New insights into the structure of polypropylene polymorphs and propylene copolymers probed by low-frequency Raman spectroscopy

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Abstract. We present a low-frequency (or low-wavenumber) Raman spectroscopy study of isotactic polypropylene, namely the different modifications - α, γ, and smectic, with a degree of crystallinity ranging from 0 to 70 %, as well as of random propylene/1-butene and propylene/1-octene copolymers with the incorporated monomer contents of 5.3 and 19.5 mol % for 1-butene and 4.5 and 24.0 mol % for 1-octene. In the Raman spectra of the propylene/1-octene copolymers and the neat isotactic polypropylene, we have found that the band at 105 cm⁻¹, which is connected to the torsion vibrations of CH₂-CHCH₃ groups in the polymer backbone, can be assigned to the vibrations of helical macromolecules in the α and γ crystallites and the smectic phase. If the smectic phase is absent in the corresponding polymer system, then the intensity of the 105 cm⁻¹ band is related to the molecular vibrations in the crystallites. We have also observed a broadening of the band at 398 cm⁻¹ accompanied by the appearance of a high-wavenumber shoulder in the Raman spectra of the copolymers with the increase in the incorporated monomer content. This experimental finding can be explained by the reduction of the degree of crystallinity, conformational disordering or by the increase in the dimensions of the crystal unit cell.

1. Introduction
Polypropylene (PP) exhibits a complex molecular and supramolecular structure, which has a major impact on its physical properties. There are three stereoisomeric forms of PP: the isotactic, syndiotactic and atactic configurations, and the macromolecules in each of these configurations can adopt different conformations. Besides PP, random copolymers of propylene with α-olefins (ethylene, 1-butene, 1-octene, etc.), which can be considered to be materials with PP-like structure, are widely used in industry [1-4].

The molecular chains of most commercially-important isotactic PP in the helical conformation can crystallize in the α, β, and γ modifications, which have the monoclinic, hexagonal, and orthorhombic lattices, respectively [1, 2, 5]. The different crystalline modifications can coexist in an isotactic PP sample, for which the total degree of crystallinity does not exceed 75%. Usually, non-crystalline regions of isotactic PP contain macromolecules in both the helical and non-helical conformations [6]. However, there is also the smectic or pseudocrystalline modification, in which the macromolecules of
isotactic PP do not form crystals but exhibit the helical conformation as well [5, 7]. Often, the smectic modification is considered to be an intermediate form between the amorphous and the crystalline states of isotactic PP.

Raman spectroscopy can potentially provide quantitative information about the configurational, conformational, and phase states of macromolecules, the content and length distribution of conformationally-ordered macromolecular segments, and about the sizes of the macromolecular crystallites. The spectral range 600–1600 cm\(^{-1}\) in the Raman and IR spectra of isotactic PP is the most important for a quantitative analysis of the phase and conformational compositions. This spectral region was investigated in numerous works, and the obtained results are summarized in our recent papers [8, 9]. However, a number of spectral lines in this region are still not precisely assigned. For example, for the line at 809 cm\(^{-1}\), whose intensity is often used to calculate the degree of crystallinity, contradictory assignments in the Raman and IR spectra can be found [8, 9]. While the range 2700–3100 cm\(^{-1}\) is less suited for quantitative structural analysis of propylene-containing materials because of strong overlap of numerous bands with large bandwidths, the range 0–600 cm\(^{-1}\) contains a number of well-separated and structure-sensitive Raman-active lines. Nevertheless, the 0–600 cm\(^{-1}\) region has been less investigated for the phase and conformational composition analysis, probably due to the relatively more demanding Raman measurements in this very low-frequency region.

The low-frequency Raman spectra of isotactic PP at room and cryogenic temperatures were studied by G.V. Fraser et al. [2] for the \(\alpha\)-modification, by P.D. Vasko and J.L. Koenig [7] for the \(\alpha\) and smectic modifications, and by J.M. Chalmers et al. [5] for the \(\alpha\), \(\beta\), \(\gamma\), and smectic modifications. It should be noted that the sample referred to as \(\gamma\) PP in the study by Chalmers et al. [5] was in reality a mixture of the \(\alpha\) and \(\gamma\) modifications with equal contents of \(\alpha\) and \(\gamma\) phases and with a total degree of crystallinity of 52%. According to the works in references [2, 5, 7], the bands at approximately 106, 171, 250, 320, 398, 460, and 530 cm\(^{-1}\) are found in the Raman spectra of all the crystalline modifications of isotactic PP (\(\alpha\), \(\beta\), and \(\gamma\)). Also, the band at approximately 50 cm\(^{-1}\) and the longitudinal acoustic mode, whose peak position is inversely proportional to the length of isotactic segments in the helical conformation [10, 11], are observed in the Raman spectra of all the crystalline forms.

In the publication by Chalmers et al. [5] however, the reported Raman spectrum of highly-crystalline \(\alpha\) PP contains the band doublet at approximately 460 cm\(^{-1}\) with the peak positions at 453 and 460 cm\(^{-1}\). Unfortunately, for the \(\beta\), \(\gamma\), and smectic forms, these authors presented only tabulated data of peak positions, without any information about the intensities and widths of the Raman bands and without reporting the Raman spectra themselves. The peak positions reported for room-temperature Raman measurements in this work showed a noticeable difference for the smectic modification as compared to the other modifications. On the contrary, P.D. Vasko and J.L. Koenig [7] reported that these peak positions in the Raman spectra of the \(\alpha\) and smectic modifications are identical. The only difference was an additional weak band at 417 cm\(^{-1}\) observed in the Raman spectra of the smectic modification at -160°C. Chalmers et al. [5] also observed a band at 413 cm\(^{-1}\) in the Raman spectra of the \(\gamma\) modification of PP at cryogenic temperature, but they did not observe this band in the case of the smectic PP.

The studies of the low-frequency Raman spectra of molten isotactic PP were reported by P.D. Vasko and J.L. Koenig [7] and by R.M. Khafagy [12] as well as by V.M. Hallmark et al. [13] and T. Hahn et al. [14], who carried out numerical calculations for simulating the isotropic Raman spectra of isotactic PP. On the one hand, the band at 398 cm\(^{-1}\) is observed in solid, smectic and melt states of isotropic PP [7]. This band is assigned either to the umbrella vibration about the tertiary carbon atom [13] in helix segments with length of at least \(n = 6\) or 9 monomer units (two or three complete turns in the helix) [14] or to the superposition of the wagging vibration of CH\(_3\)-groups (\(\delta(CH)\)) and the bending vibration of CH-groups (\(\delta(CH)\)) [12]. On the other hand, the calculated spectrum contains a broad shoulder band on the high-wavenumber side of the 398 cm\(^{-1}\) band [13, 14]. This shoulder was assigned to the vibrations of conformational defects in the macromolecules [13].
However, only a little shift (~ 2 cm⁻¹) of this band without any appearance of a high-wavenumber broad shoulder was found in the Raman spectra recorded when solid isotactic PP was heated up to and above the melting temperature in the experimental work by R.M. Khafagy [12]. Moreover, this author suggested that the 398 cm⁻¹ band depends only on the molecular configuration. Also, the high-wavenumber shift of the band at 398 cm⁻¹ was observed in the Raman spectra of isotactic PP-halloysite nanocomposites upon increase in the halloysite content, and this was explained by a drop in the degree of crystallinity of the polymer upon loading it with the filler [15].

Modern developments in PP synthesis allow to produce PP-based functional materials with different structural characteristics and with properties varying in a wide range. In particular, samples with 100 % content of the γ modification in the crystalline phase can be synthesized [8].

In the present work, we have studied the low-frequency Raman spectra of the α, γ, and smectic PP polymorphs, fully amorphous PP, and random copolymers, which include propylene/1-butene and propylene/1-octene copolymers with various comonomer content.

2. Experimental

| Table 1. Degree of crystallinity of the investigated copolymers and PP samples |
|---------------------------------|-----------------|-----------------|
| Polymer system                  | Content of 1-octene or 1-butene (mol %) | Degree of crystallinity (CR) based on X-ray analysis (%) |
|---------------------------------|--------------------------------------|---------------------------------------------------|
| propylene/1-octene copolymers   | 24.0                                  | 0                                                  |
| (CPOs)                          | 4.5                                   | (42% of α phase + 12% of γ phase)                  |
| propylene/1-butene copolymers   | 19.5                                  | 55 (α phase)                                      |
| (CPBs)                          | 5.3                                   | 55                                                |
| isotactic α PP (α-iPP-f)        | 0                                     | 55 (α phase)                                      |
| smectic isotactic PP (smectic iPP) | 0                             | smectic                                           |
| Nascent forms of PP             |                                       |                                                   |
| isotactic α PP (α-iPP)          | 0                                     | 68 (α phase)                                      |
| isometric γ PP (γ-iPP)          | 0                                     | 10 (γ phase)                                      |
| amorphous PP (amorphous PP)     | 0                                     | 20 (γ phase)                                      |
| isotactic polybutene (iPB)      | 0                                     | 35 (γ phase)                                      |
|                                 | 0                                     | 70 (γ phase)                                      |

As recapitulated in Table 1, the studied random copolymers of propylene (C₃H₆) with 1-octene (C₈H₁₈), denoted as CPO, contain 24.0 and 4.5 mol % of 1-octene, while the random copolymers of propylene with 1-butene (C₄H₈), denoted as CPB, contain 19.5 and 5.3 mol % of 1-butene. The CPO and CPB samples as well as the samples of the α and smectic modifications of isotactic PP (α-iPP-f and smectic iPP, respectively) were fabricated as films with a thickness of 1.5 mm. We also have investigated the nascent forms of the α and γ modifications of isotactic PP and isotactic polybutene as well as the fully-amorphous PP, referred to as α-iPP, γ-iPP, iPB, and amorphous PP, respectively.

The CPO and CPB copolymers and the α modification of isotactic PP were synthesized in the medium of liquid propylene over the homogeneous metallocene catalyst of C₂-symmetry, rac-Me₂Si(4-Ph-2-MeInd)₂ZrCl₂/MAO. The synthesis method and X-ray analysis data were published earlier in references [3,4]. The amorphous PP sample and the γ-iPP samples with a degree of
crystallinity of 10, 20, and 35% were synthesized in the medium of liquid propylene over the homogeneous metallocene catalyst of C\textsubscript{1}-symmetry C\textsubscript{2}\textsubscript{H}\textsubscript{4}(Flu)(5,6cyclopenta-2-MeInd)ZrCl\textsubscript{2}/MAO. The corresponding synthesis methods and X-ray analysis data were described in earlier studies [16, 17].

Similar information about the γ-iPP sample with the degree of crystallinity of 70% can be found in a different study reported earlier [18]. Smectic iPP was prepared by melting of the isotactic PP at 200\degreeC followed by subsequent pressing and quenching in icy water. Table 1 summarizes the description of the samples under study and the values of the degree of crystallinity, which were determined by X-ray analysis [3, 4, 16-18].

To record Raman spectra from the polymer films, we used the 514.5 nm line of an Ar\textsuperscript{+} laser source (Innova 308 series, Coherent, U.S.) for excitation. The scattered light was analyzed by a triple monochromator (T6400, Jobin Yvon, France) using a 1800-grooves-per-mm diffraction grating and a slit width of 100 \(\mu\)m in order to achieve a spectral resolution of approximately 2 \(\text{cm}^{-1}\). A liquid-N\textsubscript{2} cooled CCD detector (CCD 3500, Jobin Yvon, France) was used for signal detection. The scattered light was collected in a micro-Raman backscattering geometry using a 50\times (N.A. 0.5) long working distance microscope objective.

The Raman spectra of the nascent PP samples were recorded by using another Raman setup consisting of a Sapphire SF 532 laser (Coherent Inc., USA) emitting at a wavelength of 532 nm for excitation, a double monochromator (U1000, Jobin Yvon, France) and a Peltier-cooled photomultiplier detector operating in photon counting regime. For this setup, the Raman spectra were recorded at 90\degree scattering with a spectral resolution of approximately about 5 \(\text{cm}^{-1}\). The Raman spectrum of toluene in the region 0-600 \(\text{cm}^{-1}\) was used for wavenumber calibration of the Raman spectrometers.

3. Results and Discussion

![Figure 1](image-url).

\textbf{Figure 1.} Raman spectra of the films of CPOs with 24.0 and 4.5 mol% of 1-octene, CPBs with 19.5 and 5.3 mol% of 1-butene, \(\alpha\) isotactic PP (\(\alpha\)-iPP-f), and smectic iPP in the region 0-900 \(\text{cm}^{-1}\).
Figure 2. Raman spectra of PP nascent forms including the α- and γ-iPP samples with different degree of crystallinity CR and the amorphous PP in the region 50-900 cm⁻¹.

Figure 1 shows the Raman spectra of the polymer films including the copolymers CPOs and CPBs, the α-modification of isotactic PP, and the smectic iPP in the region 0-900 cm⁻¹. Figure 2 presents the Raman spectra of the studied α and γ modifications of PP nascent forms with different degree of crystallinity (CR), as well as that of the amorphous PP in the region 50-900 cm⁻¹. Figures 3 and 4 illustrate the evolution of the bands at 105 and 398 cm⁻¹ observed in the spectra of the polymer films and the PP nascent forms when changes in their supramolecular structure occur. Figure 5 compares the Raman spectra of CPBs and iPB in the regions 30-150 cm⁻¹ and 325-450 cm⁻¹. Except for the spectrum of iPB, intensities in all the Raman spectra in figures 1-5 are normalized to the peak intensity of the band at 398 cm⁻¹. Intensity in the iPB spectrum is normalized to the peak intensity of the band at 374 cm⁻¹ and is scaled by factor of 3 for a clearer presentation.

The strongest changes in the spectral region 0-600 cm⁻¹ due to variations in the supramolecular structure of the copolymers and PPs are observed for the 105 and 398 cm⁻¹ bands (Figures 3 and 4). In contrast to this, we have not observed any shifts of the peak positions of the bands at 175, 250, 319, 455, and 530 cm⁻¹ in the Raman spectra of all the copolymers and PPs, although these bands show a weak dependence of their peak intensities on the type (α, γ, or smectic) of modification (Figure 4). For instance, as can be seen in Figures 3 and 4, the ratio of the peak intensities of the bands at 530 and 455 cm⁻¹ for smectic iPP is slightly lower compared with that for the α-modification of isotactic PP with CR = 55% (the sample α-iPP-f). Also, this ratio decreases more clearly with the reduction of CR of the neat γ-modification samples. Thus, we consider that there are no significant fingerprints in the spectra in the region 0-600 cm⁻¹, which allow for discrimination of the types (the α, γ or smectic) of the isotactic PP modification.
Figure 3. Raman spectra of the films of CPOs with 24.0 and 4.5 mol % of 1-octene, CPBs with 19.5 and 5.3 mol % of 1-butene, isotactic α-PP (α-iPP-f, film), and smectic iPP in the region 0-550 cm⁻¹.

Figure 4. Raman spectra of the PP nascent forms including the α- and γ-iPP samples with different degree of crystallinity CR and the amorphous PP in the region 50-550 cm⁻¹.

For all the samples, except CPBs, the intensity of the band at 105 cm⁻¹ diminishes and the band at 398 cm⁻¹ is broadening together with the appearance of a high-wavenumber shoulder, when the degree of crystallinity of the sample decreases. Such an evolution of these bands well correlates with the changes of the spectral features in the region 800-850 cm⁻¹ (Figures 1 and 2).

If the smectic phase is absent, then the Raman bands at 809 and 841 cm⁻¹ should be assigned to the vibrations of helical macromolecules, localized in the crystalline and amorphous phases, respectively [6, 8, 9]. These bands are overlapping with the band at approximately 830 cm⁻¹, which is assigned to the vibrations of macromolecules in non-helical conformation [6, 8, 9].

According to the X-ray analysis data, the smectic phase is absent in the samples of the CPOs, α- and γ - iPPs. This means that the decrease in the intensity of the Raman band at 809 cm⁻¹ and the increase and broadening of the band at 841 cm⁻¹ are explained by the reduction of degree of crystallinity CR and the growth of conformational disorder in the amorphous phase [9]. Thus, the band at 105 cm⁻¹ (the torsion vibrations of the CH₂-CHCH₃ groups in the chain backbone) can be assigned to helical macromolecules in the α and γ crystallites and the smectic phase in the Raman spectra of the CPOs and isotactic PP.

Taking into account the evolution of the Raman bands at 809 and 841 cm⁻¹, we assume that the broadening of the band at 398 cm⁻¹ with the appearance of a high-wavenumber shoulder is due to the increase in the content of macromolecules in non-helical conformations. This assumption is in a good agreement with the result of theoretical treatment, which was presented by V.M. Hallmark et al. [13].
The behavior of the bands at 105 and 398 cm$^{-1}$ in the Raman spectra of CPBs differs from the evolution of the same bands in the Raman spectra of CPOs and different PP modifications. The band observed at 398 cm$^{-1}$ in the spectrum of CPB with 5.3 mol % of 1-butene exhibits a shift toward lower wavenumbers in the spectrum of CPB with 19.5 mol % of 1-butene, being observed in this case at 394 cm$^{-1}$. Simultaneously, additional lines at approximately 97 and 406 cm$^{-1}$ appear in the spectrum of CPB with 19.5 mol % of 1-butene (Figures 3 and 5). However, the degree of crystallinity of CPBs with 5.3 and 19.5 mol % contents of 1-butene is the same (CR=55 %). The Raman spectrum of iPB in the region 25-425 cm$^{-1}$ contains two bands at 61-75 cm$^{-1}$ and 375 cm$^{-1}$ (Figure 5). The broad band at 61-75 cm$^{-1}$, which appears as a shoulder band on the tail of Rayleigh scattering, partially overlaps with the PP Raman band at 105 cm$^{-1}$. It would be possible that the additional scattering at 97 cm$^{-1}$ in the CPB spectrum is due to the sufficiently long iPB segments, which are formed in CPBs at a high content of 1-butene [3]. However, the iPB Raman band at 375 cm$^{-1}$ extends up to 400 cm$^{-1}$, therefore, the Raman band at 406 cm$^{-1}$ in the CPB spectrum cannot be due to vibrations of the 1-butene segments. Note that similar effects are not observed in the spectra of CPOs and the samples of the γ-modification of PP.

Earlier X-ray studies showed that macromolecules in the studied samples of CPB form a crystalline lattice similar to that of the α-modification of isotactic PP, but with enlarged unit-cell dimensions and an area of the cross-section of helical macromolecules in comparison with neat α-PP [3]. In other words, the growth of 1-butene content results in the expansion of the unit cell. Therefore, the expansion of the unit cell due to the incorporation of 1-butene in the PP chains allows to explain the appearance of both additional lines at approximately 97 and 406 cm$^{-1}$. The unit cell of the α-modification of isotactic PP consists of four macromolecules. The point group symmetry of an infinitely-long helical macromolecule of isotactic PP is C$_3$, and the vibrational spectrum consists of the A- and the doubly-degenerated E-symmetry vibrations [2]. The splitting of the band at 105 cm$^{-1}$ (A+E mixed symmetry) into two lines was observed at cryogenic temperatures [2, 5]. Theoretical considerations [20] of the vibrational spectrum of isotactic PP suggest two bands at approximately 400 cm$^{-1}$, namely, at 398 cm$^{-1}$ (A-symmetry, $\omega$ (CH$_2$) + $\delta$ (CH)) and at 408 cm$^{-1}$ (E-symmetry, $\omega$ (CH$_2$) + $\delta$ (CH)) + rocking (CH$_2$). The changes in the unit cell parameters or in the cross-section of
the PP helical chain affect the inter- and intramolecular interaction, and as a consequence, the frequencies of the molecular vibrations are also changed.

Probably, this explains the splitting of the band at 398 cm\(^{-1}\) or an increase in the scattering cross-section of the band at 408 cm\(^{-1}\). Thus, in principle, the reasons of the change of the band shape at 398 cm\(^{-1}\) can be different for neat isotactic PP, CPOs and CPBs.

4. Conclusions
We have studied low-frequency Raman spectra of different polypropylene (PP) polymorphs (\(\alpha\), \(\gamma\), and smectic modifications), as well as those of a fully amorphous PP and of the random propylene/1-butene and propylene/1-octene copolymers with various comonomer content.

We have found that the band at 105 cm\(^{-1}\) (the torsion vibrations of the CH\(_2\)-CHCH\(_3\) groups in the chain backbone) can be assigned to the helical macromolecules in the \(\alpha\) and \(\gamma\) crystallites and the smectic phase in the Raman spectra of the propylene/1-octene copolymers and neat isotactic PP. If the smectic phase is absent, the intensity of the band at 105 cm\(^{-1}\) can be assigned to the vibrations of macromolecules in the crystallites.

The band at 398 cm\(^{-1}\) shows a broadening toward the high-wavenumber side when the degree of crystallinity of PP decreases or when the content of the incorporated monomer (1-butene or 1-octene) increases. We suggest two possible explanations of this effect: namely, the growth of the degree of conformational disorder (for the neat PP and the copolymers of propylene with 1-octene) and the increase in the dimensions of the unit cell or in the cross-section of helixes, which can appear due to the incorporation of 1-butene. As a matter of fact, the growth of the unit cell dimensions and of the cross-section of the copolymer helical chains should be taken into account for the interpretation of the Raman spectra of propylene copolymers. Additional studies are planned to clarify the behavior of the band at 398 cm\(^{-1}\).

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