Received: 14 August 2018 | Revised: 5 December 2018 | Accepted: 5 December 2018

DOI: 10.1002/jrs.5554

RESEARCH ARTICLE

WILEY Journal of RAMAN SPECTROSCOPY

Characterizing chemical composition of polyolefin-based copolymers from spectral features in the C—H stretching region

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Funding information
Agencia Nacional de Promoción Científica y Tecnológica, Fondo para la Investigación Científica y Tecnológica, Grant/Award Number: PICT14-1919; National Agency for the Promotion of Science and Technology, Grant/Award Number: PICT14-1919

Abstract

The comonomer content of a series of commercial ethylene–octene (Engage®, Infuse®), ethylene–butene (Engage), and ethylene–propylene (Versify®, Nordel®) copolymers is investigated using the Raman spectroscopy. The analysis relies upon the different content of methyl, methylene, and methine groups of each copolymer and focuses on the spectral features of the C—H stretching region. Raman spectra of a series of molecules with well-defined content of methyl, methylene, and methine groups (alkanes and well-defined polymer chains) are first addressed to rationalize the complex spectral features arising from different stretching modes, their Fermi resonance, and the different molecular conformations. Results are interpreted on the base of recent work on the topic. A curve-fitting procedure is proposed to resolve contributions arising from CH_2 and CH_3 groups. The sum of intensity of bands at 2,855 and 2,865 cm^{-1} (symmetric C—H stretching and Fermi resonance) correlates linearly with CH_2 content whereas that at 2,880 cm^{-1} (symmetric C—H stretching) does with CH_3 content. With that base, Raman spectra of ethylene-based copolymers are analyzed to quantify comonomer content. Results are compared with independent results from ^{13}C nuclear magnetic resonance analysis with good agreement between the methods. Overall, it highlights the importance of Raman spectroscopy as versatile tool for process monitoring, quality control, or sample identification not only at academics but also in industrial environments.

KEYWORDS

C—H stretching, chemical composition, copolymers, polyethylene, Raman spectroscopy

1 | INTRODUCTION

Ethylene- and propylene-based polyolefins represent the largest volume of sales in the plastic industry due to their excellent cost/performance value, easy processability, and recyclability. Over the last decades, these commodities have continued evolving. For instance, copolymerization with 1-alkenes (propylene, 1-butene, 1-octene, etc) has been the most effective way of creating new families of materials with improved properties.[1] Ethylene copolymers with elastomeric behavior that retain thermoplastic-like processability, which advantageously

replace traditional nonrecyclable cross-linking rubbers in several applications, or polypropylene copolymers with improved performance at subambient temperatures are some examples of the many new applications niches of polyolefin copolymers.[2,3]

The incorporation of some 1-alkene units in a polyethylene or polypropylene chain introduces the so-called *short branching*, which causes a disruption in chain regularity. The content and distribution of branches along the polymer backbone determine the length of crystallizable sequences so affecting crystal content, melting temperature ranges, and the glass transition temperature of the material. Ultimately, those properties define stress–strain behavior, permeability, temperature ranges of use, processing conditions, or eventual adhesion of the copolymer to other substrates. Thus, comonomer content (and its distribution) becomes the key tool to tailor copolymer properties for targeted applications.

The quantification of comonomer content in 1-alkene-based copolymers is commonly approached by ^{13}C nuclear magnetic resonance (^{13}C NMR), a highly sensitive technique that provides valuable structural information such as comonomer composition and distribution, tacticity, monomer misinsertions, or the presence of regio and stereo defects. As a disadvantage, NMR requires sample preparation, complex instrumentation, and very long acquisition times that turns out not very suitable for industrial environments or rapid in-line determinations. Raman spectroscopy can overcome these limitations with some extra advantages, such as the ability of spatially resolve measurements in the case of Raman microscopy. On the negative side, peak overlapping in Raman spectra frequently impedes the isolation and identification of those structural features that usually appear well resolved in a high-frequency NMR spectrum. At this point, it should also be considered that comonomer contents on the order of 10 mol % for the case of poly(ethylene-co-1-octene) imply that any technique should be able to detect the presence of about one methyl (or one methine) group over 22 methylenes ones.

Most of the Raman studies in polyolefins have been carried out in the low wavenumber and fingerprint C—C region. The longitudinal acoustic modes below 500 cm^{-1} have been used to probe crystal thickness[4,5] or order state of the amorphous phase[6] whereas skeletal modes between 500 and 1,500 cm^{-1} have been useful to quantify crystal content or chain orientation.[7–9] Recently, changes in the Raman spectral profiles of polyethylene chains due to the incorporation of comonomers such as 1-hexene, 1-octene, or propylene have been analyzed, with particular focus in the 500- to 1,500-cm^{-1} region.[10,11] However, the complex spectral patterns composed of several superposed peaks have precluded attempts to establish a reliable method for comonomer quantification.[10] A spectral region much less explored in polymer analytics is that between 2,800 and 3,100 cm^{-1}, where C—H stretching modes arise. These vibrational modes are the strongest features of the Raman spectrum, appear well isolated from the rest of the peaks, and are highly sensitive to structural changes. This spectral region can be useful for the elucidation of chemical composition of polymer chains with comonomers such as ethylene, propylene, 1-butene, or 1-octene as they differ in the proportion of methine, methylene, or methyl groups, and those are expected to yield specific C—H stretching signatures.

The analysis of the C—H stretching region has shown to be challenging and particularly complex, because of the several vibrational modes coupled with Fermi resonance and crystal splittings. Seminal work carried out by Snyder et al. established the basis of spectral assignment and Fermi interactions of methylene units in the C—H stretching region.[12,13] Snyder's work was in major part motivated by the interest in understanding chain ordering in biological membranes, composed of rather long hydrocarbon chains that assemble with majority of CH_2 groups. Less attention has been paid to specific spectral signatures of methyl and methine units until recent years, when several authors have specifically addressed the topic. For instance, Wang et al. examined several short-chain alcohols at the liquid/air interface using the sum-frequency generation (SFG) vibrational spectroscopy, and they found new spectral features of CH_2 and CH_3 groups, which were assigned to Fermi interaction.[14] Very recently, Liu et al published a series of studies using deuteration to isolate specific Raman signatures of the CH, CH_2, and CH_3 groups in 1- and 2-propanol molecules.[15,16] Supported by quantum chemistry calculations, the authors discerned overlapping spectral features arising from each of these groups and provided a well-founded peak assignment.

The application of this new insights in the context of polymer analysis is not only of academic interest but also very useful for process monitoring, quality control, or sample identification in industrial applications.[17] For instance, the development of rapid and reliable methods for quantification of comonomer content in the case of polyolefin-based copolymers would contribute to further extend the application of Raman spectroscopy beyond the well-established crystallinity–density correlations used in industry,[18] thus providing a rather complete product characterization with a single technique. In a wider perspective, the ability to monitor structural changes of a polymer chain due to monomer incorporation has some common roots with other important kind of phenomena such as degradation, cross-linking, or

chemical modification, also addressable within the same framework.

In this work, we approach the problem of quantifying comonomer content on a series of commercial ethylene-based copolymers with 1-butene, 1-octene, and propylene, based upon spectral information of the C—H stretching region. To provide a base for our analysis, the C—H stretching region of a series of alkanes and well-defined polymer chains containing known amounts of CH, CH_2, and CH_3 units is first analyzed and interpreted in the framework of recent work on the topic. The proposed spectral assignment is used to interpret the Raman spectra of a series of copolymers and to predict their comonomer content. Several commercial grades of ethylene–octene (Engage®, Infuse®), ethylene–butene (Engage), and ethylene–propylene (Versify®, Nordel®) copolymers are analyzed. Results of the methodology are primarily compared with those obtained by ^{13}C NMR.

2 | EXPERIMENTAL

2.1 | Samples

Octadecanol, tetradecanol, dodecanol, decane, heptane, octane, pentane, and 2,5-dimethylhexane were purchased from Aldrich. The three Polywax samples (PX500, PX1000, and PX3000), composed by linear polyethylene chains, were provided by Baker–Petrolite. The polypropylene sample (Cuyolen 1100N) was provided by Petroquímica Cuyo. Table 1 summarizes all the characteristics of these samples. Engage, Infuse, Nordel, and Versify are trademarks of commercial grades produced by Dow. Samples were provided in pellets form and used as received.

Table 2 shows the chemical composition of the copolymers, where Engage, Infuse, Nordel, and Versify are referred to as E, I, N, and V, respectively. Characterization of most of the copolymers was carried out by ^{13}C NMR. Representative ^{13}C NMR spectra are shown in Figures S1–S3. The primary information yielded by ^{13}C NMR is comonomer mol % (third column, Table 2) from the analysis of triads (see Supporting Information). The results of the fourth and fifth columns of Table 2 are derived from those of the third column along with the comonomer molecular structure. For instance, the incorporation of 1-butene units implies the addition of two CH_2 groups, one CH and one CH_3 per molecule. Similarly, incorporation of 1-octene implies the addition of six CH_2 groups, one CH and one CH_3 per molecule whereas that of propylene units, it implies the incorporation of one of each of those groups per molecule. More details on the above can be found in the Supporting Information. For some grades, data of comonomer content provided by the manufacturer were also available.[19]

TABLE 1 Chemical composition of the model molecules used in this work

Sample	$CH/CH_2/CH_3$ weight ratio	$CH/CH_2/CH_3$ weight fraction
PX3000	0/150/1[a]	0/0.99/0.01
PX1000	0/49/1[a]	0/0.98/0.02
PX500	0/24/1[a]	0/0.956/0.044
Octadecanol	0/15.7/1	0/0.94/0.06
Tetradecanol	0/11.5/1	0/0.92/0.08
Dodecanol	0/10.1/1	0/0.91/0.09
Decane	0/3.7/1	0/0.79/0.21
Octane	0/2.8/1	0/0.74/0.26
Heptane	0/2.3/1	0/0.7/0.3
Pentane	0/1.38/1	0/0.58/0.42
2,5 dimethyl hexane	0.43/0.45/1	0.23/0.24/0.53
Polypropylene	0.86/0.92/1	0.31/0.33/0.36

[a]Measured by ^{13}C nuclear magnetic resonance.

2.2 | Raman spectroscopy

Raman spectra were acquired in a Renishaw inVia reflex system equipped with charge-coupled device detector of 1,040 × 256 pixels. A 785-nm diode laser (300 mW) was used as excitation source in combination with a grating of 1,200 grooves/mm and slit openings of 65 μm, which yield a spectral resolution of about 4 cm^{-1}. The laser power was kept below 10% to avoid sample damage. A 50× (0.5 numerical aperture) long working distance (8 mm) Leica metallurgical objective was used in the excitation and collection paths. Spectra were typically acquired in 10 s with at least four accumulations. Raman spectra above room temperature were taken in a Linkam stage (THM-600) under N_2 atmosphere.

2.3 | ^{13}C NMR

The ^{13}C NMR spectra were recorded at 120°C with an acquisition time of 1.5 s, pulse width of 74° and pulse delay of 4 s on a Varian Inova 300 spectrometer operating at 75 MHz for ^{13}C. Polymer solutions were prepared with o-diclorobenzene, benzene-d_6 (20 vol %) in a 5-mm sample tube. Copolymer compositions were determined from standard analysis of triads, see also Supporting Information for more details.[20,21]

TABLE 2 Chemical composition of the copolymers used in this work as measured by ^{13}C nuclear magnetic resonance, except where indicated

Sample	Monomer–comonomer	Comonomer mol %	$CH/CH_2/CH_3$ weight ratio	$CH/CH_2/CH_3$ weight fraction
E7447	Ethylene–butene	22.0	0.87/8.45/1	0.084/0.82/0.097
E7256	Ethylene–butene	13.2	0.87/14.24/1	0.054/0.883/0.062
E8130	Ethylene–octene	16[a]	0.86/15.34/1	0.05/0.89/0.058
E8407	Ethylene–octene	12.4 (14[a])	0.88/18.96/1	0.042/0.91/0.048
E8411	Ethylene–octene	10.1 (11[a])	0.86/21.95/1	0.036/0.992/0.042
I9100	Ethylene–octene	9.7	0.88/23.13/1	0.035/0.925/0.04
I9530	Ethylene–octene	10.3	0.88/21.93/1	0.037/0.921/0.042
I9807	Ethylene–octene	12.5	0.86/18.55/1	0.042/0.909/0.049
I9507	Ethylene–octene	13.9	0.87/17.02/1	0.046/0.902/0.053
N4640	Ethylene–propylene	32[a]	1/4.66/1	0.15/0.7/0.15
N4520	Ethylene–propylene	37[a]	1/3.88/1	0.17/0.66/0.17
V3401	Propylene–ethylene	25.0	0.87/1.56/1	0.253/0.455/0.292
V4301	Propylene–ethylene	14.0	1.15/1.43/1	0.279/0.399/0.322
V3300	Propylene–ethylene	12.0	0.87/1.19/1	0.284/0.389/0.327

[a]Comonomer content provided by the manufacturer.[19]

2.4 | Peak fitting

Curve fitting was carried out using the Wire software v3.4 (Renishaw). Spectra were baseline subtracted using the cubic spline interpolation at specific Raman shifts (2,600, 2,780, 3,100 and 3,300 cm^{-1}). A fixed number of peaks were used in all the calculations. Peaks were fitted using a free combination of Gaussian and Lorentzian functions. Initial values for peaks positions were taken as 2,855, 2,865, 2,880, 2,890, 2,910, 2,925, 2,940, and 2,965 cm^{-1}, although they were set free to vary. On the basis of previous studies and our own examination of the problem, full widths at the half maximum were limited to values below 15 cm^{-1} for the first three peaks and below 35 cm^{-1} for the rest.[12,13]

3 | RESULTS

3.1 | Spectral assignment in the C—H stretching region

We start revisiting the spectral signatures of methylene groups, as observed in PX3000. This sample, with a molecular weight of about 3,000 g/mol, can be seen as a polymethylene chain as the nominal weight ratio of CH_2/CH_3 groups is above 100, see Table 1. Figure 1 shows nonpolarized Raman spectra of PX3000 in the C—H stretching region at room temperature and at 160°C. Table 3 summarizes the corresponding vibrational modes and assignments, based on earlier work of Snyder[12,13] and that more recent by Liu,[15,16] for further reference. At room temperature, PX3000 is semicrystalline whereas at 160°C, above its melting temperature, it is in the liquid or melt state. The spectrum at room temperature shows two intense bands at 2,853 and

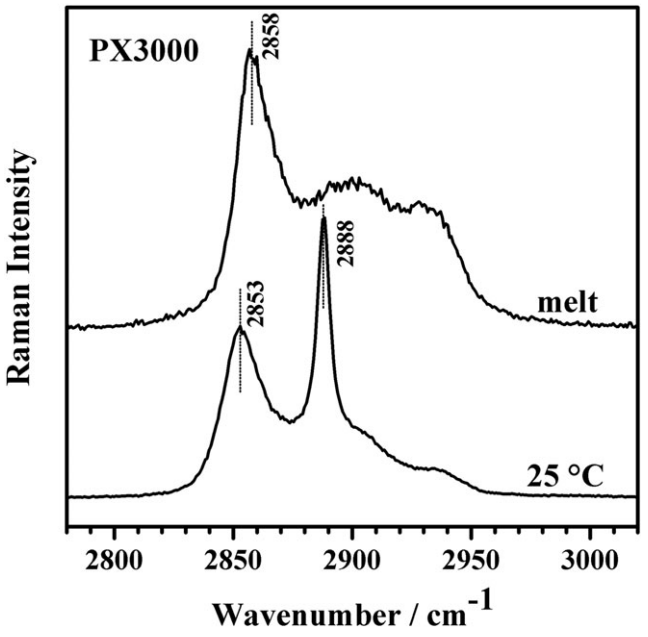

FIGURE 1 Raman spectra of PX3000 in the C—H stretching region at 25°C (semicrystalline) and 160°C (melt state)

TABLE 3 Spectral assignment in the C—H stretching region

Group	Wave number/cm^{-1}	Assignment	
		Snyder et al.	Liu et al.
CH_2	2,850–2,860	ν_S	ν_{FR}
	2,865	ν_{FR}	ν_{FR}
	2,880–2,890[a]	ν_A	-
	2,900; 2,925	ν_{FR}	ν_S
CH_3	2,880	ν_S	ν_{FR}
	2,938	ν_{FR}	ν_S
	2,950	ν_A	-
	2,965	ν_A	ν_A
CH	2,880–2,890	-	ν_S

[a]Well defined at room temperature and characteristic of the crystal state. Notations: ν_A: asymmetric C—H stretching; ν_{FR}: Fermi resonance between stretching modes and bending overtones; ν_S: symmetric C—H stretching.

2,888 cm^{-1}, assigned by Snyder to ν_S (CH_2) and ν_A (CH_2), respectively. The right-hand shoulders of the peak 2,888 cm^{-1} are assigned to Fermi resonance between the fundamental ν_S (CH_2) and methylene bending-modes overtones.[12] Notice that the line at 2,853 cm^{-1} is rather broad and may well underline two superposed peaks, most likely, another band arising from Fermi resonance of ν_S (CH_2). No contributions of bands of methyl groups are observed due to the very high CH_2/CH_3 ratio of this sample.

Most of these features remain in the spectrum of PX3000 in the melt state but under a rather different spectral envelop. The symmetric stretching mode ν_S (CH_2) persists as a band at 2,858 cm^{-1}. Once again, that band is rather broad (about 20 cm^{-1} full width at half maximum [FWHM]) and may well mask two superposed peaks. The sharp band observed at 2,888 cm^{-1} in the semicrystalline sample is most likely broaden and hidden under a broad envelop at 2,900 that also includes, as assigned by Snyder, the ν_A (CH_2) mode. The fact that the band at 2,888 cm^{-1} is sensitive to intermolecular interaction arising from the orthorhombic crystal structure of the polymethylene chain certainly complicates the composition analysis as it adds another degree of freedom to the spectral profile. Therefore, further discussions will be exclusively centered on samples in the liquid state. However, that peak could be used as indicator of crystal content, as others found in the fingerprint region.[7,12]

Overall, Snyder assignments need to be revised in view of the more recent studies of vibrational modes of the C—H stretching region. For instance, Liu et al. used deuteration to isolate specific Raman signatures of the CH_2 group of the n-propanol molecule founding that it gives rise to two peaks at 2,854 and 2,873 cm^{-1}, assigned to Fermi resonance components, along with other two at 2,917 and 2,941 cm^{-1}, assigned to symmetric stretching, ν_S (CH_2), see Table 3.[16] The coupling with other CH_2 groups or the lack of strong intermolecular interactions as occur in polymethylene chains may explain the differences with our work. Antisymmetric stretching modes are observed as weak and broad bands, most likely overlapped by the stronger ν_A (CH_2) peaks.[16] Therefore, one of the most important differences with Snyder is the assignation of 2,888 cm^{-1} as ν_A (CH_2), which, in the framework of Liu, should be most likely assigned as a Fermi resonant component. It definitively makes sense considering that Fermi resonance is very sensitive to changes in molecular environments as occurs when passing from ordered chains in the crystal to disordered chains in the melt state. Another case of study is that of Wang et al. who examined several n-alcohols (up to eight C atoms) using the SFG vibrational spectroscopy. The assignment proposed by Wang et al. is in rather well agreement with that of Snyder but with some differences, for instance, some extra peaks observed in the SFG spectra at 2,905 cm^{-1} and assigned to Fermi interaction. Certainly, the broad band underneath 2,900 cm^{-1} observed in melt PX3000 is a complex region that includes several peaks resulting from Fermi interaction but that turns out hard to be resolved by conventional Raman.

Spectral signatures of the methyl group are expected to emerge in samples with lower CH_2/CH_3 weight ratio (wCH_2/wCH_3), such as short linear hydrocarbons. Figure 2 shows conventional Raman spectra of heptane (2.3/1) and decane (3.7/1), compared with increasingly

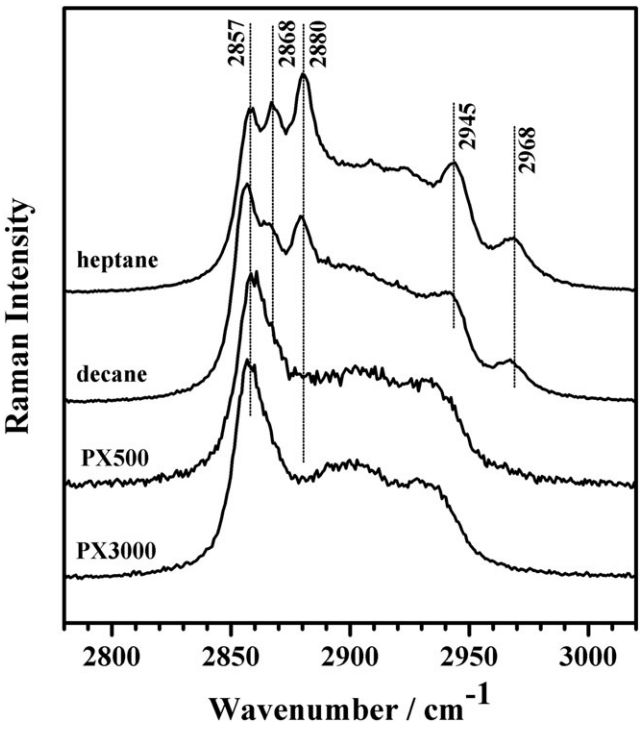

FIGURE 2 Raman spectra in the C—H stretching region of linear chains in the liquid state

longer chains as PX500 (24/1) and PX3000 (150/1), all of them in the liquid state. In heptane, we observe three peaks in the 2,850- to 2,900-cm^{-1} region. On the basis of Snyder, the peak at 2,857 cm^{-1} can be assigned to ν_S (CH_2) whereas the peak at 2,880 is a characteristic of CH_3 groups, with ν_S (CH_3) as a typical assignment. Peaks at 2,945 and 2,968 cm^{-1} are also a characteristic of CH_3 that are assigned to ν_A (CH_3).[12,13] Once again, the broad band between 2,900 and 2,950 is most likely composed of several contributions arising from CH_2 and CH_3 groups that cannot be easily resolved. Finally, let us address the assignment of the band at 2,868 cm^{-1}. Notice how this peak, prominent in heptane, becomes a shoulder in decane and eventually disappears in longer polymethylene chains. Considering that the band at 2,858 cm^{-1} in the melt PX3000 spectra shows some asymmetry consistent with the existence of a hidden band at its right hand, a reasonable assignment for the band at 2,868 cm^{-1} could be as a Fermi resonant component of 2,858 cm^{-1}. The apparent increase in intensity of 2,868 cm^{-1} with methyl content can be explained by the increasing contribution of 2,880-cm^{-1} band tail.

These assignments are in a major part confirmed by recent studies. The assignment based on the SFG spectra by Wang is similar to that of Snyder, except for a band at 2,935 cm^{-1}, most likely analogue to ours 2,945 cm^{-1}, assigned to Fermi resonance.[14] The work by Liu shows that the isolated response of terminal CH_3 groups of the deuterated 1-propanol is composed of three major bands at 2,876, 2,935, and 2,967 cm^{-1}, assigned to Fermi resonance, ν_S (CH_3) and ν_A (CH_3), respectively.[15] The assignation proposed by Snyder is inverted in the first two bands and agrees with the last one, see Table 3.

The contribution of methine groups can be analyzed from Raman spectra of species with larger amount of them, such as polypropylene and 2,5-dimethylhexane. Raman spectra are shown in Figure 3 along with that of heptane. In 2,5-dimethylhexane, the weight ratio of $CH/CH_2/CH_3$ groups is 1.00/1.08/2.31; that is, the molecule has comparable amounts of CH and CH_2 and about the double of CH_3 groups. In polypropylene, this ratio is 1/1.08/1.15; that is, it has comparable amounts of each of the groups. The spectrum of polypropylene has the same set of peaks that of decane, despite a somewhat larger peak broadening. The broad peak at 2,850 cm^{-1} can be ascribed to CH_2 groups, whereas those at 2,878 and 2,963 cm^{-1} to specific features of CH_3. Remarkably, no signatures of CH groups are observed. The shoulder observed at the right hand of the peak at 2,880 cm^{-1} might be due to CH contributions, most likely superposed with the broad band at 2,900 characteristics of CH_2 groups.

The same arguments explain the spectrum of 2,5-dimethylhexane, where the shoulder at the right hand

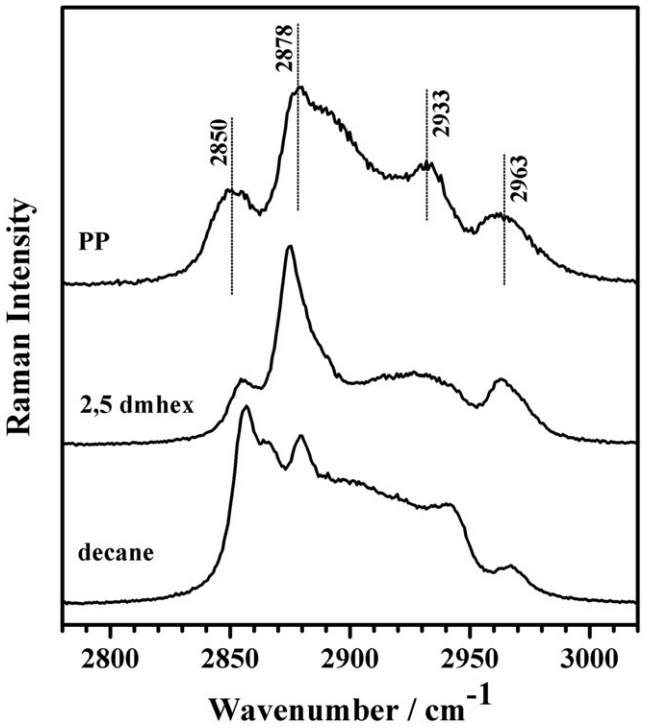

FIGURE 3 Raman spectra of samples with higher CH group content in the liquid state

of the peak at 2,880 cm^{-1} can be explained by the minor proportion of CH_2 and CH of that molecule in comparison with PP. Summarizing, the spectral features of methine groups seem to be difficult to capture. This elusive character is confirmed by experiments carried out Wang et al. and by Liu et al. In 2-propanol, the isolated response of the CH group appears as a very broad band (FWHM > 50 cm^{-1}) centered in the range of 2,880–2,890 cm^{-1}. Minor and very broad features in SFG spectrum of 2-propanol observed at about 2,920 cm^{-1} are ascribed to ν_S (CH).

3.2 | Curve-fitting analysis

On the basis of the above, a curve-fitting analysis of Raman spectra was carried out with the aim of isolating individual contributions of CH_3, CH_2, and CH groups and eventually establishing quantitative relationships between band intensities and their relative contents. Overall, analysis based on peak heights did not yield reliable results, most likely due to the extensive peak overlapping. The fitting focuses on the 2,850- to 2,890-cm^{-1} range, as it is at that region where contributions of CH_3 and CH_2 groups can be better resolved. Two peaks at about 2,855 and 2,865 cm^{-1} were used to fit contributions ascribed to CH_2 groups, whereas one at about 2,880 cm^{-1} was used to account for CH_3 units. The region above

2,890 cm^{-1} is overcrowded with several modes, so the main objective of the fitting was the quantification of the total area of spectral profile for normalization purposes; peaks at about 2,890, 2,900, 2,925, 2,940, and 2,965 cm^{-1} were used with this aim. As above discussed, CH contributions are most likely included in the band at 2,900 cm^{-1}, but they are anticipated to be difficult to isolate due to the superposition with other modes, as seen in the example of polypropylene.

Examples of fittings are given in Figure 4 for several of the compounds of Table 1. The experimental data are shown with circles whereas the individual peaks and overall fitted spectrum are shown with solid lines. In all the cases, it is seen a very good quality of data fit. Methylene contributions (2,855 and 2,865 cm^{-1}) are well resolved from that of methyl groups (2,880 cm^{-1}), whereas the rest of the spectrum is adequately reproduced with a combination of the other five peaks. We see that the methyl contributions are major in 2,5-dimethylhexane and gradually decrease from heptane to decane, reaching a minimum in PX500.

Peak intensities are related with the content of the different groups composing the molecule. For instance, the areas of the well-resolved bands at 2,855 and 2,865 cm^{-1} can be related with the weight fraction of CH_2 units. Similarly, the area of peak at about 2,880 cm^{-1} should reflect the content of CH_3 groups. If we assume that cross sections of those groups are independent of the chemical structure of the rest of the molecule, we would expect rather common molecular-independent behavior of CH_2 and CH_3 contributions. Figure 5 shows a plot that relates actual weight fractions of CH_2 and CH_3 groups versus the normalized peak areas for all the samples of Table 1. Notice that the plot includes a variety of molecular structures such as linear molecules (n-alkanes), long chain alcohols, or branched alkanes with large CH content (polypropylene; 2,5-dimethylhexane). Normalization was carried out by dividing individual peak areas by the area of spectral envelope between 2,760 and 3,100 cm^{-1}. Both plots show a well-behaved linear behavior that passes through origin, which verifies the peak assignment, and, in some way, the fact that cross sections of CH_2 and CH_3 groups behave rather independently chemical structure of the molecule. It is also seen in the sample like PX500 that peak areas of CH_3 contributions are much smaller than those of CH_2. In this sense, the quantification of methyl groups can be considered reliable in samples with CH_3 content above 1/50, as found in the PX1000 sample. In samples with lower CH_3 contents, the peak at 2,880 cm^{-1} is hard to be resolved from the rest of the spectral profile.

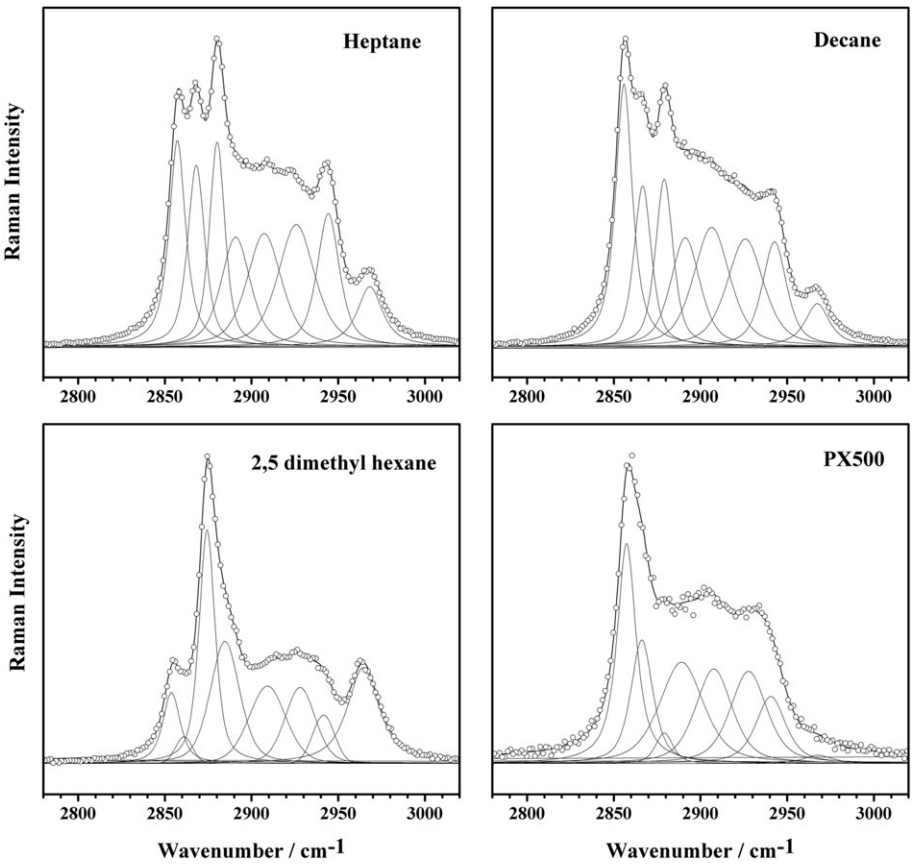

FIGURE 4 Examples of curve-fitting analysis in the CH stretching region

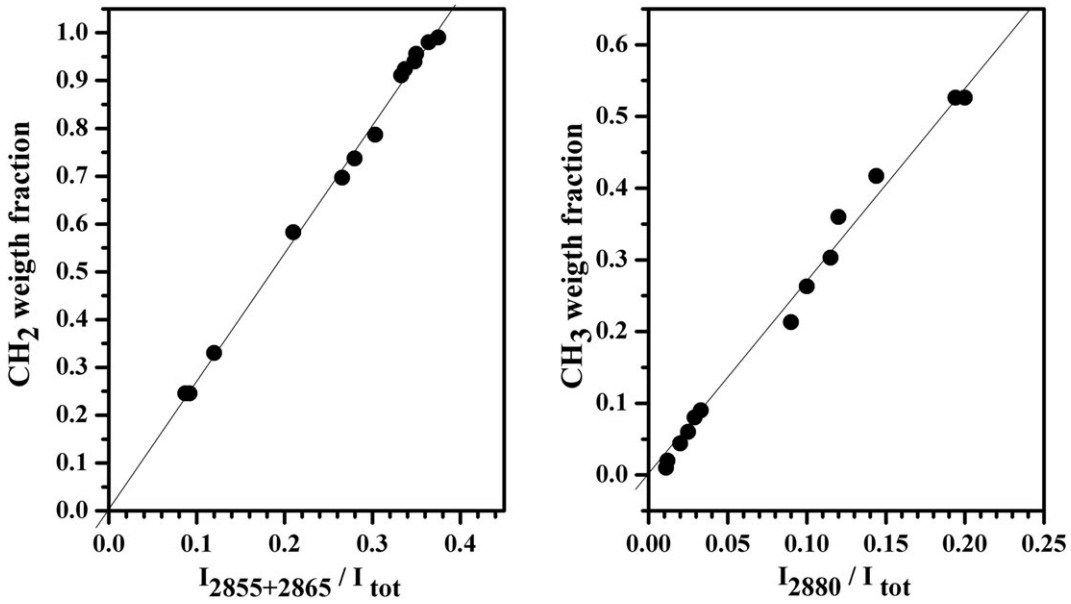

FIGURE 5 Plots relating weight fractions of CH_2 and CH_3 groups and peak areas for the samples of Table 1

3.3 | Analysis of chemical composition of copolymers chains

We apply the above-described peak assignment to the analysis of chemical composition of polymer chains with different amounts of CH, CH_2, and CH_3 units. Table 2 summarizes the series of commercial ethylene-based copolymers analyzed. The chemical compositions of most of the samples (comonomer mol %) were determined by ^{13}C NMR, see Supporting Information for representative ^{13}C-NMR spectra and equations used to perform the calculations. For some of the samples, chemical composition data provided by the manufacturer were also available. Weight fractions of CH, CH_2, and CH_3 groups reported in Table 2 contents were derived from these data and the knowledge of the comonomer molecular structure, see Supporting Information. The Engage series (E) are random ethylene–octene or ethylene–butene copolymers with ethylene contents below 22 mol %. The Infuse series (I) are ethylene–octene copolymers with a blocky architecture and octene contents in the range of 9.7–13.9 mol %. Nordel samples (N) are essentially random ethylene–propylene copolymers with comparable mass fractions of ethylene and propylene units. Versify series (V) are propylene–ethylene-based copolymers, some of them with a blocky structure, and ethylene content between 12 and 25 mol %.[22] Depending on their comonomer type and content, the copolymers have different CH_2/CH_3 ratio, going from weight fractions of CH_3 groups of about 0.04 for I9100 to 0.327 for V3300.

Raman spectra of some of these samples are shown in Figure 6, in comparison with the polymethylene model chain given by PX3000. As the samples are semi-crystalline at room temperature, spectra were taken at 160°C, in the melt state. In the case of the E7447 sample, an ethylene-based copolymer with 22 mol % of butene, the spectral profile is similar to that of PX3000, with the band at 2,855-cm^{-1} characteristic of CH_2 units as the main spectral feature. However, it can be observed in E7447 an increase in intensity around 2,880 cm^{-1}, indicative of a larger content of CH_3 groups bearing at the butene units, in comparison with PX3000.

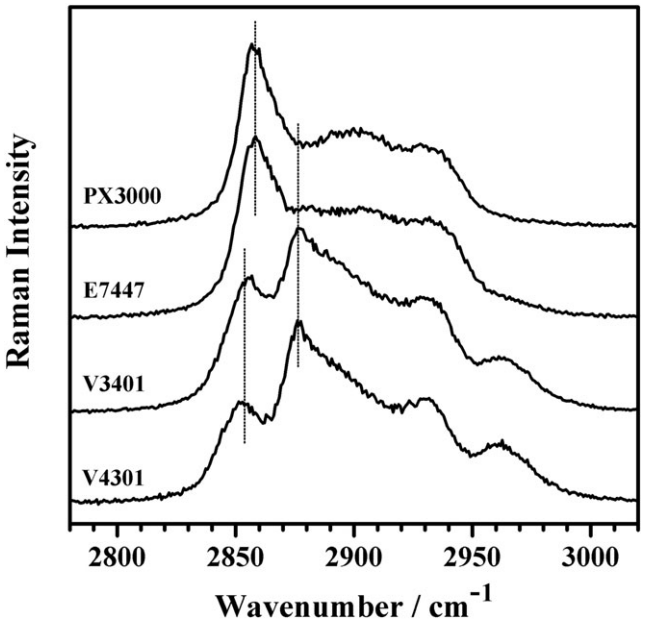

FIGURE 6 Raman spectra in the melt state of representative polyolefinic copolymers

The spectrum of V3401, a polypropylene-based copolymer with 25 mol % of ethylene, clearly reveals a very high content of CH_3 as the peak at 2,880 cm^{-1} is now the major one. The propylene content is anticipated to be even higher in V4301, as seen by the larger intensity of the 2,880-cm^{-1} peak compared with that at 2,855 cm^{-1}.

A curve-fitting analysis was performed in the copolymer samples that quantify contents of CH_2 and CH_3 units. Fittings were performed with the same set of peaks and conditions employed in the analysis of model compounds. Typical examples of fittings are shown in Figure 7. Overall, we see that the experimental spectra are well reproduced in all the cases. The peaks relevant

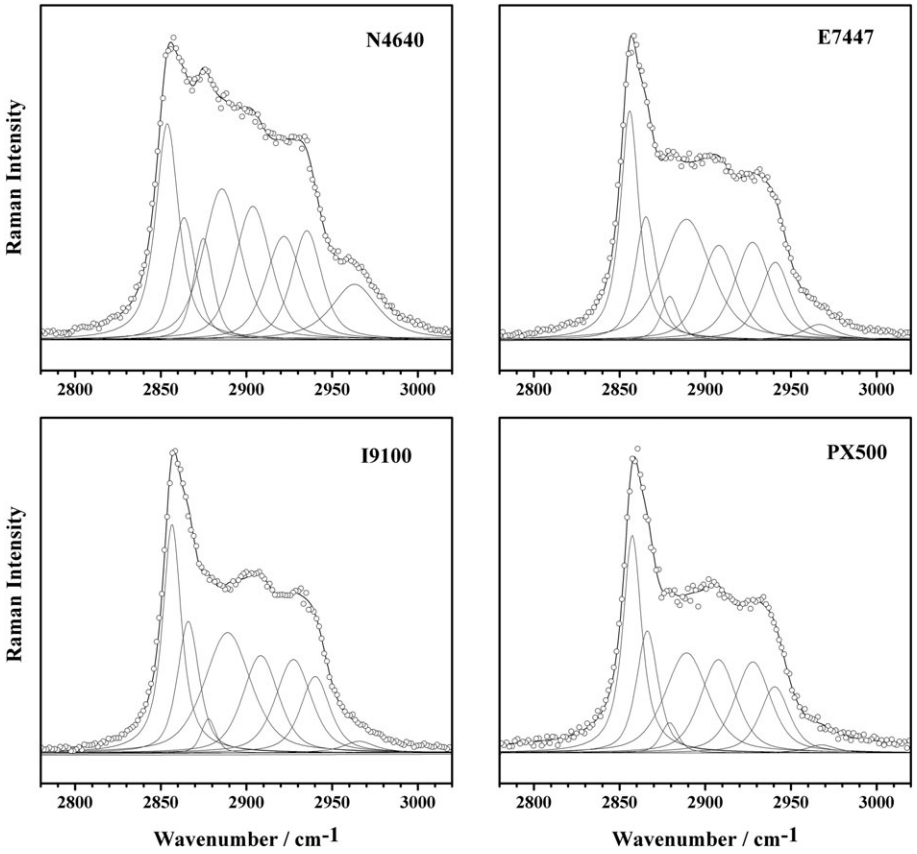

FIGURE 7 Examples of curve-fitting analysis in the CH stretching region for polymer samples

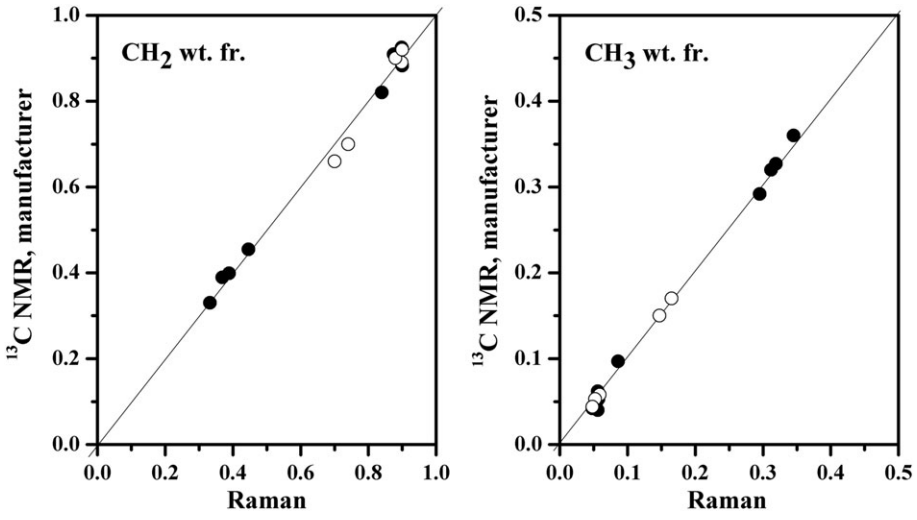

FIGURE 8 Comparison of chemical composition of Engage, Infuse, Nordel, and Versify copolymers determined by Raman with ^{13}C nuclear magnetic resonance (filled symbols) and manufacturer data (hollow symbols)

for the analysis of CH_2 and CH_3 content (2,855, 2,685, and 2,880) appear well defined whereas the rest of the peaks adequately reproduces the spectral envelop necessary for intensity normalization. From the areas of peaks at 2,855 and 2,865 cm^{-1} (CH_2 units) and 2,880 cm^{-1} (CH_3 units) along with the calibration plot shown in Figure 5, CH_2 and CH_3 weight fractions were obtained. The results are shown in Figure 8, compared with those derived from ^{13}C-NMR analysis and manufacturer data (Table 2, fifth column). As observed in the analysis of model compounds, Raman data compare very well those obtained from independent sources, remarkable considering the structural variety of copolymers analyzed.

Now reversing the calculations carried out with NMR (or manufacturer) data to obtain group weight fractions from comonomer mol %, see Figure S2, values of comonomer content can be obtained from group weight fractions measured by Raman. At this point, notice that the comonomer content can be obtained from either CH_2 or CH_3 weight fractions. An analysis of the error propagation in this calculation was carried out, see Figure S3. It is found that the error propagation is smaller from weight fractions of CH_3 groups than that from CH_2 in the case of Engage and Infuse grades. On the other hand, somewhat smaller error propagation is predicted when calculations are performed from CH_2 weight contents in Versify grades and from CH_3 contents in Nordel. Table 4 summarizes calculations from Raman data in comparison with those measured by ^{13}C NMR or provided by the manufacturer. Overall, we see a very good agreement between data. Some discrepancies are observed in grades with very low 1-octene content (e.g., I9100), with a tendency to overestimation by the part of Raman. It might explained by the low amount of CH_3 of groups in those samples, close to the detection limit, as already observed in the analysis of PX1000 or PX3000. In those cases, it turns out difficult to resolve the CH_3 contribution from the rest of the spectrum, and curve fitting leads to overestimate CH_3 content, see Figure 5. A more detailed analysis over a specific family of products with a wider composition range may contribute to improve the method predicting capabilities as the approach has been presented in general way, with the idea to cover several copolymer families.

TABLE 4 Chemical composition of the copolymers as determined by Raman, ^{13}C nuclear magnetic resonance, and the manufacturer

	Comonomer (mol %)		
Sample	^{13}C NMR	Raman	Manufacturer
E7447	22.0	19.1	-
E7256	13.2	11.7	-
E8130	-	16.4	16
E8407	12.4	13.7	14
E8411	10.1	12.3	11
I9100	9.7	14.0	-
I9530	10.3	12.3	-
I9807	12.5	14.4	-
I9507	13.9	15.6	-
N4640	-	31.2	32
N4520	-	36.2	37
V3401	25.0	23.5	-
V4301	14.0	12.2	-
V3300	12.0	12.0	-

4 | CONCLUSIONS

It has been shown how the Raman spectrum of the prominent C—H stretching region can be used for the analysis of comonomer content in polyolefinic copolymers. Substantial peak overlapping, because of different stretching modes, Fermi resonances, and Raman scattering of molecules ordered in a crystal lattice, yielded a complex spectral profile. The analysis in the melt state contributed to clean up the spectral region avoiding the appearance of extrapeaks due to crystal splitting, in turn dependent on crystal content. In the melt state, spectral features of methylene and methyl groups appeared well defined and could be reasonably well isolated by curve-fitting analysis. Contributions from methine groups were much harder to detect and did not yield narrow peaks even in molecules with substantial amounts of those groups. Linear correlations between Raman intensity of specific bands and methylene and methyl mass content allowed a reliable quantification of chemical composition in several families of industrial copolymers, yielding results that compare very well with the obtained from ^{13}C NMR. Relatively simple and less expensive instrumentation, short acquisition times plus the ability to perform spatially resolved measurements are some extra advantages of Raman spectroscopy with respect to the powerful ^{13}C NMR. The need for melting some of the samples may appear as a complicated aspect of sample preparation, although is a simple step, easy to implement in modern instrumentation.

The analysis of monomer content is very important for process monitoring, quality control, or sample identification in industrial production of ethylene-based copolymers. On the other hand, comonomer composition is a proprietary information of the manufacturer, but that knowledge is crucial for the design of new products or

applications. In a wider perspective, quantification of methyl and methylene groups is also useful to understand structural changes in the polymer chain due to other important kind of phenomena such as degradation, cross-linking, or chemical modification.

ACKNOWLEDGEMENTS

J. P. Tomba acknowledges Agencia Nacional de Promoción Científica y Tecnológica, Fondo para la Investigación Científica y Tecnológica (PICT14-1919) for financial support and Mariela P. Desimone for measuring part of the Raman spectra.

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REFERENCES

[1] P. Steve Chum, K. W. Swogger, *Prog. Polym. Sci.* **2008**, *33*, 797.

[2] H. P. Wang, D. U. Khariwala, W. Cheung, S. P. Chum, A. Hiltner, E. Baer, *Macromolecules* **2007**, *40*, 2852.

[3] H. P. Wang, P. Ansems, S. P. Chum, A. Hiltner, E. Baer, *Macromolecules* **2006**, *39*, 1488.

[4] M. Glotin, L. Mandelkern, *J. Polym. Sci. Polym. Lett. Ed.* **1983**, *21*, 807.

[5] J. P. Tomba, J. M. Carella, J. M. Pastor, *J Polym Sci B* **2005**, *43*, 3083.

[6] V. Crupi, D. Majolino, P. Migliardo, V. Venuti, *J. Mol. Struct.* **1998**, *448*, 261.

[7] G. R. Strobl, W. Hagedorn, *J Polym Sci B* **1978**, *16*, 1181.

[8] M. Glotin, L. Mandelkern, *Colloid Polym. Sci.* **1982**, *260*, 182.

[9] M. Pigeon, R. E. Prud'homme, M. Pezolet, *Macromolecules* **1991**, *24*, 5687.

[10] Y. V. Zavgorodneva, K. A. Prokhorova, L. A. Novokshonovac, T. M. Ushakovac, E. E. Starchakc, V. G. Krasheninnikovc, G. Y. Nikolaevaa, E. A. Sagitovaa, P. P. Pashinina, M. A. Gusevae, P. Donfackd, B. von der Kammerd, A. Maternyd, *Laser Phys.* **2012**, *22*, 730.

[11] J. P. Tomba, C. D. Mana, C. J. Perez, P. M. Desimone, G. Barrera Galland, *Polym. Test.* **2016**, *52*, 71.

[12] R. G. Snyder, S. L. Hsut, S. Krimm, *Spectrochim. Acta* **1978**, *34A*, 395.

[13] R. G. Snyder, H. L. Strauss, C. A. Elliger, *J. Phys. Chem.* **1982**, *86*, 5145.

[14] R. Lu, W. Gan, B. Wu, Z. Zhang, Y. Guo, H. Wang, *J. Phys. Chem. B* **2005**, *109*, 14118.

[15] Y. Yu, Y. Wang, N. Hu, K. Lin, X. Zhou, S. Liu, *J. Raman Spectrosc.* **2014**, *45*, 259.

[16] Y. Yu, Y. Wang, K. Lin, X. Zhou, S. Liu, J. Sun, *J. Raman Spectrosc.* **2016**, *47*, 1385.

[17] N. Everall, B. King, *Macromol. Symp.* **1999**, *141*, 103.

[18] K. P. J. Williams, N. J. Everall, *J. Raman Spectrosc.* **1995**, *26*, 427.

[19] http://www.matweb.com/search/GetMatlsByTradename.aspx?tn=Engage%C2%AE; https://www.dow.com/elastomers/products/

[20] G. B. Galland, R. F. de Souza, R. S. Mauler, F. F. Nunes, *Macromolecules* **1999**, *32*, 1620.

[21] M. A. Da Silva, G. B. Galland, *J. Polym. Sci. C: Polym. Chem.* **2008**, *46*, 947.

[22] M. Desimone, C. D. Mana, C. J. Perez, J. M. Carella, J. P. Tomba, *Appl. Spectrosc.* **2015**, *69*, 1505.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

How to cite this article: Tomba JP, Silva LI, García Genga M, Barrera Galland G, Perez CJ. Characterizing chemical composition of polyolefin-based copolymers from spectral features in the C—H stretching region. *J Raman Spectrosc*. 2018;1–11. https://doi.org/10.1002/jrs.5554