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CHAIN MICROSTRUCTURE OF POLY(VINYLIDENE FLUORIDE) BY 282 MHz ^{19}F-NMR SPECTROSCOPY

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ABSTRACT

Based on the effects of solvent and temperature on the 282-MHz ^{19}F-NMR spectrum of poly(vinylidene fluoride), PVF_2, in perdeuterated dimethylacetamide (DMA-d9) solution at -20°C, nine minor CF_2 resonances that are due to structures in the vicinity of reversed monomer enchainments have been identified. ^{19}F-^{19}F spin-spin decoupling and two-dimensional ^{19}F-correlation spectroscopy (^{19}F-2D COSY) have been used to assign these resonances. In several cases these assignments differ from those made previously.

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INTRODUCTION

Unless prepared by special methods [1], poly(vinylidene fluoride), PVF_2, contains 2.5-5.0% reverse enchainments, viz.

$$-CH_2-CF_2-CH_2-CF_2-CF_2-CH_2-CH_2-CF_2-CH_2-CF_2-,$$

Reverse

where $-CH_2-CF_2-$ (or $\rightarrow$) is a normal enchainment and $-CF_2-CH_2-$ (or $\leftarrow$) is a reverse enchainment.

Due to the low concentration of reverse enchainments, the probability that two reverse enchainments occur together is very low. Consequently, the NMR spectra of PVF_2 can be interpreted for the most part in terms of a polymer that contains only isolated reversed enchainments. Starting in 1960, a considerable number of papers on the ^{19}F-NMR spectra of PVF_2 have appeared. Initially Naylor and Lasoski [2] detected separate signals for CF_2 units in $-CH_2-CF_2-CH_2-$ and $-CH_2-CF_2-CF_2-CH_2-$ structures, the latter being associated with reverse enchainments. Later, Wilson [3] and Wilson and Santee [4] reported the observation of four ^{19}F-NMR signals in the 56.4-MHz ^{19}F-NMR spectra of PVF_2 in *N,N*-dimethylacetamide (DMA) solution. These were assigned to CF_2 units in $-CF_2-CH_2-CF_2^*-CH_2-CF_2-$ (designated A), $-CF_2-CH_2-CF_2^*-CH_2-CH_2-$ (designated B), and $-CH_2-CF_2^*-CF_2^*-CH_2-CH_2-$ (designated C and D) structures, where signals B, C, and D are due to CF_2 groups in the vicinity of a reverse enchainment. As more and more powerful NMR spectrometers became available, additional signals due to CF_2 units more remote from the reverse enchainment became discernable [5-8] and efforts were made to assign these by use of RIS (rotational isomeric state) calculation [9], empirical chemical shift calculation [7, 9], double resonance experiments [10, 11], and correlation spectroscopy [12]. In most of these studies, spectra obtained by using a single solvent and a single measurement temperature were examined. This has led to some confusion because the chemical shifts of some of the signals have been found to be very sensitive to solvent and temperature [8, 13].

Based on extensive studies of the influence of solvent and temperature on the ^{19}F-NMR spectra of PVF_2, Lin and Lin [8, 13] developed conditions for recording PVF_2 spectra with the highest level of definition. This work initially led to a very early recognition that more than three minor resonances associated with the reverse enchainments could be identified. In 1979, variation in solvent composition permitted an additional four signals to be de-

tected [8], and efforts to assign these peaks by ^{19}F-^{19}F decoupling experiments were initiated [11]. These led to an approximate set of assignments in 1986 [11]. Concurrent with these studies, others have used ^{19}F-^{19}F spin-spin decoupling and ^{19}F-2D COSY experiments to make assignments for these additional minor resonances [10, 12]. Unfortunately, detailed information in support of the assignments is not given in some cases, and in other cases the spectra presented seem to have been misassigned [10, 12]. The purpose of this communication is (a) to show that proper selection of solvent and temperature allows a total of nine minor resonances to be detected, (b) to make assignments for all nine minor resonances based on ^{19}F-^{19}F decoupling experiments and on ^{19}F-2D COSY experiments, and (c) to correct misassignments that appeared in the earlier literature.

EXPERIMENTAL

1. Materials

The principal PVF_2 sample used in this work was from Polysciences, Inc. The number-average molecular weight was about 60 000, and 4.0% of the monomer units were present in reverse enchainments. Other PVF_2 samples studied were Kynar 401 with a $\bar{M}_n$ of about 500 000 and 4.8% reverse monomer enchainments (from Pennwalt Co.) and a γ-ray-initiated PVF_2 with a $\bar{M}_n$ of about 40 000 and 2.5% reverse monomer enchainments.

The DMA-d9 employed for the NMR studies was obtained from the Cambridge Isotope Laboratories and the Chemical Dynamics Corporation.

2. NMR Measurements

The concentration of solutions for NMR measurements was 20 mg PVF_2 in 0.5 mL of DMA-d9 (40 mg/mL) for most experiments. The concentrations for studying the effect of concentration on chemical shifts were in the range of 20 to 200 mg/mL. The sample solutions were contained in 5 mm outside diameter sample tubes.

A Bruker WH-300 NMR spectrometer with an Aspect 2000 computer was used for temperature variation studies and for ^{19}F-^{19}F decoupling experiments. Its ^{19}F radiofrequency (RF) was 282.358 MHz. The frequency of the ^{1}H decoupler was modified so that it could be used in ^{19}F-^{19}F decoupling experiments. The 90° pulse width was 10.2 μs.

A Bruker/IBM AF-300 NMR spectrometer, also operated at 282.358 MHz, was used for ^{19}F-NMR T_1 measurements and to provide the delay time for

the 2D COSY experiments. It was equipped with an Aspect 3000 computer and an array processor.

The T_1 measurements were done at -12°C by using the inverse recovery pulse sequence [14]. ^{19}F-^{19}F two-dimensional [15] correlation spectroscopy was done at -12°C by the standard COSY pulse sequence [16, 17]. The data memory sizes for the full-range contour plots of PVF_2 solutions were 1024 words for one dimension and 512 words for the other dimension with 512-word zero filling. The sweep width was 8.5 kHz.

^1H-decoupled ^{19}F-^{19}F decoupling spectra were taken with the WH-300 spectrometer to which a ^1H-broad-band decoupling channel from the AF-300 spectrometer was connected. The ability to do this is an advantage of having two identical spectrometers in the same laboratory.

Measurement temperatures ranged from -40 to +120°C, controlled to within an accuracy to ±0.5°C. It was difficult to run long-term experiments at low temperatures because the PVF_2-DMA-d9 solutions tended to gel slowly or freeze below -15°C. A 40 mg/mL solution was stable for more than 8 h at -12°C, but it was unusable after 1 h at -15°C, after 20 min at -20°C, and after about 3 min at -30°C. Consequently, 2D-experiments were conducted at -12°C.

RESULTS AND DISCUSSION

Prior to considering the results of this paper, it is necessary to define the nomenclature that will be used. Shown below is a segment of PVF_2 in the vicinity of a reverse enchainment. The CF_2 groups that are very remote from a reverse enchainment are referred to simply by A. CF_2 groups that follow a reverse enchainment are assigned odd numbers, the numbers increasing as the distance from the reverse enchainment increase; the CF_2 units that precede a reverse enchainment are similarly assigned even numbers.

$$\begin{array}{cccccccccccccc} & A & & A_8 & & A_6 & & A_4 & & A_2 & A_1 & & & \\ -CH_2-&CF_2-&CH_2-&CF_2-&CH_2-&CF_2-&CH_2-&CF_2-&CH_2-&CF_2-&CF_2-&CH_2 & & \\ \longrightarrow & & \longrightarrow & & \longrightarrow & & \longrightarrow & & \longrightarrow & & \longleftarrow & & & \\ & A_3 & & A_5 & & A_7 & & A_9 & & A & & & & \\ -CH_2-&CF_2-&CH_2-&CF_2-&CH_2-&CF_2-&CH_2-&CF_2-&CH_2-&CF_2-&- & & & \\ & \longrightarrow & & \longrightarrow & & \longrightarrow & & \longrightarrow & & \longrightarrow & & & & \end{array}$$

All chemical shifts are given positive values for signals downfield from the internal reference peak of $CFCl_3$ and negative values for upfield signals. It was noted that the chemical shifts of the major CF_2 peak (A) and the $CFCl_3$

peak itself changed slightly with temperature. Therefore, for convenience, the major CF_2 line, instead of the $CFCl_3$ line, was used as a reference for studying the effects of temperature, sample concentration, and solvent on the chemical shifts of PVF_2. In this system the signals upfield from the major CF_2 line (A) are given positive values and signals downfield from it are given negative values.

1. One-Dimensional (1D) ^{19}F-NMR Spectrum

The 1D ^{19}F-NMR spectrum of PVF_2 in DMA-d9 solution at -20°C in Fig. 1 shows a total of 10 signals. According to early studies of Wilson [3] and Wilson and Santee [4], the most upfield peaks, A_1 and A_2, are head-to-head CF_2 resonances due to one reverse monomer enchainment, and the third highest field peak (-92.9 ppm from $CFCl_3$) is due to A_3. The signals at -90.7, -91.5, -89.5, and -89.7 ppm from $CFCl_3$ are A_5, A_4, A_6, and A_7 peaks, respectively.

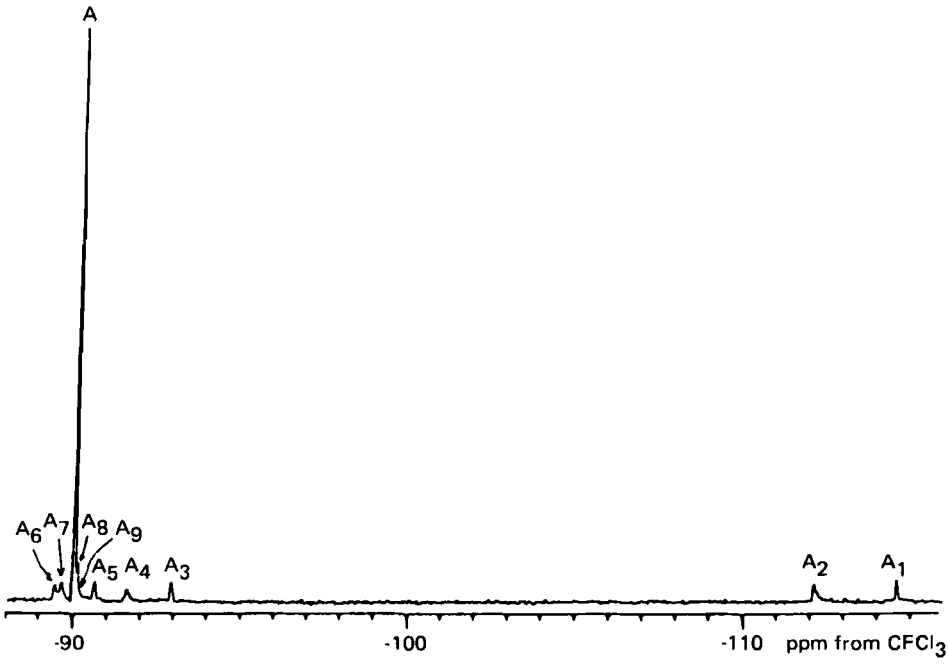

FIG. 1. 282 MHz ^{1}H-decoupled ^{19}F-NMR spectrum of PVF_2 (40 mg/mL) in DMA-d9 at -20°C.

These peaks were first observed by Lin [8] using DMA as the solvent at -10°C and were assigned incorrectly to A_7, A_5, A_6, and A_4, respectively. Lin has also observed two additional signals at -90.2 and -90.3 ppm from $CFCl_3$ and has attributed them to A_8 and A_9 CF_2 units [11]. These assignments have been confirmed by ^{19}F-2D COSY results that are discussed later in this paper.

2. Temperature and Solvent Studies

It is important to pay attention to the conditions under which the spectra are recorded, because the chemical shifts of some of the signals change dramatically with temperature and solvent choice. The spectrum shown in Fig. 1 was the best attainable after an extensive study of the effects of solvent and temperature on spectrum quality. Our studies [8] have included investigations of acetone-d6, acetophenone, benzaldehyde, *N,N*-diethylacetamide, *N,N*-dimethylacetamide [both protonated (DMA) and deuterated (DMA-d9)], deuterated

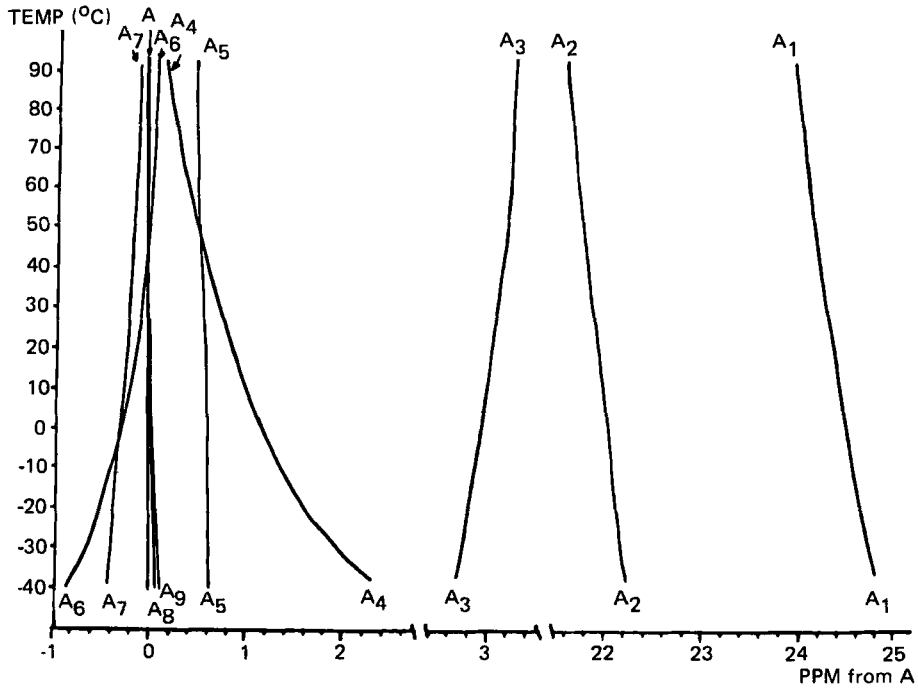

FIG. 2. Variation of chemical shifts with temperature in the 282-MHz ^{19}F-NMR spectra of PVF_2 (40 mg/mL) in DMA-d9).

N,N-dimethylformamide (DMF-d7), deuterated dimethylsulfoxide, ethylene carbonate, deuterated nitrobenzene, deuterated nitromethane, and deuterated tetrahydrofuran as solvents and temperatures ranging from -40 to +120°C. The effects of temperature and sample concentration on the spectra obtained with DMA-d9 as a solvent are of special interest and are discussed below. Notice that DMA-d9 affords better peak separation than DMA. Figure 2 shows the effect of temperature on the relative chemical shifts of PVF_2 in DMF-d9 when the concentration is 40 mg/mL. It can be seen that the chemical shifts of all peaks are sensitive to temperature, especially A_4 and A_6. It is interesting, furthermore, to note that peaks due to CF_2 units at the left of a reverse enchainment (even-numbered ones) are more sensitive to temperature than the others. It is possible that this is due to a chain corformation effect.

Concentration does not have a very large effect on chemical shift. For example, Fig. 3 shows that variation of the polymer concentrations from 20

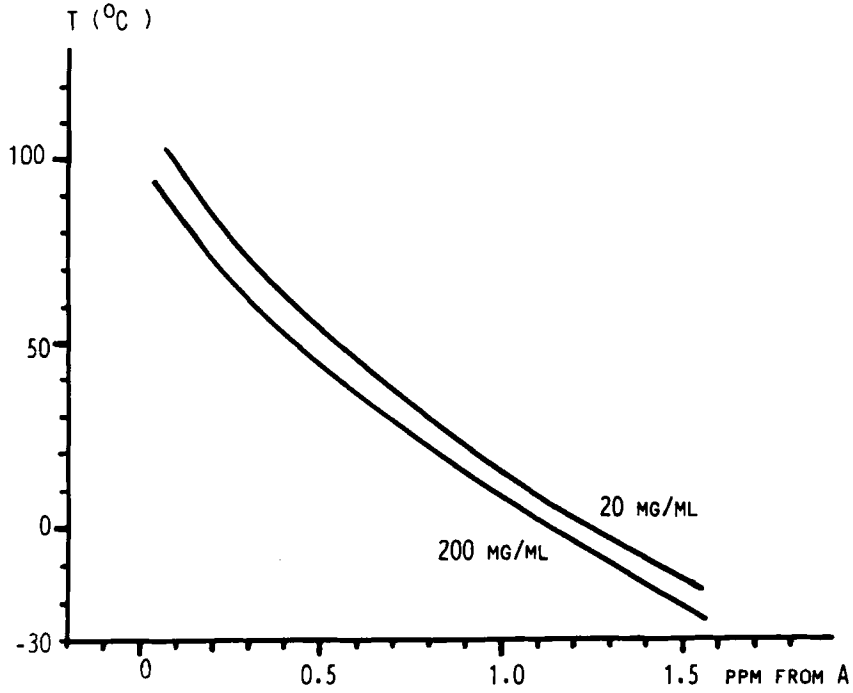

FIG. 3. Effect of sample concentration on the temperature dependence of the chemical shift of the A_4 signal. Data for PVF_2 in DMA-d9 solution.

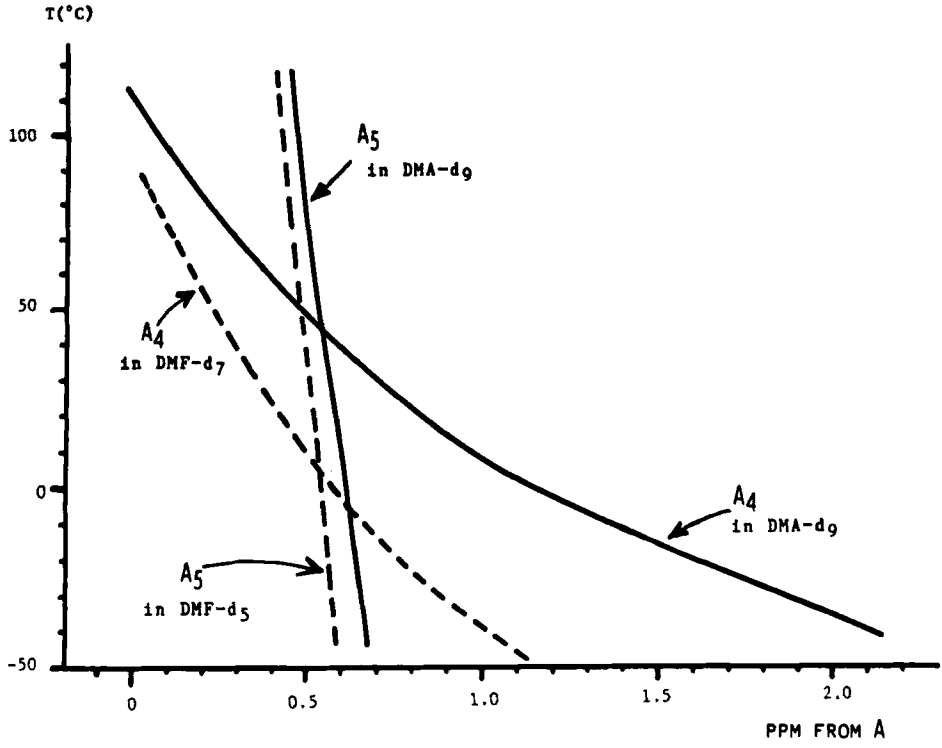

FIG. 4. Chemical shift changes of A_4 and A_5 vs temperature for PVF_2 in DMA-d9 and DMF-d7. The solution concentration in both cases was 40 mg/mL.

to 200 mg/mL had a very small effect on the chemical shift of the A_4 resonance, which is the most sensitive one to temperature and solvent choice.

Figure 4 shows that the chemical shifts of the A_4 and A_5 peaks are affected by temperature to a much greater extent when DMA-d9 is the solvent than when DMF-d7 is used. It can be seen that failure to appreciate the changes of chemical shift with solvent and temperature could cause confusion in peak identification, and it seems that this has, in fact, happened.

To eliminate confusion when the spectra of PVF_2 in DMA-d9 are studied, empirical equations that describe the relationships between chemical shifts and temperature (T, °K) were developed. These have the form $\phi = \phi_0 + \phi_1 T + \phi_2 T^2$, where ϕ is the chemical shift of a peak, and ϕ_0, ϕ_1, and ϕ_2 are empirical constants. ϕ_0 is the chemical shift at $T = 0$ K. Table 1 lists the parameters that were developed from the data by a curve-fitting routine.

TABLE 1. ϕ_0, ϕ_1, and ϕ_2 Values for PVF_2 Resonances (40 mg/mL in DMA-d9)[a]

	ϕ_0	ϕ_1	ϕ_2
A_6	-5.011	0.0270	-0.0000358
A_7	-1.305	0.00501	-0.00000383
A_9	0.960	-0.00413	0.00000381
A_8	0.662	-0.00327	0.00000386
A_5	0.630	0.000991	-0.00000383
A_4	10.494	-0.0507	0.0000613
A_3	0.107	0.0154	-0.0000171
A_2	22.941	-0.00187	-0.00000462
A_1	27.036	-0.0120	0.0000101

[a]Reference A = 0 for $\phi = \phi_0 + \phi_1 T + \mu_2 T^2$.

3. ^{19}F-^{19}F Homodecoupling Experiments

^{19}F-^{19}F homodecoupling experiments were done to verify some of the assignments discussed above and to establish others. While some experiments were done in ^1H-coupled systems, it proved very advantageous to investigate ^1H-decoupled spectra. The ^1H-decoupled ^{19}F-^{19}F homodecouplings of PVF_2 in DMA-d9 at +15°C are shown in Fig. 5, where it can be seen that irradiation of the A_1 peak sharpens the A_2 and A_3 peaks, while irradiation of the A_2 peak perturbs the A_1 and A_4 peaks, and irradiation of the A_3 peak sharpens the A_1 peak and influences the shape of the A_5 signal. Similarly, irradiation of the A_4 peak influences the A_2 and A_6 peaks, irradiation of the A_5 peak perturbs the A_3 and A_7 peaks, and the line widths of the A_6 and A_7 peaks are narrowed when the A_8 and A_9 peaks are irradiated simultaneously (at +15°C the chemical shifts of A_8 and A_9 could not be separated). Finally, the shape of the A_4 peak is altered when A_6 is irradiated, and A_5 is changed when A_7 is irradiated. These phenomena demonstrate the existence of 3-, 4-, and 5-bond couplings between neighboring fluorine nuclei in the polymers, and they pinpoint the positions of the CF_2 groups responsible for the defect resonances relative to a reverse enchainment and to each other. Proton decoupled ^{19}F-^{19}F spin-spin decoupling is thus an important technique for studying the chain microstructure of PVF_2. Unfortunately the A_8 and A_9

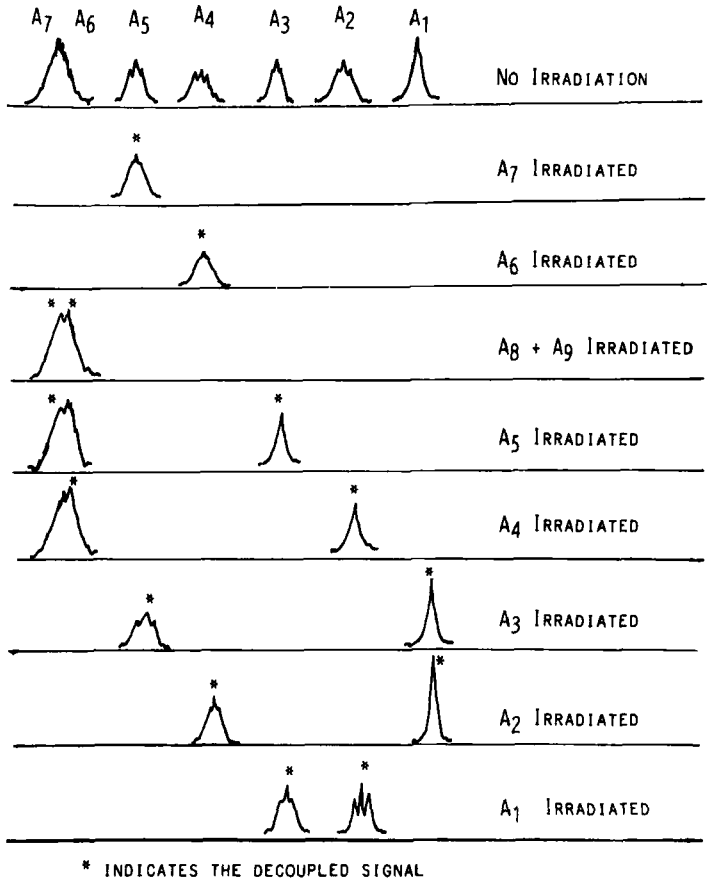

FIG. 5. Effect of selective decoupling on defect resonances of PVF_2 in DMA-d9 (40 mg/mL) at +15°C.

assignments cannot be made with certainty by this approach because of the small difference of their chemical shifts. ^{19}F 2D COSY provides a way around this difficulty.

4. ^{19}F 2D COSY Experiments

Cais and Kometani [12] have previously reported a ^{19}F 2D COSY study of an aregic PVF_2 sample. Their spectrum, which was of polymer in DMF-d7 solution at 25°C, did not permit separate A_4 and A_5 resonances to be observed.

Their spectrum revealed (A_1,A_2), [A_2, (A_4 + A_5)], and [A_3, (A_4 + A_5)] correlations but did not show an (A_1, A_3) correlation. By working with samples in dimethylacetamide-d9 at -12°C and using ^{1}H-decoupling, it was possible for us to obtain improved spectra that allowed a large number of correlations to be demonstrated. Thus, Fig. 6 shows the full-range ^{19}F-2D COSY contour plot of PVF_2. It clearly demonstrates (A_1, A_2), (A_2, A_4), (A_3, A_5), and (A_1, A_3) correlations. Figure 7, an expansion of the -90 to -95 ppm region, clearly shows the (A_5, A_7) and (A_4, A_6) correlations. Figure 8 shows an expanded ^{1}H-decoupled ^{19}F-2D COSY spectrum obtained with higher data resolution (512 words for one dimension, 256 words for the other dimension with 256 words zero filling, and a 1.3-kHz sweep width over the -90.2 to -94.8 ppm range). It contains what are believed to be correlations for (A_6, A_8) and (A_7, A_9). Although one must be careful in interpreting correlations of low-intensity signals that are observed in the vicinity of a strong signal, we believe that these particular correlation peaks (A_6, A_8) and (A_7, A_9) are real since they have been reproduced several times.

Based on these correlation results, assignments for the A_1, A_2, A_3, A_4, A_5, A_6, A_7, A_8, and A_9 signals are easily made. The assignments for A_1-A_7 made from ^{19}F-2D COSY studies are in agreement with those made in the ^{19}F-^{19}F decoupling studies discussed above [11]. The correlations between (A_6, A_8) and (A_7, A_9) signals enable us to correct the misassignments of the A_8 and A_9 signals made in the previous ^{19}F-^{19}F decoupling studies [11].

5. Conflicts with Previous Assignments

Since the assignments developed above differ from some assignments in the earlier reports, it seems worthwhile to discuss these differences.

Weisgerber et al. [5], studied a spectrum recorded at 170°C and assigned the peak at 90.2 ppm (A_4) to chain branching. Since this peak is clearly shown to be associated with reverse enchainment and since no evidence exists for branching in PVF_2, it seems that this assignment should be discounted.

Ferguson and Brame [7] reported 188 MHz ^{19}F-spectra of PVF_2 in DMA at an unspecified temperature. They assigned the resonance at 92.2 ppm to A_4 only and did not recognize that A_5 should also be observed in the region. In a later paper, Ferguson and Ovenall [10] reported 376 MHz ^{19}F-spectra recorded in DMA (which behaves differently from DMA-d9) at 27°C. They listed separate resonances for peaks at 92.22 and 92.20 ppm and attributed them to A_4 (B_1 + B_2 in their nomenclature) and A_5 (B_3 + B_4 in their nomen-

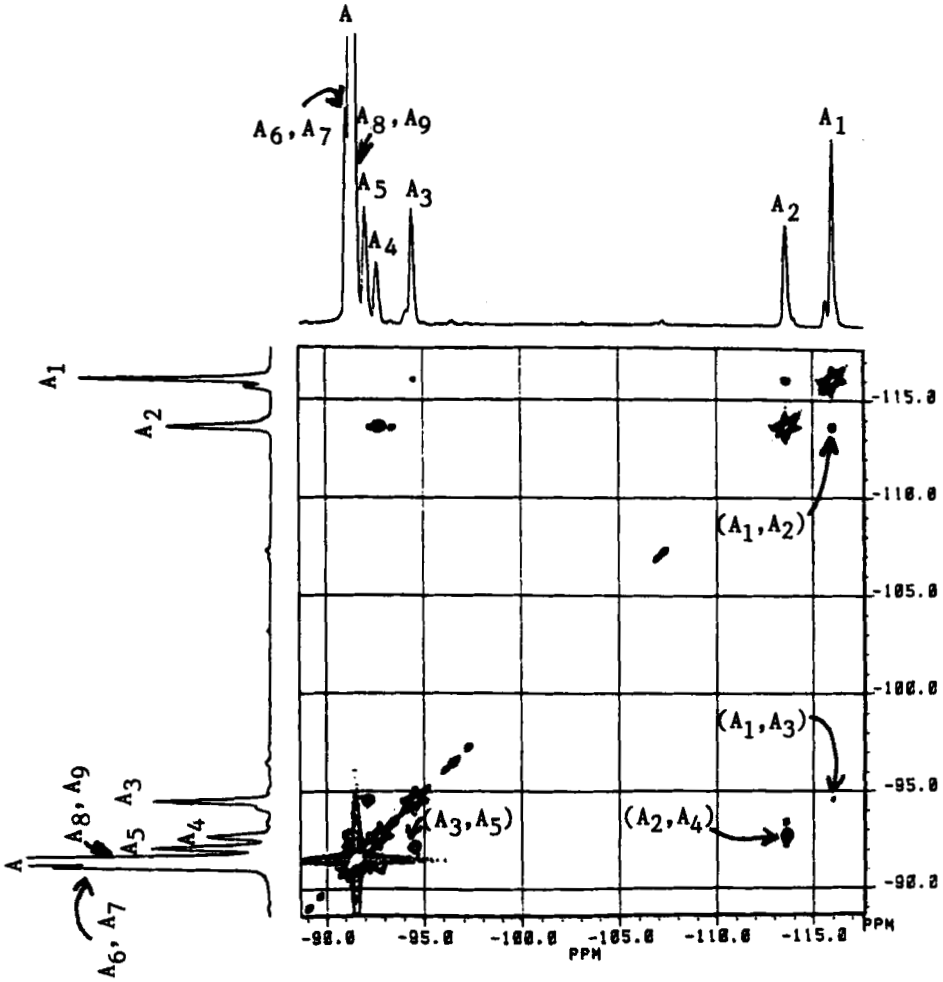

FIG. 6. 282 MHz ^{1}H-coupled ^{19}F2D COSY of PVF_2 (40 mg/mL) in DMA-d9 at -12°C.

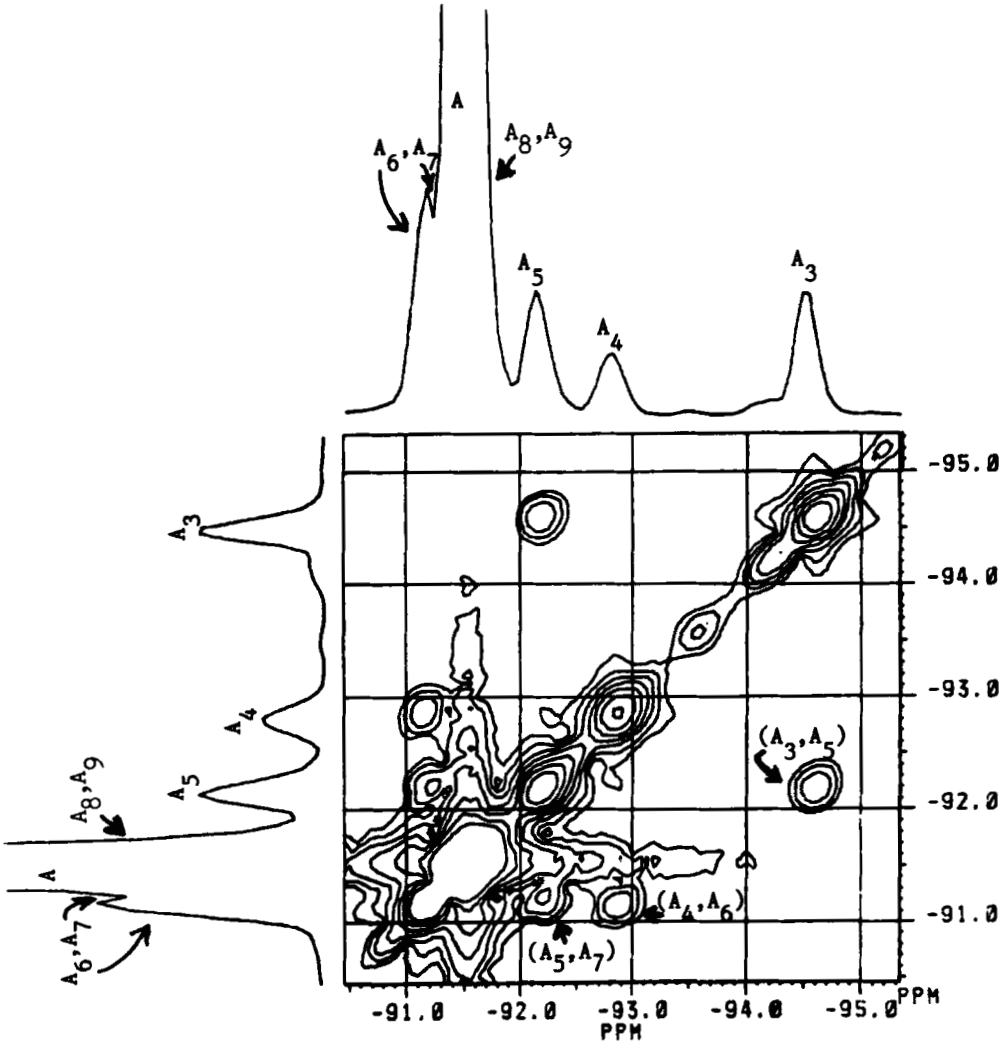

FIG. 7. Expanded region of -89.45 to -95.35 ppm from Fig. 6.

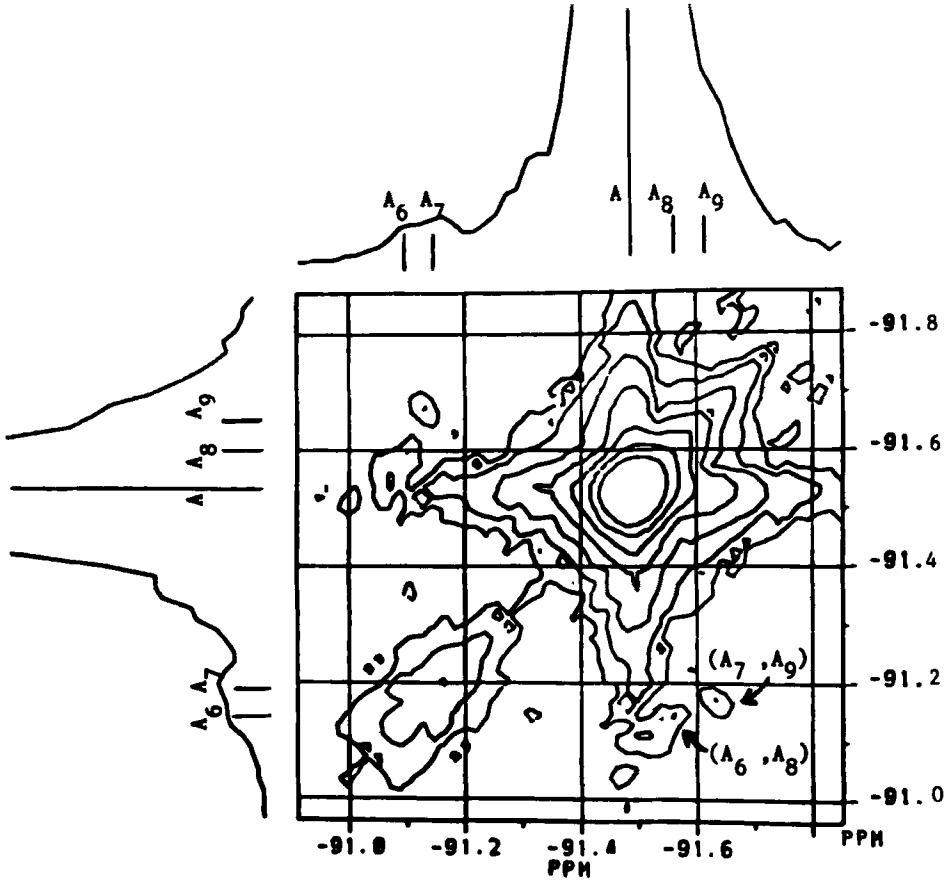

FIG. 8. 282-MHz ^{1}H-decoupled ^{19}F 2D COSY of PVF_2 (40 mg/mL) in DMA-d9 at -12°C.

clature), respectively. However, based on the work reported here, these assignments should be reversed.

Louchikov et al. [18] reported 376 MHz spectra of PVF_2 apparently in DMF-d7, at 40°C based on the chemical shifts reported. We believe that peaks designated S^{A}_{112}, S^{A}_{121}, and S^{A}_{212} should be assigned to A_7, A_4, and A_5 and not to A_6, A_5, and A_4, as they have done.

Cais and Kometani [1, 12] studied PVF_2 in DMF-d7 at 25°C and made assignments consistent with those of Louchikov [18] and of Ferguson and

Ovenall [10], so their assignments must also be revised. In a subsequent 188 MHz 2D COSY study on aregic PVF_2 (in DMF-d7 at 30°C) [12], they also failed to observe separate A_4 and A_5 resonances and did not observe an (A_1, A_3) correlation. Their assignments for the C, E, and H peaks are equivalent to A_3, A_2, and A_1 in this work, but the B peak should be considered to be due to A_4 and A_5.

Finally, Tonelli et al. [9] tried to use the RIS model to assign the resonance observed at about 91.8 ppm of PVF_2 in DMF-d7 at 21°C from a 84.6-MHz spectrometer. Unfortunately, the RIS model employed did not allow for substantial solvent and temperature effects, and this peak was mistakenly assigned to A_4. It should be assigned to A_5 (see Fig. 4).

CONCLUSIONS

Although the chain microstructure of PVF_2 has been studied for the last 27 years [1-13, 18] by ^{19}F-NMR spectroscopy with different experimental techniques and theoretical calculations, the peak assignments were not confirmed, especially those of the new peaks (A_4, A_5, A_6, A_7, A_8, and A_9). The results from this work confirm the old assignments of peaks B, C, and D from Wilson [3], and Wilson and Santee [4]. These three peaks are equivalent to A_3, A_2, and A_1, respectively. The correlations of (A_1, A_3), (A_1, A_2), and (A_2, A_3) from ^{19}F-2D COSY confirm the existence of the head-head-tail-tail sequences in the PVF_2 molecular chain.

Finally, we conclude that all peaks $A_1, \ldots, A_9$ of the PVF_2 molecular chain have been resolved by taking advantage of the improved spectral definition that is obtained with DMA-d9 as solvent at temperatures below 30°C. The assignments for these peaks have been confirmed through ^{19}F-^{19}F decoupling and ^{19}F-2D COSY experiments.

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