Characterization of the Structure and Crystalline Polymorphism Present in Aliphatic Polyketones by Raman Spectroscopy

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ABSTRACT: Raman spectroscopy has been used for the first time for the characterization of perfectly 1:1 alternating α-olefin:carbon monoxide aliphatic polyketones produced by the polymerization of ethene with carbon monoxide (ECO polymers) and mixtures of ethene and propene with carbon monoxide (EPCO polymers). A procedure to determine the methyl branch content arising from propene incorporation in EPCO polymers was established. This is based on the good correlation found between the intensity of a Raman band assigned to $-CH_3$ bending and the propene incorporation determined by ^1H NMR spectroscopy. A measure of the relative degree of crystallinity was made from the CO stretching band, and this was correlated with the heat of fusion determined by differential scanning calorimetry. Band shapes in the range assigned to $-CH_2-$ bending were attributed to factor group splitting effects (correlation splitting) and were interpreted to infer the presence of the two crystal forms (α and *β*) which have previously been identified by X-ray diffraction for aliphatic polyketones.

Introduction

Aliphatic polyketones are a family of polymers prepared by the polymerization of α-olefins and carbon monoxide in a perfectly 1:1 alternating sequence using palladium catalysts.[1] These polymers are semicrystalline 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, fiber, and blend applications.[2]

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 °C. Lower melting point polymers can be produced by incorporation of propene 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 paper, aliphatic polyketones derived from ethene and carbon monoxide will be designated ECO, and those derived from ethene, propene, and carbon monoxide will be designated EPCO.

Some X-ray diffraction characterization of the crystalline structure of aliphatic polyketones has been reported.[3] 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 α and *β* forms.[3] 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 center chain relative to the corner chains. In the α form the carbonyl groups are closer together than in the *β* one. Also, the angle between the molecular plane and the *bc* plane is 26° for the α form whereas it is 40° for the *β* form. The α form with orthorhombic symmetry (space group *Pbnm*-no. 62 or D_{2h}^{16} 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 *β* form also possesses an orthorhombic symmetry (space group *Pnam*-no. 62 or D_{2h}^{16}) with same settings to that of orthorhombic polyethylene and is reported to have crystal density of typically 1.26 g/cm^3. This *β* phase has a less efficient lattice packing, and it is thought to coexist with the α form in ECO polymers and to be exclusively present in EPCO polymers above 2.5 mol % of propene.[3] A transition attributed to a phase change from the α to the *β* form has been observed in ECO at temperatures between 110 and 125 °C by differential scanning calorimetry.[3] The processes of spinning and drawing leads to the transformation of the *β*-rich symmetry into oriented α-rich symmetry.

Raman spectroscopy has become widely used for the characterization of chemical and physical features of polymers due to the recent improvements in detection, user-friendliness, and fluorescence rejection. For instance, studies can be found devoted to crystallinity content[4]/type[5]/perfection,[6] conformational changes,[7] molecular orientation,[8] molecular stress and relaxation,[9,10] etc. The purpose of the work reported in this paper was to demonstrate the potential of Raman spectroscopy for the characterization of the structure and crystalline forms present in aliphatic polyketones.

Experimental Section

Materials. The aliphatic polyketones, ECO and EPCO, used in this study were synthesized at BP Chemicals using a proprietary catalyst.

The polymers were studied as powders supplied from the production process without further treatment. An ECO sample was also studied as a 150 *μ*m film, compression molded using an electrically heated hydraulic press above the melting point, and cooled under pressure at 15 °C/min to room temperature.

The mole percent of propene in EPCO polymers, as measured by ^1H NMR, is given between parentheses attached to the code EPCO throughout the paper. As an example, EPCO(2.9) designates a polymer comprising 2.9 mol % of

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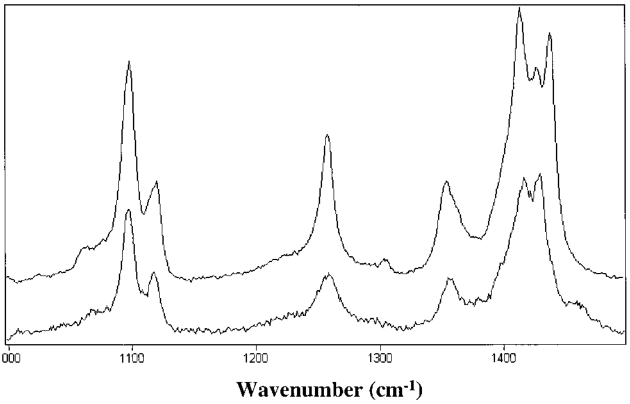

Figure 1. Raman spectra of ECO and EPCO(4.6) in the range 1000−1500 cm^{-1}.

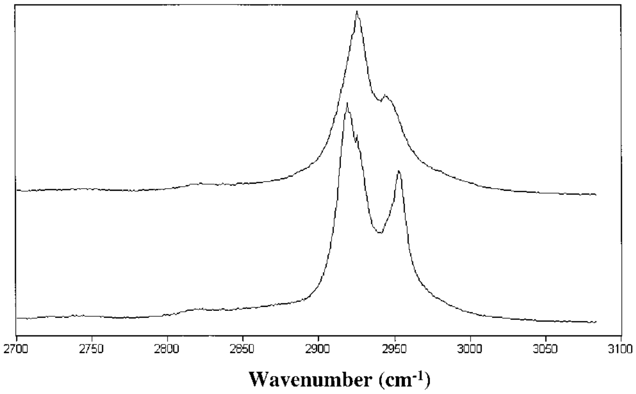

Figure 2. Raman spectra of ECO and EPCO(4.6) in the range 2700−3100 cm^{-1}.

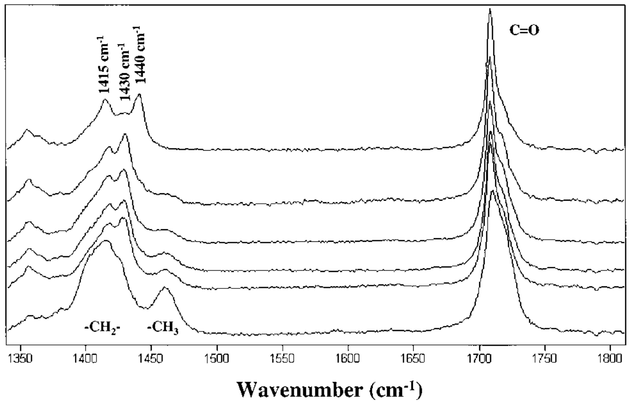

Figure 3. Raman spectra in the range 1350−1800 cm^{-1} of, from top to bottom, ECO, EPCO(2.9), EPCO(4.6), EPCO(6.4), EPCO(7.4), and EPCO(13.4) materials.

propene, 47.1 mol % of ethene, and 50 mol % of carbon monoxide. The typical weight-average molecular weight (M_w) determined by gel permeation chromatography is around 130 000 relative to PMMA standards, and the polydispersity index is around 2.

Raman Equipment. The spectra were recorded with a Raman system[11] comprising of a JY THR1000 single monochromator, Wright instruments CCD camera, and a Ti sapphire laser at 752 nm, with a Kaiser holographic edge filter. Typically 50 mW of laser light was used at the sample with a ×20 long distance microscope objective. Integration times were around 20 s, and the spectral resolution is 3 cm^{-1}. The Raman spectra were calibrated for potential spectrometer variations resulting in artificial band shifts by recording the Raman spectrum of a polyethylene pellet prior to every two or three polyketone samples.

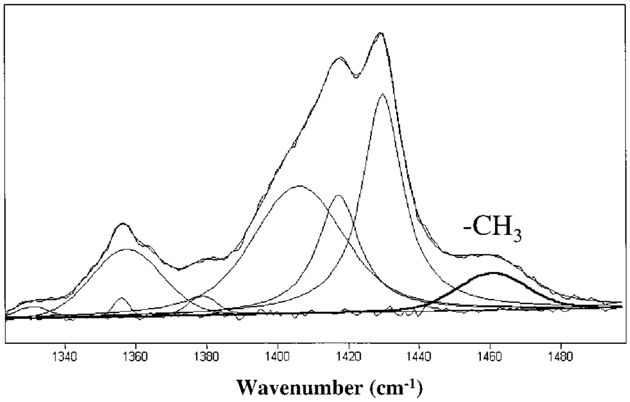

Figure 4. Example of curve fitting in the range 1320−1500 cm^{-1}.

A heating stage (Linkam TH600) with an accuracy in temperature control of ±0.1 °C was attached to the microcroscope of the LabRam (Dilor S.A.) Raman system in order to conduct Raman experiments at different temperatures. A 632 nm excitation source (He−Ne), with typically 16 mW at the sample, 1800 grooves/mm diffraction gratings, 300 μm pinhole, and a ×50 long working distance objective were the conditions used for acquiring Raman spectra.

Curve fitting of the Raman experimental profiles was carried out with the GRAMS Research 2000 software package from Galactic industries. Voigt (convolution of Lorentzian and Gaussian) profiles, no restrictions, and linear baseline conditions were utilized.

Differential Scanning Calorimetry (DSC). DSC curves were recorded in a Perkin-Elmer DSC 7 calorimeter at a heating speed of 10 °C/min from 0 to 270 °C on typically 4 mg of sample. The calibration of the DSC was carried out with standard samples of indium and tin.

Results and Discusion

Raman Spectrum of Aliphatic Polyketones. Figures 1 and 2 show the Raman spectra of ex-reactor ECO and EPCO(4.6) powder over the ranges 1000−1500 and 2700−3100 cm^{-1}, respectively. Figure 1 shows two sharp peaks around 1100 cm^{-1} tentatively attributed to C−C stretching (ν) motions, a sharp band at 1260 cm^{-1} which could be assigned to $-CH_2-$ twisting (γ_t), and a group of bands from 1350 to 1500 cm^{-1} assigned, at least in part, to $-CH_2-$ bending (δ). Figure 2 shows the $-CH_2-$ symmetric (ν_s) and asymmetric (ν_a) stretching bands at around 2915 and 2945 cm^{-1}, respectively.

Figure 3 shows the Raman spectra of a range of samples over the range 1325−1850 cm^{-1}. This range shows spectral variations between samples. The spectral features have been assigned by analogy with accepted assignments for other polymers. Thus, the intense band around 1710 cm^{-1} is attributed to C═O stretching (ν), and bands in the range from 1400 to 1500 cm^{-1} are attributed to $-CH_2-$ and $-CH_3$ bending (δ) motions.

Branching Content in EPCO Polymers. The band at ca. 1460 cm^{-1} was found to increase with increasing propene level in the EPCO samples. This band is absent in the ECO polymer (see Figures 1 and 3). As a consequence, this band is likely to arise from a $-CH_3$ bending motion. Moreover, it compares well with the position of this mode in the Raman spectrum of polypropylene.[12] The bands in this region of the spectrum were deconvoluted as shown in Figure 4. The ratio of the area of the 1460 cm^{-1} band to the area under the broad C═O stretching feature centered at 1710 cm^{-1} gives a good linear correlation with the level of propene as determined by ^{1}H NMR (see Figure 5). In perfectly alternat-

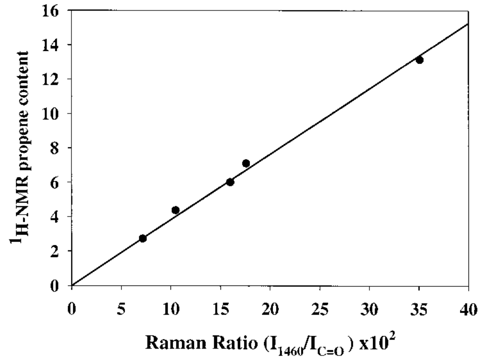

Figure 5. ^{1}H NMR mole percent of propene versus the Raman ratio $I_{1460}/I_{C=O}$ ($r^2 = 0.996$), where I_{1460} is the area of the band at 1460 cm^{-1} assigned to $-CH_3$ bending and $I_{C=O}$ is the area of the C=O stretching band centered at 1710 cm^{-1}.

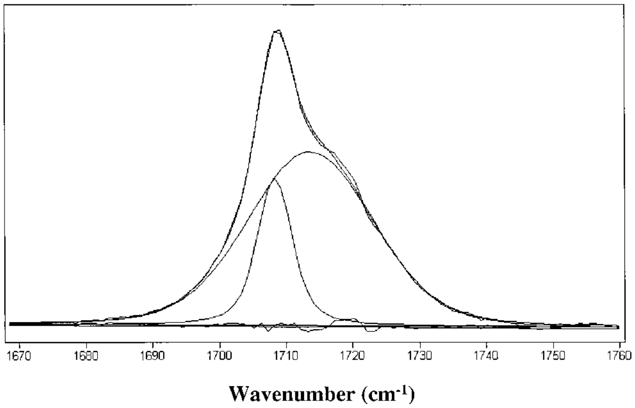

Figure 6. Example of curve fitting in the range of the C=O stretching band.

ing aliphatic polyketones the incorporation of carbon monoxide is always 50 mol %; therefore, the C=O stretching band can serve as an internal standard. It has been reported[13] that in EPCO polymers while most of the propene undergoes 1,2-incorporation $-CO-CH_2-CH(CH_3)-CO-$, a small proportion undergoes 1,3-incorporation $-CO-CH_2-CH_2-CH_2-CO-$. The ^{1}H NMR propene content was corrected for this marginal 1,3-incorporation (no more than 6% of the total propene incorporation) along the chain. The propene units that have undergone 1,3-incorporation are not accounted for in the Raman method which measures $-CH_3$ groups. The Raman method allows the rapid estimation of methyl contents in the solid state without the need for sample preparation or alteration. Furthermore, reliable analysis of branch content as a function of molecular weight could be achieved by coupling a Raman spectrometer with gel permeation chromatography (GPC).

Molecular Order in EPCO Polymers. From Figure 3, it can be seen that the C=O stretching band (at ca. 1709 cm^{-1}) broadens toward higher wavenumber. The broadening increases with increasing propene content. This C=O band was deconvoluted into two, i.e., a sharp band at ca. 1708 cm^{-1} and a broad band at ca. 1710 cm^{-1} (see Figure 6). The latter develops with increasing propene content. Since the propene is expected to cause molecular disorder along the chain, these features can be assigned to C=O segments with regular longitudinal order (in all-trans conformation) and to C=O segments with nonregular longitudinal order (in gauche conformations), respectively. To a first approximation, the all-trans segments should be mostly within crystals. As a consequence, two Raman methods are proposed to obtain an estimate of the degree of crystallinity in aliphatic polyketones (see Figure 7). In one procedure the area of the band centered at high wavenumber relative to the total area of the C=O stretching band can be used. In another procedure the wavenumber of the peak of the C=O band can be correlated with the degree of crystallinity. The peak position shifts to higher wavenumber with decreasing crystallinity, i.e., as the band broadens. This procedure has been successfully applied to poly(ether ether ketone) (PEEK).[14] The first procedure requires mathematical deconvolution of the experimentally measured band, while the second requires precise location of the band peak. In Figure 7, both the band peak position and the band area, determined by the curve-fitting procedure outlined above, are correlated with the heat of fusion as determined by differential scanning calorimetry. In both cases a reasonable correlation is obtained.

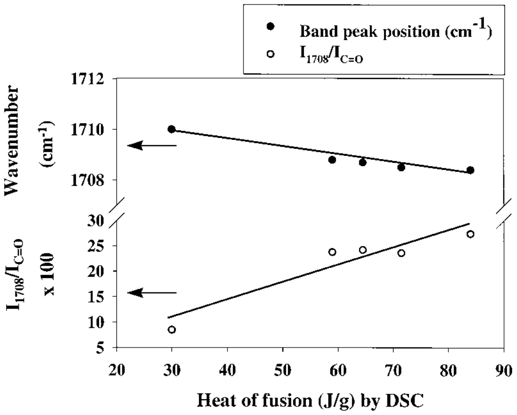

Figure 7. Peak position (cm^{-1}) of the C=O stretching band (filled circles) and Raman ratio $I_{1708}/I_{C=O}$ (empty circles) versus the heat of fusion (J/g) as determined by DSC for the EPCO samples.

Crystalline Polymorphism. The $-CH_2-$ bending region of the Raman spectrum of aliphatic polyketones, 1400−1500 cm^{-1}, is found to show some peculiar structural features that are attributed, from the discussion that follows, to the two different crystalline polymorphs reported for aliphatic polyketones. A band at 1440 cm^{-1} is distinct in the spectrum of ECO (see Figure 3). It features very weakly in the spectrum of EPCO(2.9), but is not discernible for the EPCO samples with higher propene incorporation. A band is evident at 1430 cm^{-1} in the spectrum of EPCO(2.9), which is weakly present in the spectrum of ECO. The band at 1415 cm^{-1} in the ECO spectrum appears slightly shifted to higher wavenumber in the spectra of the EPCO samples, i.e., at 1418 cm^{-1}. Furthermore, in the EPCO samples the intensity of the bands at 1430 and 1418 cm^{-1} decreases with increasing propene incorporation. A broad band can be discerned at 1410 cm^{-1}, and its intensity increases with increasing propene level. It is known that crystallinity decreases with increasing propene incorporation in these aliphatic polyketones (see Figure 7). It is proposed, therefore, that the band at 1410 cm^{-1} originates from the amorphous phase while the bands at 1415 (1418 for EPCO), 1430, and 1440 cm^{-1} arise from the crystalline phase.

To provide an explanation for the alterations observed in these crystalline bands, an analogy is drawn with the vibrational assignments of the spectrum of polyethylene in the $-CH_2-$ bending region. It is well-known that

Table 1. Number of Modes and Relationship (Correlation Table) between Symmetry Species for Single-Chain and Crystals of α and *β* ECO Polymer[a]

[&]Factor Group Single-Chain Isomorphous with D_{2h}	Factor Group Site Isomorphous with C_{2h} x 2 (two ECO chains per lattice)	Factor Group Crystal Isomorphous with D_{2h}
7 A_g	7 A_g x 2	7 A_g, 7 B_{1g} (Raman)
6 B_{1g}	6 A_g x 2	6 A_g, 6 B_{1g} (Raman)
7 B_{2g}	7 B_g x 2	7 B_{2g}, 7 B_{3g} (Raman)
4 B_{3g}	4 B_g x 2	4 B_{2g}, 4 B_{3g} (Raman)
4 A_u	4 A_u x 2	4 A_u, 4 B_{1u} (Silent, IR)
7 B_{1u}	7 A_u x 2	7 A_u, 7 B_{1u} (Silent, IR)
6 B_{2u}	6 B_u x 2	6 B_{2u}, 6 B_{3u} (IR)
7 B_{3u}	7 B_u x 2	7 B_{2u}, 7 B_{3u} (IR)
Total = 48		Total = 96

Point group D_{2h} with symmetry elements E, C2(z), C2(y), C2(x), i, σ(xy), σ(xz) and σ(yz). Point group C_{2h} with symmetry elements E, C2, i, σ_h. z was defined along the chain axis, and the plane xz was defined to contain the chain axis and the carbonyl groups (C=O).

[&] The number of modes for the single-chain comes from the following analysis:

The characters of the reducible representation (Γ_{red}) for the single-chain can be calculated as follows:

	E	C2(z)	C2(y)	C2(x)	i	σ(xy)	σ(xz)	σ(yz)
Number of Unshifted Atoms	16	0	0	4	0	4	8	0
Contribution	3	-1	-1	-1	-3	1	1	1
Γ_{red} (Product of the above)	48	0	0	-4	0	4	8	0

Using the character table for D_{2h}, the contribution of the irreducible factor group representations to the reducible representation can be easily obtained[17]:

$$\Gamma_{red} = 7\ A_g + 6\ B_{1g} + 7\ B_{2g} + 4\ B_{3g} + 4\ A_u + 7B_{1u} + 6B_{2u} + 7\ B_{3u}$$

[a] The number of fundamental modes for the ECO single chain is 3*N* of which 3*N* − 4 are genuine vibrational modes. *N* is the number of atoms in the repeat unit $-CH_2-CO-CH_2-CH_2-CO-CH_2-$, i.e., 16.

polyethylene crystallizes in an orthorhombic lattice (space group *Pnam*-no. 62 or D_{2h}^{16} in Schoenflies nomenclature) which contains two chains per unit cell with different orientations with respect to each other. The vibrational interaction between these two chains within the orthorhombic lattice together with a Fermi resonance is thought to give rise to the complex band shape seen in the $-CH_2-$ bending range of the polyethylene Raman spectrum.[15] This vibrational interaction resulting in splitting of the single-chain vibrational-active modes is predicted by group theory and is called factor group splitting (ref 16 and references therein) or correlation splitting.[15,17] Thus, a $-CH_2-$ bending factor group splitting phenomenon, i.e., correlation splitting of single-chain $-CH_2-$ bending Raman-active mode (A_g) into two components (A_g and B_{1g}) in the crystal, is thought to give rise to the bands at 1415 and 1440 cm^{-1} in polyethylene. However, due to the complex band profile seen in this Raman range, some discussion remains as to both the assigment of the latter band (1440 cm^{-1}) to the cited splitting and its symmetry.[15] The cited splitting is only observed at room temperature in the $-CH_2-$ bending vibrations (Raman-active A_g and B_{1g} and IR-active B_{2u} and B_{3u}) and in the $-CH_2-$ rocking modes (IR-active B_{2u} and B_{3u}). 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.[15] The fact that the separation between the components of the Raman $-CH_2-$ 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. Factor group splitting effects have also been observed in other polymers such as orthorhombic poly(oxymethylene).[15] The hexagonal form of poly(oxymethylene) contains only one chain per unit cell and therefore does not result in correlation splitting. In crystals with only one chain per unit cell another type of splitting can occur 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). As the factor group splitting phenomenon in polymers is the result of an interchain interaction within the lattice, alterations in the lattice may lead to variations in the intensity of the splitting. Thus, deterioration of the orthorhombic crystallinity in polyethylene by cold drawing[6] or by introduction of branches[18] results in alterations in the separation of the two components of the factor group splitting. These alterations are caused by the creation of small (with lower crystal density) and ill-defined (with defects) orthorhombic crystals which in turn lead to a decrease in the interchain interaction and to a decrease in the overall separation of the splitting components. During cold drawing, these alterations are also caused by phase transformation from orthorhombic to monoclinic (or triclinic). Oligomers of polyethylene crystallizing in other symmetries such as monoclinic (or triclinic) do not show factor group splitting as one of the bands associated with this splitting phenomenon disappears from the Raman spectrum.[5]

Aliphatic polyketones also crystallize in an orthorhombic lattice (space group *Pnam*-no. 62 for the β crystal and the same space group but different setting *Pbnm*-no. 62 for the α crystal) with two chains in an all-trans conformation very similar to that of polyethylene, but with the *c* axis increased by 3 times to account for the carbonyl group (chain repeat unit $-CH_2-CO-CH_2-CH_2-CO-CH_2-$ for ECO versus $-CH_2-CH_2-$ for polyethylene) and a higher packing density attributed to dipole effects.[3] As a consequence, interchain interactions within the unit cell resulting in correlation splitting could be responsible for the band profiles observed in Figure 3 in the $-CH_2-$ bending region. In this context, a factor group correlation analysis predicting the symmetry of the ECO single-chain vibrational modes in the crystals was carried out as described in ref 17, and the results are summarized in Table 1. The factor group of the single chain, site, and crystal for the ECO polymer are analogous to those calculated for polyethylene.[3] From Table 1 it is expected that the single-chain modes will split in the crystal, and therefore factor group splitting is feasible to be observed in the Raman spectrum of polyketones.

Differences in the spectra of EPCO and ECO in Figure 3 are attributed to the decrease in the splitting separation of a potential factor group splitting phenomenon, i.e., from 1440 to 1415 cm^{-1} for ECO to 1430−1418 cm^{-1} for EPCO. Klop et al.[3] observed by X-ray diffraction two crystalline forms, α and β, 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 β modification was present. An interpretation of the Raman spectra of ECO and EPCO polymers consistent with this is proposed (see Figure 8). The band at 1440 cm^{-1} is assigned to one of the components of the splitting arising from α form crystals. The band at 1430 cm^{-1} is assigned to one of the components of the splitting attributed to the β 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 vs 1440−1418 cm^{-1}, could arise from a decrease in interchain interaction associated with the cell expansion and chain rearrangements of the β form. In summary, the Raman spectrum of ECO shows three bands that can be attributed to the mixture of α and β forms as opposed to the Raman spectra of EPCO materials (above 2.9 mol % propene incorporation) which only show the β phase.

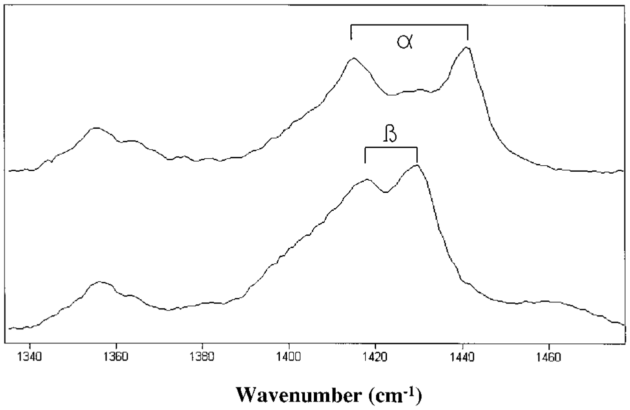

Figure 8. Raman spectra in the range 1340−1480 cm^{-1} of ECO and EPCO(4.6).

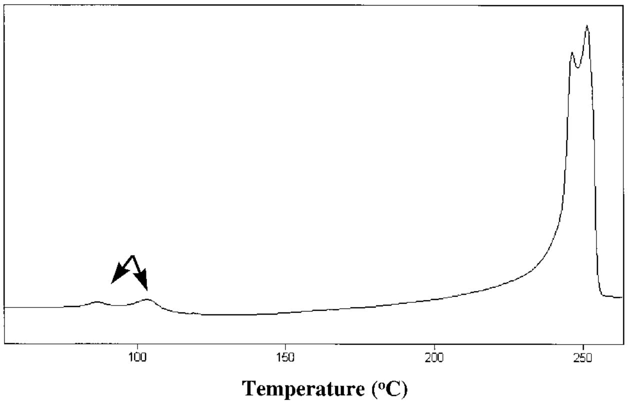

Figure 9. DSC curve for the ECO film. Back arrows indicate α to β phase transition endotherms.

To further substantiate the proposed assignments for the Raman bands, Raman experiments were carried out at different temperatures on a compression molded film of the ECO sample. The DSC experiments showed two small endothermic peaks at 85 and 105 °C which were assigned to the α to β transition (see Figure 9) after the work of Klop et al.[3] These small endothermic peaks were not seen in the EPCO polymers. Figure 10 shows the Raman spectrum of the ECO sample taken at 23, 100, and 200 °C (well below the melting point of the sample at 253 °C) and to 23 °C after heating to 200 °C. 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 trans-

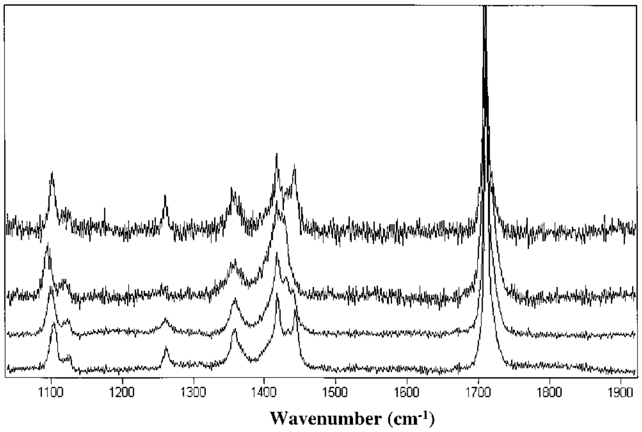

Figure 10. Raman spectra of a compression molded film of the ECO sample at, from bottom to top, 23 °C, 100 °C, 200 °C, and cooled back to 23 °C.

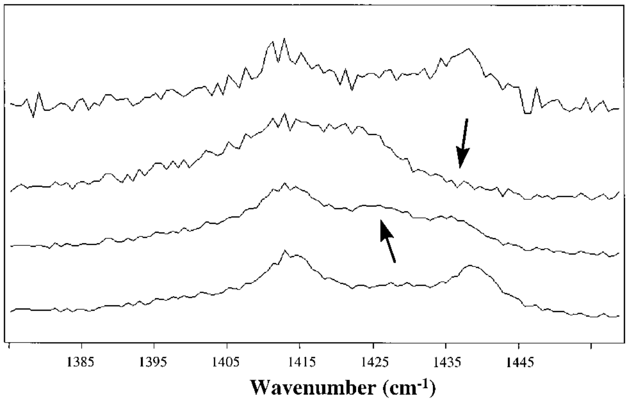

Figure 11. Magnification of Figure 10 in the range of the $-CH_2-$ bending (1375−1460 cm^{-1}).

formation 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 are in good agreement with the observations reported by Klop et al.[3] Figure 11 shows that the band at 1440 cm^{-1} not only decreases in intensity, on heating from 23 to 100 °C, but also 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. Moreover, a decrease in the separation between the bands at 1430 and 1418 cm^{-1} has been measured with increasing the propene content in EPCO polymers.[19] This separation correlates extremely well with the observed decrease in crystalline density (cell expansion) as determined by WAXS.[19] Thus, as the crystalline density decreases, driven by the introduction of an increasing number of disrupting units (methyl branches) throughout the ECO chain, a weakening in the factor group splitting is suggested caused by a decrease in the interchain interaction. The fact that the unit-cell expansion is mostly due to the enlargement of the *a* cell parameter, attributable to the lateral separation of the two interacting chains within the orthorhombic lattice, explains the observed change in the splitting for the perpendicular to the chain direction $-CH_2-$ bending mode. Finally, an excellent quantitative agreement has been found[19] between the content of the ratio α/*β* as calculated by both (i) Raman using the band at 1440 cm^{-1} normalized to the internal standard and (ii) WAXS using the ratio of the plain (210) for the α and *β* forms at angles 31° and 29°, respectively.

Conclusions

Raman spectroscopy has been shown to be useful for the phase structure characterization of a series of aliphatic polyketones, perfectly 1:1 alternating polymers of ethene with carbon monoxide (ECO), and mixtures of ethene and propene with carbon monoxide (EPCO). The level of methyl branches arising from propene incorporation in EPCO polymers can be determined quantitatively from the intensity of the 1460 cm^{-1} band after calibration with polymers of known propene incorporation. The relative degree of crystallinity can be determined from the carbonyl stretching band. The form of the crystalline phase present in aliphatic polyketones, polymorphs α and *β*, can be derived from bands in the $-CH_2-$ bending region of the spectrum, 1400−1500 cm^{-1}, attributed to factor group splitting.

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