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# Communications to the Editor

## Synthesis and Two-Dimensional $^{19}F$ NMR of Highly Aregic Poly(vinylidene fluoride)

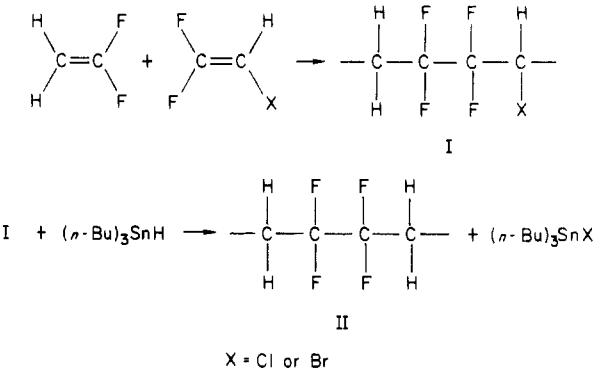
The free-radical polymerization of vinylidene fluoride ($VF_2$) is not completely regiospecific, so that the polymer $PVF_2$ contains occasional inverted or reversed monomer units as structural defects in an otherwise completely head-to-tail (isoregic) sequence.[1,2] The extent of reversed units depends weakly on temperature and varies over the limited range 3.5–6% under practical synthesis conditions.[3] This variation in defect content is too small to impart substantial differences in polymer properties. Therefore it would be desirable to have a series of $PVF_2$ samples with a much wider range of regioirregular monomer sequences to investigate structure–property correlations in detail, but heretofore such materials have been unrealized.

The structure of highly aregic $PVF_2$ may be approximated by introduction of the "pseudo" head-to-head ($-CF_2-CF_2-$) linkage by copolymerization of $VF_2$ with tetrafluoroethylene ($F_4E$).[4] However, $VF_2$–$F_4E$ copolymers are not true regioisomers of $PVF_2$ in that they lack a tail-to-tail ($-CH_2-CH_2-$) linkage corresponding to each $F_4E$ unit introduced.[5] The 1:1 alternating copolymer of ethylene with $F_4E$ (e.g., Du Pont Tefzel) is a genuine regioisomer of $PVF_2$, but its structure is one extreme having 50% reversed units (syndioregic).

Our prior syntheses of $PVF_2$ have aimed at reducing the level of defects typically found in commercial materials. Thus we have achieved just 2.8% reversed units by deuterium labeling[6] and essentially the pure isoregic structure (i.e., no reversals) by the reductive dechlorination of poly(1,1-dichloro-2,2-difluoroethylene).[7] We now extend these studies to access the range of reversals above those in commercial samples. This report focuses on the novel synthesis of such materials and their characterization by fluorine-19 NMR.

Furthermore, by having $PVF_2$ samples with high (e.g., 18%) defect levels it is now feasible to perform two-dimensional *J*-correlated (COSY) experiments[8,9] and observe the connectivities between the signals from isoregic and aregic sequences. This experiment is extremely difficult with commercial $PVF_2$ where the aregic resonances are weak so that the 2D cross peaks are easily confused with artifacts generated by the intense ridges[8] radiating from the main isoregic peak. Fluorine-19 COSY spectra of commercial $PVF_2$ have been recorded but not published by Ferguson and Ovenall.[10] To date the only published 2D fluorine-19 homonuclear correlated experiment on polymers is the work on poly(vinyl fluoride) by Bruch et al.[11] Our present study with highly aregic $PVF_2$ has allowed us to verify in an absolute manner the main regiosequence assignments in the fluorine-19 NMR spectrum of $PVF_2$.

**Scheme I**




Our synthetic procedure is outlined in Scheme I. The precursor polymer I is made by copolymerization of $VF_2$ with either 1-chloro-2,2-difluoroethylene ($CVF_2$) or 1-bromo-2,2-difluoroethylene ($BVF_2$). We find that the chlorinated or brominated monomers are attacked at their $CF_2$ carbon by the growing $-CH_2CF_2\cdot$ radical, so that after reductive dechlorination or debromination with tri-*n*-butyltin hydride they become a reversed $VF_2$ unit in the final polymer II, which is therefore a regioisomer of $PVF_2$. A significant feature of the above scheme is the ability to control the level of reversed $VF_2$ units introduced via the comonomer units by varying the feed ratio in the initial copolymerization mixture.

Vinylidene fluoride was obtained from SCM Speciality Chemicals and purified by repeated freeze–degass–thaw cycles on a vacuum line after it had been passed through a column of silica gel for drying and removal of inhibitor. The comonomers $BVF_2$ and $CVF_2$ were also obtained from SCM and purified in an identical manner. The respective monomers were measured by their gas pressure in a calibrated volume and condensed in an ampule containing the initiator trichloroacetyl peroxide (TCAP), which was prepared and added as described previously.[6]

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Table I
Details of the Preparation of Poly(vinylidene fluoride) (A) and the Copolymers with Chlorovinylidene Fluoride (B–F) and Bromovinylidene Fluoride (G–J)[a]

| | feed composn | | | | | | | copolym composn | |
|---|---|---|---|---|---|---|---|---|---|
| sample | mol % $VF_2$ | mol % $CVF_2$ | mol % $BVF_2$ | init concn, mol % | polymn temp, °C | polymn time, h | yield, wt % | mol % $CVF_2$ | mol % $BVF_2$ |
| A | 100 | 0 | 0 | 1.0 | 0 | 41 | 50 | 0 | 0 |
| B | 93 | 7 | 0 | 1.0 | −15 | 44 | 8 | 6.6 | 0 |
| C | 90 | 10 | 0 | 1.0 | −15 | 132 | 11 | 9.6 | 0 |
| D | 87 | 13 | 0 | 0.5 | −15 | 44 | 10 | 11.2 | 0 |
| E | 75 | 25 | 0 | 0.5 | −15 | 64 | 5 | *b* | 0 |
| F | 76 | 24 | 0 | 0.5 | 0 | 24 | 4 | *b* | 0 |
| G | 95 | 0 | 5 | 1.0 | 0 | 18 | 22 | 0 | 4.5 |
| H | 90 | 0 | 10 | 1.0 | 0 | 18 | 9 | 0 | 8.1 |
| I | 85 | 0 | 15 | 1.0 | 0 | 18 | 2 | 0 | 9.7 |
| J | 50 | 0 | 50 | 1.0 | 0 | 40 | 0.5 | 0 | 42.3 |

[a] The initiator was trichloroacetyl peroxide in all cases. [b] Not recorded.

The ampule was sealed under vacuum after the monomers had been frozen with liquid nitrogen and then warmed to −80 °C at which point the monomers were mixed. The tube was transferred to a steel autoclave and pressurized to ca. 20 atm to reduce the pressure differential on the ampule at the more elevated polymerization temperatures. After a suitable period the autoclave was chilled to −80 °C and depressurized, and the ampules were removed and frozen in liquid nitrogen. The copolymers were recovered in methanol after unreacted monomers had first been removed under vacuum. The composition of the copolymers was determined by 500-MHz proton NMR. Experimental details pertaining to the NMR experiments are given in the figure captions.

Table I gives details of the preparation of a series of precursor copolymers I. A significant result is that the comonomers $CVF_2$ and $BVF_2$ retard the polymerization of $VF_2$. Both yield and molecular weight (estimated from melt viscosity and film strength) of the copolymer decrease with increasing $CVF_2$ or $BVF_2$ content. We found that neither $CVF_2$ nor $BVF_2$ homopolymerizes to any degree under these conditions.

These observations indicate that abstraction of the proton on $CVF_2$ or $BVF_2$ is quite facile so that chain transfer competes with chain propagation. Thus we were unable to prepare copolymers with more than 50 mol % $CVF_2$ or $BVF_2$. In other words the reactivity ratio associated with these comonomer units is effectively zero, so that they are always flanked by $VF_2$ units in the respective copolymers. Chain termination steps were more pronounced with $BVF_2$ as the comonomer unit, so $CVF_2$ is the preferred choice in preparation of the precursor polymer I.

The fluorine-19 NMR spectra of two precursor polymers are shown in Figure 1. There are three distinct regions corresponding to the central fluorines in $-CH_2-CF_2-CH_2-$, $-CF_2-CF_2-CHX-$, and $-CF_2-CF_2-CH_2-$ sequences (X = Cl or Br). The compositions of the precursor copolymers were obtained more readily from 500-MHz proton NMR spectra, by comparing the areas of the $-CH_2-$ resonances at 3.0 and 2.4 ppm (head-to-tail and tail-to-tail $VF_2$ sequences) to the −CHCl− or −CHBr− methine proton resonance at 4.9 ppm. These spectra indicate that the comonomer unit does not form the $-CF_2-CHX-CF_2-$ sequence, which, after reduction, would correspond to the regular head-to-tail $VF_2$ sequence.

After replacement of X by H according to Scheme I the appropriate regioisomer of $PVF_2$ is obtained. The procedure for this step has been described previously.[12] Analysis by X-ray fluorescence spectroscopy showed that removal of chlorine or bromine was complete. Infrared spectra of

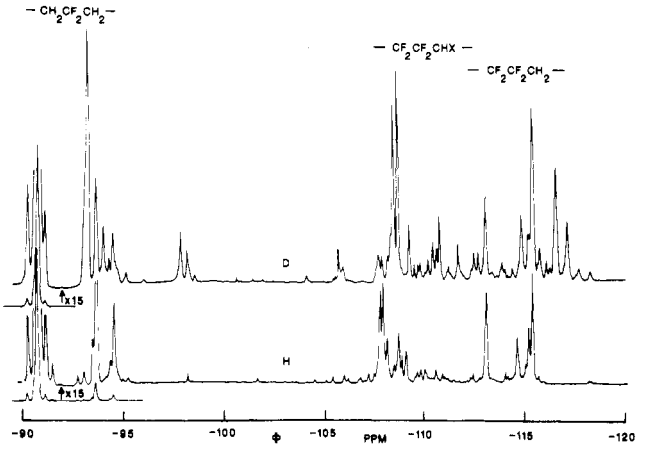


**Figure 1.** Proton-decoupled 470-MHz fluorine-19 NMR spectra of copolymers D and H, which are precursors to aregic $PVF_2$. The samples were observed at 25 °C as 10% solutions in dimethylformamide-$d_7$ on a JEOL GX-500 spectrometer. The sweep width was 20 kHz with 132K points, and 800 transients were accumulated with a delay of 10 s between successive 90° (8 μs) pulses. The CHX carbon (X = Cl in D; X = Br in H) is an asymmetric center and renders nearby geminal fluorines nonequivalent with an attendant increase in spectral complexity, particularly in the upfield regions.

films cast from dimethylformamide solution onto silicon wafers were obtained with an Analect fx-6260 FTIR and were entirely consistent with the $PVF_2$ structure. The only difference from conventional $PVF_2$ IR spectra was an increase in absorbance at 1453, 1323, and 666 $cm^{-1}$. These bands have been assigned to the head–head, tail–tail structures by Kobayashi et al.[13]

The fluorine-19 NMR spectra of the product highly aregic $PVF_2$ samples II were analyzed for composition and regiosequence distribution according to our published procedure.[14] Some representative one-dimensional spectra are shown in Figure 2. These spectra are far more sensitive to regiosequence defect structure than IR spectra, and the NMR peaks from the highly aregic samples agree exactly in chemical shift with those from conventional $PVF_2$ but have greater intensity owing to the increased defect levels. There are some new peaks with very low intensities which indicate that anomalous structures are present. These are end groups and possibly branch points resulting from the facile chain-transfer steps involving the chloro or bromo comonomer units. The above spectroscopic data show that the reduced polymers are genuine regioisomers of $PVF_2$.

The compositions, melting points, and equilibrium phases for a series of aregic compositions are given in Table

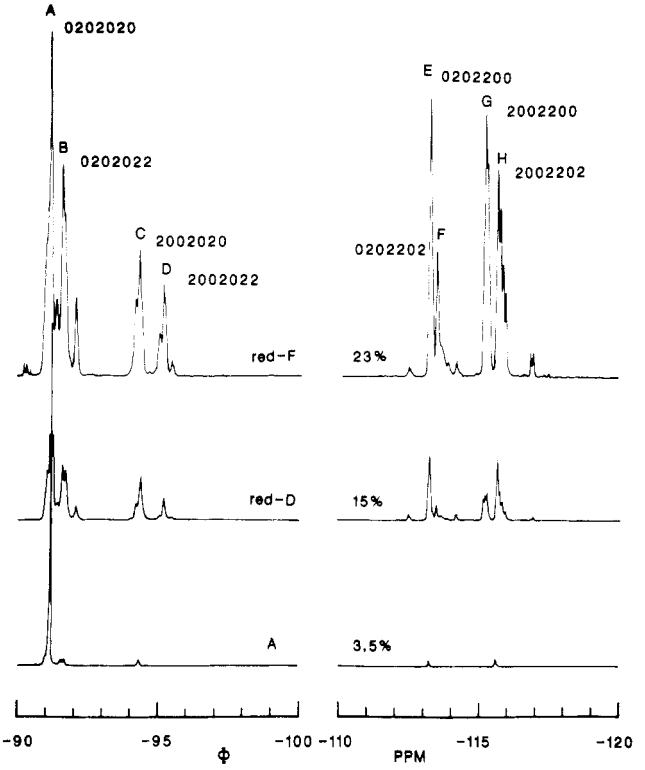


**Figure 2.** Proton-decoupled 470-MHz fluorine-19 NMR spectra of aregic $PVF_2$ samples A, red-D, and red-F having 3.5, 15, and 23% defects, respectively. The samples were observed at 25 °C as 10% solutions in dimethylformamide-$d_7$ on a JEOL GX-500 spectrometer. The sweep width was 20 kHz with 132K points, and 800 transients were accumulated with a pulse delay of 10 s using 90° (8 μs) pulses. The eight distinct regiosequence heptads (A–H) are assigned according to ref 14 to the carbon sequences as shown (0 = $CH_2$, 2 = $CF_2$). Most heptad peaks have quartet fine structure indicating a higher order sensitivity to 11-carbon sequences (monomer sequence hexads). The three spectra are vertically scaled so that the isoregic peak A has the same intensity in each.

**Table II**
**Melting Points and Crystalline Phases as a Function of Defect Levels in Poly(vinylidene fluoride) Obtained by Homopolymerization (A) and by Reduction of Precursor Copolymers (red-B–red-F)**

| sample | % defect | $T_m$, °C | crystalline phase |
|---|---|---|---|
| A | 3.5 | 180 | α |
| red-B | 11 | 145 | α |
| red-C | 14 | 135 | β |
| red-D | 15 | 122 | β |
| red-E | 18 | 137 | β |
| red-F | 23 | 140 | β |

II. We note that the percent defect in the reduced samples equals the mole percent comonomer unit (Table I) plus the 3.5%, which is inherent to $VF_2$ additions at 0 °C. This is further evidence that the comonomer units add exclusively with the head-to-head orientation. Initially the melting point decreases with increasing head-to-head structure and passes through a minimum at ca. 15% reversals. A similar behavior is seen in $VF_2$–$F_4E$ copolymers, which exhibit a minimum $T_m$ of ca. 130 °C at 20 mol % $F_4E$.[15] Another interesting finding is that the β phase of $PVF_2$ becomes more stable than the α phase between 11 and 14% defects, in good agreement with the crossover point of 10% predicted by Lando et al.[5]

The two-dimensional *J*-correlated (2D COSY) fluorine-19 NMR spectrum of aregic $PVF_2$ with 18% reversals is shown in Figure 3. The off-diagonal or cross peaks

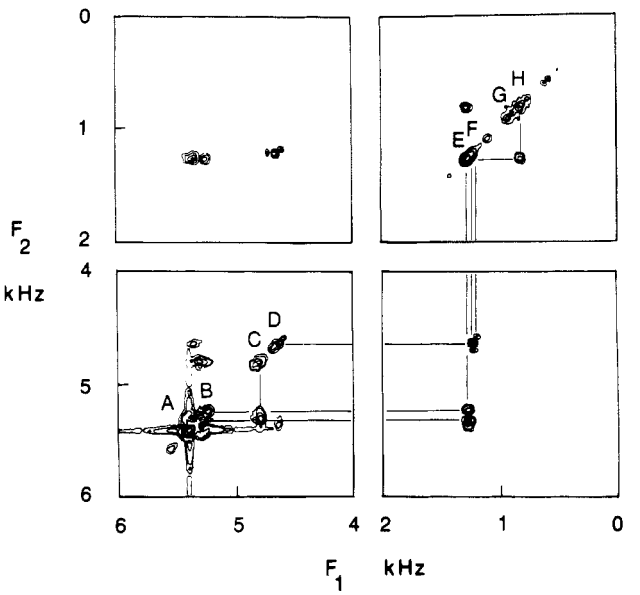


**Figure 3.** Absolute value contour plot of the 188-MHz fluorine-19 2D *J*-correlated spectrum of aregic $PVF_2$ with 18% defects. The polymer was observed as a 10% solution in dimethylformamide-$d_7$ at 30 °C on a Varian XL-200 with broad-band proton decoupling. A total of 64 transients was accumulated for each of 256 spectra with 1024 points covering 7000 Hz in both dimensions. The central region (2000 × 2000 Hz) contains no signals and has been removed for clarity.

observed indicate a connectivity between fluorine pairs which have a nonzero scalar coupling, either through three bonds (vicinal) or four bonds.[11] Longer range couplings can be ignored, and since the geminal fluorines are always equivalent in $PVF_2$ (except perhaps next to end groups or branch points) the large two-bond coupling[12] is not manifest. The observed cross peaks can be rationalized on the basis of regiosequence heptad sequences S7, which give rise to eight distinct one-dimensional peaks A–H,[14] as assigned in Figure 2.

It is a simple matter to examine the S7 sequences and establish the connectivity map allowing just three- and four-bond homonuclear fluorine couplings. In this way the necessary connectivities become A–B, A–C, B–C, B–E, B–F, D–E, D–F (four bond), and E–H (three bond). Implicit in this scheme is the correctness of the A–H sequence assignments, proposed by Fergusion and Brame[16] and calculated empirically by Tonelli et al.,[17] which can now be tested rigorously by the 2D experiment.

As Figure 3 shows all expected connectivities are observed except for B–F, which can only be established within the carbon sequence 0202022020 (0 = $CH_2$, 2 = $CF_2$) having two adjacent reversed units. The likelihood of two consecutive monomer reversals is low (–$CF_2$–CHX– units are never adjacent in the precursor copolymer), so the cross peak is extremely weak and not detected by our experiment. Likewise we could not detect cross peaks to the weak peaks we believe are due to end groups and branches, so they did not interfere with the analysis.

We have determined the assignments of peaks A and G from the model isoregic and syndioregic polymers.[7,18] Given just these two and the connectivities observed in Figure 3 the assignments of peaks B, C, D, E, F, and H can be uniquely established as indicated. These are in complete agreement with previous work.[14,16,17] Close inspection of the cross peaks in Figure 3 shows fine structure which indicates that higher order regiosequences are resolved. The 1D spectra in Figure 2 are in fact sensitive to 11-carbon sequences,[10,19] which will be assigned in a forthcoming detailed publication.

As a final point we note that Scheme I increases the fraction of reversed units in $PVF_2$ because the comonomer unit is attacked by the growing $VF_2$ radical (which has the $-CH_2-CF_2\cdot$ orientation[6]) at the $CF_2$ carbon and not the CFX carbon. Presumably this occurs to minimize steric and electrostatic repulsion forces which are accentuated by the bulky X halogen. Clearly this scheme can be made more general by the appropriate choice of comonomer pairs, and we are presently examining its utility for preparing highly aregic poly(vinyl fluoride) and poly(trifluoroethylene) as well.

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**Registry No.** $(VF_2)$ (homopolymer), 24937-79-9.

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## Accurate Lattice Constants for Tara Gum

Tara gum, obtained from the seed endosperm of *Caesalpinia spinosa*, is a galactomannan of the same general structure as guar and locust bean or carob gums.[1] As such, it has a linear 1→4-linked main chain of β-D-mannose with α-D-galactosyl substituents linked 1→6 to about one-third of the mannose residues. The structure is best represented by a mannobiose repeat in the main chain with variable

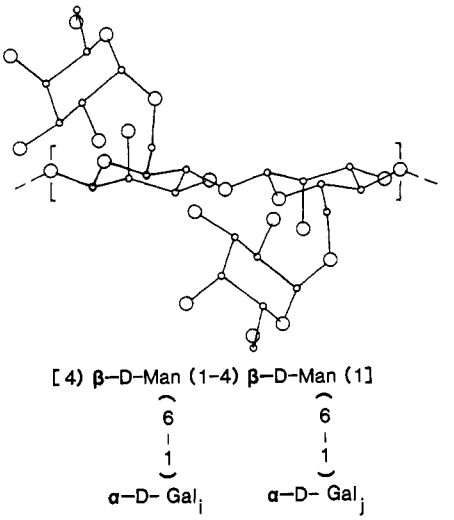


**Figure 1.** Generalized primary structure model for the crystallographic repeat of a galactomannan such as tara gum. Symbols $Gal_i$ and $Gal_j$ denote D-galactose residues of mole fractions $x_i$ and $y_i$ attached to residues $i$ and $j$ of the poly[(1→4)-β-D-mannose] chain.

mole fractions of galactose, $x_i$ and $x_j$, attached to the adjacent mannose residues $i$ and $j$; see Figure 1. The sum of $x_i$ and $x_j$ should equal twice the galactose substitution or DS. In this model regular alternation of substituted and free mannosyl residues as was originally proposed for guar[2] would take the form $x_i = 2(DS)$ and $x_j = 0$. A truly random arrangement would take the form $x_i = x_j = DS$ and irregular distributions of the type now most widely believed to exist[3] could have any value of $x_i$ and $x_j$ subject to the constraint on their sum.

Commercially, galactomannans are of importance in a diversity of applications because of the precise control over hydrorheology which they offer. The galactomannans and their parent compound mannan also present interesting structural problems in the attempt to correlate galactose content and distribution with molecular interactions and hydrodynamic properties.[3] In this context the simplest model to consider is the effect of galactose content on self-association in crystalline domains. Our laboratory is currently making a survey of several galactomannans and the initial diffraction data for one of these, tara gum, is the subject of this communication.

Materials and Methods. The original material was a gift from Dr. Gordon C. Towle of Celanese Corp. This material was precipitated from water with 95% ethanol, dissolved in water, and dialyzed exhaustively against water at 4 °C before lyophilization and storage. Samples were redissolved in water after grinding with a mortar and pestle at liquid nitrogen temperatures and 1% solutions were dried on Teflon blocks into clear, tough films. The water used in all procedures was glass distilled. Small (2 mm × 8 mm) pieces of these films were glued on to plastic supports and then suspended under a load of 10–20 g while being stored at 95% relative humidity and 50 °C. After 24 h they had extended to 300% of their initial length. The resulting films were highly birefringent as evidenced by their sharp extinction upon rotation between crossed polarizers in the polarizing microscope. These films were annealed by heating them to 105–115 °C in a sealed container with a small amount of water. X-ray diffraction data was collected at 81% relative humidity and room temperature using nickel-filtered Cu Kα radiation from a Philips sealed-tube generator. Diffraction patterns were recorded on Kodak No-Screen film.

Results and Discussion. The X-ray diffraction pattern

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