^{13}C NMR of polyolefins with a new high temperature 10 mm cryoprobe

Zhe Zhou [a,*], Rainer Kümmerle [b], James C. Stevens [a], David Redwine [c], Yiyong He [c], Xiaohua Qiu [c], Rongjuan Cong [a], Jerzy Klosin [c], Nikki Montañez [d], Gordon Roof [c]

[a] The Dow Chemical Company, Freeport, TX 77541, USA
[b] Bruker BioSpin AG, NMR Division, Industriestrasse 26, CH-8117 Fällanden, Switzerland
[c] The Dow Chemical Company, Midland, MI 48667, USA
[d] Kelly, Freeport, TX 77541, USA

ARTICLE INFO

ABSTRACT

Recently, a high temperature 10 mm cryoprobe was developed. This probe provides a significant sensitivity enhancement for ^{13}C NMR of polyolefins at a sample temperature of 120–135 °C, as compared to conventional probes. This greatly increases the speed of NMR studies of comonomer content, sequence distribution, stereo- and regioerrors, saturated chain end, unsaturation, and diffusion of polymers. In this contribution, we first compare the ^{13}C NMR sensitivity of this probe with conventional probes. Then, we demonstrate one of the advantages of this probe in its ability to perform 2D Incredible Natural Abundance Double Quantum Transfer Experiment (2D INADEQUATE) in a relatively short period of time. The 2D INADEQUATE has been rarely used for polymer studies because of its inherently very low sensitivity. It becomes even more challenging for studying infrequent polyolefin microstructures, as low probability microstructures represent a small fraction of carbons in the sample. Here, the 2D INADEQUATE experiment was used to assign the ^{13}C NMR peaks of 2,1-insertion regioerrors in a poly(propylene-co-1-octene) copolymer.

1. Introduction

Microstructural characterization of polymers is critical for understanding polymer properties, the mechanism of polymerization, and for developing NMR methods for analyzing related polymers. The most important method for studying polymer microstructure is ^{13}C NMR spectroscopy. This powerful method suffers, however, from inherently low sensitivity, which makes the study both time-consuming and not practical for minor structures.

To address the sensitivity issue, cryoprobes were developed with signal-to-noise (S/N) ratios typically 3–4 times higher per scan than that of conventional probes. This sensitivity enhancement is especially significant because in Fourier Transform NMR spectroscopy the cumulative S/N ratio is proportional to the square root of the number of collected scans. The S/N ratio obtained in an NMR measurement is proportional to the ratio of induced signal over noise voltage. The efficiency of NMR probes can be optimized by either modifying the RF coil design, which affects RF coil efficiency and/or reducing RF coil resistance by cooling the RF coil with cryogenic liquids or gases. The latter is more important for cryoprobes. The first commercially available cryoprobes were

introduced in the late 90's. Significant technical difficulties in probe design had to be overcome to allow sample analysis at ambient temperature while observing NMR signal with high frequency antenna at cryogenically low temperatures located only a few millimeters away from the sample. Additional complication arises from the limited amount of space in the probe (superconducting magnets for high resolution NMR have a bore of 54 mm in diameter) and the high magnetic field (10–22 T for the RF coil area, depending on the magnet type up to a Tesla or more for the preamplifier electronics in the magnet stray field) in which the cold RF electronics need to function properly. Cooling the RF coil and resonance circuit to roughly 19 K and preamplifier electronics integrated in the probe to 77 K reduces the amount of thermal noise from the electronics and can yield a S/N gain of a factor of 4 compared to similar conventional probe technology. Cooling is delivered using compressed He gas which is expanded using a two stage Gifford McMahon cryocooler. Two closed cooling circuit loops can be used, one for the RF coil area and the other for the cold preamplifier part. This allows efficient decoupling of the required cooling (power or capacity) for the RF coil and preamplifier electronics and offers the highest RF power tolerance for demanding NMR experiments.

Five millimeter NMR cryoprobes with sample temperature capabilities of up to 80 °C have been available for over a decade and used mainly in the structural studies of biomolecules [1]. The 10 mm cryoprobe presented here pushed further the technical

limits in probe design. The larger NMR tube diameter is beneficial for polymer NMR studies, due to the increased sample volume in the active region of the probe. The increased sample diameter, however, leads to a further reduction of available space to accommodate thermal insulation, vacuum, RF coils, and pulsed field gradient coil. In addition, polyolefin NMR studies are conducted often at high sample temperatures (120–135 °C). It has been very challenging to accommodate the increased radiation of the hot 10 mm NMR sample while maintaining the RF coil at ~19 K in the development of the high temperature cryoprobe. The increased sample temperature range leads to increased material stress, thus careful choice of construction materials has to be made. Compared to a conventional broadband observe (BBO) 10 mm probe, the new 10 mm cryoprobe achieves a S/N increase of ~4.8 (Table 1) for ambient temperature ^{13}C analysis. When measuring at high sample temperature (398 K, 125 °C), the S/N gain increases further as the RF coil temperature of the cryoprobe doesnot change, whereas for conventional probes, the RF coil temperature is practically identical to the sample temperature. Cryogenically cooled preamplifiers are built in for all channels, e.g. ^{13}C, ^1H and ^2H (lock). The latter also allows the realization of significant sensitivity gains on the lock channel which allows working with lower contents of deuterated solvents.

With this 10 mm high temperature cryoprobe, ^{13}C NMR spectra with the desired S/N ratio can be acquired in a much shorter time than previously possible. This probe is also a powerful tool for studying low concentration features in polymers, for example, regio- and stereoerrors and chain ends. In this paper, we present the cryoprobe sensitivity compared with conventional probes, and the ^{13}C NMR assignments of low level of regio- and stereoerror in poly(propylene-co-1-octene) (P/O) using 2D Incredible Natural Abundance Double Quantum Transfer Experiment (INADEQUATE).

2. Experimental

The high density polyethylene (HDPE), poly(ethylene-co-1-octene) (E/O) and P/O copolymers were synthesized by The Dow Chemical Company. HDPE (0.45 g) was placed into a Norell 10 mm NMR tube followed by 3 g of 1,1,2,2-tetrachloroethane-d$_2$ (TCE-d$_2$)/ortho-dichlorobenzene (ODCB) (w:w, 1:1). Oxygen was reduced by a nitrogen purge via a pipette inserted for ca. 4 min. The tube was capped and placed in an aluminum heating block at 150 °C for several hours. The sample was periodically checked for homogeneity and mixed manually as necessary. A homogeneous mixture was evident by visualization of the uniform distribution of the polymer in solution with no apparent areas of high solvent concentration or air pockets. The E/O copolymer sample (0.25 g) was added to a Wilmad thin-wall 10 mm NMR tube with 3.2 g of stock solvent, then purged in the N$_2$ box for 2 h. The stock solvent was made by dissolving 4 g of perdeuterated 1,4-dichlorobenzene in 39.2 g of ODCB with 0.025 M

Cr(acac)$_3$. The sample tube was then heated in a heating block 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. P/O copolymer (1.5 g) was added to a Wilmad thin-wall 10 mm NMR tube with 1.5 g of stock solvent for the INADEQUATE and HOESY experiments, then purged in a N$_2$ box for 2 h. The stock solvent was made by dissolving 4 g of perdeuterated 1,4-dichlorobenzene in 39.2 g of ODCB. The sample tube was then heated in a heating block at 150 °C. The sample tube was repeatedly vortexed and heated. The sample tube was then left in the heating block for at least 24 h to achieve sample homogenization.

All NMR experiments were carried out on a Bruker 400 MHz spectrometer with a 10 mm DUAL (proton and carbon) cryoprobe at 25 °C for the ASTM sample and at 125 °C for polymer samples. The ^{13}C transmitter offset was 32.5 ppm and the ^1H decoupler offset was 1.5 ppm.

The ^1H–^{13}C HOESY experiments were performed with an acquisition time of 0.135 s, a relaxation delay of 2.0 s and a mixing time of 0.2 s. Sixty four transients per increment were accumulated in a matrix of 2 K (t_2) × 512 (t_1) data points. SW$_2$ 7575.8 Hz and SW$_1$ 6009.6 Hz. The data was processed with 90° shifted sine bell weighting functions and zero filling to form a 4K × 1K matrix prior to the Fourier transformation. The INADEQUATE was performed with an acquisition time of 0.41 s and a pulse delay of 4.0 s. 320–384 transients per increment were acquired in a matrix of 4 K (t_2) × 140 (t_1) data points. SW$_2$ 5040.3 Hz and SW$_1$ 10080.6 Hz. Phase cycling was done according to Bourdonneau's method [2]. The data was processed with 90° shifted sine bell weighting functions and zero filling to form a 4K × 1K matrix prior to the Fourier transformation.

3. Results and discussion

3.1. The cryoprobe

Probe sensitivity is of primary importance in NMR spectroscopy as sensitivity gains account for a reduction of the power of two of the NMR time. Thus, in order to double the sensitivity of an NMR experiment it is necessary to quadruple the NMR time. S/N ratios of three samples measured with three different probes are listed in Table 1. The sensitivity increase is about 5.5-fold for the cryoprobe when compared with the conventional 10 mm broadband observe (BBO) probe for ^{13}C NMR analysis of the HDPE and the E/O samples. This translates into a 30-fold decrease in signal averaging time. The sensitivity of this 400 MHz cryoprobe is estimated to be higher than that of a conventional 10 mm carbon selective probe on 1 GHz spectrometer (calculated based on 400 MHz DUL S/N ratio and 1 GHz field strength). Such sensitivity enhancement allows for much more rapid analyses of the comonomer content, sequence distribution, tacticity, and other microstructural details of various polyolefins, especially in blends and block copolymers where the concentration of the individual structures is reduced.

In addition to sensitivity, lineshape and B_1 homogeneity are important parameters to characterize new probes. The B_0 homogeneity was achieved with 3D triple axis ^1H gradient shimming (using the probe Z-gradient and the X and Y room-temperature shims, non-spinning) as well as on-axis Z-gradient shimming (^1H, or ^2H). ^1H lineshape was measured with 0.3% CHCl$_3$ in acetone-d$_6$. Half width is 0.6 Hz and hump is 6.3/15.2 Hz (0.55%/0.11%) with sample spinning. Non-spinning values are 0.76 Hz (half width) and 12.1/23.0 Hz (hump at 0.55%/0.11%). Lineshape for ^{13}C detection was measured with the ASTM sample (40% dioxane in C$_6$D$_6$) using a power gated decoupled experiment. With the sample spinning, the half width is 0.11 Hz and the hump is 1.5/3.0 Hz (0.55%/

Table 1
^{13}C NMR S/N ratios of different 10 mm probes.

| Sample	S/N ratio		
	400 MHz BBO	400 MHz DUL	400 MHz Cryo DUL
ASTM	558	625	2677
HDPE	1858		10311
E/O	1274		7010

ASTM is 40% dioxane in 60% C$_6$D$_6$. S/N ratio with single scan, 3.5 Hz line broadening and 40 ppm noise region. S/N for HDPE and E/O samples (the octene content for the E/O sample is 12.2 mol%). With 4 scans, 2 Hz line broadening and 2 ppm noise region, taken on backbone methylene peak. Measurement at 125 °C sample temperature.
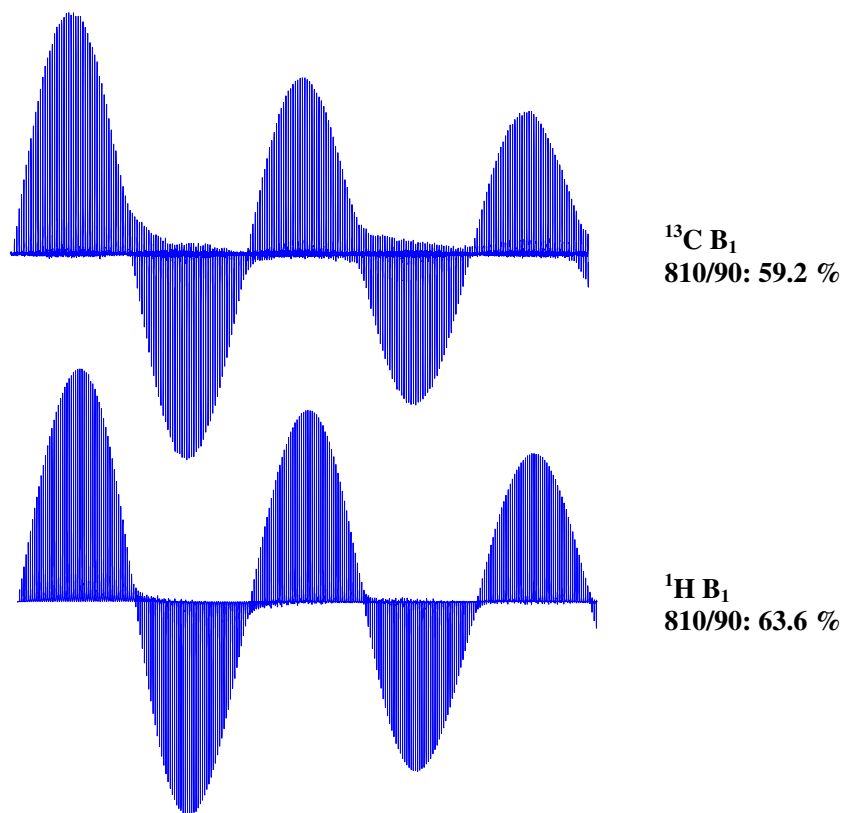
Fig. 1. The B_1 homogeneity measurement in a direct observe fashion at 120 °C with 0.6 wt% HDPE for ^1H and 2.0 wt% HDPE for ^{13}C in TCE-d_2 containing 0.0125 M Cr(acac)$_3$. The signal is from methylene of the polymer chain.

0.11%), non-spinning half width is 0.13 Hz and hump is 2.0/3.9 Hz (0.55%/0.11%). The B_1 homogeneities were measured using 0.6 wt% HDPE for ^1H and 2.0 wt% HDPE for ^{13}C in TCE-d_2 containing 0.0125 M Cr(acac)$_3$ at 120 °C using a direct measurement (nutation). Both spectra have been processed with a 75° shifted sine bell and the data is shown in the Fig. 1.
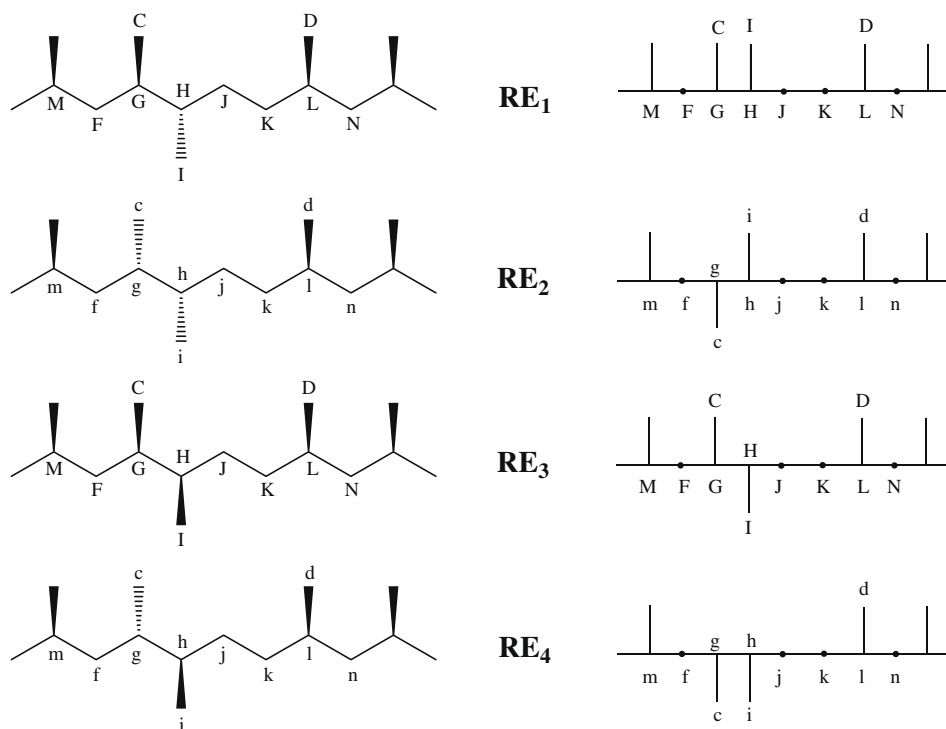
Fig. 2. 3D structures and Fisher projections of 2,1-insertion regioerrors in iPP.
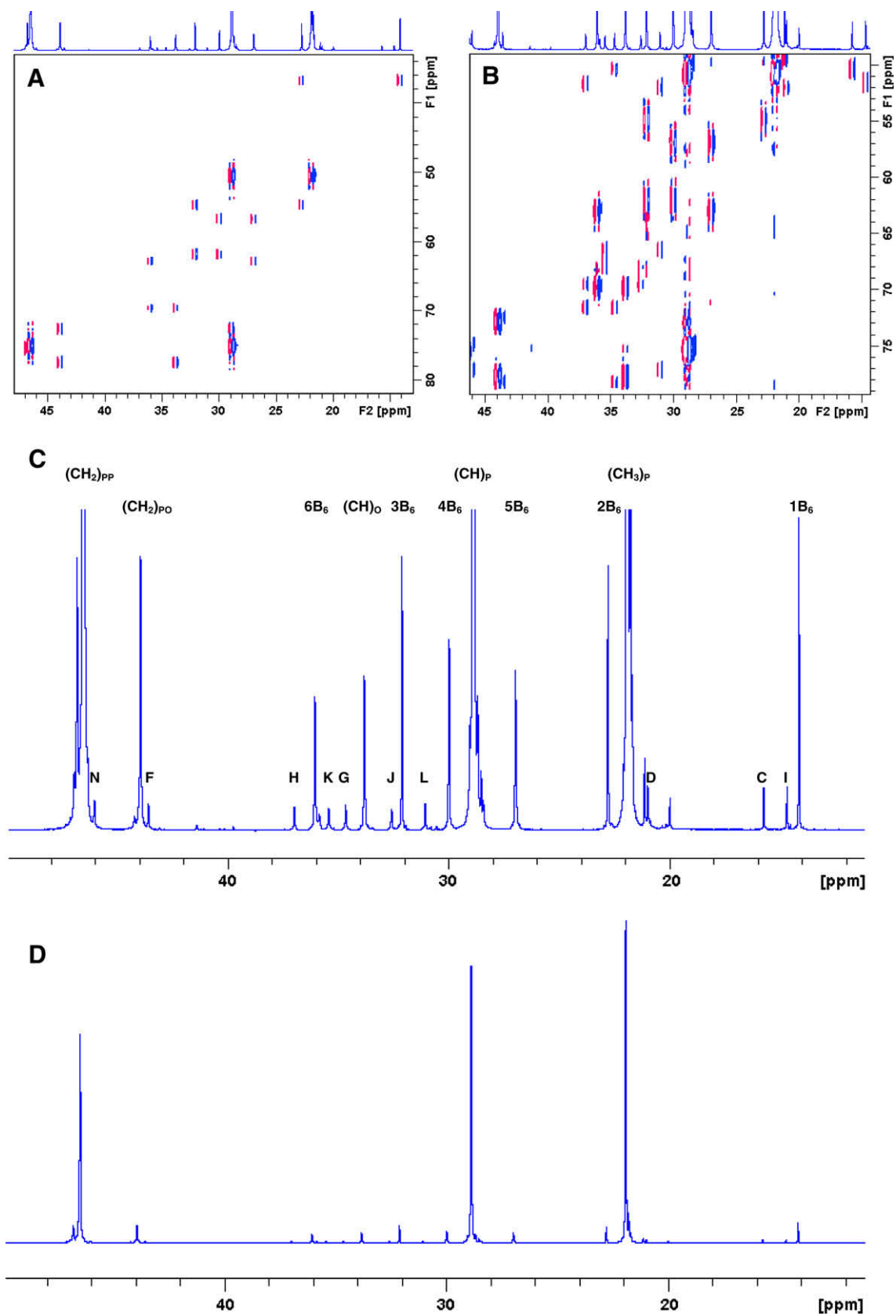
Fig. 3. NMR of P/O copolymer. (A) Fragment of 2D INADEQUATE spectra showing carbon–carbon connectivity of octene. (B) Fragment of 2D INADEQUATE spectra showing the 2,1-inverse insertion in P/O. (C) 1D ^{13}C NMR with the carbon peak assignments based on A and B. (D) 1D ^{13}C NMR of the P/O.

3.2. ^{13}C NMR assignments of a P/O and 2,1-insertion regioerror of propylene in the polymer

^{13}C NMR assignments of minor components and infrequent structures in polymers can be challenging, however, these microstructures are important. For example, the regioerrors can influence the polymeric properties as well as provide detailed insight into the mechanism of the polymerization catalyst. A few NMR studies of the related errors in polypropylene have been undertaken [3–10]. The studies were based mainly on additive ^{13}C chemical shift rules and model compounds. Asakura et al. characterized a highly regioirregular homo polypropylene sample containing about 40 mol% inverse insertion with 2D INADEQUATE [8,11,12] on a 400 MHz NMR spectrometer using a conventional probe. The S/N ratio of the reported spectrum was low and the spectrum was extremely complex due to the high level of inverted units, which resulted in ambiguous interpretation [8]. This new high temperature 10 mm cryoprobe can be a powerful tool to tackle these issues, especially when 2D INADEQUATE is needed due to dramatic sensitivity increase [13].

Here, we examined a P/O copolymer with an octene content of only 4 mol% and an average propylene run length of 25 (assuming Bernoullian statistics), prepared using representative procatalyst [*N*-[2,6-bis(1-methylethyl)phenyl]-4-(2-ethyl-3-benzofuranyl-κC4)-1-methyl-α-[2,4,6-tris(1-methylethyl)phenyl]-1H-imidazole-2-methanaminato(2-)-κN2,κN3]dimethyl-hafnium [14–16]. The most common regioerror observed in the long propylene sequence is an isolated 2,1-misinsertion, which can exist in one of four diastereoisomeric forms depending on stereochemical relationship between the methyl groups. These four sequences labeled RE$_1$–RE$_4$ are shown in Fig. 2 with 3D structures and Fisher projections [13,17].

Fig. 3 shows the NMR spectra of the P/O copolymer. The 2D INADEQUATE experiment took 2.6 days. We estimate that about 2.6 months of NMR instrument time would have been required to obtain a comparable 2D INADEQUATE spectrum with a conventional 10 mm BBO probe at 400 MHz. The carbon network of the octene is shown clearly in Fig. 3A. The F$_2$ dimension is a regular 1D ^{13}C NMR with ^{13}C–^{13}C coupling. Since two coupled spins share the same double quantum frequency in the F$_1$ dimension, correlations are made by following horizontal traces parallel to F$_2$. Carbon connectivity is established by a sequence of horizontal, vertical, and horizontal steps. Lowering the display threshold in Fig. 3A, reveals the connectivity of the regioerror which is present at only 0.55 mol% (Fig. 3B). The chemical shift assignments of the P/O are shown in Fig. 3C. Fig. 3D shows the ^{13}C 1D spectrum of the P/O scaled so that the main propylene peaks are not truncated and it can be seen that the intensity of the regioerror peaks are very low.

Having established carbon connectivity for the regioerror in the long propylene sequence in the P/O, we then set out to obtain the stereochemical identity of this regioerror, using ^{1}H–^{13}C HOESY [18]. The chemical shift difference of the two protons corresponding to peak *F* and the two protons corresponding to peak *N* in Fig. 4 are 0.42 and 0.37 ppm, respectively. It is well known that the two diastereotopic methylene protons in iPP have different chemical shifts and the difference is about 0.41 ppm [19]. However, the two homotopic methylene protons in syndiotactic polypropylene have the same chemical shift [19]. This means that the regioerror in the P/O is either RE$_1$ or RE$_3$ (see the structures in Fig. 2). Based on the ^{13}C chemical shift prediction for regioerrors in iPP [13], the regioerror in the P/O can be assigned to RE$_3$.

4. Conclusions

The 10 mm high temperature cryoprobe provides much higher sensitivity compared to conventional probes. Many polyolefin microstructures can be investigated in a short acquisition time, whereas they were previously inaccessible. For example, the 2,1-insertion regioerrors in a P/O copolymer were examined and assigned unambiguously using 2D INADEQUATE spectroscopy. These microstructural characterization studies are important for understanding the mechanism of the catalysts and for understanding the effects of low probability structural features on the polymer physical properties.

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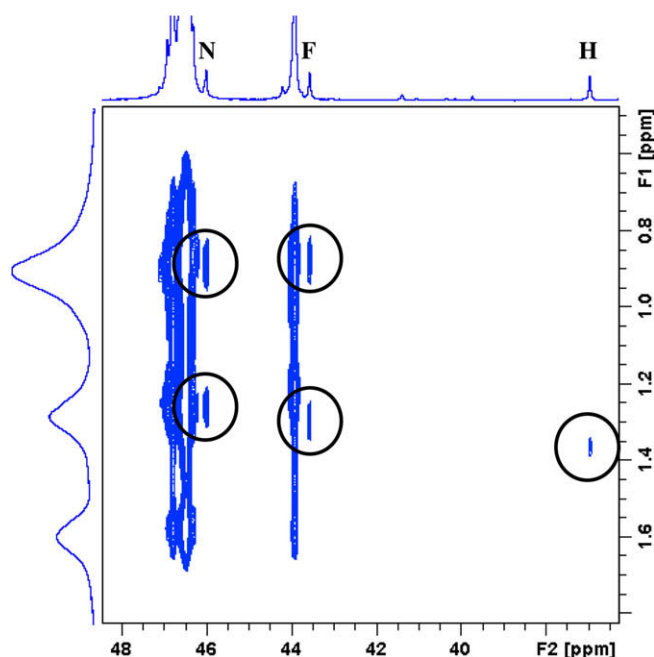

Fig. 4. Fragment of the HOESY (^{1}H–^{13}C) spectrum of the P/O. The mixing time is 0.2 s.

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