

Improved quantitative solution state ^{13}C NMR analysis of ethylene-1-octene copolymers

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Abstract

In order to acquire fully quantitative, high signal-to-noise ^{13}C NMR spectra of ethylene-1-octene copolymers in a relatively short period of time, a detailed protocol has been developed, based on the addition of an optimised amount of the relaxation agent chromium(III)triacetylacetonate and without using nuclear overhauser enhancement (NOE). Compared to classical measurements with NOE, the proposed measuring protocol additionally offers a gain in signal-to-noise of 16%, which corresponds to a gain in experimental time of 34%. It allows precise and accurate quantification of all resonances, including small one's related to, e.g. comonomer inversion, and offers more refined information towards the determination of chemical shift and peak area measurements and the development of statistical chain microstructure models.

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1. Introduction

Copolymers formed by ethylene and higher α -olefins are important commercial products for which great efforts have been made to find new catalysts [1–3]. Several systems, including heterogeneous [4–6] as well as homogeneous [7–10] systems, have been reported. The ability to analyze the microstructure of these copolymers is important for the development of models which describe polymerization mechanisms and the structure–property relationships, e.g. in crystallization [11,12] and morphology [9,13,14] models [15]. Although ^{13}C NMR has been the most successful analytical tool to characterize the copolymer composition as well as the sequence distribution [16–18], it has been difficult to obtain fully quantitative carbon NMR data due to poorly defined NMR factors as the nuclear overhauser effect (NOE) and the long T_1 C relaxation decay times. Horii et al. [19] as well as Hansen et al. [20] state that, based on T_1 C decay time and NOE measurements, internal quantitative

consistency between peak intensities only exists under ‘no-NOE’ conditions. According to Hansen et al. quantitative analysis, based on ^{13}C NMR ‘NOE’ spectra, is restricted to the use of signals that have the same NOE effect or requires corrections for the signals that have uncomplete NOE’s. However, since the correlation times of molecular motion (τ_c) are dependent on variables like temperature and concentration, these corrections will be not generally applicable. These quantification drawbacks still hamper a detailed spectral analysis, which is the prerequisite to develop improved structural microchain models and often limits the added value of refined algorithms (e.g. simplex method).

1.1. Nuclear overhauser effect

Despite several precautions with respect to T_1 relaxation, pulse length, signal-to-noise ratio, digital resolution, filter bandwidth, etc. ^{13}C spectra acquired under full broad-band proton decoupling are often not quantitative due to unequal NOE’s [19–21]. A complete NOE enhancement—a constant which is independent of the internuclear distance and

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is given by

$$\eta = \gamma_{\text{H}}/2\gamma_{^{13}\text{C}} = (A_{\text{S}} - A_0)/A_0 = 1.99 \quad (1)$$

where γ is the gyromagnetic ratio, A_0 is the carbon intensity before proton irradiation and A_{S} is the carbon intensity when the protons are irradiated—is only observed if (a) the extreme narrowing condition is met ($\omega_0^2\tau_c^2 \ll 1$; fast tumbling), (b) the carbon spins relax only by intramolecular dipolar interactions with protons and (c) proton irradiation is continued for a very long time compared with all the T_1 relaxation times (steady state build up). According to relation (1), a full NOE results in a time gain of roughly a factor nine, since the gain in signal-to-noise (S/N) corresponds to about three ($A_{\text{S}} = 2.99A_0$ since $\gamma_{\text{H}} \approx 3.98\gamma_{^{13}\text{C}}$). Of course, in any practical case, other relaxation processes (e.g. via paramagnetic impurities, spin rotation relaxation of freely rotating groups such as CH_3 at higher temperature, etc.) will contribute so that the NOE enhancement will be less and not equal for all carbon environments. Furthermore, if the extreme narrowing condition is not met ($\omega_0^2\tau_c^2 \gg 1$), the NOE decreases with increasing τ_c . One way to achieve comparable integrals is by using the inverse gated decoupling technique in which the decoupler is on during the pulse and FID acquisition, but off during the long preparation delay [22]. This, however, results in a dramatic loss of sensitivity due to the lost NOE and explains why most ^{13}C NMR studies on ethylene-1-octene copolymers make use of the NOE enhancement. Without NOE, fully quantitative ^{13}C spectroscopy, for which a preparation of five times the longest T_1 has to be respected, becomes almost impossible due to the long T_1 relaxation times of the side-chain carbons (up to about 11 s).

1.2. Relaxation agent

A way to avoid NOE, and to decrease the T_1 relaxation decay times at the same time, is to add a shiftless relaxation reagent like chromium(III)triacetylacetonate ($\text{Cr}(\text{acac})_3$). Because the gyromagnetic ratio of an unpaired electron is roughly 1000 times larger than this of protons, the carbon T_1 relaxation will be rapid, being dominated by the unpaired electron. The use of $\text{Cr}(\text{acac})_3$ allows to acquire fully quantitative carbon spectra of these copolymers in the inverse gated decoupling mode in a comparable, or even shorter, period of time as by using NOE. The addition of $\text{Cr}(\text{acac})_3$ must be made cautiously, as an excess will increase relaxation rates so much that the resonances will become broadened (fast T_2 relaxation) and difficult to detect. Although some authors already have reported the use of $\text{Cr}(\text{acac})_3$ to study ethylene-1-octene copolymers [23–27], no systematic study is published so far.

This report describes the development of a fast, $\text{Cr}(\text{acac})_3$ based protocol to acquire fully quantitative ^{13}C spectra of ethylene-1-octene copolymers without NOE but with a high S/N ratio. Especially when the determination of small resonances becomes important, e.g. to study inverted

Table 1

Sample characteristics of the metallocene based ethylene-1-octene copolymers EO-4082-M and EO-2711-M

| Material | Mol% octene ^a | Density (kg/m ³) | M_n^b (kg/mol) | M_w^b (kg/mol) | M_z^b (kg/mol) |
|-----------|--------------------------|---------------------------------|---------------------|---------------------|---------------------|
| EO-4082-M | 18.7 | 848 | 39 | 87 | 155 |
| EO-2711-M | 5.6 | 900 | 36 | 88 | 155 |

^a as measured by ^{13}C Nuclear Magnetic Resonance (NMR).

^b number, weight and z-average molecular weight as measured by size exclusion chromatography-differential viscosimetry (SEC-DV), conventional calibration.

structures (2,1-insertions) in ethylene-1-octene copolymers, unequal NOE's have to be avoided to preserve the quantitative character. Moreover, the method is applicable to other copolymers of ethylene and higher α -olefins as well, and creates possibilities towards quantitative results at higher magnetic fields.

2. Experimental

Two ethylene-1-octene copolymers (EO-4082-M and EO-2711-M) were produced in a continuously stirred tank reactor (CSTR) using different, Boron-activated metallocenes (see Table 1).

2.1. NMR sample preparation

All NMR samples were prepared according the following procedure: after swelling 300 mg of copolymer in 1 ml 1,2,4-trichlorobenzene for about 1 h at 130 °C, the solution is further diluted by the addition of 1.4 ml 1,2,4-trichlorobenzene. After homogenizing the solution by vortex mixing, a variable amount of the relaxation agent ($\text{Cr}(\text{acac})_3$) is added. After homogenizing, 0.6 ml C_6D_6 (lock solvent) is added to a final copolymer concentration of 10 V% (300 mg copolymer in 3 ml solvent mixture). The concentration of $\text{Cr}(\text{acac})_3$ varies between 0 and 100 mM. Addition of chromium ions results in purple coloured solutions due to absorption of visible light. This offers a help to reveal possible heterogeneities of the solutions.

To evaluate the effect of the copolymer concentration and viscosity of the solutions on the NMR spectral resolution and the chemical shifts, a less concentrated copolymer solution of 8 V% was prepared that contains 45 mM of $\text{Cr}(\text{acac})_3$.

2.2. NMR measurements

^{13}C NMR spectra were recorded at 120 °C on a Varian Inova 400 (9.4 T) spectrometer in a dedicated 10 mm carbon probe. Spectral parameters used were: a spectral width of 22 kHz, a similar filter bandwidth [28], a 78° pulse angle of 13 μs , an acquisition time of 1.8 s and a preparation

Table 2

Influence of NOE enhancement on the S/N and experimental time of the ^{13}C spectrum of a native EO-4082-M solution of 10 V% at 120 °C. The time index of 100 corresponds to an experimental time of about 2 h 40 min (175 scans)

| Entry | NOE | S/N ratio | Time index |
|-------|-----|-------------|------------|
| 1 | No | 592 | 100 |
| 2 | Yes | 1485 | 100 |
| 3 | No | 1485 | 629 |

delay of five times the longest T_1C decay time (of the methyl resonance). The T_1C of the methyl group varies between 10.59 s, in the absence of $\text{Cr}(\text{acac})_3$, and 0.97 s in the presence of 80 mM $\text{Cr}(\text{acac})_3$. The T_1C decay times were measured by means of the Inversion Recovery method. For solutions containing relaxation reagent, the NOE effect was always eliminated by Inverse Gated Decoupling while solutions without relaxation agent were measured with and without NOE enhancement. The S/N ratios were measured in a specific spectral region of 1000 Hz: between 0 and 100 ppm, the region with the best S/N was selected. The spectral resolution was optimised by shimming the homogeneity of the magnetic field around the sample volume starting from a shim set obtained by means of a 'blanco' solvent sample (2.4 ml 1,2,4-trichlorobenzene and 0.6 ml C_6D_6) at 120 °C. For the copolymer solutions, the line width of the 1,2,4-trichlorobenzene resonances always is < 1 Hz. Identical conditions were used to measure the T_1C decay times on an Inova 300 spectrometer.

3. Results and discussion

3.1. NOE and quantitative ^{13}C spectroscopy

Even if the pulse repetition delays are much longer than the T_1C relaxation times, uncomplete NOE's, by which different carbons receive different amounts of NOE enhancement, often result in non-quantitative integrals [27]. Uncomplete NOE's occur if the correlation times of molecular motion fall outside the extreme narrowing range or because the carbon magnetisation does not completely relax by the intramolecular dipole-dipole mechanism [29–31]. Competing relaxation mechanisms like intermolecular dipole–dipole relaxation (via solvent molecules,

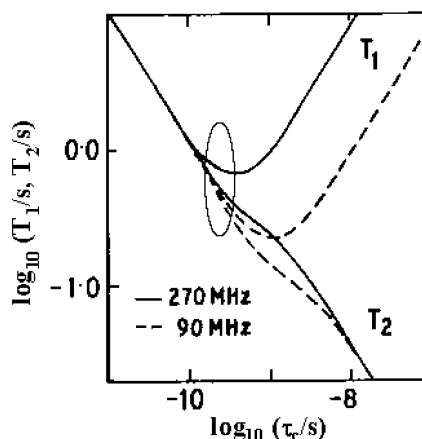


Fig. 1. Dependency of the T_1 and T_2 decay times on the correlation time of molecular motion.

identical solute molecules or paramagnetic impurities) and spin–rotation relaxation (for highly mobile carbons, e.g. side-chain methyl carbons) will reduce the NOE enhancement.

Table 2 shows the influence of NOE enhancement on the S/N and experimental time of the ^{13}C spectrum of ethylene-1-octene copolymers. While a complete NOE should improve the S/N by a factor three or reduce the experimental time by a factor nine ($S/N \sim t^{1/2}$), Table 2 shows factors of, respectively, 2.5 (entry 1 and 2) and 6.3 (entry 2 and 3) which indicates that the NOE effect is not complete. Although it is not the purpose of this study to explore the uncomplete NOE, the T_1C decay times of all carbon resonances were determined at different magnetic field strengths in order to check if the extreme narrowing range (ENR) condition is met. Increasing the field strength results in a significant increase of the decay times for all carbon resonances. Table 3 shows the results for a set of representative resonances obtained at carbon resonance frequencies of 100 and 75 MHz. Although required under slightly different experimental conditions, the table further presents the data reported by De Pooter et al. at 50 MHz [32].

The field dependency of T_1C , being relatively the smallest for the mobile methyl group (1B6), demonstrates that the ENR condition is not fully met. On the other hand, since the decay times increase upon raising the temperature (data not presented), the correlation times have to be

Table 3

T_1C decay times of some representative resonances at various magnetic field strengths as measured on the same 10 V% solution of native EO-4082-M at 120 °C. The 95% confidence limit for T_1C is about 1%. An overview of the signal nomenclature used can be found elsewhere [33]

| Carbon resonance frequency | T_1C (s) | | | | |
|----------------------------|-----------------------------|----------------------------|----------------|----------------|----------------|
| | S ₈₈ (29.98 ppm) | T ₈₈ (38.2 ppm) | 3B6 (32.2 ppm) | 2B6 (22.8 ppm) | 1B6 (14.0 ppm) |
| 100 MHz | 2.01 | 1.33 | 5.27 | 7.81 | 10.59 |
| 75 MHz | 1.76 | 1.14 | 5.04 | 7.39 | 9.71 |
| 50 MHz [32] | 1.60 | 1.06 | 4.24 | 6.21 | 9.57 |

Table 4

T_1C decay times of some representative resonances at various concentrations of $\text{Cr}(\text{acac})_3$ and copolymer (EO-4082-M) at 120 °C. The 95% confidence limit for T_1C is about 1%

| Concentrations | T_1C (s) | | | | | |
|-----------------------|------------|-------------------------|-------------------------|------|------|-------|
| | Copolymer | δS_δ | δT_δ | 3B6 | 2B6 | 1B6 |
| Cr(acac) ₃ | | | | | | |
| 0 | 10 V% | 2.01 | 1.33 | 5.27 | 7.81 | 10.59 |
| 10 mM | 10 V% | 1.50 | 1.10 | 3.14 | 3.92 | 4.66 |
| 20 mM | 10 V% | 1.29 | 0.94 | 2.15 | 3.08 | 3.43 |
| 30 mM | 10 V% | 1.09 | 0.86 | 2.15 | 2.49 | 2.65 |
| 45 mM | 10 V% | 0.92 | 0.77 | 1.41 | 1.54 | 1.66 |
| | 8 V% | 0.79 | 0.70 | 1.16 | 1.26 | 1.34 |
| 50 mM | 10 V% | 0.84 | 0.74 | 1.23 | 1.36 | 1.45 |
| 80 mM | 10 V% | 0.65 | 0.59 | 0.89 | 0.91 | 0.97 |

situated rather close to the ENR (Fig. 1: between the T_1 minimum and the ENR).

Possibly, other relaxation mechanisms also play a role in the uncomplete NOE enhancement (see 3.4. applications of protocol).

3.2. Relaxation reagent based ^{13}C NMR protocol

To obtain quantitative ^{13}C NMR information without using the questionable NOE, a strategy based on inverse gated decoupling and the use of chromium(III)triacetyl-acetate ($\text{Cr}(\text{acac})_3$) as a relaxation reagent was developed.

Table 4 shows the gradual decrease of the T_1C relaxation times at 120 °C as a function of increasing $\text{Cr}(\text{acac})_3$ concentration for a set of representative carbon signals. Fig. 2 visualizes the effect for the resonances 1B6 (methyl) and 2B6. A $\text{Cr}(\text{acac})_3$ concentration of 80 mM reduces the long

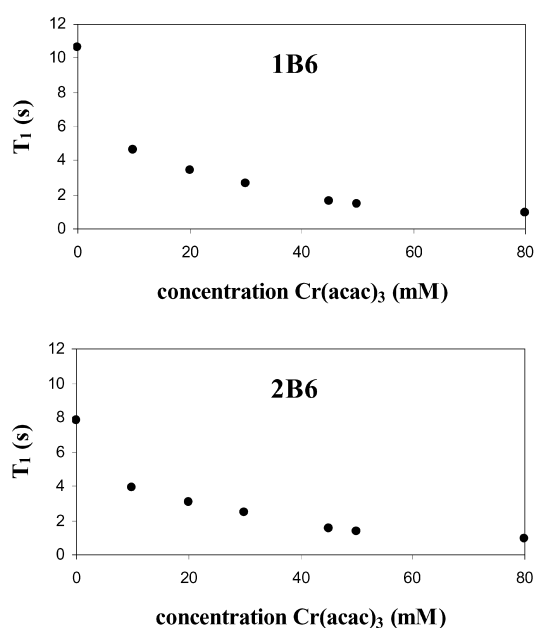


Fig. 2. T_1C decay time versus $\text{Cr}(\text{acac})_3$ concentration for the resonances 1B6 and 2B6 of a 10 V% solution of EO-4082-M at 120 °C.

Table 5

Effect of $\text{Cr}(\text{acac})_3$ on the experimental time and S/N for a 10 V% solution of EO-4082-M at 120 °C. The acquisition time used is 1.8 s and the preparation delay equals five times the T_1C of the 1B6 resonance

| [Cr(Acac) ₃] | T_1C (s) for 1B6 | NOE | # scans | Time (min) | Time index | S/N |
|--------------------------|--------------------|-----|---------|------------|------------|-----|
| 0 | 10.59 | Yes | 186 | 170 | 100 | 800 |
| 45 mM | 1.66 | No | 1010 | 170 | 100 | 800 |
| 80 mM | 0.97 | No | 1010 | 112 | 65.9 | 800 |
| 80 mM | 0.97 | No | 1530 | 170 | 100 | 925 |

decay times of the 1B6 and 2B6 resonance from initial values of 10.59 and 7.81 s to 0.97 and 0.91 s, respectively. Upon increasing the concentration of the relaxation reagent, the chemical shift and linewidth were followed cautiously: concentrations of $\text{Cr}(\text{acac})_3$ higher than 80 mM start to influence the line broadening (solvent resonances > 1 Hz.). Since the T_1C decay time of the methyl resonance was already strongly reduced by using 80 mM of $\text{Cr}(\text{acac})_3$, the T_1C 's were not determined at higher $\text{Cr}(\text{acac})_3$ concentrations.

Besides a fixed $\text{Cr}(\text{acac})_3$ concentration of 80 mM, the proposed procedure is optimised for a copolymer concentration of 10 V% and a measuring temperature of 120 °C. The latter because elevation of the temperature to 130 °C did not result in any improvement of the spectral resolution on one hand, but leads to longer T_1C decay times and higher degradation risks on the other hand. Also a more diluted copolymer solution of 8 V% (see Table 4) did not result in any improvement of the spectral resolution. Since a higher polymer concentration (viscosity) would certainly favor a shorter spin-lattice relaxation time [20] (see Fig. 1), Table 4 further shows that the $\text{Cr}(\text{acac})_3$ /copolymer concentration ratio—rather than the absolute $\text{Cr}(\text{acac})_3$ concentration—determines the T_1C decay times.

3.3. Gain of time or signal-to-noise ratio

Since the pulse repetition rate is dominated by the T_1C relaxation of the 1B6 resonance (preparation delay of 5 times T_1C), addition of $\text{Cr}(\text{acac})_3$ results in a serious reduction of the experimental time. The total time to acquire a scan, being the sum of the preparation delay and the FID acquisition (1.8 s) is reduced by a factor of $(5 \times 10.59 + 1.8)/(5 \times 0.97 + 1.8) = 8.2$. Compared to measurements without relaxation reagent but with NOE, the $\text{Cr}(\text{acac})_3$ based procedure is still 34% faster in time. An overview of some experimental results is presented in Table 5, in which the entries are comparable either by experimental time or S/N.

At a $\text{Cr}(\text{acac})_3$ concentration of 45 mM, the gain in experimental time due to the shorter T_1C decay times exactly compensates the loss due to the disabled NOE (entry 2). Further increase of the $\text{Cr}(\text{acac})_3$ concentration to

Table 6a

Influence of incomplete NOE's on the integrated value of some representative resonances for 10 V% solutions at 120 °C

| Integrated values | | | $\gamma S_\gamma + \gamma S_\delta + \delta S_\delta + 4B_6$ (28.5–31.4 ppm) | 3B6 ^a (32.2 ppm) | 2B6 (22.8 ppm) | 1B6 (14.0 ppm) |
|-------------------|-----------------------------|----------|--|-----------------------------|----------------|----------------|
| EO-4082-M | 80 mM Cr(acac) ₃ | no NOE | 68.60 | 10.00 | 10.24 | 10.17 |
| | Native | full NOE | 61.74 | 10.00 | 9.88 | 9.60 |
| EO-2711-M | 80 mM Cr(acac) ₃ | no NOE | 338.68 | 10.00 | 9.94 | 10.03 |
| | Native | full NOE | 292.02 | 10.00 | 9.62 | 9.08 |

^a Reference signal.

80 mM leads to a time gain of 34% (entry 1 and 3) or a gain in *S/N* of 16% (entry 1 and 4).

3.4. Applications of protocol

Fig. 3 shows a quantitative ¹³C NMR spectrum of EO-4082-M obtained by the proposed protocol. Please note that the *S/N* ratio, obtained in a time period of about 8 h, is much higher than normally observed in literature. Even the small αS_α signals of EOOE (± 40.3 ppm) and OOOE (± 41.0 ppm) sequences can be easily determined.

Table 6a shows the integrated values obtained for both ethylene-1-octene copolymers with rather extreme octene contents. The intensity of the resonance 3B6 has been chosen as internal reference, as Hansen et al. [20] demonstrated that the NOE for this signal is full (2.97). For native solutions, the use of NOE clearly results in a significant underestimation of the spectral region between 28.5–31.5 ppm, which becomes more pronounced at lower octene content. The classical triad distribution [34] (Table 6b) clearly shows an underestimation of the EEE and an overestimation of the EOE and OEE sequences, while no significant differences are observed for the other triads. Consequently, also the branch distribution is effected by NOE, especially for high octene contents.

Table 6a further shows that the intensity of the side-chain carbons decreases towards the highly mobile methyl group. The mechanism of spin rotation relaxation possibly can be responsible for the latter phenomenon.

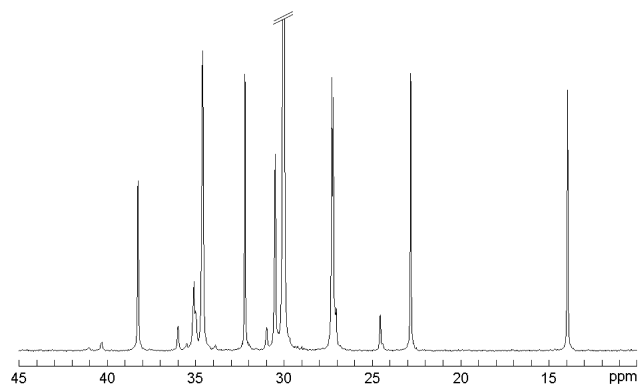


Fig. 3. ¹³C NMR spectrum of a 10 V% solution of EO-4082-M in the presence of 80 mM Cr(acac)₃ as a relaxation reagent. The experimental time was about 8 h. The small sharp peaks around 29 ppm show the presence of traces of free 1-octene.

Fig. 4 shows both the normal and APT (Attached Proton Test) carbon spectra of a Vanadium based, CSTR-produced ethylene-1-octene copolymer (EO-289-V; inversion $\approx 25\%$) with an octene content of about 30.3 mol%. The normal spectrum clearly shows the additional small resonances related to inverted comonomer units [35]. The APT spectrum, in which methine and methyl signals have negative and methylene signals have positive intensities, allows the assignment of the methine signals from inverted octene units. The resonances $\delta T_\gamma/\gamma T_\gamma/\beta T_\gamma$ are situated around 38.6, 39.0 and 36.3 ppm, respectively, and their relative presence was determined to be 74, 14 and 12%, respectively, which, as expected, demonstrates that the contribution of the δT_γ signal is the most prominent. The resonances of the inverted methylenes of inverted units [36] are also clearly observed around 31.6 ppm (αS_β) and 27.8 ppm (βS_γ) and, within integration error, the intensity

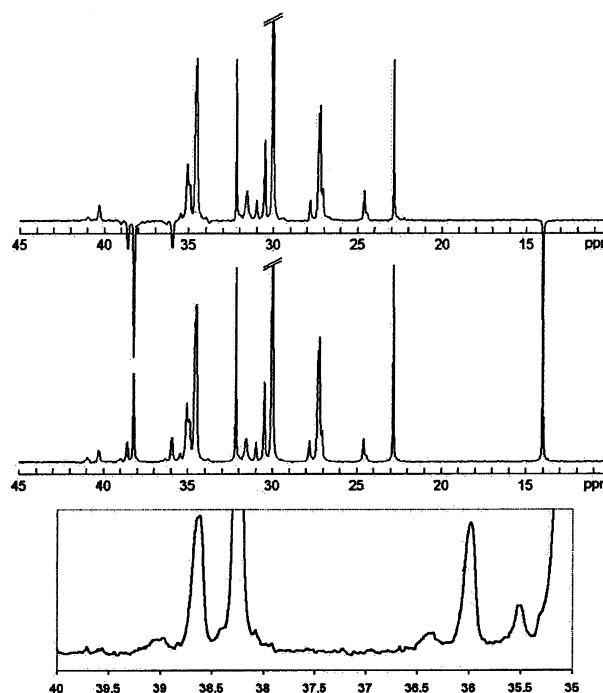


Fig. 4. APT (Attached Proton Test—top) and normal (bottom) carbon spectrum of sample EO-289-V. The 35–40 ppm region of the normal spectrum is enlarged to see the δT_γ (38.6), γT_γ (39.0) and βT_γ (36.3 ppm) signals.

Table 6b

Influence of incomplete NOE's on the triad distribution for 10 V% solutions at 120 °C

| Triad distribution | | | EOE | OEE | EEE | Branches/1000C |
|--------------------|-----------------------------|----------|-------|-------|-------|----------------|
| EO-4082-M | 80 mM Cr(acac) ₃ | no NOE | 15.45 | 26.62 | 50.35 | 93.5 |
| | Native | full NOE | 16.67 | 27.32 | 48.32 | 99.2 |
| EO-2711-M | 80 mM Cr(acac) ₃ | no NOE | 4.85 | 8.65 | 85.44 | 27.9 |
| | Native | full NOE | 5.01 | 10.06 | 84.08 | 26.9 |

of the former obeys Eq. 2:

$$\alpha S_{\beta} = \delta T_{\gamma} + 2_{\gamma} T_{\gamma} + \beta T_{\gamma} \quad (2)$$

Although the methine resonances related to inverted comonomer units appear in the same order of succession in the spectrum as for ethylene–propylene copolymers [37], the exact chemical shifts of these units in ethylene-1-octene copolymers are not published before. For the improvement of kinetic models, these signals are of tremendous relevance, since inversions affect termination and propagation probabilities. Furthermore, quantitative information on inversion-related signals will benefit the reliability of calculated catalyst characteristics, like the reactivity ratios.

Thus, the proposed ¹³C NMR measuring protocol is faster, more sensitive, fully quantitative, and applicable to other branched polyethylenes (although the Cr(acac)₃ concentration can probably be lowered for copolymers of ethylene and shorter α -olefins due to the shorter T_1C decay time of the methyl group). The ability to analyze the microstructure of these copolymers in more detail is important for the development of more refined models and algorithms to describe the copolymerization process. Finally, the protocol also offers excellent opportunities towards quantitative measurements at higher field (resolution) spectrometers.

4. Conclusions

In this paper it is demonstrated that the quantitative character of ¹³C NMR spectra of branched polyethylenes is questionable if acquired with NOE enhancement. A clear field strength dependency of the T_1C decay times is demonstrated. A fully quantitative and even faster procedure is presented based on inverse gated decoupling and the use of chromium(III)tri-acetylacetonate as a relaxation reagent. The loss of NOE enhancement is more than compensated by the strong decrease of the T_1C relaxation times. The latter allows a much faster pulse sequence repetition rate and results in an appreciable gain in experimental time (34% for comparable S/N).

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