DOI: 10.1002/masy.201051067

Raman Structural Study of Copolymers of Propylene with Ethylene and High Olefins

Konstantin Chernyshov,[1] *Dmitry Gen,*[1] *Yuri Shemouratov,*[1] *Kirill Prokhorov,*[1] *Gulnara Nikolaeva,**[1] *Elena Sagitova,*[1] *Pavel Pashinin,*[1] *Anton Kovalchuk,*[2,3] *Alla Klyamkina,*[2] *Polina Nedorezova,*[2] *Boris Shklyaruk,*[4] *Valery Optov*[2]

Summary: Nascent form of random copolymers of propylene with ethylene, 1-butene, 1-hexene, 1-octene, and 4-methyl-1-pentene was studied by Raman spectroscopy. The most significant spectral alterations with a change in propylene content were observed in two lines at 809 and 841 cm^{-1}. The first line corresponds to vibrations of polypropylene helical chains in the crystalline phase, while the second one is associated with vibrations of polypropylene helical chains having isomeric defects. Raman data confirm that conformational composition and phase state of copolymer macromolecules strongly depend on the comonomer content as well as on the size of the comonomer units.

Keywords: conformational analysis; copolymerization; crystallinity; polypropylene; Raman spectroscopy

Introduction

An important task of the modern applied polymer science is the development of materials with a set of pre-specified physical and chemical properties. An effective and inexpensive way of achieving this goal is the modernization of existing production technologies of widely used polymers. Isotactic polypropylene (PP) ranks the second place among polyolefins according to its output in the world industry due to its low cost and good properties. Isotactic PP can be found in four crystalline forms.[1,2] They are α, β, γ, and smectic modifications, which correspond to monoclinic, hexagonal, orthorhombic, and pseudo-hexagonal lattices, respectively.[1,2] However, only α modification has commercial importance.

Copolymerization of propylene with a number of olefins seems to be a promising and feasible approach of modifying industrially important characteristics of α-PP. Variations in relative content of comonomers, catalyst type and synthesis conditions allow tuning materials properties, such as mechanical, thermophysical, optical, etc., in a predictable manner and on a wide range. For example, recently synthesized with homogeneous isospecific catalytic system copolymers of propylene with ethylene, 1-hexene, and 4-methyl-1-pentene[3,4] differ significantly in mechanical characteristics. Depending on the relative content of the comonomers, tensile behavior of these materials[3,4] varied from rigid and quite brittle for the homopolymer to pronounced elastic for the copolymers.

Production of these random copolymers becomes possible due to development of the new highly-active homogeneous metallocene catalysts.[5] These catalysts allow producing polymers with a high yield, and obtaining polymer materials with improved structural

---

[1] A.M. Prokhorov General Physics Institute, Russian Academy of Sciences, 38 Vavilov St., 119991 Moscow, Russia
Fax: +(499)1352055;
E-mail: nikolaeva@kapella.gpi.ru

[2] N.N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 4 Kosygin St., 119991 Moscow, Russia

[3] Center for Composite Materials, University of Delaware, 101 Academy St., Newark (DE), 19716 USA

[4] A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 29 Leninsky Pr., 119991 Moscow, Russia

parameters such as high molecular weight, narrow molecular weight distribution, high stereoregularity, and highly homogeneous composition. The best metallocene isospecific catalyst can provide neat PP with the content of isotactic [mmmm] pentads up to 98 molar %. It was found out that the copolymers synthesized with such catalyst have almost ideal random distribution of comonomers along the copolymer chain.[3,4] Random distribution of comonomers leads to a significant reduction of the degree of crystallinity even with a small content of the incorporated monomer, and, thus, to a substantial and predictable modification of physical and chemical properties of copolymers.

It is important to note that significant alteration of the structure of propylene-based random copolymers (the degree of crystallinity, molecular weight, etc.) and, correspondingly, significant changes in the properties of the products are observed at low amounts of incorporated monomer units, below 10 molar %. This suggests possibility of fabricating new polymeric materials with improved set of physical and chemical properties using virtually the conventional synthesis technology as for the plain isotactic PP at comparable manufacturing cost.

In this contribution we present Raman study of five recently developed grades of random copolymers of propylene (C_3H_6) with ethylene (C_2H_4), 1-butene (C_4H_8), 1-hexene (C_6H_{12}), 1-octene (C_8H_{16}), and 4-methyl-1-pentene (C_6H_{12}).

Raman spectroscopy provides information on many structural characteristics, namely, chemical composition, conformational and phase composition, macromolecular orientation, molecular mobility[6], etc. However, vibrational spectra of propylene-based copolymers are still unknown, and even spectra of different configurations and modifications of neat PP are under discussion.

The most important aims of our study are identifying the phase composition, that is the relative content of different crystalline and non-crystalline phases, and determining the conformational composition, that is the relative content of different conformers. The possibility to analyze all structural phases of a polymer material by only one technique is a significant advantage of Raman spectroscopy compared with other traditional methods of polymer characterization, like X-ray analysis or differential scanning calorimetry (DSC).

Also, note that 4-methyl-1-pentene and 1-hexene are isomers. The choice of these materials allowed us to investigate the influence of both size and conformation of the incorporated monomer on the final copolymer structure. Corresponding Raman study could be interesting not only for the potential commercial applications, but also for basic research.

Experimental Part

Copolymers of propylene (C_3H_6) with ethylene (C_2H_4), 1-butene (C_4H_8), 1-hexene (C_6H_{12}), 1-octene (C_8H_{16}), and 4-methyl-1-pentene (C_6H_{12}) were synthesized in the medium of liquid propylene over homogeneous metallocene catalyst rac-Me2Si(4-Ph-2-MeInd)2ZrCl2, activated by methylaluminoxane.[3,4,7–9]

The molar content of the comonomers was measured by NMR C^{13} and IR-spectroscopy. Detailed description of the synthesis, X-ray analysis and DSC data, and mechanical characteristics of the neat PP and copolymers were published earlier.[3,4,7–9] It was found that Young's modulus decreased while the elongation at break increased with growing the content of the incorporated monomer.[3,4,7–9] This indicates that the copolymers become more plastic. The description of the experimental setup for measurements of X-ray analysis spectra as well as DSC curves was also published.[3,4,7–9] The X-ray analysis of the samples showed that the neat PP contains only crystallites of the α-modification.[3,4,7–9]

Traces of the γ-modification were found in several samples. The X-ray analysis and DSC data (Table 1) revealed that the degree of crystallinity of the copolymers decreased with the growth of content of the incorporated monomer.[3,4,7–9]

Table 1.
Degree of crystallinity, measured by X-ray analysis, and heat of fusion, measured by DSC, for copolymers as function of comonomer content.

Incorporated monomer	Content of incorporated monomer, mol. %	Degree of crystallinity, measured by X-ray analysis, %	Heat of fusion, measured by DSC, J/g
ethylene	0	70	109
	2	70	76
	10	46	50
	21	35	17
	25	15	5
1-butene	0	67	109
	0.5	69	117
	0.9	71	106
	1.8	60	101
	5.3	62	91
	19.5	52	73
	30	52	51
1-hexene	0	74	116
	1	68	111
	2	65	91
	4	56	71
	7	47	41
1-octene	0	68	109
	1.5	63	114
	2.1	60	97
	3.6	57	68
	4.5	54	64
	8.4	41	59
	24	0	0
4-methyl-1-pentene	0	74	116
	1	69	97
	2	65	86
	6	57	40

The Raman setup consisted of an Ar^+-Kr^+ laser (Stabilite 2018, Spectra-Physics, USA), a double monochromator (U1000, Jobin Yvon, France) and a 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 $5\,cm^{-1}$.

In this research we studied non-polarized Raman spectra of the copolymers in nascent form. That is the form in which the materials were taken from the reactor directly after synthesis without additional processing or thermal treatment. Recording of polarized Raman spectra of the nascent form of polymers is not reasonable because of depolarization effects on the exciting and scattered radiation due to multiple reflections and refractions.

Results and Discussion

Raman spectra in the range of stretching vibrations of C–C bonds and deformation vibrations of CH_2 and CH_3 groups of copolymers of propylene with ethylene, 1-butene, 1-hexene, 1-octene, and 4-methyl-1-pentene are shown in Figures 1–5, respectively.

Raman spectra of the propylene/ethylene copolymers in the range of stretching vibrations of CH_2 and CH_3 groups are presented in Figure 6. Generally, the spectra of the copolymers with a low propylene content are noisy due to low degree of crystallinity (Table 1).

The most noticeable changes in the spectra of the copolymers are observed in the region about $800\,cm^{-1}$ (Figures 1–5). Taking into account the published data,[10,11] we propose that the lines at

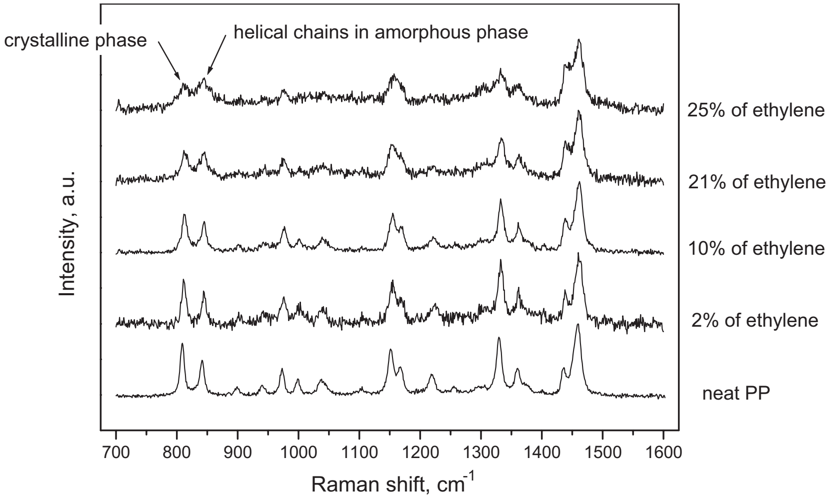

Figure 1.
Raman spectra of propylene/ethylene copolymers in the range of stretching vibrations of C—C bonds and deformation vibrations of CH_2 and CH_3 groups.

809 and 841 cm^{-1} in the spectra of the copolymers correspond to the vibrations of propylene sequences. After analyzing and comparing the spectra of all the samples (Figures 1–5) we conclude that the spectra of the copolymers under study exhibit very similar monotonic alterations in the peak intensity ratio and widths of these Raman bands with a change in the propylene content. However, the detailed analysis of the copolymers spectra provides us with important information about its structure.

An interesting feature in the spectra of the propylene/1-butene copolymers (Figure 2) is appearance of a line at 767 cm^{-1} at 1-butene content, exceeding 20 molar %. We consider

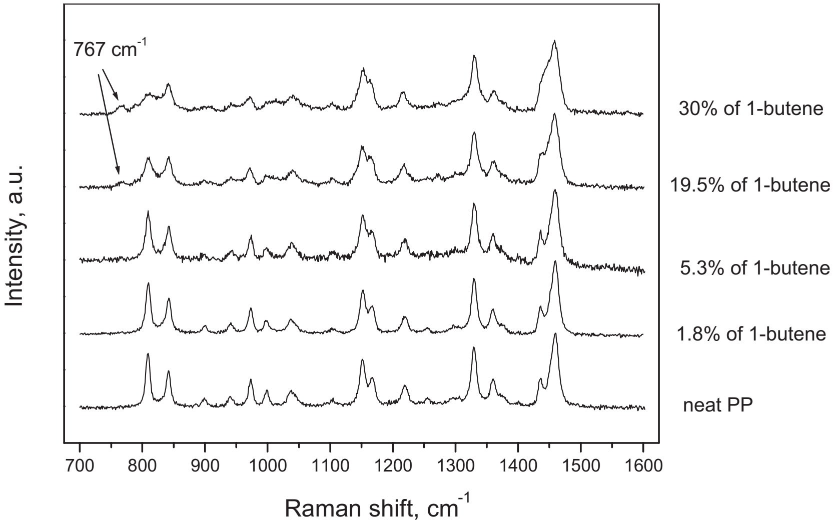

Figure 2.
Raman spectra of propylene/1-butene copolymers in the range of stretching vibrations of C—C bonds and deformation vibrations of CH_2 and CH_3 groups.

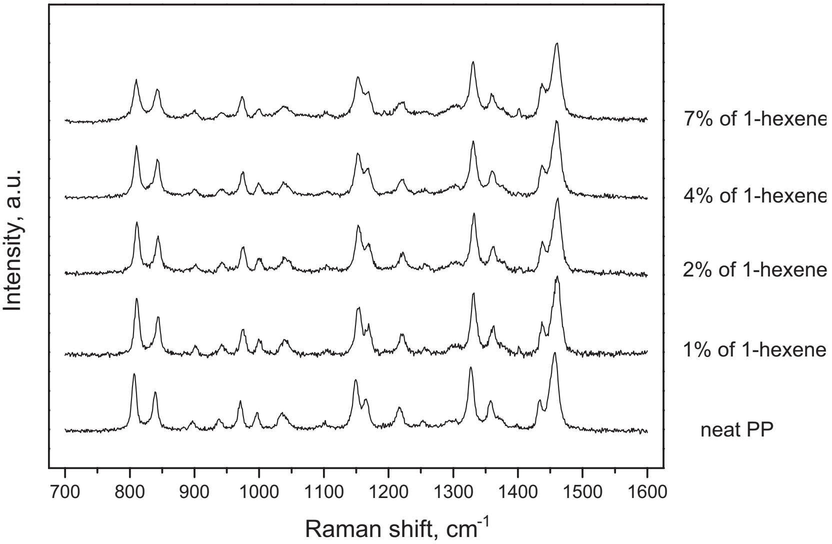

Figure 3.
Raman spectra of propylene/1-hexene copolymers in the range of stretching vibrations of C—C bonds and deformation vibrations of CH_2 and CH_3 groups.

that this effect is due to the formation of sufficiently long butene sequences in the copolymer chain.[10] This conclusion perfectly agrees with the X-ray analysis data, which also have revealed appearance of polybutene at these contents of the comonomers.[12]

For the analysis of Raman bands around 800 - 850 cm^{-1} we used results of A.S. Nielsen and co-workers.[13] These authors proposed a Raman method for determination of the phase composition of neat isotactic PP.[13] The method is based on the assumption that three lines in this

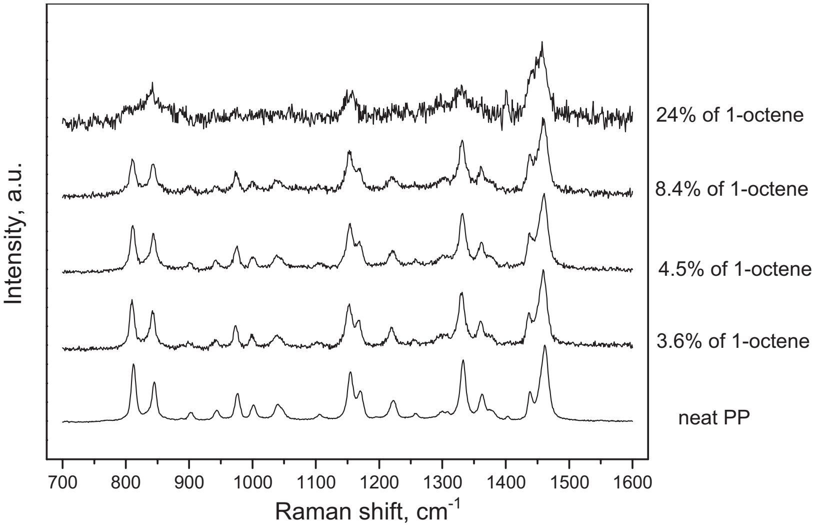

Figure 4.
Raman spectra of propylene/1-octene copolymers in the range of stretching vibrations of C—C bonds and deformation vibrations of CH_2 and CH_3 groups.

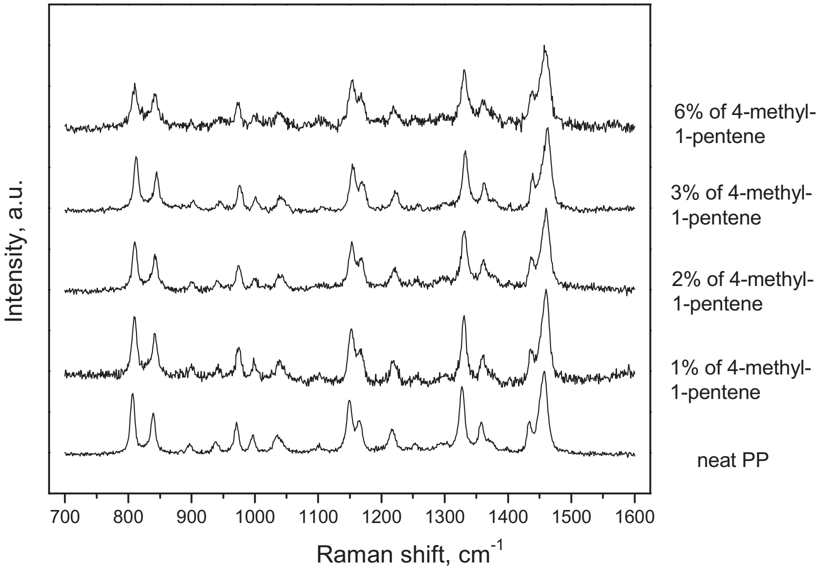

Figure 5.
Raman spectra of propylene/4-methyl-1-pentene copolymers in the range of stretching vibrations of C—C bonds and deformation vibrations of CH_2 and CH_3 groups.

spectral region belong to three different phases of isotactic PP:

a) The line at 809 cm^{-1} was ascribed to vibrations of PP helical chains in the crystalline phase.[13] This line was observed in Raman spectra of all crystalline modifications of isotactic PP.[1] The only feature of the line that appears in the low-temperature α-PP spectrum is splitting due to intermolecular interaction in the monoclinic lattice.[1] The line at 809 cm^{-1} corresponds to the superposition of wagging vibration of

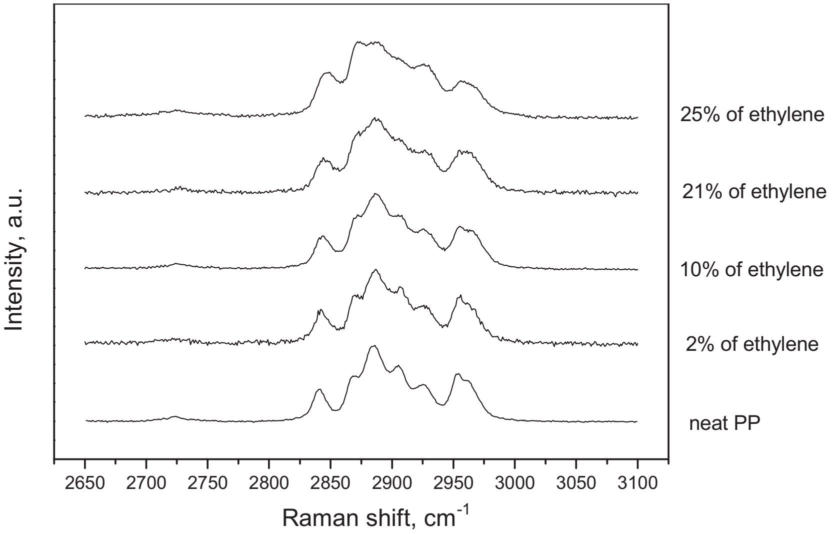

Figure 6.
Raman spectra of propylene/ethylene copolymers in the range of stretching vibrations of CH_2 and CH_3 groups.

CH_2 groups, stretching vibration of C–C bonds, and stretching vibration of C–CH_3 groups.[14]

b) The line at 841 cm^{-1} is the superposition of wagging vibrations of CH_2 and CH_3 groups, and stretching vibration of C–C bonds.[14] This line relates to PP helical chains with significant amount of conformational defects, localized in the amorphous phase.[13].

c) Relatively broad and weak band at 830 cm^{-1} belongs to vibrations of non-helical chains in the amorphous phase.[13]

A.S. Nielsen and co-workers[13] proposed that the content of each phase can be determined by division of integral intensity of the corresponding line to the reference intensity that is the sum of integral intensities of these three lines.

It can be seen from Figures 1–5 that intensities of the lines at 809 and 841 cm^{-1} monotonically decrease with the decrease in propylene content. The intensity of the line at 809 cm^{-1} diminishes faster than that of the line at 841 cm^{-1}. That means that the content of helical chains in both the crystalline and amorphous phases decreases with the growth of the incorporated monomer content. However, the content of helical chains in the crystalline phase decreases faster than that in the amorphous phase.

As it was mentioned above, the α-phase has a major contribution to the crystalline phase of the copolymers, while the effect of the γ-phase is much smaller. Therefore, proceeding from the fact that the line at 809 cm^{-1} corresponds to both α- and γ-phases,[1] we concluded that our Raman data confirm the reduction of the total content of α- and γ- phases in the copolymers with the decrease in propylene content.

The deconvolution analysis of the spectra of our samples has not revealed the third line (830 cm^{-1}), which corresponds to non-helical chains in the amorphous phase. Thus, we considered the ratio $I_{809}/(I_{809} + I_{841})$ of integral intensities of the lines at 809 and 841 cm^{-1} as Raman measure of the content of crystalline phases of isotactic PP in our copolymers (Figure 7). The point which corresponds to zero content of the incorporated monomer belongs to the neat PP. This intensity ratio was corrected taking into consideration the content of the comonomers. This correction procedure is necessary, because the intensity ratio $I_{809}/(I_{809} + I_{841})$ represents the content of crystalline phases of isotactic PP relative to the content of propylene, not to the sum content of both comonomers.

The intensity ratio at Figure 7 decreases with the growth of content of the incorporated monomer. This clearly indicates a reduction in the degree of crystallinity of the copolymers. And, as can be seen, the ratio $I_{809}/(I_{809} + I_{841})$ lowers faster with complication in the structure of the comonomer, except 1-butene. The degree of crystallinity of the propylene/1-butene copolymers decreases slower compared with the other copolymers due to incorporation of 1-butene into the PP monoclinic lattice without the lattice destruction, but with a little increase of unit cell dimensions.[12]

All the techniques – Raman spectroscopy (Figure 7), X-ray analysis and DSC (Table 1), indicate the decrease in the degree of crystallinity of the copolymers with the growth of content of the incorporated monomer, but there are noticeable discrepancies between the data, obtained by different methods. Probably, the reason for these discrepancies is the different sensitivity of the methods relative to the analysis of the crystalline phase. The X-ray analysis and DSC data account for both the α- and γ- modifications of isotactic PP as well as for polybutene in the case of the copolymers of propylene with 1-butene. Raman spectroscopy data, namely intensity of the line at 809 cm^{-1}, account for only the α- and γ- modifications of isotactic PP. The sensitivity of the methods depends on sizes of the crystallites and content of the lattices defects. Moreover, for all techniques an error of measurement rapidly increases with the decrease in the degree of crystallinity.

In Figure 8 we compare the X-ray analysis data as to the degree of crystallinity

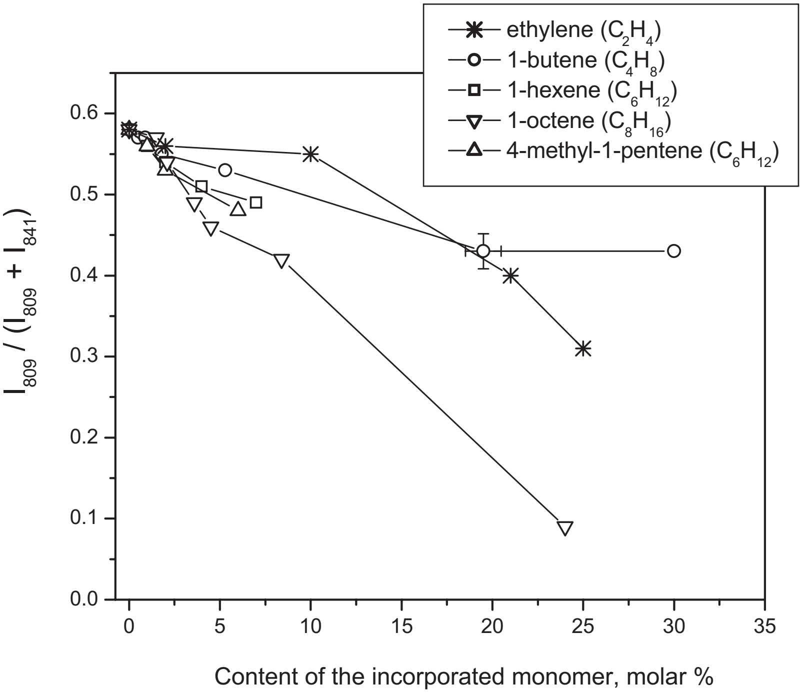

Figure 7.
Ratio $I_{809}/(I_{809}+I_{841})$ of integral Raman intensities of lines at 809 and 841 cm^{-1} as a function of comonomer content.

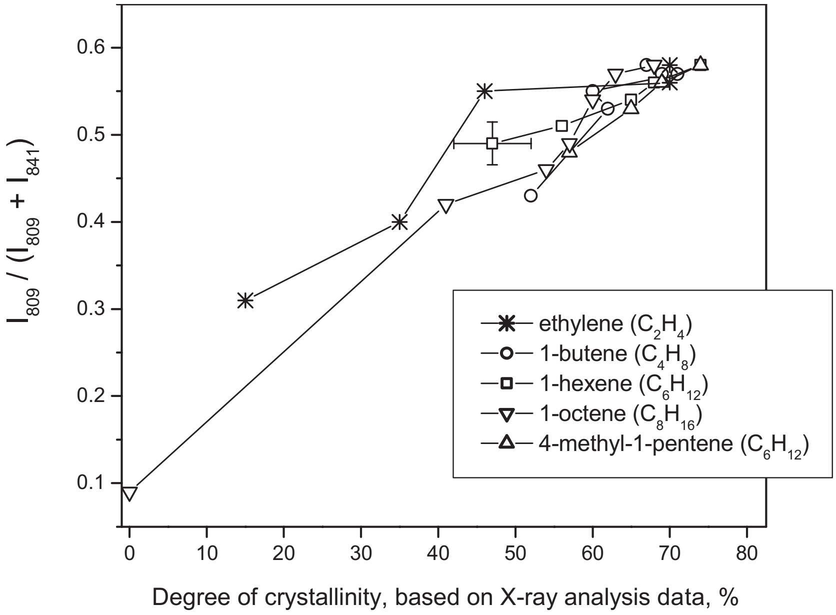

Figure 8.
Ratio $I_{809}/(I_{809}+I_{841})$ of integral Raman intensities of lines at 809 and 841 cm^{-1} as a function of degree of crystallinity of the copolymers, measured by X-ray analysis.

and the ratio of intensities of Raman lines $I_{809}/(I_{809}+I_{841})$. At first sight one can expect the linear dependence for the data, presented in Figure 8.. But after detailed analysis the deviation of the data from a straight line is not surprising. It is known from publications[10,11] that long sequences of 1-butene and 4-methyl-1-pentene can contribute to Raman intensity in the region about 800 cm^{-1}. Taking into account that both lines at 809 and 841 cm^{-1} significantly increase their widths (up to 25 cm^{-1}) with the increase in content of the incorporated monomer, it is reasonable to suppose that even weak lines from sequences of the incorporated monomers can contribute to integral intensity of the lines at 809 and 841 cm^{-1}. Moreover, the lines with such large width cannot be correctly ascribed to a crystalline phase, although the peak positions of the lines remain unchanged. Thus, for the case of the copolymers with a high content of the incorporated monomer, it is more appropriate to use peak intensities instead of integral intensities.

The line at 1460 cm^{-1} which is observed in all our spectra corresponds to the deformation vibration of CH_3 groups of PP macromolecules.[14] However, deformation vibrations of CH_2 groups can be also observed at the same frequency in the spectra of organic molecules containing polymethylene chains.[15,16] Thus, in the spectra of the copolymers under our study at this frequency one can observe superposition of the lines, corresponding to the vibrations of both CH_2 and CH_3 groups.

Contents of CH_2 and CH_3 groups differ for the six monomers studied in the present work. Thus, strictly speaking, the line at 1460 cm^{-1} cannot be proven to be a reference line for comparison of the spectra of the copolymers. However, this line is the most intense in the region from 700 to 1600 cm^{-1}, and its spectral characteristics do not vary considerably with the decrease in propylene content compared with the other lines in this spectral region. So, in the absence of another reliable reference line, we used intensity of the line at 1460 cm^{-1} as the reference intensity.

The comparison of the Raman peak intensity ratio I_{809}/I_{1460} with the degree of crystallinity measured by X-ray analysis is shown in Figure 9. The general agreement between the results obtained by these two techniques is quite good. More detailed observation shows that the curve for 4-methyl-1-pentene is located slightly lower, because this copolymer has more CH_3 groups in its structure, and, thus, the intensity of the line at 1460 cm^{-1} should be higher. The curve for 1-butene is also positioned lower. We propose unambiguous explanation for this feature. As we mentioned at the beginning of this section, the presence of polybutene was detected in the propylene/1-butene copolymers. Contributions of polybutene and PP into the degree of crystallinity could not be distinguished by X-ray analysis. But Raman spectroscopy has an advantage in determination of particular contributions from different polymers. The intensity of the line at 809 cm^{-1} accounts for only the crystalline phases of isotactic PP.

So, taking into account different chemical structure of the monomers under study, we suggest estimating the content of PP helical chains in the crystalline phases of the copolymers using the peak intensity ratio of two very pronounced Raman lines at 809 and 1460 cm^{-1}.

Figure 10 shows ratio I_{809}/I_{841} of peak intensities of the lines at 809 and 841 cm^{-1} corresponding to vibrations of PP helical chains in the crystalline and amorphous phases, respectively as a function of content of the comonomer. For all copolymers under study the content of the crystalline phase decreases faster than the content of helical chains in the amorphous regions. At low content of the incorporated monomers the curves almost coincide for all copolymers. At large content of the incorporated monomers one can observe a drastic drop of the dependence for the propylene/1-octene copolymers. It is an understandable result, because 1-octene is the biggest monomer under study, and therefore it

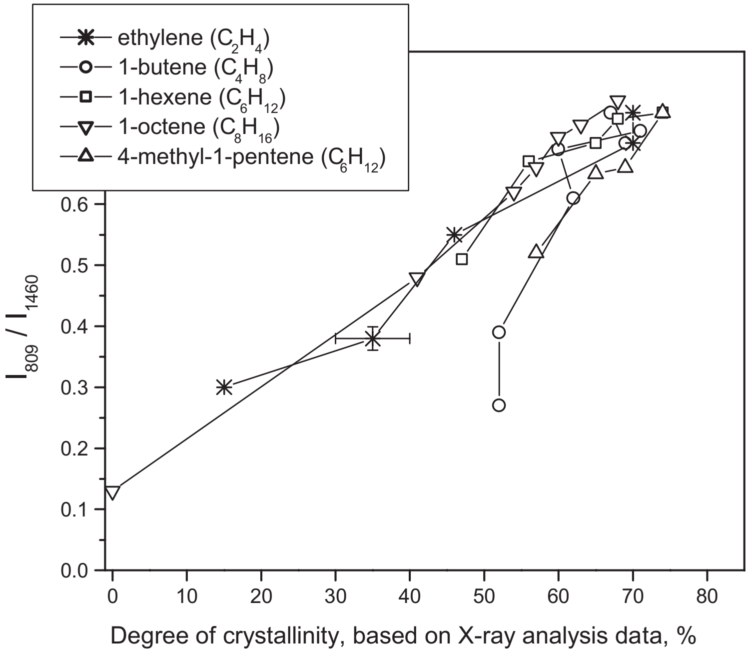

Figure 9.
Ratio I_{809}/I_{1460} of peak Raman intensities of lines at 809 and 1460 cm^{-1} as a function of degree of crystallinity of copolymers measured by X-ray analysis.

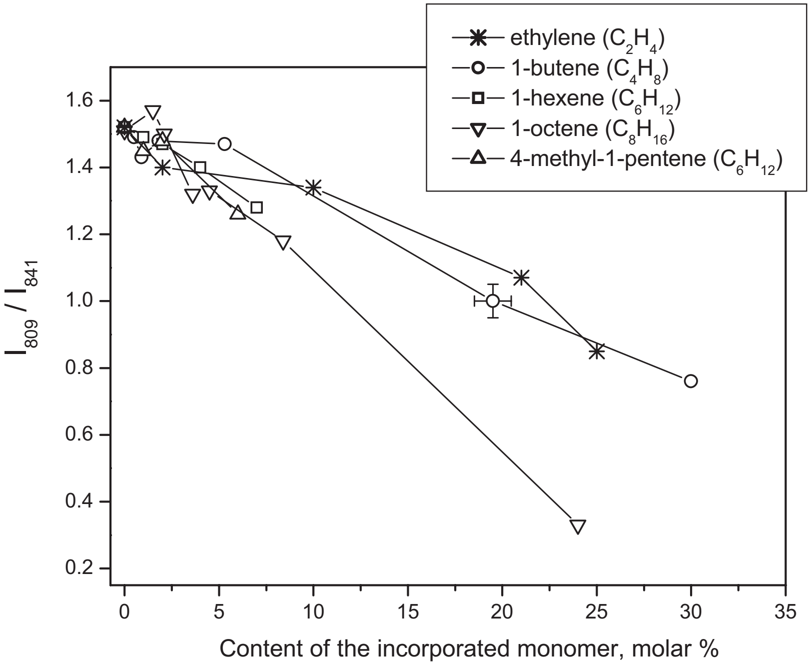

Figure 10.
Ratio I_{809}/I_{841} of peak Raman intensities of lines at 809 and 841 cm^{-1} as a function of content of incorporated monomer.

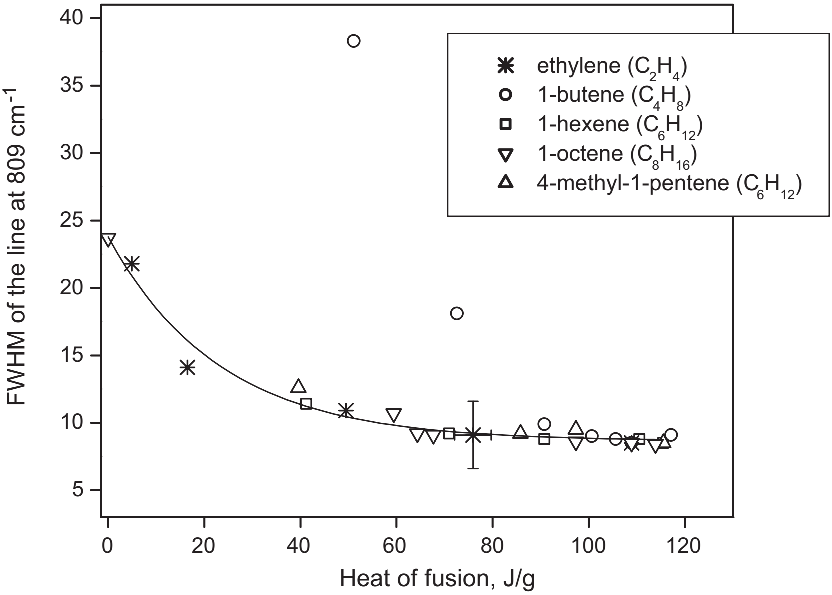

Figure 11.
Full width at the half maximum (FWHM) of line at 809 cm^{-1} as a function of heat of fusion measured by DSC.

should have the most pronounced influence on the helical conformation of PP macromolecule. We did not find any significant difference between the curves for the copolymers with ethylene and 1-butene, which differ from propylene in one C atom.

Figure 11 demonstrates the dependence of full width at half maximum of the line at 809 cm^{-1} upon the heat of fusion, measured by the DSC technique. All experimental points fit the monotonous curve except for the data for propylene/1-butene copolymers. As it was discussed above, the presence of polybutene gives a significant contribution to the DSC heat of fusion for propylene/1-butene copolymers. This presence of polybutene can be seen in Figure 2 as the appearance of 767 cm^{-1} line for 30% and 19.5% of 1-butene content.

Thus, not only the intensity but also the width of Raman line at 809 cm^{-1} can be used for the estimation of the degree of crystallinity of the propylene-based copolymers.

We found out that Raman spectra of the copolymers in the range of stretching vibrations of CH_2 and CH_3 groups are less informative due to strong overlapping of the bands (Figure 6). Computational deconvolution analysis of this spectral region has shown that the main spectral alterations were caused by the broadening of Raman bands with the decrease in the degree of crystallinity of the copolymers.

Conclusion

We carried out Raman study of five recently developed random copolymers of propylene with ethylene, 1-butene, 1-hexene, 1-octene, and 4-methyl-1-pentene synthesized with homogeneous isospecific catalytic system. We found out that changes in Raman spectra with the growth of content of the incorporated monomer are generally similar for all copolymers and are mainly caused by the alteration of the degree of crystallinity and the conformational composition of macromolecules. The intensity and width of the line at 809 cm^{-1} are sensitive to the degree of crystallinity of the propylene-based copolymers. Raman data revealed that contents of helical chains in the crystalline α- and γ- phases of PP and in the amorphous phase of the copolymers decrease with the increase in the content of the incorporated monomer. The content of helical chains in the crystalline phase decreases faster than that in the amorphous phase.

Acknowledgements: This work is supported by the Russian Foundation for Basic Research (project code 08-02-00909-a) and the Grant of the President of the Russian Federation for the Support of Leading Scientific Schools (3675.2010.2).

[1] J. M. Chalmers, H. G. M. Edwards, J. S. Lees, D. A. Long, M. W. Mackenzie, H. A. Willis, *J. Raman Spectrosc.* **1991**, *22*, 613.

[2] S. Bruckner, S. V. Meille, V. Petraccone, B. Pirozzi, *Prog. Polym. Sci.* **1991**, *16*, 361.

[3] A. A. Koval'chuk, A. N. Klyamkina, A. M. Aladyshev, P. M. Nedorezova, E. M. Antipov, *Polym. Bull.* **2006**, *56*, 145.

[4] A. A. Koval'chuk, A. N. Klyamkina, A. M. Aladyshev, V. A. Optov, B. F. Shklyaruk, V. I. Kleiner, E. M. Antipov, *Int. Polym. Sci. Technol.* **2006**, *33*, 21.

[5] "*Metallocene-Based Polyolefins: Preparation, Properties and Technology*", J. Scheirs, W. Kaminsky, Eds., J. Wiley & Sons, New York 2000, V, *1–2*.

[6] P. C. Painter, M. M. Coleman, J. L. Koenig, "*The theory of vibrational spectroscopy and its application to polymeric materials*", Wiley-Interscience, New York 1982.

[7] P. M. Nedorezova, V. I. Tsvetkova, A. M. Aladyshev, D. V. Savinov, A. N. Klyamkina, V. A. Optov, D. A. Lemenovskii, *Polym. Sci. A* **2001**, *43*, 356.

[8] P. M. Nedorezova, A. V. Chapurina, A. A. Koval'chuk, A. N. Klyamkina, A. M. Aladyshev, V. A. Optov, B. F. Shklyaruk, *Polym. Sci. B* **2009**, *52*, 15.

[9] P .M. Nedorezova, A. A. Koval'chuk, A. N. Klyamkina, A. M. Aladyshev, V. I. Tsvetkova, D. A. Lemenovskii, B. F. Shklyaryk, *Book of abstracts of III International Conference "Catalysis: fundamentals and application*", July 4 – July 8, 2007, Novosibirsk, Russia **2007**, *2*, 324.

[10] M. Abenoza, A. Armengaud, *Polymer* **1981**, *22*, 1345.

[11] E. J. J. Samuel, S. Mohan, *Spectrochim. Acta A* **2004**, *60*, 19.

[12] A. A. Koval'chuk, A. N. Klyamkina, P. M. Nedorezova, B. F. Shklyaruk, to be published.

[13] A. S. Nielsen, D. N. Batchelder, R. Pyrz, *Polymer* **2002**, *43*, 2671.

[14] R. G. Snyder, J. H. Schachtschneider, *Spectrochim. Acta* **1964**, *20*, 853.

[15] C. C. Naylor, R. J. Meier, B. J. Kip, K. P. J. Williams, S. M. Mason, N. Conroy, D. L. Gerrard, *Macromolecules* **1995**, *28*, 2969.

[16] Yu. V. Shemouratov, K. A. Prokhorov, Yu. G. Nikolaeva, P. P. Pashinin, A. A. Kovalchuk, A. N. Klyamkina, P. M. Nedorezova, K. V. Demidenok, Yu. A. Lebedev, E. M. Antipov, *Laser Phys.* **2008**, *18*, 554.