# Use of $^1$H/$^{13}$C/$^{19}$F Triple Resonance 3D-NMR to Characterize the Stereosequences in Poly(vinyl fluoride)

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Ⓢ *Supporting Information*

**ABSTRACT:** Tacticity has an enormous influence on the physical and chemical properties of polymers. There is considerable work using 1D NMR and empirical rules to study the stereosequences in polymers. This work shows that $^1$H/$^{13}$C/$^{19}$F 3D NMR experiments can provide superior resolution and atomic connectivity information, so that unambiguous resonance assignments can be made for poly(vinyl fluoride) (PVF). Compared to prior work on 3D NMR studies of stereosequence effects in fluoropolymers, the 3D NMR pulse sequence used in this work is based on single quantum coherence transfer, which eliminates the complicated splitting patterns resulting from evolution of multiple-quantum coherence. In addition, selective excitation of the $^{19}$F nuclei of interest significantly reduces the folding of peaks from other spectral regions. This greatly simplifies the spectra and makes the assignment of resonances much easier. Based on these results, it is possible to assign the $^{19}$F resonances to the pentad level. For example, consider the resonances of mm-centered sequences, which are not well resolved in $^{19}$F−$^{19}$F COSY 2D NMR spectrum. $^1$H/$^{13}$C/$^{19}$F 3D NMR data provide clear evidence for all of the three pentad structures: mmmm, mmmr, and rmmr. Examples showing the resonance assignments of head-to-tail sequences are presented.
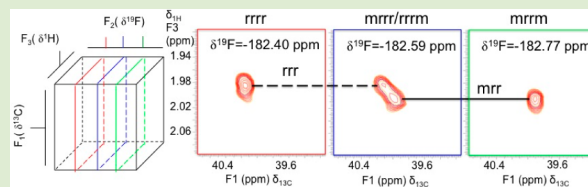
It is generally recognized that microstructural features such as regiochemistry, monomer composition, monomer sequence, tacticity (stereosequences), branching and chain ends have a significant influence on the chemical, physical, and mechanical properties of polymers. In recent years, powerful new synthetic methods have had a dramatic impact on the ability of controlling these polymer structures. It is equally important to have good analytical methods for characterizing and quantifying the structures present in polymers. This preliminary communication demonstrates the use of $^1$H/$^{13}$C/$^{19}$F triple resonance 3D NMR for characterizing the resonances from different stereosequences (tacticity) present in poly(vinyl fluoride) (PVF).

Tacticity has an important influence on the physical and mechanical properties of polymers. Prominent examples include the influence of tacticity on the crystallinity, glass transition temperature, melting temperature, degradation temperature, heat capacity, and viscoelastic properties of polypropylene, polystyrene, and poly(methyl methacrylate).[1] Tacticity has also been shown to influence the miscibility of these polymers in blends with other each other and with other polymers.

NMR is one of the most powerful methods for determining the structures, resonance assignments, and quantity of structure components in polymers.[2] A recent review[3] summarizes the applications of 1D and 2D NMR to the characterization of the structures in fluoropolymers and, in particular, PVF. In addition to probing structure−property relationships, NMR can also reveal information related to polymerization mechanisms,[4]

which can provide polymer chemists insight to obtaining polymers with desired properties. Improved analysis of chain structure can also benefit studies correlating the effect of polymerization conditions with polymer properties. Previous research by Aronson et al.[5] have demonstrated that the melting points of PVF samples were dependent on polymerization temperature and pressure and resulting differences in branching and regioregularity were evident by 1D $^{19}$F NMR results.

In earlier work, the stereosequences were determined by comparing the spectra of the polymers with those of stereoregular compounds.[6] The advent of 2D NMR greatly facilitated the characterization of stereosequences in polymers by providing better resolution and atomic connectivity information.[7,8] However, due to severe signal overlap, for some polymers even 2D NMR cannot provide sufficient resolution for unambiguous resonance assignment. 3D NMR structure characterization could provide additional information about such structure−property relationships.

Earlier published work showed the advantages of using triple resonance 3D NMR to study the microstructures in polymers.[9,10] In this study, a modified $^1$H/$^{13}$C/$^{19}$F 3D NMR sequence was used to study the microstructures in PVF. Earlier, $^1$H/$^{13}$C/$^{19}$F 3D NMR work was done on an extensively modified research grade NMR spectrometer, which was not generally available at the time. The work described in this

communication was performed on a 5 year old 500 MHz NMR instrument purchased with standard accessories, which can and should be purchased by any researcher who must use NMR to help characterize fluorinated materials.

Benefiting from the large spectral dispersion in $^{19}$F chemical shifts, Bruch et al.[7,8] used $^{19}$F$-^{19}$F COSY (correlation spectroscopy) and $^{19}$F-HOMO2DJ (homonuclear 2D-J) experiments to characterize the stereosequences and defect structures of PVF. Due to the poor resolution in $^1$H and $^{13}$C NMR spectra, there is limited work involving use of these data to study the regio- and stereosequence effects in PVF. Simultaneous $^1$H and $^{19}$F decoupling greatly improves the resolution of peaks in the $^{13}$C NMR spectrum, so that Tonelli et al.[11] and Schilling[12] were able to identify the carbon resonances of H$-$T, H$-$H, and T$-$T structures. However, there was still insufficient resolution to observe the effect of stereosequences in the $^{13}$C NMR spectrum. By dispersing the resonances into a third dimension in the $^1$H/$^{13}$C/$^{19}$F 3D NMR spectra, it is possible to assign the resonances of CFH-centered sequences to the pentad level in the $^{19}$F dimension, and to resolve and assign the resonances of CH$_2$-centered sequences to the tetrad level in the $^{13}$C dimension.

Some of the structural variations in PVF are shown in Scheme 1, in which the same nomenclature for CFHs and
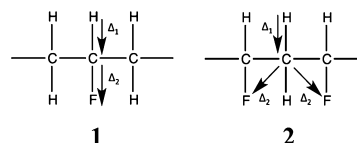
**Scheme 1. Structural Variations in PVF**
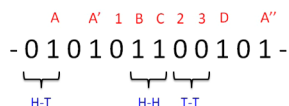
CH$_2$s are used as those found in Bruch's study: 1 indicates CFH groups having one fluorine attached to carbon, and 0 indicates CH$_2$ groups having no fluorines attached to carbon. As for regio-sequences, there could be H$-$T (head-to-tail, indicated by A, A′, A″, and D), H$-$H (head-to-head, indicated by B and C), and T$-$T (tail-to-tail, indicated by 2 and 3) structures. Among the H$-$T fluorine atoms, A indicates the fluorines in long sequences of $-0101-$ units, while A′ and D indicate the fluorines adjacent to the H$-$H and T$-$T fluorines, respectively. In addition, due to the presence of stereogenic centers, stereosequence effects can also be seen in the

spectrum. As a result, complicated splitting patterns can be observed in the $^{19}$F and $^{13}$C NMR spectra. In this communication, the stereosequence assignments for H$-$T (A) fluorines were made unambiguously based on the $^1$H/$^{13}$C/$^{19}$F 3D NMR experiment.

In this study, the polymer was obtained from E. I. du Pont de Nemours and Co. and used as received. PVF samples were prepared by free radical polymerization in a continuous aqueous dispersion process using methods previously disclosed.[13,14] The NMR sample was prepared by dissolving 128 mg PVF powder in about 700 $\mu$L DMSO-$d_6$ solvent at high temperature. The solution is homogeneous, clear, and transparent at 110 °C, but will turn cloudy at room temperature. A detailed description for NMR sample preparation is included in the Supporting Information. To characterize the stereo-

sequences in PVF, the $^1$H/$^{13}$C/$^{19}$F 3D NMR experiment based on single quantum coherence transfer was conducted. The pulse sequence used and a detailed description of how the elements of this sequence work are shown in the Supporting Information. In this sequence, $\Delta_2$ delays can be optimized based on 1-bond (170 Hz) or 2-bond (20$-$40 Hz) $^{19}$F$-^{13}$C coupling constants. Therefore, different atomic connectivity information can be obtained, as shown in (1) and (2). Compared with the previously used 3D NMR sequence,[9] one of the most important advantages of the current method is to reduce the complicated splitting patterns resulting from multiple-quantum coherence evolution. In addition, due to regio- and stereosequence effects, the $^{19}$F spectrum of PVF shows very large chemical shift dispersion. Typically, only a small portion of the $^{19}$F window is examined in 3D NMR experiments to obtain adequate digital resolution. As a result, the folded peaks from other regions can make the 3D NMR data extremely difficult to analyze if there are many peaks. To overcome this problem, only the $^{19}$F nuclei of interest were
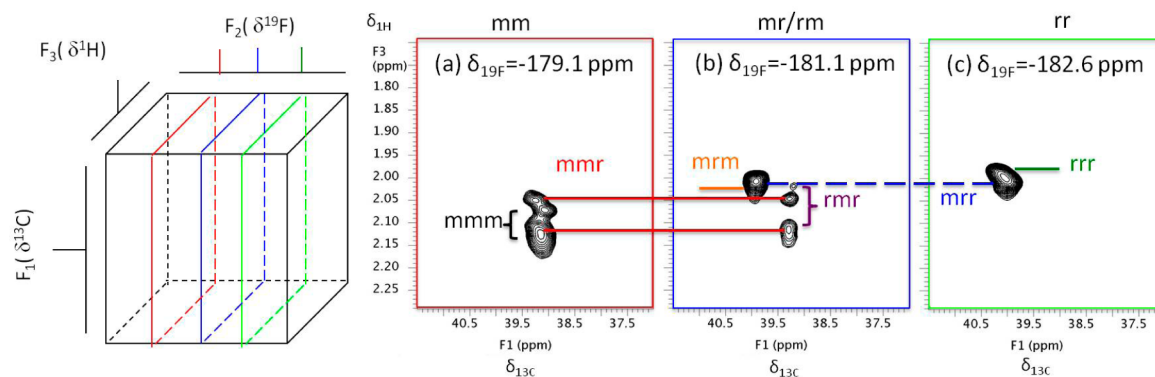
**Figure 1.** Low resolution H$-$C planes from the 500 MHz two bond $^1$H/$^{13}$C/$^{19}$F 3D NMR spectrum of PVF (183 mg/mL in DMSO) at 110 °C: (a) $\delta_{19F} = -179.1$ ppm, (b) $\delta_{19F} = -181.1$ ppm, and (c) $\delta_{19F} = -182.6$ ppm. For example, in the f$_1$f$_3$ slice corresponding to $\delta_{19F} = -179.1$ ppm (a), the resonances of both carbons are correlated with two nonequivalent protons. Therefore, the $^{19}$F between these methylene groups must exist in mm triads. Furthermore, the tetrad sequences can be assigned based on triad sequences and by inspecting for the same correlations in different planes. Take the mmr sequence, for example, the cross-peaks connected by the red lines show up in both mm and mr planes, therefore, this set of crosspeaks was assigned to the mmr sequence.

excited. This greatly simplified the spectra and made the assignment of resonances much easier.

Figure 1 shows selected H−C ($f_1 f_3$) chemical shift planes from a $^1H/^{13}C/^{19}F$ 3D NMR spectrum, in which $\Delta_2$ was optimized based on $^2J_{FC}$. As a consequence, correlations are observed among the atoms as illustrated on structure **2**. Based on the patterns of cross-peaks in individual planes, the triad sequences can be determined. The two methylene protons in m-dyads are nonequivalent. As a result, the resonances of methylene carbons in m-dyads will be correlated with two different proton resonances. By comparison, the resonances of methylene carbons in r-dyads should show a correlation to a single proton resonance, as the two protons attached to this carbon are chemically equivalent. In the $f_1 f_3$ slice corresponding to $\delta_{19F} = -179.1$ ppm (Figure 1a), the resonances of both carbons are correlated with two nonequivalent protons. Therefore, the $^{19}F$ between these methylene groups must exist in mm triads. In the $f_1 f_3$ slice with $\delta_{19F} = -182.6$ ppm (Figure 1c), both methylene carbon resonances show correlations with equivalent protons. This indicates that these methylene groups are present in r-dyads, and the $^{19}F$ atoms with chemical shift corresponding to this slice must be centered in rr triads. In the $f_1 f_3$ slice with $\delta_{19F} = -181.1$ ppm (Figure 1b), cross-peaks from methylene groups having both equivalent and nonequivalent methylene protons can be observed. Thus, the $^{19}F$ atoms producing the cross-peaks in this plane must be present in mr/rm triads.

Once the triad sequences are determined, they can be used as the basis to assign the cross-peaks of tetrad sequences by inspecting for the same correlations in different $^{19}F$ chemical shift planes. For example, the pair of cross-peaks indicated by black brackets in Figure 1a do not show up in any other planes. They are therefore assigned to the methylene groups of mmm tetrad sequences (**3**), because the resonances of the central methylene group are correlated with the resonances of mm fluorines on both sides. The pair of cross-peaks aligned with the red (solid) lines in Figure 1a is also observed in Figure 1b, which corresponds to the fluorine atoms in mr/rm triads. Therefore, this set of cross-peaks in Figure 1a is assigned to the methylenes in mmr tetrad sequences. The cross-peaks of these methylene groups are correlated with the resonances of mm fluorine atoms on one side, and with the resonances of mr
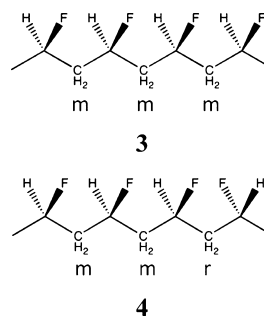


fluorine atoms on the other side (**4**). In Figure 1b, cross-peaks from two sets of methylene groups with nonequivalent protons, mmr and rmr, are expected. Because the mmr sequence has been assigned to the cross-peaks aligned with the solid red lines, the more upfield set of peaks in the $^1H$ dimension, indicated by purple brackets, must be attributed to the methylene groups centered in rmr tetrads. The intensity of the cross-peaks attributed to rmr tetrads is very weak in this slice. Stronger correlations produced by rmr sequences can be seen in the adjoining plane, which is included in the Supporting Information. The cross-peaks of other tetrad sequences can be assigned in the same way, and the results are labeled in Figure 1.

Due to better dispersion in the $^{19}F$ dimension, it is possible to assign the signals of CFH-centered sequences to the pentad level. For mm-centered sequences, there are three possible pentad sequences: mmmm, mmmr and rmmr. Figure 2 shows selected $f_1 f_3$ slices from the region of mm type fluorine resonances. Based on previous assignments, it is known that the upfield resonances in the $^1H$ chemical shift dimension (highlighted with dashed lines) are attributed to mmr tetrads, while the downfield pair of resonances in the $^1H$ chemical shift dimension (highlighted with solid lines) is attributed to mmm tetrads.

In Figure 2c, only one set of cross-peaks is seen. This indicates that the fluorine resonance at this frequency should be correlated with the resonances of protons in mmm sequences on both side. Therefore, this fluorine chemical shift must be attributed to mmmm pentad sequences. The symmetrical pentad sequence rmmr can be assigned in a similar way to the plane in Figure 2a, at $\delta_{19F} = -179.06$ ppm. In Figure 2b, cross-
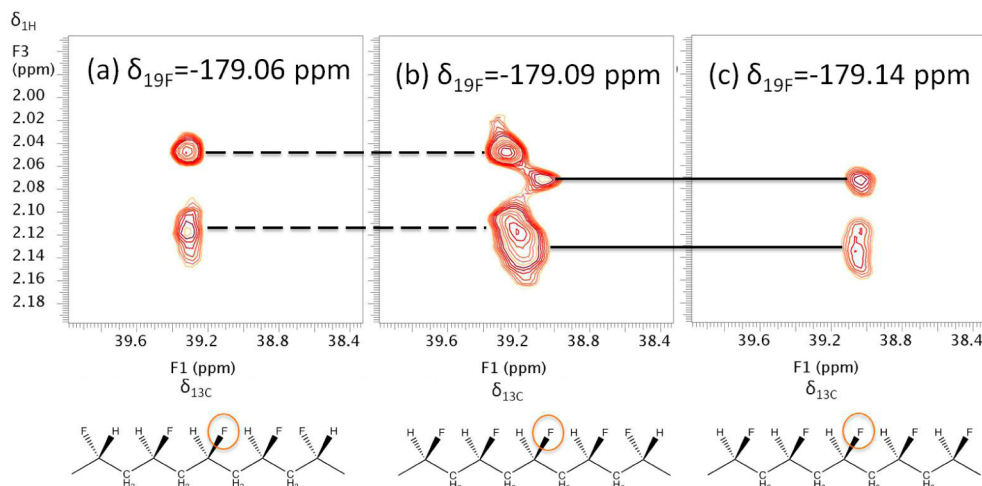


**Figure 2.** Selected $f_1 f_3$ (HC) planes from the 500 MHz two-bond $^1H/^{13}C/^{19}F$ 3D NMR spectrum at different $^{19}F$ chemical shifts (110 °C): (a) $\delta_{19F} = -179.06$ ppm, (b) $\delta_{19F} = -179.09$ ppm, and (c) $\delta_{19F} = -179.14$ ppm.

peaks from two types or methylene groups are observed, one from mmm sequences and the other from mmr sequence. Therefore, the $^{19}$F responsible for the cross-peaks in this slice must exist in unsymmetrical mmmr pentad sequences. Similar reasoning can be used to make resonance assignments for the mr/rm- and rr-centered pentad sequences; these results are summarized in the Supporting Information.

Due to severe signal overlap, it is difficult to obtain resonance assignments for $CH_2$-centered sequences even with the 2D
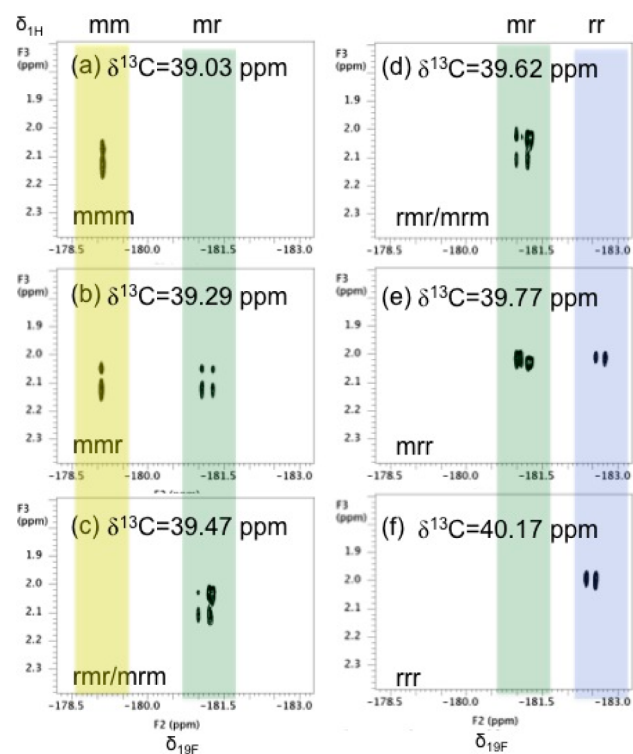


**Figure 3.** Selected $f_2f_3$ (H−F) slices from $^1H/^{13}C/^{19}F$ 3D NMR spectrum at different $^{13}C$ frequencies (110 °C): (a) $\delta_{13C}$ = 39.03 ppm, (b) $\delta_{13C}$ = 39.29 ppm, (c) $\delta_{13C}$ = 39.47 ppm, (d) $\delta_{13C}$ = 39.62 ppm, (e) $\delta_{13C}$ = 39.77 ppm, and (f) $\delta_{13C}$ = 40.17 ppm.

NMR data. Figure 3 shows selected H−F planes from the $^1H/^{13}C/^{19}F$ 3D NMR spectrum in which $\Delta_2$ was optimized based on $^2J_{FC}$. According to the above assignments, triads can be determined based on the $^{19}F$ chemical shifts. The peaks highlighted in yellow, green, and blue are attributed to the fluorine atoms in mm, mr/rm, and rr sequences, respectively.

In Figure 3a ($\delta_{13C}$ = 39.03 ppm) there is a correlation to the resonance of only one type of fluorine atom (mm). The proton resonance of the attached $CH_2$ groups must be correlated with the resonances of mm fluorine atoms on both sides. Therefore, the $^{13}C$ chemical shift of this plane must be attributed to the $CH_2$ carbons in mmm sequences. In the $f_2f_3$ slice at $\delta_{13C}$ = 39.29 ppm (Figure 3b), two types of $^{19}F$ are observed from mm and mr triads. This indicates that the carbon resonance of the methylene group responsible for the cross-peaks in this plane must be correlated with the resonances of mm fluorines on one side and mr fluorines on the other side. Therefore, the carbon resonance at this frequency is assigned to mmr tetrads. The r-centered tetrad sequences were assigned in a similar way, and the results are shown in Figure 3. In Figure 3c,d, the resonances for rmr and mrm sequences are not well resolved.

In conclusion, $^1H/^{13}C/^{19}F$ 3D NMR experiment can provide phenomenal resolution and unequivocal atomic connectivity information for studying the microstructures of PVF and of fluorine-containing polymers in general. Due to the presence of two sensitive nuclei, this experiment can be conducted on commonly available instruments and without isotopic labeling. Unambiguous resonance assignments were made for all three nuclei in the H-T structures. The stereosequences for $CH_2$-centered sequences, which were not resolved in the 1D and the 2D NMR spectra, can be resolved in 3D NMR spectra due to the dispersion in $^{19}F$ chemical shift dimension. These experiments are relatively easy to implement on modern NMR instruments, and data can be obtained in relatively short experiment times (ca. 11 h in the case of the spectra presented here). The characterization of other structure features in PVF, including the stereosequences in the H−H and T−T regions is under study and will be reported in a later paper.

## ■ ASSOCIATED CONTENT

**ⓢ Supporting Information**

Figures showing 1D NMR spectra, additional planes from the 3D NMR spectra of PVF, a detailed description of the NMR sample preparation, and the $^1H/^{13}C/^{19}F$ 3D NMR sequence are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

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## ■ ACKNOWLEDGMENTS

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