

Nuclear Magnetic Resonance Spectra of Isobutylene—Chlorotrifluoroethylene Copolymer. II. Interpretation of Fluorine Resonances in Terms of Tetrads and Their Temperature Dependence

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ABSTRACT: Proton and fluorine NMR spectra of chlorotrifluoroethylene—*isobutylene* copolymers with various compositions were measured. The fluorine resonances are explained in terms of tetrads, and the methyl resonances on the other hand, are interpreted in terms of triads. Not only the geminal fluorine atoms but also the geminal methyl groups were found to become nonequivalent to each other under the influence of one or two asymmetric centers in the copolymer chain. It was also found that the fluorine spectra show a marked temperature dependence in the range of 70 to 120°C. This suggests that the copolymers have rather high potential barriers for internal rotation, probably, because of their bulky substituents. A statistical treatment was made for the polymerization process, and the results suggest that there exists a penultimate effect in this copolymerization reaction.

KEY WORDS Penultimate Effect / Markov Process / Tetrad / NMR / Conformation / Copolymer / Isobutylene / Chlorotrifluoroethylene /

In recent years, nuclear magnetic resonance has turned out to be a powerful tool for the analysis of polymer and copolymer structures. Almost all the works, however, have been concerned with proton nuclei, and the studies of polymer structures by the measurements of fluorine resonances have been meager so far. Ferguson¹ analyzed the compositional structure of vinylidene fluoride—hexafluoropropylene copolymer by magnetic resonance of fluorine nuclei, and Naylor and Lasoski² showed the presence of a small amount of “head to head” or “tail to tail” structures in poly(vinylidene fluoride) by the investigation of ¹⁹F NMR, which was supported by a recent detailed work.³ Tiers and Bovey⁴ investigated the configurational structure of polychlorotrifluoroethylene using its model compounds. Recently both proton and fluorine resonance spectra were measured of tetrafluoroethylene—*isobutylene* copolymers by the authors,⁵ and it was found that the CF₂ resonances can be interpreted successfully in terms of tetrads while the proton resonances are explained by triads. The spectra of tetrafluoroethylene—*isobutylene*

isobutylene copolymer are not too complicated to be interpreted because the material being examined as a good symmetry in structure. The spectra of chlorotrifluoroethylene—*isobutylene* copolymer, however, are more complicated owing to the symmetries in the polymer chain, and include quite interesting problems. In a previous paper⁶ proton and fluorine resonances were measured only of a copolymer of which the composition was 50:50, and it was confirmed spectroscopically that the copolymer has alternating structure. In the present work, the measurements were carried out at various temperatures for the copolymers deviating from the alternating structure, and a statistical treatment was made for the polymerization process.

EXPERIMENTAL

All the samples were prepared by copolymerizations of chlorotrifluoroethylene with *isobutylene* by means of γ -ray irradiation from a Co-60 source. The copolymerizations were carried out at 25°C in stainless steel vessels, and stopped at

low conversions (12–20%). The composition of copolymers was determined by an elemental analysis. Proton and fluorine NMR spectra were measured at 70–135°C using tetrachloroethylene as a solvent. A model 4H-100 spectrometer (JEOL) was employed for the measurements of 100-MHz (for ^1H) and 94-MHz (for ^{19}F) spectra.

RESULTS AND DISCUSSION

In Figure 1 is shown a typical 100-MHz proton spectrum of a copolymer of which the composition has deviated from the alternating structure.

There appear seven sharp peaks in the region of methyl resonances, and their relative intensities are remarkably dependent on the composition of copolymers. Five of the seven peaks at the higher field are not seen in the spectrum of the alternating copolymer. A tentative assignment is given for methyl resonances on the basis of triads (tetrads for the peaks at 8.80 and at 8.85 τ) as shown in Table I. Weak resonances at 8.9–9.0 τ are probably attributed to terminal methyl groups, though the definite assignments are not known so far.

The nonequivalence of the central methyl

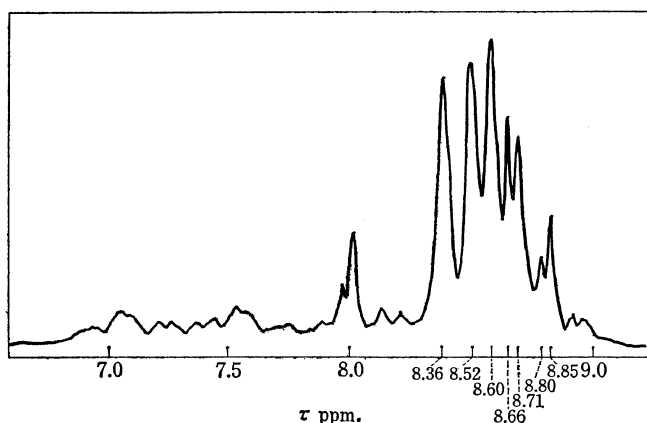


Figure 1. A 100-MHz proton spectrum of a copolymer with 0.41 mol% of CTFE at 120°C.

Table I. Assignment of methyl resonances

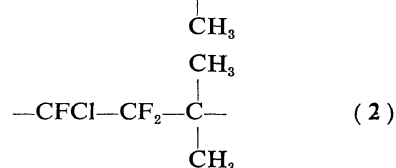
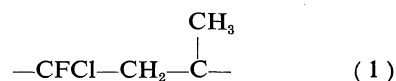
Structure	Notation	Methyl resonance, τ	
$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CFCl}-\text{CH}_2-\text{C}-\text{CF}_2-\text{CFCl}- \\ \\ \text{CH}_3 \end{array}$	FIF	8.36	8.52
$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ -\text{C}-\text{CH}_2-\text{C}-\text{CF}_2-\text{CFCl}- \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	IIF	3.60	
$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ -\text{CFCl}-\text{CH}_2-\text{C}-\text{CH}_2-\text{C}- \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	FII	3.66	3.71
$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\ \quad \quad \\ -\text{C}-\text{CH}_2-\text{C}-\text{CH}_2-\text{C}- \\ \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$	III	8.80 (IIIF)	8.85 (IIII)

NMR Spectra of IB—CITE Copolymer

groups in the FIF triad has already been discussed in a previous paper.⁶ It is of great interest to consider the reason why the central methyl groups are doublets in the FII and III triads. As to the methyl resonances in the FII triad, there seem to be two possible explanations. One is the interpretation by the effect of the asymmetric carbon at a second nearest position. In the case of low molecular weight compounds,^{7,8} it is known from that geminal protons or geminal methyl groups become nonequivalent by the effect of an asymmetric center at the second nearest position. This may be the first example of this type of nonequivalence in polymeric systems. Another is the interpretation in terms of tetrads. If the effect of the substituents at the third nearest carbon atoms on the chemical shift of the central methyl groups is strong enough to be detected, the spectra should be analyzed on the basis of tetrads, not of triads. Consequently, the resonance assigned to the FII triad splits to two peaks attributed the FIIF and FIII tetrads. The relative intensity of these two peaks is supposed to be dependent on the composition of copolymers and the FIIF peak should be stronger in intensity than the FIII peak owing to the alternating tendency in this copolymeriza-

tion. However, the two peaks at 8.66 and 8.71 τ were found to have almost equal intensities in all the spectra obtained. Thus, the latter explanation is rejected, and the former is accepted.

It should be noted that the methyl resonance in IIF is a singlet, while that in FII is a doublet. This means that the influence of the asymmetric center is so strong in the structure 1 that the nonequivalence of the methyl groups can be observed, but that in the structure 2 the influence is not so strong for the nonequivalence to be detected.



The spacing of the doublet assigned to FIF is about 16 Hz and is much larger than that (5 Hz) of the doublet attributed to FII. This gives the evidence that both types of asymmetric centers **1** and **2** participate in causing the nonequivalence of the central methyl groups in the

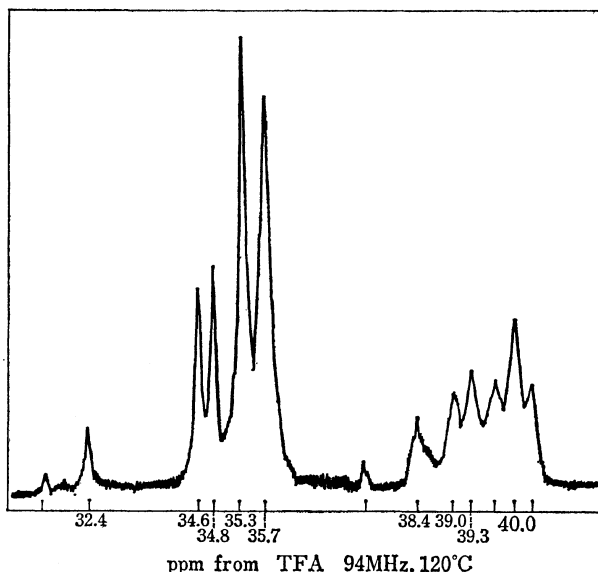


Figure 2. A 94-MHz fluorine spectrum of a copolymer with 0.43 mol% of CTFE at 120°C.

FIF triad, and suggests that the copolymer is stereospecific (probably isotactic) as already discussed in a previous paper.⁶

There is no reason for the splitting of methyl resonance in the III triad, as far as triads are considered. The two peaks assigned to III, however, can be explained if tetrads are taken into account. Thus, the peaks at 8.80 and 8.85 τ were attributed to IIIF and IIII, respectively. As already mentioned above, the peak IIIF should be stronger in intensity than the peak IIII. But in all the spectra obtained, the intensity of the IIII peak was stronger than that of the peak IIIF, and furthermore, when the copolymerizations are carried out at lower temperatures, the relative intensity of IIII to IIIF tends to increase. It has already been reported⁵ that the polymerization of isobutylene takes place independently *via* a cationic mechanism at lower temperatures in the isobutylene—tetrafluoroethylene system, and that the methyl resonance of polyisobutylene appears at 8.85 τ . Therefore, it is concluded that the homopolymer of isobutylene is responsible for most of the IIII peak.

In Figure 2 is indicated a typical 94-MHz. ¹⁹F spectrum of a copolymer deviated from the alternating structure. In a previous paper,⁶ it was reported that the spectrum of the alternating copolymer was composed of an AB-type quartet centered at about 35.5 ppm and a triplet at 40.0 ppm from trifluoroacetic acid as a reference, which was assigned to the CF₂ and the CFCI resonances, respectively. There appears an additional quartet at the lower field (31.7, 34.6, 34.8, and 37.6 ppm) and two extra peaks at 39.0 and 39.3 ppm in the present spectrum. These new peaks are explained in terms of tetrads on the analogy of tetrafluoroethylene—*isobutylene* copolymers, and the assignment is given in Table II. Here all the chlorotrifluoroethylene units are assumed to be isolated from one another in the copolymer, which is consistent with the

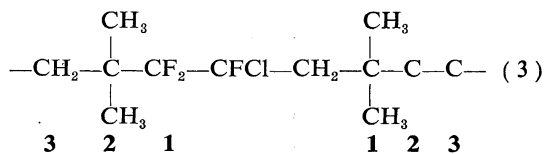
monomer reactivity ratios of this system ($r_{IB}=0.04$ and $r_{CTFE}=0.00$).⁹

It should be noted that the CFCI resonance assigned to IFII is not a triplet, but appears to be a doublet. The CFCI resonances are supposed to be explained as X-parts of ABX spectra, if vicinal ¹⁹F—¹⁹F coupling constants are negligibly small as in the present case. The CFCI resonance appearing at the lower field probably comprises six peaks, that is, two unresolved doublets observed at 39.0 and 39.3 ppm and two weak outer peaks overlapping with neighboring signals. Vicinal ¹⁹F—¹H coupling constants were calculated on this basis as follows.

$$\text{IFII} \quad |J_{AX} + J_{BX}| = 28 \sim 29 \text{ Hz}$$

$$\text{IFIF} \quad |J_{AX} + J_{BX}| = 54 \sim 56 \text{ Hz (120}^\circ\text{C)}$$

It is of great interest that the value $|J_{AX} + J_{BX}|$ in IFII is approximately a half of that in IFIF. Since the vicinal coupling constant is remarkably dependent on the internal rotation angle about the related bond, the above result suggests that the substituents on the carbon atoms no. 2 (and probably also of no. 3) in the formula 3 affect to a great extent the internal rotation potential about the CFCI—CH₂ bond, and that the spectra are quite sensitive to the conformational structure of the polymer segment.



This tempted the authors to investigate the temperature dependence of the spectra, and it was found that the ¹⁹F spectra, above all the CF₂ resonances, showed a marked temperature dependence as in Figure 3. The temperature dependence of the related parameters is listed in Table III.

Evidently the values $|J_{AX} + J_{BX}|$ and δ_{FFgem} increase with decreasing temperature, while J_{FFgem} is almost constant or decreases slightly with decreasing temperature. The value $|J_{AX} + J_{BX}|$ seems to be rather large in IFIF since the vicinal ¹⁹F—¹H coupling constant is usually not larger than 30 Hz.¹⁰ However, it is known that the vicinal coupling constant between ¹⁹F and ¹H is quite sensitive to the dihedral angle between the

Table II. Assignment of fluorine resonances

Resonance	Structure	Pattern	Position, ppm
CF ₂	IIFI	Quartet	Centered at 34.7
CF ₂	FIFI	Quartet	Centered at 35.5
CFCI	IFII	Doublet (?)	39.3 and 39.0
CFCI	IFIF	Triplet	Centered at 40.0

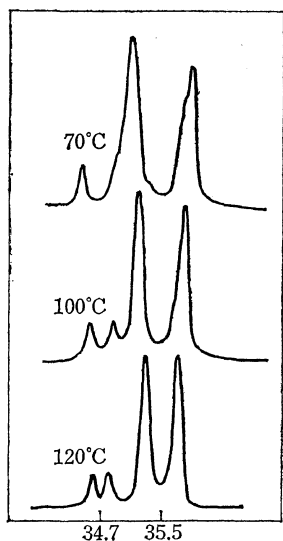


Figure 3. Temperature dependence of the central doublet of the CE_2 resonances (94 MHz).

Table III. Temperature dependence of the related parameters

Temp, °C	$ J_{\text{AX}} + J_{\text{BX}} $, Hz	$\delta_{\text{FFgem}}^{\text{b}}$, Hz		$J_{\text{FFgem}}^{\text{c}}$, Hz
		FIFI ^a	IIFI ^a	
120	55	153	113	265
100	60	131	140	263
70	72	211	154	258

^a Signals from which the parameters were calculated.

^b δ_{FFgem} , difference of chemical shifts between the geminal fluorine atoms.

^c J_{FFgem} , geminal ^{19}F — ^{19}F coupling constant.

CCF plane and the CCH plane. Bovey, *et al.*,¹¹ observed the high value of 43.5 Hz as a vicinal ^{19}F — ^1H coupling constant for a *trans* conformation in cyclohexyl fluoride, and Gutowsky, *et al.*,¹² found that J_{HFtrans} is about 37.3 Hz in a substituted fluoroalkane.

It is very interesting to note the difference between the values of δ_{FFgem} calculated from the FIFI and IIFI signals. It was deduced in a previous paper⁶ that the two geminal ^{19}F nuclei become nonequivalent under the influence of the asymmetric center at the nearest neighboring position and that the effect of the third neighboring asymmetric carbon might be negligible. The

above result, however, shows that the effect of the nearest neighboring asymmetric center is strong enough to cause the geminal fluorine nuclei to be nonequivalent, and furthermore, that the contribution of the asymmetric carbon at the third neighboring position is not negligible because it evidently enhances the nonequivalence of the geminal fluorines.

According to Price, the sequence distribution in copolymers can be treated by means of Markoffian statistics. If third order Markoffian statistics¹³ are applied to the present system as in a previous paper,⁵ the following relations are obtained.

$$V_{\text{IIF}} = V_{\text{FII}} \quad (4)$$

$$V_{\text{FFI}} = V_{\text{IFF}} \quad (5)$$

$$V_{\text{IIF}} + V_{\text{FIF}} = V_{\text{IFI}} + V_{\text{IFF}} \quad (6)$$

where V_{IIF} , V_{FII} , V_{FFI} , etc., refer to the relative concentrations of the corresponding triad components. In the present case,

$$V_{\text{FFF}} = V_{\text{FFI}} = V_{\text{IFF}} = 0 \quad (7)$$

If $P_{\text{III/I}}$, $P_{\text{IFI/I}}$, and $P_{\text{FII/I}}$ are defined as the probabilities with which the growing chains with the respective end groups III, IFI, and FII add to an isobutylene monomer, then, V_{III} , V_{IIF} , V_{FII} , V_{IFI} , and V_{FIF} are expressed by using these probabilities as in the eq 8—11.

$$V_{\text{III}} = -CP_{\text{IFI/I}}P_{\text{FII/I}} \quad (8)$$

$$V_{\text{IIF}} = V_{\text{FII}} = -CP_{\text{IFI/I}}(1 - P_{\text{III/I}}) \quad (9)$$

$$V_{\text{IFI}} = -C(1 - P_{\text{III/I}}) \quad (10)$$

$$V_{\text{FIF}} = -C(1 - P_{\text{III/I}})(1 - P_{\text{IFI/I}}) \quad (11)$$

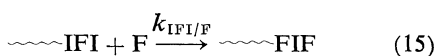
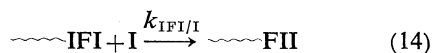
where C is a constant value. From these relations the eq 12 and 13 are obtained.

$$\frac{V_{\text{IIF}}}{V_{\text{IFI}}} = P_{\text{IFI/I}} = \frac{r_{\text{IFI}}M_{\text{I}}}{M_{\text{F}} + r_{\text{IFI}}M_{\text{I}}} \quad (12)$$

$$\begin{aligned} \frac{V_{\text{III}}}{V_{\text{IIF}}} &= \frac{P_{\text{FII/I}}}{1 - P_{\text{III/I}}} \\ &= \left(\frac{M_{\text{I}}}{M_{\text{F}}}\right) \left(\frac{M_{\text{F}} + M_{\text{I}}r_{\text{III}}}{M_{\text{F}} + M_{\text{I}}r_{\text{FII}}}\right) r_{\text{FII}} \end{aligned} \quad (13)$$

where M_{I} and M_{F} are the mole fractions of isobutylene and chlorotrifluoroethylene in the monomer mixture, respectively, and r_{FFI} , r_{III} , and r_{FII} are the relative reactivity ratios defined

by the eq 16, etc.,



$$r_{\text{IFI}} = \frac{k_{\text{IFI/I}}}{k_{\text{IFI/F}}} \quad (16)$$

The eq 13 is rewritten as follows.

$$a^2 u \left(\frac{1}{r_{\text{FII}}} \right) - r_{\text{III}} = a(1-u) \quad (17)$$

where $a = M_{\text{F}}/M_{\text{I}}$ and $u = V_{\text{III}}/V_{\text{IIF}}$. Therefore, it follows that if $a(1-u)$ is plotted versus $a^2 u$, then a straight line should be obtained, and that r_{FII} and r_{III} are determined from its slope and the intercept from the ordinate. The mole fraction of chlorotrifluoroethylene in the copolymer, m_{F} , is given by the eq 18, and the relative ratios of the tetrad components should be expressed by the triad components as written in the eq 19 and 20.

$$m_{\text{F}} = \frac{V_{\text{IIF}} + V_{\text{FFI}} + V_{\text{IFI}} + V_{\text{FFF}}}{V_{\text{III}} + V_{\text{IIF}} + V_{\text{IFI}} + V_{\text{FII}} + V_{\text{IFF}} + V_{\text{FIF}} + V_{\text{FFI}} + V_{\text{FFF}}} = V_{\text{IFI}} \quad (18)$$

Table IV. Relative concentrations of the triad components

No.	CTFE, mol % in monomer mixture M_{F}	Conversion, %	CTFE ^a , mol % in copolymer	V, %				
				FIF	IIF	FII	III ^b	IFI ^c
A	7.6	13.7	35.9	23.6	14.5	15.6	8.2	38.1
B	10.9	20.8	—	25.0	14.6	14.9	5.9	39.7
C	12.8	17.1	—	29.2	12.4	12.9	4.0	41.6
D	14.0	13.6	39.3	29.2	12.2	12.6	3.2	42.2
E	17.0	15.3	—	31.8	11.6	11.0	2.4	43.2
F	19.6	18.5	—	33.0	10.6	11.0	1.9	43.5
G	23.4	17.6	45.2	40.6	6.0	6.2	1.0	46.2
H	74.4	12.2	49.0	47.2	1.6	1.7	0.9	48.7

^a CTFE concentrations in the copolymers were determined from elemental analyses.

^b $V_{\text{III}}(\%)$ was determined as the sum of V_{IIIF} and V_{III}^* , where V_{III}^* was calculated according to the following equation, assuming $r_{\text{III}} = 0.04$.

$$\frac{V_{\text{III}}^*}{V_{\text{IIIF}}} = \frac{V_{\text{III}} P_{\text{III/I}}}{V_{\text{III}} P_{\text{III/F}}} = \frac{P_{\text{III/I}}}{1 - P_{\text{III/I}}} = r_{\text{III}} \frac{M_{\text{I}}}{M_{\text{F}}}$$

^c V_{IFI} was calculated in accordance with the eq 6.

$$\frac{V_{\text{IFI}}}{V_{\text{FIFI}}} = \frac{V_{\text{IIF}} P_{\text{IIF/I}}}{V_{\text{FIF}} P_{\text{FIF/I}}} = \frac{V_{\text{IIF}}}{V_{\text{FIF}}} \quad (19)$$

$$\frac{V_{\text{FII}}}{V_{\text{FIF}}} = \frac{V_{\text{IFI}} P_{\text{IFI/I}}}{V_{\text{IFI}} P_{\text{IFI/F}}} = \frac{P_{\text{IFI/I}}}{1 - P_{\text{IFI/I}}} = r_{\text{IFI}} \frac{M_{\text{I}}}{M_{\text{F}}} \quad (20)$$

In Table IV the relative concentrations of the triads are shown together with the polymerization conditions. According to the eq 2, V_{IFI} should be equal to V_{FII} , and a fairly good agreement is obtained between the experimental results and the theory. The chlorotrifluoroethylene contents of the copolymers determined from elemental analyses seem to be a little lower than those obtained from NMR data (V_{IFI}) in the samples polymerized at the lower chlorotrifluoroethylene

Table V. Verifications of the equations

No.	$\frac{V_{\text{IIF}}}{V_{\text{FIFI}}}$	$\frac{V_{\text{IIF}}}{V_{\text{FIF}}}$	r_{IFI}^a
A	0.64	0.68	0.040
B	0.58	0.58	0.053
C	0.44	0.43	0.048
D	0.42	0.41	0.058
E	0.34	0.36	0.065
F	0.31	0.32	0.065
G	0.18	0.15	0.040
H	~0	0.03	—

^a Calculated from the eq 12.

concentrations in the monomer mixtures. Probably this is due to the fact that the values in

the NMR data contain the contribution of neither polyisobutylene nor the end groups of the polymer chains.

The relative intensity ratio of tetrads, V_{IIFI}/V_{FIFI} , which was determined from the ^{19}F spectra, is almost equal to that of triads, V_{IIF}/V_{FIF} , obtained from the methyl resonances, as shown in Table V. This agreement suggests that the present copolymerization reaction is expressed in terms of a third or lower order Markoff process. A plot of $a(1-u)$ vs. a^2u is given in Figure 4,

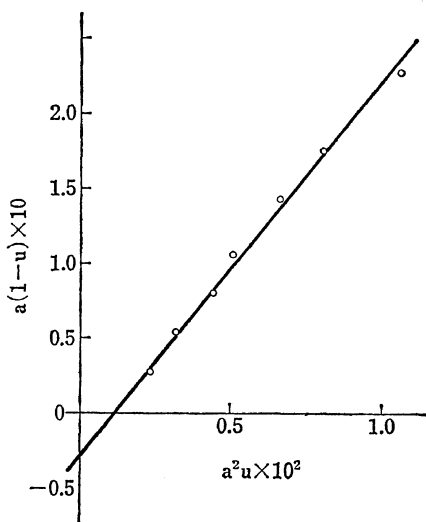


Figure 4. A plot of $a(1-u)$ vs. a^2u .

where the mean values of the initial and final concentrations are used as M_F and M_I . The plot gives a straight line, from which r_{III} and r_{FII} are determined as follows.

$$r_{III} = 0.030$$

$$r_{FII} = 0.038$$

On the other hand, the value of r_{IFI} in Table V is somewhat scattered, and it may be difficult to derive a decisive conclusion from these data. However, when r_{III} and r_{FII} are compared with values of r_{IFI} , it appears that although the difference between the values of r_{III} and r_{FII} is meaningless, the value of r_{IFI} is clearly different from the values of r_{III} and r_{FII} . This means that the present copolymerization reaction is expressed as a second order Markoff process, or that there exists a penultimate effect in this copolymerization reaction.

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