Tacticity of Poly(1-chloro-1-fluoroethylene) Fluoropolymer Determined Using $^1H/^{13}C/^{19}F$ Triple-Resonance 3D-NMR

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Ordinarily, it is possible to distinguish between mm/rr and mr/rm triad stereosequences using standard NMR experiments; however, distinction between the resonances of mm and rr triads can only be made if a spectrum from a stereoregular polymer of known relative configuration is available. Recently, triple-resonance 3D-NMR techniques combined with isotopic labeling have provided powerful tools for biomolecular structure determination.[1−3] These tools have tremendous potential applications in polymer chemistry.[4] This communication reports the use of a 3D-$^1H/^{13}C/^{19}F$ triple-resonance NMR experiment to unambiguously determine the resonance assignments for mm, mr/rm, and rr triad stereosequences in poly(1-chloro-1-fluoroethylene) (PCFE, **1**) without resorting to the preparation of stereoregular polymer with known relative configuration. Additionally, this technique provides significantly better dispersion than 1D- and 2D-NMR methods, enabling the resolution of resonances from tetrad sequences.

Figure 1 shows the ^1H, ^{19}F, and ^{13}C spectra of PCFE. For a fluorine-containing polymer with random stereochemistry, the NMR spectra have enormous complexity, arising from the various stereosequences found in the polymer as well as the presence of $^{19}F-^1H$ and $^{19}F-^{13}C$ couplings. Figure 1a shows the ^1H spectrum of PCFE obtained with ^{19}F broad-band decoupling. The spectrum is still too complex to interpret because of limited chemical shift dispersion. The ^{13}C spectrum of PCFE (Figure 1c) shows two resonances which arise from the quaternary and methylene carbons. The doublet at 108 ppm results from the one-bond $^{19}F-^{13}C$ coupling; tacticity has no perceptible influence on the appearance of the ^{13}C spectrum. There are three groups of resonances in the ^{19}F spectrum (Figure 1b) of PCFE. Cais and Kometani[5] originally assigned these resonances to rr, mr/rm, and mm in order of increasing field strength; however, no justification for this assignment was described. ^{19}F chemical shifts are usually more sensitive to structural differences than are the ^1H or ^{13}C chemical shifts. Therefore, ^1H and/or ^{13}C resonance assignments can be made through a 3D-NMR experiment which disperses signals based on the ^{19}F chemical shifts.

The HNCA pulse sequence[6] is normally used in conjunction with ^{13}C and ^{15}N isotopic labeling to assign the backbone resonances of proteins. Berger[7] described a modified version of the original sequence and used it together with $^1H/^{31}P/^{13}C$ triple resonance to study low molecular weight organophosphorus species. Figure 2 shows a modified version of these sequences which was used in this work. The only differences between this sequence and earlier published sequences are the substitutions of ^{13}C and ^{19}F for ^{15}N and ^{13}C, respectively, and the addition of the BIRD[8] nulling sequence during period A. Since ^{19}F has proton-like NMR characteristics, including 100% natural abundance and a large magnetogyric ratio (γ), the isotopic labeling required in biochemistry is unnecessary with fluoropolymers. The

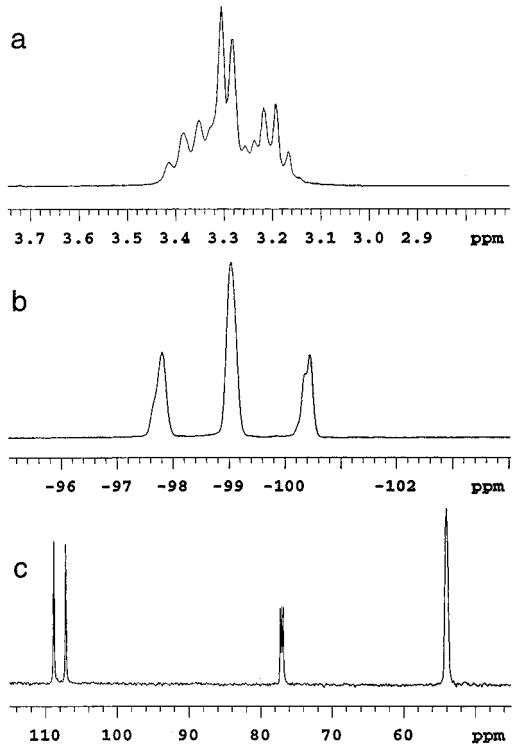

Figure 1. 1D-NMR spectra of PCFE in $CDCl_3$ collected at 25 °C: (a) 600 MHz ^1H spectrum with ^{19}F decoupling; (b) 564 MHz ^{19}F spectrum with ^1H decoupling ($CFCl_3$ is used for a chemical shift reference); (c) 150 MHz ^{13}C spectrum with ^1H decoupling (the group of resonances centered at 77 ppm is from $CDCl_3$ solvent).

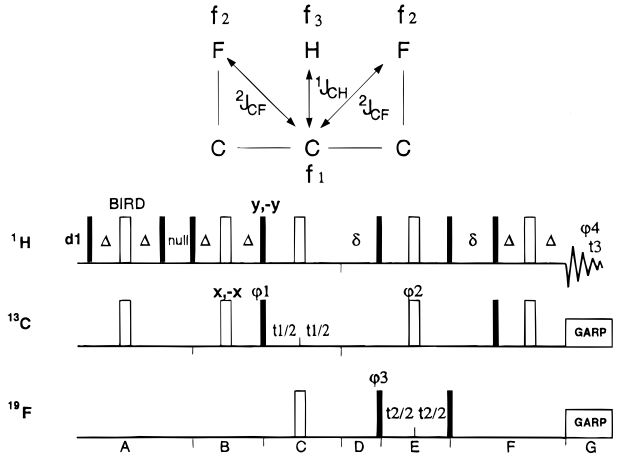

Figure 2. Pulse sequence for 3D-$^1H/^{13}C/^{19}F$ NMR correlation experiment: $\varphi_1 = x$; $\varphi_2 = (x)_4, (y)_4, (-x)_4, (-y)_4$; $\varphi_3 = x, -x, -x, x$; $\varphi_4 = x, -x, -x, x, -x, x, x, -x$. φ_1 is incremented during t_1, and φ_3 is incremented during t_2 to provide a hypercomplex phase-sensitive 3D data set.[12]

BIRD sequence during period A aids in suppression of undesired signal components from ^1H not coupled to ^{13}C. The transfer of coherence between spins occurs via the path ^1H to ^{13}C (via $^1J_{CH}$ during period B), ^{13}C chemical shift evolution (period C), development of $^1H/^{13}C/^{19}F$ coherence (based on evolution of $^2J_{CF}$ coupling, period D), evolution of ^{19}F chemical shift (period E), sequential transfer of magnetization back to ^1H (by retracing the path of coherence transfer, period F), and finally ^1H detection (with ^{13}C and ^{19}F GARP[9] decoupling during the acquisition time, period G). Since this is a ^1H-detected experiment, the sensitivity gains associated with detection of the high-γ nucleus are realized. This

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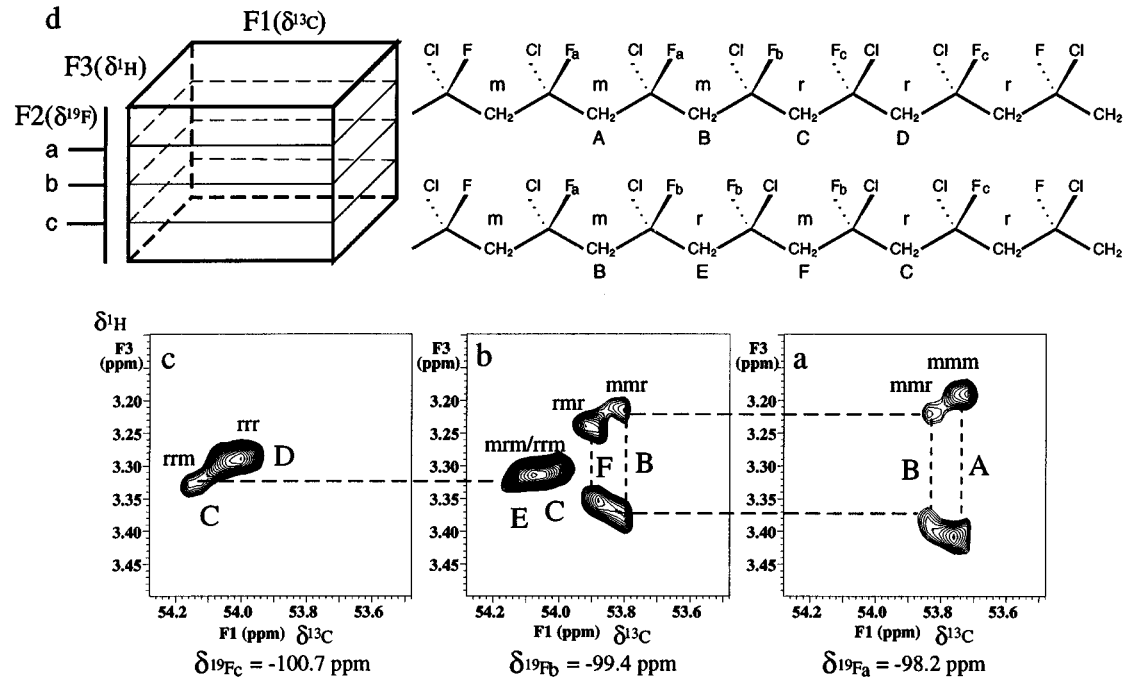

Figure 3. 3D-HCF NMR spectrum of PCFE with f_1f_3 slices at different ^{19}F frequencies: (a) f_1f_3 slice at $\delta^{19}_F = -98.2$ ppm; (b) f_1f_3 slice at $\delta^{19}_F = -99.4$ ppm; (c) f_1f_3 slice at $\delta^{19}_F = -100.7$ ppm; (d) schematic illustration of the 3D spectrum showing the relative positions of the slices. The spectrum was obtained on a Varian Unityplus 600 MHz spectrometer at 25 °C, with 90° pulses for ^1H, ^{13}C, and ^{19}F of 10.8, 16.0, and 20.5 μs, respectively, relaxation delay 1 s, $\Delta = 1.65$ ms $(1/(4 \times {}^1J_{CH}))$, $\delta = 12.5$ ms $(1/(2 \times {}^2J_{CF}))$, 8 transients for each of 2 × 32 increments during t_1 and 2 × 32 increments during t_2, a 3000 Hz spectral window in f_3, a 380 Hz spectral window in f_1, and a 4000 Hz spectral window in f_2 dimensions. The total experiment time was 14 h. The data were zero filled to 256 × 128 × 128 and weighted with a Gaussian function before Fourier transformation.

sequence provides a map of correlations between ^1H, ^{13}C, and ^{19}F chemical shifts of atoms which are related by the one- and two-bond couplings within H−C−C−F fragments as shown by the partial structure in Figure 2.

The 3D-$^1H/^{13}C/^{19}F$ NMR spectrum of PCFE is shown in Figure 3; f_1f_3 ($^1H/^{13}C$) slices at the three different ^{19}F chemical shifts are shown in Figures 3a−c, and the relative positions of these slices within the 3D spectrum are shown in Figure 3d. At each ^{19}F chemical shift, sets of cross peaks to at least two different ^{13}C resonances are observed, one for each geminal methylene group. Methylene carbons in m diads show correlations to the resonances of the two nonequivalent, directly bonded protons (e.g., the A and B pairs of cross peaks in Figure 3a). The methylene carbons in r diads are attached to ^1H atoms which are essentially chemically equivalent[10] and therefore exhibit a correlation to a single ^1H resonance (e.g., cross peaks C and D in Figure 3c). In the slice at $\delta^{19}_F = -98.2$ ppm (Figure 3a), both carbon resonances from adjacent methylenes show cross peaks to two proton resonances; therefore, this ^{19}F must be centered in an mm triad (type a fluorines in the structures in Figure 3). In the slice at $\delta^{19}_F = -100.7$ ppm (Figure 3c), both methylene carbon resonances show cross peaks to single proton resonances; therefore, this ^{19}F must be centered in an rr triad (type c fluorines). In the slice at $\delta^{19}_F = -99.4$ ppm (Figure 3b), one methylene carbon resonance shows a cross peak to a single proton resonance and the second methylene shows a cross peak to two proton resonances; therefore, this ^{19}F must be centered in an mr triad (type b fluorines). Although the 1D-^{19}F NMR spectrum shows only a single peak for the C−F centered mr/rm triads, the 3D-NMR spectrum clearly shows four sets of cross peaks from several possible tetrad structures (B, C, E, and F in Figure 3b).

Once the triad stereosequences are determined from examination of single slices, the relative stereochemistry of adjacent diads in the chain can be determined by looking for identical C−H cross peaks in different ^{19}F slices. For example, in Figure 3a, the A pair of cross peaks do not occur in the other two slices; therefore, methylene A only shows cross peaks to ^{19}F atoms in mm triads and must be centered in an mmm tetrad. The B pair of cross peaks in Figure 3a also occurs in Figure 3b; therefore, these cross peaks indicate that methylene B is coupled to ^{19}F centered in an mm triad on one side (cross peaks B, Figure 3a) and to ^{19}F centered in an mr triad on the other side (cross peaks B, Figure 3b). Similar arguments can be used to assign the ^1H and ^{13}C resonances of all possible tetrads; the remaining cross peaks in Figure 3 are labeled with the assignments of the methylenes from the structures shown.

By taking advantage of the sensitivity of the ^{19}F chemical shift to structural variations, ^1H and ^{13}C resonance assignments can be determined through a 3D- $^1H/^{13}C/^{19}F$ NMR correlation experiment. The 3D-NMR experiment provides information which could not possibly be obtained from 1D- or 2D-NMR experiments. This capability of the 3D-NMR experiment is partly a result of the tremendous chemical shift dispersion provided by three frequency dimensions and is partly a result of the unique ability of 3D-NMR experiments to simultaneously relate the shifts of three coupled nuclei. While the results described in this paper rely on the presence of ^{19}F as the third nucleus in a fluoropolymer, similar results could be obtained from hydrocarbon-based polymers by substitution of selective excitation of a unique group of proton resonances with shaped pulses in place of the ^{19}F pulse train.[11]

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