>
<td>PE</td>
<td>4.1</td>
<td>415</td>
<td>9.9</td>
<td>0.60</td>
</tr>
<tr>
<td>PC</td>
<td>3.7</td>
<td>506</td>
<td>11.0</td>
<td>0.72</td>
</tr>
<tr>
<td>POK-high</td>
<td>6.2</td>
<td>551</td>
<td>11.3</td>
<td>0.78 (a)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.73 (β)</td>
</tr>
</tbody>
</table>

Source: ref. 50. (PEO, Polyethylene oxide; PC, Polyglycolic acid)

Therefore, a compilation is made in Table VIII of the results of the extrapolations for
the low-molecular-weight polyketone homolog series and melting data for several other
polymers. The estimated range for the entropy of fusion covers the range expected for
flexible chain polymers. All-carbon backbone macromolecules with all-trans
conformations in the crystalline state show a significant volume change upon melting,
which can be understood in terms of the difference in packing fraction in the
crystalline state and the amorphous state at room temperature. Both the POK-a and the POK-β crystal structure show an all-trans conformation of the polymer backbone and therefore the change in packing fraction upon melting is expected to be similar to the value for polyethylene and polyglycolic acid\(^6\) for which these changes amount to 14 and 11\(^\%\), respectively.

The change in packing fraction upon melting will be reflected in a high entropy of fusion, and the true value for the heat of fusion will likely be at the upper end of the 4-6.2 kJ/(mol chain atoms) range. Therefore, the high melting point of the perfectly alternating copolymer is not due to a low entropy of fusion but to a (very] high enthalpy of fusion.

**Polyketone as a Starting Material for Fibers**

From the presented crystal structure, a first approximation to the theoretical chain modulus can be derived simply by substituting an all-trans polyethylene chain in the POK-a unit cell. Values for the theoretical modulus of polyethylene are reported in the literature, but show a considerable variation (186-380 GPa\(^6\)). Maximum Young's moduli up to 264 GPa can be achieved nowadays after hot drawing a gel spun polyethylene fiber\(^6\). Therefore, a value for the theoretical modulus amounting to 350 GPa, which is based on experimental results obtained by Fanconi and Rabolt\(^6\), seems to predict the theoretical modulus of polyethylene most realistically. Correction of this value for the slightly lower crosssection of the POK-a unit cell compared with the cross-section of the polyethylene unit cell leads to a prediction of a theoretical modulus of 360 GPa for the perfectly alternating copolymer. In this approach the elastic constants for the two bond types are taken equal, as in the case of polyethylene.

The crystallinity of the oriented fibers can be calculated from the enthalpy of fusion. For the highly drawn fiber (185 J/g) the crystallinity will be between 55 and 85\(^\%\). On the basis of our experience with other gel spun flexible chain polymers (e.g., polyamide 6 and polyvinyl alcohol), this value is reasonable. For an estimate of the crystallinity on the basis of the measured density of the drawn fiber (i.e., 1.32 g/cm\(^3\)) the
amorphous density is required. Based on the estimated crystallinity of oriented POK-C₂ fibers an amorphous density (ρₐ) of 1.2 g/cm³ is obtained after substitution of ρₓ=1.38 g/cm³, ρᵧ=1.32 g/cm³ and Xₓ = 0.7 in expression (6).

\[
X_x = \frac{\rho - \rho_a}{\rho_c - \rho_a}
\]  

(6)

As in the case of polyethylene, the amorphous density at room temperature is approximately 15 % less than the crystalline density. The estimate for the amorphous density of polyketone is consistent with the expected difference between the crystalline density and the amorphous density at room temperature.

Another interesting feature of polyketone fibers is the presence of strong lateral forces due to the dipole interactions of the carbonyl groups. It was concluded that the high melting point is a result of the strong lateral forces in the crystal. Moreover, increased lateral forces will improve properties governed by the interactions in transversal direction of the fibers (e.g., compressive strength and creep resistance).

2.5 Conclusions

The perfectly alternating polyketone copolymer is an interesting starting material for fiber applications. The crystal structure of this polymer was determined and turns out to have a very dense packing. Owing to the all-trans conformation of the polymer chain in the crystal lattice and the small chain cross-section, high moduli can be achieved in well-oriented crystalline material. The crystallinity in oriented fibers will exceed 50 %. Rather strong interactions between the polymer chains result in a high melting point of the material, whereas the mechanical properties governed by transverse interactions (e.g., creep resistance and compressive strength) will be superior to those of polyethylene fibers.
2.6 References and Notes


27. In order to avoid confusion with polyaryl ketones like PEEK and PEK we have abbreviated this polymer as polyolefin ketone; POK.


34. G. Hoentjen and A.J. Witteveen. Internal report Akzo. 3,6,9-undecanetrione was prepared according to a similar synthesis route as described in ref. 35.


