

High-Temperature Pulsed-Field-Gradient Multidimensional NMR of Polymers

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The application of pulsed-field-gradient (PFG) techniques has been particularly important in providing the ability to detect 2D and 3D NMR cross peaks from minor structural components in synthetic organic polymers. The lack of mobility in a large percentage of polymers leads to rapid T_2 relaxation which prevents the use of pulse sequences, such as the HMBC experiment, that operate based on coherence transfer via small, long-range J couplings. High-temperature NMR increases molecular motion with corresponding line narrowing (e.g., polyethylenes are typically analyzed at 120°C). However, until now, the requirement for high temperature has precluded the use of PFG methods. Here we present data from a new probe which is capable of performing high-temperature PFG coherence selection experiments at temperatures typical of those used in many polymer analyses. We illustrate the performance of this probe with PFG-HMBC spectra of a copolymer from ethylene/1-hexene/1-butene at 120°C. © 1999 Academic Press

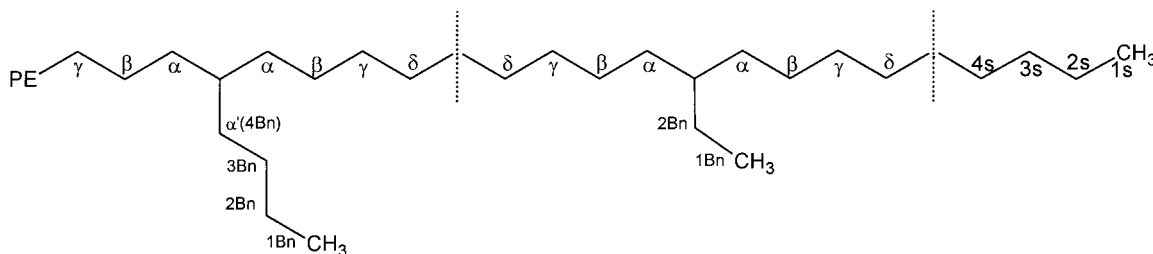
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NMR has had a tremendous influence on our ability to characterize polymers and to understand their chemistry. It is generally recognized that a relatively small number of key structures such as long-chain branches, cross links, and reactive chain ends can have a dramatic influence on a polymer's properties. The sensitivity of modern NMR instruments has provided the capability to routinely detect signals from these structures which have low occurrence levels in a polymer

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chain. However, the number and proximity of these resonances makes it difficult to assign peaks based on traditional comparison of shifts with model compounds. Two-dimensional (2D) NMR methods, particularly heteronuclear multiple-quantum coherence (HMQC) (1, 2) and heteronuclear multiple-bond correlation (HMBC) (3) NMR experiments, have become valuable techniques for elucidating chemical structures and proving resonance assignments. These experiments have also become effective methods for investigating the microstructures of polymers (4, 5).

The application of pulsed-field-gradient (PFG) techniques (6, 7) has been particularly important in providing the ability to detect 2D and 3D NMR cross peaks from minor structural components in synthetic organic polymers (8–10). The lack of mobility in a large percentage of polymers leads to rapid T_2 relaxation which prevents the use of pulse sequences, such as the HMBC experiment, that operate based on coherence transfer via small, long-range J couplings. To circumvent this problem, high-temperature NMR is used to increase molecular motion with corresponding line narrowing (e.g., polyethylenes are typically analyzed at 120°C). However, until now, the requirement for high temperature has precluded the use of PFG methods. Here we present data from a new probe which is capable of performing high-temperature PFG coherence selection experiments at temperatures typical of those used in many polymer analyses. We illustrate the performance of this probe with PFG-HMBC spectra of a copolymer from ethylene/1-hexene/1-butene (1) at 120°C.



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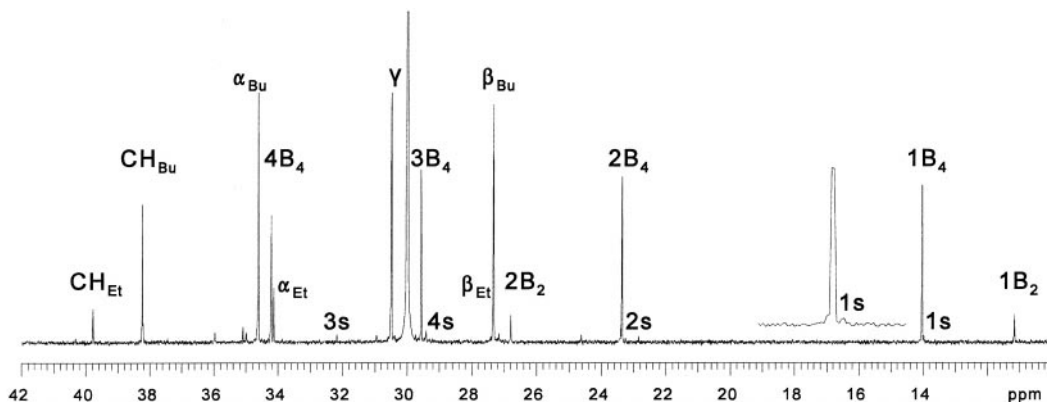


FIG. 1. 1D 188.6-MHz ^{13}C NMR spectra of polyethylene, **1**. The polymer used in this study was purchased from Aldrich Chemical Co. ($M_n \approx 50,000$). The largest methylene peak was used as a reference (30.0 ppm).

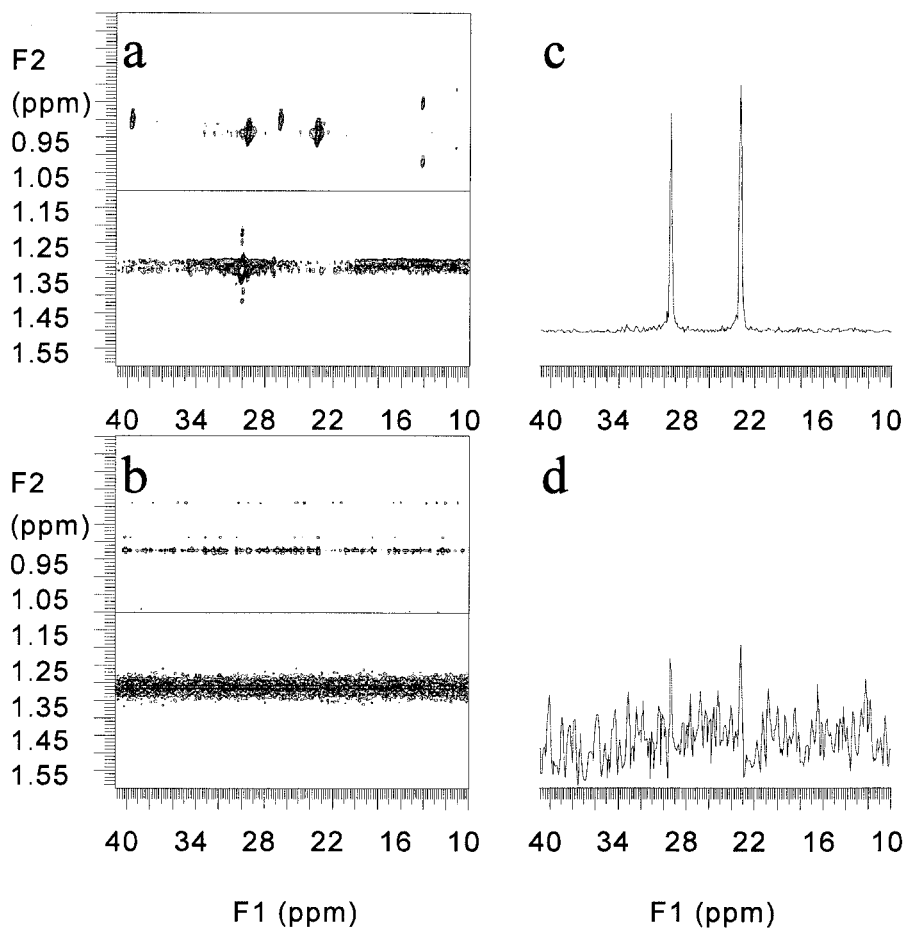


FIG. 2. HMBC spectra of **1** (10% w/w) in 40% benzene- d_6 and 1,2,4-trichlorobenzene. (a) PFG-HMBC; (b) standard phase-cycled HMBC; (c) slice from (a) at $\delta_{\text{H}} = 0.91$; and (d) slice from (b) at $\delta_{\text{H}} = 0.91$. The 2D NMR spectra were obtained at 120°C with a relaxation delay of 4.0 s, $\Delta = 1.79$ ms (based on $^1J_{\text{CH}} = 140$ Hz), and an acquisition time of 0.345; eight transients were averaged for each of 1024 increments during t_1 . The evolution time was incremented to provide the equivalent of a 13.9-kHz spectral window in the F_1 dimension; and a 1-kHz spectral window was used in the F_2 dimension. The gradient pulses were 2.0 ms long and were 0.100 and 0.075 T/m (for the first and second PFG pulses) (9, 10). The total experiment time was about 10 h. Data were zero filled to 4096×2048 and weighted with a shifted sine-bell function before Fourier transformation. The top half of each spectrum was plotted with $6\times$ vertical amplification to reveal the weak signals from low occurrence structures.

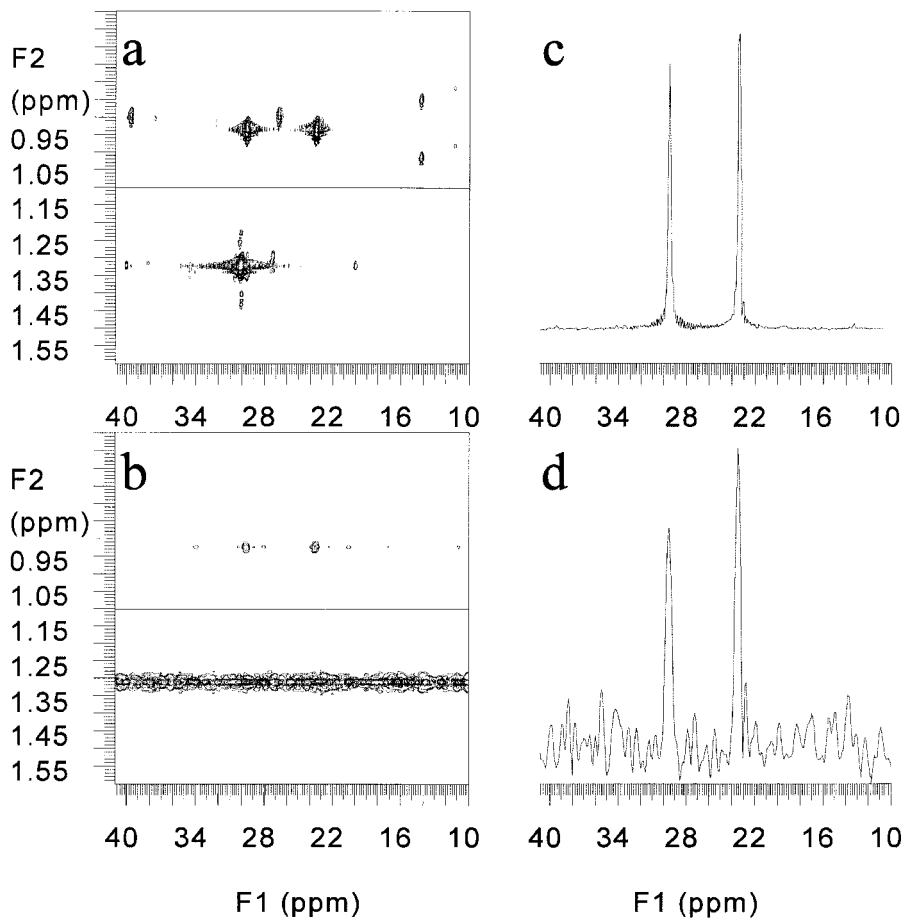


FIG. 3. HMBC spectra obtained from **1** at 120°C, by signal averaging 64 transients per t_1 increment: (a) gradient HMBC spectrum; (b) standard phase-cycled HMBC spectrum; slice from (a) at $\delta_{\text{H}} = 0.91$; and (d) slice from (b) at $\delta_{\text{H}} = 0.91$. The top half of each spectrum is plotted at 6 \times vertical amplification to reveal cross peaks from chain ends and butyl branches. All other acquisition parameters were the same as those used for the spectra in Fig. 2.

High-resolution ^{13}C NMR has been successfully used to assign the carbon resonances for branches in polyethylene and copolymers of ethylene and α -olefins (11–16). These assignments have been made with the aid of modified Grant–Paul chemical shift rules (17), Lindeman–Adams methods (18), comparison with the spectra of model compounds, and the study of model copolymers (19). It is now possible in 1D NMR to detect many signals from minor components such as chain ends and branches, which are present at a level of one part in 10^3 – 10^6 . ^{13}C NMR analyses of these materials are commonly obtained from a sample of the swelled polymer in 1,2,4-trichlorobenzene (TCB) at 120°C. Under these conditions, relaxation times are several seconds and linewidths can be extremely narrow.

The spectra shown here were obtained from a sample of **1** (10%, w/w) in TCB with 40% benzene- d_6 as a lock solvent. Data were collected on a Varian Unityplus 750-MHz spectrometer with a Nalorac $^1\text{H}/^2\text{H}/^{13}\text{C}/\text{X}$ 5-mm gradient probe designed to operate up to 130°C. The 90° pulse widths for ^1H and ^{13}C were 10.5 and 30.0 μs , respectively. On cursory examination,

the 188.6-MHz ^{13}C NMR spectrum of **1** (Fig. 1) shows 17 resonances (20) which are attributed to 1B_4 (14.05 ppm), 2B_4 (23.37 ppm), 3B_4 (β' , 29.57 ppm), and 4B_4 (α_{Bu} , 34.23 ppm) of the butyl branches; $\alpha_{\text{Bu}}\delta^+$ (34.63 ppm), $\beta_{\text{Bu}}\delta^+$ (27.34 ppm), $\gamma_{\text{Bu/Et}}\delta^+$ (30.49 ppm), methine (38.24 ppm), and $\delta^+\delta^+$ (30 ppm) of the hexyl branches; and 1s (13.99 ppm), 2s (22.84 ppm), and 3s (32.18 ppm) resonances from the end of the main chain. The α_{Bu} and α_{Bu} (4B_4) carbons are very different and produce two resonances in the region 34–35 ppm with an intensity ratio of 2:1. These assignments are consistent with those previously reported (16). Additional resonances can be seen from 1B_2 (11.16 ppm), 2B_2 (26.80 ppm), α_{Et} (34.15 ppm), β_{Et} (27.36 ppm), and methine (39.79 ppm) of the ethyl branches.

The PFG-HMBC and the standard phase-cycled HMBC 2D NMR spectra of **1** are shown in Figs. 2a and 2b, respectively. They were both obtained by averaging eight transient per t_1 increment. These spectra exhibit correlations between the ^1H and ^{13}C resonances of methine, methylene, and methyl groups which are separated by two and three bonds. Chemical shift correlations provide unequivocal resonance assignments when

peaks have similar chemical shifts and comparisons with the shifts of model compounds are ambiguous. The plot of the aliphatic region from the standard HMBC spectrum of **1** in Fig. 2b is dominated by artifacts associated with the C–H correlations from the main-chain repeat units. They are so intense that the noise ridges arising from imperfect cancellation of coherence from ^1H atoms bound to ^{13}C obscure any resonances that would provide useful structural information. Only correlations from the 2B_4 and 3B_4 structures can be seen. The ability of the PFG-HMBC experiment to select the desired coherence pathway in one scan results in a much higher quality spectrum as shown in Fig. 2a. Three groups of resonances are observed along different proton chemical shifts in the methyl region. They are assigned to 2B_2 and methine resonances from ethyl branches, 2B_4 and 3B_4 resonances from butyl branches, and 2s and 3s resonances from chain ends. Weak doublets from HMQC “leakage” of 1B_2 and 1B_4 one-bond correlations are also observed at $\delta_{13\text{C}} = 11.16$ and 14.05 .

Figures 2c and 2d show slices at $\delta_{1\text{H}} = 0.91$ (with peaks attributed to the methylene carbons in butyl branches), from the PFG-HMBC and standard phase-cycled HMBC spectra in Figs. 2a and 2b, respectively. The t_1 noise level in the slice from the phase-cycled HMBC spectrum (Fig. 2d) is approximately 10 times higher than the noise level in a similar slice from the PFG-HMBC spectrum (Fig. 2c).

Figures 3a and 3b show the PFG-HMBC and the phase-cycled HMBC spectra of **1** obtained by averaging 64 transients per t_1 increment. These experiments permitted collection of data with a complete phase cycle (to compensate for imperfect pulses, etc.) for coherence selection. As in the above spectrum, the HMBC spectrum of **1** is dominated by the C–H correlations from the $\delta^+\delta^+$ methylene units. The peaks from 1B_2 , 2B_2 , CH_{Et} , 1B_4 , 1s , 2s , and 3s are not seen in Fig. 3b. Three groups of resonances along different proton chemical shifts in the methyl region are also observed as discussed above in relation to Fig. 2. In the methylene region of the ^1H chemical shift dimension, correlations to the α , α' , β , γ , and $\delta^+\delta^+$ ^{13}C resonances are observed in Fig. 3a. The assignments in the methyl and methylene areas of the 1D spectrum are confirmed by the PFG-HMBC NMR spectra described above.

The data presented here indicate the tremendous potential for using ultrahigh-field NMR to study structure–property relationships of important polymers. The PFG experiments provide much better coherence selection than difference methods based on phase cycling alone. The PFG-HMBC experiment provides an additional significant advantage from a 100-fold improvement in the dynamic range of the experiment over phase-cycled HMBC. This is a consequence of the fact that the signals from 99% of the ^1H 's not coupled to ^{13}C are suppressed by PFG coherence selection, and never pass through the instrument's receiver system.

The high-temperature gradient probe extends the use of PFG 2D and 3D NMR experiments to high-melting and/or low-solubility polymers and materials which must be heated to increase

mobility. Much better spectra can be obtained, enabling detection of the resonances from minor structures. When the sensitivity is good, the PFG spectra can be obtained by averaging only two to eight transients per t_1 increment, resulting in shorter data collection times. In cases when the signal-to-noise is poor, more t_1 increments can be collected with fewer transients per increment to provide a spectrum with better signal-to-noise as well as better resolution in the F_1 dimension.

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