*Macromolecules* **1980**, *13*, 1630–1634

# Fluorine-19 Nuclear Magnetic Resonance of Tetrafluoroethylene–Olefin Terpolymers

**Kenkichi Ishigure,* Shojiro Watanabe, Yoneho Tabata, and Keichi Oshima**

*Department of Nuclear Engineering, University of Tokyo, Bunkyo-ku, Tokyo, Japan.*
*Received November 6, 1979*

ABSTRACT: $^{19}F$ NMR spectra of tetrafluoroethylene–ethylene–isobutylene, tetrafluoroethylene–propylene–isobutylene, and tetrafluoroethylene–ethylene–propylene terpolymers prepared with constant tetrafluoroethylene monomer concentrations (50–60 mol %) and varying olefin monomer charge ratios were measured. It was found that the fluorine spectra can be interpreted by means of tetrads and that the terpolymers have alternating tetrafluoroethylene and olefin units under the conditions used. On the basis of the NMR assignments, the monomer reactivity ratios were estimated.

We have shown in a series of papers[1-7] that $^{19}F$ NMR is a very powerful tool for the analysis of the structures of fluorine-containing copolymers. $^{19}F$ NMR made it possible to analyze the tetrad monomer sequences in tetrafluoroethylene–propylene and tetrafluoroethylene–isobutylene copolymers and indicated that both copolymers had highly alternating structures when prepared below room temperature within a certain range of monomer charage ratio.

In the present paper, we report the $^{19}F$ NMR spectra of the terpolymers of tetrafluoroethylene (TFE)–ethylene (E)–isobutylene (IB), TFE–IB–propylene (P), and TFE–E–P and show that these spectra give valuable information on the monomer sequences of these terpolymers.

## Experimental Section

All of the terpolymers were prepared by $\gamma$ irradiation of the monomer mixtures in glass ampules. The concentration of TFE in the monomer mixtures was chosen to be 50–60 mol % in order to produce highly alternating terpolymers of TFE and olefin. The monomer charge ratios were widely varied with respect to the olefins. The conversions were usually kept low (around 5%). When the terpolymers were prepared with TFE concentrations larger than 65 mol % or smaller than 45 mol %, the $^{19}F$ NMR spectra of the terpolymers showed resonances attributable to sequences with consecutive TFE or olefin monomer units, respectively. In some experiments deuterated olefins were used to prepare the terpolymers. Propylene-$d_6$ and isobutylene-$d_8$ were prepared by the dehydration of isopropyl alcohol-$d_8$ and *tert*-butyl alcohol-$d_{10}$, respectively, at 400 °C on $Al_2O_3$ catalyst, which was obtained by activation of aluminum hydroxide at 350 °C. $^{19}F$ NMR spectra were measured with a JEOL Model PS100 spectrometer operated at 94 MHz. Benzotrifluoride was used as an internal standard for fluorine, and chemical shifts on the $\phi^*$ (ppm) scale were evaluated by adding 63.7 ($\phi$ value of benzotrifluoride) to chemical shifts relative to benzotrifluoride.

## Results and Discussion

**Assignment of Spectra. 1. TFE–E–IB Terpolymer.** A typical $^{19}F$ NMR spectrum of TFE–E–IB terpolymer is shown in Figure 1, where five major resonance peaks together with three minor ones are numbered from low to high magnetic field. When the terpolymers were prepared with approximately constant tetrafluoroethylene concentrations (50–60 mol %) but widely varying ethylene/isobutylene ratios (2–8), no additional peaks appeared in the spectra, and peaks 2, 7, and 8 were always observed to be of very low intensity and especially weak at the high ethylene/isobutylene monomer charge ratio.

On the other hand, the five major peaks, 1, 3, 4, 5, and 6, change their relative intensities with varying ethylene/isobutylene monomer ratio. On the basis of this result and the NMR data of the TFE–olefin copolymers, the minor peaks, 2, 7, and 8, are assigned to the monomer sequences with more than two successive TFE units. It is assumed that under the present conditions the terpolymer has a highly alternating structure with respect to the TFE unit and either of the olefin units, ethylene or isobutylene; the olefin units are distributed at their sites according to the monomer charge ratio and the relative reactivities. The tetrad monomer sequences in the present terpolymer systems are analogous to those of TFE–olefin copolymers. The following notation is used for the eight tetrads relevant to the fluorine resonances in the present system: $-CF_2CH_2C(CH_3)_2CF_2{*}CF_2CH_2C(CH_3)_2-$, FIF*I; $-CF_2CH_2C(CH_3)_2CF_2{*}CF_2CH_2CH_2-$, FIF*E; $-CF_2CH_2CH_2CF_2{*}CF_2CH_2C(CH_3)_2-$, FEF*I; $-CF_2CH_2CH_2CF_2{*}CF_2CH_2CH_2-$, FEF*E; $-CH_2CH_2CF_2CF_2{*}CH_2CH_2CF_2-$, EF*EF; $-CH_2C(CH_3)_2CF_2CF_2{*}CH_2CH_2CF_2-$, IF*EF; $-CH_2CH_2CF_2CF_2{*}CH_2C(CH_3)_2CF_2-$, EF*IF; $-CH_2C(CH_3)_2CF_2CF_2{*}CH_2C(CH_3)_2CF_2-$, IF*IF.

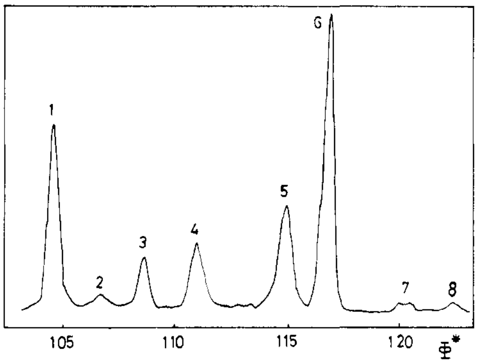

**Figure 1.** 94-MHz $^{19}F$ NMR spectrum of TFE–E–IB terpolymer prepared with 55 mol % tetrafluoroethylene monomer concentration and 3.5 ethylene/isobutylene monomer charge ratio. The measurement was carried out at 60 °C, using THF as solvent.

Here, the designations F, I, and E refer to the tetrafluoroethylene, isobutylene, and ethylene units, respectively. Of these eight tetrads, FEF*E and EF*EF are assumed to appear at the same position in the spectrum. Accordingly, seven resonance peaks may appear if the chemical shift differences are large enough to separate the resonance corresponding to these tetrads. However, these tetrads are responsible for only five peaks in Figure 1. This suggests superposition of the resonance peaks.

It is readily seen from the NMR data for the TFE–IB copolymer[3] that IF*IF and FIF*I contribute to resonance peaks 1 and 6, respectively. It is also known[3] that IF*II and IIF*I, if present, appear at magnetic fields 0.5 and 0.8 ppm lower than IF*IF and FIF*I, respectively. Neither of these resonances was observed, even when samples were prepared with lower ethylene/isobutylene monomer charge ratios. This result is quite consistent with the assumption

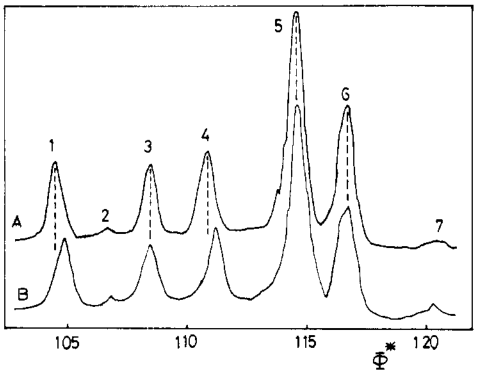

**Figure 2.** Comparison of $^{19}$F NMR spectra of TFE-E-IB and TFE-E-IB-$d_8$ terpolymers: (A) nondeuterated sample prepared with 58 mol % tetrafluoroethylene monomer concentration and 7.5 ethylene/isobutylene monomer charge ratio; (B) deuterated (IB-$d_8$) sample prepared with 57 mol % tetrafluoroethylene monomer concentration and 8.3 ethylene/isobutylene-$d_8$ monomer charge ratio. The measurement was carried out at 100 °C, using THF as solvent.

of an alternating structure for this terpolymer.

According to an empirical rule concerning the relation between chemical shifts and chemical structures of substituted fluorohydrocarbons,[8] the CF$_2$ resonances assigned to the eight tetrad sequences should appear from low to high magnetic field in the following order: IF*IF < IF*EF, EF*IF < EF*EF = FEF*E < FEF*I < FIF*E < FIF*I. It is not possible to determine from the empirical rule whether or not IF*EF will appear at higher magnetic field than EF*IF.

As is shown in Figures 1 and 2, resonance peak 5 increases in intensity for the sample prepared with the higher ethylene/isobutylene monomer charge ratio. Thus, it is inferred that a major contribution to peak 5 comes from EF*EF and FEF*E. It is anticipated from the sequence structures that the chemical shift differences between FIF*I and FIF*E and between FEF*I and FEF*E are very small, since only the substituents at the third neighboring carbon are different between these sequences. Thus, peaks 6 and 5 are assigned to FIF*I + FIF*E and FEF*I + FEF*E + EF*EF, respectively.

In Figure 2 the $^{19}$F NMR spectrum of the sample prepared with isobutylene-$d_8$ is compared with that of the nondeuterated sample. Since the vicinal F-D coupling is much smaller than the corresponding F-H coupling, it is expected that narrowing of the EF*IF and IF*IF peaks will occur when the IB units of EF*IF and IF*IF are deuterated. In Figure 2B the narrowing is not seen clearly, but resonance shifts of approximately 0.3-0.4 ppm to higher magnetic field relative to the other peaks are observed only with peaks 1 and 4. This is probably due to isotope shifts, which have been previously observed with the TFE-P-$d_6$ copolymer.[4] Thus, peaks 4 and 3 are assigned to EF*IF and IF*EF, respectively. The reason that the narrowing was not observed with peaks 1 and 4 may possibly be due to the high viscosity of the sample solution. The deuterated sample was prepared with the high ethylene/isobutylene charge ratio, which causes high molecular weight of the terpolymer and, consequently, high viscosity of the sample solution.

Finally, peak 2 is tentatively assigned to FIF*F according to the empirical chemical shift rule.

**2. TFE-P-IB Terpolymer.** In Figure 3 a typical $^{19}$F NMR spectrum of the TFE-P-IB terpolymer is compared with that of the TFE-P-IB-$d_6$ terpolymer. Twelve resonance peaks appear, as numbered in the figure. In this system the spectra are made more complicated by asymmetric centers introduced by the propylene units.

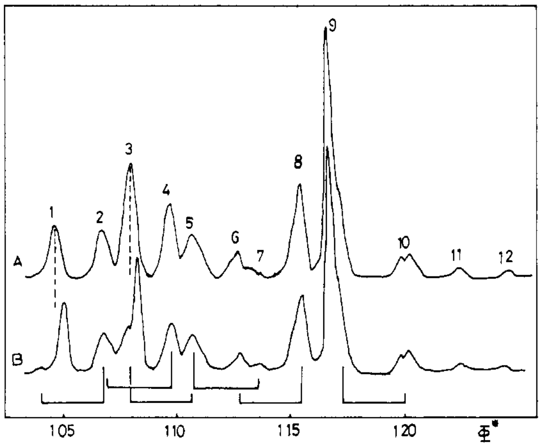

**Figure 3.** 94-MHz $^{19}$F NMR spectra of TFE-P-IB and TFE-P-IB-$d_8$ terpolymers: (A) nondeuterated sample prepared with 60 mol % tetrafluoroethylene monomer concentration and 6.9 propylene/isobutylene monomer charge ratio; (B) deuterated (IB-$d_8$) sample prepared with 60 mol % tetrafluoroethylene concentration and 6.0 propylene/isobutylene monomer charge ratio. The measurement was carried out at 60 °C, using THF as solvent.

Minor peaks 11 and 12 are assigned to the sequences with consecutive TFE monomer units. The resonances assigned to the sequences with consecutive isobutylene or propylene units were not observed in this system under the present conditions. Therefore, it is assumed that this ternary system also gives highly alternating TFE-olefin polymers, as was observed in the TFE-E-IB system.

Now the empirical rule concerning the chemical shifts of substituted fluorohydrocarbons mentioned above gives the order of the relevant tetrad resonances from low to high magnetic field as follows: IF*IF < PF*IF, IF*PF < PF*PF < FPF*P < FP*FI < FIF*P < FIF*I. Here the rule can tell nothing about the order between PF*IF and IF*PF. It is known from the $^{19}$F NMR data for the TFE-P copolymer[4] that both FPF*P and PF*PF show two partly overlapping AB quartets, some components of which have further fine structure. This arises from nonequivalence of geminal fluorine nuclei induced by the asymmetric carbons of the chains. It is readily seen from the data of the TFE-P copolymer that FPF*P corresponds to peaks 6, 8, 9, and 10. In the case of the TFE-P copolymer FPF*P comprises two sets of AB quartets, but here the resonances assigned to FPF*P are not well resolved. The reason will be described later. The central part of the AB quartets assigned to PF*PF corresponds to peaks 4 and 5, and the outer part overlaps somewhat with other peaks, as shown by the stick spectrum in Figure 3B. Peak 1 is assigned to IF*IF, and FIF*I makes a contribution to peak 9. If it is recalled that the chemical shift difference between FIF*I and FIF*P is small, it is reasonable to assume that FIF*P makes a contribution to peak 9, overlapping with FIF*I. It will be difficult for the same reason to differentiate FPF*I from FPF*P. Thus, FPF*I is considered to overlap FPF*P, appearing as an AB quartet. This is probably the reason that the resonances assigned to FPF*P are not as well resolved as in the TFE-P copolymers.

Now PF*IF and IF*PF remain unassigned. If the spectrum of the deuterated sample (TFE-P-IB-$d_8$) is compared closely with that of the nondeuterated one, it is readily seen that narrowing and relatively high-field shifts take place with peaks 1 and 3 in the former spectrum. Thus, peak 3 is assigned to PF*IF. It is apparent in the spectrum of the deuterated sample that peak 3 is

Table I
Tentative Assignment of the $^{19}$F Spectrum of TFE-P-IB Terpolymer

| peak no. | pattern | assignment |
|---|---|---|
| 1 | singlet | IF*IF |
| 2, 3 | central part of AB quartet | IF*PF |
| 3 | singlet | PF*IF |
| 4, 5 | central part of AB quartet | PF*PF |
| 6, 8, 9, 10 | AB quartet | FPF*P + FPF*I |
| 9 | singlet | FIP*I + FIF*P |

Table II
Tentative Assignment of the $^{19}$F Spectra of TFE-E-P Terpolymer

| peak no. | pattern | assignment |
|---|---|---|
| 1, 2, 3 | part of AB quartet | PF*PF |
| 4 | singlet | PF*EF |
| 5, 6 | central part of AB quartet | EP*PF |
| 7 | singlet | EF*EF + FEF*E |
| 5, 7, 8, 9 | AB quartet | FPF*P |

composed of two components. It is therefore tentatively assumed that IF*PF appears as an AB quartet, of which the central part corresponds to peaks 2 and 3 and the outer part is somewhat overlapping, as shown by the stick spectrum in Figure 3B.

The tentative assignment mentioned above is summarized in Table I.

**3. TFE–E–P Terpolymer.** Figure 4 compares a typical $^{19}$F NMR spectrum of a TFE–E–P terpolymer with that of a TFE–E–P-$d_6$ terpolymer.

It is assumed, as in the previous cases, that this terpolymer has a highly alternating structure with respect to TFE and either of the olefins, ethylene or propylene. The order of the chemical shifts for resonances assigned to the relevant eight tetrads, according to the empirical rules, is as follows: PF*PF < PF*EF, EF*PF < EF*EF = FEF*E < FEF*P < FPF*E < FPF*P.

It is seen from the NMR data for the TFE–P copolymers that resonances 2 and 3 correspond to the central part of the AB quartets assigned to PF*PF and that resonances 9 and 8 and parts of 7 and 5 are attributable to FPF*P.

The lower field part of the group of resonances designated 8 has a higher intensity than the higher field part of 8 and does not show any fine structure, while in the TFE–P copolymer the former is approximately equal in intensity to the latter and splits into a triplet in the nondeuterated sample and into a doublet in the deuterated sample. This is due to the partial superposition of FPF*E on FPF*P. Thus, the lower field parts of resonances 8 and 9 include the higher field half of an AB quartet assigned to FPF*E. The lower field half of FPF*E is probably merged in resonances 7 and 5. It is found from comparison with the spectrum of the TFE–E–IB terpolymer that resonance 7 includes EF*EF, FEF*E, and, probably, FEF*P.

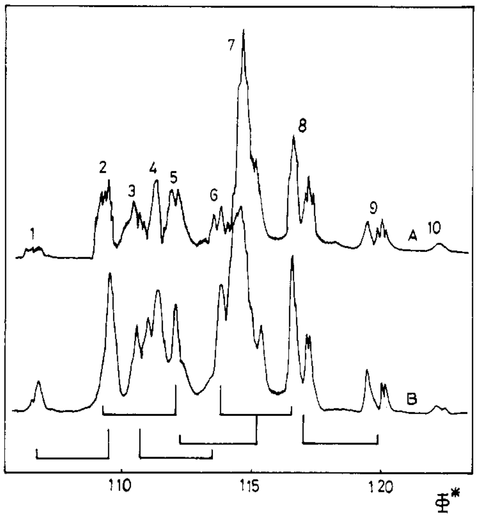

**Figure 4.** 94-MHz $^{19}$F NMR spectra of TFE–E–P and TFE–E–P-$d_8$ terpolymers: (A) nondeuterated sample prepared with 50 mol % tetrafluoroethylene monomer concentration and 1.0 ethylene/propylene monomer charge ratio; (B) deuterated (P-$d_6$) sample prepared with 53 mol % tetrafluoroethylene monomer concentration and 1.1 ethylene/propylene-$d_6$ monomer charge ratio. The measurement was carried out at 60 °C, using THF as solvent.

It is to be noted that resonances 5 and 6 become singlets in the deuterated sample and that peak 4 remains unchanged by deuteration. Therefore, peak 4 is assigned to PF*EF, and resonances 5 and 6 are assigned to the central part of the AB quartet of EF*PF.

The above tentative assignment is summarized in Table II.

**4. Chemical Shifts of Fluorohydrocarbon Chains.** In the previous sections assignments are given to the fluorine resonances related to the eighteen tetrad sequences of the "alternating" TFE–E–I, TFE–P–I, and TFE–E–P terpolymers. It is worthwhile to make comparisons among the chemical shifts of these resonances. Two series of comparisons are shown in Tables III and IV. It is to be noted that the chemical shifts change regularly, corresponding to the variation of the sequence structures. When the sequence structures are represented as shown in 1, the successive substitution of hydrogen at the X

$$-CH_2C(X_1)(X_2)CF_2CF_2{*}CH_2C(Y_1)(Y_2)CF_2-$$
1

position for the methyl group shifts the central $CF_2$ resonance toward lower magnetic field by approximately 3 ppm, while substitution of hydrogen at the Y position gives a 1.5–2-ppm low-field shift for the $CF_2$ resonance. This close correlation between the chemical shifts and the sequence structures may justify the tentative assignment of the resonances mentioned above.

Table III
Chemical Shifts of Tetrad Sequences

| sequence structure | notation | pattern | $\phi^*$ | $\Delta\phi^*$ |
|---|---|---|---|---|
| $-CH_2CH_2CF_2CF_2{*}CH_2CH_2CF_2-$ | EF*EF | singlet | 114.4 | |
| $-CH_2CH(CH_3)CF_2CF_2{*}CH_2CH_2CF_2-$ | PF*EF | singlet | 111.2 | 3.2 |
| $-CH_2C(CH_3)_2CF_2CF_2{*}CH_2CH_2CF_2-$ | IF*EF | singlet | 108.6 | 2.6 |
| $-CH_2CH_2CF_2CF_2{*}CH_2CH(CH_3)CF_2-$ | EF*PF | AB quartet | 112.8 | |
| $-CH_2CH(CH_3)CF_2CF_2{*}CH_2CH(CH_3)CF_2-$ | PF*PF | AB quartet | 109.8 | 3.0 |
| $-CH_2C(CH_3)_2CF_2CF_2CH_2CH(CH_3)CF_2-$ | IF*PF | AB quartet | 107.1 | 2.7 |
| $-CH_2CH_2CF_2CF_2{*}CH_2C(CH_3)_2CF_2-$ | EF*IF | singlet | 110.9 | |
| $-CH_2CH(CH_3)CF_2CF_2{*}CH_2C(CH_3)_2CF_2-$ | PF*IF | singlet | 107.7 | 3.2 |
| $-CH_2C(CH_3)_2CF_2CF_2{*}CH_2C(CH_3)_2CF_2-$ | IF*IF | singlet | 104.6 | 3.1 |

Table IV
Chemical Shifts of Tetrad Sequences

| sequence structure | notation | pattern | $\phi^*$ | $\Delta\phi^*$ |
|---|---|---|---|---|
| $-CH_2CH_2CF_2CF_2{}^*CH_2CH_2CF_2-$ | EF*EF | singlet | 114.4 | |
| $-CH_2CH_2CF_2CF_2{}^*CH_2CH(CH_3)CF_2-$ | EF*PF | AB quartet | 112.8 | 1.6 |
| $-CH_2CH_2CF_2CF_2{}^*CH_2C(CH_3)_2CF_2-$ | EF*IF | singlet | 110.9 | 1.9 |
| $-CH_2CH(CH_3)CF_2CF_2{}^*CH_2CH_2CF_2-$ | PF*EF | singlet | 111.2 | |
| $-CH_2CH(CH_3)CF_2CF_2{}^*CH_2CH(CH_3)CF_2-$ | PF*PF | AB quartet | 109.8 | 1.4 |
| $-CH_2CH(CH_3)CF_2CF_2{}^*CH_2C(CH_3)_2CF_2-$ | PF*IF | singlet | 107.7 | 2.1 |
| $-CH_2C(CH_3)_2CF_2CF_2{}^*CH_2CH_2CF_2-$ | IF*EF | singlet | 108.6 | |
| $-CH_2C(CH_3)_2CF_2CF_2{}^*CH_2CH(CH_3)CF_2-$ | IF*PF | AB quartet | 107.1 | 1.5 |
| $-CH_2C(CH_3)_2CF_2CF_2{}^*CH_2C(CH_3)_2CF_2-$ | IF*IF | singlet | 104.6 | 2.5 |

Table V
Chemical Shift Difference between Nonequivalent Geminal Fluorine Nuclei in the Tetrads of Type 3

| sequence structure | $\Delta\nu$[a] |
|---|---|
| $-CH_2CH_2CF_2CF_2{}^*CH_2CH(CH_3)CF_2-$ | 3.4 |
| $-CH_2CH(CH_3)CF_2CF_2{}^*CH_2CH(CH_3)CF_2-$ | 2.6 |
| $-CH_2C(CH_3)_2CF_2CF_2{}^*CH_2CH(CH_3)CF_2-$ | 2.7 |

[a] In ppm.

It is interesting to note that in tetrad sequences of type 3, where one of the second neighboring carbons is asym-

$$-CH_2CH(CH_3)CF_2CF_2{}^*CH_2C(Y)_2CF_2-$$

2

$$-CH_2C(X)_2CF_2CF_2{}^*CH_2CH(CH_3)CF_2-$$

3

etric, the central geminal fluorine nuclei are always nonequivalent, whereas they are apparently equivalent in type 2. This is inferred to be probably due to the difference in the conformation of the sequences, but further explanation is not possible at present. Table V summarizes the chemical shift differences between the nonequivalent nuclei in the tetrads of type 3.

**5. Monomer Reactivity Ratios.** On the basis of the above assignments it is possible to determine the monomer reactivity ratios in the present terpolymerization systems. It is assumed that a first-order Markov process is applicable to the present terpolymerization processes

$$X\cdot + Y \xrightarrow{k_{X/Y}} \sim\!\sim Y\cdot \tag{1}$$

A transition probability $P_{X/Y}$ is defined as the probability of the transition of a terminal radical X to a terminal radical Y by addition to a monomer Y. Accordingly, $P_{X/Y}$ is expressed by eq 2, where $k_{A/B}$ refers to the rate constant

$$P_{X/Y} = \frac{k_{X/Y}M_Y}{k_{X/X}M_X + k_{X/Y}M_Y + k_{X/Z}M_Z} \tag{2}$$

for the addition reaction of a terminal radical A to a monomer B and $M_A$ refers to the concentration of A in the monomer mixture. It is assumed that in all three systems there are no sequences with consecutive olefin units under the present conditions. Thus, relations 3–6 are obtained.

$$P_{E/E} = P_{E/P} = P_{E/I} = 0 \tag{3}$$

$$P_{P/E} = P_{P/P} = P_{P/I} = 0 \tag{4}$$

$$P_{I/E} = P_{I/P} = P_{I/I} = 0 \tag{5}$$

$$P_{E/F} = P_{P/F} = P_{I/F} = 1 \tag{6}$$

In each system the following relationships are used to estimate the reactivity ratios.

Table VI
Monomer Contents and Reactivity Ratios[a] Calculated from NMR Data for TFE-E-I Terpolymers

| | sample no. | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| $M_F$ | 0.51 | 0.53 | 0.55 | 0.57 |
| $M_E/M_I$ | 1.9 | 2.2 | 3.5 | 8.3 |
| {E} | 0.11 | 0.10 | 0.16 | 0.27 |
| {I} | 0.39 | 0.37 | 0.33 | 0.23 |
| {F} | 0.50 | 0.52 | 0.51 | 0.50 |
| $k_{F/I}/k_{F/E}$ | 13.9 ± 1.2 | 11.2 ± 1.2 | 12.8 ± 1.2 | 11.5 ± 1.2 |

[a] A rough measure of error level based on the error estimation of the components in eq 7.

**i. TFE–E–I System.**

$$\frac{I_1}{I_3} = \frac{\mathrm{IFIF}}{\mathrm{IFEF}} = \frac{\{\mathrm{I}\}P_{I/F}P_{F/I}P_{I/F}}{\{\mathrm{I}\}P_{I/F}P_{F/E}P_{E/F}} = \frac{P_{F/I}}{P_{F/E}} = \frac{k_{F/I}M_I}{k_{F/E}M_E} \tag{7}$$

$$\frac{I_4}{I_1} = \frac{\mathrm{EFIF}}{\mathrm{IFIF}} = \frac{\{\mathrm{E}\}}{\{\mathrm{I}\}} \tag{8}$$

$$\frac{I_6 + I_2}{I_1} = \frac{\mathrm{FIFI} + \mathrm{FIFE} + \mathrm{FIFF}}{\mathrm{IFIF}} = \frac{\{\mathrm{F}\}}{\{\mathrm{I}\}} \tag{9}$$

Here, {E}, {I}, and {F} refer to the monomer contents in the terpolymers and $I_i$ stand for the intensities of the corresponding resonance peaks in the spectra.

Table VI summarizes the monomer contents and the reactivity ratios calculated by the above relations together with the monomer charge ratios. It is seen that the addition of isobutylene to the terminal tetrafluoroethylene radical is approximately 12 times faster than that of ethylene.

**ii. TFE–P–IB System.** In this system, relationships 10–12 are used to calculate the reactivity ratios independently.

$$\frac{\mathrm{IFIF}}{\mathrm{IFPF}} = \frac{P_{F/I}}{P_{F/P}} = \frac{k_{F/I}M_I}{k_{F/P}M_P} \tag{10}$$

$$\frac{\mathrm{PFIF}}{\mathrm{PFPF}} = \frac{P_{F/I}}{P_{F/P}} \tag{11}$$

$$\frac{\mathrm{FIFI} + \mathrm{FIFP}}{\mathrm{FPFP} + \mathrm{FPFI}} = \frac{(P_{F/I})^2 + P_{F/I}P_{F/P}}{(P_{F/P})^2 + P_{F/P}P_{F/I}} = \frac{P_{F/I}}{P_{F/P}} \tag{12}$$

It is not straightforward to estimate the relative intensities of some resonances because of the severe overlapping of the resonances in this system. The procedures for estimating the intensities of the overlapping resonances used above are as follows: $W = I_2 - 0.15I_4$, IFPF = $2W \times 1.16$, IFIF = $I_1 - 0.16W$; PFIF = $I_3 - W$, PFPF = $1.15(I_4 + I_5$

Table VII
Monomer Reactivity Ratios[a] Calculated from NMR Data for TFE-P-IB Terpolymers

| | sample no. | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| $M_F$ | 0.60 | 0.62 | 0.60 | 0.53 |
| $M_P/M_I$ | 2.8 | 6.0 | 6.9 | 9.8 |
| $k_{F/I}/k_{F/P}$ | | | | |
| eq 10 | 3.5 ± 0.4 | 3.8 ± 0.4 | 3.4 ± 0.4 | 2.9 ± 0.4 |
| eq 11 | 2.8 ± 0.4 | 3.7 ± 0.4 | 3.1 ± 0.4 | 2.9 ± 0.4 |
| eq 12 | 3.2 ± 0.3 | 3.7 ± 0.3 | 3.2 ± 0.3 | 3.1 ± 0.3 |

[a] A rough measure of error level based on the error estimation of the components in each equation.

Table VIII
Monomer Reactivity Ratios[a] Calculated from NMR Data for TFE-E-P Terpolymers

| | sample no. | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| $M_F$ | 0.50 | 0.50 | 0.50 | 0.50 |
| $M_E/M_P$ | 0.33 | 0.50 | 1.0 | 3.0 |
| $k_{F/P}/k_{F/E}$ | 3.2 ± 0.5 | 2.7 ± 0.5 | 2.8 ± 0.5 | 4.0 ± 0.5 |

[a] A rough measure of error level based on the error estimation of the components in eq 13.

$- 0.16W)$, FPFP + FPFI = $2(I_6 + I_8)$, FIFI + FIFP = $I_9 - I_8$. Here, $I_i$ refer to the intensities of the corresponding peaks in the spectra and $W$ corresponds to the intensity of half of the central doublet assigned to IF*PF. The coefficients 0.15 and 0.16 are the calculated intensity ratios of the outer peak to the central one for the AB quartets assigned to PF*PF and IF*PE, respectively.

Table VII lists the monomer reactivity ratios obtained in the three procedures. The values are in quite good agreement among the procedures.

**iii. TFE–E–P Terpolymer.** Because of more severe overlapping of the resonances, only one relation (eq 13) is used for the calculation of the reactivity ratio.

$$\frac{\text{PFPF}}{\text{PFEF}} = \frac{P_{F/P}}{P_{F/E}} = \frac{k_{F/P}M_P}{k_{F/E}M_E} \tag{13}$$

$$\text{PFEF} = I_4$$

$$\text{PFPF} = 2[I_1 + I_2 - (I_5 - I_9) \times 0.22]$$

Here the coefficient 0.22 is the calculated intensity ratio of the outer peak to the central one for the AB quartet assigned to EF*PF.

Table VIII summarizes the monomer reactivity ratios together with the monomer charge ratios. If the average values in Tables VII an VIII are used for $k_{F/I}/k_{F/P}$ and $k_{F/P}/k_{F/E}$, the value of 10.6 is obtained for the product of those

$$k_{F/I}/k_{F/E} = (k_{F/I}/k_{F/P}) \times (k_{F/P}/k_{F/E}) = 3.3 \times 3.2 = 10.6$$

This is in fairly good agreement with the values in Table IV, if the errors involved and assumptions used in the NMR analysis are taken into account.

## References and Notes

(1) Ishigure, K.; Tabata, Y.; Oshima, K. *Macromolecules* **1970**, *3*, 27.
(2) Ishigure, K.; Tabata, Y.; Oshima, K. *Polym. J.* **1971**, *2*, 321.
(3) Ishigure, K.; Tabata, Y. *Macromolecules* **1970**, *3*, 450.
(4) Ishigure, K.; Tabata, Y.; Oshima, K. *Macromolecules* **1973**, *6*, 584.
(5) Ishigure, K.; Tabata, Y.; Oshima, K., *Macromolecules* **1975**, *8*, 177.
(6) Ishigure, K.; Ohashi, H.; Tabata, Y.; Oshima, K. *Macromolecules* **1976**, *9*, 290.
(7) Ishigure, K.; Ohashi, H.; Tabata, Y.; Oshima, K. *Macromolecules* **1977**, *10*, 567.
(8) Ferguson, R. C. *J. Am. Chem. Soc.* **1960**, *82*, 2416.