Regularity modes in Raman spectra of polyolefins: Part I. Propylene/olefin copolymers☆

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ABSTRACT

Behavior of the regularity modes of isotactic polypropylene is analyzed in Raman spectra of a number of random propylene/olefin copolymers. The regularity modes at 809, 841, 973, 998, and $1220\,cm^{-1}$ decrease in intensity with growth of the content of the incorporated monomer. For the lines at 809, 973, and $1220\,cm^{-1}$ the rate of intensity damping varies depending on the structure of the incorporated monomer. The type of the incorporated monomer has inconsiderable effect on the evolution of intensity of the regularity bands at 841 and $998\,cm^{-1}$. Anomalous behavior of the mode at $1220\,cm^{-1}$ was observed for the propylene/1-butene copolymers.

1. Introduction

Isotactic polypropylene (iPP) is widely-used polymer with good physical-chemical properties and relatively low cost. The structure and properties of iPP have been extensively investigated by different methods. Mechanical, thermophysical, optical and other properties of iPP can be further improved or modified by the insertion of random chain branching in the polymer chain through copolymerization of propylene with linear, branched or cyclic olefins. Technological advance in this field was achieved first of all owing to development of very effective metallocene catalysts, which ensure synthesis of random olefin copolymers with content of the incorporated monomer in a wide range. Such copolymers are also of significant interest for academic research, since their vibrational spectra, molecular and supramolecular structure and properties differ from that of the homopolymers.

Using differential scanning calorimetry (DSC), X-ray analysis and mechanical testing it was revealed that decrease in the propylene content leads to significant and monotonous changes in the structure of the random propylene copolymers, namely, to decrease in the degree of crystallinity, the melting/crystallization temperature, and the Young modulus, and increase in the elongation at break [1–7].

Raman spectroscopy is a powerful and nondestructive method to analyze polymer structure, in particular, in terms of chemical and phase compositions, contents of different configurational and conformational states, and orientational order of macromolecules. Important information about the content and length distribution of sequences of conformationally ordered segments of macromolecules can be obtained from the analysis of the so-called regularity modes.

Assignment of the Raman lines of the most practically important α-modification of iPP can be found in [8–15]. The behavior of the regularity modes in Raman and IR spectra of neat iPP as a function of temperature was investigated in [10,16–23]. IR spectroscopy was used to study the iPP regularity bands in spectra of random propylene copolymers with ethylene [24], 1-butene [25], 1-pentene [26], and 1-hexene [7,27].

It was shown that the type of the incorporated monomer has a non-trivial influence on the copolymer molecular and supramolecular structure. For example, 1-butene co-units can be included in the monoclinic crystalline lattice of iPP with the expansion of the unit cell and also can cause appearance of the orthorhombic crystalline phase of neat iPP [4,25]. In turn, the propylene copolymers with 1-pentene and 1-hexene are able to crystallize with formation of the trigonal form, and this new form was clearly detected already at 8% of the incorporated comonomer [26,27].

The relationship between appearance of the specific regularity bands in the iPP IR spectrum and the length n of sequences of

monomer units in helical conformation has been well established [24,28]. The minimum n values for appearance of the bands at 973, 998, 841, and 1220 cm^{-1} are 2–4, 5–10, 12–14, and about 14 monomer units, respectively. Appearance of the IR line at 809 cm^{-1} was attributed to presence of the conformationally ordered sequences of isotactic segments in the helical conformation with minimal length n of about 7 [25–27] and of about 15 monomer units [16,17]. It is important to note that practically all the published investigations of the iPP regularity modes were carried out using IR spectroscopy, while Raman spectroscopy was used in a few papers.

Studying the random propylene copolymers with ethylene, 1-butene, 1-pentene, 1-hexene, 1-octene, and 4-methyl-1-pentene, we revealed that the Raman method of evaluation of phase composition of iPP [15] can be applied for characterization of random propylene copolymers [29–32]. We showed that the total content of isotactic chains in the helical conformation decreases with reduction of the propylene content and with growth of the length of the side chain of the incorporated monomer. Furthermore, the content of isotactic chains in the helical conformation in the crystalline phase falls faster than that in the amorphous phase [29–32].

In this work, we focus on behavior of the iPP regularity modes in Raman spectra of random propylene/olefin copolymers as a function of the content and chemical structure of the incorporated monomer.

2. Experimental

We studied the nascent form of random copolymers of propylene (C_3H_6) with ethylene (C_2H_4), 1-butene (C_4H_8), 1-pentene (C_5H_{10}), 1-hexene (C_6H_{12}), 1-octene (C_8H_{16}), and 4-methyl-1-pentene (C_6H_{12}), synthesized in the medium of liquid propylene over homogeneous metallocene catalyst rac-Me$_2$Si(4-Ph-2-MeInd)$_2$ZrCl$_2$, activated by methylaluminoxane. Method of synthesis as well as DSC, X-ray analysis, and mechanical testing data for these materials were described in detail in [2–7]. The molar content of the comonomers in the synthesized copolymers was measured by ^{13}C NMR spectroscopy.

The Raman setup consisted of an Ar$^+$-Kr$^+$ laser (Stabilite 2018, Spectra-Physics, USA), a double monochromator (U1000, Jobin Yvon, France) and Peltier-element cooled photomultiplier detector operating in photon counting regime. The wavelength of excitation light was 472.7 nm. Spectra were recorded at 90°-scattering with spectral resolution of 5 cm^{-1}. The measurement error of the intensity ratios of the Raman lines was from 5 to 15% in dependence of the band intensity. The diameter of the laser spot on a sample was about 2 mm. This allows us to measure the average characteristics of the copolymer samples instead of local characteristics of a small particle of the copolymer nascent form (powder). We purposely did not use any treatment (moulding, pressing) of our samples, because it is well known that such treatment causes change of the copolymer sample structure.

We carried out analysis of our Raman spectra using homemade software. Spectral characteristics of the Raman lines were evaluated based on fitting of the experimental spectra. Shape of each line was described by the weighted sum of Lorentz and Gauss functions:

$$y = A_0 \left[\mu \frac{2}{\pi} \frac{\gamma}{4(\nu - \nu_0)^2 + \gamma^2} + (1 - \mu) \frac{2\sqrt{\ln 2}}{\sqrt{\pi}\gamma} \exp\left(-\frac{4\ln 2}{\gamma^2}(\nu - \nu_0)^2\right) \right],$$

where μ—the weighting factor of the Lorentz/Gauss contributions to the line profile ($0 \leq \mu \leq 1$); A_0, ν_0 and γ—the integral intensity,
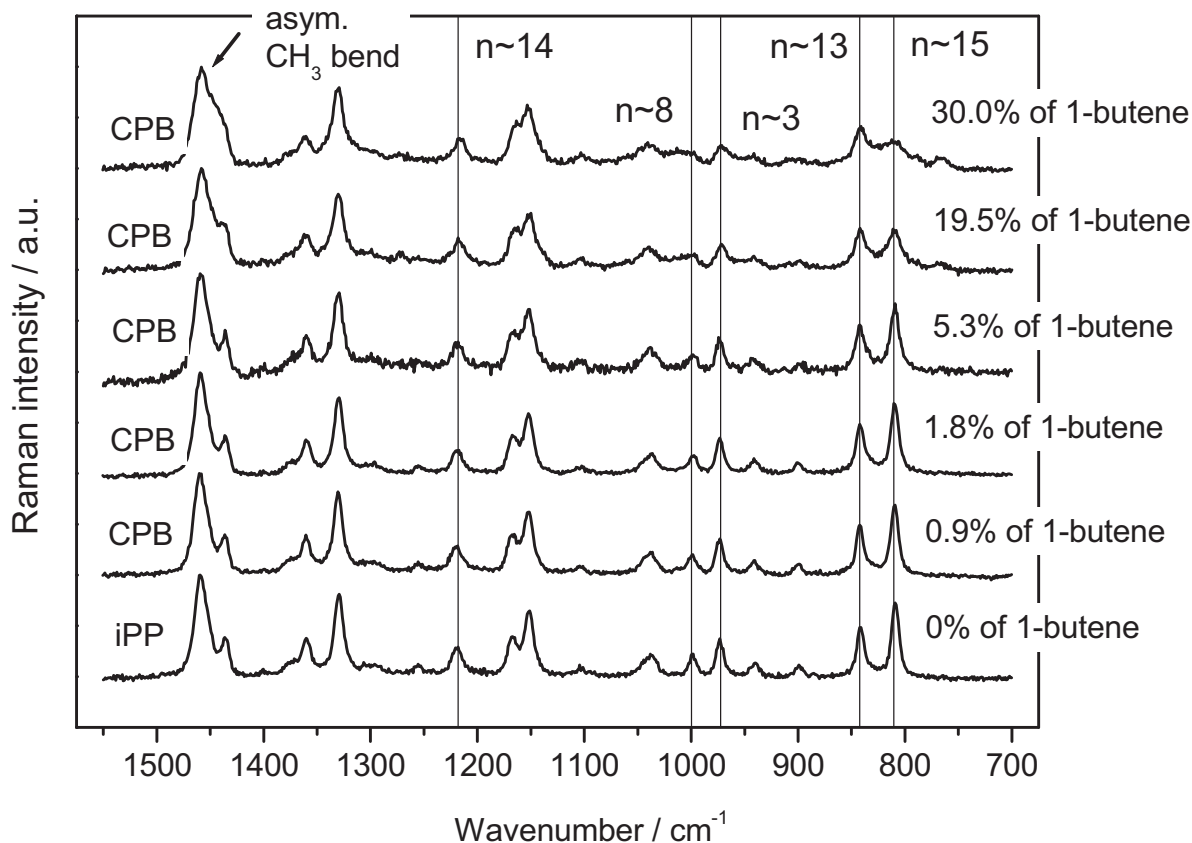

Fig. 1. Raman spectra of the propylene/1-butene copolymers (CPBs) in the region 700–1550 cm^{-1}.