Fluorine-19 Nuclear Magnetic Resonance of Trifluoroethylene–Isobutylene Copolymers Prepared by γ-Ray Induced Copolymerization. Head-to-Head and Tail-to-Tail Structures

Kenkichi Ishigure,* Hirotada Ohashi, Yoneho Tabata, and Keichi Oshima

Department of Nuclear Engineering, University of Tokyo, Tokyo, Japan.

Received October 28, 1976

ABSTRACT: ^{19}F-NMR spectra were measured of trifluoroethylene–isobutylene copolymers and their deuterated compounds were prepared by γ-ray induced copolymerization. The CF_2 resonances of the copolymer samples having excess trifluoroethylene concentration are too complicated to interpret, and the assignments were made only with the samples having approximately equimolar concentration. The CF_2 resonances were interpreted in terms of tetrads, while the CFH resonances were interpreted in terms of triads. It was found that abnormal head-to-head and tail-to-tail structures amount to approximately 50% in the copolymers, and it was inferred from this result that a growing radical with a terminal isobutylene unit adds to trifluoroethylene almost in a random direction in the course of the polymerization. Terminal groups of types CF_2H and CF_3 were observed to be present in the copolymers, and the mechanism for the formation of these terminal groups was discussed.

In a series of papers[1-7] we have shown that ^{19}F NMR gives useful information on the structure of fluorine-containing copolymers such as monomer sequence distribution and configurational and conformational structures of copolymers. As is well known, chemical shifts of fluorine nuclei are so large in comparison with proton chemical shifts that ^{19}F NMR is quite useful for detecting and analyzing abnormal "head-to-head and tail-to-tail" structures in polymers. As early as 1960, Naylor and Lasoski[8] detected the presence of head-to-head and tail-to-tail structures in poly(vinylidene fluoride) by ^{19}F NMR. This was followed by the detailed work of Wilson and Santee.[9] Ferguson[10] investigated the structure of vinylidene fluoride–hexafluoropropylene copolymers by ^{19}F NMR and found the existence of similar abnormal structures in these copolymers. It was reported by Lawson et al.[11] that ^{19}F NMR of trifluoronitrosomethane–tetrafluoroethylene copolymer shows the presence of abnormal structures caused by irregular addition of trifluoronitrosomethane to tetrafluoroethylene terminal unit. In the present paper, ^{19}F-NMR spectra were measured of trifluoroethylene–isobutylene copolymers and their deuterated compounds, and it was found that a large amount of head-to-head and tail-to-tail structure is present in the copolymers.

Experimental Section

Trifluoroethylene was prepared by debromochlorination of 1-bromo-2-chlorotrifluoroethane (Showa Denko Co.) with zinc dust in ethanol at about 80 °C.[12] Trifluoroethylene-d_1 was synthesized as follows: chlorotrifluoroethylene was prepared by the treatment of 1,1,2-trichlorotrifluoroethane with zinc dust in ethanol. Deuterium bromide (Canada Merck Co.) was added to chlorotrifluoroethylene, under the exposure of UV light from an ultrahigh pressure mercury lamp in a Pyrex high-pressure vessel,[13] to obtain 1-bromo-2-chlorotrifluoroethane-d_1. This material was converted to trifluoroethylene-d_1 according to the procedure mentioned above.

$$CF_2ClCFCl_2 \xrightarrow[Zn]{} CF_2{=}CFCl \xrightarrow[DBr]{h\nu} CF_2BrCFDCl \xrightarrow[Zn]{} CF_2{=}CFD$$

Isobutylene-d_8 was synthesized by dehydration of *tert*-butyl-d_8 alcohol (Canada Merck Co.) at about 400 °C over Al_2O_3. The Al_2O_3 was prepared from aluminum hydroxide that had been prepared by the neutralization of aqueous aluminum sulfate with potassium hydroxide. Trifluoroethylene-d_1 and isobutylene-d_8 were found to contain about 10 and 8% of hydrogen, respectively, by means of mass spectroscopy.

All copolymer samples were obtained by γ-ray initiated polymerizations of monomer mixtures, and copolymer compositions were determined from elemental analysis. The monomer reactivity ratios of this system were found to be 0.02 for trifluoroethylene and 0.7 for isobutylene at 30 °C.[14] These values show that in this system the copolymers obtained are not so highly alternating as in the previous systems.[1-7] In the present paper, we are concerned mainly with copolymer samples having an approximately equimolar composition. These were prepared from monomer mixtures containing approximately 83 mol % trifluoroethylene.

^{19}F-NMR spectra were measured with a JEOL Model PS100 spectrometer operated at 94 MHz in the temperature range of 60 to 120 °C. Benzo trifluoride was used as solvent or as internal reference standard, and chemical shifts are expressed in terms of Φ^* values (ppm) evaluated by the addition of 63.7 (Φ value of benzo trifluoride) to the chemical shift of the relevant resonance relative to benzo trifluoride.

Results and Discussion

(1) CF_2 Resonances. A typical ^{19}F-NMR spectrum of an approximately 50:50 trifluoroethylene–isobutylene copolymer is shown for the CF_2 region in Figure 1. It is peculiar that the spectrum is very complicated in comparison with the spectrum of an alternating chlorotrifluoroethylene–isobutylene copolymer,[6] which is considered to be a homologue of the present copolymer. The main resonance peaks are numbered from low to high magnetic field as indicated in Figure 1. Out of the 16 peaks, peaks 1, 3, and 5, as well as the weak peaks between 11 and 12, seem to be due to nonalternating sequences since their intensities are weak when the copolymers have a nearly 50:50 composition. Peak 16 is rather sharp compared with the other resonances, and shows a marked dependence on the condition of the sample preparation, especially, the polymerization temperature and the monomer feed ratio.

Hence, 12 peaks, 2, 4, 6, 7, 8, 9, 10, 11, 12, 13, 14, and 15, are closely related to the CF_2 resonances of alternating sequences of the copolymer. The following relation among the line separations suggests that the 12 peaks are composed of three sets of AB type quartets, Q_1, Q_2, and Q_3.

$$4 - 2 = 7 - 6 = 2.8 \text{ ppm}$$

$$10 - 8 = 14 - 12 = 2.9 \text{ ppm}$$

$$11 - 9 = 15 - 13 = 2.9 \text{ ppm}$$

Q_1: 2, 4, 6, and 7

Q_2: 8, 10, 12, and 14

Q_3: 9, 11, 13, and 15

The 56.4-MHz ^{19}F-NMR spectrum of the copolymer was found to support the above assignment. As in the case of chlorotrifluoroethylene–isobutylene copolymers, two geminal F nuclei are considered to be nonequivalent in this copolymer

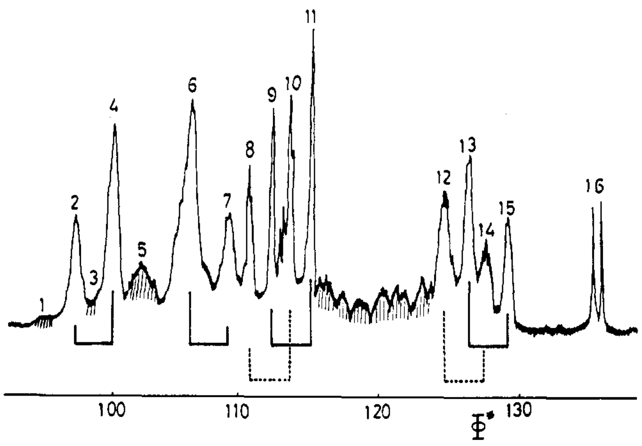


Figure 1. CF_2 part of ^{19}F-NMR spectrum of approximately 50:50 trifluoroethylene–isobutylene copolymer:solvent = benzo trifluoride, 60 °C.

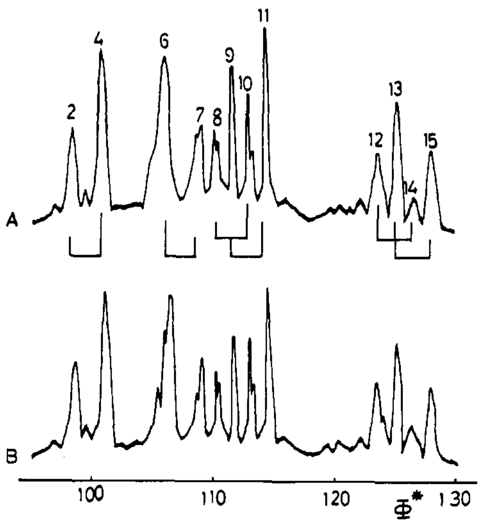


Figure 2. CF_2 part of ^{19}F-NMR spectra of deuterated trifluoroethylene–isobutylene copolymers with approximately 50:50 composition in benzo trifluoride at 60 °C: (A) a copolymer of trifluoroethylene-d_1 and isobutylene; (B) a copolymer of trifluoroethylene-d_1 and isobutylene-d_8.

owing to the presence of asymmetric groups in the main chain.

However, it should be noted that of these three quartets the most downfield one is separated by about 17 ppm from the most upfield one. This chemical shift difference between two CF_2 resonances is too large to be explained in terms of differences in stereochemical environments of the CF_2 groups. Therefore, in order to interpret the CF_2 resonances of the copolymer, it seems essential to consider abnormal bonding structures, such as head-to-head and tail-to-tail structures. Since these abnormal structures were found, as already mentioned, in the polymers of vinyl fluoride and vinylidene fluoride, it is reasonable to consider that abnormal addition reactions occur in the copolymerization of trifluoroethylene.

Now it is assumed that isobutylene adds in the usual head-to-tail fashion to a terminal radical in the course of the copolymerization reaction. This assumption will be justified by the fact that any unusual bonding structure is not observed either in chlorotrifluoroethylene–isobutylene[1,2,6] or tetrafluoroethylene–isobutylene copolymers.[3] Thus, four alternating types of sequences with central trifluoroethylene units are considered in terms of tetrads, as shown below.

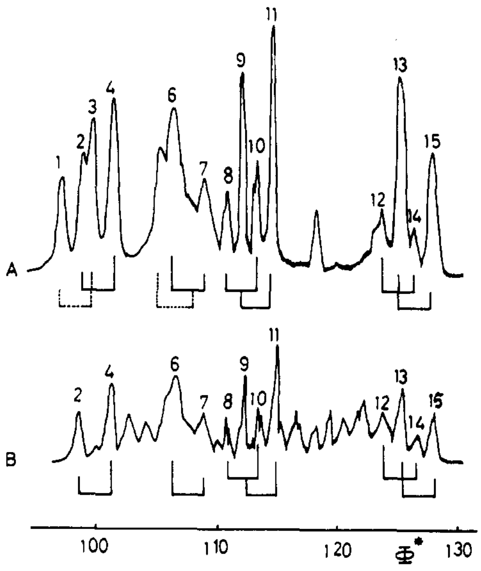
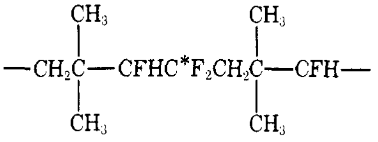
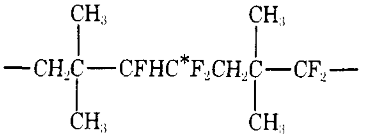


Figure 3. (A) CF_2 part of ^{19}F-NMR spectrum of isobutylene rich copolymer:solvent = benzo trifluoride, 60 °C. (B) CF_2 part of ^{19}F-NMR spectrum of trifluoroethylene rich copolymer:solvent = benzo trifluoride, 100 °C.



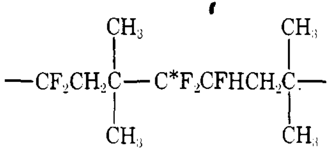
$$-CH_2\overset{CH_3}{\underset{CH_3}{C}}-CFHC^*F_2CH_2\overset{CH_3}{\underset{CH_3}{C}}-CFH-$$

IN*IN



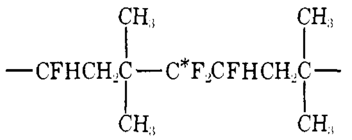
$$-CH_2\overset{CH_3}{\underset{CH_3}{C}}-CFHC^*F_2CH_2\overset{CH_3}{\underset{CH_3}{C}}-CF_2-$$

IN*IA



$$-CF_2CH_2\overset{CH_3}{\underset{CH_3}{C}}-C^*F_2CFHCH_2\overset{CH_3}{\underset{CH_3}{C}}-$$

NIA*I



$$-CFHCH_2\overset{CH_3}{\underset{CH_3}{C}}-C^*F_2CFHCH_2\overset{CH_3}{\underset{CH_3}{C}}-$$

AIA*I

Here $-CFHCF_2-$ and $-CF_2CFH-$ units arising from the addition of a terminal radical to trifluoroethylene on CFH and CF_2, respectively, are expressed by N and A, and I refers to an isobutylene unit which adds to terminal radicals in the usual head-to-tail fashion.

According to an empirical rule concerning the relation between chemical shifts and chemical structures of substituted fluorohydrocarbons,[10] the CF_2 resonances assigned to the above four sequences should appear from low to high magnetic field in the following order.

$$IN^*IN < IN^*IA < AIA^*I < NIA^*I$$

The chemical shift differences between the CF_2 resonances of two groups of the sequences, one containing N* and another containing A*, are considered to be rather large, because the

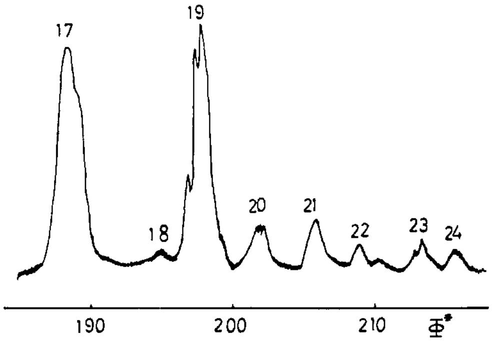


Figure 4. CFH part of ^{19}F-NMR spectrum of approximately 50:50 trifluoroethylene-isobutylene copolymer:solvent = benzo trifluoride, 60 °C.

substituents are different with three positions (1, 2, and $\bar{2}$) of four neighboring and next neighboring carbons. Therefore, two quartets, Q_2 and Q_3, at higher magnetic fields are tentatively assigned to AIA*I and NIA*I, respectively. The downfield quartet Q_1 is rather broad compared with Q_2 and Q_3, and is assigned to IN*IA + IN*IN with poor resolution.

In Figure 2 are shown the CF_2 parts of ^{19}F-NMR spectra of deuterated copolymers which were prepared approximately under the same condition as the sample used in Figure 1. The upfield quartets, Q_2 and Q_3, are seen to be subject to no marked change by the deuteration of isobutylene unit as expected from the structure. The low-field quartet, Q_1, on the other hand, is narrower in the spectrum of the isobutylene-d_8 copolymer than in the spectrum of the isobutylene copolymers and its fine structure is better defined. This is considered to result from a decrease in the vicinal F-H coupling constants in IN*IN and IN*IA. This result seems to support the tentative assignment given above.

In Figure 3 are indicated the CF_2 parts of ^{19}F-NMR spectra of trifluoroethylene-isobutylene copolymers that contain excess isobutylene and excess trifluoroethylene. The spectrum of the isobutylene-rich copolymer (A in Figure 3) is appreciably different from the spectrum in Figure 1. With increasing content of isobutylene in the copolymer, peaks 1 and 3 increase in intensity with corresponding shoulders at about $105\Phi^*$ and $108\Phi^*$, and it is readily found that these four components make an AB type quartet, which is tentatively assigned to IN*II.

It should be noted that in Figure 3A the intensity ratio of the quartet Q_3 to Q_2 is much higher than in Figure 1. Thus, it is readily inferred that the quartet Q_3 comprises two components fortuitously overlapping each other. One component is NIA*I as was mentioned earlier, and the other is tentatively assigned to IIA*I.

The spectrum of the trifluoroethylene-rich copolymer is quite complicated, including many peaks appearing with increasing trifluoroethylene content as shown in Figure 3B. These extra resonance peaks are considered to be due to copolymer sequences having two or more successive trifluoroethylene units. It is, however, quite difficult at present to assign these peaks. Therefore, in the present paper we are concerned mainly with the NMR spectra of the approximately alternating copolymers in which the extra resonances are quite low in intensity.

(2) CFH Resonances. In Figure 4 is shown the CFH part of ^{19}F-NMR spectrum of approximately 50:50 trifluoroethylene-isobutylene copolymer. At least eight multiplets are seen as numbered in spectrum A. The five upfield peaks, 20, 21, 22, 23, and 24, increase in intensity with increasing trifluoroethylene contents, while peak 18 is most intense in the spectrum of the isobutylene-rich copolymer. Therefore, peaks 17 and 19 are assigned to alternating sequences of monomer units. The CFH resonances are rather broad with poor separation of the peaks, suggesting the overlap of resonances. Therefore, we will try to explain the CFH resonances in terms of triads at first. If we consider only the alternating triad sequences, two sequences shown below are closely related to the resonances under consideration. Accordingly, CFH resonance of the alternating copolymer is expected to split into two components with appreciable chemical shift difference.

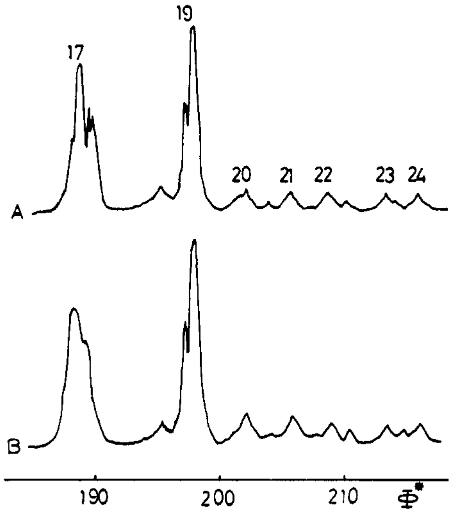
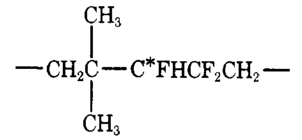
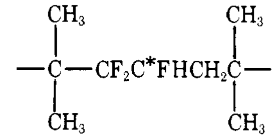


Figure 5. CFD part of ^{19}F-NMR spectra of deuterated copolymers: (A) trifluoroethylene-d_1-isobutylene-d_8 copolymer; (B) trifluoroethylene-d_1-isobutylene copolymer.



$-CH_2\overset{CH_3}{\underset{CH_3}{C}}-C^*FHCF_2CH_2-$

IN*I



$-\overset{CH_3}{\underset{CH_3}{C}}-CF_2C^*FHCH_2\overset{CH_3}{\underset{CH_3}{C}}-$

IA*I

If the CFH parts of the deuterated copolymers in Figure 5 are compared closely, it will be readily seen that peak 17 in the spectrum A is markedly narrowed and well resolved in comparison with the one in spectrum B, while peak 19 is not changed. The narrowing of peak 17 in spectrum A is considered to arise from the decrease in vicinal F-H coupling by deuteration of isobutylene units. Thus, peaks 17 and 19 are assigned to IA*I and IN*I, respectively. The empirical rule regarding the chemical shifts of fluorinated hydrocarbons and their substituents predicts that IN*I appears at higher magnetic field than IA*I. The above assignment is in agreement with the prediction.

In spectrum A of Figure 5 peaks 17 and 19 apparently show fine structures, which suggests that IA*I and IN*I are partly overlapping with the resonances due to the sequences arising from the deviation from the alternating structures. According to the empirical chemical shift rule, NA*I and AA*I appear around IA*I, and IN*N and IN*A around IN*I. Therefore, the fine structures of peaks 17 and 19 are attributed to these resonances overlapping partly.

It does not seem easy to explain peak 18 consistently in terms of triads. This resonance increases with increasing isobutylene content in the copolymer as mentioned already. Hence, there is no way other than introducing a tetrad to ex-

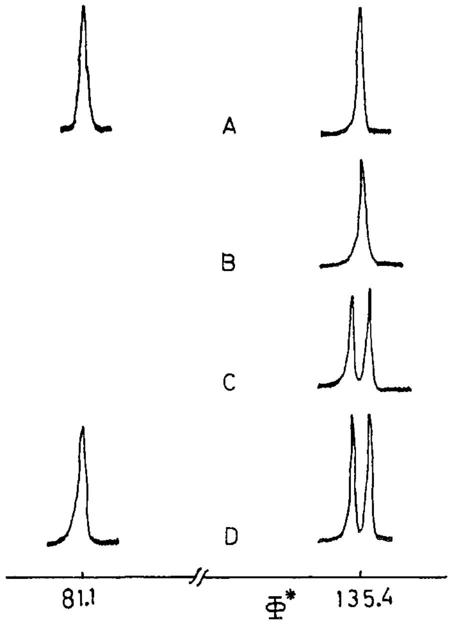


Figure 6. ^{19}F-NMR spectra of terminal groups of trifluoroethylene–isobutylene copolymer and its deuterated compounds:solvent = benzo trifluoride, 60 °C. (A) An approximately alternating copolymer of trifluoroethylene-d_1 and isobutylene-d_8. (B) An approximately alternating copolymer of trifluoroethylene-d_1 and isobutylene. (C) An approximately alternating copolymer of trifluoroethylene and isobutylene-d_8. (D) An approximately alternating copolymer of trifluoroethylene and isobutylene.

plain this resonance. We assign peak 18 to IIN*I, though we do not know why only IIN*I is separated so clearly from other components. Thus, strictly speaking, peak 19 is assigned to IN*I + IN*N + IN*A exclusive to IIN*I. The contribution of the latter two components is small in the approximately 50:50 copolymer.

The resonance peaks, 20 to 24, are due to the other sequences with more than two consecutive trifluoroethylene units, for instance, IA*A, AN*I, NN*I, AN*N, etc. However, further assignment of the resonances is quite difficult at present owing to bitter overlapping of the resonances.

(3) Terminal Groups. The doublet (16) at ca. 135Φ* in Figure 1 is unusually sharp compared to the other peaks, and the intensity depends on the polymerization condition, especially monomer concentration and temperature. The relative intensity of the doublet decreases with increasing polymerization temperature or with decreasing trifluoroethylene concentration.

As is indicated in Figure 6, the doublet becomes a singlet when the trifluoroethylene units are deuterated, but not when the isobutylene units are deuterated. Thus, the splitting of this resonance is attributed to coupling to a proton of trifluoroethylene, and the coupling constant was estimated to be 55 Hz. This resonance is attributed to a terminal $CF_2\mathit{CF_2H}$ group on the basis of the data of low molecular weight compounds. Literature data show[15] that the $\mathit{CF_2H}$ group of n-$C_6F_{13}CF_2H$ is observed at 137.6Φ and that the geminal F–H coupling constant of CF_2HCF_2H is about 52 Hz.

Molecular weights of the copolymer samples were measured by vapor pressure osmometry to be in the range of 2000 to 4000, depending on the polymerization condition. Therefore, it is not unreasonable to conclude that terminal groups are observable with appreciable intensity by NMR. So the possibility of finding other types of terminal groups was sought again for all the region of fluorine resonance, and another resonance having an intensity comparable to CF_2H resonance was found at about 81Φ* as shown in Figure 6. This resonance is tentatively assigned to the terminal CF_3 group, considering that CF_3 resonances of perfluorohydrocarbons appear at 81 to 82Φ.[15] In Table I are shown the relative intensities of these terminal groups with their temperature dependence.

It is rather interesting to consider how these terminal groups are formed. There are three processes, initiation, termination, and chain transfer, that can lead to terminal CF_2H groups.

The possible reactions concerned with the terminal CF_2H group are given as follows.

Initiation Reactions

$$F\cdot + CFH{=}CF_2 \rightarrow \mathit{CF_2H}CF_2\cdot \tag{1}$$

$$H\cdot + CF_2{=}CFH \rightarrow \mathit{CF_2H}CFH\cdot \tag{2}$$

Termination Reactions

$$\text{-}CF_2CFH\cdot + F\cdot \rightarrow \text{-}CF_2\mathit{CF_2H} \tag{3}$$

$$\text{-}CFHCF_2\cdot + H\cdot \rightarrow \text{-}CFH\mathit{CF_2H} \tag{4}$$

Chain Transfer Reactions

$$\text{-}CFHCF_2\cdot + H\text{–}C \rightarrow \text{-}CFH\mathit{CF_2H} \tag{5}$$

$$\text{-}CF_2CFH\cdot + F\text{–}C \rightarrow \text{-}CF_2\mathit{CF_2H} \tag{6}$$

Of these reactions, (2), (4), and (5) can be ruled out by the deuteration experiments, while (6) is also rather improbable because of high C–F bond energy. There seems to be no reason to eliminate reaction 3. This type of termination, however, would occur less frequently than the usual polymer radical–polymer radical termination.

Thus, we assume that reactions 1 and 7 are the main sources of the corresponding terminal groups.

$$F\cdot + CF_2{=}CFH \rightarrow \mathit{CF_3}CFH\cdot \tag{7}$$

Table I
Values[a] of the Parameters Determined from NMR Data

Origin	Rel intensity	Samples A, at 0 °C	B, at 30 °C	C, at 50 °C
Terminal	$-CF_2H$/total CF_2) × 100	1.60 ± 0.1	0.8 ± 0.1	0.8 ± 0.1
Terminal	$-CF_2H/-CF_3$	0.8 ± 0.1		1.2 ± 0.1
CF_2	α = INI/IAI	0.67 ± 0.05	0.84 ± 0.05	0.92 ± 0.05
CF_2	β = (NIAI + IIAI)/AIAI	0.99 ± 0.05	1.17 ± 0.05	1.39 ± 0.05
CF_2	γ = INII/(ININ + INIA)	0.098 ± 0.03	1.12 ± 0.03	0.18 ± 0.03
CFH	δ = IN/AI	0.99 ± 0.05	1.07 ± 0.05	1.13 ± 0.05
CFH	ϵ = (AA + 2AN + NN)/(AI + IN)	0.30 ± 0.03	0.26 ± 0.03	0.23 ± 0.03

[a] The intensity of the relevant resonance peak was measured from the area under the resonance curve. Considerable error was involved in this measurement, and the approximate error limit was determined after several times measurement.

(4) Copolymer Sequence. On the basis of the above assignments, we can estimate the parameters α, β, γ, δ, and ϵ from the intensities of the component peaks of the CF_2 and the CFH resonances as shown below,

$$\alpha = \frac{\mathrm{INI}}{\mathrm{IAI}} = \frac{\mathrm{INII + ININ + INIA}}{\mathrm{IIAI + AIAI + NIAI}} = \frac{(1) + (3) + (2) + (4)}{(8) + (9) + (10) + (11)}$$

$$\beta = \frac{\mathrm{NIAI + IIAI}}{\mathrm{AIAI}} = \frac{(9) + (11)}{(8) + (10)}$$

$$\gamma = \frac{\mathrm{INII}}{\mathrm{ININ + INIA}} = \frac{(1) + (3)}{(2) + (4)}$$

$$\delta = \frac{\mathrm{IN}}{\mathrm{AI}} = \frac{\mathrm{INI + INN + INA}}{\mathrm{IAI + NAI + AAI}} = \frac{(18) + (19)}{(17)}$$

$$\epsilon = \frac{\mathrm{AA + 2AN + NN}}{\mathrm{AI = IN}} = \frac{(20) + (21) + (22) + (23) + (24)}{(17) + (18) + (19)}$$

where the number in a parentheses refers to the peak number in the ^{19}F-NMR spectra.

In Table I is shown the dependence of these parameters on the polymerization temperature. The precision of the parameter values is not high because of the overlapping of the resonances.

It is not straightforward to estimate A and N contents from the data given in Table I. We define a transition probability, $P_{X/Y}$, as a probability of the transition of a terminal radical X· to a terminal radical Y· by the addition to a monomer Y.

$$P_{X/Y}\!: \quad -X\cdot + Y \rightarrow -Y\cdot$$

Then, the parameters are represented using the transition probabilities on the assumption that a first-order Markov process is applicable to the present copolymerization process, as follows.

$$\alpha = \frac{\{I\} \cdot P_{I/N} \cdot P_{N/I}}{\{I\} \cdot P_{I/A} \cdot P_{A/I}} = \frac{P_{I/N} \cdot P_{N/I}}{P_{I/A} \cdot P_{A/I}} \tag{8}$$

$$\beta = \frac{\mathrm{NIAI + IIAI}}{\mathrm{AIAI}} = \frac{\{N\}P_{N/I} + \{I\}P_{I/I}}{\{A\}P_{A/I}} \tag{9}$$

$$\beta = \frac{\{I\} - \{A\}P_{A/I}}{\{A\}P_{A/I}} = \frac{\{I\}}{\{A\}}\frac{1}{P_{A/I}} - 1 \tag{10}$$

$$\gamma = \frac{\mathrm{INII}}{\mathrm{ININ + INIA}} = \frac{\mathrm{INII}}{\mathrm{INI - INII}} = \frac{P_{I/I}}{1 - P_{I/I}} \tag{11}$$

$$\delta = \frac{\mathrm{IN}}{\mathrm{AI}} = \frac{\{I\}P_{I/N}}{\{A\}P_{A/I}} \tag{12}$$

$$\epsilon = \frac{\{A\} + \{N\}}{\mathrm{AI + IN}} - 1 = \frac{\{A\} + \{N\}}{\{A\}P_{A/I} + \{I\}P_{I/N}} - 1 \tag{13}$$

From these parameters, transition probabilities and copolymer compositions are estimated on the assumption of the steady state as shown below.

$$P_{I/I} = \frac{\gamma}{\gamma + 1} \tag{14}$$

$$P_{I/N} = \frac{\delta}{\beta + 1} \tag{15}$$

$$P_{I/A} = 1 - P_{I/I} - P_{I/N} \tag{16}$$

$$\frac{\{A\} + \{N\}}{\{I\}} = \frac{1 + \delta}{\delta}(\epsilon + 1)P_{I/N} \tag{17}$$

$$\frac{\{N\}}{\{A\}} = \left(\frac{1}{\alpha}\right)\left(\frac{P_{I/N}}{P_{I/A}}\right)\left\{\beta - \left(\frac{I}{A + N}\right)\frac{\gamma(1 + \delta)(1 + \epsilon)}{\gamma + 1}\right\} \tag{18}$$

Here, {I}, {A}, and {N} refer to the mole fractional concentrations of isobutylene and of A and N units of trifluoroethylene in the copolymer, respectively.

Table II
The Values of the Transition Probabilities and the Copolymer Composition

	Samples		
	A, at 0 °C	B, at 30 °C	C, at 50 °C
M_F[a]	0.83	0.83	0.84
{I}(exptl)	0.47	0.48	0.48
{I}(NMR)	0.44	0.46	0.48
$P_{I/I}$	0.089	0.11	0.15
$P_{I/N}$	0.50	0.49	0.47
$P_{I/A}$	0.41	0.40	0.38
{N}/({A} + {N})	0.60	0.57	0.58
r_I	0.67	0.78	1.1

[a] In the preparation of the samples, the conversions were approximately 10%, and the average M_F values are shown.

Table III
Temperature Dependence of the Ratios of the Reaction Rate Constants

	Polymerization temp, °C		
	0	30	50
k_N/k_A	1.2	1.2	1.2
k_1/k_7	1.2		1.8

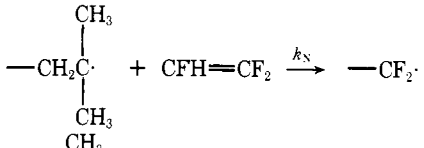
In Table II are shown the values of the transition probabilities and A and N concentration estimated from NMR data. It is to be noted that the transition probabilities are dependent on the monomer composition in the copolymerization reaction. So the mole fraction of trifluoroethylene in the monomer mixture, M_F, is shown in Table II. The isobutylene contents derived from NMR, {I}(NMR), seem to be in fairly good agreement with the experimental values from elemental analyses, {I}(exptl), if the experimental errors in the determination of the parameters, $\alpha \sim \epsilon$, are taken into account.

The monomer reactivity ratio, r_I, determined from $P_{I/I}$ also agrees with that estimated from elemental analysis (0.7 at 30 °C) within the limit of experimental errors.

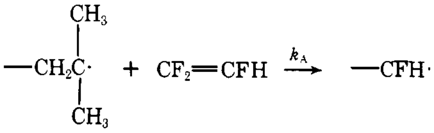
The temperature dependence of {N} appears not to be straight, but this may be due to the complicated procedure in the determination of these values, as seen from eq 18.

Roughly speaking, in this system the abnormal head-to-head and tail-to-tail structures amount to approximately 50% and reactions 19 and 20 take place almost at random. This may be the first case that the addition polymerization takes place in the random direction as far as we know.

The transition probabilities, $P_{I/I}$, $P_{I/N}$, and $P_{I/A}$, appear to slightly depend on the polymerization temperature, but the variation of the values, $P_{I/N}$ and $P_{I/A}$, corresponds to the increase of $P_{I/I}$ with temperature.



$$-CH_2\overset{CH_3}{\underset{CH_3}{C}}\cdot + CFH{=}CF_2 \xrightarrow{k_N} -CF_2\cdot \tag{19}$$



$$-CH_2\overset{CH_3}{\underset{CH_3}{C}}\cdot + CF_2{=}CFH \xrightarrow{k_A} -CFH\cdot \tag{20}$$

As is shown in Table III, the ratio $P_{I/N}/P_{I/A}$ is scarcely dependent on temperature. This ratio corresponds to the ratio of the rate constants for reactions 19 and 20.

If we assume that the terminal groups stated in the previous section arise mainly from reactions 1 and 7, respectively, then it is possible to estimate the rate constant ratio of reactions

1 and 7. This ratio is also given in Table III. It is interesting to note that the correspondence is rather good between the values of these ratios.

As is already mentioned, the steady state was assumed in the above statistical analysis of the monomer sequence distribution. We should, however, bear in mind that the validity of this treatment is limited because of the low molecular weights of the present copolymers. The preliminary result of the application of the statistical analysis for finite chain[16] showed that in the present system the statistical analysis for infinite chain is applicable approximately to the copolymers having the molecular weights larger than 2500.

References and Notes

(1) K. Ishigure, Y. Tabata, and K. Oshima, *Macromolecules*, **3**, 27 (1970).
(2) K. Ishigure, Y. Tabata, and K. Oshima, *Polym. J.*, **2**, 321 (1971).
(3) K. Ishigure and Y. Tabata, *Macromolecules*, **3**, 450 (1970).
(4) K. Ishigure, Y. Tabata, and K. Oshima, *Macromolecules*, **6**, 584 (1973).
(5) K. Ishigure, Y. Tabata, and K. Oshima, *Macromolecules*, **8**, 177 (1975).
(6) K. Ishigure, H. Ohashi, Y. Tabata, and K. Oshima, *Macromolecules*, **9**, 290 (1976).
(7) G. Kojima, H. Wachi, K. Ishigure, and Y. Tabata, *J. Polym. Sci.*, **14**, 1317 (1976).
(8) R. E. Naylor, Jr., and S. W. Lasoski, Jr., *J. Polym. Sci.*, **44**, 1 (1960).
(9) C. W. Wilson, III, and E. R. Santee, Jr., *J. Polym. Sci., Part C*, **8**, 97 (1965).
(10) R. C. Ferguson, *J. Am. Chem. Soc.*, **82**, 2416 (1960).
(11) D. D. Lawson and J. D. Ingham, *J. Polym. Sci., Part B*, **6**, 181 (1968).
(12) R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 3747 (1954).
(13) J. P. Park, M. L. Sharrah, and J. R. Lasher, *J. Am. Chem. Soc.*, **71**, 2339 (1949).
(14) K. Ishigure, Y. Tabata, and K. Oshima, to be published.
(15) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, N.Y., 1969, p 211.
(16) G. G. Lowry, "Markov Chains and Monte Carlo Calculations in Polymer Science", Marcel Dekker, New York, N.Y., 1970, p 187.

NMR Studies of Polymerization of 1,3-Dienes with Bis(π-crotylnickel iodide)

V. A. Kormer* and M. I. Lobach

S. V. Lebedev Synthetic Rubber Research Institute, Leningrad, 198035, USSR.

Received October 18, 1976

ABSTRACT: High-resolution NMR studies have been made of the polymerization of 1,3-dienes with bis(π-crotylnickel iodide). The observed proton resonances of the reaction products of this complex with butadiene, isoprene, 2-ethyl-, 2-isopropyl-, and 2-*tert*-butylbutadienes, 2,3-dimethylbutadiene, 1,3-pentadienes, and 4-methyl-1,3-pentadiene indicate that the end unit of the propagating polymer chain is of π-allylic structure. The type of an alkyl substituent greatly influences the relative content of syn and anti isomers in these adducts.

It can be said without exaggeration that NMR spectroscopy contributed much to the progress of π-allylic compound chemistry, for it made possible a more penetrating insight into the nature of metal–carbon bonds. Successful application of NMR spectroscopy was reported in a series of papers on polymerization of 1,3-dienes using organic compounds of lithium,[1-8] palladium,[9-13] and nickel[14-24] published almost simultaneously.

In the present paper, the results of NMR studies on the reactions of 1,3-dienes of various structure with bis(π-crotylnickel iodide) and its deuterated analogues which were carried out in our laboratory are summarized. To our mind, these studies have revealed some fundamental trends in the coordination polymerization which can contribute first of all to a better understanding of stereocontrol phenomena.

Experimental Section

Perdeuteriobutadiene was prepared from hexachlorobutadiene[25] and 1,1,4,4-tetradeuteriobutadiene was prepared by thermal decomposition of 2,5-dihydrothiophene-*2,2,5,5*-d_4 dioxide.[26] Similarly 1,1,4,4-tetradeuterioisoprene was prepared from isoprene-d_4 sulfone.[3] Complexes $(C_4H_7NiI)_2$, $(C_4D_5H_2NiI)_2$, and $(C_4D_7NiI)_2$ were synthesized from corresponding crotyl iodide and carbonylnickel.[27] All hydrocarbons used were dried over calcium hydride.

The reactions of 1,3-dienes with π-crotylnickel complexes in benzene solution were carried out under argon in glass vessels fitted with baffle-boards. 1,3-Diene was charged into the upper part of the vessel, with the lower part being filled with the complex solution containing a small amount of tetramethylsilane used as an internal standard for NMR measurements.

NMR spectra were recorded using a Jeol Co. JNM + 3H-60 NMR spectrometer and a Bruker HX-90 spectrometer.

Results and Discussion

Reaction with Butadiene. NMR spectra of the reaction mixtures indicated that, first, the addition of bis(π-crotylnickel iodide) to butadiene is a relatively slow process which allows a clear-cut differentiation of the reaction by separate stages to be made; second, all the molecules of the crotyl complex are involved in the reaction; and, third, after each act of insertion the π-allylic bond is regenerated in the adducts.

The ^{1}H NMR spectrum of bis(π-crotylnickel iodide) (Figure 1) shows five resonances: three doublets at τ 7.01 (H^b), 8.50 (H^c), and 8.86 (syn-CH_3), and two multiplets at τ 5.32 (H^a) and 7.30 (H^d). In the presence of perdeuteriobutadiene a gradual weakening of these signals is observed and new signals at τ 7.95, 8.38, and 4.55 (Figure 2) appear which characterize protons of the crotyl group separated from the metal. After a definite period of time a full disappearance of the initial complex resonances is observed. The change of signal intensities in this reaction provides information on the insertion of the first butadiene molecules.

It should be noted, however, that in the spectrum of a reaction mixture consisting of the perdeuterated complex and butadiene (Figure 3) the signals of a substituted π-crotyl ligand appear: the protons H^a (τ 5.30), H^b (τ 7.02), H^c (τ 8.50), H^d (τ 7.30), and the methylene group protons in α-position to the allylic carbon atom (τ 8.37). The insertion of the second and other diene molecules does not lead to any change in these signal intensities and results in the appearance of methylene (τ 7.95) and methine (τ 4.55) proton resonances in the spectrum.