^{19}F NMR Chemical Shifts and the Microstructure of Fluoro Polymers

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ABSTRACT: Chemical shifts observed for the various fluorine atoms in the ^{19}F NMR spectra of poly(vinylidene fluoride), poly(vinyl fluoride), poly(fluoromethylene), and poly(trifluoroethylene) are calculated as functions of stereosequence and defect structure. This is accomplished by assuming a shielding effect for a fluorine atom in a gauche arrangement with another fluorine or carbon atom separated by three bonds (γ substituent) relative to their trans arrangement. Calculation of bond conformation probabilities in the various fluoro polymer stereosequences and defect structures permits the prediction of ^{19}F NMR chemical shifts. This approach is successfully applied to elucidate the microstructures of the four fluoro polymers under study. The shielding γ effects found for the ^{19}F nuclei in these fluoro polymers are several-fold greater than the γ effects operating on their ^{13}C nuclei and on the carbon atoms in non-fluorine-containing polymers.

Introduction

^{13}C NMR spectra of vinyl homo- and copolymers can be predicted[1] from analysis of the numbers and kinds of γ interactions involving each carbon atom type in the polymer. Each nonhydrogen γ substituent in a three-bond gauche arrangement (see Figure 1) with a given carbon atom produces an upfield chemical shift of that carbon resonance relative to their trans arrangement. Polymer chain conformational characteristics, as manifested by calculated bond rotation probabilities, can be utilized to evaluate the frequency with which such γ gauche interactions occur.

The sensitivity of vinyl homo- and copolymer ^{13}C chemical shifts to stereosequence and comonomer sequence results from the dependence of bond rotation probabilities on the same microstructural features. A dispersion of ^{13}C chemical shifts reflecting the different possible microstructures found along the vinyl polymer chain is produced by the γ gauche effects. The magnitudes of the upfield γ effects and their frequencies of occurrence, as obtained from the bond rotation probabilities, constitute the only information needed to calculate the effects of polymer microstructure on the observed ^{13}C NMR chemical shifts.

The ^{13}C NMR chemical shifts observed in a wide variety of vinyl homo- and copolymers have been successfully predicted following the γ-effect approach.[2-9] Recently,[10] we extended the γ-effect method to the calculation of the ^{13}C NMR chemical shifts exhibited by the fluoro polymers poly(vinylidene fluoride) (PVF$_2$), poly(vinyl fluoride) (PVF), poly(fluoromethylene) (PFM), and poly(trifluoroethylene) (PF$_3$E). Successful prediction of the ^{13}C NMR chemical shifts observed for these fluoro polymers served to confirm their conformational characteristics as embodied in the rotational isomeric state (RIS) models recently developed[11,12] for each by one of us.

The aim of the present investigation is to determine whether or not the ^{19}F NMR chemical shifts observed for these fluoro polymers can be understood in terms of γ effects similar in nature to those which apparently govern their ^{13}C NMR chemical shifts.[10] We seek to learn if the microstructurally sensitive ^{19}F NMR chemical shifts exhibited by fluoro polymers can be predicted from knowledge of their conformational characteristics and the magnitudes of their possible γ gauche interactions.

Experimental Section

Materials. The details of the synthesis of the PFM employed in this study have been previously reported.[13] PF$_3$E was synthesized at 0 °C by the polymerization of bulk monomer in a sealed glass ampule with trichloroacetyl peroxide initiator. Regioregular PF$_3$E was obtained by reductive dechlorination of poly(1-chloro-1,2,3-trifluoroethene) (Kel-F) with tributyltin hydride. Complete details of these procedures will be published separately.[14] PVF was a commercial sample purchased from Aldrich Chemical Co. Two samples of PVF$_2$ were employed: Kynar 821, a product of Penwalt Corp. (see Figure 3a), and a commercial product of Kureha Chemical Industry Co. (see Figure 3b).

^{19}F NMR Measurements. A Bruker WH-90 spectrometer was used to record the 84.66-MHz ^{19}F NMR spectra of PFM and PVF$_2$. The 188.22-MHz ^{19}F NMR spectra of PVF, PVF$_2$, and PF$_3$E were recorded on a Varian XL-200 spectrometer. The experimental conditions for each polymer regarding solvent, sample concentration (% (w/v)), observation temperature (°C), number of accumulations, 90° pulse width (μs), pulse delay time (s), spectral window (kHz), and memory size are as follows: PFM—dioxane-d_8, 10, 70, 1236, 3.4, 3.0, 4, 8K; PF$_3$E—acetone-d_6, 10, 20, 200, 9.0, 3.7, 24, 32K; PVF—Me$_2$SO-d_6, 11, 100, 200, 8.0, 5.0, 8, 32K; PVF$_2$ (188.22 MHz)—DMF-d_7, 11, 21, 150, 8.0, 2.0, 8, 32K; PVF$_2$ (84.66 MHz)—DMF-d_7, 20, 28, 300, 4.0, 4.0, 3, 16K.

All spectra except that of PVF$_2$ at 84.66 MHz were recorded under conditions of broad-band proton decoupling. C$_6$F$_6$ (163 ppm vs. CFCl$_3$) was employed as an internal reference except in the case of PFM, where no reference was used. For the PVF and PVF$_2$ samples, maximum fluorine T_1 values were determined. Delay times greater than $5T_{1\,\max}$ were used in measuring defect concentrations in these materials.

Calculation of ^{19}F NMR Chemical Shifts

Matrix methods[15] are used to obtain bond rotation probabilities from the RIS models recently developed[11,12] for each of the fluoro polymers under investigation. The numbers of F- - -F and F- - -C γ gauche interactions ($\gamma_{F,F}$ and $\gamma_{F,C}$) are obtained from the calculated bond rotation probabilities. Comparison of the relative ^{19}F NMR chemical shifts observed in these fluoro polymers with those calculated through adjustment of $\gamma_{F,F}$ and $\gamma_{F,C}$ to achieve closest agreement serves to determine their magnitudes.

Having derived $\gamma_{F,F}$ and $\gamma_{F,C}$ from a comparison of the observed and calculated ^{19}F NMR chemical shifts, we compare the magnitudes of the γ effects derived from each of the fluoro polymers to test their consistency. The effects of stereosequence and structural defects are considered in the calculation of ^{19}F chemical shifts for each of the fluoro polymers.

^{19}F NMR Chemical Shifts for Poly(vinylidene fluoride). The ^{19}F NMR spectrum of PVF$_2$ free of structural defects should contain a single resonance due to the absence of asymmetric centers. Occasional head-to-head:tail-to-tail (H-H:T-T) addition of monomer units (see Figure 2) does produce an asymmetric environment and should result in chemical shifts for the fluorine atoms in the immediate vicinity of the H-H:T-T defect which are not eqivalent to the more abundant fluorines in the head-to-tail (H-T) portions of the PVF$_2$ chains.[16] The ^{19}F NMR spectrum of PVF$_2$ measured at 84.6 MHz and presented in Figure 3a clearly manifests the nonequiva-

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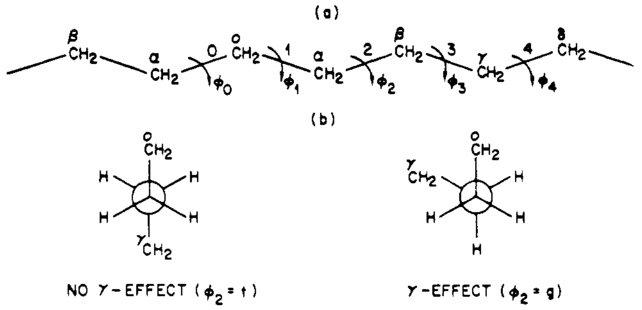

Figure 1. (a) Portion of a paraffinic hydrocarbon chain in the all-trans, planar-zigzag conformation. (b) Newman projection along bond 2 in (a) illustrating the γ effect.

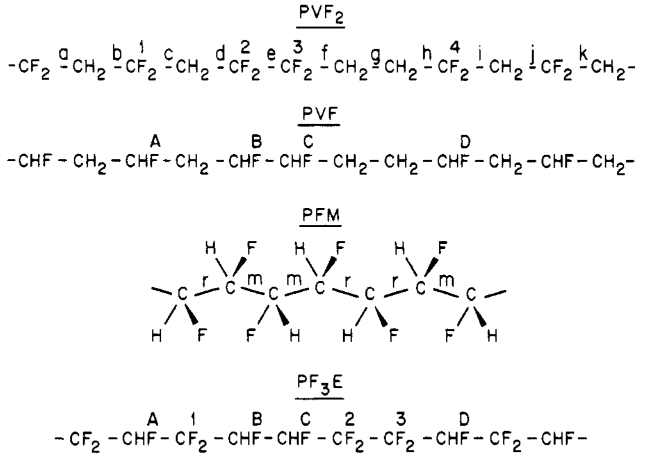

Figure 2. Schematic drawings of portions of PVF_2, PVF, PFM, and PF_3E chains illustrating H-H:T-T defect and stereosequence microstructures.

lence of the abundant H-T and rarer H-H:T-T fluorine chemical shifts. H-T fluorines resonate at 91.6 ppm (relative to $CFCl_3$) while H-H:T-T defect peaks are observed at 3.2 (4), 22.0 (2), and 24.0 (3) ppm upfield from the H-T resonance.

We write expressions for the relative ^{19}F NMR chemical shifts (ν) of H-T and H-H:T-T fluorines in terms of γ effects ($\gamma_{F,F}$ and $\gamma_{F,C}$) and the bond rotation probabilities (P) which determine the frequences of γ gauche effects. From Figure 2 we obtain

$$\nu_F^{H-T} = (1 + P_t)\gamma_{F,C}$$

$$\nu_F^2 = (1 + 0.5P_{t,d} + 0.5P_{t,e})\gamma_{F,C} + (1.5 - 0.5P_{t,e})\gamma_{F,F}$$

$$\nu_F^3 = (1 + 0.5P_{t,e} + 0.5P_{t,f})\gamma_{F,C} + (1.5 - 0.5P_{t,e})\gamma_{F,F}$$

$$\nu_F^4 = (1 + 0.5P_{t,h} + 0.5P_{t,i})\gamma_{F,C}$$

Bond rotation probabilities P_t, $P_{t,d}$, $P_{t,e}$, $P_{t,f}$, $P_{t,h}$, and $P_{t,i}$, where t signifies the trans (0°) conformation, are evaluated from the RIS model developed previously by one of us[11] for H-T and H-H:T-T PVF_2.

From the expressions written for ν_F and the calculated bond rotation probabilities, it is apparent that ν_F^{H-T} and ν_F^4 are most similar. Hence, $\nu_F^4 - \nu_F^{H-T} = 3.2$ ppm, which leads directly to $\gamma_{F,C} = 30$ ppm upfield, or shielding. By elimination, $|\nu_F^2 - \nu_F^3| = 2.0$ ppm, which yields $\gamma_{F,F} = 15$ ppm upfield, or shielding. Substitution of $\gamma_{F,F} = 15$ ppm and $\gamma_{F,C} = 30$ ppm into the expressions for ν_F leads to calculated relative ^{19}F chemical shifts which compare favorably with the observed ^{19}F resonances as shown in Figure 3c.

At 188 MHz four additional defect peaks (1, 5, 6, and 7) appear in the ^{19}F NMR spectrum of PVF_2 (see Figure 3b). These additional peaks were also observed by Ferguson and Brame,[17] who assigned them to the defect structures drawn in Figure 3b based on α-, β-, and γ-substituent effects derived from the CF_2 resonances observed in various saturated linear chains. In addition to ν_F^{H-T}, ν_F^2, ν_F^3, and ν_F^4, ^{19}F chemical shifts were also calculated for the defect CF_2 fluorines 1, 5, 6, and 7. ^{19}F γ effects (γ_{F,CH_2}, γ_{F,CF_2}, and $\gamma_{F,F}$) were varied and least-squares fitted to produce the best agreement between observed and calculated chemical shifts. Good agreement was achieved for $\gamma_{F,CH_2} = \gamma_{F,CF_2} = 25$–$30$ ppm and $\gamma_{F,F} = 15$ ppm (see Figure 3c), confirming the assignments proposed by Ferguson and Brame[17] and the γ effects derived from the defect resonances 2, 3, and 4 observed at the lower magnetic field. In our initial calculations of the ^{19}F NMR chemical shifts for the remaining three fluoro polymers, $\gamma_{F,C} = 30$ ppm and $\gamma_{F,F} = 15$ ppm upfield will be assumed.

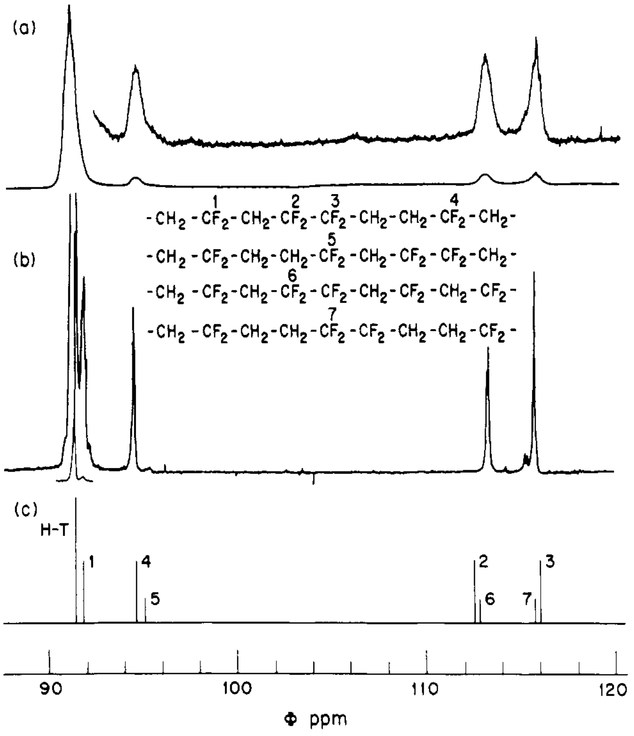

Figure 3. Observed and calculated ^{19}F NMR spectra of PVF_2: (a) measured at 84.6 MHz; (b) measured at 188.2 MHz; (c) calculated. Vertical expansion in (a) is ×8, in (b) ×40.

In our considerations of possible defect structures in PVF_2 we have neglected the possibility of chain branching. This class of defect structures will be investigated in future work.

^{19}F NMR Chemical Shifts for Poly(fluoromethylene). The monomer units (*cis*- or *trans*-1,2-difluoroethylene) of PFM[13] preclude the differentiation between their H-T and H-H:T-T addition and result in the attachment of a single fluorine atom to each backbone carbon atom. Stereosequence, aside from the possibility of branching, remains as the single structural feature of importance in characterizing the microstructure of PFM.

Because each backbone carbon is asymmetric, i.e., asymmetric centers are separated by a single C-C bond in PFM (see Figure 2) rather than two C-C bonds as in PVF and PF_3E, we have considered the effects of stereosequence up to the nonad level, resulting in the estimation of bond rotation probabilities for 136 different stereoisomers. Our recently derived[12] RIS model for PFM was used to calculate the bond rotation probabilities for all nonad stereosequences.

In Figure 4 the observed ^{19}F NMR spectrum of PFM[13] is compared to the calculated ^{19}F chemical shifts obtained

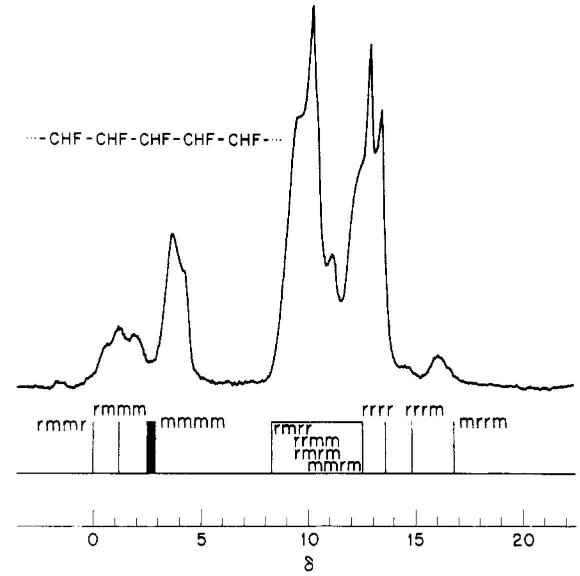

Figure 4. Observed (84.6 MHz) and calculated ^{19}F NMR spectra of PFM.

using $\gamma_{F,C}$ = 20 ppm and $\gamma_{F,F}$ = 10 ppm upfield, or shielding. Only ^{19}F chemical shifts calculated for pentads by averaging over all PFM nonads are presented, with the nonad sensitivity of a given ^{19}F chemical shift indicated by its width.

There is general agreement between calculated and observed resonances, indicating that conformationally sensitive γ effects are the source of the stereosequence-dependent dispersion of ^{19}F chemical shifts in PFM. Adoption of Bernoullian polymerization statistics permits a faithful simulation[13] of the observed spectrum (see Figure 4) and clearly indicates that the sample of PFM investigated here is predominantly atactic, with P_m = 0.42.

^{19}F NMR Chemical Shifts for Poly(vinyl fluoride). Characterization of the microstructure of PVF requires knowledge of stereosequence and H-H:T-T defect content. Bond rotation probabilities are obtained from a recently developed[12] RIS model of PVF which incorporates the effects of both H-H:T-T defect structures and stereosequence. In H-T portions of PVF, stereosequence effects to the pentad level are considered, while all possible octad stereosequences encompassing a single H-H:T-T defect (see Figure 2) were treated.

A comparison of the observed ^{19}F NMR spectrum of PVF with the ^{19}F chemical shifts calculated for γ_{F,CH_2} = $\gamma_{F,CHF}$ = 35 ppm and $\gamma_{F,F}$ = 25 ppm is presented in Figure 5. The agreement is excellent and permits a detailed assignment of the observed peaks. The observed effects of stereosequence and H-H:T-T defects are both reproduced by the calculated ^{19}F NMR chemical shifts.

Weigert[18] has presented peak assignments for the ^{19}F NMR spectrum of PVF based on analogies drawn from the methyl carbon region of the ^{13}C NMR spectrum of atactic polypropylene[19] and the ^{19}F NMR spectra of a series of 2-halo-3-fluorobutanes.[20] Although his assignments for the H-T ^{19}F resonances (mm, mr, and rr in order with increasing magnetic field) agree with ours (P_m = 0.43), there are differences between the two assignments for the H-H:T-T peaks.

Both assignments agree that H-H fluorines B and C (see Figure 5) in the racemic (r) configuration should resonate upfield from their meso (m) arrangement, which is also the observed and calculated order in PFM (see Figure 4). However, Weigert assigns the defect peaks labeled 1, 2, 3, 4, 5, and 6 to defect fluorines B(m*m*), C(*m*), B(r*m*), B(m*r*), C(*r*), and B(r*r*), where the italic r or m denotes the relative configuration of the H-H fluorines B and C (see PFM stereostructure in Figure 2 for r and m configurations). Our calculated ^{19}F chemical shifts indicate that peaks 1-6 are due to B(m*m*), B(r*m*), C(*m*), B(m*r*), C(*r*), and B(r*r*).

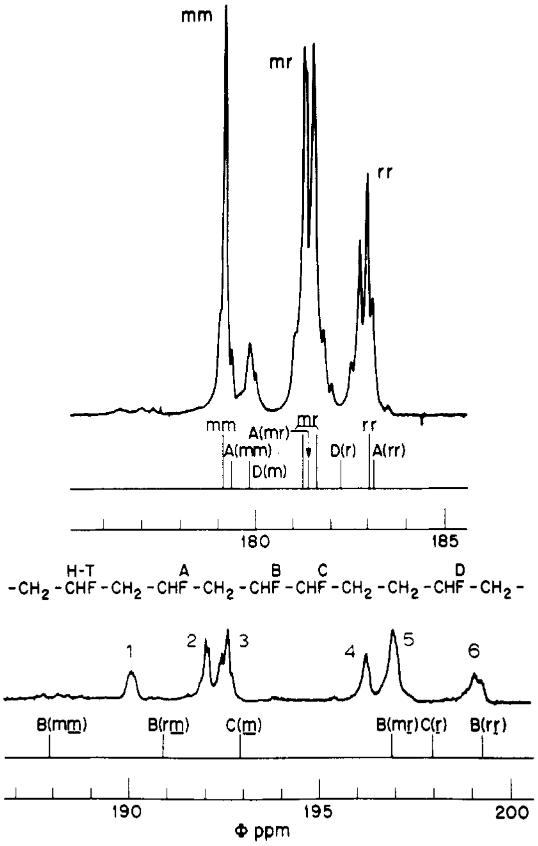

Figure 5. Observed (188.2 MHz) and calculated ^{19}F NMR spectra of PVF.

The intensities (*I*) of H-H B and C resonances should be equal, which according to Weigert's assignments means *I*(1) + *I*(3) + *I*(4) + *I*(6) should equal *I*(2) + *I*(5). However, it is clear that Weigert's assignment gives too much intensity to the H-H fluorine B, while our assignment is consistent with the expected 1:1 intensity ratio for H-H fluorines B and C.

The minor peaks to the high-field side of H-T(mm) and between H-T(mr) and H-T(rr) are assigned to D(m) and D(r) by Weigert, while the ^{19}F chemical shifts we calculated for A(mm), A(mr), and A(rr) together with D(m) and D(r) closely correspond to these peaks of minor intensity in the H-T portion of the spectrum.

Half the ratio of the intensity of H-H fluorines B and C to the total intensity yields an estimate of 11.6 mol % H-H:T-T addition. Independent ^{13}C NMR analysis[10] of the same PVF sample yields 10.6 mol % of H-H:T-T addition, confirming our ^{19}F NMR assignments.

^{19}F NMR Chemical Shifts for Poly(trifluoroethylene). As expected from our discussion of ^{19}F NMR chemical shifts in PVF, stereosequence and H-H:T-T defect content are also both important features of PF_3E microstructure. The calculation of ^{19}F NMR chemical shifts for PF_3E was conducted in a manner identical with that described for PVF except bond rotation probabilities were obtained from the RIS model[12] appropriate to PF_3E.

A comparison of ^{19}F NMR chemical shifts calculated from the previously derived[12] RIS model for PF_3E with those observed in the spectrum of regioregular PF_3E (all H-T addition) (see Figure 6) made apparent the failure of this RIS model to yield calculated ^{19}F chemical shifts

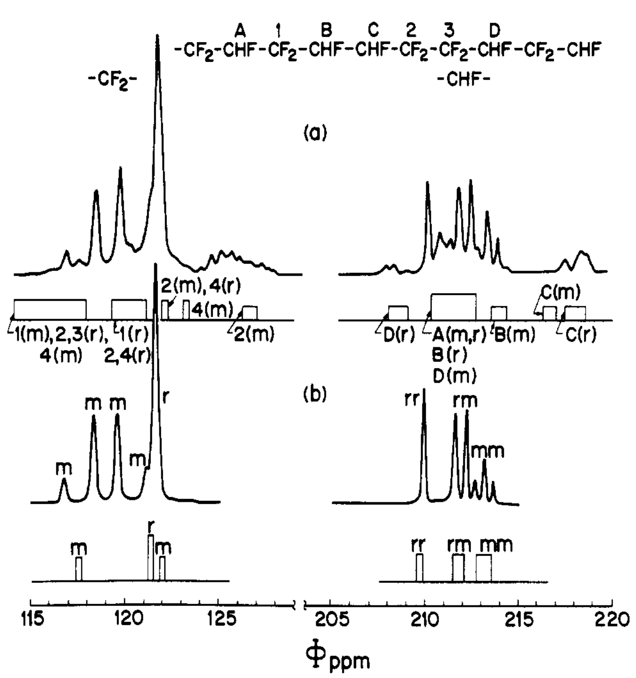

Figure 6. Observed (188.2 MHz) and calculated ^{19}F NMR spectra of PF$_3$E: (a) PF$_3$E containing H-H:T-T defects; (b) regioregular PF$_3$E.

in agreement with the observed. As an example, in the CHF region the over all spread in the calculated ^{19}F chemical shifts due to stereosequence effects was $\sim$0.5 ppm, while the observed spread (see Figure 6) is close to 4 ppm.

The failure of the RIS model for PF$_3$E,[12] as derived from conformational energy estimates, to predict the observed ^{19}F NMR spectra led us to rederive a RIS model which does correctly predict the observed ^{19}F NMR chemical shifts. Statistical weights reflecting the probabilities of all possible backbone rotational states were treated as parameters and selected to provide calculated ^{19}F NMR chemical shifts which agreed with the observed spectra. (Details of the development of the RIS model for PF$_3$E from the observed ^{19}F NMR spectra will be presented shortly.[21])

In Figure 6 we compare the calculated ^{19}F NMR chemical shifts to the observed spectrum of PF$_3$E. The agreement is good for both CHF and CF$_2$ fluorines, with γ effects in the range observed for the other three fluoro polymers treated here; i.e., $\gamma_{\mathrm{F,CHF}} = 20$ ppm, $\gamma_{\mathrm{F,CF_2}} = 28$ ppm, and $\gamma_{\mathrm{F,F}} = 10$ ppm. From the intensity of the most upfield CHF resonances corresponding to T-T fluorine C, we estimate that our PF$_3$E sample has 11.6 mol % H-H:T-T addition. This percent H-H:T-T addition is lower than the $\sim$50% H-H:T-T addition we previously estimated for a commercial sample of PF$_3$E using ^{13}C NMR.[10] However, as mentioned above, our previously developed RIS model for PF$_3$E[12] was in error, and the 50% H-H:T-T estimate obtained by ^{13}C NMR is probably also wrong. We will shortly reanalyze the ^{13}C NMR spectrum of PF$_3$E using the RIS model developed[21] by comparison of calculated and observed ^{19}F NMR chemical shifts.

The calculated order of resonances for regioregular PF$_3$E is in good agreement with the experimental assignment.[14] Spin-spin coupling between the CF$_2$ fluorines (see below) provides an unambigous means for making the stereosequence assignments[14] in regioregular PF$_3$E.

In Figure 6a the calculated ^{19}F chemical shift of racemic C(r) T-T CHF fluorine comes upfield from its meso (m) arrangement[22] in a manner similar to that observed for H-H fluorines in PVF and for m and r dyads in PFM. The racemic arrangement of -CHFCHF- units is clearly favored over the meso configuration for the PF$_3$E studied here.

Yagi[23] attempted to deduce microstructural information from the 56.5-MHz ^{19}F NMR spectrum of PF$_3$E. However, the poor resolution of his spectrum (CF$_2$ region) resulted in the absence of resonances below 119 ppm and above 126 ppm, which are clearly seen in the CF$_2$ region of our spectrum obtained at 188.22 MHz. The microstructural conclusions drawn by Yagi concerning PF$_3$E are almost certainly in error. This latter judgment receives support from the observation that the ^{19}F chemical shifts calculated for the fluorine nuclei belonging to CF$_2$ groups are inequivalent if either or both the nearest or next-nearest neighbors are asymmetric CHF groups. As an example, in the sequence -CF$_2$-CHF$\overset{1}{-}$CF$_2\overset{2}{-}$CHF-CF$_2$- the fluorines belonging to the central CF$_2$ group are in a gauche arrangement with the terminal CF$_2$ carbons, with probabilities $(2.0 - P_{1,g^-} - P_{2,g^+})$ and $(2.0 - P_{1,g^+} - P_{2,g^-})$. Since $P_{1\ \mathrm{or}\ 2,g^+} \neq P_{1\ \mathrm{or}\ 2,g^-}$ in a meso (m) dyad, the two fluorine nuclei will resonate at different frequencies even though they belong to the same symmetric CF$_2$ group and are part of a H-T PF$_3$E chain segment. The clearly separated resonances predicted for the CF$_2$ fluorines when at least one of their neighbors is an asymmetric CHF group can be seen in Figure 6, where the chemical shifts calculated for the H-T and H-H:T-T (1, 2, 3, and 4) CF$_2$ fluorines are separated into distinct regions whose widths reflect the sensitivity to stereosequence. Yagi's analysis of the CF$_2$ region of his PF$_3$E spectrum did not take into account the inequivalence of fluorines belonging to the same CF$_2$ groups.

In addition, the magnetic inequivalence of CF$_2$ fluorines results in long-range spin-spin coupling, producing multiple resonances. This is seen clearly in the spectrum of regioregular PF$_3$E (Figure 6b), where in the CF$_2$ region the two inequivalent CF$_2$ fluorines residing in a meso (m) dyad are further split into an AB quartet.[14] On the other hand, the CF$_2$ fluorines in racemic (r) dyads are equivalent and yield a single resonance. Yagi did not account for the multiple resonances produced by the spin-spin coupling of inequivalent CF$_2$ ^{19}F nuclei.

In the CHF region of the ^{19}F NMR spectrum of PF$_3$E (see Figure 6a), there appears to be a clear separation of the "normal" H-T and "defect" T-T peaks, thereby providing an unambiguous analaysis of PF$_3$E microstructure. Judging from the CF$_2$ region of Yagi's ^{19}F NMR spectrum, we believe he most likely would not have resolved the meso (m) and racemic (r) T-T fluorine peaks for C, seen clearly in the CHF region of our PF$_3$E spectrum in Figure 6a.

Discussion and Conclusions

Our ability to correctly predict the ^{19}F chemical shifts as a function of microstructure (stereosequence and/or defect content) in the four fluoro polymers investigated indicates that, like ^{13}C nuclei,[1] ^{19}F chemical shifts are sensitive to their numbers and kinds of γ substituents. The γ effects upon both ^{13}C and ^{19}F nuclei are shielding and produce upfield chemical shifts relative to the unsubstituted nuclei. Apparently, the shielding effect produced by γ substituents requires a gauche arrangement between them and the observed ^{13}C or ^{19}F atom.

This required gauche arrangement is the source of the conformational sensitivity of ^{13}C and ^{19}F chemical shifts, because the local polymer chain conformation is sensitive to stereosequence and defect structures. With the demonstration that ^{19}F, as well as ^{13}C, chemical shifts are

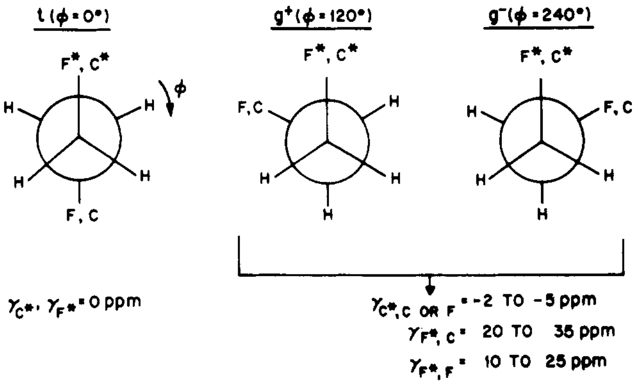

Figure 7. Schematic illustration of ^{13}C and ^{19}F γ effects in fluoro polymers.

sensitive to the gauche arrangement of γ substituents, it becomes increasingly important to understand the underlying cause(s) for the shielding γ effects.[24]

We have demonstrated that with a single consistent set of γ effects ($\gamma_{F,C}$ = 20–35 ppm and $\gamma_{F,F}$ = 10–25 ppm) the microstructurally sensitive ^{19}F NMR chemical shifts of fluoro polymers can be predicted. Because the method of calculating the ^{19}F chemical shifts requires evaluation of the number of gauche arrangements between the ^{19}F nuclei and their γ substituents, as obtained from bond conformation probabilities, it is apparent that the RIS models previously developed for these fluoro polymers,[11,12] with the exception of PF$_3$E, provide realistic descriptions of their conformational characteristics.

We previously[10] drew a similar conclusion when we were able to successfully account for the ^{13}C chemical shifts exhibited by the same fluoro polymers. However, the much larger magnitudes of the γ effects[25] on ^{19}F nuclei (10–35 ppm), compared to ^{13}C nuclei (−2 to −5 ppm) (see Figure 7), make the prediction of ^{19}F chemical shifts a much more sensitive test of fluoro polymers conformational characteristics. It appears that the RIS models[11,12] developed for PVF$_2$, PFM, and PVF pass this test.

Our ability to identify the H–H and T–T defect resonances in the ^{19}F NMR spectra of PVF$_2$, PVF, and PF$_3$E enables us to estimate the abundance of such defects. Measurement of the intensities of the defect peaks and comparison to the total intensity of all observable resonances yield the following estimates of H–H:T–T addition in these fluoro polymers: PVF$_2$ (Kureha sample, Figure 3b, 3.4%), PVF (11.6%), and PF$_3$E (11.6%). In the cases of PVF$_2$ and PVF, these compare favorably with the 3.3% and 10.6% defect contents estimated from our ^{13}C NMR analysis[10] of the same fluoro polymer samples.

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(22) In PFM, PVF, and PF$_3$E the racemic (r) arrangement of -CHFCHF- fluorines (see Figure 2) is observed to resonate upfield from the meso (m) arrangement, as predicted by the calculated ^{19}F NMR chemical shifts. Recently, Segre (Segre, A. L., private communication) synthesized and separated the racemic and meso isomers of 2,3-difluorobutane and recorded their ^{19}F NMR spectra. She finds the fluorine nuclei in the racemic isomer to resonate ca. 3 ppm upfield from the fluorines in the meso isomer. This observation confirms our calculated ^{19}F NMR chemical shifts for the -CHFCHF- fragments in PFM, PVF, and PF$_3$E and strengthens our assignment of the upfield peaks to the racemic isomer in each instance.
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(25) γ effects on both ^{13}C and ^{19}F nuclei are shielding and produce upfield shifts. However, by convention ^{13}C chemical shifts decrease (Me$_4$Si scale) and ^{19}F chemical shifts increase with increasing magnetic field. As a consequence, $\gamma_{C,X}$ are negative and $\gamma_{F,X}$ are positive (see Figure 7).