ones raises the interesting question of what is the cause of their enhanced reactivity in a propagation process. Two factors should be considered. In the course of addition the cation has to be transferred from the terminal carbanion to the new negative center formed by the addition of monomer. This requires a partial dissociation of the cation which is more facile for the loose than for the tight pair, provided the solvation is not intramolecular. Alternatively, the higher reactivity of the loose pair may arise from the increase in its dipole.

It seems that the latter factor is more important in determining the reactivity of ion pairs. The transfer of Na^+ ion is easier even in the "tight" $\sim\sim S^-,Na^+$ ion pair than in the "stretched" $\sim\sim VP^-,Na^+$ pair; this is evident when the relevant dissociation processes are compared. Nevertheless, the latter is much more reactive than the former. We do not imply, however, that the facile dissociation of ion pairs does not contribute to their reactivity. Quite to the contrary, this is still a factor which enhances the reactivity of a pair, other things being equal. Indeed, the ease of dissociation may be responsible for the higher reactivity of *solvent separated* $\sim\sim S^-,Na^+$ in THF when compared with the "stretched" $\sim\sim(2\text{-}VP)^-,Na^+$.

The activation energy of propagation appears to be similar for the free $\sim\sim(2\text{-}VP)^-$ anion and for the $\sim\sim(2\text{-}VP)^-,Na^+$ ion pairs, about 7–8 kcal/mol. It is interesting to note the same relation in the living polystyrene system; the activation energy of propagation of the free $\sim\sim S^-$ ion is about 5–6 kcal/mol and that of the loose $\sim\sim S^-,Na^+$ ion pair in THF was deduced to be also about 6 kcal/mol. The significance of this relation cannot yet be evaluated.

The effect of solvent upon the propagation constant, $k_{\pm}$, of $\sim\sim(2\text{-}VP)^-,Na^+$ calls for comments. It may appear surprising that the $k_{\pm}$ is greater in THP and dioxane than in THF. However, the relatively high reactivity of $\sim\sim S^-,Na^+$ in THF, and even more so in DME,[12] when compared with its reactivity in dioxane or THP results from the substantial contribution of the loose pairs to the overall reactivity. In THP or dioxane we observed the growth of tight pairs only whereas the reactivity of tight pairs in THF is not known. On the other hand, in the $\sim\sim VP^-,Na^+$ system we are concerned with the reactivities of "stretched" ion pairs which may be only slightly influenced by the solvent. The relatively high reactivity of the $\sim\sim(2\text{-}VP)^-,Cs^+$, when compared with the sodium salt, becomes plausible when the idea of internal solvation by the polymer is accepted.

Finally, it should be remarked that similar effects arising from the intramolecular solvation of the cation have been observed recently in the system living poly-*o*-methoxystyrene.[13] Here again the favorable location of the *o*-methoxy group makes possible the intramolecular solvation of the cation and the reactivity of this polymer is indeed much higher than that of the living polymer derived from the *p*-methoxy styrene.

Acknowledgment. We gratefully acknowledge the financial support of this investigation to the National Science Foundation and to the Petroleum Research Fund administered by the American Chemical Society.

(12) T. Shimomura, J. Smid, and M. Szwarc, *J. Amer. Chem. Soc.*, **89**, 5743 (1967).

(13) J. Geerts, M. van Beylen, and G. Smets, *J. Polym. Sci., Part A-1*, 2859 (1969).

Nuclear Magnetic Resonance Spectra of a Isobutylene–Chlorotrifluoroethylene Copolymer

Kenkichi Ishigure, Yoneho Tabata, and Keichi Oshima

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

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ABSTRACT: High-resolution nmr spectra were measured at 94 MHz (100 MHz) and 56.4 MHz for both ^{19}F and ^{1}H nuclei of chlorotrifluoroethylene–iosbutylene copolymers polymerized by γ irradiation. It was concluded from the nmr spectra that the copolymers have completely alternating structure and that a propagating isobutylene radical adds to chlorotrifluoroethylene monomer on the carbon atom with two fluorine substituents in the polymerization reaction. The CF_2 resonance was found to be an AB-type quartet, being affected by the nearest neighboring asymmetric center of $-CFCl-$. The methyl resonance, a doublet with equal intensity, seems to suggest the possibility of the stereospecific structure of the polymers.

Many successful results have been obtained in determining the microstructure of polymers and copolymers by means of nuclear magnetic resonance (nmr) measurements. Most of them, however, are concerned with proton spectra of polymers and there are few investigations of the structure of polymers by fluorine spectra.[1-3]

It has been reported by the authors that several kinds of fluorine-containing polymers can be obtained by copolymerization induced by ionizing radiation.[4] The structure of isobutylene (IB)–chlorotrifluoro-

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

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

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

(4) Y. Tabata, K. Ishigure, H. Shibano, K. Oshima, and H. Sobue, Proceedings of Conference on Industrial Uses of Large Radiation Sources, Vol. 1, 1963, p 179.

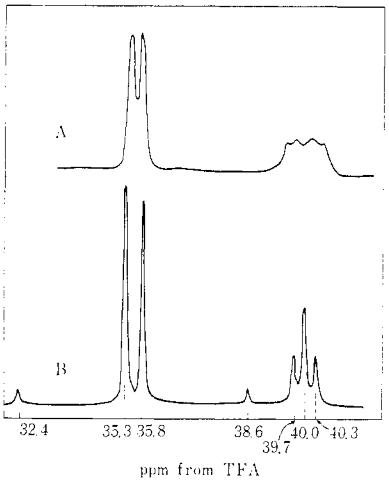


Figure 1. A, Fluorine nmr spectrum of IB–CTFE copolymer with mole fraction 0.478 CTFE at 56 MHz (solvent C_2Cl_4, temperature 100°); B, fluorine nmr spectrum of IB–CTFE copolymer with mole fraction 0.478 CTFE at 94 MHz (solvent C_2Cl_4, temperature 100°).

ethylene (CTFE) copolymers obtained by the radiation process has been investigated in our laboratory by both fluorine and proton nmr spectra.

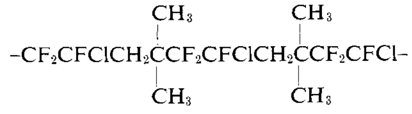
The samples were prepared by γ-ray-induced copolymerization of CTFE with IB at 0°. The concentrations of CTFE in the copolymers were determined from elemental analysis. Copolymers obtained from the monomer mixtures with higher concentrations of CTFE were found to contain approximately 50 mol % of CTFE and to be highly crystalline by X-ray diffraction. It may be concluded that these copolymers have an exactly alternating structure. Nmr spectra of both fluorine and proton were measured at 100° with a spectrometer of Japan Electron Optics Co. Ltd., operating at 56.4 and 94 MHz (100 MHz in the case of proton).

In Figure 1 are shown typical fluorine nmr spectra of the assumed alternating copolymer measured at 56.4 and 94 MHz. A comparatively sharp doublet and an unresolved broad singlet are found at higher fields of 35.5 and 40.0 ppm in the 56.4-MHz spectrum, respectively, from trifluoroacetic acid (TFA) as an internal standard. The separation between the two peaks of the doublet at the lower field is about 0.3 ppm (~17 Hz) and the relative intensity ratio of the doublet to the broad singlet is approximately 2:1. The doublet is assigned to the $-CF_2-$ group and the singlet at the higher field to the –CFCl– group. According to Tiers and Bovey,[2] CF_2 and CFCl units in polychlorotrifluoroethylene show broad resonance peaks at fields of *ca.* 28–29 ppm and *ca.* 49–51 ppm from TFA, respectively. No observable peaks were found in any other regions than shown in Figure 1 as far as the spectra of the copolymers are concerned. Therefore, it is concluded that the CTFE units are isolated from each other and have no CTFE unit as nearest neighbors in the copolymers. This conclusion can be supported also by the copolymerization data. The monomer reactivity ratios, $r_{C_4H_8}$ and $r_{C_2F_3Cl}$, were estimated[5] to be 0.04 and 0.00, respectively, and these values mean that a propagating CTFE radical adds only to IB monomer, and not to CTFE.

The spectrum at 94 MHz is obviously somewhat different from that at 56.4 MHz. Two new peaks of equal intensity appear at 32.4 and 38.6 ppm, and the separation between the components of the doublet increases from 0.3 ppm in the 56.4-MHz spectrum to 0.5 ppm (48 Hz) in the 94-MHz spectrum. The peak at 40.0 ppm assigned to –CFCl– unit splits to a triplet, of which the components almost equally spaced have the relative intensities in the ratio of 1:2:1. The splitting of the –CFCl– resonance seems to be due to a coupling with two equivalent nuclei with $^1/_2$ spin, and the coupling constants are estimated to be about 30 Hz at 100°, provided they are equal to each other. It is known that the coupling constant J_{FF} between adjacent –CFCl– and $-CF_2-$ groups is rather small (*ca.* 3–5 Hz),[2] and, on the other hand, the vicinal coupling constant J_{HF} is comparatively large (*ca.* 10–30 Hz) in comparison with J_{FF}. Thus it may be concluded that the –CFCl– group has the unit of $-CH_2-$, but not the unit of $-C(CH_3)_2-$, as the nearest neighbor. The –CFCl– resonance should be represented as a X part of ABX spectrum. In the 94-MHz resonance the spectrum is rather simple owing to the "deceptive" nature, and $|J_{AX} + J_{BX}|$ was obtained to be about 60 Hz at 100° from the outer spacing of the triplet. In the 56.4-MHz spectrum, on the other hand, the CFL resonance appears more complicated because of the absence of the deceptive nature.

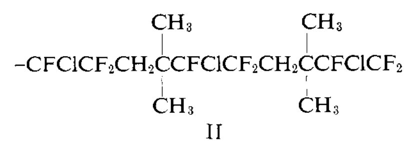
The doublet around 35.5 ppm with the outer two peaks, which are assigned to the $-CF_2-$ group, are explained as an AB-type quartet. The coupling constant between geminal fluorine atoms has been reported to be about 280 Hz,[2] and the value is in fairly good agreement with our experimental one (263 Hz). Based on the above $\delta\nu$ and $J_{FF_{gem}}$ values, the relative intensity ratios among the components of the quartet in 94- and 56.4-MHz resonances were calculated to be 0.09:1:1:0.09 and 0.04:1:1:0.04. The former calculated values agree well with our experimental result; in the 56.4-MHz spectrum the outer peaks of the quartet are too weak in intensity to be observed. The separation between the central peaks of the quartet was calculated to be about 18 Hz in the 56.4-MHz resonance, which is nearly equal to the experimental value of 17 Hz.

It is very interesting to analyze the structure of the IB–CTFE copolymer from these experimental results, since there are two possibilities in the regular alternating structure (I and II). It is known that when a propagating radical adds to an isobutylene monomer, the addition takes place on the unsubstituted carbon



$$-CF_2CFClCH_2\overset{CH_3}{\underset{CH_3}{C}}CF_2CFClCH_2\overset{CH_3}{\underset{CH_3}{C}}CF_2CFCl-$$

I

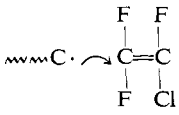


$$-CFClCF_2CH_2\overset{CH_3}{\underset{CH_3}{C}}CFClCF_2CH_2\overset{CH_3}{\underset{CH_3}{C}}CFClCF_2$$

II

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

atom of the monomer. This is also supported theoretically.[6] In the case of CTFE, it has not been known so far on which side of the carbon atoms the growing radical attacks. It is quite evident from the results shown above that the copolymers obtained under the present conditions correspond to the structure of type I. This means that the growing end attacks the CTFE monomer on the carbon atom with two fluorine substituents in the radical process.



$$\sim\sim C\cdot \curvearrowright \overset{F}{\underset{F}{C}}=\overset{F}{\underset{Cl}{C}}$$

I

The nonequivalence of two fluorine nuclei in the $-CF_2-$ group may be due principally to the asymmetric carbon atom at its nearest neighbor, and the effect of the third neighboring one may be negligible.

The 100-MHz proton spectrum of the copolymer is shown in Figure 2. It is known[7] that polyisobutylene shows methyl and methylene resonances at τ 8.85 and 8.52. The doublet centered at 8.44 and weak shoulders at 8.60 ~ 8.85 are assigned to methyl groups, and the complex resonances at 6.85 ~ 8.02 are attributed to methylene groups. The doublet, of which components at 8.36 and 8.52 are of equal intensity, is due to the regular alternating structure and the other shoulders at 8.60 ~ 8.85 to the nonregular structures. It is very interesting to consider the methyl resonance of the regular alternating copolymer. A pair of methyl groups attached to the same carbon atom have two asymmetric centers at the second nearest positions. The situation is rather similar to that in the methylene resonance of vinyl type polymers ($-CHXCH_2CHX-$), but it should be noted that while the "racemic" methylene protons are equivalent in vinyl type polymers, two methyl groups corresponding to the "racemic" structure do not become equivalent in our copolymer because of the absence of symmetry. There are two possible explanations for the methyl resonance of a doublet with equal intensity.

If all the asymmetric carbon atoms take the regular steric configuration, such as *dddd*. . . , *llll*. . . , or *dldldl*. . . , then the two methyl groups may be nonequivalent and the methyl resonance will split to a doublet with equal intensity. Thus, if there appears only one doublet with equal intensity, the polymers have a stereoregular (probably isotactic) structure. If it is assumed, however, that the asymmetric carbon atoms have a random configuration, then the methyl resonance should split, principally, to three or more resonance peaks corresponding to "*meso*" and "racemic" structures. Provided that the separations among the resonance peaks are small, all the peaks may be difficult to resolve and it follows that it is, apparently, the stereoconfiguration of only one, on either side, of the two nearest asymmetric centers that predominantly affects the chemical shifts of the methyl resonance, and that the contribution from another one is not enough for splitting.

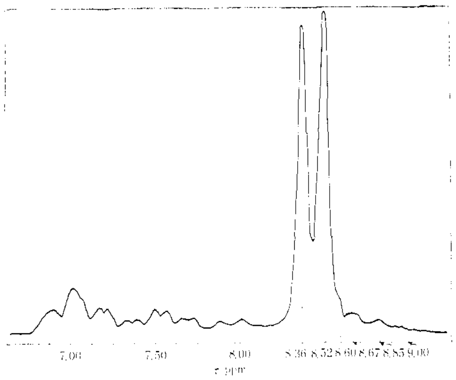


Figure 2. Proton nmr spectrum of IB–CTFE copolymer with mole fraction 0.478 CTFE at 100 MHz (solvent C_2Cl_4, temperature 100°).

The methylene resonances are spread widely and are very complicated. If it is assumed that only the nearest CFCl group contributes to the nonequivalence of the methylene protons, neglecting the effects of third nearest one, and that the long-range coupling constant between methylene protons and fluorines ($J_{CF_2-CH_2}$) is negligibly small, then the methylene resonance can be expressed in terms of the AB part of an ABX-type spectrum. The methylene resonances are not well resolved and are too complicated to be analyzed on this basis.

It seems to be quite an interesting problem whether the polymers obtained are stereospecific or not. The appearance of the methyl resonance and the simple $-CF_2-$ resonance may seem to indicate a stereoregular structure. It appears rather unusual that the radical polymerization induced by γ radiation should proceed quite stereospecifically, although the steric effects of bulky substituents have to be taken into account in the present system.

Further work is now under progress and the results are to be published elsewhere.

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(6) K. Hayashi, T. Tonezawa, C. Nagata, S. Okamura, and K. Fukui, *J. Polym. Sci.*, **20**, 537 (1956).

(7) T. Fischer, J. B. Kinsinger, and C. W. Wilson, III, *ibid., Part B*, **4**, 379 (1966).