Fluorine-19 Nuclear Magnetic Resonance of Chlorotrifluoroethylene–Propylene Alternating Copolymer

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ABSTRACT: ^{19}F nmr spectra at 94 MHz were observed for chlorotrifluoroethylene–propylene copolymers prepared by γ-ray irradiation at different temperatures. The analysis of the spectra showed that the copolymers have a regular alternating structure over a wide range of monomer charge ratio, as expected from monomer reactivity ratios. It was found that the spectra can be explained in terms of tetrads with regard to CF_2 resonances but in terms of triads with regard to CFCl resonances, although they are rather complicated owing to the configurational structures of the copolymers. The CF_2 resonances are separated into two groups of AB-type quartets, one comprising apparently two components having a larger chemical shift difference, δ_{AB}, and the other composed of four quartets with a smaller δ_{AB} value. The CFCl resonance splits into four components partly overlapping with the CF_2 resonances. From the relative intensities of the CF_2 resonances the copolymers were estimated to be more isotactic when they are polymerized at lower temperature and to approach a random configuration with increasing polymerization temperature.

It has been shown in previous papers by the authors that ^{19}F nmr is a powerful tool for the investigation of the structures of fluorine-containing copolymers, and useful information has been obtained on sequential and/or configurational structures of tetrafluoroethylene–isobutylene,[1] chlorotrifluoroethylene–isobutylene,[2,3] and tetrafluoroethylene–propylene[4,5] copolymers. In these copolymers, however, the fact that either two components of the copolymer are symmetric or only one component has an asymmetric center made the ^{19}F nmr spectra rather easier to interpret. In the present paper the analyses are carried out on ^{19}F nmr spectra of chlorotrifluoroethylene–propylene copolymers which are, as will be seen later, complicated on account of the asymmetries of the two monomer components.

It has been reported previously[6] that chlorotrifluoroethylene easily copolymerizes by radiation with olefins such as ethylene, propylene, or isobutylene over a wide temperature range, and that the compositions of the copolymers are very close to a 1:1 mol ratio over a wide range of monomer charge ratio. For instance, the monomer reactivity ratios reported for the chlorotrifluoroethylene–propylene system are 0.00 ($\gamma_{CF_2=CFCl}$) and 0.06 ($\gamma_{C_3H_6}$), suggesting an alternating structure for this copolymer. Here the authors are concerned only with the assumed alternating copolymer of chlorotrifluoroethylene and propylene.

Experimental Section

Chlorotrifluoroethylene was prepared by dechlorination of 1,1,2-trichlorotrifluoroethane with zinc dust in ethanol. Hexadeuteriopropylene was supplied by Merck and Co. of Canada and was used without further purification. All the copolymer samples were prepared by radiation-induced copolymerizations in the temperature range of −78 to 50°. The concentrations of chlorotrifluoroethylene in monomer mixtures were chosen to be 70–85 mol % and the reactions were usually stopped at low conversions (less than 10%) so that the copolymers obtained are highly alternating. ^{19}F nmr spectra were measured with a JEOL Model PS-100 spectrometer operated mainly at 94 MHz in the temperature range of 25 to 150°. Benzo trifluoride was used as solvent or as internal reference standard, and chemical shifts are expressed in terms of Φ^* values (ppm), which are 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

In Figure 1 a 94-MHz ^{19}F spectrum of an assumed chlorotrifluoroethylene–propylene copolymer is shown in comparison with a 56.4-MHz spectrum. As usual with ^{19}F spectra, spectral parameters, especially chemical shifts, are quite dependent on the measuring temperature and on solvent, and the reliability of chemical shift values is not as high for fluorine resonances as for proton resonances. It is apparent that two doublets at *ca.* $\Phi^* = 106$ and at *ca* $\Phi^* = 109$ and two multiplets at *ca.* $\Phi^* = 118$ and at *ca.* $\Phi^* = 121$ in the 94-MHz spectrum correspond to the resonances at $\Phi^* = 105$ and at $\Phi^* = 110$ and to the multiplets at *ca.* $\Phi^* = 118$ and at *ca.* $\Phi^* = 123$, respectively, in the 56.4-MHz spectrum. The separations between the two doublets and between the two multiplets in the 94-MHz spectrum are 265 Hz and in quite good agreement with those between the corresponding resonances in the 56.4-MHz spectrum, if they are expressed in terms of frequency (Hz). Thus, the two doublets at lower magnetic field and the two multiplets at higher field are considered as components of an AB quartet with a large coupling constant J_{AB}, if the fine structures of each component are neglected.

In Figure 2 the ^{19}F spectrum of a copolymer which is rich in chlorotrifluoroethylene and deviates from an alternating structure is shown. The shadowed parts, which are shown somewhat exaggerated, increase in intensity with increasing chlorotrifluoroethylene content in the copolymer. These new resonances will be mostly attributed to the sequences with two consecutive chlorotrifluoroethylene units. According to Bovey,[7] CFCl resonances in polychlorotrifluoroethylene appear at higher magnetic fields, $\Phi^* = 125.6$ and 127, than CF_2 resonances at $\Phi^* = 104.2$ and 106.0. Therefore, the two peaks at *ca.* $\Phi^* = 127$ in Figure 2 may be assigned to the CFCl resonance at the asterisk position in the following sequence of the copolymer.

$$-CH_2-CH(CH_3)-CF_2-\overset{*}{C}FCl-CF_2-CFCl-CH_2- \quad (1)$$

This resonance is used as a good measure for the deviation of the copolymer from alternating structure. The other new resonances are more or less overlapping and are too complicated to assign. At any rate the two peaks at *ca.* $\Phi^* = 127$ are so weak in Figure 1 that it is concluded that this copolymer sample has a quite strongly alternating structure.

In Figure 3 ^{19}F spectra of chlorotrifluoroethylene–propylene-d_6 alternating copolymer are shown. The upper spectrum was measured at 120°, and is better resolved than the one measured at lower temperature. All the resonance peaks are numbered as shown in the figure. The multiplet centered at *ca.* $\Phi^* = 118$ is separated into three portions (the peaks numbered 9, 10, and 11 in Figure 3B) at 120°, each of which seems to have further fine structure. As is al-

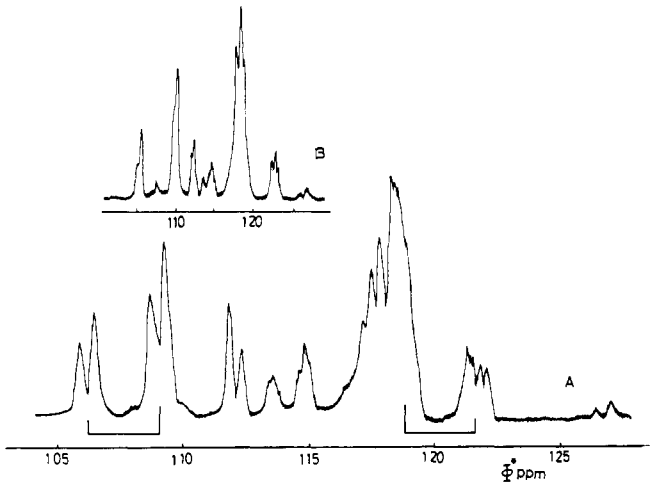


Figure 1. ^{19}F nmr spectra (94 and 56.4 MHz) of alternating chlorotrifluoroethylene–propylene copolymer: (A) 94 MHz, 100°; (B) 56.4 MHz, 100°.

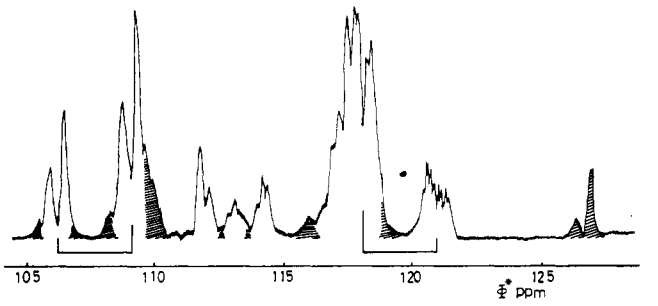


Figure 2. ^{19}F nmr spectra (94 MHz) of chlorotrifluoroethylene rich copolymer (120°).

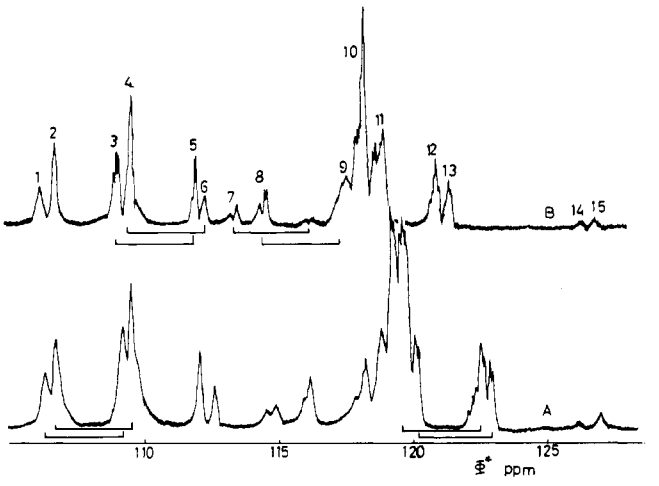


Figure 3. ^{19}F nmr spectra (94 MHz) of chlorotrifluoroethylene–propylene-d_6 alternating copolymer: (A) 60°; (B) 120°.

ready seen, the peaks 12 and 13 are the highest magnetic field components of two AB quartets assigned to CF_2 resonances, and the central peaks corresponding to the peaks 12 and 13 are merged in the peaks 10 and 11, respectively. Now the peaks 1, 2, 3, 4, 12, 13, and the central portions corresponding to 12 and 13 are assigned to CF_2 groups, the other peaks 5–9 and the rest of 10 and 11 are supposed to be CFCl resonances. However, the intensity of CF_2 resonances assigned above is much lower than two thirds of the total fluorine resonance intensity. This means that other resonances than the above two AB quartets should be assigned to CF_2 resonances. If the spectra in Figure 3 are examined closely, it is found that the resonances 7 and 8 markedly shift toward lower magnetic field at higher temperature, while the chemical shifts of the peaks 5 and 6 are rather independent of temperature. This temperature dependence seems to be usual with AB quartet spectra of fluorine resonances in polymers. For instance, two quartets composed of 1, 3, a part of 10, and 12, and 2, 4, a part of 11 and 13 show quite similar temperature dependence, as seen in Figure 3. This suggests that the peaks 5, 6, 7, and 8 may be the central parts of the other AB quartets and should be assigned to CF_2 resonances. In Figure 3B weak resonances are found at *ca.* $\Phi^* = 116$ and in the 56.4-MHz spectrum, on the other hand, a small peak exists at about $\Phi^* = 107$ which does not find a corresponding resonance in the 94-MHz spectra. These resonances would be attributed to the outer parts of AB quartets, which are masked in Figures 3A and 2 by overlapping, if the peaks 5–8 are assigned to CF_2 resonances.

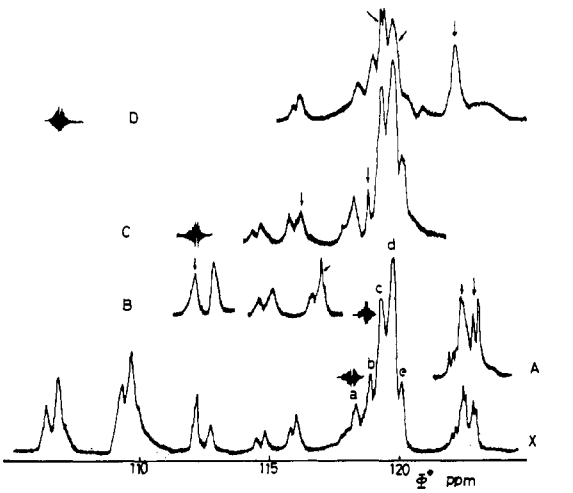


Figure 4. ^{19}F–^{19}F homonuclear spin decoupled spectra of chlorotrifluoroethylene–propylene-d_6 alternating copolymer: X, unirradiated spectrum; A–D, irradiated spectra, ((◆) irradiated position, (↓) changed position).

To confirm the above point, fluorine–fluorine homonuclear decoupling was used and the results are given in Figure 4. The lowest spectrum is the unirradiated one, which is corresponding to Figure 3A but is poorly resolved owing to frequency sweep measurement. If the approximate centers of the peaks 1 and 2 are irradiated, the resonances, d, e, 12, and 13 change noticeably and peak c, normally a singlet, becomes a doublet, as shown in Figure 4D. The changes of the resonances d, e, 12, and 13 are taken for granted, because these are the higher field halves of the AB quartets. The splitting of the peak c, however, seems rather interesting and suggests that this splitting arises from the vicinal F–F couplings. Thus, the peak c may be attributed to CFCl resonances.

When the peak 5 is irradiated, the resonances 8 decrease their intensity markedly and the resonance b becomes very thin (Figure 4C). If the peak b is irradiated, conversely, the resonance 5 decreases its intensity and resonances 8 change (Figure 4B). These results clearly show that the resonances 5 and 8 are the central parts of AB type quartets, of which the outer peaks are merged in other resonances. It is evident that the higher field outer peaks corresponding to the resonances 8 are superimposed on the peak b. The thin peak b observed in Figure 4C is probably not a decoupled component of the AB quartet assigned to CF_2, but a part of the CFCl resonance decoupled from the CF_2 resonances.

The irradiation of peak a gives a sharp splitting of the resonance 13 and a partial perturbation of the fine struc-

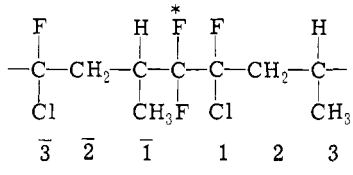
tures of the resonance 12 (Figure 4A). Thus, the fine structures of the resonances 12 and 13 are concluded to be due to vicinal F–F couplings.

Now the homonuclear decoupling experiments lead to the following conclusions: (1) resonances 5, 6, 7, and 8 are the central parts of four AB quartets, resonance 5 pairing with 8 and resonance 6 pairing with 7; and (2) the multiplet at *ca.* $\Phi^* = 119$ observed as five peaks (a, b, c, d, and e) in Figure 4 comprises intricately overlapping resonances, at least four CFCl resonances, four outer peaks of AB quartets corresponding to 7 and 8, and the central resonances corresponding to 12 and 13.

From the above discussion, it is apparent that there are two kinds of CF_2 resonances, one comprising at least two AB quartets with larger chemical shift difference, δ_{AB}, and the other comprising four AB quartets with smaller δ_{AB}. The CFCl resonances appear in the region of $\Phi^* = 117$–120 and have at least four components (a, b, c, and d partly overlapping).

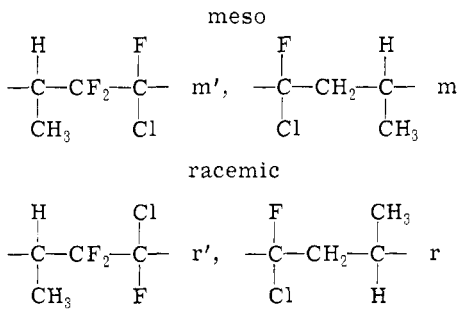
These splittings of the resonances CF_2 and CFCl are considered to arise from the differences in the configurations of the copolymer, since the copolymer used is highly alternating and should not show any appreciable resonances attributed to the deviation from an alternating structure.

It has been found from a series of studies by the present authors that when the central CF_2 resonances in these types of copolymer chains are considered, the substituents on the six carbons at the first, second, and third neighboring positions have the possibility of affecting the chemical shifts of the resonances. This means that the spectra are usually explained in terms of tetrads:



(2)

Therefore, it is reasonable to think that the configurations of the four asymmetric carbons ($\bar{3}$, $\bar{1}$, 1, and 3) in formula (2) affect the chemical shift difference (δ_{AB}) of the central CF_2 resonance in the present copolymer. If meso and racemic structures are defined and noted as shown in the formulas below, where main chain carbons are assumed to be stretched into planar zigzag forms, then the tetrad sequence shown by formula (2) has the possibility of the following eight configurations; mm′m, rm′m, mm′r, rm′r, mr′m, rr′m, mr′r, and rr′r.

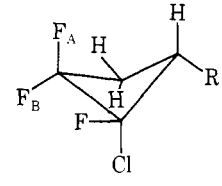


Consequently, the CF_2 resonances are expected to comprise eight components provided that the copolymer takes approximately random configurations and that each configuration gives a resonance in which the chemical shifts are sufficiently separated. The CFCl resonance is considered to split into four components, m′m, m′r, r′m, and r′r, under the same conditions.

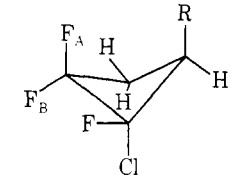
The CF_2 resonances are considered in detail first. The chemical shift difference δ_{AB} between geminal fluorine nuclei is dependent on the configurations of the four asymmetric centers in the tetrad sequence (2), as mentioned earlier. However, two adjacent asymmetric carbons probably have a stronger effect on the chemical shift of the CF_2 resonance than the other remote ones. It may be presumed that the eight components of the CF_2 resonances are separated into two groups, one composed of mm′m, mm′r, rm′m, and rm′r and the other including mr′m, rr′m, mr′r, and rr′r, and that the values of the chemical shift difference, δ_{AB}, would be substantially different between these two groups of resonances. This prediction seems to coincide with the experimental result observed. Two groups of AB quartets are assigned to the CF_2 resonances, as already mentioned. The one group, consisting apparently of two quartets, shows larger values of the chemical shift difference, δ_{AB}, than the other, comprising four AB quartets. It will be readily found that the former group contains more than two components, if the resonance peaks 12 and 13 in Figure 3 are examined more closely. It was shown by the decoupling technique that the fine structures of the peaks 12 and 13 are partly due to vicinal couplings to the CFCl groups, but the complicated splittings of the resonances cannot be explained only by the vicinal coupling unless overlapping of the other components is assumed to occur. It would be reasonable to consider that the four partly overlapping AB quartets constitute this group of resonances, although it is not so easy to separate them by inspection of the fine structures of peaks 12 and 13. Thus, two groups of AB quartets are considered to correspond to two groups of tetrad sequences, one containing m′ and the other containing r′.

The next problem is to find which group of the resonances corresponds to the sequences containing m′ or l′. At first, let us consider the dyad expressed in terms of m′ or r′. The situation is rather complicated owing to the presence of three substituents, CH_3, F, and Cl, and the lack of symmetry in the r′ configuration.

Ernst[8] investigated the ^{19}F nmr spectra of several substituted trifluorochlorocyclobutanes which commonly occur as mixtures of the two cis and trans isomers shown in formulas I and II. In all four cases studied, where R was CH:



cis
I



trans
II

CH_2, CN, C_6H_5, and $C(CH_3)_2$:CH_2, the values of the chemical shift difference between the geminal fluorine nuclei, δ_{AB}, were much larger for cis isomers than for trans isomers. The former are in the range of 18.5–20.5 ppm and the latter are between 0.5 and 4.5 ppm. On the other hand, it was reported by Tarrant, *et al.*,[9] that the ^{19}F spectrum of mixtures of *cis*- and *trans*-methyltrifluorochlorocyclobutanes (R = CH_3 in I and II) shows two kinds of δ_{AB} values, one 19.94 ppm and the other 3.42 ppm. These results seem to suggest that in this copolymer the value of δ_{AB} is larger for m′ configurations than for r′ configurations. Therefore, it would be reasonable to assign the quartets with larger δ_{AB} to mm′m, rm′m, mm′r, and rm′r and the quartets with smaller δ_{AB} to mr′m, rr′m, mr′r, and rr′r.

Through the above discussion it was assumed that the copolymer always takes the regular head-to-tail structure shown in formula (2), and this implies that the propagating radical with a terminal propylene unit always adds to chlo-

Table I
Relative Intensities of the Resonances for the Samples Prepared at Different Temperatures

		A −78°	B −35°	C 25°
1		3.6	4.2	3.3
2		6.4	5.0	4.3
3	1′	6.2	6.3	5.1
	5′	1.4	1.6	2.2
4	2′	10.2	8.2	7.4
	6′	0.2	0.5	0.7
5		4.4	4.7	6.2
6		2.2	2.8	3.8
7		2.4	2.7	3.6
8		4.6	5.2	6.0
9 + 10 + 11	7′	0.4	0.5	0.7
	8′	1.4	1.7	2.1
		32.4	34.0	33.4
	12′	9.8	13.8	13.2
	13′	5.8		
12		6.0		
			8.7	8.1
13		3.0		
Total		100.0	99.9	100.1

Table II
Temperature Dependence of σ_R and σ_F Values

	Temp, °C		
	−78	−35	25
σ_R	0.75	0.70	0.62
σ_F	0.70	0.67	0.65

Table III
Calculated Relative Probabilities for Several Tetrads and Triads

		−78°	−35°	25°
CF_2	$P_{mm'm}$	0.49	0.45	0.42
	$P_{mm'r}$	0.21	0.22	0.23
	$P_{rm'm}$	0.21	0.22	0.23
	$P_{rm'r}$	0.09	0.11	0.12
	$(P_{mm'm} + P_{rm'r})/(P_{mm'r} + P_{rm'm})$	1.4	1.3	1.2
	$(P_{mm'r} + P_{rm'm} + P_{rm'r})/P_{mm'm}$	1.0	1.3	1.4
CFCl	$P_{m'm}$	0.53	0.47	0.40
	$P_{m'r}$	0.22	0.23	0.22
	$P_{r'm}$	0.18	0.20	0.25
	$P_{r'r}$	0.08	0.10	0.13

rotrifluoroethylene at the CF_2 group. This assumption is based on the results for the chlorotrifluoroethylene–isobutylene copolymer reported by the authors,[2] and is not contradictory to the result for polychlorotrifluoroethylene,[7] the ^{19}F spectrum of which was explained on the assumption of regular head-to-tail structure.

$$\sim CH_2CH(CH_3)\cdot \overset{CF_2=CFCl}{\longrightarrow} \sim CF_2CFCl\cdot \quad (3)$$

It should be noted that the chemical structures of the cyclic codimers prepared by thermal reaction of chlorotrifluoroethylene with the appropriate olefins have nothing to do with the chemical structures of the corresponding copolymers. It is also known[10] that chlorotrifluoroethylene gives head-to-head or tail-to-tail cyclic dimers by thermal reaction, although polychlorotrifluoroethylene has regular head-to-tail structure.

The distribution of configurational sequences of this copolymer is dealt with rather quantitatively on the basis of Bernoulli trials which are known to occur often in radical polymerization processes. If a completely alternating structure is assumed, the probabilities of finding tetrad sequences indicated by subscripts, P_{XYZ}'s, are given as follows

$$\begin{aligned} P_{mm'm} &= \sigma_F^2\sigma_R & P_{rr'r} &= (1-\sigma_F)^2(1-\sigma_R) \\ P_{mm'r} &= \sigma_F(1-\sigma_F)\sigma_R & P_{rr'm} &= (1-\sigma_F)(1-\sigma_R)\sigma_F \\ P_{rm'm} &= (1-\sigma_F)\sigma_F\sigma_R & P_{mr'r} &= (1-\sigma_F)(1-\sigma_R)\sigma_F \\ P_{rm'r} &= (1-\sigma_F)^2\sigma_R & P_{mr'm} &= \sigma_F^2(1-\sigma_R) \end{aligned} \quad (4)$$

where σ_F and σ_R are the probabilities of the addition of terminal radical, ~CFCl ·, to propylene in the meso configuration and of the addition of terminal radical, ~CH(CH$_3$) ·, to chlorotrifluoroethylene in the meso configuration, respectively, corresponding to coisotacticity parameter, σ, commonly employed in copolymerization systems.[11] It is worthwhile to note that in this system it is necessary in principle to use two parameters, σ_F and σ_R, since intervening fluorine atoms would have a different effect from that of intervening hydrogen atoms on the interactions of the substituents, CH_3 Cl, and F, in the course of the addition of propagating radical to monomer.

In Table I the relative intensities of the resonances, estimated from the relative areas under the resonance curves, are compared among the three samples prepared at different temperatures. As evident from the discussion above, the peaks 3 and 4 contain some contributions from the outer peaks (5′ and 6′) corresponding to resonances 5 and 6, respectively, and the multiplet centered at *ca.* Φ^* = 119 (9, 10, and 11) also includes the central parts corresponding to peaks 12 and 13, and the outer parts corresponding to the peaks 8 and 7 (only in the lower temperature measurement). The relative intensities of those merged peaks expressed by the numbers with primes were estimated by theoretical calculations which were carried out using measured chemical shift difference, δ_{AB}, and coupling constants J_{AB}.

If the relative intensities of 13′, 12′, 8′, and 7′ are subtracted from those of 9, 10, and 11, the remainder is supposed to be ascribed to the CFCl resonances. This value is seen from the table to be approximately equal to 33%, and seems to justify the assignment given above.

It is interesting to note that the relative intensities of some resonances vary slightly with polymerization temperature. For instance, the sum of the relative intensities of the peaks 5, 5′, 6, 6′, 7, 7′, 8, and 8′ is 17.2% at −78°, 19.7% at −35°, and 25.3% at 25°, increasing with rising temperature. Correspondingly, the relative intensities of the other two quartets decrease with increasing temperature. This shows that the copolymer configuration changes with polymerization temperature.

As already mentioned, the four quartets with smaller chamical shift difference, δ_{AB}, are assigned to rr′r, rr′m, mr′r, and mr′m and the quartets with larger δ_{AB} to mm′m, mm′r, rm′m, and rm′r. The parameter σ_R is readily calculated from eq 5, using the relations in (4)

$$\frac{P_{mm'm} + P_{mm'r} + P_{rm'm} + P_{rm'r}}{P_{rr'r} + P_{rr'm} + P_{mr'r} + P_{mr'm}} = \frac{\sigma_R}{1-\sigma_R} = \frac{I_1 + I_{1'} + I_2 + I_{2'} + I_{12'} + I_{12} + I_{13'} + I_{13}}{I_{5'} + I_5 + I_{6'} + I_6 + I_7 + I_{7'} + I_8 + I_{8'}} \quad (5)$$

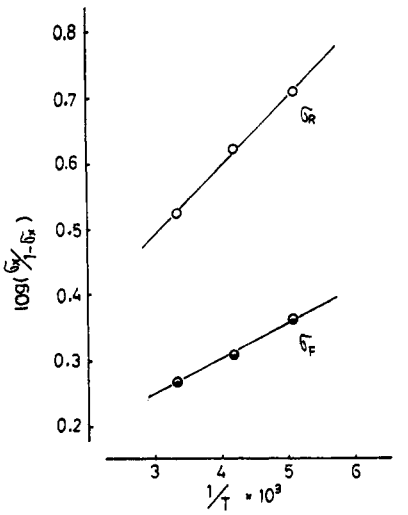


Figure 5. Plot of log $(\sigma_X/(1-\sigma_X))$ *vs.* $1/T$: ○, σ_R; ●, σ_F.

where I refers to the relative intensity of the related resonance. When the resonances 7 and 8 are closely examined, it is noted that the lower field component of 8 is approximately equal in intensity to the higher field component of resonance 7. Since $P_{rr'm}$ is equal to $P_{mr'r}$ on the basis of Bernoulli processes as shown in eq 4, it would be appropriate to assign these two components with corresponding outer part to rr'm and mr'r. The value of σ_R calculated suggests that this copolymer does not take random configurations but is rich in meso configurations, especially at lower temperature. Therefore, it seems reasonable to assign the higher field component of 8 with corresponding outer part to mr'm and the lower field component of 7 with related outer peak to rr'r. Now it is possible to calculate the value of σ_F according to eq 6. The temperature dependence

$$\frac{P_{rr'r} + P_{rr'm}}{P_{mr'r} + P_{mr'm}} = \frac{P_{rr'r} + P_{mr'r}}{P_{rr'm} + P_{mr'm}} = \frac{1-\sigma_F}{\sigma_F} = \frac{I_{6'} + I_6 + I_7 + I_{7'}}{I_{5'} + I_5 + I_8 + I_{8'}} \quad (6)$$

of σ_R and σ_F values is indicated in Table II. It is interesting to note that the difference between the values of σ_R and σ_F is significant but not large. If the copolymer takes random configurations, then σ_R and σ_F are supposed to be equal to 0.5. It is seen that the copolymer is more isotactic at lower temperature and approaches a random configuration with increasing polymerization temperature. In the case of polychlorotrifluoroethylene which was presumably prepared by radical initiators, the polymer was reported to be predominantly syndiotactic rather than random, and this might appear inconsistent with the present result. However, the interactions occur among electronegative polar substituents in polychlorotrifluoroethylene and would be quite different from those in this copolymer. It has been reported[10] that the copolymer of methyl acrylate and styrene shows a parameter σ of 0.80 at 60° and of 0.85 at −25°, *i.e.*, increasing isotacticity with decreasing polymerization temperature, and this is a very similar situation to the present case.

In Figure 5, the value of log $(\sigma_X/(1-\sigma_X))$ is plotted versus the reciprocal of the polymerization temperature (°K), and from these lines the differences between activation enthalpies, ΔH_m^* and ΔH_r^*, are estimated as follows.

$$\sigma_R: \Delta H_m^* - \Delta H_r^* = -0.46 \text{ kcal/mol}$$
$$\sigma_F: \Delta H_m^* - \Delta H_r^* = -0.24 \text{ kcal/mol}$$

These values are comparable to the reported ones for other systems.[10]

It will be recalled that when the values of σ_R and σ_F were determined from the intensities of the CF_2 resonances, no consideration was given to the relative intensity ratio of the two quartets assigned to mm'm, rm'm, mm'r, and rm'r. It is straightforward to calculate the probabilities, P_{XYZ}'s, for these tetrads using the values given in Table II. As shown in Table III, there may be two possible combinations which can reasonably explain the resonances. One possibility is that the inner quartet (2, 2', 12', and 12) is assigned to mm'm and rm'r overlapping each other, and the outer (1, 1', 13', and 13) to mm'r and mm'r. The other possibility is that the outer quartet is assigned to mm'm and the inner to the other three. The relative intensity ratio of the inner quartet to the outer is calculated to be 1.7 at −78°, 1.3 at −35°, and 1.4 at −25° from Table I. If these values are compared to those in Table III, the former assignment would be more probable, though, tentatively, the later might seem more reasonable.

It is rather difficult to obtain unambiguous information from the CFCl resonances because of strong overlapping of the resonances. There seem to be at least four components for the CFCl resonances which appear in the region of $\Phi^* = 117$ to 120. It would be appropriate to assign these four components to the related triads, m'm, m'r, r'm, and r'r. It should be noted that the CFCl resonances are interpreted stereochemically in terms of triads rather than tetrads. The relative probabilities of finding these triads are calculated from the values of σ_R and σ_F and are shown in Table III. From these values and the decoupling experiment the probable assignment is derived as follows: peak a is assigned to m'r, peak b to r'r, peak c to m'm, and the resonance merged in d to r'm. This assignment is rather tentative and there remains some ambiguity in it.

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