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Raman structural study of random olefin copolymers

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Abstract

In this work we present Raman study of random copolymers of ethylene and propylene with a number of α -olefins, and investigation of the relationships between the spectral characteristics of the Raman lines and the copolymer structural properties. For both the copolymers we observed rapid decrease in the crystallinity and conformational order as the content of the incorporated monomer increases.

Introduction

Polyethylene (PE) and isotactic polypropylene (PP) are important industrial polymers with useful physical and chemical properties. However, their properties can be further enhanced by the induction of chain branching through copolymerization with α -olefins. Random copolymers are promising industrial thermoplastics, as they exhibit strong dependence of the crystallinity on the incorporated monomer content. This behavior can be exploited for tuning the copolymer mechanical characteristics from a rigid to an elastic state. Moreover, the vibrational spectra, the molecular and supramolecular structure, and the deformation mechanisms of copolymers demonstrate new interesting features, making them of significant interest for academic research.

Using homogeneous metallocene catalytic systems, based on the complexes of metallocenes and methylaluminumoxane (MAO), it is possible to produce polymers with a high yield, and to obtain polymer materials with improved structural parameters such as narrow molecular weight distribution, high stereoregularity, and high

compositional uniformity. Homogeneous catalysts have higher selectivity with respect to the incorporation of higher α -olefins in a polymer molecule as compared to the conventional Ziegler-Natta catalysts [1,2]. These catalysts are very effective for the synthesis of both ethylene and propylene copolymers. In particular, the use of homogeneous single-site catalysts makes it possible to synthesize ethylene- and propylene-based copolymers with high content of the incorporated monomer and, therefore, to increase chain branching and to vary the copolymer properties within a wide range.

Raman spectroscopy is a highly informative technique for the study of both the crystalline and the amorphous phases of polymers. The possibility to analyze all structural phases of a polymer material by only one technique is a significant advantage of Raman spectroscopy compared with traditional methods of polymer characterization, such as X-ray diffraction analysis and differential scanning calorimetry (DSC). In the case of copolymers, the amorphous phase structure is especially important, since the crystallinity of these materials is typically low. Raman structural analysis does not require any sample preparation in this case. The polymer and copolymer structures can be explicitly studied by Raman spectroscopy in terms of the chemical and phase compositions, the contents of different conformers in the amorphous phase, and the molecular orientation.

In this work, random copolymers of both ethylene and propylene with a number of α -olefins are studied by Raman spectroscopy, and the relationships between the spectral characteristics of the Raman lines and the structural properties

(crystallinity and conformational order) of the two copolymer systems are investigated.

Results and Discussion

Random Copolymers of Ethylene and 1-Hexene

Many works [3-6] reported so far about the investigation of ethylene/1-hexene copolymers (CEHs) lack extensive studies of the CEH Raman spectra and their dependence on the material structure, especially for the CEHs with high content of 1-hexene. The reason might lay in the fact that these copolymers are relatively novel materials. We recently reported a detailed Raman study of CEHs [7], and here we briefly summarize our previous findings.

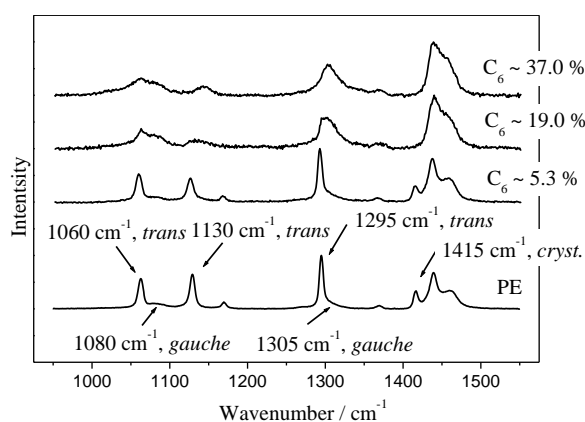


Fig. 1. Raman spectra of the CEHs and neat PE.

We have studied the nascent form of CEHs, produced following the method described in [8]. CEHs with 1-hexene content ranging from 1.9 to 7.4 mole % and from 10.9 to 37.0 mole % were synthesized in the presence of the catalysts $\text{Me}_2\text{Si}(2\text{-Me-4Ph-Ind})_2\text{ZrCl}_2/\text{MAO}$ and $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$, respectively.

The Raman spectra of the copolymers were measured using the 488 nm excitation line of an Ar^+-Kr^+ laser (Stabilite 2018, Spectra-Physics, USA), a double-pass monochromator (U1000, Jobin Yvon, France), and a photomultiplier detector operating in the photon counting mode. Non-polarized Raman spectra were recorded at room temperature employing a right-angle scattering geometry. The spectral resolution was 5 cm^{-1} .

In order to ease the interpretation of the CEH spectra, Raman spectra of a neat PE film at 24 and 136°C were also recorded. The melting temperature of the neat PE film was 128°C . The PE film used here was produced by compression molding at 180°C and subsequent quenching in cold water.

Fig. 1 shows the Raman spectra of CEHs in the region comprising both the stretching vibrations of

C-C bonds and the deformation vibrations of CH_2 and CH_3 groups. As demonstrated in our previous study [7], the copolymer spectra depend significantly on the 1-hexene content. In particular, the relative intensities of the bands around 1060, 1130, 1295, and 1415 cm^{-1} decrease with the increase in the content of 1-hexene. On the contrary, a concomitant increase in intensities of the broad bands with peak positions at 1080 and 1305 cm^{-1} is also observed.

The lines at 1060 and 1130 cm^{-1} correspond respectively to the asymmetric and symmetric stretching vibrations of C-C bonds of *trans*-conformers localized in both the crystalline and amorphous phases of PE [9]. The line at 1415 cm^{-1} is assigned to the bending vibrations of CH_2 groups of *trans*-conformers in the PE orthorhombic crystalline phase [9]. The broad band at about 1080 cm^{-1} corresponds to the stretching vibrations of the C-C bonds of *gauche*-conformers in the amorphous phase of PE [9]. The line at 1295 cm^{-1} belongs to the twisting vibrations of the CH_2 groups of *trans*-conformers in both the crystalline and amorphous phases of PE [9]. The band with peak position at 1305 cm^{-1} is assigned to the twisting vibrations of CH_2 groups of macromolecules with significant amounts of *gauche*-conformers in the amorphous phase of PE [9].

Therefore, in the light of the above assignment, the changes observed in the Raman spectra of the CEHs indicate that the increase in 1-hexene content leads to a decrease in the content of crystallites having the PE-like orthorhombic crystal lattice and in the total content of *trans*-conformers. Simultaneously, the content of *gauche*-conformers in the amorphous phase of CEHs increases.

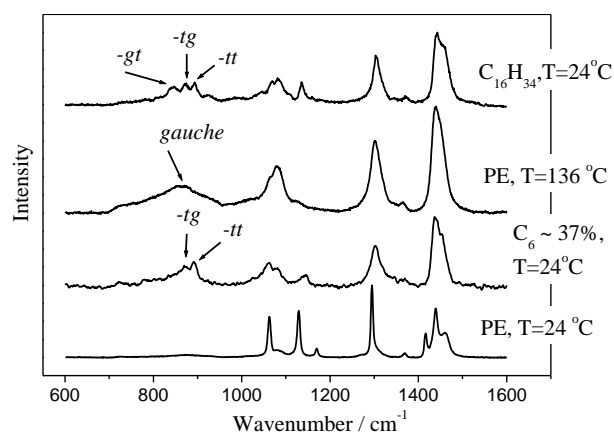


Fig. 2. Raman spectra of the neat PE, recorded at 24 and 136°C , the CEH with 37% of 1-hexene, and the n-alkane $\text{C}_{16}\text{H}_{34}$.

In Fig. 2, the Raman spectra of the CEH with 37% of 1-hexene, neat PE film, PE melt, and of liquid (at normal conditions) n-alkane $\text{C}_{16}\text{H}_{34}$ are compared. Note that the relative content of CH_2 and CH_3 groups is close for the n-alkane $\text{C}_{16}\text{H}_{34}$ and the CEH

with 37.0% of 1-hexene. The crystallinity for all these samples, except the PE film, is equal to 0. The crystallinity of the neat PE film is 60 % from X-ray diffraction analysis.

According to the results of the papers [7,10-12], the Raman bands at 870 and 890 cm^{-1} in the spectrum of the CEH with 37.0% of 1-hexene (see Fig. 2) belong to the stretching vibrations of C-C bonds of the terminal segments $-(\text{CH}_2)_4-\text{CH}_3$ in *-tg* and *-tt* conformers, respectively. Also, the broad band spreading from 830 to 910 cm^{-1} was assigned to the vibrations of *gauche*-conformers [7,10-13]. Therefore, the presence of these spectral features evidences a significant proportion of *-tg* and *-tt* conformers in the lateral chains of the CEH with 37.0% of 1-hexene as well as a significant amount of *gauche*-conformers in the copolymer macromolecules.

Table 1 summarizes the melting temperature and crystallinity of CEHs, based on DSC and Raman spectroscopy data. The CEH crystallinity, based on Raman data, is calculated by using the formula [9]:

$$CR_2 = \frac{I_{1415}}{(I_{1295} + I_{1305}) \times k}, \quad (1)$$

where I_{1415} , I_{1295} , and I_{1305} are the integral intensities of the lines at 1415, 1295, and 1305 cm^{-1} , respectively, and k is a normalization coefficient, which is determined by the experimental conditions of recording the Raman spectra. For our experiments this coefficient was equal to 0.43. This value was calculated from Raman spectra of solid n-alkanes.

It is clear from Table 1 that the CEH crystallinity, based on two methods – DSC and Raman spectroscopy, consistently decreases with the increase in 1-hexene content.

Table 1. Melting temperature and crystallinity of CEHs, based on DSC and Raman spectroscopy data

1-hexene content in CEH, mole %	T_m , °C DSC	CR_1 , % DSC	CR_2 , % Raman
0	128	65	55
1.9	134	37	46
5.3	129	35	36
7.4	98	0	5
10.9	-	0	5
19.0	-	0	0
37.0	-	0	0

Summing up, we have found that the CEH structure and the Raman spectra depend strongly on the 1-hexene content. Increase in the 1-hexene content leads to decrease in the content of the PE-like orthorhombic crystalline phase and in the total content of *trans*-conformers. Simultaneously, the

increase in the content of *gauche*-conformers is observed. We have demonstrated that the CEH crystallinity can be quantified by using the equation suggested for neat PE [9]. The Raman signature at about 800 cm^{-1} provides information about the conformations of the lateral chains of the CEHs with high 1-hexene content.

Random Copolymers of Propylene and α -Olefins

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}), and 1-octene (C_8H_{16}) were synthesized in the medium of liquid propylene over homogeneous metallocene catalyst $\text{rac-Me}_2\text{Si}(4\text{-Ph-2-MeInd})_2\text{ZrCl}_2$, activated by methylaluminoxane. For the sake of comparison, two samples of neat PP were synthesized using catalysts - $\text{rac-Me}_2\text{Si}(4\text{-Ph-2-MeInd})_2\text{ZrCl}_2$ and $\text{C}_2\text{H}_4(5,6\text{cyclopenta-2-MeInd})(\text{Flu})\text{ZrCl}_2$.

Crystallinity of these samples, based on X-ray analysis data, was 73 and 10%, respectively.

The mole content of the comonomers in the copolymers was measured by NMR C^{13} . Detailed description of the synthesis, X-ray analysis and DSC data, and mechanical characteristics of the copolymers were published earlier [14-18]. In particular, it was found that the copolymers become more elastic with growing content of the incorporated monomer.

Isotactic PP can be found in smectic form and in α , β , and γ crystalline forms, which correspond respectively to the monoclinic, hexagonal, and orthorhombic lattices [19,20]. Only the α modification of PP has commercial importance. The X-ray analysis of the samples showed that the neat PP contains only crystallites of the α -modification. Minor traces of the γ -modification were found in several copolymers. The X-ray analysis and DSC data revealed that the copolymer crystallinity decreased as the content of the incorporated monomer increased.

The Raman setup and the spectra acquisition parameters were the same as already described above.

In our recent papers [21-23] we presented Raman studies of the copolymers of propylene with α -olefins. Here we summarize all the previous results with the aim to make general conclusions on the dependence of the copolymer structure and Raman spectra on the chemical structure and content of the comonomers.

As an example, Fig. 3 demonstrates the Raman spectra in the range of the stretching vibrations of C-C bonds and deformation vibrations of CH_2 and CH_3 groups of random propylene/1-butene

copolymers (CPBs). For comparison, we also present Raman spectra of two neat PP samples with crystallinity of 73 % (bottom spectrum) and 10% (top spectrum). The most significant spectral alterations related to the change in propylene content were observed at the two lines at 809 and 841 cm^{-1} .

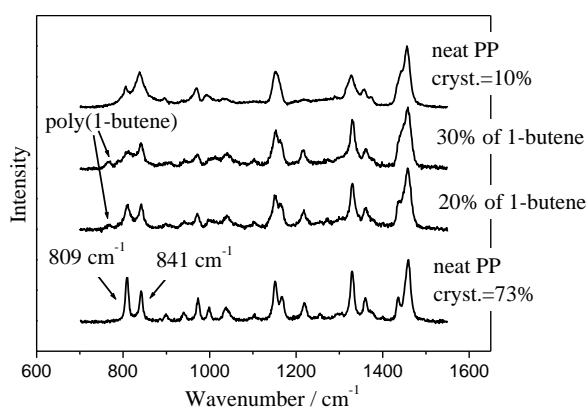


Fig. 3. Raman spectra of the CPBs and neat PP.

A Raman method for the determination of the phase composition of neat isotactic PP was proposed in reference [24]. The method is based on the assumption that three Raman lines at about 809, 841, and 830 cm^{-1} belong to three different phases of isotactic PP. Firstly, the 809 cm^{-1} line corresponds to the vibrations of PP isotactic chains in helical conformation in the crystalline phase [24]. This line was observed in the Raman spectra of all crystalline modifications of isotactic PP [19]. Secondly, the 841 cm^{-1} line is associated with the vibrations of PP isotactic chains in helical conformation, but having isomeric defects [24], and thus localized in the amorphous phase. Thirdly, the relatively broad and weak band at 830 cm^{-1} belongs to the vibrations of non-helical chains in the amorphous phase [24]. Therefore, the content of each PP phase can be determined by relative integral intensity of the corresponding line to the reference intensity that is the sum of the integral intensities of all three lines [24].

It can be seen from Fig. 3 that the intensities of the lines at 809 and 841 cm^{-1} monotonically decrease with the increase in the 1-butene content. The 809 cm^{-1} line exhibits faster intensity decrease. That means that the content of isotactic chains in helical conformation in both the crystalline and amorphous phases decreases with the growth of the 1-butene content. However, the content of helical chains in the crystalline phase decreases faster than that in the amorphous phase.

The line at about 767 cm^{-1} (see Fig. 3) is due to the formation of sufficiently long butene sequences in the copolymer chain. This conclusion perfectly agrees with the X-ray analysis data, which also

have revealed the appearance of polybutene at high contents of 1-butene [18].

After analyzing and comparing the data for all the propylene copolymers under study [21-23] we conclude that the copolymer Raman spectra exhibit very similar monotonic alterations with a change in the propylene content. Noteworthy, the deconvolution analysis of the copolymer spectra has not revealed a third line at about 830 cm^{-1} (corresponding to non-helical chains in the amorphous phase). Thus, we have considered the ratio $I_{809}/(I_{809} + I_{841})$ of integral intensities of the lines at 809 and 841 cm^{-1} as the Raman measure of the content of crystalline phase of isotactic PP in our copolymers. Fig. 4 shows this ratio as a function of the incorporated monomer content. The 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 of the contents of both monomers.

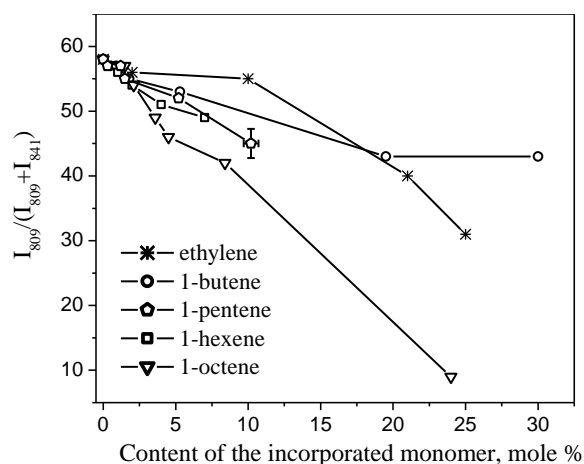


Fig. 4. The crystallinity of the propylene/olefin copolymers, based on the Raman spectroscopy data, as a function of the incorporated monomer content.

The intensity ratio $I_{809}/(I_{809} + I_{841})$ decreases with the growth of the content of the incorporated monomer (see Fig. 4). This clearly indicates a reduction in the copolymer crystallinity. In general, the ratio $I_{809}/(I_{809} + I_{841})$ lowers faster with complication in the structure of the incorporated monomer, except 1-butene. The crystallinity of the propylene/1-butene copolymers decreases slower as 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 the unit cell dimensions [18].

It is worth to mention that at low content of the incorporated monomer (less than 2 mole %) the decrease in the copolymer crystallinity slightly depends on the size of the incorporated monomer

(see Fig. 4). At high content of the incorporated monomer the copolymer crystallinity lowers faster as the size of the incorporated monomer increases.

In summary, the crystallinity and conformational order in the propylene-based copolymers decrease with the increase in the incorporated monomer content, and this tendency is more pronounced with the increase in the size of the incorporated monomer unit. The values of the copolymer crystallinity, determined by Raman spectroscopy, X-ray diffraction analysis, and DSC, are fully consistent, and also explain well the change in the copolymer mechanical properties [14-18].

Conclusions

Raman spectroscopic investigation of a number of ethylene and propylene copolymers have led us to the general conclusion that the conformational composition and the phase state of copolymer macromolecules depend strongly on the content and chemical structure of the incorporated monomer. General tendency is the decrease in crystallinity and conformational order with the growth of the incorporated monomer content. Raman spectroscopy is therefore a rather informative and convenient tool for detailed structural characterization of random copolymers of ethylene and propylene.

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