An NMR Study of Poly(vinylidene fluoride) Structure by ^{1}H, ^{13}C, and ^{19}F Triple Resonance Method

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ABSTRACT: ^{1}H, ^{13}C, and ^{19}F triple resonance NMR experiments on poly(vinylidene fluoride) (PVDF) in solution were carried out in order to provide a detailed primary structural analysis of PVDF. The ^{19}F NMR signals were measured by the ^{1}H broad-band decoupled ^{19}F J-correlated 2D NMR and ^{1}H–^{19}F J-correlated two dimensional (2D) methods, and the ^{13}C NMR signals were measured by the ^{1}H broad-band decoupled ^{19}F–^{13}C J-correlated 2D method. On the basis of the spectral analysis, a complete primary-structural analysis of PVDF was carried out. From these results, it was demonstrated that the ^{1}H, ^{13}C, and ^{19}F triple resonance NMR method is a very useful means for analysing primary-structure of fluoropolymers.
KEY WORDS   Poly(vinylidene fluoride) / 2D NMR / Triple Resonance / Primary Structure / COSY /

NMR spectroscopy is a powerful method for studying the microstructure of fluoropolymers, using ^{13}C and ^{19}F nuclei. Since both ^{19}F and ^{13}C nuclei have a wide chemical shift range, ^{13}C and ^{19}F chemical shifts are very sensitive to structural variation. In general, solution-state ^{13}C and ^{19}F spectra of fluoropolymers are complicated because of the existence of various kinds of regio-irregular structures and stereochemical structures, and sometimes spin coupling splittings among ^{1}H, ^{13}C, and ^{19}F nuclei. This makes spectral analysis of the structure of the polymers difficult. For overcoming such a situation, it is very useful to use 2D NMR methods. 2D NMR methods, however, have been used only to a limited extent in synthetic fluoropolymers.[1]

Recently, 2D NMR studies on the primary structure of poly(vinylidene fluoride) (PVDF) have been carried out[2] in addition to the one-dimensional (1D) NMR studies reported previously.[3] Nevertheless, further complete analysis of the primary structure of the polymer is needed.

The purpose of this work is to carry out further detailed analysis of the primary structure of PVDF by means of the hetero-nuclear 2D NMR technique developed by in our laboratory. The resolved resonances in the observed 390 MHz ^{19}F NMR spectra of PVDF have been assigned by the reported ^{1}H broad-band decoupling ^{19}F J-correlated 2D method[1] and our ^{1}H–^{19}F J-correlated 2D method. The resolved resonances in simultaneous ^{1}H and ^{19}F broad-band decoupling ^{13}C NMR spectrum have been assigned by our ^{1}H broad-band decoupling ^{13}C–^{19}F J-correlated 2D method. On the basis of these results, a complete structural analysis of the stereochemical structures and regio-irregular structures of PVDF has been carried out.

EXPERIMENTAL

Materials

The PVDF samples used in this work are

prepared by emulsion polymerization at 50°C. This reaction was initiated with di-n-propyl peroxydicarbonate.

NMR measurements

376 MHz ^{19}F, 400 MHz ^{1}H and 100 MHz ^{13}C NMR spectra have been recorded on a JEOL α-400 spectrometer using a ^{1}H, ^{13}C, and ^{19}F triple resonance tuned probe. All the experiments have been carried out at about 10 w/v% solution of PVDF in dimethylsulfoxide-d_6 (DMSO-d_6) at 80°C.

^{19}F NMR spectra have been recorded under ^{1}H broad-band decoupling. ^{19}F chemical shifts are relative to CFCl$_3$.

^{13}C NMR spectra have been recorded under simultaneous ^{1}H and ^{19}F decoupling. The ^{1}H broad-band decoupling was carried out with Garp decouple sequence. As the ^{19}F NMR spectrum has resonances with a wide range of chemical shifts, the ^{19}F decoupling was achieved with the MPF8 decouple pulse sequence.[4] In this experiments, irradiation point was set at 134.5 kHz (about -105 ppm).

The ^{1}H broad-band decoupled ^{19}F J-correlated 2D (^{19}F COSY with ^{1}H decoupling) NMR experiments were performed using the modified ^{1}H COSY pulse sequence. The ^{19}F 90° pulse width was 9.2 μs. The ^{1}H decoupled ^{19}F COSY spectra were obtained with 20 scans for each of 512 FIDs which contain 4096 data points in the F$_2$ dimension over a spectral width of 16.0 kHz. A relaxation delay of 1.8 s was used. Zero-filling in the F$_1$ dimension was produced by a 4094 × 1024 data matrix with a digital resolution of 39.1 Hz per point for the F$_2$ dimension and 15.63 Hz per point for the F$_1$ dimension, respectively. For 2D Fourier transformation a sine-bell squared window function was used for both of the dimensions. The transformed data were then symmetrized.

The ^{1}H–^{19}F J-correlated 2D (^{1}H–^{19}F COSY) NMR experiments were performed using the modified ^{13}C–^{1}H heteronuclear COSY pulse sequence. The ^{1}H 90° pulse width
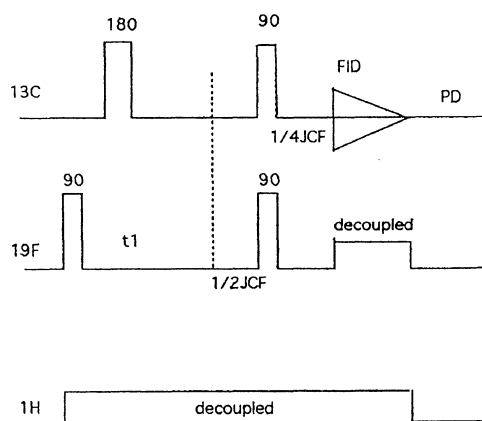

Figure 1. The pulse sequence for ^{1}H decoupled ^{13}C–^{19}F J-correlated 2D NMR measurement.

was 15.7 μs and the ^{19}F 90° pulse width 9.2 μs. The spectra were acquired with 8 scans for each of 512 FIDs which contain 512 data points in the F$_2$ dimension. The F$_2$ spectral width was 1.2 kHz and the F$_1$ spectral width 13 kHz. Zero-filling in the F$_1$ dimension was produced by a 1024 × 512 data matrix with a digital resolution of 22.63 Hz per point in the F$_2$ dimension and 3.13 Hz per point in the F$_1$ dimension. For 2D Fourier transformation a sine-bell square window function was used for both of the dimensions.

The ^{1}H broad-band decoupled ^{13}C–^{19}F J-correlated 2D NMR experiments (^{13}C–^{19}F COSY with ^{1}H decoupling) were performed using the pulse sequence as shown Figure 1. The ^{13}C 90° pulse width was 20.0 μs and the ^{19}F 90° pulse width 9.2 μs. The spectra were acquired with 320 scans for each of the 512 FIDs which contain 1024 data points in the F$_2$ dimension. The F$_2$ spectral width was 10 kHz and the F$_1$ spectral width 10 kHz, respectively. Zero-filling in the F$_1$ dimension was produced by a 1024 × 1024 data matrix with digital resolution of 9.77 Hz per point in the F$_2$ dimension and 20.41 Hz per point in the F$_1$ dimension, respectively. For 2D Fourier transformation a sine-bell square window function was used for both of the dimensions.

RESULTS AND DISCUSSION

^{19}F NMR spectral Analysis

During the polymerization of vinylidene fluoride, head-to-head (H-H) and tail-to-tail (T-T) additions of the monomer units produce non-symmetric environments as regio-irregular structures. The existence of the H-H and T-T structures results in a ^{19}F chemical shift distribution. The corresponding ^{19}F NMR signals were assigned by ^{19}F COSY experiments[1] and the γ-effect.[5]

376 MHz ^{19}F NMR spectra of PVDF are reproduced in Figure 2, where (a) shows ^{19}F NMR spectra without ^1H broad-band decoupling and (b) shows ^{19}F NMR spectra with ^1H broad-band decoupling. By ^1H broad-band decoupling each of the signals becomes sharp and so new peaks appear by resolution of overlapped peaks. The spectral analysis is not easy because the spectrum is complicated with a number of weak peaks. To assign these peaks reasonably, ^1H decoupling ^{19}F J-correlated 2D NMR (^{19}F COSY with ^1H decoupling) experiments on the connectivities between the peaks were carried out. The spectra obtained are shown in Figure 3. Figure 3 (a) shows a ^1H decoupled ^{19}F COSY spectrum in the range -91.0 to -96.0 ppm, corresponding to the $CH_2C\underline{F}_2CH_2$ moiety. Figure 3 (b) shows a ^1H decoupled ^{19}F COSY spectrum in the range -113.0 to -117.0 ppm, corresponding to the $CH_2C\underline{F}_2C\underline{F}_2CH_2$ moiety. The observed cross-peaks indicate a connectivity between a pair of fluorine atoms in which there exists a scalar J coupling through three or four bonds. The
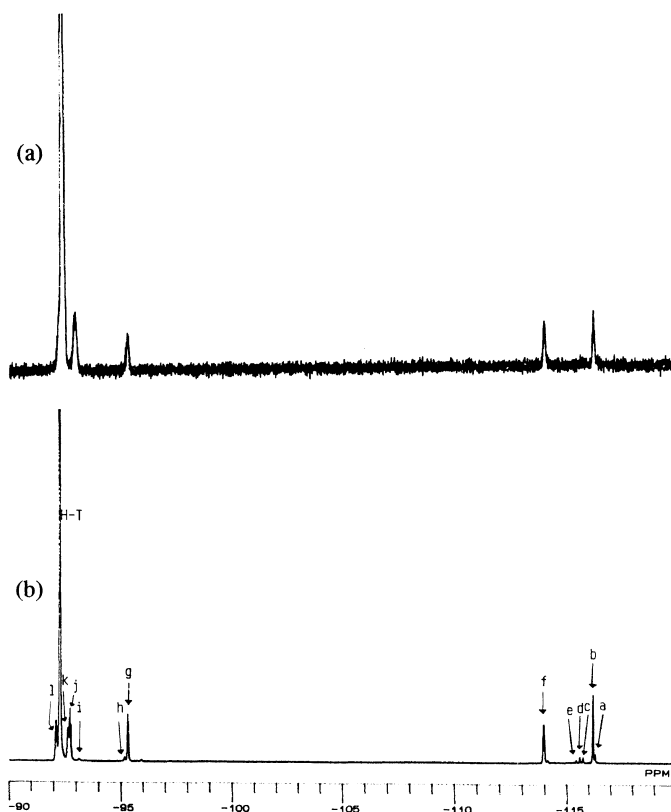

Figure 2. ^{19}F NMR spectra for PVDF without ^1H broad-band decouping (a) with ^1H broad-band decoupling (b).
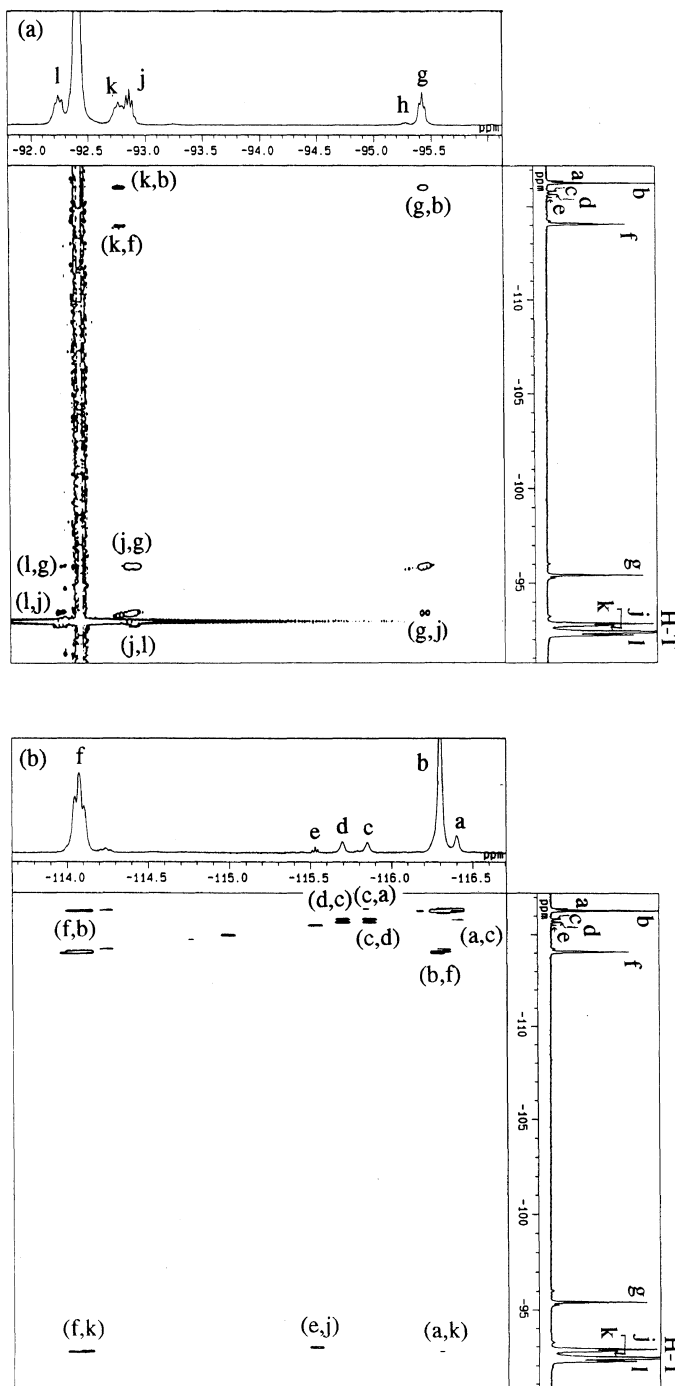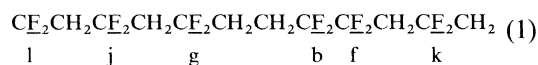
Figure 3. Contour plot ^{1}H decoupled ^{19}F J-correlated 2D NMR of PVDF. The positive contour only is shown. Expanded region of -92.0 to -96.0 ppm (a) and expanded region of -113.0 to -117.0 ppm (b).

assignment is easily made by confirming the existence of the correlated peaks. According to these experimental results, the connectivities between peaks l and j, peaks g and b, peaks j and g, peaks f and b, and peaks k and f were clarified. On the basis of these connectivities, the irregular structures of PVDF were determined as follows.

$$\underset{\text{l}}{C\underline{F}_2}CH_2\underset{\text{j}}{C\underline{F}_2}CH_2\underset{\text{g}}{C\underline{F}_2}CH_2CH_2\underset{\text{b}}{C\underline{F}_2}\underset{\text{f}}{C\underline{F}_2}CH_2\underset{\text{k}}{C\underline{F}_2}CH_2 \quad (1)$$

In Table I are shown ^{19}F chemical shifts of PVDF compared with calculated ^{19}F chemical shifts by Tonelli *et al*. These assignments support reasonably those assigned with the γ-effect calculation.

As mentioned above, the ^{19}F spectrum of PVDF was successfully assigned by ^{19}F COSY

Table I. [19]F chemical shifts of PVDF compared with calculated ^{19}F chemical shifts

Peak No.	Experimental chemical shift	Calculated chemical shift[a]
	ppm	ppm
a	−116.40	—
b	−116.30	−116.0
c	−115.85	—
d	−115.69	—
e	−115.83	—
f	−114.08	−112.3
g	−95.42	−94.4
h	−95.38	—
i	−93.24	—
j	−92.85	—
k	−92.76	—
l	−92.24	−92.0

[a] Calculated ^{19}F chemical shifts were read from ref 4.
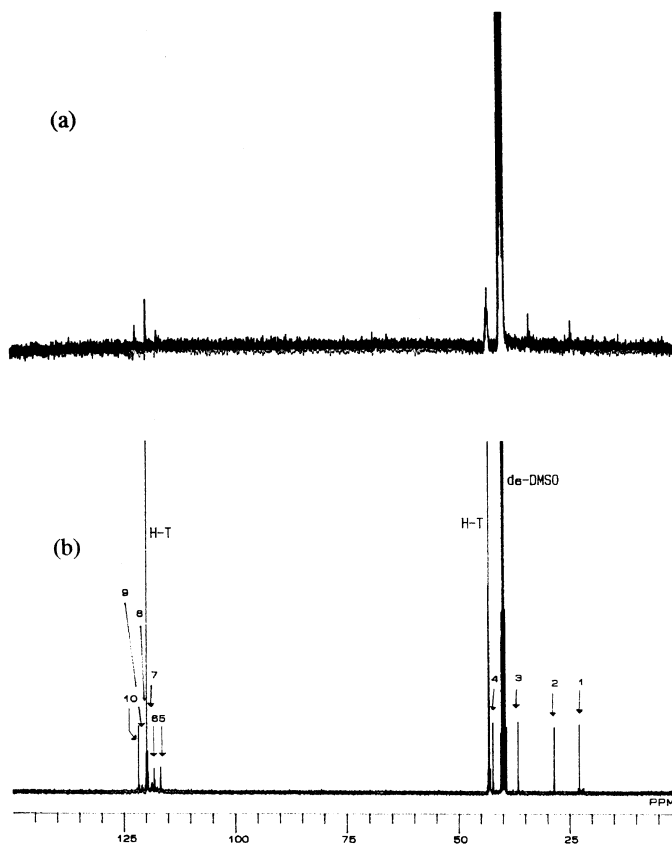
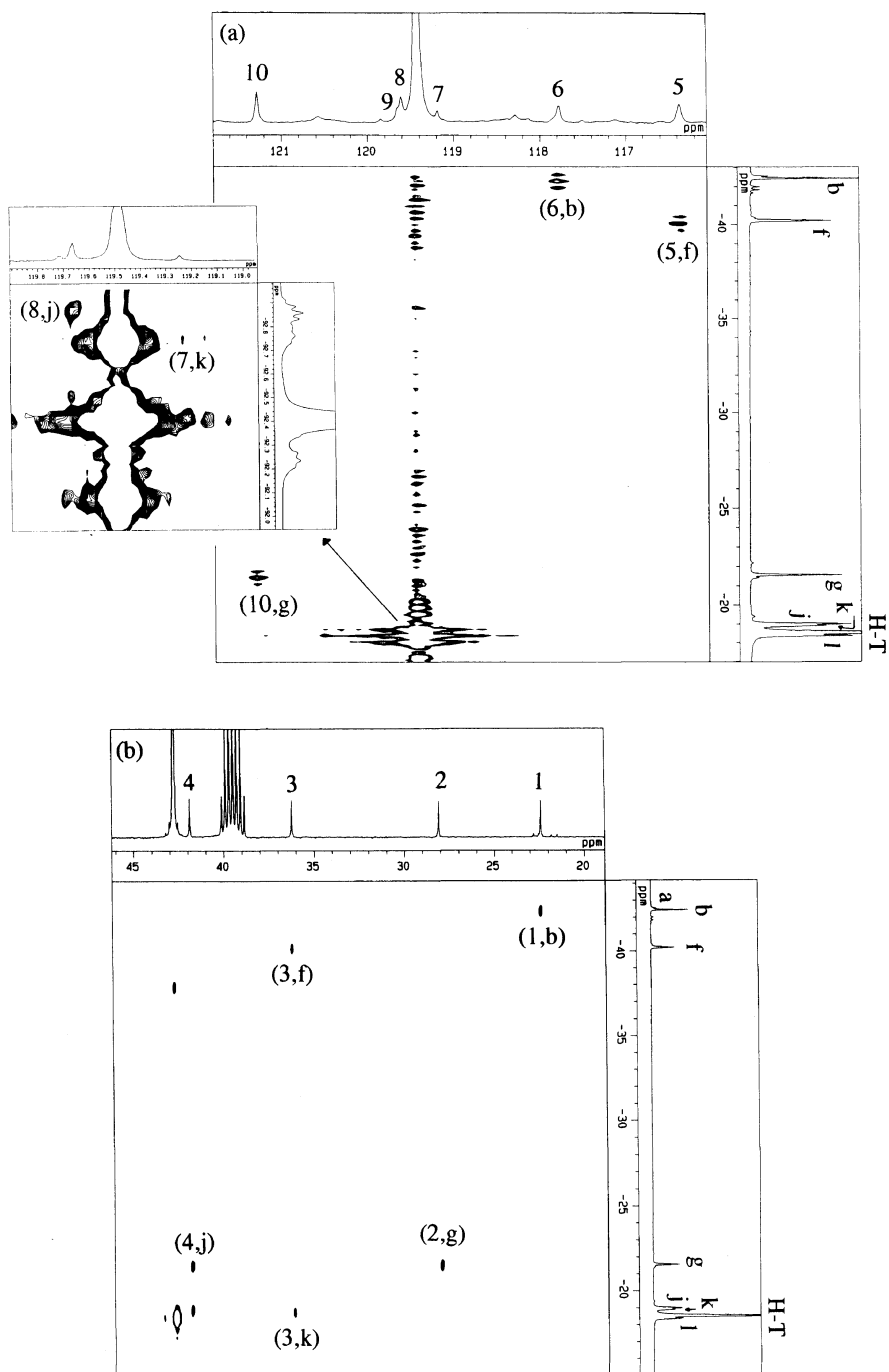**Figure 4.** ^{13}C NMR spectra for PVDF ^{1}H decoupling(a) and simultaneous ^{1}H and ^{19}F decoupling (b).

Figure 5. Contour plot of ¹H decoupled ¹³C–¹⁹F J-correlated 2D NMR of PVDF with the pulse sequence of Figure 1. The positive contour only is shown. The delays are setting by 1.25 ms (a) and 12.5 ms (b).
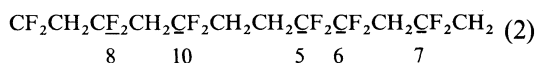
NMR with ^{1}H decoupling COSY method.

^{13}C NMR Spectral Analysis

In Figure 4, ^{13}C NMR spectra of PVDF are shown. A ^{13}C NMR spectrum (Figure 4 (a)) with low signal-to-noise ratio was obtained by ^{1}H broad-band decoupling in spite of a number of accumulations. The low signal-to-noise ratio is the result of the J_{C-F} coupling that produces multiplets and the absence of an NOE from ^{19}F nuclei. On the other hand, as shown in Figure 4 (b), a ^{13}C NMR spectrum with high signal-to-noise ratio was obtained by ^{1}H and ^{19}F decouplings. The ^{13}C signals for the CF$_2$ carbons with seven kinds of magnetically unequivalent environments appear in the vicinity of 120 ppm, while the ^{13}C signals for the CH$_2$ carbons with five kinds of magnetically-unequivalent environments appear in the chemical shift range from 20 to 50 ppm. So, it is clear that the ^{13}C chemical shifts reflect the structural environment as with the case of ^{19}F chemical shifts.

Next, we address with the assignment for ^{13}C signals of PVDF by ^{13}C–^{19}F J-correlated 2D NMR ^{1}H broad-band decoupling (^{13}C–^{19}F COSY NMR with ^{1}H decoupling) methods as shown Figure 1. First, the ^{13}C-^{19}F COSY NMR with ^{1}H decoupling was observed by setting the delay time to 1.25 ms, because the ^{13}C signal with direct C–F J-coupling constant of a few hundred Hz is enhanced. In this way, the cross-peaks can be observed between a pair of ^{13}C and ^{19}F nuclei which are interacting through a C–F J-coupling constant of a few hundred Hz. From these experimental results, the large C–F coupling constant of 400 Hz shows that the ^{13}C and ^{19}F nuclei are directly connected to each other. As shown in Figure 5 (a), the peaks 5 and 6 for the ^{13}C signal correlate with the peaks f and b for the ^{19}F signal, respectively. Hence, the peaks 5 and 6 can be assigned to the carbons in the H–H structure. Similarly, the peaks 7, 8, and 10 for the ^{13}C signal correlate with the peaks k, j, and g for the ^{19}F signal, respectively. From the

correlated peaks obtained, the CF$_2$ carbon peaks of PVDF can be assigned as follows.

$$CF_2CH_2C\underset{8}{F}_2CH_2\underset{10}{C}F_2CH_2CH_2C\underset{5}{F}_2\underset{6}{C}F_2CH_2\underset{7}{C}F_2CH_2 \quad (2)$$

Next, the ^{13}C–^{19}F COSY NMR with ^{1}H decoupling was observed by setting the delay time to 12.5 ms, because the ^{13}C signal with geminal C–F J-coupling constant of a few tens Hz is enhanced. In this way, the cross-peak can be observed selectivity between a pair of ^{13}C and ^{19}F nuclei which are interacting through the C–F J-coupling with a few tens Hz. From these experimental results, the C–F J-coupling constant of a few tens Hz obtained shows that the ^{13}C and ^{19}F nuclei connect vicinally with each other. As shown in Figure 5 (b), peak 3 for the ^{13}C nuclei correlates with peaks f and k for the ^{19}F nuclei. In this way the necessary connectivities between peaks 1 and b, peaks 2 and g, peaks 4 and g, and peaks 4 and j can be made. From these correlated peaks, the CH$_2$ carbon signals of PVDF can be assigned as follows.

$$CF_2CH_2CF_2C\underset{4}{H}_2CF_2\underset{2}{C}H_2\underset{1}{C}H_2CF_2 CF_2\underset{3}{C}H_2CF_2CH_2 \quad (3)$$
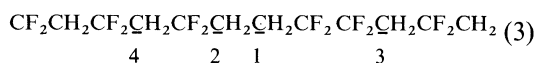
From the ^{13}C–^{19}F J-correlated ^{1}H decoupled 2D method, the ^{13}C signals of PVDF

Table II. ^{13}C chemical shifts of PVDF compared with calculated ^{13}C chemical shifts

Peak No.	Experimental chemical shift	Calculated chemical shift[a]
	ppm	ppm
1	22.79	22.8
2	28.46	31.0
3	36.63	38.0
4	42.28	44.0
5	118.14	119.3
6	118.65	118.0
7	119.55	—
8	119.98	—
9	120.03	—
10	121.65	122.8

[a] Calculated ^{13}C chemical shifts were read from ref 5.

can be assigned to the structures (3) and (4). In Table II are shown ^{13}C chemical shifts of PVDF compared with calculated ^{19}F chemical shifts by Tonelli *et al*. The assignment of the ^{13}C signals of PVDF, which previously has been made only by the empirical γ-effect calculation[6] has now been rigorously supported by the 2D experiments. Further more new ^{13}C signals have been assigned.

Finally, it can be concluded that the PVDF sample prepared by emulsion polymerization has a very complicated primary structure with regio-irregularities and that ^{1}H, ^{13}C, and ^{19}F triple resonance NMR method is a very useful means for analyzing the primary-structure of fluoropolymers.

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