Using Raman spectroscopy to determine the structure of copolymers and polymer blends

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Abstract. We present Raman structural study of two grades of random propylene/1-octene copolymers with low and high molecular weights and the 1-octene content up to 4.5 mole %. The copolymer spectra are compared with the spectra of the α, γ, and smectic modifications of isotactic polypropylene. Raman investigation has showed that the degree of crystallinity and conformational order of the copolymer macromolecules slightly decrease with the growth of the 1-octene content. The degree of crystallinity is slightly higher for the samples of the high-molecular-weight grade compared to the low-molecular-weight one. Furthermore, we present Raman spectra of polyethylene/polypropylene (90/10) blends, mixed in the polyethylene melt at three different temperatures, corresponding to three different states of polypropylene macromolecules. It was concluded that the degree of crystallinity and conformational order of the polyethylene macromolecules in the blends are the highest for the temperature, at which polypropylene macromolecules have lost their packing and conformational order.

1. Introduction
Along with a filler loading, copolymerization and blending are effective and inexpensive ways of polymer structure modification. In principle, these three ways allow purposeful and wide-range variation in the material properties and, as a consequence, creation of state-of-the-art functional materials for new high-tech applications. To make development of a new material maximally efficient, researchers need an informative, non-destructive and fast method of quantitative structural characterization. Raman spectroscopy is exactly the method, which meets all these requirements. Its main advantage is the ability to provide quantitative information on the macromolecules in different configurational, conformational, and phase states, including description of various crystalline modifications and amorphous regions with different state of order.

In this contribution we put an emphasis on Raman structural study of random propylene copolymers and polyethylene/polypropylene (PE/PP) blends, which are practically important materials due to their excellent physical-chemical properties and relatively low cost. Interpretation of the
copolymers were synthesized in the medium of liquid propylene over the homogeneous metallocene catalyst of C2-symmetry Me2SiInd2ZrCl2 by using the method, described in [1]. We compare the Raman spectra of these copolymers with the spectra of the nascent form of the random propylene/1-octene copolymers, synthesized in the medium of liquid propylene over the homogeneous metallocene catalyst of C2-symmetry rac-Me2Si(4-Ph-2-MeInd)2ZrCl2 (Series 2, table 1, samples α-iPP2 and C2-4.5). Method of the synthesis as well as differential scanning calorimetry (DSC), X-ray analysis, and mechanical testing data for the copolymers from the Series 2 were published in [1]. Raman spectra of the copolymers of the Series 2 with the 1-octene content up to 24 mole % are analyzed in detail in [2,3].

Two series of the copolymers differ mainly in molecular weight (Mw), measured by gel permeation chromatography (table 1, [1]). Table 1 also summarizes data on the degree of crystallinity, determined by X-ray analysis, DSC and Raman spectroscopy (for details see Results and Discussion section). The mole content of the comonomers in the copolymers was measured by 13C NMR spectroscopy [1].

Table 1. The degree of crystallinity of the propylene/1-octene copolymers and neat PP samples, measured by X-ray analysis, DSC and Raman spectroscopy.

| Sample / Molecular weight | Crystallinity, % | X-ray analysis | DSC | Raman spectroscopy |
|---------------------------|------------------|----------------|-----|--------------------|
|                           |                  |                |     | Iref/I109(I109/I1463) |
| Propylene/1-octene copolymers, Series 1, catalyst Me2SiInd2ZrCl2 |                  |                |     |                     |
| α-iPP1 (isotactic), Mw=49 800 |                  |                |     |                     |
| copolymer (C1-0.7) 0.7% of 1-octene, Mw=45 200 | 68 (α phase) | 65 | 53 (0.95) |
| copolymer (C1-4.4) 4.4% of 1-octene, Mw=30 800 | 60 (α phase) | 57 | 50 (0.87) |
| Propylene/1-octene copolymers, Series 2, catalyst rac-Me2Si(4-Ph-2-MeInd)2ZrCl2 |                  |                |     |                     |
| α-iPP2 (isotactic), Mw=742 400 |                  |                |     |                     |
| copolymer (C2-4.5) 4.5% of 1-octene, Mw=220 500 | 54 (42% α phase + 12% γ phase) | 39 | 51 (spectrum was recorded using 473 nm wavelength) |
| Neat PP samples |                  |                |     |                     |
| s-iPP3 (isotactic) |                  | smectic | smectic | 43 (1.50) |
| PP4 (isotactic with a large amount of stereodefects) | 0 | 0 | 0 (0) |
| γ-iPP5 (isotactic with a regulated amount of stereodefects) | 10 (γ phase) | no data | 10 (0.42) |
| γ-iPP6 (isotactic with a regulated amount of stereodefects) | 20 (γ phase) | no data | 29 (0.54) |
| γ-iPP7 (isotactic with a regulated amount of stereodefects) | 35 (γ phase) | no data | 34 (0.70) |
| γ-iPP8 (isotactic) | 70 (γ phase) | no data | 53 (1.06) |
| sPP9 (syndiotactic) | 30 | no data | - |

All the samples under study were in the nascent form. The only exception was the smectic modification (s-iPP3), which was prepared in a form of thick and transparent film by melting of the PP granules at 200°C and subsequent pressing and quenching in icy water.
The fully-amorphous PP sample (PP4) and the PP samples of the γ modification with the degree of crystallinity of 10% (γ-IPP5), 20% (γ-IPP6), and 35% (γ-IPP7) were synthesized in the medium of liquid propylene over the homogeneous metallocene catalyst of C1 symmetry C2H4(Flu)(5,6cyclopenta-2-MeInd)MtCl2 in accordance with the method [4,5]. The method allows to produce an isotactic PP with a regulated amount of stereodefects and, thus, to get the neat γ modification with variable degree of crystallinity. X-ray analysis, DSC, and mechanical data for these samples are also presented in [4,5].

![Raman spectra of the nascent powder of α-IPP2](image)

Figure 1. Raman spectra of the nascent powder of α-IPP2: A – the region 750 – 1550 cm⁻¹, B – the region 750 – 920 cm⁻¹, C - the region 2750 – 3050 cm⁻¹. The spectra are normalized to the peak intensity of the line at 1463 cm⁻¹ (A), 809 cm⁻¹ (B) and 2883 cm⁻¹ (C). λ – the excitation wavelength.

The method of synthesis of the neat γ modification of isotactic PP with the degree of crystallinity of 70% (γ-IPP8) and the corresponding X-ray analysis data are described in [6]. The same information for the syndiotactic PP (sPP9) is presented in [7].

Isotropic films of the blends of 90 mass % of PE and 10 mass % of isotactic PP were produced by mixing in the PE melt at three temperatures of 155, 165 and 190°C with subsequent pressing and quenching in room-temperature water. The films of the neat PE and neat PP were prepared at 150 and 190°C, respectively. The melting temperatures of the neat PE and neat PP were 128 and 165°C respectively. The relative content of the blend components was chosen in accordance with the works [8-10], where new technology for producing the all-polymer composites was proposed.
The Raman setup consisted of a Sapphire SF 532 laser (Coherent Inc., USA), a double monochromator (U1000, Jobin Yvon, France) and Peltier-element cooled photomultiplier detector, operating in photon counting regime. The excitation wavelength was 532 nm. Spectra were recorded at 90°-scattering with spectral resolution of 5 cm⁻¹.

In the course of preliminary measurements with different excitation wavelengths (473 and 488 nm from Ar+-Kr+ Stabilite 2018 laser (Spectra Physics, USA) and 532 nm from Sapphire SF 532 laser (Coherent Inc., USA)) we found out that the relative intensities of the isotactic PP Raman lines can be affected by the choice of the excitation wavelength. In particular, it can be seen from figure 1A that the intensities of the lines at 809 and 841 cm⁻¹ increase noticeably relative to the intensity of the line at 1463 cm⁻¹ with growth of the excitation wavelength. Integral intensities of the lines at 809 and 841 cm⁻¹ are used for evaluation of the degree of crystallinity and conformational order of macromolecules of isotactic PP [11], while the line at 1463 cm⁻¹ (the deformation vibration of CH₃ groups) often serves as a reference line due to the fact, that its intensity is less dependent on the degree of crystallinity and conformational order of macromolecules (for example, [12,13]).

The relative intensities in the narrow spectral region 750 – 920 cm⁻¹ (figure 1B) as well as in the region 2750 – 3050 cm⁻¹ (figure 1C) are independent of the excitation wavelength. Thus, care should be taken when comparing the intensities of the isotactic PP Raman lines in the region 750 – 1550 cm⁻¹, if the spectra are recorded using different excitation wavelengths. However, the degree of crystallinity and conformational order of isotactic PP macromolecules, evaluated as the ratios of integral intensities of the lines in the region 750 – 920 cm⁻¹ [11], do not depend on the excitation wavelength.

It is important that the line at 809 cm⁻¹, which integral intensity was proposed to be a measure of the degree of crystallinity of isotactic PP [11], is observed in a Raman spectrum of smectic isotactic PP [14]. Thus, the degree of crystallinity, evaluated from Raman spectra using the method [11], accounts for the smectic phase or similar states of isotactic PP macromolecules. Besides, it should be noted that the degree of crystallinity, evaluated from data of different techniques, should not coincide exactly because of different nature of physical effects, which form the basis of the methods. But the trends in the changes of the degree of crystallinity, evaluated by different techniques, should be the same. The error of measurement of the degree of crystallinity is similar for all the methods, used in this work, and is about 5 – 15%, depending on the absolute value of this parameter.

3. Results and Discussion

3.1. Propylene/1-octene copolymers and polymorphs of isotactic PP
Assignment of the Raman-active lines of isotactic and syndiotactic PP can be found in [11,14-19] and in [20-25] respectively. The relationships between appearance of the regularity bands in the isotactic PP vibrational spectrum and the length n of sequences of monomer units in the helical conformation have been established [13,26]. The minimum values of n, at which the bands at 973, 998, 841, and 1220 cm⁻¹ appear in the isotactic PP vibrational spectrum, are 2-4, 5-10, 12-14, and about 14 monomer units respectively (see detailed literature review in [27]). Appearance of the line at 809 cm⁻¹ was attributed to the minimal length n of about 7 [28-30] and of about 15 monomer units [31,32].

The line at 809 cm⁻¹ was assigned to the vibrations of isotactic PP helical chains in the crystalline phases with the monoclinic, hexagonal, and orthorhombic crystalline lattices and in the smectic phase [11,14]. Ratio of integral intensity I₈₀₉ of this line and the total integral intensity Iₖₑₙ in the spectral region from 750 to 890 cm⁻¹ is used as a measure of the degree of crystallinity of isotactic PP ([11], table 1). The line at 841 cm⁻¹ was assigned to the vibrations of isotactic PP helical chains with significant amount of conformational defects, localized in the amorphous phase [11].

The Raman spectra of the copolymers from the Series 1 as well as the spectra of the polymorphs of isotactic PP and the spectrum of the syndiotactic PP are presented in figures 2ABC. The spectrum of the syndiotactic PP looks very different from the spectra of the isotactic PPs, especially in the region 750 – 1550 cm⁻¹, where practically all the regularity bands of isotactic PP are localized. The spectrum of the smectic modification differs from the spectrum of the α modification mainly in the enhancement
of the relative intensities of the lines at 809 and 841 cm\(^{-1}\) and in the form of the intensity distribution in the region 2750 – 3050 cm\(^{-1}\).

Figure 2. Raman spectra of the propylene/1-octene copolymers and neat PPs in the regions 750 – 1550 cm\(^{-1}\) (A), 2750 – 3050 cm\(^{-1}\) (B), and 750 – 885 cm\(^{-1}\) (C). The spectra are normalized to the peak intensity of the line at 1463 cm\(^{-1}\) (A), 2883 cm\(^{-1}\) (B) and 841 cm\(^{-1}\) (C). The numbers on the left side are the degree of crystallinity, measured by X-ray analysis.
When comparing the copolymer spectra, the spectrum of the α modification (with the degree of crystallinity of 68%) and the spectrum of the fully-amorphous PP, it is clear that the intensities of the regularity bands at 809, 841, 973, 998, and 1220 cm$^{-1}$ monotonously decrease with the increase in the 1-octene content (and/or with the reduction of the degree of crystallinity) with the most pronounced effect, observed for the lines at 809 and 1220 cm$^{-1}$, which are related to the highest n values.

The intensity of the line at 809 cm$^{-1}$, normalized to the intensity of the line at 841 cm$^{-1}$, is slightly higher in the spectra of the neat PP and the copolymer from the Series 2 in comparison with the spectra of the samples from the Series 1 (figure 2C). It means that the degree of crystallinity is slightly higher for the samples of the high-molecular-weight grade as compared to the low-molecular-weight one.

Figures 3AB show the Raman spectra of various polymorphs of isotactic PP. The spectra of the α modification with the degree of crystallinity of 68% and the γ modification with the degree of crystallinity of 70% are very similar. The most significant difference is observed in the range at about 2960 cm$^{-1}$ for the doublet of the lines, assigned to the asymmetric stretching vibrations of CH$_3$ groups [33]. As in the case of the α modification, for the γ modification the intensities of the regularity bands at 809, 841, 973, 998, and 1220 cm$^{-1}$ decrease with the reduction of the degree of crystallinity with the most pronounced effect, observed for the lines at 809 and 1220 cm$^{-1}$.

### 3.2. PE/PP blends

Raman spectrum of PE is well investigated, and almost all the PE Raman-active lines are reliably assigned [34-39]. The Raman-active regularity bands for a PE macromolecule in the trans-conformation are observed at 1062, 1130, 1170, 1295, 2850, and 2881 cm$^{-1}$ and are assigned to the sequences of trans-conformers with the minimal length n of 6–8, 18, 18, 18, 6–8, and 18 CH$_2$ groups respectively [40]. The line at 1417 cm$^{-1}$ belongs to the vibrations of the macromolecules in the trans-conformation in the orthorhombic crystalline phase [35]. Structure of PE/PP blends was analyzed by Raman spectroscopy in a number of works [10,41-52]. However, Raman investigation of structure of PE/PP blends as a function of temperature of the polymer mixing was not carried out before.

Figures 4AB show Raman spectra of the neat PE and the blends of 90 mass % of PE and 10 mass % of isotactic PP, produced by mixing in the PE melt at three temperatures of 155, 165, and 190°C. The spectra were normalized to the peak intensity of the line at 2850 cm$^{-1}$ [40].

As it was indicated above, the melting temperatures of the neat PE and the neat PP were 128°C and 165°C respectively. Thus, the blends were mixed at three temperatures, at which the PE was in the state of a melt, where the orthorhombic crystalline phase and the trans-conformation of the PE macromolecules were destroyed. At 155°C PP macromolecules should retain both the helical conformation and packing in the crystalline lattice. At 165°C we expect destruction of the PP crystallites, but retention of the helical conformation of the PP macromolecules for the most part. At 190°C all the PP crystallites should be destroyed, and the helical conformation of the PP macromolecules should be strongly disturbed. Thus, we expect the different structure and, as a consequence, different Raman spectra for the blends, mixed at these three temperatures.

The spectra of the blends turned out to be similar to the spectrum of the neat PE. This is due to the low PP content in the blends and, thus, to weakness of the PP Raman lines. For the blend, prepared at 155°C, we observed decrease in the intensities of all the PE regularity bands as well as of the line at 1417 cm$^{-1}$. It means that the degree of crystallinity and conformational order of the PE macromolecules for this blend are lower compared with other two blends and the neat PE. Thus, the solid PP particles more strongly disturb the conformational ordering and crystallization of the PE macromolecules during cooling compared with the separated PP macromolecules uniformly-distributed over the blend.

The peak intensities of all the PE regularity bands as well as of the line at 1417 cm$^{-1}$ are slightly higher for the blend, prepared at 190°C, compared with the blend, mixed at 165°C. This means that the most perfect structure of PE is obtained at the mixing temperature of 190°C.
Figure 5 presents the temperature-dependent Raman spectra of the isotactic PP α-iPP2 (with the melting temperature of 164°C) in the region 750 – 1550 cm\(^{-1}\). The intensities of all the isotactic PP regularity bands are lower at 175°C compared with the spectrum, measured at 25°C. It is an indication of disruption of the macromolecular packing and conformational order.

![Figure 5](image)

Figure 3. Raman spectra of various polymorphs of isotactic PP in the regions 750 – 1550 cm\(^{-1}\) (A) and 2750 – 3050 cm\(^{-1}\) (B). The spectra are normalized to the peak intensity of the line at 1463 cm\(^{-1}\) (A) and 2883 cm\(^{-1}\) (B). The numbers are the degree of crystallinity, measured by X-ray analysis.
Figure 4. Raman spectra of the PE/PP blends in the regions 750 – 1550 cm$^{-1}$ (A) and 2750 – 3050 cm$^{-1}$ (B). The spectra are normalized to the peak intensity of the line at 2850 cm$^{-1}$. The numbers are the temperatures, at which the polymers were mixed.

Figure 5. Raman spectra of the isotactic PP α-IPP2 with the melting temperature of 164°C in the region 750 – 1550 cm$^{-1}$ at various temperatures. The spectra are normalized to the peak intensity of the line at 1463 cm$^{-1}$.

Significant amount of the conformationally-ordered segments is still present at temperatures, exceeding the melting point (figure 5). In the temperature region from 60 to 166°C the intensity of the line at 809 cm$^{-1}$ (relative to the intensity of the line at 1463 cm$^{-1}$) is higher compared with the
spectrum, recorded at 25°C. We explain this fact by the increase in the content of the smectic modification, which is formed due to destruction of the PP crystallites. This explanation is confirmed by higher intensity of the line at 809 cm⁻¹ in the spectrum of the smectic modification compared to the spectrum of the α and γ modifications, measured at room temperature (figures 2A, 3A).

4. Conclusion

Based on Raman spectroscopy data we found out that the degree of crystallinity and conformational order of macromolecules of the propylene/1-octene copolymers decrease with the growth of the 1-octene content. The degree of crystallinity is slightly higher for the neat polypropylene and the copolymer of the high-molecular-weight grade compared to the low-molecular-weight one. Raman study of the polyethylene/polypropylene blends revealed that the degree of crystallinity and conformational order of the polyethylene macromolecules are the highest for the mixing temperature, at which the polypropylene macromolecules completely lost their packing and conformational order.

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