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TESTING

## Morphological Raman analysis of short chain branched ethylene and propylene metallocenic copolymers

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## ARTICLE INFO

## Keywords:

Raman  
Short chain branches  
Polypropylene  
Polyethylene  
Metalloenic  
Olefin copolymers

## ABSTRACT

Spectroscopic features in the Raman spectra of semicrystalline polyolefins that characterize different phase morphologies are reported. With growing incorporation of different 1-olefins, changes in the spectra due to different short chain branches are identified for polyethylene and polypropylene, both isotactic and syndiotactic. Bands were assigned to crystalline, semicrystalline and amorphous contents, and quantification was approached with the use of internal reference bands. The degree of crystallinity and the conformational order of the copolymers decrease with the increase in short chain branches content, and the behavior of larger short chains is different depending on the type of polymer analyzed. A semi ordered interphase was found, assigned and followed in all cases, as well as the evolution of amorphous phase with comonomer incorporation.

## 1. Introduction

Semicrystalline polymers have a heterogeneous microstructure consisting of crystalline and amorphous phases. Consequently, polymer properties are highly influenced by its crystalline morphology [1–19]. Other methods that provide quantitative measurements of the degree of crystallinity are available for the morphological characterization, as differential scanning calorimetry (DSC). The determination of crystallinity from this method is based on the assumption of a two-phase structure, which may indeed not be the case. Previous studies on semicrystalline polymers using vibrational spectroscopy have shown the existence of an intermediate transitional phase or interphase [1–6,20–36], consisting on semi-ordered, or short-range ordered systems that are frequent in polyolefins.

Raman spectroscopy is a fast and nondestructive method to probe the conformational states of the polymer chains. Thus, differentiation in the vibrational spectrum of chains in crystals with unique conformations must be expected [1,2,20–30,33–46]. Contents of different configurational and conformational states, order and length distribution of sequences can be potentially identified and related to chains in specific 'phases' [37–39].

For example, an interfacial region is present between crystalline lamellas and the amorphous phase of polyethylene (PE) and its short chain branched (SCB) copolymers. Mutter et al. [20] even split this

interfacial region in interfacial crystal and liquid like components, which were thoroughly examined through free volume models [3–6]. Each of these phases was estimated through different bands, or their deconvolution, in the Raman spectrum [1,3–6,20,27–30,33–36]. Their intensities and positions depend on the degree of crystallinity of the sample [21,22]. Similar three phase morphologies with ordered helicoidal structures and sequences, exist in isotactic polypropylene (iPP) copolymers [2,24–26,42–45]. Still, there is not a common consensus on the estimation of each of the phases through Raman analysis. As long as known, neither there are studies involving copolymers of syndiotactic polypropylene (sPP), though it is known that the homopolymer also follows ordered helicoidal and all-trans structures, as well as an amorphous phase.

In this work we use Raman spectroscopy to characterize ethylene and propylene metallocenic copolymers. Metallocene catalysts made possible the synthesis of 1-olefin copolymers with well-defined structures, homogeneous comonomer composition, and narrow molecular weight distribution [1,5–14]. The introduction of a chosen 1-olefin during ethylene or propylene polymerization induces the insertion of SCB of a desired length. Comonomers of different length were used, in order to compare between different sizes of SCB in the morphologies. Also, both iso and syndio tacticities were taking into account for the propylene metallocenic copolymers. The effect of growing amounts of comonomer on the morphologies of all the polyolefins was studied.

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**Table 1**  
Reaction conditions for the different syntheses.

Polymer	T (°C)	Stir (rad/s)	P (kPa)	Catalytic system	Reactor
PEX#	60	52	200	[Et(Ind) <sub>2</sub> ]ZrCl <sub>2</sub> /MAO	Parr, 1 l
iPPX#	40	105	300	[Me <sub>2</sub> Si(2Me-Ind) <sub>2</sub> ]ZrCl <sub>2</sub> /MAO	Buchi, 1 l
sPPX#	55	105	200	[Ph <sub>2</sub> C(Flu)(Cp)]ZrCl <sub>2</sub> /MAO	Buchi, 1 l

## 2. Experimental

The syntheses of the polymers were carried in toluene for 30 min, under the conditions shown in Table 1. Polymerizations were then stopped with methanol acidified with HCl (2%). The resulting polymers were precipitated and then washed with methanol and acetone. Finally, the product was dried at room temperature. The tacticity and the amount of comonomer incorporated in the copolymers were measured by <sup>13</sup>C NMR at 90 °C using a Varian Inova 300 spectrometer operating at 75 Hz [1,7–10,12]. The nomenclature employed in this work to identify the copolymers is of the type PEX#, iPPX#, sPPX# where X and # are letters and numbers that identify, respectively, the comonomer used (H = 1-hexene, OD = 1-octadecene), and the approximate molar amount in percentage of comonomer incorporated to the polymer (Table 2).

The Raman spectra of the polymers were obtained on a confocal LabRam Dilor S.A. microspectrometer. The amount of crystalline, amorphous and interfacial polymer contents was determined from the analysis of the internal mode region of the Raman spectra (800 - 1550 cm<sup>-1</sup>). The excitation source was a He/Ne laser (632.817 nm). The scattered light was collected by a microscope, followed by a notch filter. For deconvolution of the overlapping band systems, the curve analysis program Grams (supplied by Galactic Industries Corp.) was used. A combination of Gaussian and Lorentzian functions so as to give the best fit to the observed spectra was performed [2,28,34,35].

The thermal transitions were determined by differential scanning calorimetry (DSC), using a Perkin-Elmer Pyris 1 calorimeter under argon atmosphere and calibrated with indium and n-heptane standards. To ensure the same thermal history for all samples, the original and irradiated copolymers were first heated to 150 °C, maintained at 150 °C for two minutes, and then cooled down to 40 °C at 10 °C/min. After this treatment, the samples were reheated at 10 °C/min, and the corresponding endotherms were recorded between 40 and 150 at 10 °C/min. The melting peaks and the corresponding areas were determined to obtain the enthalpy (ΔH<sub>f</sub>) of fusion. To estimate the degree of crystallinity (X<sub>c</sub>) of the polymer, we used a ΔH<sub>f</sub> value of 288 J/g for the melting enthalpy for 100% crystalline PE [47], and of 148 J/g for the melting enthalpy of 100% crystalline iPP [48].

**Table 2**  
Monomer incorporation in the synthesized polymers.

Polymer	% comonomer
PE	–
PEH3	3.3
PEH9	9.2
PEH16	16.1
PEOD5	4.8
PEOD7	6.8
iPP	–
iPPH4	3.7
iPPH9	9.2
iPPOD3	3.0
sPP	–
sPPH3	3.1
sPPH16	16.1
sPPOD6	6.1

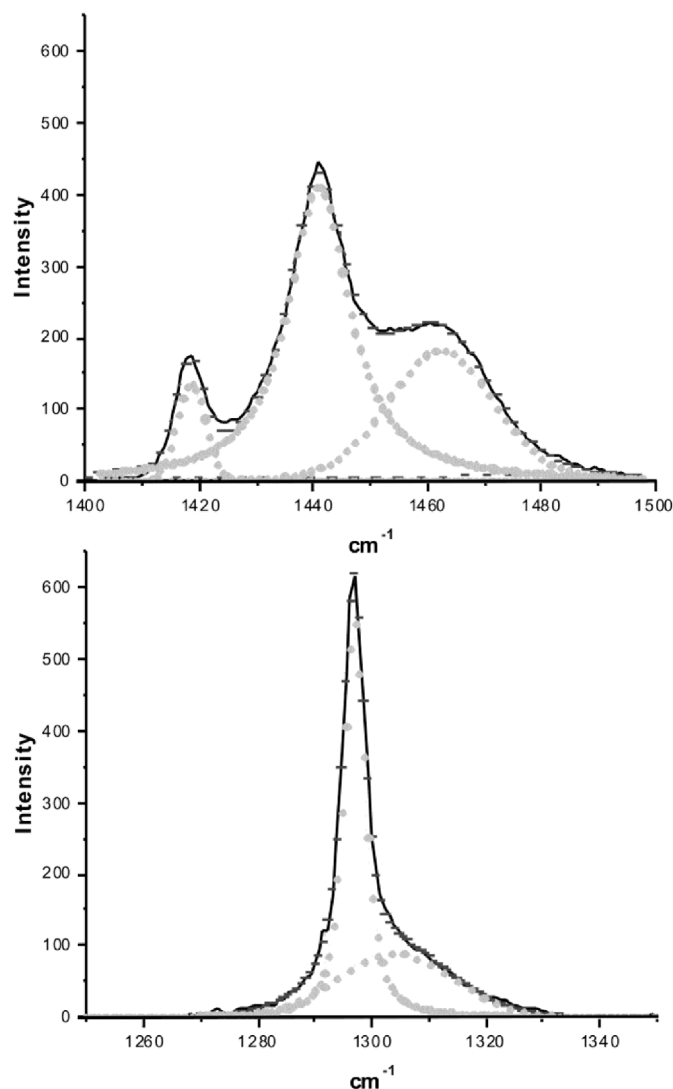


Fig. 1. Deconvolution of PEH3. Black solid line represents the original spectra, while the grey dashed line, the deconvolution adjustment. Dotted bands represent the respective deconvoluted bands at 1298 cm<sup>-1</sup>, 1304 cm<sup>-1</sup>, 1419 cm<sup>-1</sup>, 1440 cm<sup>-1</sup> and 1460 cm<sup>-1</sup>.

## 3. Results and discussion

### 3.1. Ethylene copolymers

To quantitatively evaluate the phase structures of the PE polymers, we analyzed their Raman CH<sub>2</sub> twisting and bending internal regions. The mass fractions of the three PE phases, namely, the orthorhombic crystalline phase, the liquid-like amorphous phase, and the disordered anisotropic interfacial phase are calculated from the measured integrated intensities of three bands. They are: a) CH<sub>2</sub> bending band at 1419 cm<sup>-1</sup> which is due to the crystalline portions alone, b) CH<sub>2</sub> twisting band located between 1303 and 1307 cm<sup>-1</sup> belonging to the amorphous phase and c) another component of the same mode at 1298 cm<sup>-1</sup> which can be attributed to both the crystalline phase and the interphase [27]. Fig. 1a shows the curve analysis performed on the polyethylene samples for the twisting at 1250 to 1350 cm<sup>-1</sup> region while Fig. 1b does the same for the 1400 to 1500 cm<sup>-1</sup> bending region. According to Strobl and Hagedorn [27], the total integrated intensity in the twisting region between 1250 cm<sup>-1</sup> and 1350 cm<sup>-1</sup>, I<sub>t</sub>, is independent of the chain conformation, i.e. the amorphous and crystalline content. It therefore provides an internal intensity standard. The amorphous content, α<sub>a</sub> (i.e. the mass fraction of the amorphous

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