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

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ABSTRACT: 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. This paper reports the use of a 3D $^{1}H/^{13}C/^{19}F$ triple resonance NMR experiment to unambiguously determine the resonance assignments for mm, mr/rm, and rr triad stereosequences in poly(1-chloro-1-fluoroethylene) without resorting to the preparation of stereoregular polymer having known relative configuration. Additionally, this technique provides significantly better dispersion than 1D- and 2D-NMR methods. Consequently, it was possible to completely resolve and assign ^{1}H, ^{13}C, and ^{19}F resonances from methylenes centered in tetrad structures and fluorine atoms centered in pentad structures.

Introduction

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]

In an earlier communication,[5] a 3D $^{1}H/^{13}C/^{19}F$ triple resonance NMR experiment was used to unambiguously determine the resonance assignments for mm, mr/rm, and rr triad stereosequences in poly(1-chloro-1-fluoroethylene) (PCFE) without resorting to the preparation of stereoregular polymer with known relative configuration. In this paper, a complete description of the technique is provided. Additionally, the significantly better dispersion in 3D-NMR compared to 1D- and 2D-NMR is used to resolve additional signals and make unequivocal assignments of the ^{1}H, ^{13}C, and ^{19}F resonances from methylene groups in tetrads and fluorines in pentad sequences.

Experimental Section

Materials. The sample of PCFE was generously provided by Prof. H. J. Harwood at The University of Akron. It was obtained by polymerization of 1-chloro-1-fluoroethylene in toluene at 46 °C using azobis(1,4-dimethyl-4-methoxyvaleronitrile) as the initiator. 1-Chloro-1-fluoroethylene was obtained from SCM Speciality Chemicals, Gainesville, FL. Azobis(1,4-dimethyl-4-methoxyvaleronitrile) was obtained from Dupont, Wilmington, DE.

NMR Measurements. The NMR spectra were collected at 25 °C on a Varian Unityplus 600 MHz NMR spectrometer equipped with three broad band rf channels and an indirect detection triple resonance probe (from Nalorac Cryogenics) with channels pretuned to the ^{1}H, ^{19}F, ^{13}C, and ^{2}H (lock) frequencies. $CDCl_3$ was used as an internal reference for ^{1}H and ^{13}C chemical shifts ($\delta^{1}H = 7.22$, $\delta^{13}C = 77.0$); $CFCl_3$ was used as an external reference ($\delta^{19}F = 0$ ppm) for ^{19}F chemical shifts.

1D-NMR. The ^{1}H spectrum of PCFE was acquired at 600 MHz with ^{19}F decoupling using a 1.0 s acquisition time, 5.0 μs (45°) pulse width and 16 transients. The ^{19}F spectrum of PCFE was acquired at 564 MHz with ^{1}H decoupling using 0.3 s acquisition time, 21.5 μs (90°) pulse width and 16 transients. The ^{13}C spectrum of PCFE was acquired at 125 MHz with Waltz-16 modulated ^{1}H decoupling and both with and without Waltz-16 modulated ^{19}F decoupling, using a 0.5 s acquisition time, 10 μs (40°) pulse width and 12 800 transients.

3D-NMR. The $^{1}H/^{13}C/^{19}F$ 3D-NMR spectrum of PCFE was obtained using the States[6] method of phase-sensitive detection in all three dimensions, using 90° pulses for ^{1}H, ^{13}C, and ^{19}F of 10.8, 16, and 20.5 μs, respectively, a relaxation delay of 1s, a delay Δ of 1.65 ms, a delay δ of 12.5 ms, and a 0.043 s acquisition time (with simultaneous GARP-modulated ^{19}F and ^{13}C decoupling); 8 transients were averaged for each of 2×32 increments during t_1 and 2×32 increments during t_2. The evolution times were incremented to provide the equivalent of a 380 Hz spectral window in the f_1 dimension, a 4000 Hz spectral window in the f_2 dimension, and a 3000 Hz spectral window in the f_3 dimension. The total experiment time was 14 h. The data were zero-filled to $256 \times 128 \times 128$ and weighted with a Gaussian function before Fourier transformation.

Results and Discussion

Figure 1 shows the ^{1}H, ^{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 from the presence of $^{1}H-^{1}H$, $^{19}F-^{1}H$, and $^{19}F-^{13}C$ couplings. Figure 1a shows the ^{1}H spectrum of PCFE with ^{19}F broad band decoupling. Even with the simplification achieved by elimination of $^{19}F-^{1}H$ couplings, the spectrum is still too complex to interpret because of limited chemical shift dispersion. The ^{13}C spectrum of PCFE with ^{1}H decoupling (Figure 1b) shows two resonances which arise from the quaternary and methylene carbons (the central triplet is the $CDCl_3$ solvent peak). When ^{19}F decoupling is applied, the doublet at 108 ppm resulting from the one-bond $^{19}F-^{13}C$ coupling collapses to a singlet (Figure 1c); the broad peak at about 54 ppm sharpens into two groups of resonances (inset in Figure 1c). Tacticity has only a small influence on the appearance of the methylene resonances in the ^{13}C spectrum and no detectable influence on the ^{13}CF(Cl) resonance. In the ^{19}F spectrum of PCFE (Figure 1d), there are three groups of resonances. Cais and Kometani[7] originally assigned these resonances to rr, mr/rm, and mm in order of increasing field strength; however, no justification for

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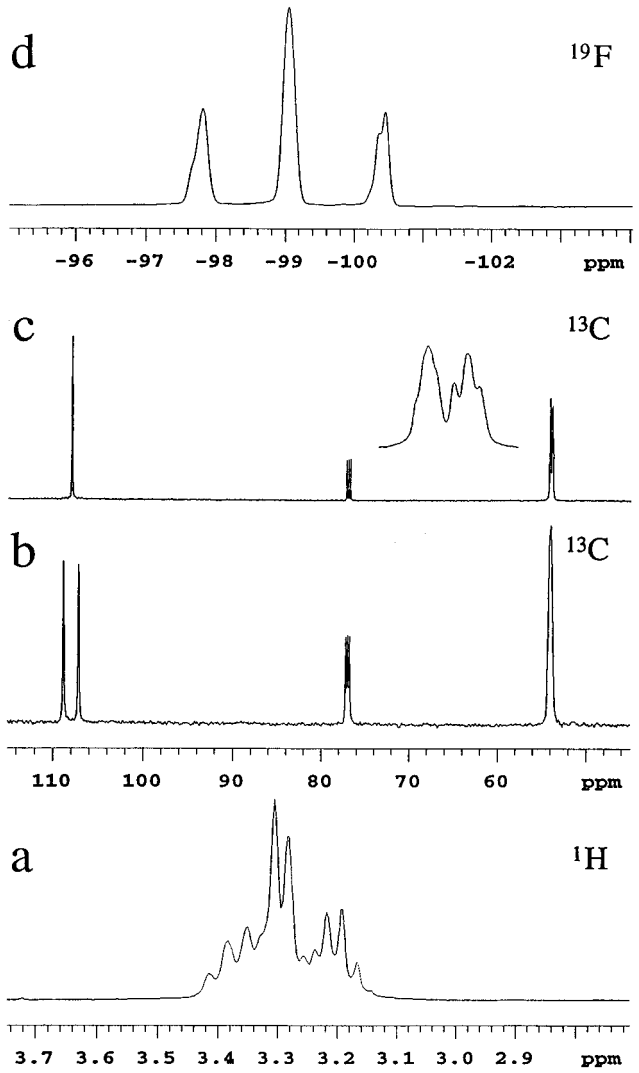

Figure 1. 1D spectra of PCFE: (a) ^{1}H spectrum with ^{19}F decoupling, (b) ^{13}C spectrum with ^{1}H decoupling, (c) ^{13}C spectrum with ^{1}H and ^{19}F decoupling, and (d) ^{19}F spectrum with ^{1}H decoupling.

this assignment was described. Because the ^{19}F chemical shifts are more sensitive to structural differences than are the ^{1}H or ^{13}C chemical shifts, it is possible to obtain ^{1}H and ^{13}C resonance assignments using a 3D ^{1}H/^{13}C/^{19}F chemical shift correlation NMR experiment which disperses signals based on the ^{19}F chemical shifts. A popular 3D-NMR sequence used by biochemists can be adapted for this purpose.

The HNCA pulse sequence[8] is normally used in conjunction with ^{13}C and ^{15}N isotopic labeling to assign the backbone resonances of proteins. Berger[9] described a modified version of the original sequence and used it together with ^{1}H/^{31}P/^{13}C triple resonance to study low molecular weight organophosphorus species. Figure 2 shows the modified version of these sequences used in this work. The 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[10] nulling sequence during period A. Since ^{19}F has protonlike NMR characteristics, including 100% abundance and a large magnetiogyric ratio (γ), the isotopic labeling required in biochemistry is unnecessary with fluoropolymers. The BIRD sequence during period A aids in suppression of undesired signal components from ^{1}H not coupled to ^{13}C. The transfer of coherence between spins occurs via the path ^{1}H to ^{13}C (via $^1J_{CH}$

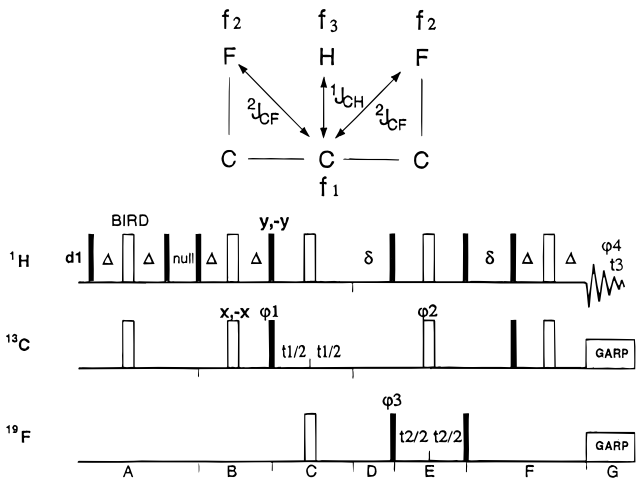

Figure 2. Pulse sequence for ^{1}H/^{13}C/^{19}F 3D-NMR correlation experiment: $\varphi_1 = x$; $\varphi_2 = (x)_4, (y)_4, (-x)_4, (-y)_4$; $\varphi_3 = x, -x, -x, x$; $\varphi_4 = x, -x, -x, x, -x, x, x, -x$; φ_1 is incremented during t_1 and φ_3 incremented during t_2 to provide a hypercomplex phase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

during period B), ^{13}C chemical shift evolution (period C), development of ^{1}H/^{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 ^{1}H (by retracing the path of coherence transfer, period F), and finally ^{1}H detection with ^{13}C and ^{19}F GARP[11] decoupling during the acquisition time (period G). Since this is a ^{1}H detected experiment, the sensitivity gains associated with observation of the high γ nucleus are realized. This sequence provides a map of correlations among ^{1}H, ^{13}C, and ^{19}F chemical shifts of atoms which are related by one- and two-bond couplings within H−C−C−F fragments as shown by the partial structure in Figure 2.

The low resolution ^{1}H/^{13}C/^{19}F 3D-NMR spectrum of PCFE is shown in Figure 3; f_1f_3 (^{1}H−^{13}C correlations) slices at the three different ^{19}F chemical shifts are shown in Figure 3a−c, and the relative positions of these slices within the 3D spectrum are schematically illustrated in Figure 3d. At each ^{19}F chemical shift, sets of crosspeaks to at least two different ^{13}C resonances are observed, one for each geminal methylene group. Methylene carbons centered in m diads show correlations to the resonances of the two nonequivalent, directly bonded protons (e.g. the A and B pairs of crosspeaks in Figure 3a). The methylene carbons centered in r diads are attached to ^{1}H atoms which are essentially chemically equivalent (although these protons are not rigorously equivalent unless the polymer is syndiotactic, remote stereochemistry has very little influence on the ^{1}H chemical shifts, and separate resonances are not observed in these data) and therefore exhibit a correlation to a single ^{1}H resonance (e.g. crosspeaks C and D in Figure 3c). The fact that methylene protons centered in m diads are nonequivalent was first used by Bovey and Tiers[12] to assign the resonances in the ^{1}H spectrum of poly(methyl methacrylate). Later, this same characteristic was used in the interpretation of polymer 2D-NMR spectra.[13]

In the slice at $\delta^{19}F = -98.2$ ppm (Figure 3a) both carbon resonances from adjacent methylenes show crosspeaks 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 crosspeaks to single proton resonances;

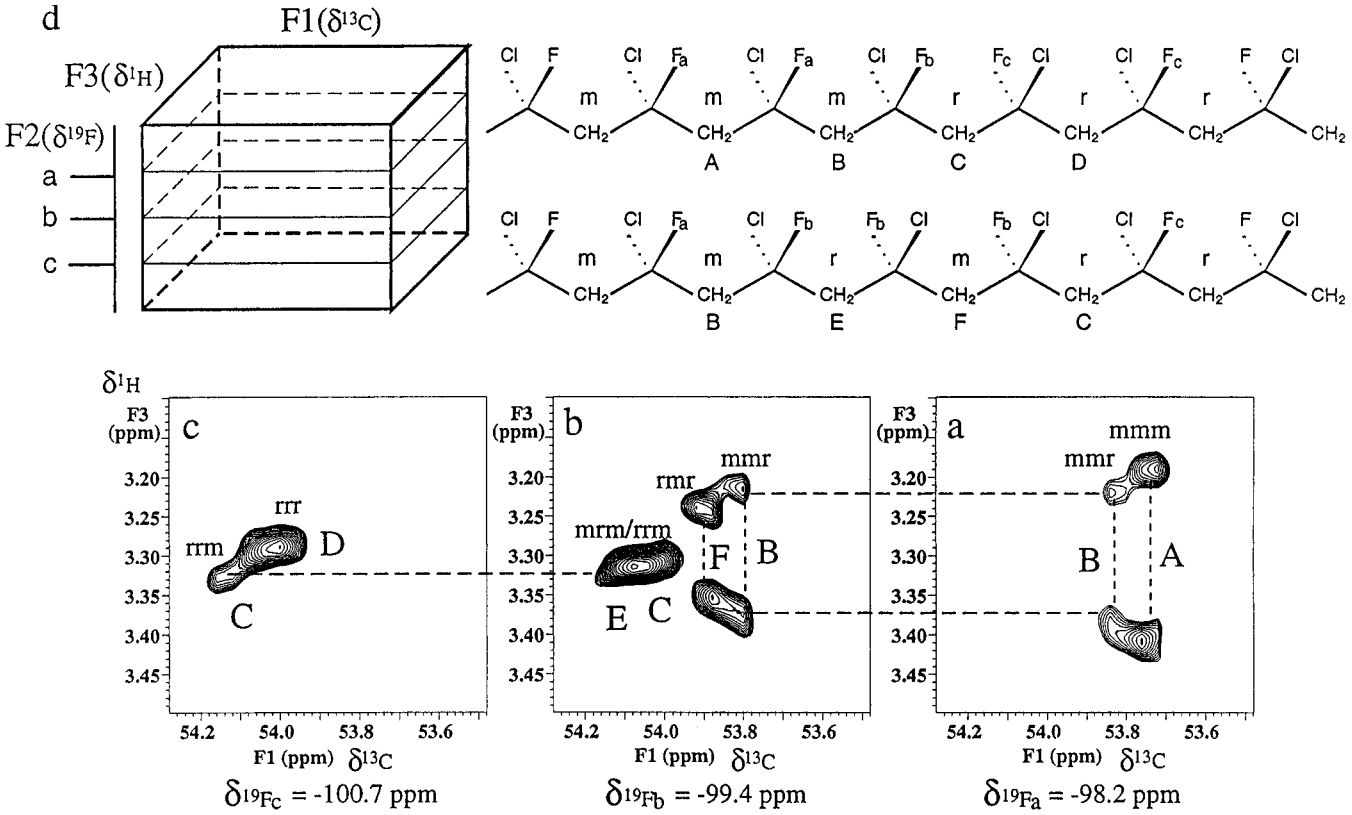

Figure 3. $^1H/^{13}C/^{19}F$ 3D-NMR spectrum of PCFE with f_1f_3 slices at different ^{19}F resonance frequencies: (a) $\delta^{19}F = -98.2$ ppm, (b) $\delta^{19}F = -99.4$ ppm, (c) $\delta^{19}F = -100.7$ ppm. (d) Schematic illustration of the 3D spectrum indicating the relative positions of the three slices.

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 crosspeak to a single proton resonance and the second methylene carbon resonance shows a crosspeak to two proton resonances; therefore, the fluorines having this shift must be centered in mr/rm triads, the $^1H/^{13}C/^{19}F$ 3D-NMR spectrum clearly shows four sets of crosspeaks 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 crosspeaks in different ^{19}F slices. For example, in Figure 3a, the A pair of crosspeaks do not occur in the other two slices; therefore, type A methylenes only show crosspeaks to ^{19}F atoms in mm triads and must be centered in mmm tetrads. The B pair of crosspeaks in Figure 3a also occur in Figure 3b, therefore, these crosspeaks indicate that methylene B is geminal to an ^{19}F centered in an mm triad on one side (crosspeaks B, Figure 3a) and geminal to an ^{19}F centered in an mr triad on the other side (crosspeaks B, Figure 3b). Similar arguments can be used to assign the ^1H and ^{13}C resonances of all possible tetrads; the remaining crosspeaks in Figure 3 are labeled with the assignments of the methylenes from the structure shown. The assignments for r-centered tetrads are not as clear as those for m-centered tetrads, especially the distinction of mrr and mrm tetrads. These can be clarified by examining f_2f_3 slices ($^1H-^{19}F$ correlations).

Figure 4 shows ^1H and ^{19}F correlations in f_2f_3 slices at selected ^{13}C chemical shifts. The slices in Figures 4a−c confirm the ^1H and ^{13}C chemical shift assignments of the m-centered tetrad sequences. For example, in Figure 4b, two kinds of ^{19}F resonances (at $\delta^{19}F = -98.2$ and −99.4) are present, which correspond to fluorines centered in mm and mr/rm triad structures, respectively. This confirms the fact that the CH_2 group between the two ^{19}F's is centered in an mmr tetrad (type B CH_2 groups in Figure 3).

In Figure 4a, only one type of ^{19}F resonance (at $\delta^{19}F = -98.2$) is present, which corresponds to fluorines centered in mm triad structures. Therefore, the CH_2 groups with $\delta^{13}C = 53.75$ are centered in mmm tetrads (type A CH_2 groups in Figure 3). Likewise, in Figure 4c only one type of ^{19}F resonance (at $\delta^{19}F = -99.4$) is present, which corresponds to fluorines centered in mr triad structures. Therefore, the CH_2 groups with $\delta^{13}C = 53.87$ are centered in rmr tetrads (type F CH_2 groups in Figure 3).

Slices in Figures 4d−f show the ^1H and ^{19}F correlations of r centered methylene tetrads. The slice in Figure 4d shows one ^{19}F peak at $\delta^{19}F = -99.4$ ppm, which is from mr/rm triads. Hence, the corresponding ^1H and ^{13}C chemical shifts must arise from mrm tetrad structures (type E CH_2 groups). In the slice shown in Figure 4e, two ^{19}F resonances (at $\delta^{19}F = -99.4$ and −100.7 ppm) are observed, corresponding to a fluorine within an mr triad on one side and a fluorine within an rr triad on the other side. Consequently, the ^{13}C resonances at $\delta^{13}C = 54.06$ must arise from a methylene centered in an mrr tetrad (type C CH_2 groups). Similar arguments apply to the slice in Figure 4f, which provides an assignment for this methylene carbon as one centered in an rrr tetrad (type D CH_2 groups).

In the 1D ^{19}F spectrum, resonances from structures further than triad stereosequences are not resolved. However, in the 3D $^1H/^{13}C/^{19}F$ spectrum, a series of ^{19}F resonances from different pentads are resolved. Figure 5a-c shows $^1H-^{13}C$ correlations in consecutive f_1f_3 slices with a slightly different ^{19}F chemical shifts in the −97.9

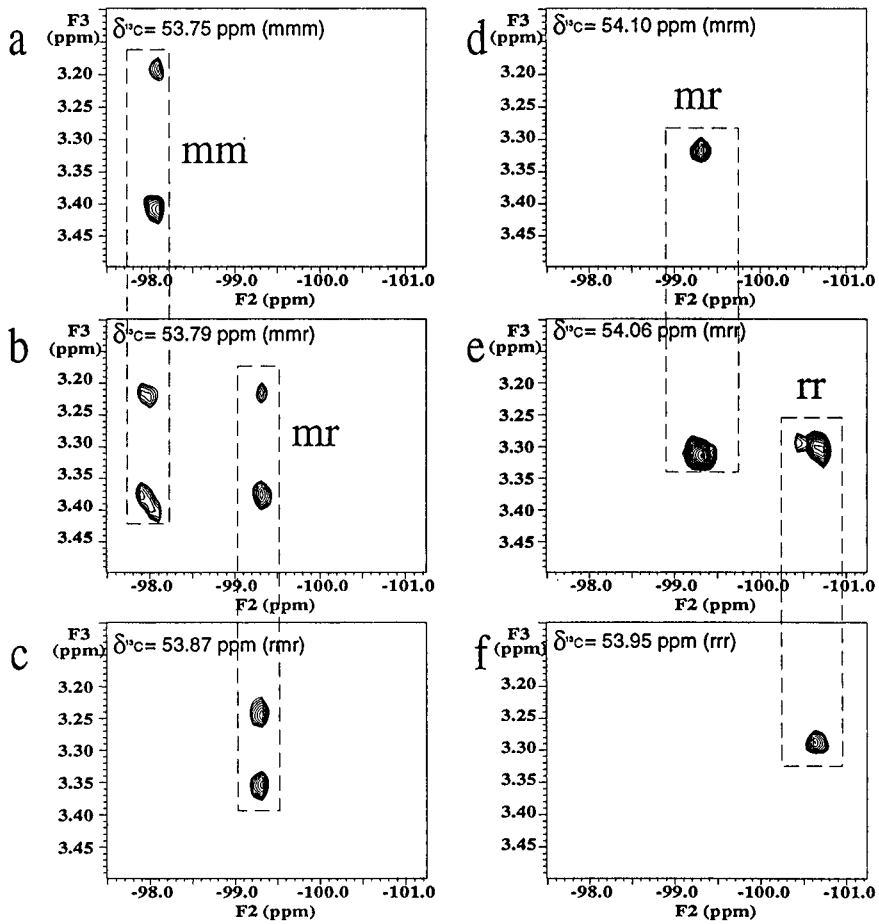

Figure 4. $^{1}H/^{13}C/^{19}F$ 3D-NMR spectrum of PCFE with f_2f_3 slices at ^{13}C resonance frequencies of methylene groups centered in m (a−c) and r (d−f) diads: (a) $\delta^{13}C = 53.75$ ppm, (b) $\delta^{13}C = 53.79$ ppm, (c) $\delta^{13}C = 53.87$ ppm, (d) $\delta^{13}C = 54.10$ ppm, (e) $\delta^{13}C = 54.06$ ppm, (f) $\delta^{13}C = 53.95$ ppm.

to −98.2 ppm region. These three slices correspond to the shift range of ^{19}F centered in mm triads as discussed above. Crosspeaks from methylene groups centered in mmm and mmr tetrads are marked on the spectra. Only one ^{13}C resonance appears in the slice in Figure 5a. This pair of CH_2 correlations only appears in slices corresponding to the shifts of ^{19}F centered in mm triads; therefore, it must be between two ^{19}F's, both of which are in mm triads. These CH_2 resonances are therefore attributed to mmm tetrads. Because there are no other ^{13}C correlations in this slice, the two CH_2's on either side of the ^{19}F at −98.16 ppm must both reside in mmm tetrads. Therefore, the ^{19}F resonance of an mmmm pentad has been resolved and identified in this slice.

In the f_1f_3 slice shown in Figure 5b, at $\delta^{19}F = -98.06$, correlations from two different types of CH_2's are detected. One of these, at $\delta^{13}C = 53.75$, occurs at the same shift as the CH_2 correlations in Figure 5a and must therefore arise from a CH_2 group centered in an mmm tetrad. The second set of CH_2 correlations, at $\delta^{13}C = 53.80$, is also present in a slice at the chemical shift of an ^{19}F centered in an mr triad (peaks F in Figure 3b) and therefore is a CH_2 centered in an mmr tetrad. Consequently, the f_1f_3 slice in Figure 5b must arise from an ^{19}F centered in an mmmr pentad.

The f_1f_3 slice in Figure 5c, at $\delta^{19}F = -97.96$, exhibits correlations from a single CH_2 at the shift of methylenes centered in mmr tetrads. Consequently, this ^{19}F links identical types of CH_2's and must be centered in an rmmr pentad.

In a similar fashion three f_1f_3 slices can be found in the shift range of ^{19}F atoms centered in rr triads; these are shown in Figure 5d−f. Because all these correlations relate a single carbon resonance to the single shift of equivalent methylene protons, the methylenes represented in these slices are all attributed to r diads.

The slice in Figure 5d, at $\delta^{19}F = -100.86$, contains only one correlation between a single ^{13}C methylene resonance of chemically equivalent methylene protons. Crosspeaks at these ^{1}H and ^{13}C chemical shifts only occur in slices at the ^{19}F chemical shifts of fluorines centered in rr triads. Therefore, the fluorines on either side of this methylene group must both be centered in rr triads and this CH_2 correlation must be from a methylene group centered in an rrr tetrad. This ^{19}F slice contains only this one $^{1}H-^{13}C$ correlation; therefore, the methylene groups on either side of the fluorine with $\delta^{19}F = -100.86$ must both be centered in rrr tetrads and this fluorine must be centered in an rrrr pentad.

The f_1f_3 slice in Figure 5e, at $\delta^{19}F = -100.66$, shows the same CH_2 correlation that was observed in Figure 5d, from a methylene centered in an rrr tetrad. A second CH_2 correlation observed in Figure 5e is also observed in slices at the ^{19}F shift of fluorines centered in mr triads. Therefore, this second CH_2 correlation arises from a methylene group centered in an mrr tetrad. Consequently, the fluorine with $\delta^{19}F = -100.66$ must be centered in an mrrr pentad.

The slice in Figure 5f shows a single correlation from a methylene group. Because this correlation exists in a slice at the shift of an ^{19}F in an rr triad, at least one of the adjacent ^{19}F's must be in an rr triad. Methylene crosspeaks at the same ^{13}C and ^{1}H shifts also occur in

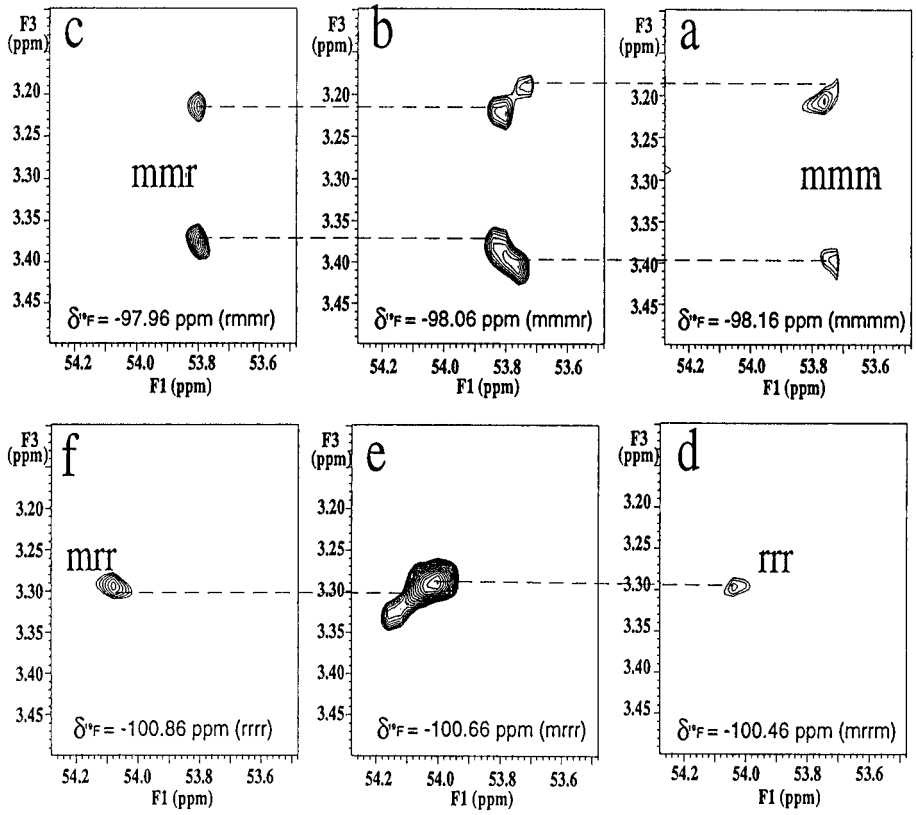

Figure 5. $^{1}H/^{13}C/^{19}F$ 3D-NMR spectrum of PCFE with f_1f_3 slices at the ^{19}F resonance frequencies of fluorines centered in mm (a−c) and rr (d−f) triads: (a) $\delta^{19}F = -98.16$ ppm, (b) $\delta^{19}F$ = -98.06 ppm, (c) $\delta^{19}F = -97.96$ ppm, (d) $\delta^{19}F = -100.46$ ppm, (e) $\delta^{19}F = -100.66$ ppm, (f) $\delta^{19}F = -100.86$ ppm.

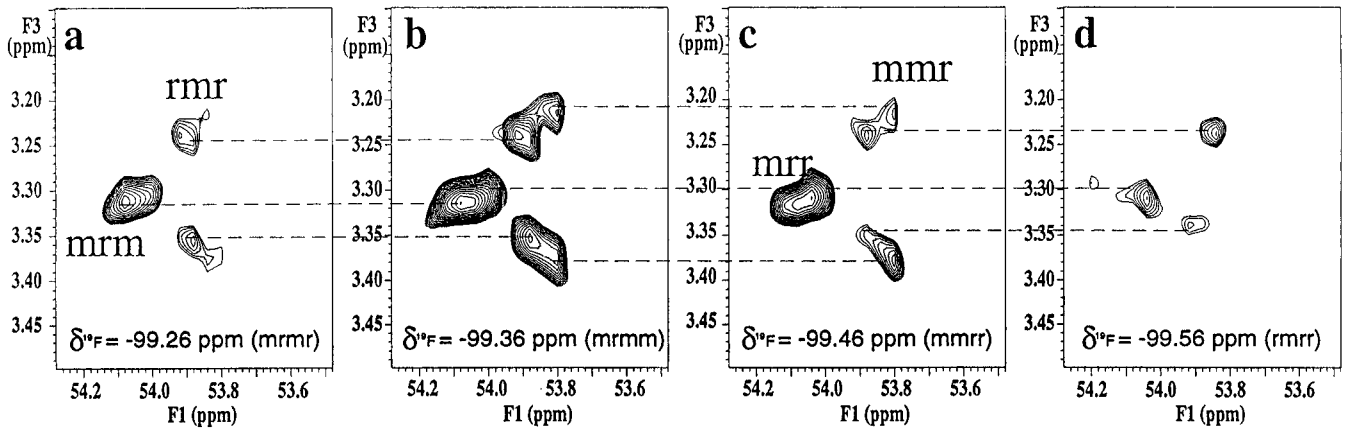

Figure 6. $^{1}H/^{13}C/^{19}F$ 3D-NMR spectrum of PCFE with f_1f_3 slices at the ^{19}F resonance frequencies of fluorines centered in mr triads: (a) $\delta^{19}F = -99.26$ ppm, (b) $\delta^{19}F = -99.36$ ppm, (c) $\delta^{19}F = -99.46$ ppm, (d) $\delta^{19}F = -99.56$ ppm.

slices at chemical shift of fluorines centered in mr triads. Therefore, the second adjacent ^{19}F must be in an mr triad, and this crosspeak arises from a CH_2 group centered in an mrr tetrad. The fluorine at $\delta^{19}F = -100.46$ only shows this one correlation, indicating that both adjoining methylenes are centered in mrr tetrads; consequently, this fluorine must be centered in an mrrm pentad.

Figure 6a−d shows consecutive slices at the ^{19}F shifts of fluorines centered in mr triads. The mm- and rr-centered pentads have a plane of symmetry through the central triad, making two of the possible pentad sequences equivalent. The middle triads of mr-centered pentads have no symmetry; therefore, there are four possible stereosequences, mmrm, mmrr, rmrmr, and rmrr. Methylene correlation patterns arising from CH_2 groups centered in mmr and mrr tetrads have already been identified in the discussions of mm and rr triad centered stereosequences above. The resonances from two additional methylene-centered tetrads, mrm and rmr, are observed in Figure 6 at $\delta^{13}C = 53.9$ and 54.1, respectively. They are easily distinguished and assigned on the basis of the fact that the central CH_2

Table 1. ^{19}F Chemical Shift Assignments for PCFE

triads	$\delta^{19}F$ (ppm)	pentads	$\delta^{19}F$ (ppm)
mm	−98.2	mmmm	−98.16
		mmmr	−98.06
		rmmr	−97.96
mr	−99.4	mmrm	−99.36
		mmrr	−99.46
		rmrm	−99.26
		rmrr	−99.56
rr	−100.7	mrrm	−100.46
		mrrr	−100.66
		rrrr	−100.86

Table 2. ^{1}H and ^{13}C Chemical Shift Assignments of PCFE

tetrads	$\delta^{13}C$ (ppm)	$\delta^{1}H$ (ppm)
mmm	53.75	3.19, 3.42
mmr	53.79	3.22, 3.39
rmr	53.87	3.24, 3.36
mrm	54.10	3.31
mrr	54.06	3.30
rrr	53.95	3.29

group has correlations to equivalent protons in the r-centered tetrads and to nonequivalent protons in the m-centered tetrads. Once these assignments are made, it is a trivial matter to assign the ^{19}F chemical shifts of different pentads by identifying the two-CH_2 tetrad patterns which are present in each f_1f_3 slice. These pentad assignments appear below each contour plot in Figure 6.

Complete ^{1}H, ^{13}C, and ^{19}F chemical shift assignments for all triads, tetrads and pentads are summarized in Tables 1 and 2.

Conclusion

Although heteronuclear 3D-NMR experiments are typically performed in conjunction with isotopic labeling, this work clearly demonstrates that useful data can be obtained without isotopic labeling, especially when high abundance, NMR active isotopes such as ^{19}F are present in the molecule. By taking the advantage of the sensitivity of the ^{19}F chemical shift to structural variations, ^{1}H and ^{13}C resonance assignments can be determined through a $^{1}H/^{13}C/^{19}F$ 3D-NMR correlation experiment. This information could not be obtained from 1D- or 2D-NMR experiments. By dispersing resonances into three dimensions, it is possible to resolve numerous methylene resonances, where only a single signal is detected in the 1D-NMR spectrum. Once these resonances are resolved, the unique ability of 3D-NMR experiments to simultaneously relate the shifts of three coupled nuclei provides unequivocal assignments for the resonances of different stereosequences. 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 other NMR active nuclei such as ^{31}P.

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