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# Improved Peak Assignments for the $^{13}\text{C}$ NMR Spectra of Poly(ethylene-*co*-1-octene)s

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**ABSTRACT:** High field NMR instruments and multidimensional NMR spectra have substantially improved our ability to assign  $^{13}\text{C}$  NMR chemical shifts of the microstructures of polyolefins including poly(ethylene-*co*-1-octene). However, simple principles of quantitative NMR still need to be obeyed, such as three  $\alpha$  methylene carbons for each methine in the EOE triad. We applied these principles to the state-of-art peak assignments for poly(ethylene-*co*-1-octene). A couple of errors were identified as well as some ambiguous assignments. These findings were incorporated into a rigorous and systematic new assignment for the resonances of the polymer.

## Introduction

Ethylene and 1-octene copolymer is a very important commercial plastic. The compositions of the copolymer as well as its sequence distribution significantly affect the material properties of the product. They also reveal details about the polymerization chemistry.  $^{13}\text{C}$  NMR has been the most successful analytical tool used to characterize the copolymer composition and sequence distribution.<sup>1</sup> However, there are still inaccuracies in the literature about the basic starting point for quantitative NMR analysis for the ethylene/1-octene copolymer.

Correct and unambiguous peak assignment is the starting point of all quantitative NMR analysis. There are a number of ways to assign carbon peaks for polymers such as Grant–Paul chemical shift rules,<sup>2</sup> spectra of model compounds, attached proton measurements,<sup>3</sup> and multidimensional NMR for single bond and multibond carbon proton connection.<sup>4–6</sup> The last approach coupled with ultrahigh field strength has demonstrated tremendous capability in chemical shift dispersion and has recently become the method of choice. Amazingly detailed assignments have been generated using this approach. While the polymer science field has benefited immensely from these detailed assignments, the authors feel strongly that a quantitative self-consistency check can make the assignments more rigorous. Quantitative self-consistency check is defined as the agreement among the integrals from peaks assigned to the same microstructure. One example is that there should be three  $\alpha$ -methylene carbons for every methine carbon in the EOE triad of ethylene/1-octene (E/O) copolymer.

Unambiguous peak assignment can benefit greatly from a rigorous and systematic way for counting each carbon in the system once and only once. While this task is trivial for small molecules, it is significantly more difficult for copolymer systems. The authors propose a scheme to assign only the carbons in the center unit of an odd  $n$ -ad to achieve this goal of counting each carbon once and only once. This scheme is rigorous in that once the “ $n$ ” in  $n$ -ad and direction of counting are determined, every carbon in a polymer chain belongs to

one and only one repeat unit and every repeat unit belongs to one and only one center unit of an odd  $n$ -ad except for the chain ends. After accounting for chain ends, every carbon in this polymer has been counted once and only once. This scheme is also systematic in that each individual  $n$ -ad can be systematically enumerated. Various accounting techniques can be programmed and employed to check that each  $n$ -ad is counted  $m$  times, where  $m$  is the number of carbons in the center unit of that  $n$ -ad. In a future report we will show that it is trivial to develop an ideal method to analyze the  $^{13}\text{C}$  NMR spectrum for the ratios of  $n$ -ads once this systematic assignment is in place.

Since it is controversial to quantitatively deconvolute peaks that are not baseline resolved, peaks discussed in this study are those that can be baseline resolved by a moderate high field instrument, i.e., 100 MHz for the  $^{13}\text{C}$  NMR Larmor frequency. Using an ultra-high-field NMR, one can usually assign copolymer systems down to the pentad level for a selected set of pentads. Therefore, for this study we used pentads for the odd  $n$ -ad system. It is straight forward to combine four related pentads into one triad to convert the assignment based on the pentad system to one based on the triad system.

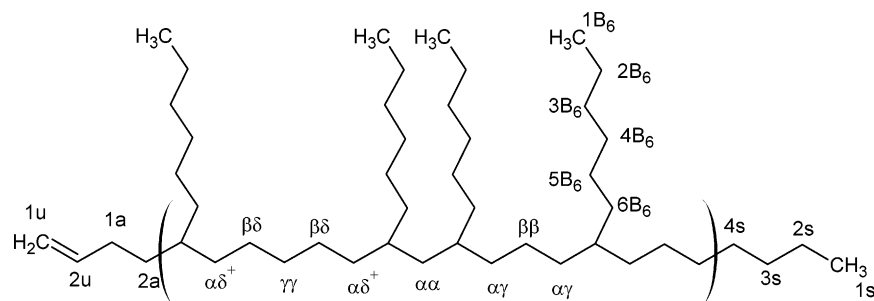
## Experimental Section

**Sample with Low Octene Concentration.** A commercial ethylene/1-octene resin with about 13 mol % octene was obtained from The Dow Chemical Company. About 0.25 g of polymer was added into a 10 mm NMR tube with 2.5 mL of stock solvent. The stock solvent was made by dissolving 2 g of perdeuterated 1,4-dichlorobenzene in 30 mL of *o*-dichlorobenzene (ODCB) with 0.033 M chromium acetylacetonate. The sample tube was then heated in a heating block set at 150 °C. The sample tube was repeatedly vortexed and heated until the solution flowed consistently from the top of the solution column to the bottom. The sample tube was then left in the heat block for at least 24 h to achieve sample homogenization.

The  $^{13}\text{C}$  NMR spectrum was taken on a Varian Inova Unity 400 MHz system. The probe temperature was set at 125 °C. The center of the spectrum was set at 32.5 ppm with spectral width set at 250 ppm. Acquisition parameters were optimized for quantitative NMR including a 14  $\mu\text{s}$  90° pulse, inverse gated  $^1\text{H}$  Waltz decoupling, 1.3 s acquisition time, 6 s delay time, and 8192 scans for data averaging. The magnet was carefully shimmed to generate a line

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Chart 1



shape of less than 1 Hz at full width half-maximum for the two high field peaks from ODCB. The  $\delta^+\delta^+$  peak, also the biggest peak in the aliphatic region, was referenced to 30.0 ppm. The raw data file was processed using Felix95, and a list of integrals with predefined integral area was generated.

**Sample with High Octene Concentration.** The sample with 87 mol % octene was obtained from The Dow Chemical Company. About 10% (w/w) of copolymer and 1,4-dichlorobenzene- $d_4$  were placed in a 5 mm NMR tube. A trace of hexamethyldisiloxane (HMDS) was added to serve as an internal chemical shift reference ( $\delta_H = 0.09$  ppm,  $\delta_C = 2.03$  ppm). The sample was rotated at 20 rpm in a Kugelrohr oven at the 120 °C for 2 h and then at 100 °C for 20 h, after which a clear uniform solution was obtained. All NMR work on this sample was done with a Varian INOVA 750 NMR spectrometer at 120 °C using a Nalorac H/C/N 5 mm PFG probe unless otherwise noted. Data were processed with Varian's VNMR software.

The 1D quantitative  $^{13}\text{C}$  NMR spectra were obtained with a 5 mm broadband ( $^{15}\text{N}$ – $^{31}\text{P}$ ) probe, with a 6.25  $\mu\text{s}$  90° pulse, 26 kHz spectral width, 1024 transients, 3.0 s acquisition time and a 45 s relaxation delay ( $5 \times T_1$ ). Spectra were obtained with inverse gated WALTZ-16<sup>7</sup> proton decoupling (decoupled spectrum without NOE). Data were zero filled to 512K and exponential weighted with 1 Hz line broadening prior to Fourier transformation. The  $^{13}\text{C}$  chemical shifts are reported relative to internal hexamethyldisiloxane at 2.03 ppm.

**2D gHSQC NMR.** The States<sup>8</sup> phase-sensitive gradient selected HSQC<sup>9</sup> NMR spectra were obtained with 90° pulse widths for  $^1\text{H}$  and  $^{13}\text{C}$  of 11.0  $\mu\text{s}$  and 15.0  $\mu\text{s}$ , respectively, a relaxation delay of 1 s, a delay  $\Delta$  set to  $1/(2 \times J_{\text{CH}})$ , ( $J_{\text{CH}} = 125$  Hz), and an acquisition time of 0.236 s with simultaneous  $^{13}\text{C}$  GARP1<sup>10</sup> decoupling, 11.3 kHz spectral width in the  $^{13}\text{C}$  ( $f_1$ ) dimension and a 2.1 kHz spectral width in the  $^1\text{H}$  ( $f_2$ ) dimension; 16 transitions were averaged for each of  $2 \times 1024$  increments during  $t_1$ . The coherence selection PFG pulses were 2.0 and 1.0 ms in duration and had amplitudes of 0.214 and 0.107 T/m, respectively. The data were acquired in phase sensitive mode where CH and  $\text{CH}_3$  cross-peaks are inverted relative to  $\text{CH}_2$  cross-peaks.<sup>11,12</sup> Linear prediction was used to forward extend the data two times its original length. Data were zero filled to provide a  $4096 \times 8192$  matrix and processed with sinebell and shifted sinebell weighting before Fourier transformation.

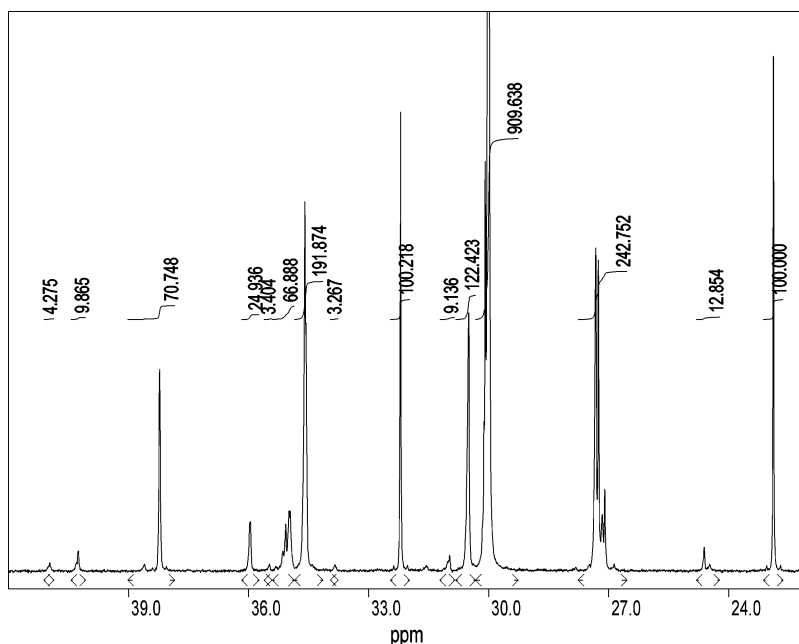
**2D gHMBC NMR.** Data were acquired with 90° pulse widths for  $^1\text{H}$  and  $^{13}\text{C}$ , which were 10.9  $\mu\text{s}$  and 15  $\mu\text{s}$ , respectively, a relaxation delay of 1 s, a 0.214 s acquisition time, a delay  $\Delta$  set to  $1/(2 \times J_{\text{CH}})$  ( $J_{\text{CH}} = 125$  Hz). Two spectra were obtained with  $\tau$  delays of 50 and 100 ms (set to  $1/(2 \times J_{\text{CH}})$ ) to obtain two separate spectra with delays optimized for two- and three-bond  $^1\text{H}$ – $^{13}\text{C}$  correlations. The strengths of two 2.0 ms gradient pulses were 0.214 T/m and 0.160 T/m, respectively; 24 transients were averaged for each of 1024  $t_1$  increments. The evolution time was incremented to provide the equivalent of an 11.3 kHz spectral width in the  $f_1$  dimension. A 2.1 kHz spectral width was used in the  $f_2$  dimension. Linear prediction was carried out in the  $f_1$  dimension to improve the digital resolution. Data were zero filled to provide a  $4096 \times 8192$  matrix and processed with sinebell and shifted sinebell weighting before Fourier transformation.

**2D HSQC-TOCSY NMR.** The spectra were obtained with 90° pulse widths for  $^1\text{H}$  and  $^{13}\text{C}$  of 8.8  $\mu\text{s}$  and 16.0  $\mu\text{s}$ , respectively, a relaxation delay of 1 s, a delay  $\Delta$  set to  $1/(2 \times J_{\text{CH}})$ , ( $J_{\text{CH}} = 125$  Hz), and an acquisition time of 0.088 s with simultaneous  $^{13}\text{C}$  GARP1 decoupling; 24 transitions were averaged for each of  $2 \times 1024$  increments during  $t_1$  with the evolution time incremented to provide the equivalent of 10.0 kHz spectral width in the  $^{13}\text{C}$  ( $f_1$ ) dimension and a 2.1 kHz spectral width in the  $^1\text{H}$  ( $f_2$ ) dimension. A spin-lock pulse was applied for a period of 40 ms with a spin-lock field of 7.8 kHz with MLEV-17 modulation. The coherence selection PFG pulses were 2.0 and 1.0 ms in duration and had amplitudes of 0.214 and 0.107 T/m, respectively. The data were acquired with phase sensitive mode based on the States method<sup>8</sup> where HSQC (one-bond) cross-peaks are inverted relative to TOCSY (multiple-bond) cross-peaks. Linear prediction was used to forward extend the data. Data were zero filled to provide a  $4096 \times 8192$  matrix and processed with sinebell and shifted sinebell weighting before Fourier transformation.

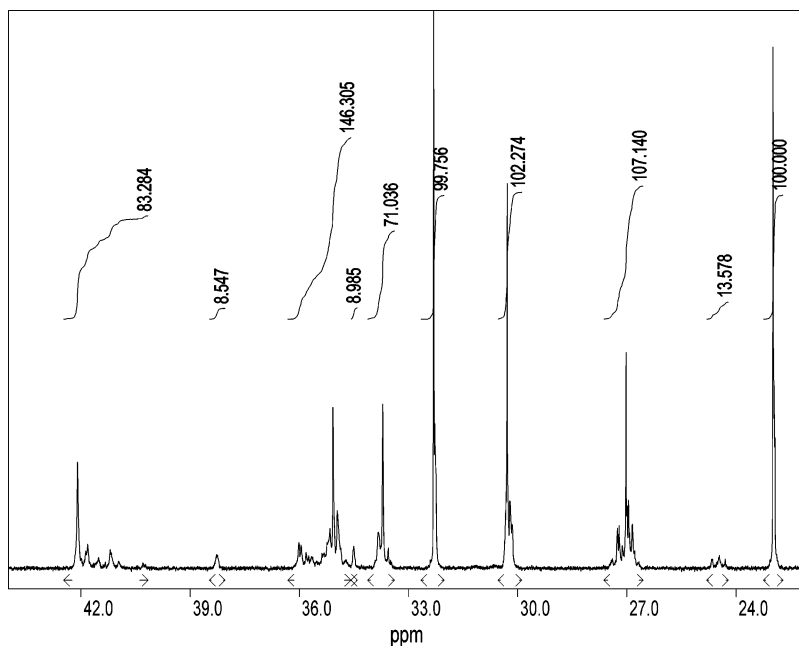
## Results and Discussion

A general structure for ethylene/1-octene copolymer is shown in Chart 1. The carbons in this structure are labeled based on nomenclature first defined by Carman<sup>13</sup> and modified by Dorman<sup>14</sup> and Randall.<sup>1</sup> Methylene carbons along the backbone are identified by a pair of Greek letters to indicate the distance to branches in either direction. Carbons in the side chains are identified by  $iB_6$  where “ $i$ ” indicates the position on the branch, starting with the methyl carbon in position 1. The saturated carbons at the end of the main chain are identified as 1s ( $\text{CH}_3$ ), 2s ( $\text{CH}_2$ ), 3s ( $\text{CH}_2$ ), etc.

**1. Incomplete Accounting of  $\alpha\gamma$  Methylenes by the Peak at 35.5 ppm.** The 2001 *Macromolecules* article by Liu et al.<sup>4</sup> contains the most detailed carbon assignments on ethylene/1-octene copolymers. After applying the quantitative self-consistency check, we have concerns about one of the assignment. The article assigned  $\alpha\gamma$  methylene carbon to two peaks at 35.65 and 35.53 ppm. These two peaks have no other contributions except the  $\alpha\gamma$  methylene carbon. The  $\alpha\gamma$  methylene carbon is only present in the OEO triad. There is another methylene carbon,  $\beta\beta$ , that is only present in the OEO triad as well. Since there are two  $\alpha\gamma$  methylene carbons for every  $\beta\beta$  methylene carbon, the integral of the  $\beta\beta$  methylene carbon (with well established assignment to peaks in the 24–25 ppm region)<sup>1</sup> can be used to check the assignment for the  $\alpha\gamma$  methylene carbon. Figure 1 shows a  $^{13}\text{C}$  NMR spectrum of a commercial ethylene/1-octene copolymer resin. In this plot, the integral for the “assigned”  $\alpha\gamma$  peaks at 35.65 and 35.53 ppm is only a third of the integral for the  $\beta\beta$  peaks at 24–25 ppm. By comparison, the disagreement between other integrals that should be the same are only 10% of the integral for the  $\beta\beta$  peaks. For example, the integral for the methine carbon and the integral for each methylene on the hexyl side chain should be the same. The sum of integrals for the methine carbon resonances at 37.8–38.5, 35.8–36.2, and 33.7–34.0 ppm is 99.0. The integral for  $2B_6$



**Figure 1.**  $^{13}\text{C}$  NMR spectrum of a commercial ethylene/1-octene resin.



**Figure 2.**  $^{13}\text{C}$  NMR spectrum of an ethylene/1-octene resin with 87 mol % octene.

methylene ( $\text{CH}_2$   $\alpha$  to  $\text{CH}_3$ ) at 22.8 ppm is 100. The integral for  $3\text{B}_6$  methylene ( $\text{CH}_2$   $\beta$  to  $\text{CH}_3$ ) at 32.2 ppm is 100.2. The chain end correction to  $2\text{B}_6$  and  $3\text{B}_6$  is minor for this polymer since the number-average molecular weight is in excess of 100 000 g/mol. That is about 2 chain ends per 10 000 carbons.

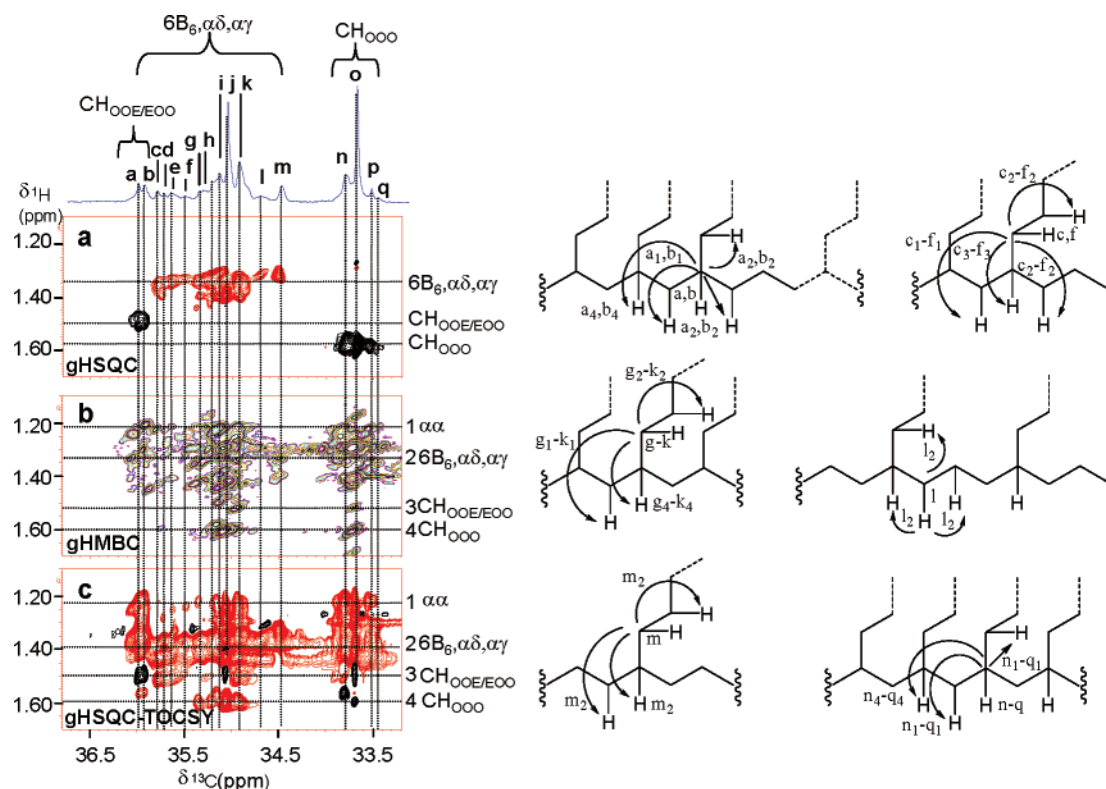
It is interesting that the integral for the “assigned”  $\alpha\gamma$  peaks at 35.5–35.7 region is of similar amplitude as the integral for the methine peak for the OOO triad at 33.8 ppm. Thus, it is reasonable to suggest that three octene units need to be present for the “assigned” peak. Combining the assignment made by Liu et al. that it is an  $\alpha\gamma$  methylene carbon, we propose to assign this peak to the  $\alpha\gamma$  methylene carbons that is also  $\gamma$  to the CH on a third octene from OEOO/OOEO structure. This carbon is  $\alpha$  to one CH and  $\gamma$  to two CHs. The rest of the  $\alpha\gamma$  methylene carbons are assigned to the region from 34.8 to 35.4 ppm.

The correction to the assignment for  $\alpha\gamma$  methylene carbon can also be substantiated by 2D NMR on E/O copolymer with

high octene level. Figure 2 shows the  $^{13}\text{C}$  NMR spectrum of an E/O copolymer with 87 mol % octene.

There are no significant  $\gamma\gamma$  and  $\gamma\delta^+$  peaks (31.6–30.4 ppm) compared to the  $\beta\beta$  peak at 24.5 ppm. Therefore, all the  $\alpha$  methylene carbons on the polymer backbone are either  $\alpha\alpha$  or  $\alpha\gamma$ . Thus, the methylene carbons in the 36.3–34.2 ppm region can only be  $\alpha\gamma$  backbone methylene carbons or  $6\text{B}_6$  methylene carbons on the hexyl side chain. The integral of the methine carbon of EOE triad at 38.2 ppm and that of the  $6\text{B}_6$  carbon of EOE triad at 34.4 ppm is the same within experimental error. Thus, all the  $\alpha$  methylene carbons downfield from 34.4 ppm in EOEOE pentad are  $\alpha\gamma$  backbone methylene carbons. Figure 3 shows the 37–33 ppm region from the gHSQC, gHMBC and gHSQC-TOCSY spectra of this copolymer. The carbon shifts in this region are labeled **a–q**; one-bond HSQC correlations are identified by single letters (**a–q**) to indicate their carbon resonance positions and the C–H bonds on the structures to

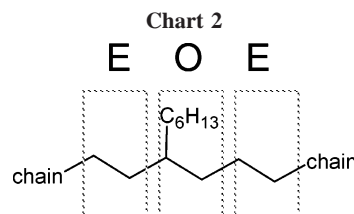




**Figure 3.**  $\text{CH}_{\text{OOE}}$ ,  $6\text{B}_6$ ,  $\alpha\gamma$ ,  $\alpha\delta$ , and  $\text{CH}_{\text{OOO}}$  regions from the (a) gHSQC, (b) gHMBC, and (c) gHSQC-TOCSY spectra of E/O copolymer with 87 mol % octene (see text).

the right of the figure are correspondingly labeled **a–q** to indicate the structure features assigned to these HSQC cross-peaks. The HMBC and HSQC-TOCSY spectra have their  $f_2$  axes ( $^1\text{H}$  chemical shift positions) labeled **1–4** so that multiple-bond correlations can be designated by a letter to indicate the  $^{13}\text{C}$  chemical shift position and a subscripted number to indicate the  $^1\text{H}$  chemical shift position of the cross-peak. The structure features assigned to these cross-peak are similarly indicated by a label (**a<sub>n</sub>**, **b<sub>n</sub>**, **c<sub>n</sub>**, ...) on each of the arrows showing multiple-bond correlations on the polymer substructures on the right side of the figure. The peak labeled **l** has no cross-peaks with CH proton resonances of OOE/EOO or OOO structures in the gHMBC and gHSQC-TOCSY spectra. Thus, we can assign peak **l** to  $\alpha\gamma$  methylene carbons in EOEOE pentads. Similarly, peak **m** is not correlated to CH proton resonances of OOE/EOO or OOO structures in the gHMBC and gHSQC-TOCSY spectra, however it does exhibit HSQC-TOCSY correlations to  $1\text{B}_6$  and possibly  $\text{CH}_{\text{EOE}}$  protons resonances and is attributed to  $6\text{B}_6$  methylene groups in EOE triads.

**2. Undercounted EEE Triad.** There is another error in the assignment by Liu et al. In this case, the carbon assignment is correct; however, the correctly assigned carbons are not completely categorized into the correct triad. Liu et al. assigned the EEE triad to the  $\delta^+\delta^+$  methylene carbons only, thus the only contribution to EEE triad came from the 30.0 ppm peak. The quantity of EEE triads was calculated by dividing the integral for the 30.0 ppm peak by two. However in a OEEEE pentad, one of the  $\gamma\delta^+$  methylene carbon belongs to the center E unit. It needs to be counted toward the EEE triad. In the extreme case where the polymer is composed of (OEEEE) $_n$  structures, using the assignments of Liu et al. will produce a calculated EEE triad quantity of only half the correct value. In fact, this mistake in counting carbons is not unique to the OEEEE pentad, it is present in all  $\text{OE(E)}_n\text{EO}$  sequences having  $n \geq 1$ . One of the  $\gamma\delta^+$  methylene carbon belongs to the (E) $_n$



unit. Therefore, the error caused by this mistake is positively related to the octene concentration at low octene level and negatively related to the octene concentration at high octene level. The maximum error occurs in the extreme case of (OEEEE) $_n$ .

The authors believe this carbon miscount is a major contributor for the disagreement in Table 3 of the article by Liu et al., between the triad numbers calculated using the method described by Randall<sup>1</sup> and those calculated using the method described in the Liu article. While the disagreement for the 3.9 mol % octene sample is minor, the disagreement is significant for the 36 mol % octene sample, the biggest discrepancy among six triads is the one for EEE. Both of the above observations are consistent with our analysis in the previous paragraph. This error can be remedied simply by adding half of the  $\gamma\delta^+$  peak to the equation Liu et al. used for calculating EEE mole fraction. Instead of  $[\text{EEE}] = k(F_4/2 - E/2)$ , the new equation becomes  $[\text{EEE}] = k(F_4/2 - E/2 + F_3/4)$ . After the correction, the comparison between the triad numbers calculated using the two methods are much closer.

**3. Ambiguous Assignment.** The article by Liu et al. contains some ambiguous assignments as well. For example, the  $\alpha\alpha$  methylene carbon in OOOE/EOOO was assigned to the 40.97 peak. However there are two  $\alpha\alpha$  methylene carbons in OOOE/EOOO, both of which are  $\gamma$  to at least one methine. The one which is  $\gamma$  to only a single methine (center methylene) can be assigned to the 40.97 peak for certain. The other  $\alpha\alpha$  carbon

Table 1. Chemical Shift Assignments of Ethylene/1-Octene Copolymer

[illegible]

can be at 41.6 or 40.97 ppm depending upon which neighbor it has (i.e., XOOOE/EOOOX, where X = O or E, respectively). Similar situations can be found for other assignments such as

methine of OOE/EOO, methine for OOO, 4B<sub>6</sub> for OOO, etc. While it may be obvious to people well versed with ethylene/1-octene <sup>13</sup>C NMR spectra as to which of the two or three

carbons in the structure the assignment is for, it is certainly not clear to people who have limited experience with this system. This situation can be avoided by assigning only one carbon at a time and by only assigning carbons in the center unit of an odd  $n$ -ad.

**New Assignment for Quantitative  $^{13}\text{C}$  NMR Analysis.** Here we propose refined assignments for ethylene/1-octene copolymer  $^{13}\text{C}$  NMR spectra based on those suggested by Liu et al. Other than improving on the deficiencies identified in the first part of the Discussion section, we also combined peaks that are not baseline resolved by a moderately high field instrument, i.e., 100 MHz Larmor frequency for  $^{13}\text{C}$  NMR. While assigning nonbaseline resolved peaks is valuable for qualitative purpose, attempting to use these assignments by employing various resolution enhancement or line deconvolution techniques will actually decrease the accuracy in the final numbers. It is important to notice that some of the baseline resolved peaks (thus individually assigned in this report) become less resolved at very high octene concentration (more than 40 mol % octene). However, most commercially important ethylene/1-octene copolymers have octene contents well below this level. The assignments included in this report target the analysis of these commercially important resins.

These resonance assignments are for ethylene/1-octene copolymers with no regio errors. In other words, each hexyl side chain is separated by an odd number of methylene carbons. The other convention employed in the assignment is that octene always starts at a backbone methine carbon and ends at its neighboring backbone methylene carbon. Chart 2 shows an illustration of this structure. It is important to note this structure is exactly the opposite of the more traditional way of propagating the  $\alpha$ -olefin, which is based on free radical polymerization. The structure drawn in Chart 2 usually occurs in the polymerization chemistry that the authors encounter. The assignment to the each respective  $n$ -ad will change if one counts octene from the other direction. However, as long as one is consistent, the end result from the quantitative analysis of the  $^{13}\text{C}$  NMR spectrum will be the same.

The chain end carbons are not listed in the assignment table and are listed in the following: 1s, 2s, 3s, and 4s are assigned to the 14.0–14.1, 22.8–23.0, 32.0–32.2, and 29.5–29.6 ppm regions, respectively.

Table 1 contains the details of the assignments. The first column lists the molecular structure that includes the carbon being assigned. The carbon being assigned is always labeled as “\*”. The second column lists the chemical shift range for the baseline resolved peak that includes all the contribution from the assigned carbon. The third column lists the pentad whose center unit contains the assigned carbon. The fourth column

lists the corresponding region number reported by Liu et al. The fourth column is listed to facilitate the comparison between this report and the article by Liu et al.

Since assigning the center unit of an odd  $n$ -ad is systematic, it is easy to check the uniqueness and completeness of the assignments. The following check was applied using Excel by sorting the third column. Thirty two distinct pentads were listed. That is exactly the number of pentads available. Each E centered pentad was listed twice, corresponding to only two carbons in each ethylene unit. Each O centered pentad was listed eight times corresponding to only eight carbons in each octene unit. After the above checks, we are reasonably confident that each carbon is counted once and only once.

## Conclusion

The results presented in this report show the utility of the quantitative self-consistency check as a tool to refine NMR peak assignments. It also demonstrates the importance of assigning only one carbon at a time and assigning each carbon once and only once. A rigorous and systematic way for achieving this goal is presented. Using this systematic approach and the quantitative self-consistency check, a quantitative NMR analyst can fully harness the tremendous potential achievable through chemical shift dispersion provided in both ultrahigh field NMR and multidimensional NMR.

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