The Factor Group Splitting Phenomenon:
A Vibrational Spectroscopy Approach to Assess
Polymer Crystallinity and Crystalline Density

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Summary: This paper gathers a number of relevant recent findings where Raman spectroscopy has been successfully applied by the author and coworkers to gain a unique structural picture about the crystalline phase present in isotropic and cold-drawn polyethylenes and in a range of aliphatic polyketone materials. In these semicrystalline polymers a relatively well-known spectroscopic phenomenon called factor group splitting (or correlation field splitting) is thought to occur. By careful analysis of the behaviour of this splitting phenomenon, chiefly in the -CH₂- bending range of the spectrum and in terms of alterations in band intensity and position, a valid approach to assess crystallinity content and morphology, crystalline polymorphism, and crystalline density is displayed. The potential of this spectroscopic phenomenon to yield information about the crystalline phase present in these polymers can therefore be regarded as analogous to that gained by wide-angle X-ray scattering.

Introduction

Vibrational Spectroscopy (Raman and IR) is an excellent and widely used tool for polymer research, since it gains information of a chemical and physical nature down to the molecular level. More in particular, Raman spectroscopy -technique traditionally considered as intricate and complementary to IR- has undergone significant advances in polymer characterisation with the advent of recent improvements in instrumentation versatility and completeness, detection, user-friendliness and fluorescence rejection. While the use of the IR and Raman techniques is undoubtedly essential for analytical purposes in polymers, Raman has also found a relevant status in the characterisation of the physical structure of polymers due to its versatility in sampling accessibility and particular spectral characteristics. For instance, structural studies can be found devoted to crystallinity content[1], conformational changes[2], molecular orientation[3], molecular stress and relaxation[4], etc. Moreover, the technique is experiencing a new revival
within an industrial environment due to both its potential as in process analyser and the availability of searchable libraries for automated sample identification.

It is well-known that the vibrational spectrum of polymers is intrinsically sensitive to the conformational state of the molecular chains\cite{5}. Therefore, the vibrational spectroscopy does not in principle probe the chain lateral or three-dimensional order (crystallinity) in polymers but only the longitudinal order, i.e., a minimum number \( n \) of chains segments with one dimensional regular conformation. In spite of that, there exits an interesting spectroscopic phenomenon called “factor group splitting” or “correlation field splitting”, which is now known for many years, and that is suspected to account for some of the multiplicity of peaks recorded in the vibrational spectrum of a number of crystalline polymers, including polyethylene\cite{6,7} and polyoxymethylene\cite{6}, and since more recently in aliphatic polyketones\cite{8}. This phenomenon can be predicted using group theory and has been widely used to calculate crystallinity content\cite{1} (three-dimensional order) in polyethylene because it causes certain fundamental vibrational modes of the chain to split only in the crystals.

We will focus in this paper on a descriptive analysis of this phenomenon to derive useful information concerning the nature of the crystalline phase present in polyethylene and cold-drawn polyethylene and in a relatively new family of materials called aliphatic polyketones.

**Polyethylene**

Figure 1 shows the superimposed Raman spectrum at room temperature and at -160°C of a polyethylene material\cite{9}. From this Figure it can be seen that by lowering temperature there is a number of bands assigned to ordered chain conformations (arising from chain segments in all-trans disposition mostly in crystals) that split into two components. This phenomenon is termed factor group splitting\cite{10,11,12} (or Davydov splitting\cite{11} or correlation field splitting\cite{7}).
Figure 1. Raman spectra in the range of, from left to right, the -CH₂- bending, the -CH₂- twisting, and the antisymmetric C-C stretching of polyethylene at 25°C and at -160°C (dotted).[9]

It is well-known that polyethylene usually crystallises in an orthorhombic lattice (space group Pnam-No.62 or D₁₆ 2h in Schoenflies nomenclature) which contains two chains per unit cell with different orientation with respect to each other[6]. The vibrational interaction between these two chains within the orthorhombic lattice is responsible for this phenomenon. This vibrational interaction resulting in splitting of the single-chain vibrational-active modes is predicted by group theory and hence the terminology factor group splitting. Factor group splitting is only observed at room temperature in the -CH₂- bending vibrations (Raman active A₅ and B₁₂ and IR active B₂₀ and B₃₆) and in the -CH₂- rocking modes (IR active B₂₀ and B₃₆). These two molecular vibrations are thought to result in a more intense interchain interaction in the crystals than other molecular vibrations because they involve motions predominantly perpendicular to the chain direction. However, at liquid N₂ temperatures the Raman spectrum shows an observable splitting of the antisymmetric C-C stretching band at 1060 cm⁻¹ (symmetry B₂₈ and B₄₆) and the -CH₂- twisting band at 1295 cm⁻¹ (symmetry B₂₈ and B₃₆)[9] (see Figure 1). Factor group splitting effects have also been observed in other polymers like orthorhombic polyoxymethylene[6]. The hexagonal form of polyoxymethylene contains only one chain per unit cell and therefore does not result in correlation field splitting. Monoclinic and hexagonal polyethylene can be obtained at high pressure and at high pressure and high temperature respectively, and neither of both result in factor group splitting[11]. In crystals with only one chain per unit cell another type of splitting can occur to degenerate vibrational modes which is called “site group splitting” or “crystal
field splitting” since it is possible to describe the factor group modes as those of a single-chain distorted by the local crystalline site symmetry (by the crystal field).

A combination of a factor group splitting together with a Fermi resonance is thought to give rise to the complex band shape seen in the -CH₂- bending range (1400-1500 cm⁻¹) of the polyethylene Raman spectrum[6]. Thus, a -CH₂- bending factor group splitting phenomenon, i.e. correlation splitting of single-chain -CH₂- bending Raman-active mode (A₁g) into two components (A₂g and B₁g) in the crystal, is thought to give rise to the bands at ca. 1415 and 1440 cm⁻¹ in polyethylene. However, due to the complex band profile seen in this Raman range some debate remains open as to both the assignment of the latter band (1440 cm⁻¹) to the cited splitting and its symmetry[6]. The fact that the separation between the components of the Raman -CH₂- bending splitting, 1415 and 1440 cm⁻¹ bands, is so high (around 25 cm⁻¹) in polyethylene is unusual, and it is thought to be caused by the simultaneous presence of the cited Fermi effect which enhances the separation.

A careful analysis of this spectroscopic phenomenon can be a very useful tool to gain qualitative and quantitative information about the crystalline phase of polyethylene. Thus, as the 1415 cm⁻¹ band (A₂g) is thought to arise only in the orthorhombic crystals Strobl and Hagedorn[1] cleverly proposed a methodology that makes use of the relative intensity of this band to determine the structural phases of isotropic (orthorhombic) polyethylene. As isotropic polyethylene is mainly orthorhombic the Raman crystallinity as determined by the use of this band is thought to give a good estimation of the polymer crystallinity content. The method determines crystallinity, amorphous (liquid-like phase) and intermediate (interfacial or interphase, region where the crystalline order is dissipated at the borderline between the crystals and the liquid-like phase) phase content by curve fitting of the experimental spectrum. Although, some discussion remains as to the use of the above method to determine the interfacial content[14], the calculation of crystallinity has usually been well accepted and widely used. A modification of the above method has also been proposed to overcome molecular orientation in stretched high density polyethylene (HDPE) and calculate the Raman (orthorhombic) crystallinity[15].
Table 1. Raman crystallinity and Raman crystallinity band position for isotropic, cold-drawn and annealed cold-drawn specimens of HDPE1. The spectra were recorded with an FT-Raman system equipped with a depolarizer in order to scramble the incident laser light and thus minimize molecular orientation effects (see Ref. 15). An error in the determination of the band position of ±0.15 cm⁻¹ for these experiments was estimated from the curve-fitting procedure (see Ref. 15 for further details).

<table>
<thead>
<tr>
<th>Sample</th>
<th>%Crystallinity by Raman</th>
<th>Crystallinity band position</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE1 Isotropic</td>
<td>60</td>
<td>1417.1</td>
</tr>
<tr>
<td>HDPE1 Cold-drawn</td>
<td>40</td>
<td>1418.0</td>
</tr>
<tr>
<td>(68% by DSC)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HDPE1 Annealed</td>
<td>67</td>
<td>1417.0</td>
</tr>
<tr>
<td>(100°C, 1h)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Sample characteristics of the polyethylene materials used. All materials except HDPE1 (ethylene-1-butene) and LDPE are ethylene-1-octene copolymers.

<table>
<thead>
<tr>
<th></th>
<th>HDPE1</th>
<th>HDPE2</th>
<th>LDPE</th>
<th>LLDPE</th>
<th>MPE1 (Metalloocene)</th>
<th>MPE2 (Metalloocene)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (Kg/m³)</td>
<td>958</td>
<td>953</td>
<td>923</td>
<td>918</td>
<td>903</td>
<td>885</td>
</tr>
<tr>
<td>M_w</td>
<td>-</td>
<td>79800</td>
<td>68000</td>
<td>82000</td>
<td>80800</td>
<td>90600</td>
</tr>
<tr>
<td>M_w/M_n</td>
<td>-</td>
<td>3.3</td>
<td>3.3</td>
<td>3.4</td>
<td>2.2</td>
<td>2.0</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>133</td>
<td>130</td>
<td>111</td>
<td>125</td>
<td>101</td>
<td>82</td>
</tr>
</tbody>
</table>

The cold-drawing process is known to induce significant structural changes in polyethylene\[^{16,17}\], i.e. molecular orientation in the straining direction, crystal fractionation, solid-solid phase transformation\[^{18,19}\] and increased unit cell volume (lower crystalline density). The analysis of the factor group splitting bands in the Raman spectrum of polyethylene proves to be sensitive to all these effects when analysed with sufficient care.
The determination of molecular orientation is beyond the scope of this paper and can be found elsewhere\textsuperscript{[3,15]}, instead we will focus on the crystallinity effects. Table 1 shows that a substantial decrease in the Raman crystallinity can be measured upon cold-drawing (at a constant strain rate of 10 mm/min until the full gauge length of the dumb-bell was necked) of a HDPE material (HDPE1 see Table 2 for materials characteristics)\textsuperscript{[15]}. As, (i) X-ray scattering did not indicate for the HDPE1 sample significant presence of solid-solid phase transformation to monoclinic symmetry and (ii) the amount of crystallizable all-trans chain segments did not seem to vary for this material, the above reduction in orthorhombic crystallinity in the cold-drawn sample was attributed to the transformation of part of the original orthorhombic crystals into a highly distorted and ill-defined crystallites accompanied by perhaps some chain unfolding and/or hexagonal phase, and some minor monoclinic phase, for all of which factor group splitting is either lacking or no longer observable\textsuperscript{[15]}. Moreover, Table 1 shows that subsequent annealing at 100°C for 1 hour, i.e. well below the polymer melting point at 133°C, of the cold-drawn specimen produces a substantial increase in the intensity of the 1415 cm\textsuperscript{-1} splitting band. Thus, subsequent annealing increases again the Raman crystallinity. Interestingly, this band does not only undergo changes in intensity but also shifts its position to higher wavenumber in cold-drawn specimens and shifts back to lower wavenumber in annealed cold-drawn specimens (see Figure 2). Determination of band areas and positions throughout the paper was carried out by curve-fitting of the experimental profile as detailed in Ref. 15 and 20. From this Figure 2, it can also be seen that the extent of the shift is material dependent\textsuperscript{[20]}, thus, the band shift is higher (and the band broader) for a low density polyethylene (LDPE, see Table 2) than for a HDPE (HDPE2), i.e. 2.3 cm\textsuperscript{-1} for the LDPE vs 1.5 cm\textsuperscript{-1} for the HDPE2. This band shift is attributed to a reduction in lattice interchain interaction due to the cell expansion. The latter observations are in agreement with X-ray results: This technique points to a decrease in crystal size (crystal fractionation) and crystalline density (lattice expansion) upon cold drawing\textsuperscript{[17,18]}. The decrease in crystalline density is due to the increase of chiefly “a” but also “b” lattice parameters; as a consequence, the interacting chains are further apart in the unit cell, effect that could cause the 1415 cm\textsuperscript{-1} band shift cited above. Upon annealing the orthorhombic crystallinity is recovered towards the flawlessness of the isotropic crystals, hence the observed band intensity rise and the recovery of its position.
Figure 2. Raman spectra (recorded with the LabRam system of Dilor S.A., 632 nm excitation source) in the -CH$_2$- bending range of HDPE2 (left) and LDPE (right) of, from top to bottom, isotropic, cold-drawn and annealed cold-drawn specimens.

In support of the above band shift argument is the observation that (i) upon decreasing temperature, i.e. enhancing the lattice interchain interaction, there is a shift of this band (1415 cm$^{-1}$) towards lower wavenumber (see Figure 1), whereas (ii) on increasing temperature, i.e. upon lattice expansion, this band shifts towards higher wavenumber (see Figure 3). Figure 3 shows that on heating a ethylene-1-butene copolymer –showing a melting endotherm ranging from -50°C to 110°C with maximum of melting at 80°C– the factor group splitting is indeed largely affected. The 1415 cm$^{-1}$ band decreases intensity as the maximum of melting is approached, and the 1415 cm$^{-1}$ and 1440 cm$^{-1}$ bands shift towards each other. Figure 3 shows that for this sample the 1415 cm$^{-1}$ band shift appears to show a linear behaviour with temperature and from the slope an apparent coefficient of thermal expansion of 0.026 cm$^{-1}$/°C can be measured. In fact from the observation of Figures 1 and 3, it is clear that is the 1415 cm$^{-1}$ band which exhibits the largest shift of the -CH$_2$- bending splitting pair. Moreover, the other vibrational modes shown in Figure 1 do also split to some extent implying an increase in interchain interaction. The observation in Figure 2 of a larger shift for the 1415 cm$^{-1}$ band in cold-drawn LDPE could be related to the long chain branches being pulled through the crystals, hence resulting in a higher damage for the crystalline morphology. As the crystalline phase is expected to be more heterogeneous in terms of size and perfection for the LDPE material, this is also suggested by its broader melting point endotherm, the band is seen broader in both the isotropic and the cold-drawn material. Consequently, this splitting phenomenon seems to be a valid tool to assess chain packing in the crystals and to study how this is affected by particular structural alterations.
Figure 3. Raman spectra (recorded at, from top to bottom, -50, -10, 30, 50, 70, 85°C) in the -CH\textsubscript{2}- bending range (left) and 1415 cm\textsuperscript{-1} band shift (right) as a function of temperature of an ethylene-1-butene copolymer. A Linkam TH600 heating stage was attached to the LabRam (Dilor S.A.) micro-Raman system operating with a laser excitation source at 632 nm to record the spectra.

Figures 4 and 5 show the alterations produced upon cold drawing on the other Raman and IR observable splittings, respectively. In Raman (Figure 4), it is seen the factor group splitting of the antisymmetric C-C stretching at ca. 1060 cm\textsuperscript{-1} and that of the -CH\textsubscript{2}- twisting band at ca. 1295 cm\textsuperscript{-1}. From the Figure, the B\textsubscript{2g} components of both doublets appear to decrease in the cold-drawn material with respect to the isotropic material. This effect by no means can be assigned to molecular orientation effects in a direction other (“b” or “a” direction of the unit cell) than the chain direction (“c” direction of the unit cell) because cold drawing produces a random molecular orientation in “a” and “b” direction\textsuperscript{[21]}. The separation of the splitting components, in cm\textsuperscript{-1}, was the same for isotropic and cold-drawn specimens, i.e. 3.1 cm\textsuperscript{-1} for the doublet at 1060 cm\textsuperscript{-1} and 2.3 cm\textsuperscript{-1} for the doublet at 1295 cm\textsuperscript{-1}.

In IR (see Figure 5), the crystalline -CH\textsubscript{2}- bending (1463 (B\textsubscript{2g}) and 1473 (B\textsubscript{3u}) cm\textsuperscript{-1} doublet) and -CH\textsubscript{2}- rocking (721 (B\textsubscript{3u}) and at 730 (B\textsubscript{3u}) cm\textsuperscript{-1}) can be seen\textsuperscript{[22]}. Orientation effects in drawn samples can be averaged in IR by calculating the structural absorbance ((A\textsubscript{ll}+2A\textsubscript{ll})/3)\textsuperscript{[23,24]}, where A\textsubscript{ll} is the absorbance of the spectrum polarised parallel to the sample molecular orientation and A\textsubscript{ll} is the absorbance of the spectrum polarised perpendicular to the sample molecular orientation. The spectra in the -CH\textsubscript{2}- rocking region show a clear difference in the relative absorption of one of the components of the doublet. The splitting separation was identical, i.e. 10.8 cm\textsuperscript{-1} and the band position of both
components was shifted 0.5 cm$^{-1}$ towards low wavenumber in the cold-drawn material. In the -CH$_2$- bending region, the spectra show much smaller intensity differences, although the 1463 cm$^{-1}$ component may have decreased slightly for the cold-drawn material. The splitting separation is 8.3 cm$^{-1}$ for the cold-drawn sample and 9.3 cm$^{-1}$ for the isotropic sample, resulting in a 1 cm$^{-1}$ decrease in the splitting separation for the cold-drawn material.

Figure 4. Raman spectra taken at -113°C in isotropic and cold-drawn (thicker line) HDPE1 in the C-C antisymmetric stretching range (top) and in the -CH$_2$- twisting range (bottom). A micro-Raman system JYU1000 spectrometer (set up with high spectral resolution 1800 grooves mm$^{-1}$ gratings) with a laser excitation source at 514 nm was used.

Figure 5. Mid-IR “structural absorbance” measurements at RT in isotropic and cold-drawn (thicker line) HDPE1 in the range of the -CH$_2$- rocking (left) and -CH$_2$- bending (right). A Bruker IFS66 FT-IR spectrometer was used.

Summarising the above results, relative intensity reduction in splitting components were seen in all the factor group split bands (although smaller for the IR active -CH$_2$-
bending around 1470 cm\(^{-1}\)). Alterations in the separation of the various splitting components was only unambiguously observed for the 1415-1440 cm\(^{-1}\) Raman doublet and the IR doublet around 1470 cm\(^{-1}\). The most obvious reason for not observing any changes in the separation of the other Raman doublets is that the effect may be too small to be detected. From the well-studied behaviour of the Raman \(-CH_2-\) bending range, it is postulated that the reduction in the relative intensity of a component in a factor group split doublet occurs because some of the crystals are excluded from contributing to this spectroscopic phenomenon; whereas a reduction in the doublet separation (doublet bands shift) is related to relatively minor alterations in the unit cell volume of the orthorhombic crystals. However, different molecular vibrations resulting in observable factor group splitting may show totally different sensitivity to unit cell alterations as we have here observed. For instance, while for the 1415-1440 cm\(^{-1}\) Raman doublet part of the crystals does not show splitting (do not contribute to the sample crystallinity), for the IR doublet at 1470 cm\(^{-1}\) virtually almost all crystals show the factor group splitting, albeit altered. So the IR crystallinity given by this band is expected to be higher than the corresponding Raman one. From the results, it turns out that the 1415 cm\(^{-1}\) Raman band (used to calculate the Raman crystallinity of the sample in the methodology of Strobl and Hagedorn) is very much sensitive to alterations in the unit cell and therefore highly defective crystals may not be included in the calculations of the crystalline phase, even though undeformed specimens are considered.

To check the influence of the crystalline morphology in the Raman \(-CH_2-\) bending splitting, a number of undeformed polyethylene grades (see Table 2 for sample characteristics) varying in molecular architecture and density were studied by Raman, DSC and WAXS\(^{[20]}\). Figure 6, shows a plot of crystallinity as determined by the use of the various techniques vs. polymer density for these materials. From this Figure, the Raman crystallinity (calculated using the 1415 cm\(^{-1}\) band)\(^{[11]}\) was found to depress more rapidly with decreasing polymer density than crystallinity by other techniques. This trend has independently been confirmed more recently in a study by Neway et al.\(^{[25]}\) carried out on a larger number of homogeneous and heterogeneous polyethylene materials. We attribute this observation to the presence of an increased number of crystals with defects and a critical drop in crystalline density, perhaps with different crystalline morphology (hexagonal phase)\(^{[26]}\), with decreasing sample density, which do not result in observable factor group splitting.
Figure 6. Raman, DSC and WAXS crystallinity as a function of sample density. Raman Cryst. Anneal. means Raman crystallinity measured in samples annealed for 1 hours at ca. 25°C below their melting point.

Figure 7, shows the position of the 1415 cm$^{-1}$ Raman band and the inverse of the maximum of the DSC melting endotherm as a function of sample density for the samples shown in Figure 6. Band positions and areas were determined by curve fitting of the experimental data as explained in ref$^{[20]}$. Instrumental frequency shifts were ruled out by observing that the position of the 1295 cm$^{-1}$ internal standard band did not shift across density. The lack of linearity of the melting point with density is due to the different molecular architecture of the materials studied here, i.e. heterogeneous (Ziegler-Natta LLDPE) vs. homogeneous (metallocene polyethylenes) incorporation of the branches along molecules and across the molecular weight. From this Figure 7, it is worth noting the reasonable correspondence in the trend of the shift of this band with decreasing density and that of the inverse of the melting point. Thus, the Raman crystallinity band seems to be able to pick up differences in the molecular architecture exhibited by the different samples in a way similar to the melting point. The band shift towards higher wavenumber with decreasing melting point and density clearly suggests that the orthorhombic crystals giving rise to this band must have an increased lattice volume, i.e. lower crystalline density. A decrease in crystalline density$^{[27]}$ is partially related to inclusion of some side-chains by some authors (unlikely here for hexyl branches), and is usually associated with defects and reduced lamella thickness. Reduction in lamella thickness is indicated by a reduction in melting point and is thought to cause cell expansion due to surface dilatometric stresses, thermal vibrations and intracrystalline defects resulting from faster crystallisation at the large undercoolings required. The fact that the cell expansion
(crystalline density drop) in polyethylene is mostly due to the enlargement of the “a” cell parameter, parameter directly responsible for the lateral separation of the two interacting chains within the orthorhombic lattice, explains the shift in position observed for the perpendicular to the chain direction -CH$_2$- bending Raman band seen in Figure 7.

Figure 7. The position of the 1415 cm$^{-1}$ Raman band and the inverse of the maximum of maximum of melting (by DSC) vs. polymer density for the samples shown in Figure 6.

**Aliphatic Polyketones**

Aliphatic polyketones are a family of polymers prepared by the polymerisation of α-olefins and carbon monoxide in a perfectly 1:1 alternating sequence using palladium catalysts$^{28}$. These polymers are semi-crystalline thermoplastics and are reported to have a useful combination of mechanical, high temperature, chemical resistance, wear resistance and barrier properties giving them significant commercial potential in a broad range of engineering, barrier packaging, fibre and blend applications$^{29}$. The simplest aliphatic polyketone is the polymer of ethene and carbon monoxide. It can be regarded as a homopolymer of the repeat unit -(CH$_2$-CH$_2$=C=O)-. It has a crystalline melting point typically between 255 and 260$^\circ$C. Lower melting polymers can be produced by incorporation of propene, butene, hexene, etc. in addition to ethene. The aliphatic polyketones derived from a mixture of ethene, propene and carbon monoxide can be regarded as random copolymers of -(CH$_2$-CH$_2$=C=O)- and -(CH$_2$-CH(CH$_3$)-C=O)- units. For brevity throughout this study, aliphatic polyketones derived from ethene and carbon monoxide will be designated ECO, those derived from ethene, propene and carbon
monoxide will be designated EPCO, those comprising butene will be designated EBCO, and those comprising hexene will be designated EHC0 polymers. The mol% of second olefin, as determined by $^1$H-NMR, is given between parenthesis attached to the sample code. As an example, EPCO(2.9) designates a terpolymer comprising 2.9 mol% of propene, 47.1 mol% of ethene and 50 mol% of carbon monoxide.

Some X-ray diffraction characterisation of the crystalline structure of aliphatic polyketones has been reported$^{30,31}$. Two orthorhombic crystalline structures (with ab unit cell projection analogous to that of polyethylene) with two polymer chains in all-trans conformation traversing the crystal lattice and a high packing density have been described in the literature for aliphatic polyketones, i.e. the so-called $\alpha$ and $\beta$ forms. The conformation of the backbone was found to be identical for the two structures, so the difference is attributed to a different orientation of the carbonyl group in the centre chain relative to the corner chains. In the $\alpha$ form the carbonyl groups are closer together than in the $\beta$ one. Also, the angle between the molecular plane and the bc plane is 26° for the $\alpha$ form whereas it is 40° for the $\beta$ form. The $\alpha$ form with orthorhombic symmetry (space group Pbnn-No.62 or D$^{16}_{2h}$ in Schoenflies nomenclature) and a crystal density of 1.39 g/cm$^3$ has been reported in well-oriented ECO. It is thought to arise from highly efficient dipolar intermolecular interactions within the lattice provided by the carbonyl groups. The $\beta$ form also possesses an orthorhombic symmetry (space group Pnam-No.62 or D$^{16}_{2h}$) with same settings to hat of orthorhombic polyethylene and is reported to have a lower crystal density of typically 1.26 g/cm$^3$.

Raman spectroscopy is also shown to be able to discern between the above polymorphs. The -CH$_2$- bending range shows clear differences between polymers showing predominantly $\alpha$ phase from those exhibiting predominantly $\beta$ phase (see Figure 8). Differences in the spectra in Figure 8, are attributed to the decrease in the splitting separation of a potential factor group splitting phenomenon, i.e. from ca. 1440 - 1415 for the $\alpha$ phase to ca. 1430 - 1418 cm$^{-1}$ for the predominantly $\beta$ phase. A factor group correlation analysis carried out for this polymer predicts the factor group splitting of the polyketone single chain vibrational modes in the crystals$^{81}$.
Figure 8. Raman spectra in the range 1350 - 1750 cm\(^{-1}\) of (top) a sample with predominantly \(\beta\) form crystallinity and (bottom) of a material with predominantly \(\alpha\) form crystallinity. A micro-Raman setup comprising a JY THR1000 single monochromator a CCD camera and a laser at 752 nm was used.

Klop et al.\(^{[1]}\) observed by X-ray diffraction two crystalline forms, \(\alpha\) and \(\beta\), in ECO and that the relative levels of each depend on sample history. They also reported the two forms were present in EPCO when the propene incorporation was less than 2.5 mol\%, but for polymers with higher propene incorporation only the \(\beta\) modification was present. An interpretation of the Raman spectra of polyketone polymers consistent with this is proposed (see Figure 9).

Figure 9. Raman spectra in the range 1350 - 1530 cm\(^{-1}\) of, from top to bottom, ECO, EHCO(4.8), EBCO(4.8), EPCO(5.1). A micro-Raman setup comprising a JY THR1000 single monochromator a CCD camera and a laser at 752 nm was used.
Thus, the band at 1440 cm$^{-1}$ is assigned to one of the components of the splitting arising from $\alpha$ form crystals. The band at 1430 cm$^{-1}$ is assigned to one of the components of the splitting attributed to the $\beta$ form crystals. The band at 1415 cm$^{-1}$ in ECO which shifts to higher wavenumber in EPCO (at 1418 cm$^{-1}$) is assigned to the other component for both splittings and is common to both polymorphs. The reduction in splitting seen for EPCO compared to ECO, i.e. 1430-1415 versus 1440-1418 cm$^{-1}$, could arise from a decrease in interchain interaction associated with the cell expansion and chain rearrangements of the $\beta$ form. In general, ECO and EHCO polymers show a mixture of the two phases whereas EPCO and EBCO polymers above a certain level of second olefin incorporation show predominantly $\beta$ phase. The reason for that behaviour is the incorporation in the crystals of the latter two types of polyketone polymers of some branches (second olefin) resulting in inability to pack into the higher density $\alpha$ phase. An excellent agreement between Raman and X-ray scattering has been found in the qualitative and quantitative determination of the polymorphs content$^{32}$. Figure 10 plots the separation between the components of the $\alpha$ and $\beta$ factor group splitting components vs. crystalline density as calculated by X-ray diffraction for an ECO and a number of EPCO materials with different propene content$^{32}$. This Figure shows that there exist a reasonable linear correlation between the crystalline density of the $\beta$ phase and the separation of the factor group splitting. However, this linear correlation does not seem to extend to the $\alpha$ phase (data point corresponding to the ECO sample). The $\alpha$ phase is known to have a slightly different chain arrangement within the lattice and therefore results in a far more efficient interchain interaction. Accordingly, a different dependence of the splitting separation with crystalline density may apply for both polymorphs.
Finally, Figure 11 shows the Raman spectrum of the ECO sample taken at 23$^\circ$C, 100$^\circ$C, 200$^\circ$C (well below the melting point of the sample at 253$^\circ$C) and to 23$^\circ$C after heating to 200$^\circ$C.
Figure 10. Separation in wavenumber between the Raman α and β -CH$_2$- splittings vs. crystalline density as determined by X-ray scattering for an ECO and various EPCO samples.

Figure 11. Raman -CH$_2$- bending range of an ECO sample at, from bottom to top, 23°C, 100°C, 200°C and cooled back to 23°C. A Linkam TH600 heating stage was attached to the LabRam (Dilor S.A.) micro-Raman system operating with a laser excitation source at 632 nm to record the spectra.

It is worth noting that DSC shows two small endothermic peaks at 85° and at 105°C which were tentatively assigned the solid-solid α to β transitions by Klop et al.[1]. At 100°C compared to 23°C the intensity of the band at 1440 cm$^{-1}$, assigned to the α phase, is reduced and the band at 1430 cm$^{-1}$, assigned to the β phase, is more pronounced. At 200°C the band at 1440 cm$^{-1}$ seems to have totally disappeared pointing to a complete phase transformation and suggesting that the sample reaches the melting point in the β form. On cooling the sample back to 23°C the α phase seems to be restored. The above
observations therefore unambiguously confirm the solid-solid phase transition occurrence on heating. Figure 11 shows that the band at 1440 cm\(^{-1}\) not only decreases in intensity, on heating from 23 to 100\(^{\circ}\)C, but simultaneously shifts to lower wavenumber. The band at 1130 cm\(^{-1}\) also shifts to lower wavenumber with increasing temperature. These band shifts relate to a decrease in interchain interaction (lattice expansion) with increasing temperature as molecular mobility within the crystal is increasingly activated.

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