Microstructure Analysis of Poly(vinyl fluoride) by Fluorine-19 Two-Dimensional *J*-Correlated NMR Spectroscopy

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ABSTRACT: Fluorine-19 NMR spectroscopy is a powerful method for studying the microstructure of fluoropolymers since ^{19}F chemical shifts are highly sensitive to structural variables. Different stereosequences have markedly different chemical shifts, and fluorines involved in head-to-head:tail-to-tail monomer inversions have significantly different chemical shifts from those of normal head-to-tail units. Complete stereosequence assignments have been made at the pentad level for isoregic poly(vinyl fluoride) from the 188-MHz ^{19}F *J*-correlated spectrum. The cross-peaks arising from four-bond scalar coupling between adjacent fluorines are visible in the 2D spectrum even though this coupling is too small to be detected in the 1D spectrum. An unexplained absence of cross-peaks between isoregic and defect fluorines prevents complete assignments of the defect resonances in commercial poly(vinyl fluoride), but partial assignments can be made from the vicinal coupling between the head-to-head fluorines. In both defect and isoregic regions of the 2D spectra, resolution of fine structure is observed which cannot be seen in the 1D spectra.

Introduction

Fluorine-19 nuclear magnetic resonance (NMR) spectroscopy is a powerful method for studying the microstructure of fluoropolymers since ^{19}F chemical shifts are highly sensitive to structural variables. Different stereosequences have markedly different chemical shifts, and fluorines involved in head-to-head:tail-to-tail inversions in the polymer chain have significantly different ^{19}F chemical shifts from those involved in normal head-to-tail additions. Fluorine-substituted ethylenes are particularly subject to the generation of inverted units, and the ^{19}F spectra of these polymers are often extremely complex. Since the physical properties of these fluoropolymers may depend strongly on the degree of stereoregularity and regioregularity of the chain, it is desirable to assign the resonances in the ^{19}F spectrum to specific sequences within the polymer. We report a novel application of ^{19}F two-dimensional *J*-correlated spectroscopy (^{19}F COSY) to the assignment of the microstructure in the ^{19}F spectrum of poly(vinyl fluoride).

Two-dimensional *J*-correlated spectroscopy (COSY) connects spins which are *J*-coupled to each other, and the resultant spectrum is a map of the entire coupling network within a molecule. This experiment has been the inspiration for a multitude of related 2D NMR experiments since it was first conceived by Jeener in 1971.[1] Proton COSY experiments have been applied extensively to line assignments in the proton spectra of proteins,[2-9] peptides,[10-12] micelle-bound glucagon,[13] and nucleic acids.[14,15] However, 2D NMR has only seen limited application to synthetic polymers. Macura and Brown[16] have applied 2D *J*-resolved spectroscopy to poly(vinyl chloride), Gerig[17] has applied ^{19}F–^{1}H 2D chemical shift correlation spectroscopy to poly(*p*-fluorostyrene), and Bruch and Bovey[18] have applied 2D NOE spectroscopy to a vinylidene chloride–isobutylene copolymer. There has been only one reported application of COSY to synthetic polymers: Ferguson and Ovenall[19] recently described a limited application of ^{19}F 2D *J*-correlated spectroscopy to poly(vinylidene fluoride). This is also the only previous extension of 2D *J*-correlated spectroscopy to fluorine; all other applications have been to proton spectra.

The pulse sequence for 2D *J*-correlated spectroscopy is shown in Figure 1. The preparation period is a relaxation delay to ensure that the spin system is in equilibrium. The first 90° pulse causes each fluorine to precess at its characteristic frequency during the evolution period of length t_1. The second 90° pulse, or mixing pulse, causes magnetization exchange between all fluorines which are *J*-coupled to each other. The final precession frequency is observed during the detection period of length t_2. The broadband proton decoupler is on during the entire sequence to remove ^{19}F–^{1}H coupling. The evolution time t_1 is systematically incremented and the resultant free induction decay is detected in t_2 for a series of t_1 values. A two-dimensional Fourier transform is performed on the resultant data matrix to yield a 2D spectrum as a function of two frequencies, ω_1 and ω_2, the precession frequencies during t_1 and t_2, respectively. Those fluorines which do not exchange magnetization have a final frequency, ω_2, which is the same as the initial frequency, ω_1. Hence, the COSY spectrum contains the normal spectrum along the diagonal corresponding to $\omega_1 = \omega_2$. The peaks along this diagonal are called *autocorrelation* or *diagonal* peaks in the 2D spectrum. Those fluorines which exchange magnetization due to *J*-coupling have a final frequency which is different from the initial precession frequency. This gives rise to *cross-correlation* or *off-diagonal* peaks connecting coupled fluorines. If two fluorines which have normal precession frequencies ω_a and ω_b are *J*-coupled, then the COSY spectrum consists of two diagonal peaks with coordinates (ω_a, ω_a) and (ω_b, ω_b) and two symmetrical off-diagonal peaks with coordinates (ω_a, ω_b) and (ω_b, ω_a). Although the diagonal peaks are generally much larger than the off-diagonal peaks, it is the off-diagonal peaks which contain the useful information in a 2D *J*-correlated spectrum. By matching all pairs of off-diagonal peaks, the complete network of connectivities via *J*-coupling can be seen in a single 2D *J*-correlated spectrum.

Experimental Section

Materials. The aregic poly(vinyl fluoride) was a commercial sample supplied by Aldrich Chemical Co. in powder form. Isoregic poly(vinyl fluoride) was prepared as described previously[20] by reductively dechlorinating a precursor polymer, poly(1-chloro-1-fluoroethylene), with tri-*n*-butyltin hydride.

$$n\mathrm{CH_2{=}CFCl} \rightarrow (\mathrm{CH_2{-}CFCl})_n \rightarrow (\mathrm{CH_2{-}CHF})_n$$

NMR Spectroscopy. All spectra were obtained in *N,N*-dimethylformamide-d_7 (DMF-d_7) solvent at a controlled temperature of 130 °C using a Varian XL-200 spectrometer operating at a ^{19}F frequency of 188.2 MHz. Broadband proton decoupling was employed in order to remove ^{19}F–^{1}H coupling in all spectra. Spin–lattice relaxation times were measured by using a 180°–τ–90° inversion–recovery pulse sequence and least-squares analysis of integrated peak intensities.

The ^{19}F 2D *J*-correlated experiment on isoregic poly(vinyl fluoride) was performed with a recycle time of 8.9 s to ensure that the maximum signal is obtained upon repetition of the pulse sequence. A total of 32 transients was accumulated for each t_1

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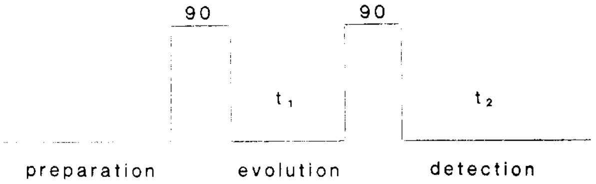


Figure 1. 2D *J*-correlated pulse sequence.

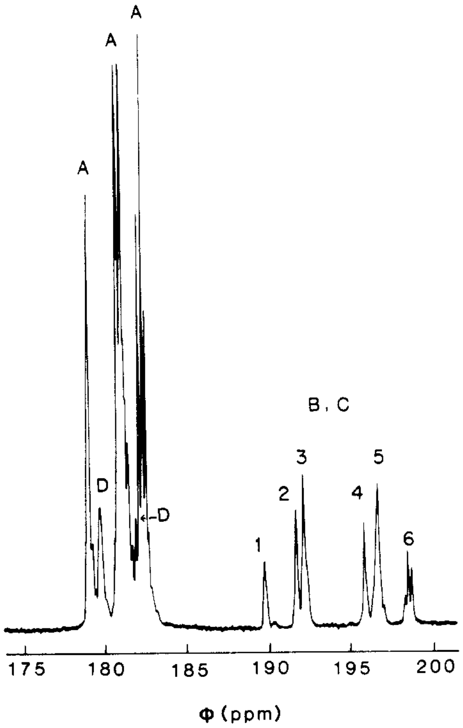


Figure 2. 188-MHz ^{19}F spectrum of an 8% solution of commercial poly(vinyl fluoride) in DMF-d_7 at 130 °C. Broadband proton decoupling was employed to remove $^{19}F-^{1}H$ coupling. A total of 16K points were accumulated over a sweepwidth of 5000 Hz. Sixteen transients were accumulated with a recycle time of 10 s.

value. The data matrix consisted of 256 spectra of 910 points each and was zero-filled to 512 by 1024 points covering 1300 Hz in both dimensions.

The ^{19}F 2D *J*-correlated experiment on commercial poly(vinyl fluoride) was performed with a recycle time of 8.5 s, and 32 transients were accumulated for each t_1 value. The matrix consisted of 256 spectra of 500 points each and was zero-filled to 512 by 512 points covering 5000 Hz in both dimensions.

In both cases, a four-cycle phase cycling routine was employed to eliminate spectral artifacts, and quadrature detection was employed in both dimensions. To improve resolution the free induction decays were multiplied by a pseudoecho window function in both dimensions prior to Fourier transformation.[21] This was necessary since an absolute value spectrum was calculated in both cases. The 2D *J*-correlated spectrum of commercial poly(vinyl fluoride) was symmetrized[22] to eliminate the ridges of "t_1 noise" running parallel to the ω_1-axis.

Results and Discussion

Commercial poly(vinyl fluoride), an optically clear, highly crystalline plastic, contains a substantial fraction of head-to-head:tail-to-tail monomer units, as first demonstrated by Wilson and Santee in 1965.[23] The 188.2-Hz ^{19}F spectrum of commercial poly(vinyl fluoride) in *N*,*N*-dimethylformamide-d_7 is shown in Figure 2. Weigert[24] made assignments for this spectrum in 1971 by analogy to the ^{13}C spectrum of atactic polypropylene, and Tonelli et al.[25] predicted the ^{19}F chemical shifts as a function of the stereosequence from bond rotation probabilities obtained from a rotational isomeric state model for poly(vinyl fluoride). Both studies agree that the large peaks in the downfield part of the spectrum are due to different stereosequences within the head-to-tail region of the polymer, while the smaller peaks throughout the spectrum arise from head-to-head:tail-to-tail defects in the chain. However, there is minor disagreement on the assignment of the fine structure, and there is no direct experimental evidence for the assignments given.

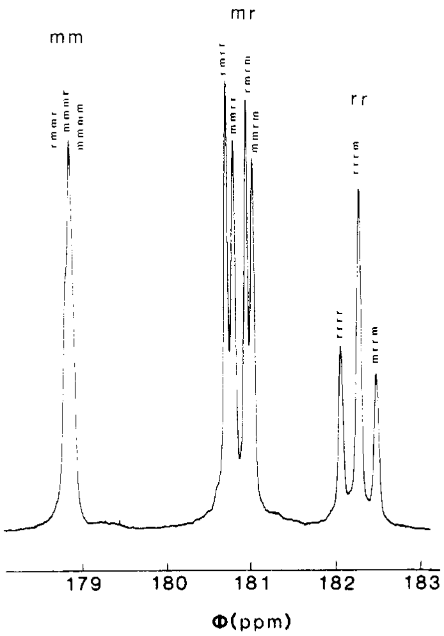
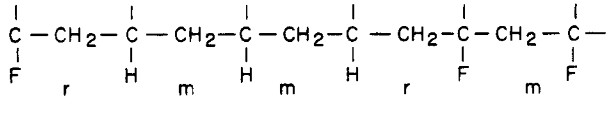


Figure 3. 188-MHz ^{19}F spectrum of an 11% solution of isoregic poly(vinyl fluoride) in DMF-d_7 at 130 °C. Broadband proton decoupling was employed to remove $^{19}F-^{1}H$ coupling. A total of 16K points were accumulated over a sweepwidth of 2000 Hz. Sixteen transients were accumulated with a recycle time of 15 s.

The ^{19}F spectrum of the isoregic poly(vinyl fluoride) is much simpler, as shown in Figure 3. The three groups of peaks have been assigned to the triad sequences mm, mr, and rr,[24,25] and the fine structure within these groups reflects sensitivity to pentad sequences.

Since the relative intensities of the lines indicate that the polymer is nearly atactic (P_m = 0.48), the pentad assignments are difficult to make on this basis. However, these assignments can be made from 2D *J*-correlated spectroscopy by taking advantage of four-bond *J*-coupling between neighboring fluorines. No $^{19}F-^{19}F$ scalar coupling can be detected as resonance splitting in the normal spectrum because of large line widths of approximately 14 Hz. However, model compounds indicate that the four-bond coupling constant between neighboring fluorines in the polymer chain should be approximately 7 Hz.[26] Although this is too small to be manifested as resonance splitting, it is large enough to give rise to off-diagonal peaks in the COSY spectrum. These off-diagonal peaks can be used to make stereosequence assignments since there is predicted coupling between the central pair of fluorines in pentad sequences which share a common hexad. Thus, for example, in the hexad sequence



$$-\underset{F}{\overset{H}{C}}-\underset{r}{CH_2}-\underset{H}{\overset{F}{C}}-\underset{m}{CH_2}-\underset{H}{\overset{F^*}{C}}-\underset{m}{CH_2}-\underset{H}{\overset{F^*}{C}}-\underset{r}{CH_2}-\underset{F}{\overset{H}{C}}-\underset{m}{CH_2}-\underset{F}{\overset{H}{C}}-$$

four-bond coupling between the indicated fluorines will result in cross-peaks connecting the rmmr and mmrm resonances in the COSY spectrum. All pentad assignments

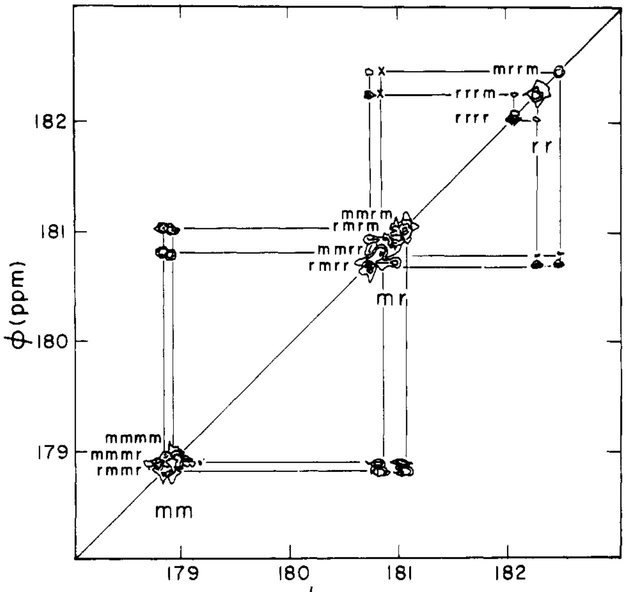


Figure 4. 188-MHz ^{19}F 2D J-correlated spectrum of an 11% solution of isoregic poly(vinyl fluoride) in DMF-d_7 at 130 °C. X denotes peaks which are visible at lower contour levels.

can be made unambiguously from the correlations observed in the COSY spectrum.

The ^{19}F COSY spectrum of isoregic poly(vinyl fluoride) is shown in Figure 4. The three upfield resonances are known to correspond to rr-centered pentads from a previous study by Cais.[20] The rrrr resonance can be identified since it can only couple to rrrm. Hence, rrrm must be the central peak since it is coupled to rrrr. The most upfield resonance must be mrrm by default.

There are four lines of approximately equal intensity in the middle of the spectrum which must correspond to mr-centered pentads. Two of these lines, rmrr and mmrr, must be coupled to both rrrm and mrrm in the rr-centered region. Two other lines, mmrm and mmrr, must be coupled to both mmmr and rmmr in the mm-centered region. Hence, mmrr can be identified immediately as the second line since it is the only line coupled to both the mm region and the rr region. Once mmrr is assigned, rmrr must be the first line since it is the only other resonance coupled to the rr region. Similarly, mmrm must be the fourth line since it is the only other line coupled to the mm region. The third line must be rmrm since it is coupled only within the mr region.

The mm-centered pentads all appear to have the same chemical shifts in the normal ^{19}F spectrum, but close analysis of the mm region of the COSY spectrum shows resolution into pentad fine structure. A slice through the mm region, shown in Figure 5, clearly reveals three peaks along the diagonal. The mmmm resonance can be assigned because it does not couple to the mr region, whereas both of the other resonances do. The mmmr resonance can be assigned on the basis of its intensity. If the pentad chemical shifts were more widely spaced it could be identified by its coupling with mmmm, but this pair of cross-peaks is too close to the diagonal to be visible.

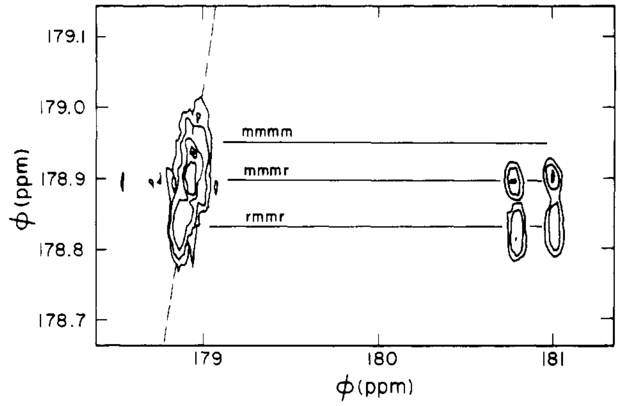
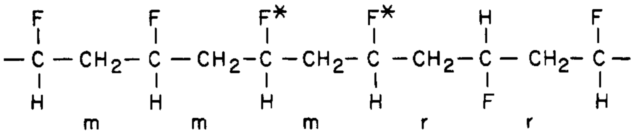


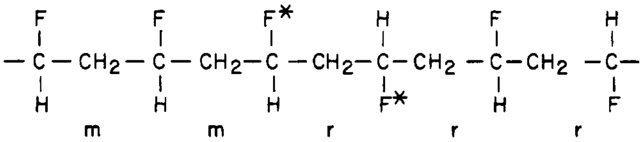
Figure 5. Expansion of the mm region of the 2D J-correlated spectrum of isoregic poly(vinyl fluoride) shown in Figure 4.

Although quantitation of 2D spectra is difficult in general, intensity comparisons can sometimes be suggestive. If the relative intensities of all off-diagonal peaks associated with the diagonal peaks assigned to mmrr and mmrm are compared, the cross-peaks to the mm region seem to be much more intense than those to the rr region. For example, the interaction between mmrr and mmmr is much stronger than the interaction between mmrr and rrrm. This implies that the indicated coupling in the sequence



$$-\underset{\substack{|\\H}}{\overset{\substack{F\\|}}{C}}-\underset{m}{CH_2}-\underset{\substack{|\\H}}{\overset{\substack{F\\|}}{C}}-\underset{m}{CH_2}-\underset{\substack{|\\H}}{\overset{\substack{F^*\\|}}{C}}-\underset{m}{CH_2}-\underset{\substack{|\\H}}{\overset{\substack{F^*\\|}}{C}}-\underset{r}{CH_2}-\underset{\substack{|\\F}}{\overset{\substack{H\\|}}{C}}-\underset{r}{CH_2}-\underset{\substack{|\\H}}{\overset{\substack{F\\|}}{C}}-$$

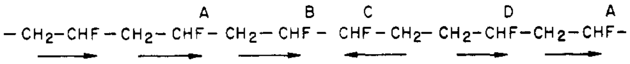
may be larger than in the sequence



$$-\underset{\substack{|\\H}}{\overset{\substack{F\\|}}{C}}-\underset{m}{CH_2}-\underset{\substack{|\\H}}{\overset{\substack{F\\|}}{C}}-\underset{m}{CH_2}-\underset{\substack{|\\H}}{\overset{\substack{F^*\\|}}{C}}-\underset{r}{CH_2}-\underset{\substack{|\\F^*}}{\overset{\substack{H\\|}}{C}}-\underset{r}{CH_2}-\underset{\substack{|\\H}}{\overset{\substack{F\\|}}{C}}-\underset{r}{CH_2}-\underset{\substack{|\\F}}{\overset{\substack{H\\|}}{C}}-$$

Rotational isomeric state calculations[27] indicate a substantial difference in the conformations of m and r sequences in poly(vinyl fluoride), but is not possible at present to offer a more detailed interpretation in terms of ^{19}F–^{19}F J coupling.

Although stereosequence assignments at the pentad level can thus be readily made from the COSY spectrum for isoregic poly(vinyl fluoride), the occurrence of inverted units in the commercial material makes assignments more difficult. The major distinct types of fluorines can be described by different stereochemical configurations associated with the following structure[24,25] (see also Figure 6)



$$-\underset{\longrightarrow}{CH_2-CHF}-\underset{\longrightarrow}{CH_2-\overset{A}{CHF}}-\underset{\longrightarrow}{CH_2-\overset{B}{CHF}}-\underset{\longleftarrow}{\overset{C}{CHF}-CH_2}-\underset{\longrightarrow}{CH_2-\overset{D}{CHF}}-\underset{\longrightarrow}{CH_2-\overset{A}{CHF}}-$$

The fluorines labeled D have similar chemical shifts to the normal isoregic fluorines, called type A, and give rise to small peaks in the downfield part of the ^{19}F spectrum shown in Figure 2. The fluorines labeled B and C have chemical shifts upfield from the A fluorines and give rise to the small peaks labeled 1–6 in Figure 2.[24,25]

If all three- and four-bond couplings were visible in the ^{19}F COSY spectrum, then all lines could be assigned in the ^{19}F spectrum of commercial poly(vinyl fluoride). Fluorines of type B and D are coupled to type A fluorines which have already been assigned in the isoregic poly(vinyl fluoride) spectrum. Once these fluorines are assigned, the C fluorines could then be assigned from the vicinal coupling between B and C. However, not all of these couplings can be detected in the 2D J-correlated spectrum of commercial poly(vinyl fluoride) shown in Figure 7. As in the isoregic case, the four-bond coupling between head-to-tail fluorines is evident in the form of cross-peaks between the different pentad resonances. However, the expected cross-peaks between isoregic fluorines and A and D fluorines are not visible in the COSY spectrum. Since these cross-peaks are

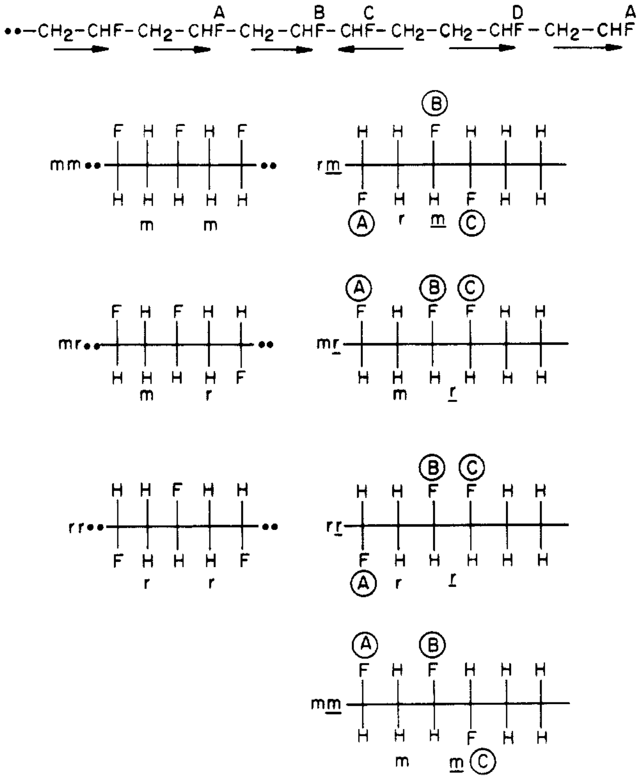


Figure 6. Isoregic (head-to-tail) and syndioregic (defect) sequences.

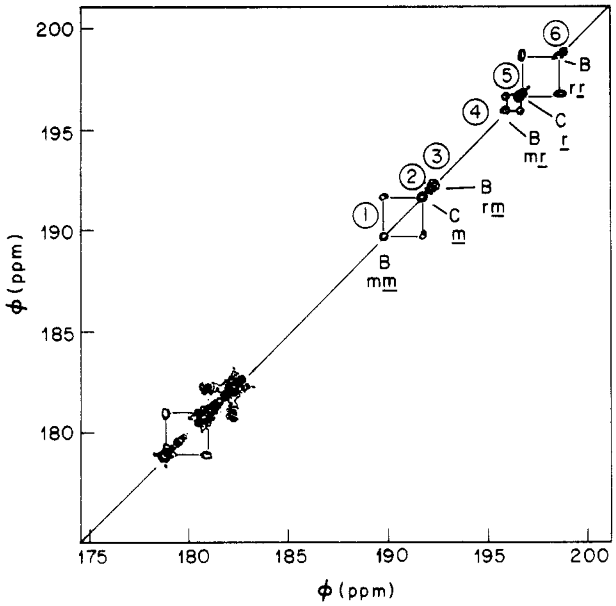


Figure 7. 188-MHz ^{19}F 2D J-correlated spectrum of an 8% solution of commercial poly(vinyl fluoride) in DMF-d_7 at 130 °C.

small compared to the isoregic diagonal and off-diagonal peaks, they are obscured in Figure 7.

However, the apparent absence of cross-peaks between A and B fluorines cannot be similarly rationalized since they would be well separated from the isoregic resonances. It might be argued that a conformational change at the defect bonds between fluorines A and B has reduced the ^{19}F–^{19}F coupling below detection in the COSY spectrum, but the RIS model[27] gives no encouragement to this idea since the conformations of these bonds appear in fact to be very little affected by the presence of fluorine C.

A more likely explanation for the absence of A and B cross-peaks is related to the fine structure associated with these cross-peaks. The B fluorines are coupled to both the

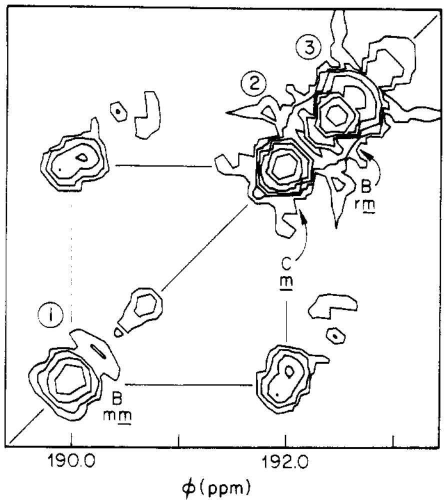


Figure 8. Expansion of peaks 1–3 in the 2D J-correlated spectrum of commercial poly(vinyl fluoride) shown in Figure 7.

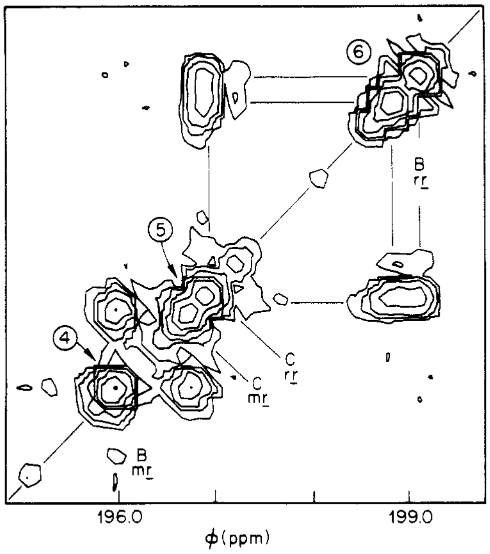


Figure 9. Expansion of peaks 4–6 in the 2D J-correlated spectrum of commercial poly(vinyl fluoride) shown in Figure 7.

A and C fluorines, whereas the C fluorines are coupled only to the B fluorines. Hence, the total cross-peak intensity is distributed over more lines in the case of the four-bond A to B cross-peaks than in the vicinal B to C cross-peaks. It is well-known that lines associated with a given cross-peak tend to mutually cancel if the resolution is poor. The four-bond cross-peaks are expected to suffer the effects of this cancellation more than the vicinal cross-peaks. Such four-bond couplings can be seen in the COSY spectrum of the isoregic portions of the commercial poly(vinyl fluoride) but are lost in the defect portions because of their much weaker intensity. (It should also be realized that the digital resolution is four times poorer in the commercial polymer's spectrum than in that of the isoregic material.)

The vicinal coupling between fluorines B and C can be used to connect B,C pairs of the same stereosequence. Weigert[24] assigned the defect peaks labeled 1 through 6 in Figure 2 to fluorines of B($m\underline{m}$), C($\underline{m}$), B($r\underline{m}$), B($m\underline{r}$), C($\underline{r}$) and B($r\underline{r}$), respectively, where m, r, $\underline{m}$, and $\underline{r}$ are as defined in Figure 6. The correlation patterns shown in Figure 7, and expanded 5-fold in Figures 8 and 9, confirm these assignments, although the absence of cross-peaks to the downfield isoregic region (vide supra) do not permit us to absolutely demonstrate them. ^{19}F chemical shifts calculated by Tonelli[25] are in agreement except for a reversal of the assignments of peaks 2 and 3.

We again observe that more fine structure can be resolved in the 2D spectra than in the conventional spectrum. Peak 3 becomes resolved into three regions, only one of which appears coupled to C($\underline{m}$) (peak 2). Thus, the assignment of peak 3 as B($r\underline{m}$) rather than C($\underline{m}$) is not necessarily inconsistent with relative intensities,[25] although detailed assignments are not at present established. In Figure 9, peaks 4 and 5 are coupled, as are peaks 5 and 6. In addition, fine structure can be seen in C($\underline{r}$), only part of which is coupled to B($r\underline{r}$); this appears to correspond to resolution of C($m\underline{r}$) and C($r\underline{r}$), as shown. The resolved fine structure in B($r\underline{r}$), all of which couples to C($r\underline{r}$), represents longer stereosequences in $r\underline{r}$, probably to the left of the defect as represented in Figure 6.

^{19}F Spin–Lattice Relaxation Measurements. To more fully characterize isoregic and commercial poly(vinyl fluoride), ^{19}F T_1 values were determined by the inversion–recovery method. They depend rather markedly on stereosequence, being shorter for syndiotactic sequences, as consistently observed for other vinyl polymers.[29] We find for *mm*, 2.79 s; for *mr*, 2.44 s; and for *rr*, 2.10 s; average error ±0.02 s. For the defect regions there is a less obvious correlation with structure. For example B($m\underline{r}$), C($m\underline{r}$), C($r\underline{r}$), and B($r\underline{r}$) all have T_1 values of 2.0 ± 0.2 s; while B($m\underline{m}$), C($\underline{m}$), and B($r\underline{m}$) showed values of 2.5 ± 0.2 s, 2.8 ± 0.2 s, and 2.0 ± 0.2 s, respectively. Thus fluorines in a head-to-head arrangement tend to show longer T_1 values when in the $\underline{m}$ configuration.

Conclusions

Complete stereosequence assignments have been made at the pentad level for isoregic poly(vinyl fluoride) from the ^{19}F 2D *J*-correlated spectrum. The cross-peaks arising from four-bond scalar coupling between adjacent fluorines are visible in the 2D spectrum even though this coupling is too small relative to the line widths to be detected as resonance splittings in the 1D spectrum. The relative magnitudes of these cross-peaks may reflect the relative magnitudes of the coupling constants and corresponding differences in conformation. An absence of cross-peaks between isoregic and defect fluorines prevents complete assignment of the syndioregic defect fluorines in commercial poly(vinyl fluoride), but partial assignments can be made from the vicinal coupling between the head-to-head fluorines. These assignments are consistent with those made by Weigert[24] and differ only slightly from those made by Tonelli et al.[25]

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