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Regularity modes in Raman spectra of polyolefins: Part II. Polyethylene and ethylene copolymers☆

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ABSTRACT

In this work, the thermal behavior of the regularity modes in Raman spectra of polyethylene with different densities and random ethylene/1-hexene copolymers with varying content of comonomer are studied. We demonstrate especially that the vibrational modes at 1062 and 2850 cm^{-1} are related to a critical sequence length of *trans*-conformers of 6–8 CH_2 groups, while the modes at 1130, 1170, 1295, and 2883 cm^{-1} indicate a critical sequence length of *trans*-conformers of 18 CH_2 groups. Upon increasing the 1-hexene content in the ethylene/1-hexene copolymers, the evolution of the intensities of the Raman modes at 1062, 1130, 1170, 1295, and 1417 cm^{-1}, normalized to the intensity of the band at 2850 cm^{-1}, is similar to the evolution of the intensities of the same modes in the Raman spectra of low density polyethylene at increasing temperature. This observation however contrasts with that in the Raman spectra of polyethylenes with middle and high densities. We suppose that these results can be explained by similarities in the structure of non-crystalline areas of low density polyethylene and the ethylene/1-hexene copolymers, which contain significant amounts of short sequences of *trans*-conformers.

1. Introduction

Raman spectra of polymers are also characterized by the so-called regularity modes; their peak positions and intensities depend on the length and content of sequences of conformationally ordered segments of macromolecules. The observation of the well-known longitudinal acoustic regularity mode of polyethylene (PE), solid *n*-alkanes and copolymers, which is localized in the low-wavenumber spectral region (0–200 cm^{-1}), allows for the evaluation of the crystallite sizes in these materials [1,2].

In the present study, we focus on the regularity modes, which contribute to the Raman spectra of PE and random ethylene copolymers in the regions 1000–1600 and 2750–3200 cm^{-1}.

Practically all Raman-active bands of PE and *n*-alkanes have been reliably assigned to characteristic chemical bonds and can be used to interpret the Raman spectra of various molecules containing polymethylene chains (fatty acids, alkylammonium salts, ethylene copolymers, etc.). The regularity modes corresponding to the vibrations of *trans*-conformers (conformationally ordered segments of CH_2-chains) are observed in the Raman spectra of PE at 1062, 1130, 1170, 1295, 1417, 2850, and 2883 cm^{-1}. The bands at 1062 and 1130 cm^{-1} have been assigned to the asymmetric (ν_{as}(C—C)) and symmetric (ν_s(C—C)) stretching vibrations of the C—C bonds, respectively [3–7]. The bands at 1170, 1295, and 1417 cm^{-1} are the rocking (r(CH_2)), twisting (τ(CH_2)), and wagging (ω(CH_2)) vibrations of the CH_2 groups, respectively [3–7]. The bands at 2850 and 2883 cm^{-1} belong to the symmetric (ν_s(CH_2)) and asymmetric (ν_{as}(CH_2)) stretching vibrations of the CH_2 groups, respectively [3–8]. To simplify further discussion we consider PE and random ethylene copolymers as systems, which consist of crystallites (orthorhombic crystalline phase) and non-crystalline areas (interphase and liquid-like amorphous phase). Macromolecules in the crystallites are in the

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all *trans*-conformation, but the non-crystalline areas contain both macromolecules in the all *trans*-conformation (interphase) and macromolecules with significant amount of *gauche*-conformers. In terms of such approach, all the above-mentioned regularity modes, except the mode at 1417 cm^{-1}, belong to the vibrations of macromolecules, localized in both the crystallites and non-crystalline areas. The mode at 1417 cm^{-1} is attributed to the vibrations of the crystallites and is usually used to calculate the degree of crystallinity (CR) of PE and related substances [4,8,9] by using Eq. (1).

$$CR = \frac{I_{1417}}{(I_{1295} + I_{1305}) \times k}, \qquad (1)$$

where I_{1417}, I_{1295}, and I_{1305} are the integral intensities of the lines at 1417, 1295, and 1305 cm^{-1}, respectively, and $k = 0.43–0.47$ is a normalization coefficient, which is determined by the experimental conditions of recording the Raman spectra. This value is usually calculated based on measurements of Raman spectra of solid *n*-alkanes.

To date, PE and *n*-alkanes as well as many substances with polymethylene chains have been extensively investigated by Raman spectroscopy [1–17], including theoretical and temperature- and pressure-dependent studies [10,11]. However, some questions concerning the behavior of their regularity modes still remain open, for which more detailed studies are needed. In particular, the value of the minimal length of the *trans*-conformer sequence, at which a certain specific band appears in the Raman spectra, still lacks consensus for some of the observed modes. Tashiro et al. studied the regularity modes in the Raman spectra of random copolymers of ethylene and deuterated ethylene, *n*-alkanes, and neat PE as a function of temperature growth [12]. It was found that the critical sequence length of *trans*-conformers, which was related to the appearance of the Raman modes at 2883 and 1062 cm^{-1}, is 4–6 and 6–8 CH$_2$ groups, respectively. The length of such *trans*-sequence corresponding to the appearance of the mode at 1295 cm^{-1} was reported to be 6 CH$_2$ groups, and for the modes at 1130 and 1170 cm^{-1}, the typical length was found to be 18 CH$_2$ groups [12]. The assignment of the modes at 1062 and 1130 cm^{-1} to the vibrations of *trans*-conformer sequences with the lengths equal to at least 4–6 and 18 CH$_2$ groups, respectively, well correlates with the experimental and theoretical studies of the wavenumber dispersion laws for the ν_{as}(C—C) and ν_s(C—C) modes for *n*-alkanes and fatty acids [13,14,18]:

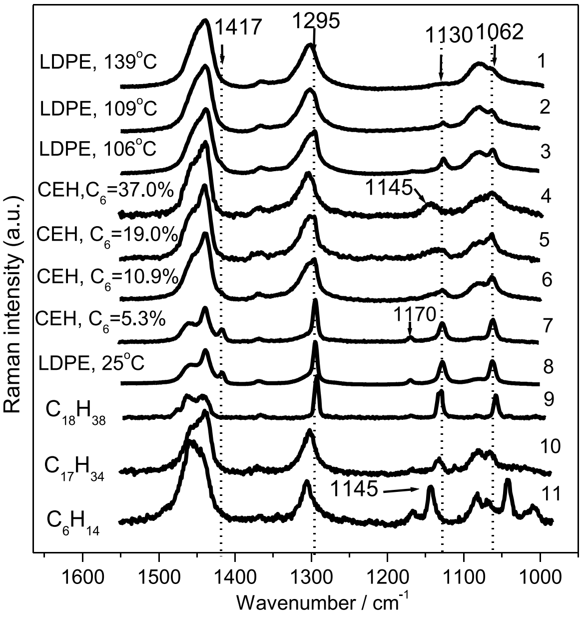

Fig. 1. Raman spectra of low density polyethylene (LDPE) at different temperatures, ethylene/1-hexene copolymer (CEH), and of *n*-alkanes in the region 1000–1600 cm^{-1}. The different traces are labeled (1–3) for LDPE spectra at high temperatures, (4–7) for CEHs spectra at different 1-hexene content, (8) for the LDPE spectrum at ambient temperature, and (9–11) for *n*-alkanes spectra with $n = 18$, 17, and 6, respectively.

It was shown that the relation given in Eq. (2) holds for the ν_{as}(C—C)–mode

$$\nu_{as}(n) = \sqrt{\nu_0^2 - \beta^2 \sin^2 \frac{\pi}{n}} \qquad (2)$$

and that in Eq. (3) for the ν_s(C—C)–mode:

$$\nu_s(n) = \sqrt{\nu_\infty^2 + \beta^2 \sin^2 \frac{\pi}{n}} \qquad (3)$$

Here n is the number of C atoms in a *trans*-chain, ν_{as} (expressed in cm^{-1}) is the wavenumber of the asymmetric C—C stretching mode, $\nu_0 = 1068.5$ cm^{-1} is the corresponding wavenumber for a hypothetical infinite *trans*-chain, ν_s and $\nu_\infty = 1130.5$ cm^{-1} are the wavenumbers of the symmetric C—C stretching mode for a finite *trans*-chain and a hypothetical infinite *trans*-chain, respectively. The *trans*-chain length L is defined as $L = aN \approx an/2$, where $a = 2.58$ Å is the size of the unit cell for *n*-alkanes (or fatty acids), and N is the amount of the unit cells along the chain. The parameter $\beta = s/a\pi c$ is a characteristic of a material, where $s = 18.6 \times 10^3$ m/s is the velocity of an elastic wave travelling along the *trans*-chain and c is the velocity of light [13,14].

Ab initio calculations of wavenumbers and intensities for the *n*-alkane C$_{16}$H$_{34}$ associate 1062 and 1130 cm^{-1} to an all *trans* sequence longer than 10 bonds [15].

The assignment of the mode at 1295 cm^{-1} to the vibrations of *trans*-conformer sequences with the length of 6 CH$_2$ groups [12] is however still ambiguous, because the τ(CH$_2$) band with such a wavenumber value appears in the Raman spectra of *n*-alkanes only if $n \geq 18$ [16]. It is possible that the previous assignment in the corresponding spectral region was overlooked due to the confusion of the mode at 1295 cm^{-1} with the nearly overlapping broad band at about 1305 cm^{-1}. The band at approx. 1305 cm^{-1} is assigned to the τ(CH$_2$) vibrations for conformationally disordered CH$_2$-chains in the solids and melt, so the vibrations of both short *trans* segments and *gauche* conformers contribute to this band [4,8,19]. However, if a *trans* sequence is going to be sufficiently long, it will start contributing to the 1295 cm^{-1} band [4,8].

In this contribution, we perform a detailed comparative study of the Raman-active regularity modes in the spectra of PE with different densities when temperature rises, of random ethylene/1-hexene copolymers with varying content of the comonomer, and of *n*-alkanes (with $n = 5–18$).

2. Materials and method

The PE films of low (LDPE, density $\rho = 0.906$ g/cm^3, melting temperature $T_m = 107$ °C), middle (MDPE, $\rho = 0.935$ g/cm^3, $T_m = 128$ °C), and high (HDPE, $\rho = 0.950$ g/cm^3, $T_m = 132$ °C) densities were heated up from 25 to 140 °C in steps of 3 °C. Raman spectra were recorded with a spectral resolution of ~2 cm^{-1} in a micro-Raman backscattering geometry using a 50× (N.A. 0.5) long working distance microscope objective for light focusing and collection and the 488 nm emission line of an Ar$^+$ laser source (Innova 308 series, Coherent, USA) for excitation. The scattered light was analyzed in a Triax monochromator (TRIAX 550, Jobin Yvon, France) using a 1200 grooves per mm diffraction grating and a slit width of 100 μm. A liquid N$_2$ cooled CCD detector (CCD 3500, Jobin Yvon, France) was used for signal detection. The laser power at the