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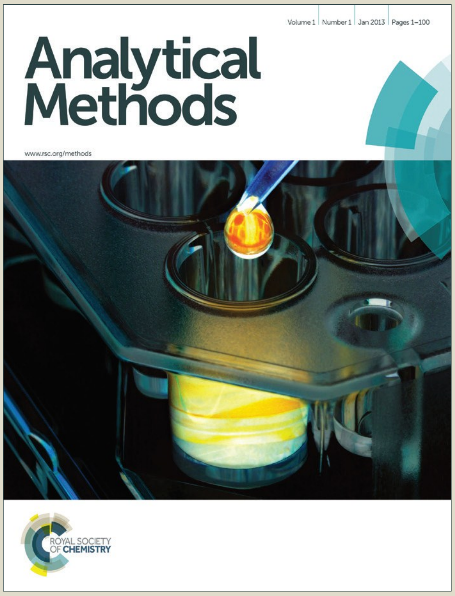

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Raman Spectroscopy as a non-destructive tool to quantify the comonomer content in ethylene/1-olefin copolymers

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Abstract:

Ethylene/1-olefin copolymers, ranging from 1-butene to 1-octadecene, have been studied with Raman spectroscopy and the spectral changes upon comonomer incorporation have been analyzed. The Raman spectra of ethylene/1-olefin copolymers are characterized by a band ensemble in the lower frequency region below 1000 cm^{-1} which is a characteristic scattering from the comonomer segments. The spectra show bands due to scattering from the polyethylene sequences which also reflect the effect of the morphological changes occurring with the increasing comonomer content. By correlating the bands characteristic of the comonomer to those of the ethylene sequences, an internal intensity standard was identified. This also caters to the effect of the experimental parameters such as sample focus and spectral acquisition time for calibration of the comonomer content. This approach was also extended to amorphous ethylene/norbornene copolymers and a similar method for quantification was developed. The major advantages of this method are the minimum amount of sample preparation, and the low sample size, enabling even micrograms of the sample to be measured. Due to these, quantification with Raman spectroscopy is uniquely suited for online quality control and liquid chromatography which require a fast and robust analytical methodology.

Keywords:

Raman spectroscopy, polyethylene, ethylene/1-olefins, comonomer content

Introduction:

Polyethylene (PE) is one of the most important industrial polymers finding a wide range of applications in durable and consumable goods, with a global consumption soaring to 76 million tons in 2010. An excellent cost/performance ratio, recyclability, ease of synthesis and processability have made the market for these polymers to grow continuously [1, 2]. PE can be classified into the homopolymer and semicrystalline copolymers of ethylene with 1-olefins containing up to 20 mol % of comonomer (Linear Low Density Polyethylene, LLDPE). Typically, 1-butene, 1-hexene and 1-octene are used as the comonomer with ethylene. Until the late 1980's PE was synthesized by free radical polymerization or by heterogeneous transition metal catalysts. The early 1990's saw the addition of metallocene catalysts to the portfolio of catalyst systems [1-5] which allow the production of copolymers which are narrowly distributed with regard to molar mass and comonomer incorporation [6]. Such, and further advances in the catalyst and process technology thus helped in gaining a better control over the structure dependent performance attributes of PE copolymerized with 1-olefins such as toughness, crack resistance and optical properties [6]. The comonomer content is a fundamental molecular parameter, which strongly influences the macroscopic polymer properties. As a consequence, there continues to be a need for analytical techniques, which are fast and require minimum effort with regard to sample preparation for quantification.

Nuclear Magnetic Resonance (NMR) has been widely used for structure elucidation of ethylene/1-olefin-copolymers and to quantify the comonomer content [7]. NMR is specific in terms of acquiring information about the microstructure such as tacticity [8], inverse insertion [9] and comonomer sequence distribution [10]. Being an absolute technique, NMR does not require a calibration, however quantitative measurements require significant amounts of sample, with the mass range depending on instrumentation and experimental parameters. Additionally, sample preparation may pose a bottleneck in high throughput environments. Fourier Transform Infrared Spectroscopy (FT-IR) has also been shown capable of such quantification but has several limitations [11, 12]. The measurement can be carried out in Attenuated Total Reflectance (ATR) and transmission mode. The first one is a surface technique, as the spectral information is retrieved from a few microns below the sample surface. The obtained spectra are affected by a number of experimental parameters such as the applied pressure, the surface area of contact and the change in the refractive index with the penetration into the sample [13]. However, quantitative information can only be retrieved from measurements in transmission mode which requires significant quantities of sample, typically a few grams, and intensive sample preparation.

Raman spectroscopy is another method of vibrational spectroscopy, which is sensitive to composition and morphological parameters like orientation and degree of crystallinity. The short spectral acquisition times and minimal sample preparation make it a predestined technique to analyze polymer blends, copolymers and polymer composites. The interaction of PE with highly conductive fillers such as carbon nanotubes has been studied by analyzing the band shifts in the Raman spectra of the nanotubes upon intercalation of PE in the nanotube bundles [14, 15]. PE/ polypropylene (PP) blends have also been quantified and being thermodynamically immiscible [16], the phase composition and crystallinity for the individual blend components has also been determined [17].

The Raman spectrum of PE is well understood and the fundamental modes of vibration have been assigned [18-20]. The internal mode region of the spectrum has been grouped into three frequency regions, namely the C-C stretching region between 1000 cm^{-1} and 1200 cm^{-1}, the CH_2 twisting modes near 1300 cm^{-1} and the CH_2 bending modes between 1400 cm^{-1} - 1500 cm^{-1} [21]. Subtle changes in the Raman spectra of olefin copolymers upon comonomer incorporation (1-olefins) have been observed, but have not been developed into a tool to quantify the comonomer content. For copolymers of propylene with 1- olefins, changes in the intensity of the bands at 809 cm^{-1} and 841 cm^{-1} were observed with increasing content of the incorporated comonomer [22]. The first of these bands corresponds to vibrations of the helically oriented PP chains in the crystalline phase, while the second one is associated with vibrations of the helically aligned PP chains with significant amounts of conformational defects, localized in the amorphous phase. When small amounts (0-20 mol %) of 1-olefinic comonomers are copolymerized with ethylene, the changes reflected in the Raman spectra are minute, and these finite details have not gained much attention to be useful for any quantification. For the case of ethylene/1-hexene copolymers changes in the Raman spectra were identified, but have not been developed as a tool for quantification of the comonomer content [23].

So far, analysis of PE by Raman spectroscopy has been limited to deriving the density, degree of crystallinity, and melting point from multivariate analysis of the Raman spectra [24, 25]. Mauler et al. investigated the influence of comonomer content on the degree of crystallinity and dynamic mechanical properties of ethylene/1-octene copolymers [26]. The Raman spectra were analyzed and a decrease in the degree of crystallinity was observed. Henceforth, developing a fast, accurate and robust method to quantify the comonomer content in ethylene copolymers by Raman spectroscopy would extend this technique further than crystallinity and density measurements, making it suitable for a rapid identification of minute sample amounts. The need for such a tool exists for quality control in polymer synthesis. A further area where a compositional analysis of small amounts of sample is required can be found in liquid chromatography, where, after removing the chromatographic solvent, trace amounts of the remaining polymer have to be analyzed. The non-destructive nature of Raman spectroscopy renders it also a good potential in forensic analysis and the analysis of very small inhomogenities in processed samples e.g., multi-layer films. In this study, we exploit the subtle changes in the Raman spectra of PE upon comonomer incorporation and understand these changes to present a new method establishing Raman spectroscopy as a tool for comonomer quantification for several industrially important ethylene/1-olefins.

Experimental:

Samples:

Samples used are detailed as in Table I below. All samples were synthesized using metallocene catalyst systems.

Table I: Sample description

Copolymer type	Notation	Content [Mol % of 1-olefin comonomer determined through NMR]	Dispersity	Supplier
ethylene /1-butene	E_{BUT}	1.57 – 10.32	3.2-4.3	Braskem, Brazil
ethylene /1-hexene	E_{HEX}	2.2 – 20.7	1.8-2.9	O. Boyron, Univ. of Lyon, Lyon France
ethylene /1-octene	E_{OCT}	0 – 13.9	2-2.2	The Dow Chemical Company, USA
ethylene /1-octadecene	E_{OCTD}	1.7-3.3	1.9-2.6	O. Boyron, Univ. of Lyon, Lyon France
ethylene /norbornene	E_{NOR}	24.5 – 60.75	1.8-1.9	Topas Advanced Polymers GmbH, Germany

Raman Spectroscopy:

Raman measurements were carried out using a WITec alpha 500 spectroscopy system. For measurements on pellets/powders, a 20× (NA 0.4) microscope objective was used to focus the laser beam and to collect the scattered light. Laser radiation having a wavelength of 532 nm with a power of about 50 mW was employed as an excitation source. The scattered light was analyzed in a 600 mm^{-1} grating spectrometer at a spectral resolution of about 1 cm^{-1}. After focusing the sample manually with the microscope, the laser spot was positioned to accumulate a single spectrum with an acquisition time of 2 s and 10 accumulations were carried out per measurement. Each spectrum was smoothened by using a Savitzky-Golay method and background subtracted.

Results and Discussions:

The Raman spectra of E_{OCT} copolymers with a comonomer content ranging from 0 – 13.9 mol % in the range of the C-C stretching and the deformation vibrations of CH_2 and CH_3 groups are shown in Fig. 1.

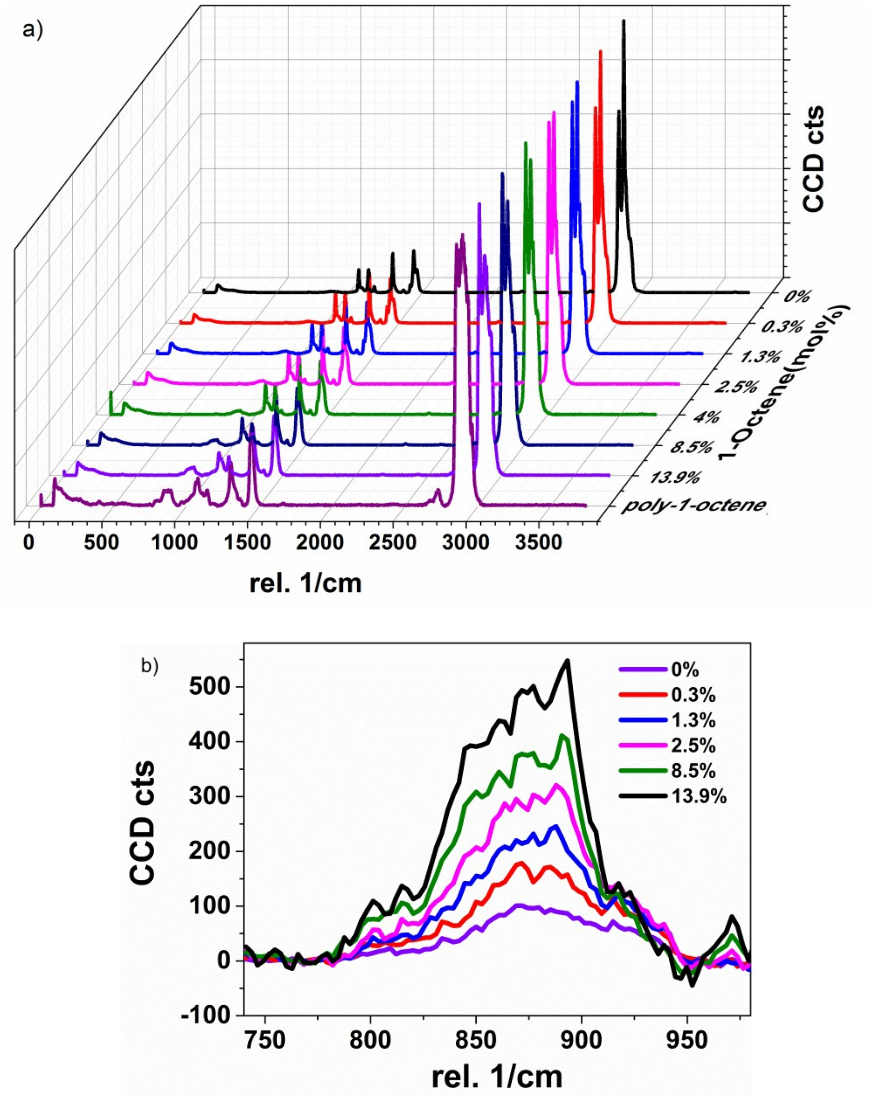

Fig. 1: a) Raman spectra of E_{OCT} with varying 1-octene content and b) Raman spectra of E_{OCT} showing the band ensemble below 1000 cm^{-1}

The spectra show pronounced differences with increasing content of the comonomer. The characteristic bands for the ethylene sequences show a marked decrease in intensity and simultaneously, the intensity of the band at 1416 cm^{-1} which has been widely used to measure the degree of crystallinity [21] also decreases. The bands in the C-C stretching region assigned at 1058 cm^{-1}, 1126 cm^{-1} and 1166 cm^{-1}, the twisting region at 1295 cm^{-1} and the bending region at 1439 cm^{-1} [20] follow a similar trend. Interestingly, the frequency region below 1000 cm^{-1} shows a band ensemble which is characteristic for the 1-octene comonomer as can be recognized from the spectrum of poly-1-

octene. This band ensemble, normalized with respect to the highest intensity band at 1058 cm^{-1}, shows a significant increase in intensity with comonomer incorporation (Fig. 1 b).

A method to predict the crystallinity of PE by Raman spectroscopy was developed by investigating the spectra of bulk-crystallized PE [19]. The spectra were analyzed to determine the content of the three distinct polymorphs, namely the orthorhombic crystalline phase, a melt like amorphous phase, and a disordered anisotropic phase. The intensity of the band at 1416 cm^{-1} was used to deduce the relative fraction of segments present in the orthorhombic phase (α_c). The relative amount of segments forming the liquid like amorphous phase (α_a) was obtained from two bands centered in the twisting region at 1303 cm^{-1} or in the stretching region at 1080 cm^{-1}. The interfacial phase (α_b) was proposed as a domain wherein the chains are in the extended *trans*-configuration, but have lost their lateral order, and the relative amount of segments forming this phase was calculated as $\alpha_b = 1 - \alpha_a - \alpha_c$. With increasing 1-octene content the Raman band characteristic for measuring the crystallinity (α_c) in the PE segments at 1416 cm^{-1} decreases in intensity and remains as a small shoulder in the sample with 8.5 mol % 1-octene. Similarly, with the increase in comonomer content the band at 1166 cm^{-1} merges with the more intense band at 1126 cm^{-1}. The alkyl branches of the comonomer are not able to enter the crystal lattice [22], and hence, an increase in the fraction of α_a and α_b is observed.

Thus, the Raman spectra reflect the effect of the decrease in band intensity of the characteristic bands from the PE segments due to the decrease in the ethylene content, the effect of the comonomer segments seen as a band ensemble and the associated changes in the phase composition due to comonomer incorporation. Broadening has also been observed in these characteristic PE bands, which is deduced to be due to the increasing content of 1-octene which shows several bands overlapping in the same frequency region as the PE segments (Fig. 1b). The above three effects limit the applicability of using solely the Raman bands of the PE segments to determine the comonomer content. However, before selecting suitable bands for quantification it has to be taken into account that the intensity of the Raman spectra varies to a great extent with experimental parameters, taking in the first instance the spectral acquisition time and the sample focus/depth [27].Fig. 2 shows the Raman spectra of linear PE measured with different acquisition times after being focused with the microscope.

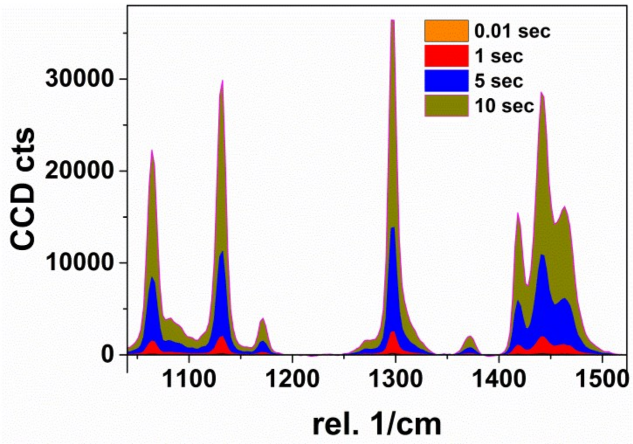

Fig. 2: Variation in signal intensity of the Raman spectra of linear PE with spectral acquisition times.

A clear dependence of the signal intensity on the acquisition time can be seen, and the intensity of the Raman signal increases with the spectral acquisition time. Additionally, in order to maximize the signal intensity and reduce the signal/noise ratio, spectral acquisition has to be preceded by proper focusing of the sample. The latter is, however, a very subtle parameter often depending on the skill of the operator, and even a few microns shift in the sample focus can have a significant influence on the signal intensity. This in turn would have a direct impact on the height/area of individual bands, thus again reducing their applicability as the sole criterion to determine the comonomer content in samples.Fig. 3 shows this effect where a sample was focused manually (same spectral acquisition time) and then Raman spectra were acquired at one micrometer levels above and below the sample. The intensity of the bands at 1295 and 1439 cm^{-1} have been plotted with the variation in sample height.

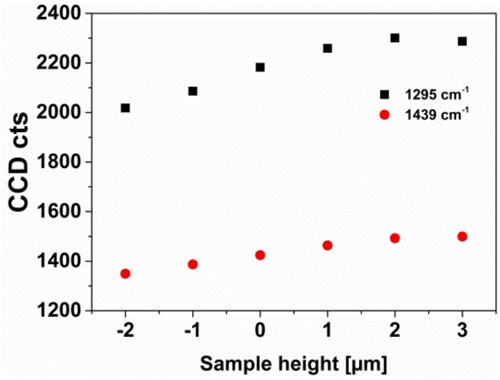

Fig. 3: Effect of sample focusing on the scattering intensity the sample

A significant variation in band intensity is seen with the shift in focus above and below the sample.

Using the spectral acquisition time of 2 seconds and focusing the samples manually, the intensity of the band at 885 cm^{-1} in the band ensemble of E_{OCT} below 1000 cm^{-1} was correlated with the comonomer content as shown inFig. 4 below.

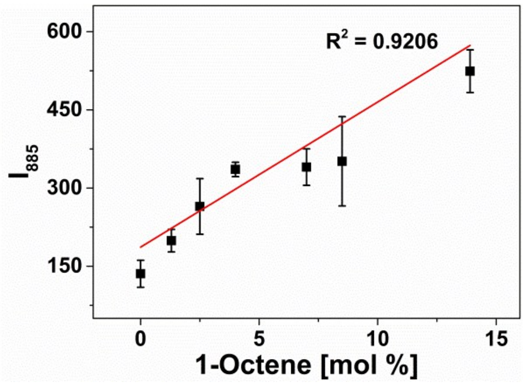

Fig. 4: Band intensity I_{855} as a function of 1-octene content

The effect of the experimental parameters on the intensity of the band at 885 cm^{-1} for determining the comonomer content is evident inFig. 4 but the correlation with the comonomer content is non-linear. Thus, for developing a method to correlate these spectral changes upon comonomer incorporation and also eliminating effect of the experimental parameters on the spectra, an internal intensity standard/reference for normalizing the intensity of the band ensemble is required. Hence, the ratio of the band intensities of the characteristic bands from the ethylene sequences to the characteristic bands emerging from the comonomer was investigated to find an internal standard which also minimizes the effect of the spectral overlap due to scattering from the comonomer sequences. Normalizing the band intensity ratio would cancel out the effect of sample focusing, and thus, reduce the number of parameters to find a suitable correlation for quantification. The high intensity bands characteristic of the PE segments at 1058 cm^{-1} (C-C stretching), 1126 cm^{-1} (C-C stretching), 1295 cm^{-1}(C-C twisting) and at 1439 cm^{-1}(C-C bending) were selected. The band ensemble characteristic for the comonomer from 700 cm^{-1}- 950 cm^{-1} shows four major bands at 844 cm^{-1}, 855 cm^{-1}, 875 cm^{-1} and 885 cm^{-1} respectively. The ratio of the intensity of the strongest band amongst these at 885 cm^{-1} to these characteristic PE bands was probed to determine a correlation which accounts for the effect of increasing comonomer content, the accompanying decrease in the ethylene content and intrinsic changes in the ratio of polymorphs. The band ratios with the respective standard deviation in the measurements in correlation with the comonomer content are presented inFig. 5.

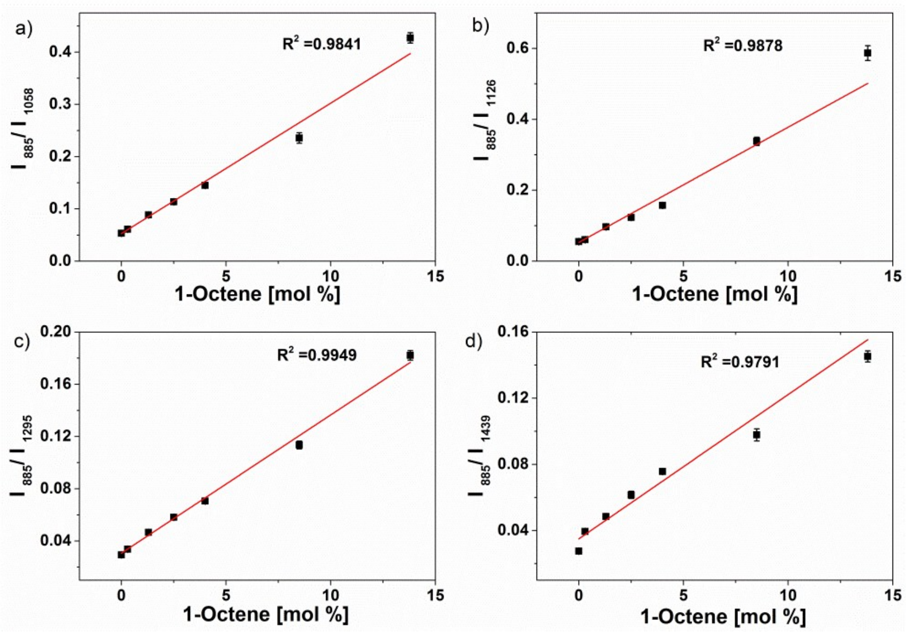

Fig. 5: Band intensity ratios a) I_{855}/ I_{1058} b) I_{855}/I_{1126} c) I_{855}/I_{1295} d) I_{855}/I_{1439} plotted as a function of 1-octene content

As seen from Fig. 5, the band at 1295 cm^{-1} in the C-C twisting region yielded the best correlation with an R^2 value of 0.9949. The band at 1439 cm^{-1} in the C-C bending region shows broadening and overlaps with a characteristic band of 1-octene at 1444 cm^{-1} yielding an R^2 value of 0.9791. This band is also seen to merge with the one at 1416 cm^{-1} used to determine the crystallinity of PE as discussed previously, and the combined effect of these two bands leads to a non-linear correlation. The band at 1058 cm^{-1} in the C-C stretching region yields an R^2 value of 0.9841, but starts to develop a shoulder due to merging with the characteristic bands of 1-octene at 1059 and 1080 cm^{-1} when the 1-octene content is increased. The other band in the stretching region at 1126 cm^{-1} gives an R^2 value of 0.9878 also merging with the band characteristic for the 1-octene comonomer at 1140 cm^{-1} showing non-linearity. Most of the characteristic Raman bands for 1-octene are in close vicinity to those for PE, however, the effect on the Raman scattering intensity of the C-C twisting mode was the least and was observed to fit excellently correlating with the comonomer content.

To verify the reproducibility and the robustness of this method, ten independent measurements were carried out per sample and a collective average of the band ratios was plotted. The deviation from the linear fitting was observed to be negligible, verifying the applicability and robustness of the method.

The Raman spectra of E_{BUT} with varying content of 1-butene in the frequency range 600-1070 cm^{-1} are shown in Fig. 6.

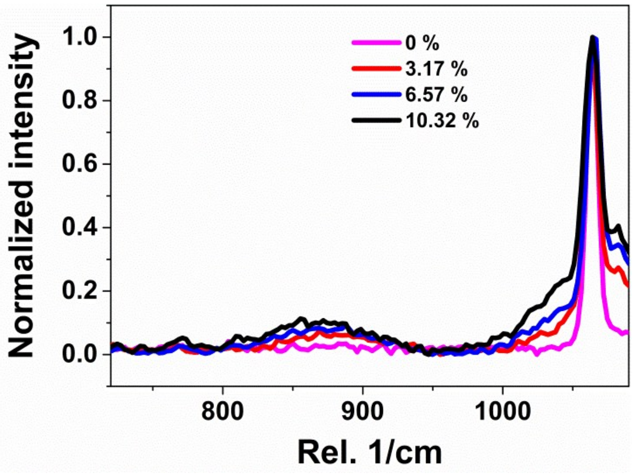

Fig. 6: Raman spectra of E_{BUT} normalized to the high intensity band at 1058 cm^{-1}

With increasing comonomer content, similar changes in the Raman spectra as observed for E_{OCT} can be seen for E_{BUT} with the decrease in intensity of ethylene sequences and the appearance of a band ensemble in the region below 1000 cm^{-1}. The latter shows a clear increase in intensity with increasing comonomer content, but was difficult to resolve in terms of individual bands due to the presence of several bands having similar intensity. On a closer inspection, the band at 869 cm^{-1} could be identified in the ensemble showing the highest variation in intensity with comonomer content. Using an analogous approach as for E_{OCT}, the bands from the three different modes of vibration for the ethylene sequences were selected to develop a method to quantify the 1-butene comonomer. The intensity of the band at 869 cm^{-1} was chosen for drawing out a correlation with the bands from the ethylene sequences to deduce a method for quantifying the content of E_{BUT}.Fig. 6 shows the intensity ratio of the band at 869 cm^{-1} to those arising from the ethylene.

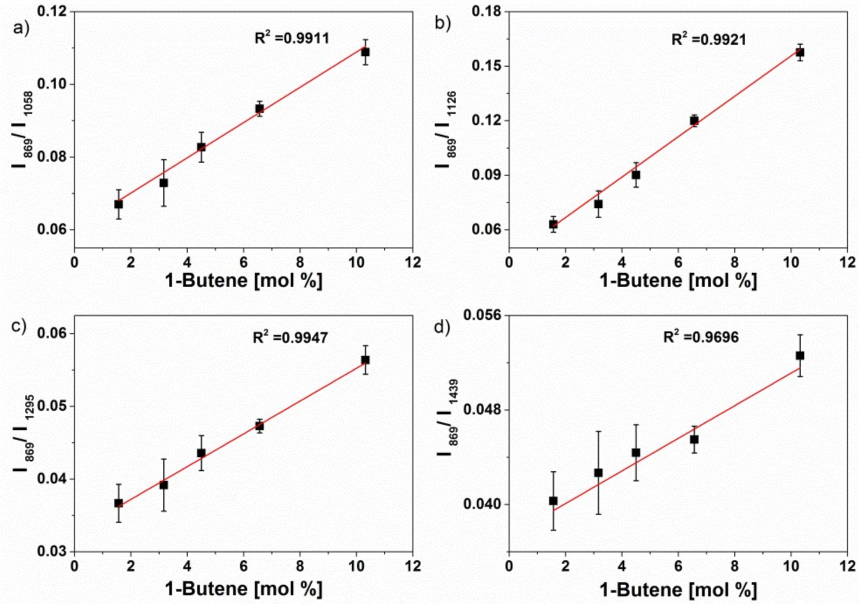

Fig. 7: Band intensity ratios a) I_{869}/ I_{1058} b) I_{869}/I_{1126} c) I_{869}/I_{1295} d) I_{869}/I_{1439} as a function of 1-butene content

In this case as well, the intensity ratio of the band at 869 cm^{-1} to the band in the C-C twisting region at 1295 cm^{-1} showed a more accurate correlation with the 1-butene content than the bands in the stretching and bending regions. The band at 1439 cm^{-1} in the C-C bending region was especially influenced by scattering from the 1-butene sequences giving an R^2 value of 0.9696. Hence, the effect of the spectral overlap of the scattering from the 1-butene sequences with the ethylene sequences and its relation with the characteristic band of the 1-butene sequences found the best synchronization with the band at 1295 cm^{-1} yielding an R^2 value of 0.9947 for quantification of E_{BUT}.

The Raman spectra of E_{HEX} with varying content of 1-hexene in the frequency range from 600-1070 cm^{-1} are shown inFig. 8.

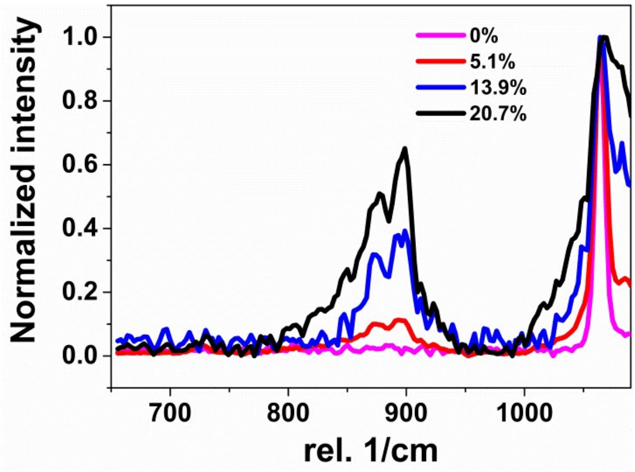

Fig. 8: Raman spectra of E_{HEX} normalized to the high intensity band at 1058 cm^{-1}

E_{HEX}, similar to E_{OCT} and E_{BUT} also shows a band ensemble in the low frequency region below 1000 cm^{-1} which grows in intensity with comonomer incorporation. The ensemble shows the presence of two prominent bands at 879 cm^{-1} and 893 cm^{-1}, with the one at 893 cm^{-1} being dominant, and in addition showing a variation in intensity with 1-hexene content. Therefore, the latter was selected as representative of 1-hexene and was used to find a correlation with the characteristic bands in the different vibrational regions for the ethylene sequences as selected earlier. The effect of band overlap and changes in the bands from the ethylene sequences was studied and the best fit for obtaining the 1-hexene content through the Raman spectra of E_{HEX} was identified (Fig. 9).

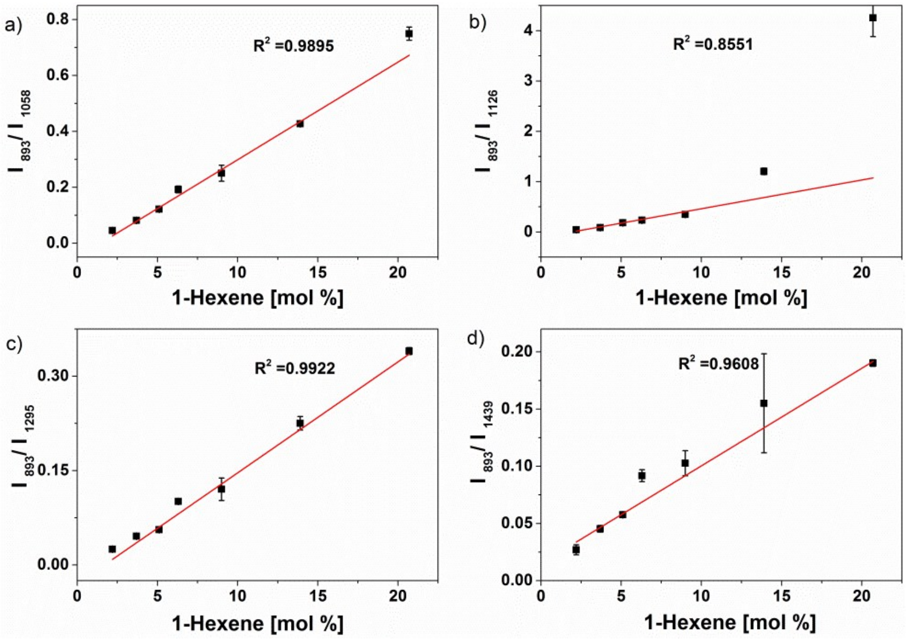

Fig. 9: Band intensity ratios a) I_{893}/ I_{1058} b) I_{893}/I_{1126} c) I_{893}/I_{1295} d) I_{893}/I_{1439} as a function of 1-hexene content

In this case, similar to E_{OCT}, the best correlation was found with the intensity ratio of the band at 893 cm^{-1} characteristic of the 1-hexene comonomer to that of the band in the C-C twisting region at 1295 cm^{-1} yielding an R^2 value of 0.9922.

The Raman spectra of E_{OCTD} with varying content of 1-octadecene in the frequency range from 600-1070 cm^{-1} are shown in Fig. 10.

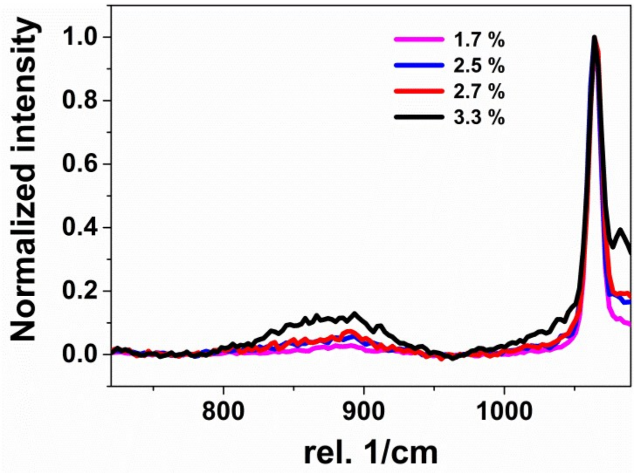

Fig. 10: Raman spectra of E_{OCTD} normalized with regard to the high intensity band at 1058 cm^{-1}

The spectra show the appearance of a band ensemble in the low frequency region below 1000 cm^{-1} as seen previously for other 1-olefins. The increasing content of 1-octadecene is also characterized by the increase in the intensity of this ensemble which becomes increasingly prominent with the increasing comonomer content. Quantification of E_{OCTD} was carried out using a similar approach of choosing the band ratios of the most prominent band in the ensemble to the characteristic bands from the scattering through the ethylene sequences. The band ensemble in this case was clearly seen, and the highest intensity band at 896 cm^{-1} was used as a representative of the scattering from 1-octadecene and its correlation with the characteristic bands from the ethylene sequences was determined (Fig.11).

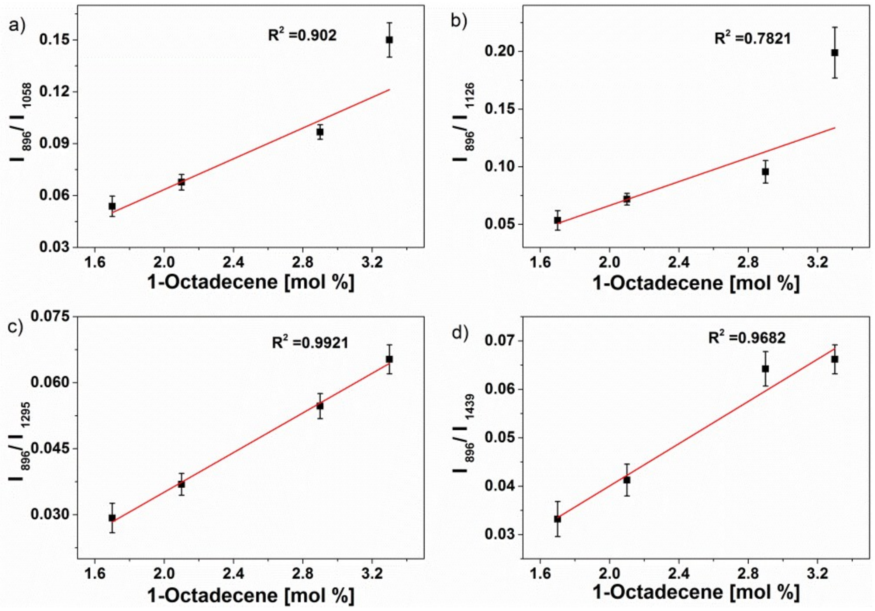

Fig.11: **Band intensity ratios a) I_{896}/ I_{1058} b) I_{896}/I_{1126} c) I_{896}/I_{1295} d) I_{896}/I_{1439} as a function of 1-octadecene content**

In this case for E_{OCTD} as well, the best linear correlation for determining the comonomer content was observed with the band in the C-C twisting region at 1295 cm^{-1}giving an R^2 value of 0.992. Here too, the effect of the spectral overlap of the scattering through 1-octadecene is pronounced in the C-C bending region.

Hence, it can be concluded that the band in the C-C twisting region at 1295 cm^{-1} can be used as an internal intensity standard for normalizing the intensity of the band ensemble to quantify the comonomer content of LLDPE. The Raman spectra of the comonomers from 1- butene to 1-octadecene have been studied and the intensity of this band to be used as an internal standard appropriate for quantification has been verified.

Quantification of Cyclic Olefin Copolymer (COC) norbornene

An interesting question is, if such a method to quantify the comonomer content can also be applied to ethylene copolymers of low crystallinity. Cyclic Olefin Copolymers (COCs) are commercially important materials, which due to their superior optical, mechanical, thermal and water barrier properties find a wide range of applications ranging from packaging films, lenses, vials, displays, and medical devices. Norbornene is frequently used as a comonomer with ethylene, including others such as cyclopentene and dicyclopentadiene [28, 29]. Copolymers of ethylene with straight chain aliphatic 1-olefins generally have lower comonomer content (up to 20 mol %) compared to COC's for which the commercially relevant comonomer content ranges from 20-60 mol %. Due to the high comonomer content, these materials are fully amorphous, and extending the applicability of this method of quantification to such amorphous materials would add another line of commercially important materials quantifiable nondestructively. At such a concentration of the comonomer, the spectrum of the comonomer starts dominating, suppressing and overlapping with the dominant bands observed due to the ethylene sequences (Fig. 10).

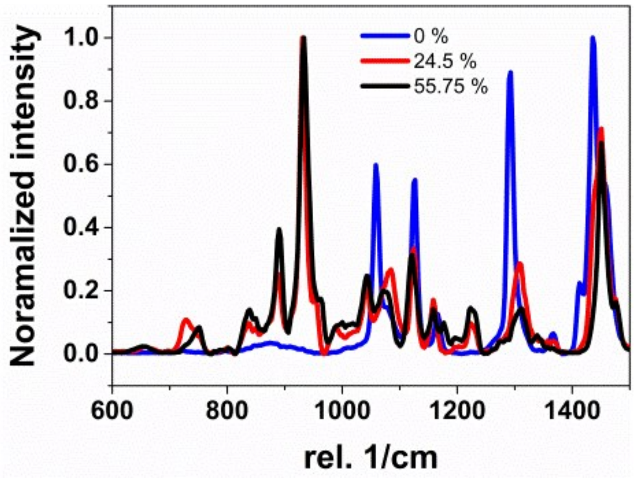

Fig. 12: Raman spectra of E_{NOR}

The bridged cyclic structure in the copolymer gives rise to several high intensity bands from 500 cm^{-1}-1500 cm^{-1}. The bands solely characteristic of the ethylene sequences are not segregable easily apart from the band at 1439 cm^{-1} which can still be seen prominently. To determine the effect of the decrease in the percentage of the ethylene sequences and the increase in the norbornene content through the Raman spectra, the intensity of the band at 1439 cm^{-1} was selected and plotted with respect to the intensity of the band at 1313 cm^{-1} attributed to the cyclic comonomer.

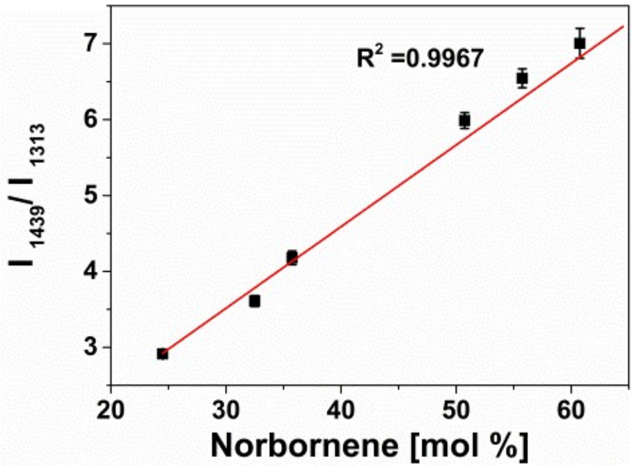

Fig. 13: Band intensity ratio I_{1439}/ I_{1313} as a function of the norbornene content

A good linear correlation (Fig. 13) substantiates the fact that the two bands chosen are appropriate to quantify the content of norbornene in COCs.

Conclusions:

Quantification of the comonomer content in linear low density polyethylene is of enormous importance for many industrial applications such as quality control and sample identification. NMR spectroscopy has been widely used for structure elucidation of copolymers, but quantitative measurements require significant amount of sample and sample preparation may pose a bottleneck, limiting its scope for applications in high throughput analysis and in cases, where measurements are limited by the amount of sample available. In this study, the potential of Raman spectroscopy has been exploited as a fast and nondestructive alternative for comonomer quantification requiring no sample preparation. The Raman spectra of ethylene/1-olefin copolymers, ranging from 1-butene to 1-octadecene show a band ensemble in the lower frequency region below 1000 cm^{-1} which results from the scattering from the comonomer sequences and increases in intensity with increasing comonomer content. Upon comonomer incorporation the spectra reflect the combined effect of the decrease in ethylene content, associated changes in the phase composition of polyethylene and increased scattering from the comonomer sequences. The band ensemble characteristic for the comonomer itself cannot be used for quantification since the intensity of the spectra is affected by the sample focus and the spectral acquisition time. These effects, together with the spectral changes upon comonomer incorporation, have been analyzed to identify an internal standard for normalizing the intensity of the band ensemble. The intensity of the band at 1295 cm^{-1} in the C-C twisting region was found to be appropriate for this purpose also accounting for the effect of the experimental parameters in the spectra. This method has also been extended for determining the comonomer content of cyclic olefin copolymers having low crystallinity where the bands arising due to scattering from the comonomer sequences start dominating. Hence, in this study the Raman spectra of copolymers of ethylene with 1-olefins ranging from 1-butene to 1-octadecene and the cyclic norbornene have been analyzed and a method has been developed to quantify the comonomer content. Due to the minimal sample preparation, fast spectral acquisition time and its nondestructive nature, the Raman spectroscopic approach would be very useful for quality controls. A strong need for such a technique also exists in liquid chromatography where the amounts of sample acquired are regularly very small.

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