Table III
Spectral Assignment of Methylene Carbon Resonances of Atactic Poly(vinyl alcohol)

Methylene Carbon Shift	Tetrad Assignments	Methylene Carbon Peak Intensities[a] Calcd	Methylene Carbon Peak Intensities[a] Obsd
45.8	rrr	0.161	0.17
45.6	rrm + mrm	0.383	0.37
45.2	mmr + rmr	0.361	0.35
44.8	mmm	0.095	0.11

[a] Obtained from the carbon-13 spectrum of sample A dissolved in Me_2SO-d_6.

Table IV
Tetrad Tacticity Determinations of Poly(vinyl alcohol)

Sample	Tetrads[a] rrr	rrm	mrm	rmr	mmr	mmm
A	0.17	0.25	0.12	0.16	0.19	0.11
B	0.04	0.06	0.08	0	0.25	0.57

[a] The tetrads were calculated from the triad data of Table I and the methylene carbon data of Table III.

carbon resonances of PVA is based on the following observations. From the triad data of sample A in Table I, it can be shown that only a single parameter is required to describe the configurational sequence of this sample. Or, in other words, the stereoregularity of the radical-polymerized poly(vinyl acetate), from which this sample is derived, obeys Bernoullian statistics.[11] This parameter, P_m, is defined as the probability that a growing polymer chain will form an m sequence. For sample A, $P_m = (mm)^{1/2} = 1 - (rr)^{1/2} = 0.456$, where mm and rr are, respectively, the fractions of isotactic and syndiotactic triads. Then the various tetrad placements in sample A can be readily calculated from P_m;[11] *i.e.*, mmm = P_m^3, mmr = $2P_m^2(1 - P_m)$, rmr = $P_m(1 - P_m)^2$, mrm = $P_m^2(1 - P_m)$, rrm = $2P_m(1 - P_m)^2$, rrr = $(1 - P_m)^3$. The calculated concentrations of the six tetrads can be made consistent with the observed methylene carbon peak intensities as shown in Table III; *i.e.*, the four lines of the methylene quartet were ascribed to the tetrads of rrr, rrm + mrm, mmr + rmr, and mmm from low to high field. It is noteworthy that these assignments are qualitatively confirmed by the peak positions and intensities of the corresponding spectrum of the highly isotactic sample B. The fact that the tetrad placements in sample A can be accounted for by the Bernoullian trial process indicates that the stereochemistry of the free-radical polymerization of vinyl acetate is independent of the configuration of the ultimate unit, the penultimate unit, as well as the penpenultimate unit of the growing polymer chain.

The tetrad distributions in the PVA samples can also be completely determined by using the following relationships of tetrads and traids: mmr = 2(mm − mmm) and mmr = 2 (rr − rrr). The calculated results are presented in Table IV.

After this article had been submitted, a similar work was published by Inoue, Chûjô, and Nishioka.[12] They report the carbon-13 spectra of poly(vinyl alcohol) dissolved in D_2O.

(11) F. A. Bovey, "Polymer Conformation and Configuration," Academic Press, New York, New York, 1969, Chapters 1 and 2.

(12) Y. Inoue, R. Chûjô, and A. Nishioka, *J. Polym. Sci., Part A-2*, **11**, 393 (1973).

---

^{19}F Nuclear Magnetic Resonance Spectra of Tetrafluoroethylene–Propylene Copolymers

Kenkichi Ishigure,* Yoneho Tabata, and Keichi Oshima

Department of Nuclear Engineering, University of Tokyo, Tokyo, Japan. *Received January 3, 1973*

ABSTRACT: High-resolution ^{19}F nmr spectra were measured at 94 MHz. of three kinds of tetrafluoroethylene–propylene copolymers, *i.e.*, alternating, tetrafluoroethylene- and propylene-rich copolymers prepared by γ-ray irradiation. The spectra were found to be quite sensitive not only to the sequence distribution but also to the configurational structure of the copolymers, and are well interpreted in terms of tetrads. It was concluded from the analysis of the spectra that the copolymers prepared in the temperature range of −78 to 30° have random configurations. Spectral parameters, especially chemical shift differences between nonequivalent nuclei, were observed to show marked temperature dependences, which were inferred to be closely related to the conformational structures of the copolymers.

Nuclear magnetic resonance has been widely applied to the investigations of polymer and copolymer structures for the past decade. Most of the work, however, has been concerned with proton resonance. Fluorine resonance has found only limited applications in this field despite the advantage of large chemical shifts.

In the previous papers[1-3] the authors have shown that ^{19}F nmr is a very powerful tool to investigate the structures of fluorine-containing copolymers such as tetrafluoroethylene (C_2F_4)–isobutylene and chlorotrifluoroethylene (C_2ClF_3)–isobutylene copolymers. The ^{19}F spectra of these copolymers have been interpreted in terms of tetrads and have given useful information concerning the sequence distribution of the copolymers. In the present work ^{19}F nmr spectra were obtained for C_2F_4–propylene (C_3H_6) copolymers and investigated in relation to their structures. As will be seen, the spectra are somewhat complicated by spin-spin coupling and by the asymmetric structures of the polymers compared to the previous cases.

Experimental Section

All copolymer samples were prepared by the γ-ray-initiated copolymerizations of the monomer mixtures at various tempera-

(1) K. Ishigure and Y. Tabata, *Macromolecules*, **3**, 450 (1970).
(2) K. Ishigure, Y. Tabata, and K. Oshima, *Macromolecules*, **3**, 27 (1970).
(3) K. Ishigure, Y. Tabata, and K. Oshima, *Polym. J.*, **2**, 321 (1971).

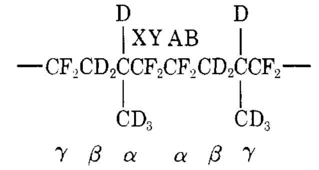
tures in the range of −78 to 30°. As deduced from the monomer reactivity ratios ($\gamma(C_2F_4) = 0.01$ and $\gamma(C_3H_6) = 0.1$),[4] this system yields copolymers of 50:50 composition, which may be assumed to have alternating structures, over a wide range of monomer compositions. The copolymers with high propylene content were obtained from copolymerization mixtures rich in propylene. On the other hand, copolymer samples with high C_2F_4 contents were obtained by Soxhlet extraction of copolymer–poly(tetrafluoroethylene) mixtures which were produced after thorough polymerization of monomer mixtures with extremely low propylene contents. Most of the ^{19}F nmr spectra were measured at 94 MHz using a Jeol spectrometer Model PS-100 (partly 4H-100) in the temperature range of 25–150°. Benzotrifluoride was usually employed as a solvent or an internal reference and chemical shifts were expressed in terms of Φ*(ppm), which was evaluated by the addition of 63.7 (Φ value of benzotrifluoride) to the chemical shift (ppm) of the relevant resonances relative to benzotrifluoride.

Results and Discussion

Alternating Copolymer. As shown in Figure 1A, the ^{19}F nmr spectrum of assumed alternating C_2F_4–C_3H_6 copolymer appears rather complicated and has fine structure. Since this complication was considered to arise partly from vicinal H–F couplings, C_2F_4-deuterated propylene-d_6 copolymer was prepared. As shown in Figure 1B, the ^{19}F nmr spectrum of the deuterated polymer still has a fine structure, which is inferred to arise from vicinal F–F couplings. It should be noted that the two spectra were measured at different temperatures. As is generally observed in fluorine resonance studies, spectral parameters, especially chemical shifts, are quite dependent on temperature in this system. The rather poor agreement between the chemical shifts of the corresponding resonances in the two spectra is due to the different temperatures of the measurements. The temperature dependence of the resonances will be discussed later.

The spectra were found to be slightly dependent on the solvent used. When they were measured at 25° using benzotrifluoride as a solvent, triplets were observed at 112.8 (b′ in Figure 2B) and 110.0 Φ*, whereas doublets at 112.7 (a) and 109.9 (b) were observed when tetrahydrofuran was the solvent. No other resonance was affected appreciably by solvent. As is shown in Figure 2B, the separations of the triplet components are almost equal to that of the doublet components observed in tetrahydrofuran. Thus, the triplet observed in benzotrifluoride is considered to be comprised of two doublets which overlap and appear to be one doublet in tetrahydrofuran.

FRFRF



$$-CF_2CD_2\overset{D}{\underset{CD_3}{C}}\overset{XY}{CF_2}\overset{AB}{CF_2}CD_2\overset{D}{\underset{CD_3}{C}}CF_2- \qquad (1)$$

$$\gamma\ \ \beta\ \ \alpha \qquad \alpha\ \ \beta\ \ \gamma$$

In this paper, copolymer sequences are expressed in terms of the arrangements of F and R, referring to C_2F_4 and olefin, respectively, as in the formula (1). Geminal fluorine nuclei on the carbon atom adjacent to $CDCD_3$ (or $CHCH_3$) groups and those on the carbon atom neighboring to CD_2 (or CH_2) groups are called XY and AB, respectively, regardless of their steric configurations. As will be seen in the later part of this paper, the effects of α, β, and γ carbon substituents must be taken into account for a consistent explanation of the chemical shifts of central CF_2 resonances (for instance, XY CF_2 in the formula (1)) in the present system. Therefore, tetrad notation is used to designate copolymer sequences with regard to the CF_2 resonances.

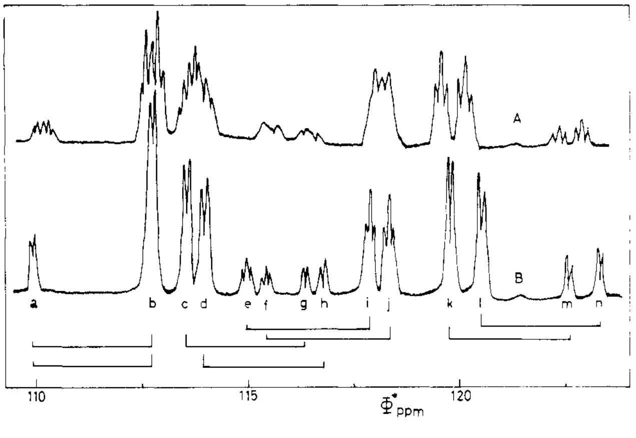


Figure 1. 94-MHz ^{19}F nmr spectra of alternating C_2F_4–C_3H_6 copolymers (C_2F_4 content ~50 mol %): solvent, tetrahydrofuran; (A) C_2F_4–C_3H_6, 60°; (B) C_2F_4–C_3H_6-d_6, 25°.

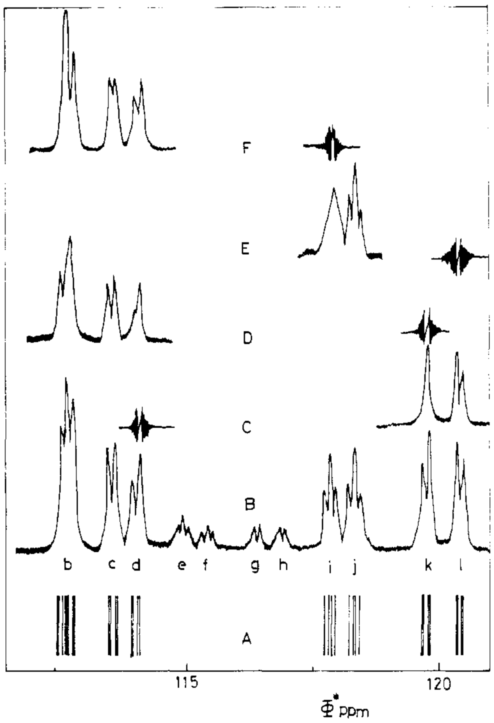
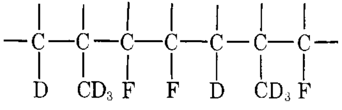


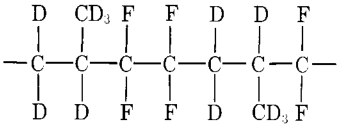
Figure 2. F–F homonuclear decoupled spectra and a calculated spectrum of an alternating C_2F_4–C_3H_6-d_6 copolymer at 25°: solvent, benzotrifluoride; (A) calculated spectrum; (B) unirradiated spectrum; (C–F) homonuclear decoupled spectra. The lowest field triplet and the two highest field doublets are not shown in B.

Stereochemical consideration leads to the recognition of two kinds of configurations for RFRF or FRFR sequences, as shown in the formulas (2) and (3), where the main chain carbon atoms are extended in a planar zigzag form. The terms "meso" and "racemic" are employed in the usual sense, but it is worth noting that AB fluorine nuclei are not equivalent in racemic RFRF structure.



$$-\overset{D}{\underset{D}{C}}-\overset{D}{\underset{CD_3}{C}}-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}-\overset{D}{\underset{D}{C}}-\overset{D}{\underset{CD_3}{C}}-\overset{F}{\underset{F}{C}}- \qquad (2)$$

meso RFRF



$$-\overset{D}{\underset{D}{C}}-\overset{CD_3}{\underset{D}{C}}-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}-\overset{D}{\underset{D}{C}}-\overset{D}{\underset{CD_3}{C}}-\overset{F}{\underset{F}{C}}- \qquad (3)$$

racemic RFRF

[4] G. Kojima and Y. Tabata, *J. Macromol. Sci.-Chem.*, 6, 417 (1972).

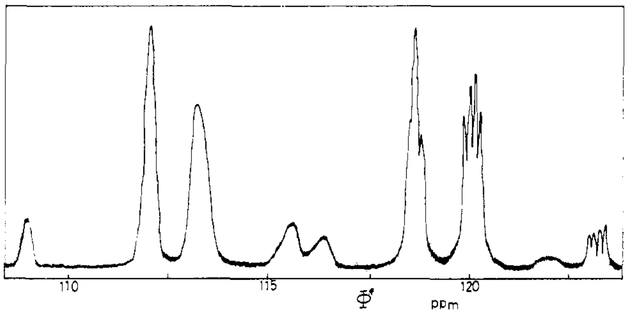


Figure 3. 94-MHz ^{19}F nmr spectrum of alternating C_2F_4–C_3H_6-d_6 copolymer at 150°: solvent, benzotrifluoride.

It has been observed in the ^{19}F nmr spectra of C_2ClF_3–isobutylene[2,3] copolymers that geminal ^{19}F nuclei are rendered nonequivalent under the influence of the adjacent asymmetric carbon, giving an AB-type quartet in which a large value of geminal F–F coupling constant (*ca.* 270 Hz) is involved. In the ^{19}F spectra of C_2F_4–isobutylene copolymers[1] the resonances of CF_2 groups neighboring to CH_2 groups were found at lower magnetic field than those of CF_2 groups neighboring to $C(CH_3)_2$ groups. It would be predicted from those results that the four CF_2 groups in the racemic and meso structures of alternating sequences will be observed as AB-type quartets, if vicinal F–F coupling constants are small enough to be negligible, as is the case with C_2ClF_3–isobutylene copolymers. Thus, in Figure 1B, the two pairs of AB-type quartets at higher magnetic field are assigned to two XY CF_2 resonances and those at lower field to two AB CF_2 resonances.

Now let us consider two pairs of the higher field quartets, disregarding the fine structure of each component due to F–F vicinal couplings. It is easy to find the corresponding components of the A or B pair, which are related to each other by a large F–F geminal couplings, as shown by brackets in Figure 1B. However, there appear to be two possible combinations of these four pairs. To see which combination is more probable, the relative intensity ratios of the components were calculated for the possible combinations from the chemical shift differences and coupling constants, as determined from the resonance positions of the components. On comparing the observed values 0.34 (I_n/I_l) and 0.21 (I_m/I_k) with the calculated values in Table I, it is readily seen that the combination A is more probable. As to the two pairs of quartets at lower field, however, the chemical shift differences are so small that the intensity ratio method could not be used to find a probable combination of the resonance components. On the other hand, the F–F spin decoupling technique was helpful for this purpose. If doublet d is irradiated, doublet k collapses, as shown in Figure 2C. Conversely the irradiation of doublet k brings about the collapse of doublet d and affects a higher field component of the triplet b′ (2D).

When doublet l is irradiated, the triplet i turns into a broad singlet without fine structure (2E). The irradiation of triplet i, in turn, affects the lower field component of triplet b′ and slightly affects the doublet c (2F). These results are qualitatively consistent with the following assignment: the outer pair (e, i, l, and n) of the quartets assigned to XY CF_2 is associated with the lower field quartet[5] (a'_l(109.8), b'_l(112.6), c(113.5), and g(116.3Φ*)) of AB CF_2 and the inner pair (f, j, k, and m) with the higher field quartet[5] (a'_h(110.0), b'_h(112.8), d(114.0), and h(116.8)) in benzotrifluoride solvent.

Table I
Possible Combinations of Resonance Components and Calculated Intensity Ratios

Combination of Components	(25° in Benzotrifluoride) Calcd Intensity Ratios[b] I_n/I_l	I_m/I_k
A e(114.9),[a] i(117.8), l(120.4), n(123.3)		
f(115.4), j(118.2), k(119.7), m(122.6)	0.32	0.20
B e(114.9), i(117.8), k(119.7), m(122.6)		
f(115.4), j(118.2), l(120.4), n(123.3)	0.25	0.27

[a] The figures in the parentheses represent the resonance positions of the labeled peaks. [b] Calculated from the usual equation for AB system.

These two groups of resonances are considered to correspond to the meso and racemic structures of FRFR and RFRF sequences. It does not seem possible at present to decide which group of the resonance is related to the meso or the racemic structure. The relative ratio of the two groups is approximately 1, being almost independent of the polymerization temperature (−78 to 30°). It is accordingly concluded that such copolymers have random configurations.

The fluorine resonances of the deuterated alternating copolymer can be treated as an ABXY system, where the coupling constants between A and B and between X and Y are comparable to the chemical shift differences δ_{AB} and δ_{XY} but the coupling constants J_{AX}, J_{AY}, J_{BX}, and J_{BY} are very small compared to δ_{AB} and δ_{XY}. Theoretical calculations were performed for this ABXY system on the basis of a perturbation method in which the couplings between AB group of nuclei and XY group of nuclei were treated as perturbation terms. Preliminary results of this calculation showed that in the 94-MHz spectra the second order terms are small enough to be negligible for an approximate simulation. In this approximation each component of the AB-type quartets comprises four partly overlapping lines. A typical result of the numerical calculations is indicated in Figure 2A, as a stick spectrum, where the parameters are assumed as follows: $J_{AX} = -2$, $J_{BX} = -13$, $J_{AY} = -20$, $J_{BY} = 4$, $J_{XY} = 271$, and $J_{AB} = 263$ Hz.

In the literature to date, the sign of vicinal F–F couplings seems to be negative,[6] though some uncertainty still remains.[7] It seems a little unlikely that one of the above vicinal coupling constants should be essentially different in sign from the rest. More detailed calculations are in progress.

As already mentioned, the spectra of this copolymer are remarkably temperature dependent. In Figure 3 is shown the spectrum measured at 150°, where only two pairs of AB-type quartets are seen. In Table II the temperature dependences of the associated parameters are listed.

It is quite interesting to note that the XY CF_2 resonance shows temperature dependence different from that of AB CF_2 resonance; δ_{XY} decreases with increasing temperature, but δ_{AB} increases. These marked temperature dependences of chemical shifts may be closely related to the conformational structure of the copolymer and probably arise from the temperature dependence of the populations of the conformers, which are separated by rather high energy barriers.

---

(5) The subscripts l and h represent the lower field and the higher field halves of the peaks a′ and b′, respectively, though only b′ is shown in Figure 2B.

(6) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, p 214.

(7) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1966, p 190.

Table II
Temperature Dependence of Spectral Parameters

Temp (°C)	XY CF_2 (Hz)				In Benzotrifluoride AB CF_2 (Hz)			
	J_{XY}	$\delta_{XY}{}^{1\,a}$	$\delta_{XY}{}^{2\,b}$	$\delta_{MR}{}^{c}$	J_{AB}	$\delta_{AB}{}^{1\,a}$	$\delta_{AB}{}^{2\,b}$	$\delta_{MR}{}^{c}$
25	271	402	302	14	263	231	271	33
100	274	363	278	10	265	242	282	14
150	~278	337	275	~8	~267	~267	~291	~8

[a] $\delta_{XY}{}^1$ and $\delta_{AB}{}^1$ are chemical shift differences between geminal fluoridine nuclei of the outer XY pair and of the associated lower field AB pair, respectively. [b] $\delta_{XY}{}^2$ and $\delta_{AB}{}^2$ are chemical shift differences between geminal fluorine nuclei of the inner XY pair and of the associated higher field AB pair, respectively. [c] δ_{MR} is chemical shift difference between the centers of the two AB-type quartets corresponding to meso and racemic structures.

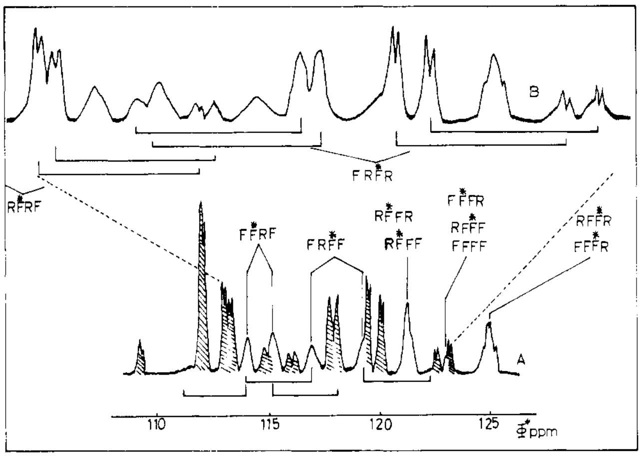
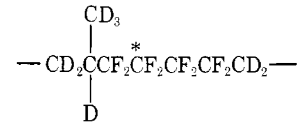


Figure 4. 94-MHz ^{19}F nmr spectrum of C_2F_4-rich C_2F_4–C_3H_6-*d*$_6$ copolymer (C_2F_4 content ~55 mol %) at 60°: solvent, tetrahydrofuran; (B) expanded spectrum of A. Shaded peaks are corresponding to the resonances appearing in Figure 1B.

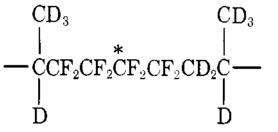
C_2F_4-Rich Copolymer. In Figure 4 the ^{19}F nmr spectrum of a C_2F_4-rich copolymer of C_2F_4 and deuterated propylene is given. There appear at least six broad peaks that are not seen in the spectrum of the alternating copolymer. These new resonances increase in intensity with increasing C_2F_4 content and are attributed to sequences of two or more consecutive C_2F_4 units. Hereafter, the tetrad notation with an asterisk, as for example, $\mathrm{R\overset{*}{F}RF}$, is used to refer to the central CF_2 resonances of the corresponding sequences. In this notation the asterisk designates the location of the central CF_2 group, the chemical shift of which is actually affected by the substituents of the neighboring three carbon atoms on each side. It should be noted that in the case of RFFR, FFFR, and RFFF the asterisk notation is essential to avoid ambiguity (see formulas (4) and (5). The new resonances are consistently assigned as indicated in Figure 4. The empirical rule[8] relating the magnitude of fluorine chemical shifts to the positions of electronegative substituents was used in making the assignment. For example, let us compare $\mathrm{R\overset{*}{F}FR}$ and $\mathrm{RF\overset{*}{F}R}$. The substituents on the α carbons are the same in both structures. The β-alkyl substituent shifts $\mathrm{R\overset{*}{F}FR}$ toward lower magnetic field relative to $\mathrm{RF\overset{*}{F}R}$, if the γ substituents are not taken into consideration. Alkyl substituents on both γ carbon atoms give rise to an additional higher field shift of $\mathrm{RF\overset{*}{F}R}$ relative to RFFR. Consequently, RFFR is at considerably higher magnetic field than $\mathrm{R\overset{*}{F}FR}$. It may appear inconsistent with the empirical rule at first sight that $\mathrm{F\overset{*}{F}RF}$ is at higher field than $\mathrm{R\overset{*}{F}RF}$. It would not be inconsistent, however, if the magnitude of the high-field shift caused by substituting fluorine atoms for β hydrogen is larger than that of the low-field shift induced by substituting fluorine atoms for β hydrogen and the β-methyl group.

$\mathrm{R\overset{*}{F}FR}$



$$-\mathrm{CD_2\underset{\displaystyle D}{\overset{\displaystyle CD_3}{C}}CF_2\overset{*}{C}F_2CF_2CF_2CD_2}- \qquad (4)$$

$\mathrm{RF\overset{*}{F}R}$



$$-\mathrm{\underset{\displaystyle D}{\overset{\displaystyle CD_3}{C}}CF_2CF_2\overset{*}{C}F_2CF_2CD_2\underset{\displaystyle D}{\overset{\displaystyle CD_3}{C}}}- \qquad (5)$$

Considering the conditions involved in preparing the C_2F_4-rich copolymers, it is reasonable to assume that sequences with consecutive C_3H_6 units are not present in the copolymers, and, in fact, there are no resonances attributable to such sequences in the spectra.

On the basis of the above assumption and of the assumption of a steady state, the following relations among the concentration of tetrad sequences are readily derived. These relations were found to hold approximately among the relative areas of the corresponding resonances within the limits of experimental error.

$$\{\mathrm{RFFF}\} = \overset{*}{\{}\mathrm{FFFR}\} \qquad (6)$$

$$\{\mathrm{RFRF}\} = \{\mathrm{FRFR}\} \qquad (7)$$

$$\begin{aligned}\{\mathrm{FFRF}\} &= \{\mathrm{RFFR}\} \quad + \quad \{\mathrm{FFFR}\} \\ &= \{\mathrm{FRFF}\} \qquad\qquad\qquad (8)^{9} \\ &= \{\mathrm{RFFR}\} \quad + \quad \{\mathrm{RFFF}\}\end{aligned}$$

It is also found from the relative areas of the resonances in Figure 4 that about 67% of C_2F_4 units are bonded in the form of -RFR-, about 30% in the form of -RFFR- and about 3% in the form of -RFFFR-, if the contribution of the structure in which four or more C_2F_4 units are successively bonded is assumed to be negligibly small.

It seems of great interest to compare the chemical shift difference $\delta\nu_*$ of geminal fluorine nuclei among $\mathrm{FR\overset{*}{F}F}$, $\mathrm{F\overset{*}{F}RF}$, and $\mathrm{R\overset{*}{F}FR}$, in which only one asymmetric center is involved. As shown in Table III, the value $\delta\nu$ of $\mathrm{FR\overset{*}{F}F}$ is comparable to that of $\mathrm{FR\overset{*}{F}R}$, though only one asymmetric center at α position is involved in the former. On the other hand, the value $\delta\nu$ of $\mathrm{F\overset{*}{F}RF}$ is much larger than that of $\mathrm{R\overset{*}{F}FR}$, although only β asymmetric carbons influence the resonances in question. These results are not well explained at present, but may be closely related to the conformational structures of the copolymer segments.

---

(8) R. C. Ferguson, *J. Amer. Chem. Soc.*, 82, 2416 (1960).

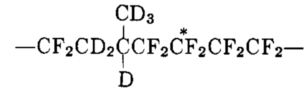
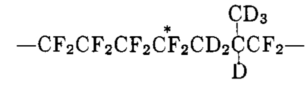
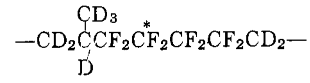
(9) The derivation of eq 8 is as follows:

$$\{\mathrm{FFR}\} = \{\mathrm{RFFR}\} + \{\mathrm{FFFR}\} = \{\mathrm{FFRF}\} + \{\mathrm{FFRR}\}$$

$$\{\mathrm{RFF}\} = \{\mathrm{RFFR}\} + \{\mathrm{RFFF}\} = \{\mathrm{FRFF}\} + \{\mathrm{RRFF}\}$$

where $\{\mathrm{FFRR}\} = \{\mathrm{RRFF}\} \simeq 0$ under the present condition.

Table III
Chemical Shift Difference between Geminal Fluorine Nuclei in Different Environments

Notation	Structure	60° H_4furan $\delta\nu$ (Hz)
$FR\overset{*}{F}F$	 $-CF_2CD_2\underset{D}{\overset{CD_3}{C}}CF_2\overset{*}{C}F_2CF_2CF_2-$	≃373
$F\overset{*}{F}RF$	 $-CF_2CF_2CF_2\overset{*}{C}F_2CD_2\underset{D}{\overset{CD_3}{C}}CF_2-$	≃241
$R\overset{*}{F}FR$	 $-CD_2\underset{D}{\overset{CD_3}{C}}CF_2\overset{*}{C}F_2CF_2CF_2CD_2-$	<80

The peaks assigned to $R\overset{*}{F}FR$ + $R\overset{*}{F}FF$ and $RF\overset{*}{F}R$ + $F\overset{*}{F}FR$ appear to have fine structures with poor resolution. These are probably due to "long-range" F–F couplings, which are known to sometimes make larger contributions than vicinal F–F couplings. This also accounts for the fact that $F\overset{*}{F}RF$ and $FR\overset{*}{F}F$ peaks are rather broad compared to other peaks.

C_3H_6-Rich Copolymer. The ^{19}F nmr spectra of C_3H_6-rich copolymers are shown in Figure 5. It is readily seen that new resonances appear between two multiplets centered at 118.6Φ* and 120.1Φ* and at the foot of the multiplet centered at 112.5Φ*. They increase in intensity with increasing C_3H_6 content. In the foregoing discussion, the spectra were interpreted in terms of tetrads, but the effect of γ substituents on chemical shifts did not appear so explicitly in the previous examples. For instance, in Figure 4 $R\overset{*}{F}FR$ seems to overlap $R\overset{*}{F}FF$, and $RF\overset{*}{F}R$ is not distinguished from $FF\overset{*}{F}R$. However, the explanation in terms of tetrad seems to be essential for the interpretation of the spectra of C_3H_6-rich copolymers. If only triads are taken into account, it is impossible to explain the spectral variation with increasing C_3H_6 content, since under the conditions for the preparation of the C_3H_6-rich copolymers, sequences with consecutive C_2F_4 units are not expected to be formed. Hence, the new resonances around 112.5Φ* and 119.3Φ* are assigned to $R\overset{*}{F}RR$ and $RR\overset{*}{F}R$, respectively. It would be predicted[8] that $R\overset{*}{F}RR$ and $RR\overset{*}{F}R$ should be at lower magnetic field than $R\overset{*}{F}RF$ and $FR\overset{*}{F}R$. This prediction seems to be valid for $R\overset{*}{F}RR$, but the situation is rather complicated in the case of $RR\overset{*}{F}R$. It is seen that the intensity of the resonance at 119.3Φ* is considerably lower than that of $R\overset{*}{F}RR$, as estimated by subtracting the area under the muliplet at 113.6Φ* from the area under the unresolved multiplet at 112.5Φ* whereas {RRFR} is found theoretically to be approximately equal to {RFRR} under the present condition. This discrepancy probably arises from partial overlapping of $RR\overset{*}{F}R$ with $FR\overset{*}{F}R$.

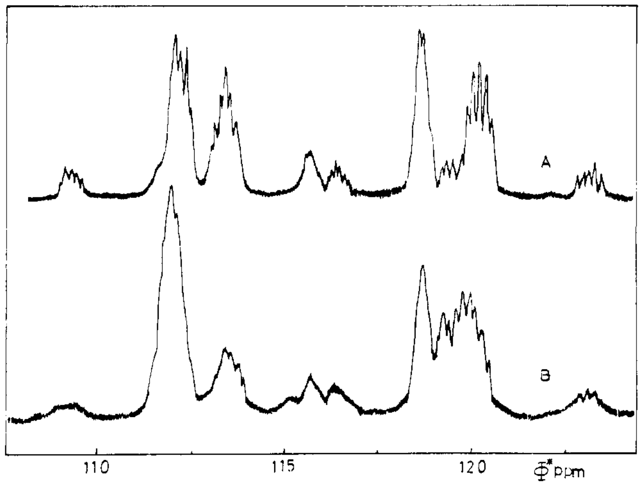
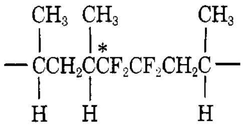


Figure 5. 94-MHz ^{19}F nmr spectra of C_3H_6-rich copolymers of C_2F_4 with C_3H_6: (A) C_2F_4 content ~40 mol %, 100°, dioxane; (B) C_2F_4 content ~35 mol %, 120°, tetrachloroethylene.

Since, three α, γ, and γ' asymmetric carbon atoms are involved in $RR\overset{*}{F}R$ structures, the resonances of this sequence may be expected to be divided into four portions corresponding to isotactic, syndiotactic, and two types of heterotactic, if the chemical shifts are large enough among the configurational structures. Unfortunately, further information has not been obtained because of the overlapping of the resonances.

$RR\overset{*}{F}R$



$$-\underset{H}{\overset{CH_3}{C}}CH_2\underset{H}{\overset{CH_3}{C}}\overset{*}{C}F_2CF_2CH_2\underset{H}{\overset{CH_3}{C}}- \quad (9)$$

The molecular weight of C_3H_6-rich copolymer tends to decrease with increasing C_3H_6 content and the M_n values of the samples measured by vapor pressure osmometry are in the range of 4000–10,000. Therefore, effects of end groups on the spectra are not expected to be serious.

It is interesting to note that the chemical shift differences $\delta\nu$ between geminal fluorine nuclei are much smaller in $R\overset{*}{F}RR$ than in $R\overset{*}{F}RF$, which shows that γ substituents as well as asymmetric centers greatly affect $\delta\nu$. Together with the results in Table III, this suggests that $\delta\nu$ is likely to increase with increasing number of CF_2 units in the sequences.

Acknowledgment. The authors thank Professor S. Fujiwara and Mr. M. Kunugi for their cooperation measuring the nmr spectra.