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ESR Spectra of γ-irradiated Linear Aliphatic Polyesters[*1]

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The ESR spectra of γ-irradiated linear aliphatic polyesters (2.2, 2.4, 2.6, 2.7, 2.8 and 6.8 polymer) have been measured at various temperatures ranging from 77°K to room temperature. Two types of spectra are obtained in these polyesters except for 2.2 polymer. The first, the six-line spectrum obtained at low temperatures was relatively short-lived and increased in signal intensity with increasing methylene groups of these polyesters. The well-resolved, second, five-line spectrum is stable even at room temperature in comparison with the former. The possible structures of two radicals were discussed.

Recently a number of ESR studies on the radical produced by γ-irradiation of low molecular weight organic and polymeric substances have been carried out. Correlations between the radical species and chemical structures of various polymers have been extensively found.[1-7] Configurations of the free radical in irradiated polyethlene and polypropylene in particular were discussed with respect to the relation of the radical decay reaction to a molecular motion in the matrices.[8,9]

In the linear aliphatic polyesters, however, no studies on the radical species produced by γ-irradiation or the behaviour of radical decay have been reported except for an anisotropic study on irradiated poly(β-propiolactone).[10] From the data obtained by the observation of ESR spectra of irradiated polyesters, the species and the site of the radical are discussed.

The crystal structures of the polyesters have been

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1) a) E. J. Lawton, J. S. Balmit and R. S. Powell, *J. Chem. Phys.*, **33**, 396, 405 (1960). b) S. Ohnishi, This Bulltin, **35**, 254 (1962).

2) M. Kashiwagi, *J. Polym. Sci.*, **A-1,** 189 (1963).

3) H. Fisher and K. H. Hellwege, *J. Polym. Sci.*, **56**, 33 (1962).

4) S. Ogawa, *J. Phys. Soc. Jap.*, **16**, 1488 (1960).

5) D. J. Ingram and M. G. Townsend, *Trans. Faraday Soc.*, **54**, 409 (1958).

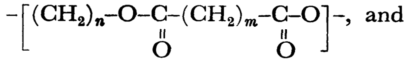
6) H. N. Rexroad and W. Gordy, *J. Chem. Phys.*, **39**, 399 (1959).

7) F. C. Thryion and M. D. Baijal, *J. Polym. Sci.*, **6**, 505 (1968).

8) S. Nara, S. Shimada, H. Kashiwabara and J. Sohma, *J. Polym. Sci.*, **6**, A-2, 1435 (1968).

9) S. Nara, H. Kashiwabara and J. Sohma, *ibid.*, **5**, A-2, 929 (1967).

10) S. Ohnishi, S. Sugimoto, K. Hayashi and I. Nitta, This Bulletin, **37**, 524 (1964).

extensively studied by many investigators.[11-14] From the results, it is apparent that the crystal structure is similar to that of polyethylene and the molecular chain conformations are planar zigzag except for poly(ethylene adipate) and the glycol parts of the polyesters with ethlene glycols. The chemical structure of the polyesters studied is expressed as  $-\left[(CH_2)_n\text{-O-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-}(CH_2)_m\text{-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-O}\right]-$, and the polyesters are denoted as *n.m* polymer hereafter. In the present paper the results deduced from ESR spectra of 2.2, 2.4, 2.6, 2.7, 2.8 and 6.8 polymer are mainly discussed.

Experimental

Samples (the 2.2, 2.4, 2.6, 2.7, 2.8 and 6.8 polymer) were prepared by polycondensation between the corresponding diol and dibasic acid using the $ZnCl_2$ as a catalyst. To obtain high molecular weight polymers, the later stage of the reaction was carried out in a vacuum keeping the pressure below 1 mmHg and bubbling argon gas through the reacting mass. The polyesters prepared as above were purified by repeated precipitation from benzene solution with methylalcohol and dried in a high vacuum at room temperature.

The samples used for ESR measurements were prepared in a 5 mmϕ glass tube with dried nitrogen atmosphere, and subjected to irradiation at 77°K. Irradiation dose was about 4 Mrad.

The ESR spectrometer used in the present study was a JES-3BSX type apparatus (Japan Electron Optics Laboratory Co., Ltd.) with 100 kHz field modulation and TE_{011} mode cavity. The ESR measurements were carried out at different temperatures from liquid nitrogen to room temperature using variable attachments for the spectrometer.

The drawn samples of 6.8 polymer were also prepared from the film obtained by means of hot pressing at melting point. Drawing was carried out at room temperature, up to 500% in draw ratio. The ESR spectra were measured on various orientations of the specimen in the applied magnetic field.

Results and Discussion

The ESR spectra of the irradiated 2.4 polymer measured at various temperatures are shown in Fig. 1. At low temperature, a single line spectrum is overlapped on a weak six-line spectrum. By raising the temperature, the signal intensity decreases gradually and the spectrum begins to split at around −140°C. At room temperature, it splits into a five-line spectrum with a hyperfine (hf) constant of about 25 gauss.

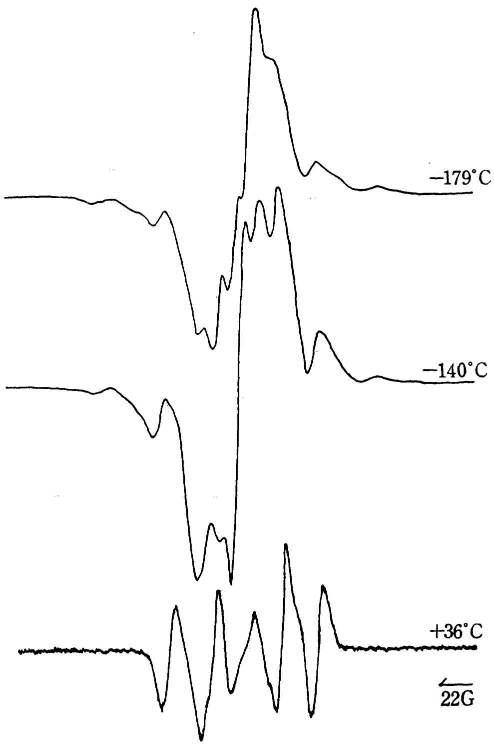
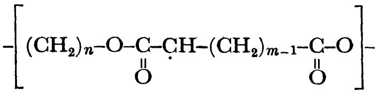
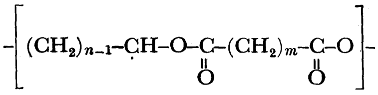
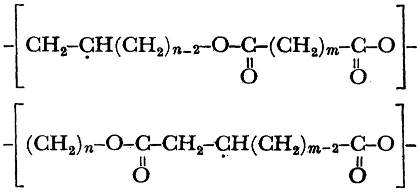


Fig. 1. The ESR spectra of γ-irradiated 2.4 polymer.

As possible species of the radical produced in these polyesters, three kinds of species are expected which are produced by abstraction of hydrogen atom from the acid or the glycol part of the main chain.[*2] The three types are those which could be produced by extracting α-hydrogen from the acid

(A) 
$$-\left[(CH_2)_n\text{-O-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-}\underset{\cdot}{C}H\text{-}(CH_2)_{m-1}\text{-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-O}\right]-$$

(B) 
$$-\left[(CH_2)_{n-1}\text{-}\underset{\cdot}{C}H\text{-O-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-}(CH_2)_m\text{-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-O}\right]-$$

(C) 
$$-\left[CH_2\text{-}\underset{\cdot}{C}H(CH_2)_{n-2}\text{-O-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-}(CH_2)_m\text{-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-O}\right]- \quad \text{or}$$
$$-\left[(CH_2)_n\text{-O-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-}CH_2\text{-}\underset{\cdot}{C}H(CH_2)_{m-2}\text{-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-O}\right]-$$

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[11] C. S. Fuller and C. J. Frosh, *J. Phys. Chem.*, **43**, 323 (1939), C. S. Fuller and C. L. Erickson, *J. Amer. Chem. Soc.*, **59**, 344 (1937).

[12] A. Turner-Jones and C. W. Bunn, *Acta Crystallogr.*, **15**, 109 (1962).

[13] Y. Chatani, A. Ueda and H. Tadokoro, Preprint of the 16th Symposium on Makromolecular Chemistry held by the Polymer Chemistry of Japan (Fukuoka, Oct., 1967) p. 41.

[14] K. Tanaka, T. Kanamoto and H. Nagai, Preprint of International Symposium on Makromolecular Chemistry, VII-147, Kyoto (1966).

[*2] At the first stage of the analysis we examined the possibility of radical production by chain scission, but the possibility was excluded on the basis of ESR spectra.

part (A), α-hydrogen from glycol part (B) and the other hydrogen from both the acid or glycol parts (C).

Type C is expected to give the same spectrum as that of the alkyl radical which has often been observed in irradiated polyethylene at low temperatures. From the experimental results, the weak six-line spectrum detected at low temperature might be assigned to type C radical, because the hf constant of the signal is about 33 gauss which equals that of polyethylene.

The spectral changes caused by the rise of temperature in the irradiated 2.6, 2.7 and 2.8 polymer are shown in Fig. 2. This behavior is similar to that of 2.4 polymer. At low temperature the weak six-line spectrum with the hf constant of 33 gauss is also observed more strongly than in that of 2.4 polymer. At room temperature the same type of five-line spectrum as detected in 2.4 polymer is also observed in each polymer. The spectrum may be attributed to either type A or type B radical.

The crystal structures of the linear aliphatic polyesters have been extensively studied by Fuller and Frosh,[11] Turner-Johns and Bunn,[12] Chatani *et al.*,[13] and Kanamoto.[14] According to their

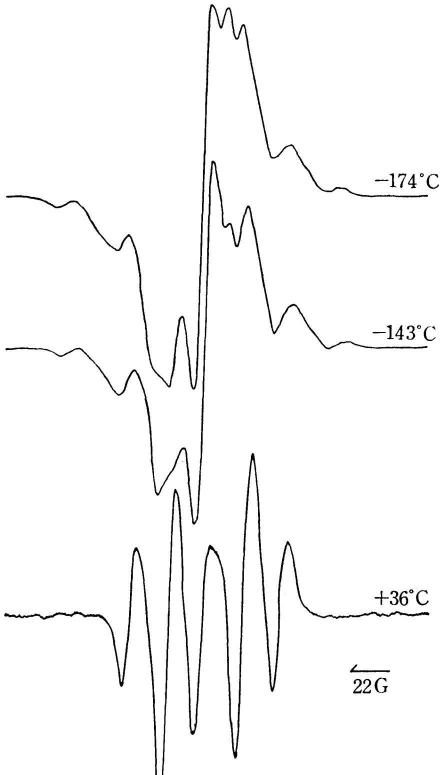

Fig. 2-a. The ESR spectra of γ-irradiated 2.6 polymer.

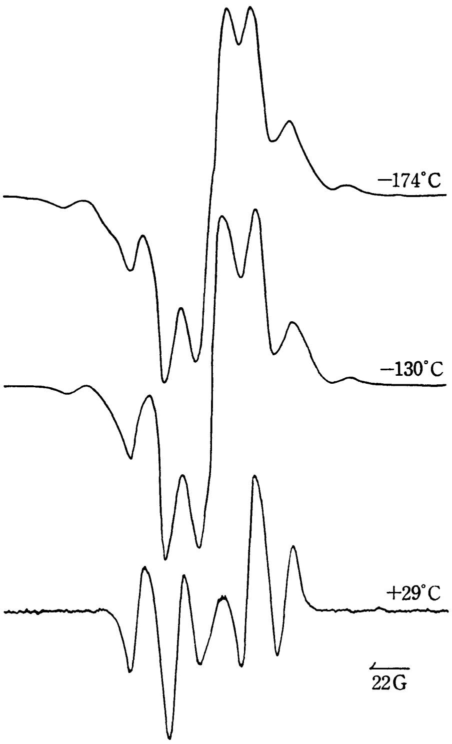

Fig. 2-b. The ESR spectra of γ-irradiated 2.7 polymer.

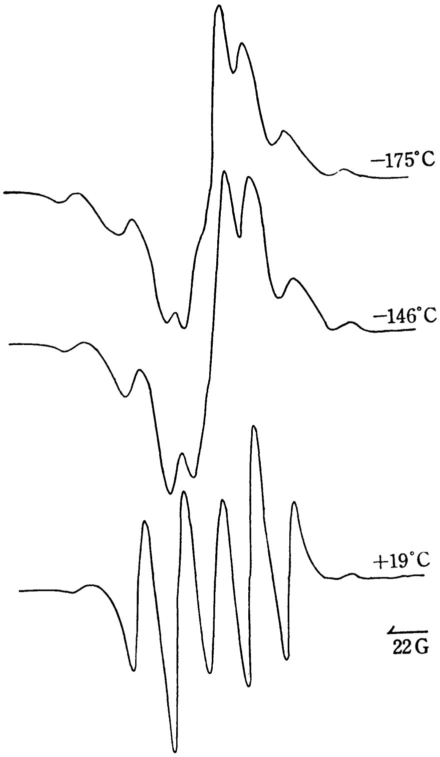

Fig. 2-c. The ESR spectra of γ-irradiated 2.8 (c), polymer.

studies, the crystal structure of these polyesters are very similar to each other and a molecular packing in planes perpendicular to the chain axis is very similar to that of polyethylene. From these results, the chain conformation of the polyesters is found to be nearly planar zigzag except for 2.2 polymer which has helical chain conformations, and for 2.4, 2.6, 2.7 and 2.8 polymers which are slightly distorted around the chain axis in glycol parts. The 6.8 polymer has a substantially planar zigzag chain conformation throughout the chain.

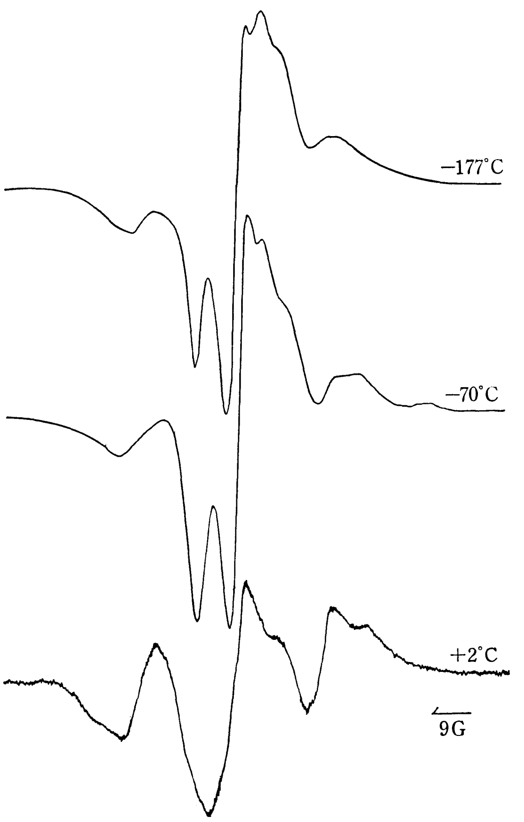

Fig. 3. The ESR spectra of γ-irradiated 2.2 polymer.

In order to obtain further information, the same experiment was performed on 2.2 polymer. As shown in Fig. 3, the spectrum at low temperature is complicated, and is not well resolved even at room temperature. On the other hand, the same type of spectrum has been observed on both irradiated poly(ethylene terephthalate)15) and powdered succinic acid,16) and the spectrum has been interpreted as the result of the interaction between an odd electron and three nonequivalent hydrogen atoms (*i.e.*, α and two β-hydrogen atoms). The nonequivalency of these hydrogen atoms in the hf interaction may be caused by distrotions of the methylene groups from the planar zigzag conformation. Considering the chemical structure of 2.2 polymer, the radical produced by irradiations is probably situated on α-carbons of diacid or diol parts. According to the crystal structure of the polymer,13) methylene groups in both parts are distorted from the planar zigzag chain conformation. From the distortion in the methylene group we can see the coincidence of the ESR spectrum of the 2.2 polymer with that of poly(ethylene terephthalate). In 2.4, 2.6, 2.7 and 2.8 polymer, as mentioned above, it is known that the ethylene glycol part of the polymers have also a slight departure from the planar chain conformation. If type B radical was produced in the polymers, unresolved signals similar to that obtained in 2.2 polymer should be expected. However, only the five-line spectrum is observed in the polyesters. This suggests that the five-line spectrum observed at room temperature could be assigned to the type A radical on the acid parts having planar zigzag chain conformation.

The effect of temperature on the ESR spectra of the 6.8 polymer was studied by raising the tem-

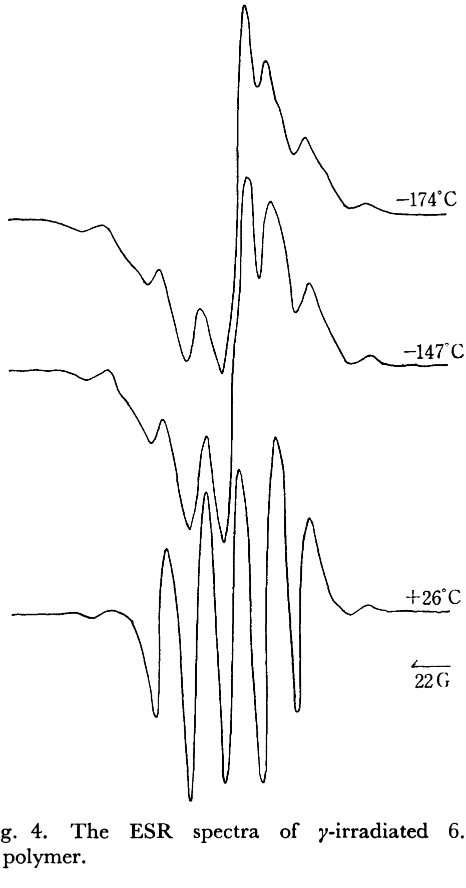

Fig. 4. The ESR spectra of γ-irradiated 6.8 polymer.

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15) D. Campbell, K. Araki and D. T. Turner, *J. Polym. Sci.*, **A-4**, 2597 (1966).

16) C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, No. 5, 1535 (1960).

perature (Fig. 4). At low temperature the six-line spectrum is larger than that of the 2.4, 2.6, 2.7 and 2.8 polymers, and decreases with rising temperature. At room temperature the five-line spectrum was also observed with a trace of type C, and the spectral pattern and the hf splitting are very similar to those of polymers described above.

The chain conformation of the polymer, as reported by Kanamoto,[14] is planar zigzag in both dibasic acid and the diol parts. If type B radical was produced in the polymer, the spectral pattern and the hf constant of the signal might be different from that of the five-line spectrum. However, the spectrum is in good agreement with that of the polyester with ethylene glycol. This indicates that type A radical is more probable than type B because of the resonance stabilization

As shown in Fig. 5, the integrated intensity ratio of the five-line spectrum is nearly 1 : 2 : 2 : 2 : 1. The intensity distribution is interpreted as the result of the interaction between an odd electron and one α-hydrogen and two equivalent β-hydrogen atoms. To obtain the anisotropic behaviour of α-hydrogen, experiments are carried out in drawn 6.8 polymer. The spectra were measured in orientation axes parallel and perpendicular to the external magnetic field. The radicals trapped in the specimen quickly disappear by the reaction with oxygen, since experiments are carried out in air without sealing the sample tube. The spectra obtained at −80°C are shown in Fig. 6-a, where type C radical remains.

Salovy and Yager[17] have reported the anisotropy in the ESR spectrum of oriented mats of solution-grown polyethylene single crystal.

In the present case, the signal intensity of type C radical will be similar to the alkyl radicals of the polyethylene studied by Salovy and Yager.

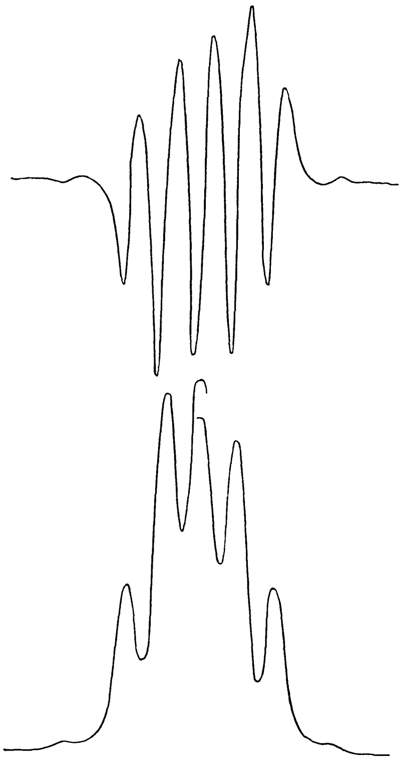

Fig. 5. The ESR spectrum of γ-irradiated 6.8 polymer at 26°C: (top) observed first derivative curve: (bottom) its integrated absorption curve.

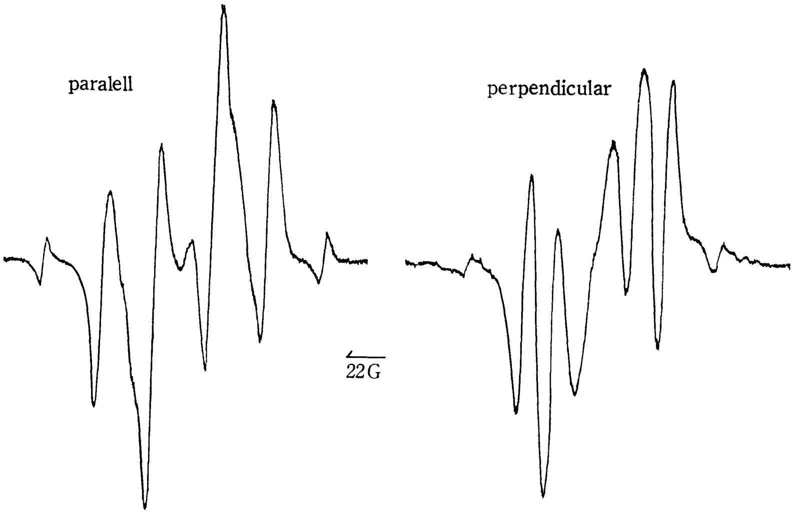

Fig. 6-a. The ESR spectra of γ-irradiated 6.8 polymer measured at −80°C. Magnetic field parallel (left) and perpendicular (right) to chain.

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[17] R. Salovy and W. A. Yager, *J. Polym. Sci.*, **A-2**, 219 (1964).

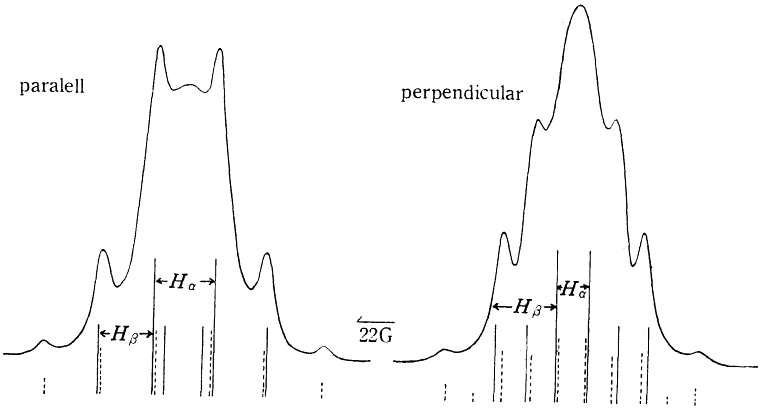

Fig. 6-b. The integrated absorption curves of γ-irradiated 6.8 polymer. Vertical dotted lines show hyperfine pattern obtained by Salovey[17] and solid lines show predicted hyperfine pattern of type A radical.

Thus, by substracting the signal intensity of polyethylene from the integrated absorption curves of our spectrum, the intensity due to type A is obtained in both orientations parallel and perpendicular to the external magnetic field, as shown in Fig. 6-b. The anisotropy of the hf constant of α-hydrogen was estimated as $A^{\alpha}_{//}=34.6$ gauss and $A^{\alpha}_{\perp}=17.3$ gauss. In oriented polymeric substances the molecular chain is aligned to the orientation axis (Y). Thus the hf constant of α-hydrogen to direction (X and Z) normal to the molecular chain is obtained as the average in hf interactions, so that $A^{\alpha}_{//}$ and $A^{\alpha}_{\perp}$ are to be A_y and $(A_x+A_z)/2$, respectively. Consequently, $A_y=34.6$ and $A_x+A_z=34.6$ are evaluated. A values are in close agreement with those of low molecular weight organic compounds.[16,18-20] The fact also permits the five-line spectrum to be attributed to type A radical.

Existence of two kinds of species is concluded. The one is relatively short-lived and gives a six-line spectrum which is attributed to type C. The other gives the five line spectrum which is stable even at room temperature. Based on the chain conformation of the polymer, it is assigned to type A radical in the acid parts.

The author wishes to thank Professor M. Takeda and Dr T. Kanamoto, Department of Chemistry, Science University of Tokyo, for their valuable advice and encouragement.

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18) H. M. McConnell, C. Heller, T. Cole and R. W. Fessenden, *J. Amer. Chem. Soc.*, **82**, 766 (1960).

19) D. Pooley and D. H. Whiffen, *Mol. Phys.*, **4**, 81 (1961).

20) I. Miyagawa and K. Itoh, *J. Chem. Phys.*, **36**, 2157 (1962).