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Carbon-13 Nuclear Magnetic Resonance Chemical Shifts and the Microstructures of the Fluoro Polymers Poly(vinylidene fluoride), Poly(fluoromethylene), Poly(vinyl fluoride), and Poly(trifluoroethylene)

A. E. Tonelli,* F. C. Schilling, and R. E. Cais

Bell Laboratories, Murray Hill, New Jersey 07974.

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ABSTRACT: Simultaneous ^1H and ^{19}F broad-band decoupled ^{13}C NMR spectra are recorded for poly(vinylidene fluoride) (PVF_2), poly(fluoromethylene) (PFM), poly(vinyl fluoride) (PVF), and poly(trifluoroethylene) (PF_3E). Observed ^{13}C chemical shifts are compared to those calculated as a function of stereoregularity and/or defect structure, i.e., head-to-head to tail-to-tail (H–H:T–T) addition of monomers. Calculated chemical shifts are obtained through enumeration of the numbers and kinds of γ effects (three-bond gauche arrangements) involving each carbon atom as dictated by the conformational characteristics of each polymer. Agreement between measured and predicted ^{13}C chemical shifts is observed for each fluoro polymer when the following γ effects are assumed: $\gamma_{CH_2,CH_2} = -5.3$, $\gamma_{CH_2,CF_2} = -2.2$, $\gamma_{CH_2,CHF} = -3.7$, $\gamma_{CH_2,F} = -3.8$, $\gamma_{CHF,C} = -5.0$, $\gamma_{CHF,F} = -3.0$, $\gamma_{CF_2,C} = -2.1$, and $\gamma_{CF_2,F} = -1.4$ ppm, where $\gamma_{a,b}$ is the upfield shift (ppm) at carbon a produced by atom or group b when in a gauche arrangement with a. This agreement permits detailed assignments of ^{13}C NMR resonances in the spectra of all four fluoro polymers, including identification of those ^{13}C resonances belonging to the carbon atoms in the H–H:T–T defects present in PVF_2, PVF, and PF_3E chains, whose abundance increases in this order. The effects of β-fluorine substituents on the ^{13}C chemical shifts in these polymers are also evaluated from the observed defect resonances.

Introduction

We have recently demonstrated[1] that the ^{13}C NMR spectra of vinyl homo- and copolymers can be predicted from analysis of the numbers and kinds of γ interactions involving each carbon atom type in the polymer chain. 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 its trans arrangement. The frequency with which such γ gauche interactions occur can be evaluated from the conformational characteristics of the polymer chain as manifested by calculated bond rotation probabilities.

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, which lead via the γ gauche effect to a dispersion of ^{13}C chemical shifts reflecting the different possible microenvironments found along the vinyl polymer chain. All that is needed to calculate the effects of polymer microstructure on ^{13}C NMR chemical shifts are the bond rotation probabilities obtained from the polymer's conformational characteristics and the magnitudes of the upfield γ effects produced by the gauche arrangements of a given carbon atom with its substituents.

This approach, which fully utilizes all the microstructural information provided by ^{13}C NMR spectroscopy, has been successfully applied to the calculation of the ^{13}C chemical shifts in a variety of vinyl homo- and copolymers.[1] Polypropylene oligomers[2,3] and homopolymer[4] and its copolymers with ethylene[5,6] and vinyl chloride,[7] poly(vinyl chloride)[8] oligomers and homopolymer and its copolymers with ethylene[9] and propylene,[7] and polystyrene[10] and its oligomers have all been treated via the γ-effect method of predicting ^{13}C chemical shifts in polymers.

In the present work we extend the application of the γ-effect method to the calculation of the ^{13}C NMR chemical shifts expected for the carbon atoms in fluoro polymers. We treat poly(vinylidene fluoride) (PVF_2), poly(vinyl fluoride) (PVF), poly(fluoromethylene) (PFM), and poly(trifluoroethylene) (PF_3E).

Three principal reasons prompted our study. First, these polymers possess fluorine atoms whose ^{19}F nuclei exhibit magnetic resonance and whose chemical shifts are at least as sensitive to polymer microstructure as their ^{13}C nuclei. In a subsquent paper[11] we shall discuss the γ-effect prediction of ^{19}F chemical shifts. Second, we were curious to learn of the magnitude of the upfield ^{13}C chemical shift produced at a carbon atom by a γ-fluorine substituent when in a gauche arrangement. Third, with the exception of PVF_2,[12] the conformational characteristics of these fluoro polymers have never been studied experimentally. We hope to test the recently predicted (by one of us) conformational characteristics[13] of PVF, PF_3E, and PFM by comparing their observed and predicted ^{13}C chemical shifts, the latter of which are derived from bond rotation probabilities as obtained[14] from their conformational models.

Experimental Section

Materials. The synthesis of the PFM employed in this study has been previously reported.[15] PF_3E was provided through the courtesy of Dr. Gordon Leader of Pennwalt Corp. PVF was a commercial sample purchased from Aldrich, and the PVF_2 employed is Kynar 301, a product of Pennwalt Corp.

Method. Spin–spin coupling between directly bonded ^{13}C and ^{19}F nuclei generally obliterates the detailed structure of the dispersion in ^{13}C NMR chemical shifts produced by different fluoro polymer microstructures. Only in the methylene carbon regions of the usual ^1H-decoupled ^{13}C NMR spectra of PVF_2 and PVF can we begin to separate the effects of ^{19}F coupling and microstructure on the ^{13}C chemical shift dispersion. Consequently, we have performed ^{13}C NMR measurements on these fluoro polymers with simultaneous decoupling of both the ^1H and ^{19}F nuclei. The details of this triple-resonance experiment will be published in the near future.[16]

The NMR spectra were recorded on a Bruker WH-90 spectrometer at a ^{13}C frequency of 22.62 MHz. In all measurements the pulse angle was 90°, and the free induction decays were stored in 8K computer locations, using a spectral window of 4000 Hz. A delay time of 6.0 s was used between pulses. For each polymer sample 10 000 scans were accumulated, except for PVF_2 where 25 000 scans were collected. Hexamethyldisiloxane (HMDS) was employed as an internal reference (2.0 ppm vs. Me_4Si). The polymer samples were observed at concentrations of 0.2 g/cm^3. PFM was observed in acetone-d_6 at 38 °C. PVF was dissolved in a 4:1 mixture of ethylene carbonate and p-dioxane-d_8 and observed at 100 °C. PVF_2 was dissolved in the same solvent mixture but observed at 75 °C. PF_3E was observed in a 4:1

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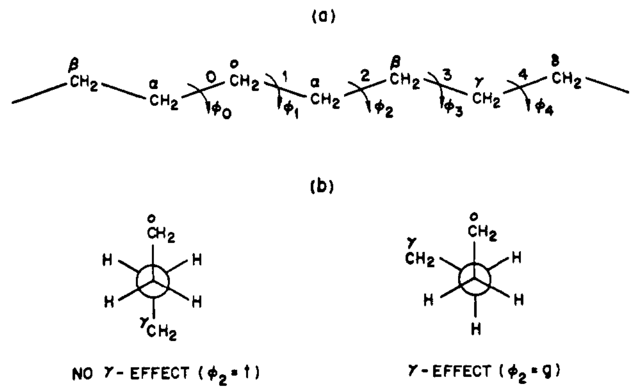

Figure 1. (a) Portion of a paraffinic hydrocarbon chain in the all-trans, planar zigzag conformation. (b) Newman projections along bond 2 in (a) illustrating the γ effect.

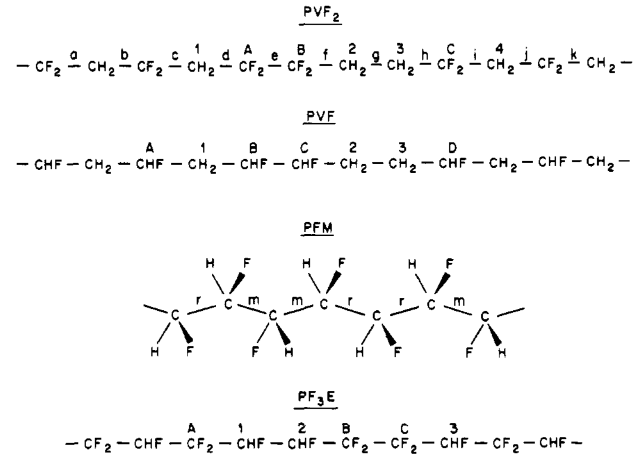

Figure 2. Schematic drawings of portions of PVF_2, PVF, PFM, and PF_3E chains illustrating H–H:T–T defect and stereosequence microstructures.

mixture of *N*,*N*-dimethylacetamide and *p*-dioxane-d_8 at 35 °C.

^{13}C NMR Chemical Shifts

Poly(vinylidene fluoride). The absence of asymmetric centers in PVF_2 should result in a simple ^{13}C NMR spectrum with single resonances for the methylene and methine carbons. However, head-to-head to tail-to-tail (H–H:T–T) addition of monomer units[17] (see Figure 2) does produce several nonequivalent environments for both carbon types and should result in ^{13}C NMR resonances which differ from their positions in head-to-tail (H–T) PVF_2. This expectation is realized in the spectrum presented in Figure 3, where in the methylene carbon region 4 resonances of low intensity appear −0.8, −8, −15, and −21 ppm upfield from the major H–T CH_2 peak.[18]

These minor upfield peaks result from occasional H–H:T–T addition of monomer units.[17] The ^{19}F NMR spectra of PVF_2 and appropriate model compounds presented by Wilson and Santee[17] and the equal intensities of the defect resonances observed here in the ^{13}C NMR spectrum of PVF_2 (Figure 3) support the H–H:T–T nature (see Figure 2) of the structural defects in PVF_2.

We may write expressions for the ^{13}C NMR chemical shifts (ν) of H–T methylenes and those methylene carbons in the vicinity of H–H:T–T defects in terms of β and γ effects and the bond rotation probabilities (P) which determine the frequencies of γ gauche effects. From Figure 2, we obtain

$$\nu_{CH_2}{}^{H-T} = 2(1 - P_t)\gamma_{CH_2,CF_2}$$

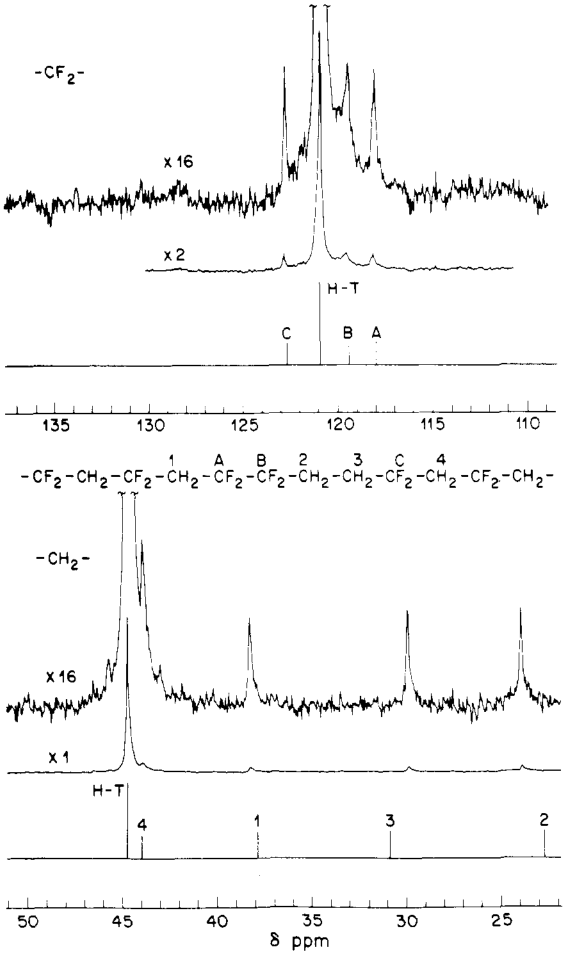

Figure 3. ^{13}C NMR spectrum and calculated ^{13}C chemical shifts for PVF_2.

where P_t is the probability of trans conformations about the bonds in H–T PVF_2.

$$\nu_{CH_2}{}^{1} = (1 - P_{b,t})\gamma_{CH_2,CF_2} + (1 - P_{e,t})\gamma_{CH_2,CH_2} + (1 + P_{e,t})\gamma_{CH_2,F}$$

$$\nu_{CH_2}{}^{2} = (2 - P_{e,t} - P_{h,t})\gamma_{CH_2,CH_2} + (2 + P_{e,t} + P_{h,t})\gamma_{CH_2,F} - \beta_{CH_2,F_2}$$

$$\nu_{CH_2}{}^{3} = (2 - P_{f,t} - P_{i,t})\gamma_{CH_2,CF_2} + (1 + P_{f,t})\gamma_{CH_2,F} - \beta_{CH_2,F_2}$$

$$\nu_{CH_2}{}^{4} = (1 - P_{h,t})\gamma_{CH_2,CH_2} + (1 - P_{k,t})\gamma_{CH_2,CF_2}$$

Bond rotation probabilities P_t, $P_{b,t}$, $P_{e,t}$, $P_{f,t}$, $P_{h,t}$, $P_{i,t}$, and $P_{k,t}$ are obtained[14] from the conformational model developed previously by one of us[12] for H–T and H–H:T–T PVF_2. Our conformational model[12] for PVF_2 correctly predicts the unperturbed dimensions and the recently measured[20] dipole moments of PVF_2 as observed in dilute solutions.

Because P_t(H–T) = $P_{k,t}$(H–H:T–T) (see Figure 2), the difference between chemical shifts of H–H:T–T methylene 4 and H–T methylene carbons reduces to $\nu_{CH_2}{}^{4} - \nu_{CH_2}{}^{H-T} = (1 - P_{h,t})\gamma_{CH_2,CH_2} - (1 - P_t)\gamma_{CH_2,CF_2} = 0.34\gamma_{CH_2,CH_2} - 0.48\gamma_{CH_2,CF_2}$. From our studies[1] of hydrocarbon polymers we know that $\gamma_{CH_2,CH_2} = -5.3$ ppm; therefore, $\nu_{CH_2}{}^{4} - \nu_{CH_2}{}^{H-T} = -1.85 - 0.48\gamma_{CH_2,CF_2}$. $\nu_{CH_2}{}^{4} - \nu_{CH_2}{}^{H-T}$ must equal −0.8 ppm because if $\nu_{CH_2}{}^{4}$ were assigned to the defect peaks −7.0, −15.0, or −21.0 ppm upfield from $\nu_{CH_2}{}^{H-T}$, then γ_{CH_2,CF_2} would have to be −11, −27, or −40 ppm, respectively. Values this large (−11 to −40 ppm) for γ_{CH_2,CF_2} are clearly unreasonable based on our experience[8,9] with vinyl chloride oligomers, homopolymer, and copolymers. Thus, $\nu_{CH_2}{}^{4}$ −

${\nu_{CH_2}}^{H-T} = -0.8$ ppm $= -1.85 - 0.48\gamma_{CH_2,CF_2}$, which leads to $\gamma_{CH_2,CF_2} = -2.2$ ppm.

H–H:T–T methylenes 2 and 3 must be most upfield from H–T CH_2 because they possess two fewer deshielding β-fluorine substituents.[21] By elimination, ${\nu_{CH_2}}^{1} - {\nu_{CH_2}}^{H-T} = -7.0$ ppm, which results in $\gamma_{CH_2,F} = -3.8$ ppm. Because H–H:T–T methylene carbon 2 has twice as many shielding γ fluorines as methylene 3, we are led to conclude ${\nu_{CH_2}}^{2} - {\nu_{CH_2}}^{H-T} = -21$ and ${\nu_{CH_2}}^{3} - {\nu_{CH_2}}^{H-T} = -15$ ppm. These expressions result in $\beta_{CH_2,F_2} = +8$ ppm.

The β and γ effects ($\beta_{CH_2,F_2} = +8$, $\gamma_{CH_2,CF_2} = -2.2$, and $\gamma_{CH_2,F} = -3.8$ ppm) derived by comparison of observed H–T and H–H:T–T methylene carbon chemical shifts result in the line spectrum drawn below the observed methylene carbon spectrum in Figure 3.

An analysis similar to that described above for the CH_2 carbons, when applied to the ^{13}C chemical shifts of the quaternary CF_2 carbon, leads to the calculated line spectrum presented below the observed CF_2 region of the PVF_2 spectrum in Figure 3. The following substituent effects are deduced from the comparison of observed and calculated CF_2 chemical shifts: $\gamma_{CF_2,C} = -2.1$, $\gamma_{CF_2,F} = -1.4$, and $\beta_{CF_2,F_2} = -5.0$ ppm. The γ effects experienced by the CF_2 carbons are less than half as large as those governing the CH_2 carbon chemical shifts.

An even more striking difference exists between the effects produced by a pair of fluorine atoms in the β position[22] upon the chemical shifts of the CH_2 and CF_2 carbons in PVF_2; $\beta_{CH_2,F_2} = +8.0$ and $\beta_{CF_2,F_2} = -5.0$ ppm. The β-fluorine atoms deshield the CH_2 carbons, as is usually observed[21] with β substituents, but the CF_2 carbons are shielded by β-fluorine atoms.

To further test the validity of the derived shielding effect produced by fluorines β to CF_2 carbons and the effects of carbons and fluorines γ to CF_2 carbons, we calculated the chemical shift expected at the central carbons in perfluorooctane and compared it to the CF_2 chemical shifts in PVF_2. The γ and β effects derived for the CF_2 carbons in PVF_2 were used along with the conformational model derived and tested for the perfluorinated alkanes and poly(tetrafluoroethylene) by Bates and Stockmayer.[23] The CF_2 carbons in H–T and H–H:T–T (C) PVF_2 do not have β-fluorine substituents, while H–H:T–T CF_2 carbons A and B in PVF_2 (see Figure 2) and the central CF_2 carbons in perfluorooctane possess two and four β fluorines, respectively. The following relative chemical shifts are calculated for the CF_2 carbons in H–T PVF_2, H–H:T–T (A, B, C) PVF_2, and perfluorooctane (PFO): ${\nu_{CF_2}}^{PFO} - {\nu_{CF_2}}^{A} = -6.6$, ${\nu_{CF_2}}^{PFO} - {\nu_{CF_2}}^{B} = -8.1$, ${\nu_{CF_2}}^{PFO} - {\nu_{CF_2}}^{H-T} = -9.5$, and ${\nu_{CF_2}}^{PFO} - {\nu_{CF_2}}^{C} = -11.3$ ppm. These compare favorably with the chemical shifts observed here for the CF_2 carbons in PVF_2 and the central CF_2 carbons in neat perfluorooctane reported by Lyerla and VanderHart,[24] i.e., 122.75 [H–H:T–T PVF_2 (C)], 120.94 (H–T PVF_2), 119.47 and 118.05 [H–H:T–T PVF_2 (B, A)], and 111.8 (perfluorooctane) ppm (ppm downfield from Me_4Si). This comparison strengthens our confidence in the γ- and β-substituent effects we derived for the CF_2 carbons in PVF_2.

The ability to calculate the relative ^{13}C NMR chemical shifts in both the CH_2 and CF_2 regions of PVF_2 confirms the previously derived conformational model of this polymer and also provides us with a set of β- and γ-substituent effects which may be used to help analyze the ^{13}C NMR spectra and therefore the microstructure of other fluoro polymers.

Poly(fluoromethylene). PFM is unique among the fluoro polymers discussed here. Each backbone carbon atom possesses a single fluorine substituent, thereby precluding any differentiation between H–T and H–H:T–T addition of monomer units (*cis*- and *trans*-1,2-difluoroethylenes).[15] Aside from the possibility of branching, stereosequence remains as the single structural feature of importance in characterizing the microstructure of PFM.

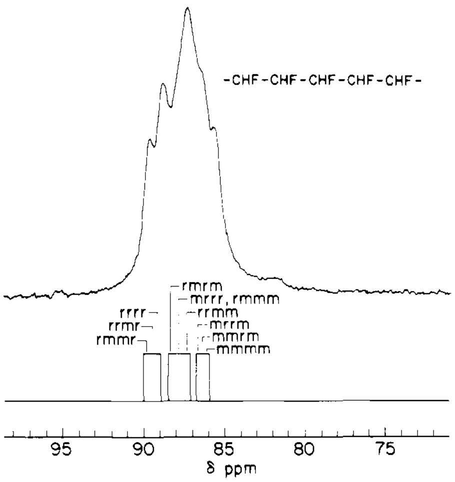

Figure 4. Same as Figure 3 except PFM instead of PVF_2.

Unlike the PVF and PF_3E vinyl polymers considered here, PFM possesses asymmetric carbon atoms separated by a single backbone bond rather than two C–C backbone bonds.[25] Consequently, in calculating ^{13}C NMR chemical shifts we have considered the effects of stereosequence up to the nonad level, resulting in the estimation of bond rotation probabilities for 136 different stereoisomers.

Bond rotation probabilities were estimated from the conformational characteristics derived previously for PFM chains[13] as a function of their stereosequence. $\gamma_{CHF,C} = -5.0$ and $\gamma_{CHF,F} = -3.0$ ppm were used to obtain calculated chemical shifts.

In Figure 4 we have presented below the observed ^{13}C NMR spectrum of PFM the calculated ^{13}C NMR chemical shifts of the ten pentads of PFM obtained by averaging over all possible nonad stereosequences. The pentads are sensitive to nonad stereosequence, resulting in a ^{13}C chemical shift dispersion of 0.2–0.5 ppm for each pentad.

The long-range sensitivity to stereosequence of the calculated PFM pentad ^{13}C chemical shifts coupled with the sensitivity of the observed[15] spectra to solvent makes a quantitative comparison of observed and predicted ^{13}C chemical shifts difficult. However, the overall observed dispersion in ^{13}C chemical shifts due to stereosequence effects (~4 ppm) is reproduced by the calculated chemical shifts.[26] In addition, the observed[15] narrowing of the ^{13}C chemical shift dispersion with increasing temperature is also predicted by the calculated chemical shifts. What is clear from the comparison of observed and calculated ^{13}C chemical shifts is that the sample of PFM employed in this study can be characterized as predominantly atactic.[15]

Poly(vinyl fluoride). The ^{13}C NMR spectra of PVF are considerably more complicated than those of PVF_2, due principally to stereosequence effects. Not only is H–H:T–T addition of monomer units more prevalent in PVF, but as in PFM we have to consider the stereosequence of the monomer units in both the H–T and H–H:T–T portions of the chain.

We adopt the substituent effects derived for the CH_2 carbons in PVF_2 and the CHF carbon in PFM when calculating the ^{13}C chemical shifts expected in PVF; i.e., $\gamma_{CH_2,CH_2} = -5.3$, $\gamma_{CH_2,CHF} = -2.2$, $\gamma_{CH_2,F} = -3.8$, $\gamma_{CHF,C} = -5.0$, and $\gamma_{CHF,F} = -3.0$ ppm. The effects of β-fluorine substituents on the CH_2 and CHF ^{13}C chemical shifts are

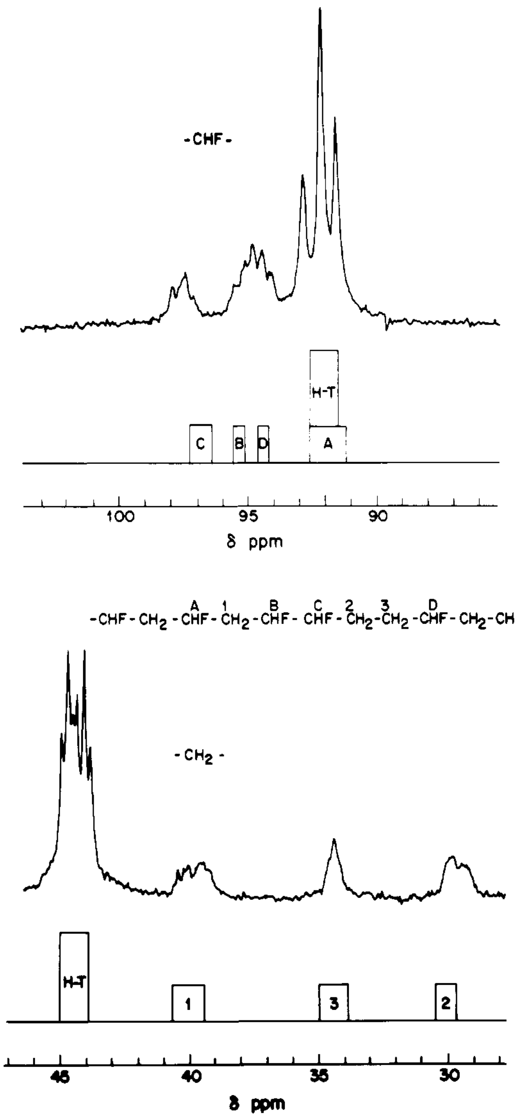

Figure 5. Same as Figure 3 except PVF instead of PVF_2.

deduced through achievement of the best agreement between observed and calculated chemical shifts. Bond rotation probabilities are obtained from the conformational model developed previously for PVF[13] by one of us, but which to date has remained experimentally untested.

A comparison of the ^{13}C NMR chemical shifts observed and calculated for PVF is presented in Figure 5. In both the CH_2 and CHF regions of the spectrum there is good agreement between the predicted ^{13}C chemical shifts and the positions of the observed resonances. This agreement is achieved for $\beta_{CH_2,F} = +6.0$ and $\beta_{CHF,F} = +1.0$ and by considering stereosequence effects to the pentad, tetrad, and octad levels for the H–T CHF, H–T CH_2, and H–H:T–T CHF and CH_2 carbons, respectively. In addition, the calculated ^{13}C chemical shifts are insensitive to the presence or absence of neighboring defects (see the next section on PF_3E for details).

Apparently the substituent effects derived for PVF_2 and PFM also apply to PVF. In addition, the conformational model proposed for PVF seems to satisfactorily describe the bond rotational probabilities in both H–T and H–H:T–T portions of PVF, thereby supporting its validity.

Poly(trifluoroethylene). For PF_3E chains we once again must consider the possibility of H–H:T–T addition of monomer units, in addition to stereosequence effects, when considering the dependence of calculated ^{13}C chemical shifts upon microstructure. In the H–T portions of PF_3E we consider the effects of stereosequence to the tetrad and pentad levels for the CF_2 and CHF carbons, respectively. When calculating the ^{13}C chemical shifts for the carbons in the vicinity of a H–H:T–T defect, we consider all possible octad stereosequences.

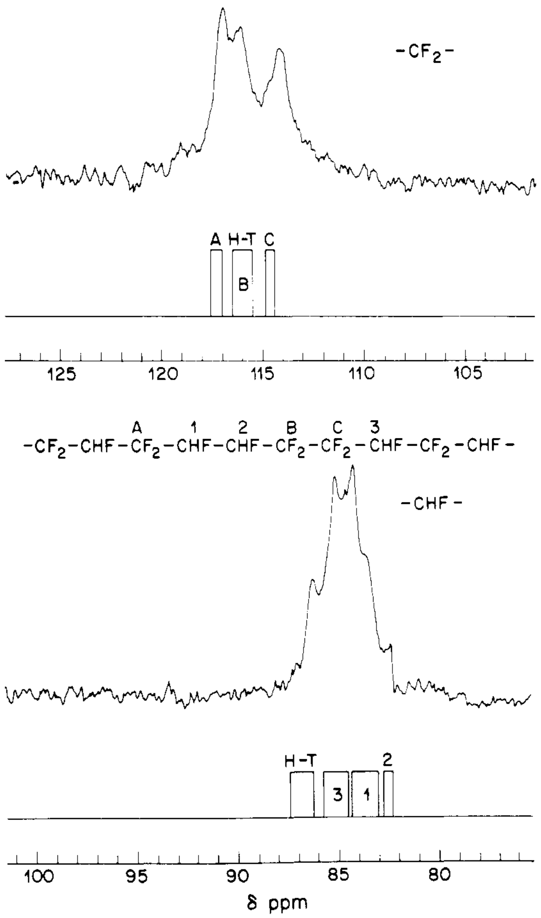

Figure 6. Same as Figure 3 except PF_3E instead of PVF_2.

The β and γ effects derived from PVF_2, PFM, and PVF are adopted for PF_3E; i.e., $\gamma_{CHF,C} = -5.0$, $\gamma_{CHF,F} = -3.0$, $\gamma_{CF_2,C} = -2.1$, $\gamma_{CF_2,F} = -1.4$, $\beta_{CHF,F} = +1$, and $\beta_{CF_2,F} = {}^1/_2\beta_{CF_2,F_2} = {}^1/_2(-5.0) = -2.5$ ppm. Bond rotation probabilities are obtained from the previously derived[13] conformational model of PF_3E.

In addition to isolated H–H:T–T defects, as seen in Figure 2, neighboring H–H:T–T defects and H–H addition of monomers followed by one or two H–T additions before a T–T monomer addition were considered when calculating ^{13}C chemical shifts. The need to consider neighboring H–H:T–T defects is apparent from comparison of observed and calculated chemical shifts (see below), which indicate that the frequency of H–H:T–T addition is at least as high as that of H–T addition. In general, the calculated ^{13}C chemical shifts for both the CF_2 and CHF carbons in H–H:T–T defects depend primarily on the numbers and kinds of β and γ substituents and show only a minor sensitivity to the presence or absence of neighboring defects. As an example, the calculated chemical shifts of CF^*_2 in the PF_3E fragments shown in Chart I differ by only 0.2 ppm.

In Figure 6 we compare the first reported ^{13}C NMR spectrum of PF_3E with the calculated ^{13}C chemical shifts. The ranges in the calculated chemical shifts for H–T and H–H:T–T carbons in both the CHF and CF_2 regions correspond to the effects of stereosequence and the presence or absence of neighboring defects. There is a good correspondence between observed resonances and predicted

Chart I

$-CF_2-CHF-CF_2-CHF-CHF-CF_2-$
$CF^*_2-CHF-CF_2-CHF-CF_2-CHF-$

$-CF_2-CHF-CF_2-CHF-CHF-CF_2-$
$CHF-CF^*_2-CF^*_2-CHF-CF_2-CHF-CF_2-$

$-CHF-CF_2-CHF-CHF-CF_2-CHF-CF_2-$
$CHF-CF^*_2-CF^*_2-CHF-CF_2-CHF-CF_2-$

$-CHF-CF_2-CHF-CHF-CF_2-CF_2-$
$CHF-CHF-CF_2-CF^*_2-CHF-CF_2-CHF-$

chemical shifts. It appears that of the polymers considered in this study, PF_3E possesses the greatest amount of H–H:T–T defect structure.

Discussion and Summary

We have extended our calculation of ^{13}C NMR chemical shifts to the fluoro polymers PVF_2, PFM, PVF, and PF_3E. A consistent set of β- and γ-substituent effects is sufficient to describe the ^{13}C chemical shifts and their dependence on chain microstructure for each of these fluoro polymers. Although nearly a dozen β and γ effects are employed in the calculation of the ^{13}C chemical shifts, there are many more independently observed resonances with which to compare, making the derived set of β and γ effects unique.

The generally good agreement achieved between the observed and calculated ^{13}C chemical shifts implies that the bond rotation probabilities used to evaluate the frequencies of the various γ effects occurring for the carbon atoms in each of the microstructural environments possible in these polymers are realistic. This provides, for the first time, direct microstructural support for the conformational models previously derived[12,13] for these chains.

Traditional measures[14] of the conformational characteristics of polymer chains, such as end-to-end distance and dipole moment, were predicted[12,13] to be relatively insensitive to microstructure (both stereosequence and defect content) for the fluoro polymers considered here. Thus, the successful testing of their conformational models as provided by the correct prediction of their ^{13}C NMR chemical shifts takes on added importance.

Not only can we study the microstructure of these polymers by comparing observed and calculated ^{13}C NMR chemical shifts, but the confidence gained in their conformational descriptions through these comparisons can now be utilized to search for the presence of similar well-behaved γ effects in their ^{19}F NMR spectra. This search is described in a subsequent paper.[11]

The detailed assignment of resonances in the ^{13}C NMR spectra of PVF_2, PVF, and PF_3E achieved by comparison to predicted ^{13}C chemical shifts permits a quantitative estimate of the H–H:T–T defect content in each fluoro polymer. Integration of defect (H–H:T–T) and normal (H–T) resonances to obtain peak areas leads to estimates of the defect content in each fluoro polymer. We find 3.2, 10.6, and ~50 mol % H–H:T–T monomer addition in the samples of PVF_2, PVF, and PF_3E, respectively, observed in the present study.

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References and Notes

(1) Tonelli, A. E.; Schilling, F. C. *Acc. Chem. Res.*, in press, and references cited therein.
(2) Tonelli, A. E. *Macromolecules* **1978**, *11*, 565.
(3) Tonelli, A. E. *Macromolecules* **1979**, *12*, 83.
(4) Schilling, F. C.; Tonelli, A. E. *Macromolecules* **1980**, *13*, 270.
(5) Tonelli, A. E. *Macromolecules* **1978**, *11*, 634.
(6) Tonelli, A. E. *Macromolecules* **1979**, *12*, 255.
(7) Tonelli, A. E.; Schilling, F. C., in preparation.
(8) Tonelli, A. E.; Schilling, F. C.; Starnes, W. H., Jr.; Shepherd, L.; Plitz, I. M. *Macromolecules* **1979**, *12*, 78.
(9) Tonelli, A. E.; Schilling, F. C. *Macromolecules* **1981**, *14*, 74.
(10) Tonelli, A. E. *Macromolecules* **1979**, *12*, 252.
(11) Tonelli, A. E.; Schilling, F. C.; Cais, R. E. *Macromolecules*, in press.
(12) Tonelli, A. E. *Macromolecules* **1976**, *9*, 547.
(13) Tonelli, A. E. *Macromolecules* **1980**, *13*, 734.
(14) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Wiley-Interscience: New York, 1969; Chapters II, IV.
(15) Cais, R. E. *Macromolecules* **1980**, *13*, 806.
(16) Schilling, F. C., in preparation.
(17) Wilson, C. W., III. *J. Polym. Sci., Part A* **1963**, *1*, 1305. Wilson, C. W., III; Santee, E. R., Jr. *J. Polym. Sci., Part C* **1965**, *8*, 97.
(18) Prior to our triple-resonance ^{13}C NMR study of PVF_2, the H–H:T–T CH_2 defect resonance observed here at –0.8 ppm upfield from H–T CH_2 carbons (see Figure 3) was obscured by long-range $^{19}F-^{13}C$ spin–spin coupling in the usual ^1H-decoupled ^{13}C NMR spectrum of PVF_2.[19]
(19) Bovey, F. A.; Schilling, F. C.; Kwei, T. K.; Frisch, H. L. *Macromolecules* **1977**, *10*, 559.
(20) Khanarian, G., unpublished observations.
(21) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; Chapters 3 and 5.
(22) The dependence of the β-fluorine substituent effect on the degree of α-fluorine substitution at the observed carbon is also observed for chlorine substituents. Measurement of the ^{13}C NMR spectra of ethane and all nine of its chlorinated derivatives led to the following observations: $\beta^0_{1,2,3}$ = +12.2, +26.3, +40.0 ppm; $\beta^1_{1,2,3}$ = +4.0, +10.4, +19.0 ppm; $\beta^2_{1,2,3}$ = +1.3, +4.9, +10.6 ppm; and $\beta^3_{1,2,3}$ = +1.0, +4.4, +9.9 ppm, where, for example, β^1_2 signifies the effect of 2 β-Cl substituents on the ^{13}C chemical shift of a carbon with a single α-Cl substituent.
(23) Bates, T. W.; Stockmayer, W. H. *Macromolecules* **1968**, *1*, 12, 17.
(24) Lyerla, J. R.; VanderHart, D. L. *J. Am. Chem. Soc.* **1976**, *98*, 1697.
(25) In H–H:T–T PVF and PF_3E, H–H and T–T asymmetric CHF carbons are also adjacent (see Figure 2) and are assigned to m and r dyads as shown for PFM.
(26) To get an idea of the sensitivity of the calculated overall dispersion in chemical shifts to $\gamma_{C,C}$ and $\gamma_{C,F}$ the following values of these γ effects lead to these dispersions: –4, –2 → 3.3 ppm; –4, –3 → 3.1 ppm; –4, –4 → 2.8 ppm; –5, –2 → 4.2 ppm; –5, –3 → 4.0 ppm; –5, –4 → 3.7 ppm; –6, –2 → 5.2 ppm; –6, –3 → 5.0 ppm; –6, –4 → 4.7 ppm; –6, –5 → 4.4 ppm; –6, –6 → 4.1 ppm. We selected $\gamma_{C,C} = -5$, $\gamma_{C,F} = -3$ based on the agreement achieved between calculated and observed ^{13}C chemical shifts in PVF as well as PFM for these γ's and because these values are similar to those derived[8,9] for chlorinated vinyl polymers.