Nuclear Magnetic Resonance of Tetrafluoroethylene–Isobutylene Copolymers Obtained by γ-Ray Irradiation

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ABSTRACT: Fluorine and proton nmr spectra of tetrafluoroethylene–isobutylene copolymers obtained by γ-ray irradiation were measured at 100 MHz (94 MHz for fluorine) and at 60 MHz (56.4 MHz). Methyl and methylene resonances were interpreted successfully in terms of triads. On the other hand, fluorine resonances were explained clearly in terms of tetrads, and it was found out that the effect due to substituents at the third nearest carbon atoms should be also taken into account to explain fluorine resonances. It was confirmed that an alternating copolymer is obtained at high concentrations of tetrafluoroethylene in the monomer mixtures.

Nuclear magnetic resonance spectroscopy has turned out to be a powerful tool for the elucidation of polymer and copolymer microstructures by recent papers. Most of this work, however, is concerned with the proton spectra of polymers except for a few examples. Ferguson[1] showed the possibility of the structural and compositional analysis of vinylidene fluoride–haxafluoropropylene copolymers by the investigation of ^{19}F nmr spectra. Naylor and Lasoski[2] studied the ^{19}F nmr spectra of poly(vinylidene fluoride) and found out the existence of small amount of "head-to-head" or "tail-to-tail" structures. Recently Wilson and Santee[3] verified the results of Naylor and Lasoski and pointed out the presence of a "head-to-head" structure also in poly(vinyl fluoride). Tiers and Bovey[4] determined the stereochemical configuration of poly(chlorotrifluoroethylene) from the analysis of ^{19}F resonances of its model compounds.

It has already been reported by the authors that tetrafluoroethylene[5–7] (TFE) and chlorotrifluoroethylene[8] are easily copolymerized with olefins, such as ethylene, propylene, or isobutylene, to give alternating copolymers by γ-ray irradiation. In a previous paper[9] it was shown that important information concerning the propagation process can be obtained from the ^{19}F nmr spectra of the copolymers. In the present paper, the structure of the tetrafluoroethylene–isobutylene copolymer is investigated using ^{1}H and ^{19}F spectra.

Experimental Section

Polymerizations were carried out at -78 to 25° by exposing a glass ampoule or a stainless-steel vessel containing a mixture of the monomers to γ-rays from a ^{60}Co source. After the irradiation, unaltered monomers were eliminated by evaporation and the residual copolymer was dried under vacuum to a constant weight. The composition of the copolymer was determined by elemental analysis. Nmr spectra were measured at 100° in a concentration range of 15–30% of the copolymers in carbon tetrachloride, since the solubility depends on the composition of copolymers. Model C-60H and Model 4H-100 spectrometers (Japan Electron Optics) were employed for the measurement at 60 MHz (56.4 MHz for ^{19}F resonance) and 100 MHz (94 MHz), respectively. Tetramethylsilane and trifluoroacetic acid were used as internal standards for the proton and fluorine resonances, respectively.

Results and Discussion

In Figure 1, 60-MHz proton spectra of the copolymers with different TFE contents are shown in comparison with that of polyisobutylene. Resonance peaks ranging from 8.6 (τ value) to 9.0 ppm are assigned to methyl groups, and smaller peaks at the lower fields than 8.5 ppm to methylene groups. Peak separations among different methyl resonances are not large enough for the analysis of the microstructure of the copolymers.

Expanded 100-MHz spectra of the copolymers are shown in Figure 2. Methyl resonances split clearly into four peaks and methylene resonances are composed of two partially overlapped triplets and two singlets. These resonance peaks are interpreted in terms of triads. There are four triad structures with a central isobutylene unit, if the regular "head-to-tail" structure is assumed between two isobutylene units.

In Table I are shown the assignments for 60- and 100-MHz proton spectra. These assignments are quite clear. Since the central methylene groups have the CF_2 group as the nearest neighbor in FII and FIF triads, the splitting of methylene resonances to triplets can be explained by the vicinal H–F coupling. The vicinal coupling constant, J_{HF}(vic), was determined as 20~21 Hz, and the value is comparable with J_{HF}(vic) (16 Hz) of poly(vinylidene fluoride) reported by Wilson and Santee.[3]

It is supposed, as reported previously,[7] that the copolymers obtained from monomer mixtures containing TFE in a higher concentration than 50 mol % have a completely alternating structure. The assumed alternating copolymers polymerized at 25° are sparingly soluble in solvents because of their high crystallinity and high molecular weight, and well-resolved proton

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

(2) R. E. Naylor and S. W. Lasoski, *J. Polym. Sci.*, **44**, 1 (1960).

(3) C. W. Wilson III and E. R. Santee, *ibid.*, *Part C*, **8**, 97 (1965).

(4) G. V. D. Tiers and F. A. Bovey, *J. Polym. Sci.*, *Part A*, **1**, 833 (1963).

(5) Y. Tabata, H. Shibano, and H. Sobue, *ibid.*, *Part A*, **2**, 1977 (1964).

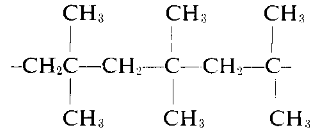
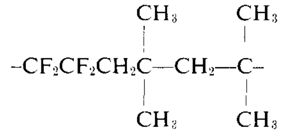
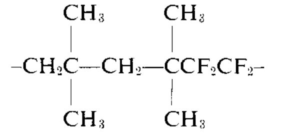
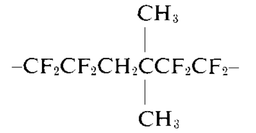
(6) Y. Tabata, K. Ishigure, and H. Sobue, *ibid.*, *Part A*, **2**, 2235 (1964).

(7) Y. Tabata, K. Ishigure, K. Oshima, and H. Sobue, *Makromol. Chem.*, **85**, 91 (1965).

(8) K. Ishigure, Y. Tabata, and K. Oshima, to be published.

(9) K. Ishigure, Y. Tabata, and K. Oshima, *Macromolecules*, **3**, 27 (1970).

TABLE I
ASSIGNMENT OF PROTON RESONANCES OF ISOBUTYLENE–TETRAFLUOROETHYLENE COPOLYMERS

Structure	Notation	100 MHz CH$_3$	100 MHz CH$_2$	60 MHz CH$_3$	60 MHz CH$_2$
 $-CH_2\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-$	III	8.85	8.53	8.87	8.55
 $-CF_2CF_2CH_2\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-$	FII	8.77 Triplet J = 20 Hz	7.87	8.79 Triplet J = 21 Hz	7.89
 $-CH_2\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}CF_2CF_2-$	IIF	8.70	8.18	8.72	8.20
 $-CF_2CF_2CH_2\underset{CH_3}{\overset{CH_3}{C}}CF_2CF_2-$	FIF	8.63 Triplet J = 21 Hz	7.60	8.66 Triplet J = 21 Hz	7.62

spectra could not be obtained. Crude copolymers obtained at $-78°$ from monomer mixtures with high concentrations of TFE are soluble in carbon tetrachloride and a typical spectrum is given in Figure 3. It apparently shows that the crude copolymer is a mixture of the alternating copolymer and isobutylene homopolymer.

As to weak peaks appearing at higher field than at 8.9 ppm in Figure 2, it is difficult so far to give a decisive assignment for them, but they are probably due to terminal methyl groups.

Fluorine 56.4-MHz spectra of the copolymers are presented in Figure 4. There appear resonance peaks at about 28 and 40 ppm to high field from a reference resonance of trifluoroacetic acid. The relative intensity of two resonances at about 40 ppm is remarkably dependent on the copolymer composition; a shoulder at 39.2 ppm, which disappears in the completely alternating copolymer, increases in intensity with increasing IB component in the copolymer. The resonances at about 28 ppm seem to possess complicated fine structures, but could not be analyzed in the figure.

Fluorine spectra of the completely alternating copolymers could be measured successfully owing to large chemical shifts of the fluorine signals, though well-resolved proton spectra were not obtained because of the low solubility of the polymers.

If there exist two or more tetrafluoroethylene units linked together in the copolymer chain, there should appear resonances corresponding to the fluorine nuclei at the positions 1, 2, 3, and 4, as shown. According to

$$-CF_2\underset{1}{CF_2}\underset{2}{CF_2}CF_2CF_2CF_2- \qquad (1)$$

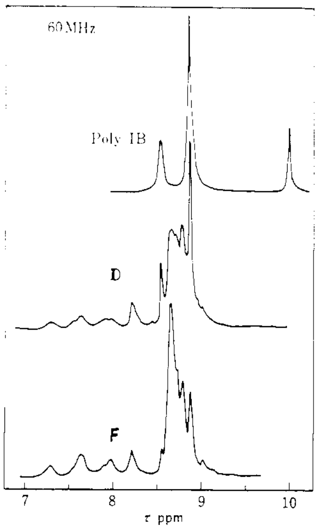


Figure 1. 60-MHz proton spectra of polyisobutylene and tetrafluoroethylene–isobutylene copolymers in CCl$_4$, at 100°: D, copolymer with 31 mol % of TFE; F, copolymer with 38 mol % of TFE.

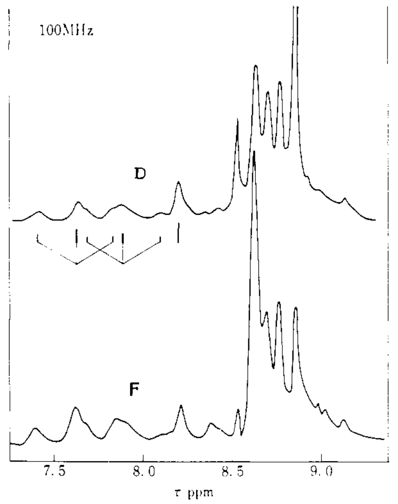


Figure 2. Expanded 100-MHz proton spectra of tetrafluoroethylene–isobutylene copolymers in CCl$_4$, at 100°: D, copolymer with 31 mol % of TFE; F, copolymer with 38 mol % of TFE.

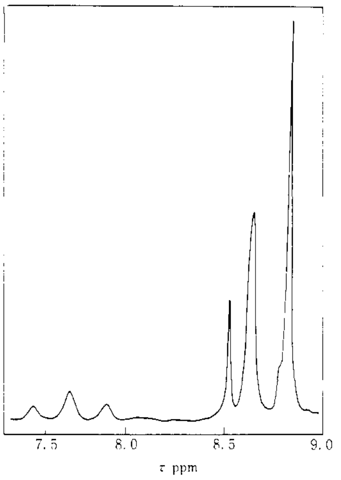
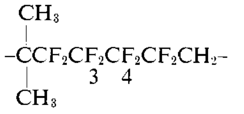
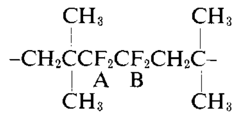


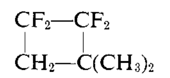
Figure 3. 100-MHz proton spectrum of a crude polymer obtained at −78° in CCl_4, at 100°.


(2)

$$\begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{-CCF_2CF_2CF_2CF_2CH_2-} \\ |\qquad 3\ \ 4 \\ \mathrm{CH_3} \end{array} \qquad (2)$$


(3)

$$\begin{array}{l} \mathrm{CH_3} \qquad\qquad \mathrm{CH_3} \\ |\qquad\qquad\qquad | \\ \mathrm{-CH_2CCF_2CF_2CH_2C-} \\ |\ \ \mathrm{A}\quad \mathrm{B}\qquad | \\ \mathrm{CH_3} \qquad\qquad \mathrm{CH_3} \end{array} \qquad (3)$$


(4)

$$\begin{array}{l} \mathrm{CF_2{-}CF_2} \\ |\qquad | \\ \mathrm{CH_2{-}C(CH_3)_2} \end{array} \qquad (4)$$

Wilson and Santee,[3] these fluorine nuclei have resonances at higher fields than 40 ppm. No observable resonances, however, were found in those regions of the spectra for the copolymers obtained under the present polymerization conditions. It is concluded that there are no structures in which two or more tetrafluoroethylene units are linked together directly, and that all the tetrafluoroethylene units are isolated from each other as indicated in structure 3.

Since the peak area of the resonance at about 28 ppm is almost equal to that of the resonance at about 40 ppm, these resonances are assigned to $-CF_2-$ groups at positions A and B in structure 3. Now one of the important problems which should be solved is: which of the two $-CF_2-$ groups appears at the higher field?

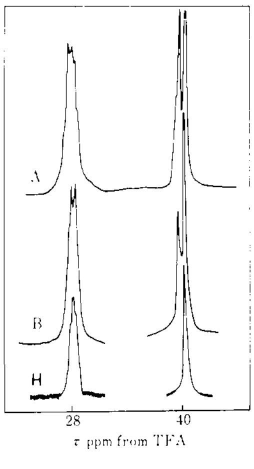


Figure 4. 56.4-MHz fluorine spectra of tetrafluoroethylene–isobutylene copolymers in CCl_4, at 100°: A, copolymer with 15 mol % of TFE; B, copolymer with 37 mol % of TFE; H, assumed an alternating copolymer.

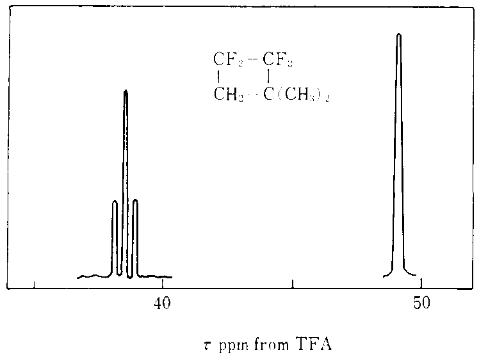


Figure 5. 56.4-MHz fluorine spectrum of the cyclic codimer of isobutylene and tetrafluoroethylene at room temperature.

A cyclic codimer of TFE and isobutylene (4) was synthesized as a model compound according to Coffman, *et al.*[10] The fluorine 56.4-MHz spectrum of the codimer is given in Figure 5. The resonance appearing at lower field is split into a triplet, while the resonance at the higher field is a singlet. The splitting of the resonance at lower field is due to the vicinal coupling between proton and fluorine nuclei (*ca.* 13 Hz), and the vicinal F–F coupling is too small to be observed in the spectrum scanned over a wide magnetic field. The result on the model compound suggests that the resonance of the $-CF_2-$ group at position A in structure 3 appears at the higher field than that of the CF_2 group at position B, although it is not certain that the result on the model can be applied to that of the copolymer because of the different conformations of a cyclic compound and of a linear polymer.

In Figure 6 are shown expanded 94-MHz spectra of the copolymers. The resonance at about 40 ppm is split clearly into two peaks and the resonance at about 28 ppm is evidently composed of two partially overlapping peaks with fine structure. The CF_2 resonance at position B should have fine structure corresponding to the vicinal H–F coupling observed in the proton spectra, while the resonance of the CF_2 group at position A might have no appreciable fine structure because

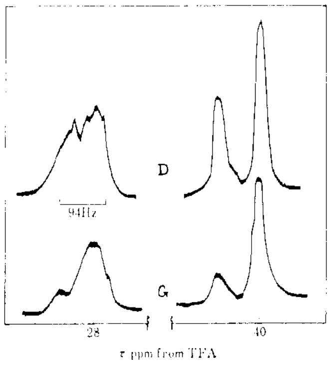


Figure 6. Expanded 94-MHz fluorine spectra of tetrafluoroethylene–isobutylene copolymers: D, copolymer with 31 mol % of TFE; G, copolymer with 39 mol % of TFE.

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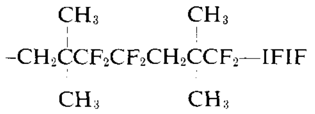
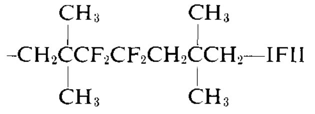
(10) D. D. Coffman, P. L. Barrick, R. D. Cramer, and M. S. Raasjh, *J. Amer. Chem. Soc.*, **71**, 490 (1949).

vicinal F–F coupling and long-range coupling between proton and fluorine may be rather weak. The two peaks at 40.0 and 39.2 ppm, therefore, can be assigned to the resonance of CF_2 group at position A, and the resonance at 27 to 28 ppm can be attributed to the CF_2 group at position B.

Now another important problem is why each of the CF_2 resonances splits to two components (40.0 and 39.2, 28.0 and 27.5 ppm). Wilson and Santee[3] reported that in fluorinated paraffins the effects of substituents on a fluorine resonance are observed when the substituents are attached to the nearest neighboring or the second nearest neighboring carbon atom, and that the effects of substituents attached to the third neighboring or more distant carbons can be neglected. If this is the case, all the resonances in the fluorine spectra of the present copolymers should be interpreted in terms of triads, but the splitting of the peaks at about 28 and 40 ppm, which is largely dependent on the copolymer composition, cannot be explained in terms of triads. The effect of a substituent at the third nearest neighboring carbon, therefore, must be taken into account, and then fluorine resonances should be interpreted in terms of tetrads. The resonance of the CF_2 group at position A in structure 3 will be split into two components corresponding to FIFI and IIFI structures, and that at position B will be split to IFIF and IFII. Ferguson[1] has pointed out that electronegative substituents have alternating effects on the chemical shift of fluorine resonances. For example, when a carbon chain is numbered as shown in (7), electronegative substituents at the no. 0 or no. 2 carbons shift the resonance of fluorine nuclei attached to no. 0 carbon to low field and those at no. 1 and no. 3 carbons to high field, in reference F-resonance of the nonsubstituted chain. This rule leads to the following assignment of the fluorine resonances (ppm): IFIF = 28.0, IFII = 27.5, FIFI = 40.0, IIFI = 39.2. The intensities of the peaks at 39.2 and 27.5 ppm decrease with decreasing isobutylene contents in the copolymer, and only two peaks appear at 28.0 and 40.0 ppm in the spectrum of the copolymer with about 50 mol % TFE as shown in Figure 4.



$$\text{-}CH_2\overset{CH_3}{\underset{CH_3}{C}}CF_2CF_2CH_2\overset{CH_3}{\underset{CH_3}{C}}CF_2\text{—IFIF} \qquad (5)$$



$$\text{-}CH_2\overset{CH_3}{\underset{CH_3}{C}}CF_2CF_2CH_2\overset{CH_3}{\underset{CH_3}{C}}CH_2\text{—IFII} \qquad (6)$$

$$\text{-}\underset{3}{C}\text{—}\underset{2}{C}\text{—}\underset{1}{C}\text{—}\underset{0}{C}\text{—}\underset{1}{C}\text{—}\underset{2}{C}\text{—}\underset{3}{C}\text{-} \qquad (7)$$

According to Price,[11] sequence distribution in copolymers can be analyzed by means of Markoffian statistics. If the relative concentrations of triad components are represented by V_{III}, V_{IIF}, V_{IFI}, . . ., and V_{FFF}, relationships 8–10 are obtained. Since in the present copolymers there exists no structure in which two or more tetrafluoroethylene units are linked together

$$V_{IIF} = V_{FII} \qquad (8)$$

$$V_{FFI} = V_{IFF} \qquad (9)$$

$$V_{IIF} + V_{FIF} = V_{IFI} + V_{IFF} \qquad (10)$$

$$V_{FFF} = V_{FFI} = V_{IFF} = 0 \qquad (11)$$

If $P_{III/I}$, $P_{IIF/I}$, $P_{IFI/I}$, . . ., and $P_{FFF/I}$ are defined as the probabilities with which the growing chains with the end groups of III, IIF, IFI, . . ., and FFF add to an isobutylene monomer, the relative triad concentrations, V_{III}, V_{IIF}, V_{IFI}, and V_{FIF} are described by these probabilities as follows

$$V_{III} = -CP_{IFI/I}P_{FII/I} \qquad (12)$$

$$V_{IIF} = V_{FII} = -CP_{IFI/I}(1 - P_{III/I}) \qquad (13)$$

$$V_{IFI} = -C(1 - P_{III/I}) \qquad (14)$$

$$V_{FIF} = -C(1 - P_{III/I})(1 - P_{IFI/I}) \qquad (15)$$

where C is a constant value. From (12), (13), and (14)

$$V_{III}/V_{IIF} = \frac{P_{FII/I}}{1 - P_{III/I}} = \left(\frac{M_I}{M_F}\right)\left(\frac{M_F + M_I r_{III}}{M_F + M_I r_{FII}}\right) r_{FII} \qquad (16)$$

$$V_{IIF}/V_{IFI} = P_{IFI/I} = \frac{r_{IFI}M_I}{M_F + r_{IFI}M_I} \qquad (17)$$

where M_I and M_F are mole fractions of isobutylene and TFE in monomer mixtures, respectively, and r_{III}, r_{FII}, and r_{IFI} are the relative reactivity ratios given by (20) etc.

$$\sim\!\!\sim III + I \xrightarrow{k_{III/I}} \sim\!\!\sim III \qquad (18)$$

$$\sim\!\!\sim III + F \xrightarrow{k_{III/F}} \sim\!\!\sim IIF \qquad (19)$$

$$r_{III} = \frac{k_{III/I}}{k_{III/F}} \qquad (20)$$

The ratio of mole fractions of the copolymer compositions, m_I/m_F, is given by (21), and the relative concentrations of tetrad components are expressed by triad concentrations

$$m_I/m_F = 1 + \frac{V_{III} + V_{IIF}}{V_{IIF} + V_{FIF}} \qquad (21)$$

$$V_{IIFI}/V_{FIFI} = \frac{V_{IIF}P_{IIF/I}}{V_{FIF}P_{FIF/I}} = \frac{V_{IIF}}{V_{FIF}} = \frac{P_{IFI/I}}{1 - P_{IFI/I}} \qquad (22)$$

$$= r_{IFI}\frac{M_I}{M_F} \qquad (23)$$

Distributions of triad concentrations, determined by the relative areas of methyl resonances, are given in Table II, where only the relative concentrations of IFI components are calculated from eq 10. It is expected from eq 8 that the value V_{IIF} is equal to V_{FII}, and experimental results are in good agreement with the theory within experimental error. As shown in Table III, the ratio of the relative tetrad concentration, V_{IIFI}/V_{FIFI}, which is determined from the peak areas of fluorine resonances, is almost equal to the value of V_{IIF}/V_{FIF}. This experimental verification of eq 22 suggests that the copolymerization reaction is expressed by a third- or lower order Markoff process. In the third and fourth columns of Table III are shown the copolymer

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(11) F. P. Price, *J. Chem. Phys.*, **36**, 209 (1962).

Table II

Relative Concentration of Triads

Sample no.	Polym cond MF, mol %	Conv, %	Relative concentration of triads V, % III	IIF	FII	FIF	IFI
A	6.5	10	11.6	18.0	18.0	17.2	35.2
B	13	10	3.8	16.2	16.0	24.0	40.0
C	14	13	2.6	13.3	12.9	29.0	42.3
D	15	32	27.0	12.4	12.4	17.9	30.3
E	19	20	2.0	8.3	8.6	36.3	44.8
F	21	32	8.5	12.1	12.0	27.6	39.7
G[a]	19	13	7.8	10.3	9.9	30.9	41.1

[a] Sample G was polymerized at 0°, while others were polymerized at 25°.

composition ratios determined from an elemental analysis and from nmr data according to eq 21. Agreement is fairly good except for the sample A, in which isobutylene content estimated from nmr data is lower than that from elemental analysis. Probably this disagreement results from the terminal group effect, which cannot be negligible in the copolymer A. The copolymer A is greaselike, and its molecular weight is not so high because it was polymerized from a monomer mixture with an extremely high isobutylene concentration. In the proton spectrum of copolymer A the resonances appearing at 9.0 ppm and at higher fields, which are assigned to the terminal methyl groups, are stronger in intensity than in the spectra of the other copolymers.

Table III

Verification of Copolymer Equations

Sample no.	V_{IIFI}/V_{FIFI}	V_{IIF}/V_{FIF}	m_I^a/m_F	m_I^b/m_F	r_{IFI}
A	1.05	1.05	1.84	5.66	0.07
B	0.60	0.67	1.50	1.64	0.10
C	0.46	0.46		1.38	0.07
D	0.67	0.69	2.30	2.23	0.12
E		0.19	1.23	1.30	0.05
F		0.44	1.52	1.63	0.11
G	0.31	0.33	1.43	1.56	0.08

[a] Calculated from nmr data according to eq 21. [b] Determined from elemental analysis.

In Table III are given r_{IFI} values estimated from nmr data using eq 17. In principle it is possible to calculate values of r_{III} and r_{FII} from these data in accordance with eq 16, and the comparison of these values with r_{IFI} may lead to the order of the Markoff process by which the copolymerization reaction is expressed. It was, however, difficult to evaluate r_{III} and r_{FII} from the ratio V_{III}/V_{IIF}. One of the reasons is in the difficulty of the precise determination of V_{III}, because trace amounts of isobutylene homopolymer may be included in the copolymer. Since a large amount of polyisobutylene is detected in the crude copolymer obtained at −78° as described previously, it may be suspected that a homopolymerization of isobutylene takes place simultaneously to some extent at 25° *via* a cationic mechanism. Further work is now in progress.

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Thermodynamic Study of Fold Surfaces of Polyethylene Single Crystals

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ABSTRACT: Calorimetric data obtained on single crystals of polyethylene are analyzed to derive information on the nature of fold surfaces. From the magnitudes of surface enthalpy and entropy, it is estimated that a fold, on the average, would consist of 20 or more segments and thus a substantial layer of disorder exists at the surface of single crystals. The surface free energy value was determined by two methods: from the customary plot of melting temperature *vs.* reciprocal lamellar thickness and from the free energy of formation of crystals calculated from the observed values of specific heat. The results of these two methods agree well. The surface enthalpy value was determined from the plot of heat of fusion *vs.* reciprocal lamellar thickness. The assumptions underlying these procedures have been analyzed and the conditions for proper evaluation of thermodynamic quantities are stated and followed. In particular, some of the crystals were cross-linked lightly in order to suppress lamellar thickening during measurements.

I. Introduction

The nature of the surfaces of folded-chain single crystals of polyethylene and other polymers has been the subject of intensive study in recent years. Despite many efforts, there still remain important questions. One of the main points of argument is concerned with the size of the folds, *i.e.*, the average number of segments that are participating in a fold. In this work we present new evidence on polyethylene single crystals, indicating that a fold would consist of 20 or more CH_2 units on the average. In other words, there appears to exist a substantial layer of disorder on the crystal surfaces amounting to an average depth of at least ten CH_2 units. This is obviously in conflict with the picture of