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Electron Spin Resonance Studies of Irradiated Single Crystals of Methacrylamide*

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Synopsis

Irradiated single crystals of methacrylamide were studied by electron spin resonance. Irradiations were made at 77 and 288°K. and measurements were made at 77, 193, and 293°K. Only chemical changes explain these spectra. The original scission is C—C breakage between ($CONH_2$) and CH_2=C(CH_3)—, and C—H breakage between CH_2=C-($CONH_2$)CH_2— and H; these small fragments react with methacrylamide and finally produce two free radicals at room temperature. These two free radicals are the ones which propagate or terminate the polymerization. The free radical transformation at the last period of polymerization is concluded to be:

$$R\dot{C}H_2(CH_3)CONH_2 \rightarrow R'R''C(CH_3)CONH\cdot$$

INTRODUCTION

It is extremely difficult to obtain a single crystal of a high polymer which is sufficiently large to permit observation of the electron spin resonance (ESR) after irradiation. Therefore, the only way to determine the exact nature of free radicals trapped in a vinyl polymer by polymerization or radiation damage seems to be to study an irradiated single crystal of its monomer. However, there are very few examples of ESR studies of irradiated single crystals of vinyl monomers. It is also difficult to prepare a single crystal of a vinyl monomer. This is partly because a monomer is readily polymerized during the evaporation of the solvent from its solution to make single crystals. The other difficulty is that most of vinyl monomers are liquid at room temperature. In this respect, acrylamide and methacrylamide have their advantages, as both of them are solid at room temperature.

EXPERIMENTAL

It was difficult to grow a good single crystal from an alcoholic solution of methacrylamide, as it readily gave very thin and fragile plates. A mixed

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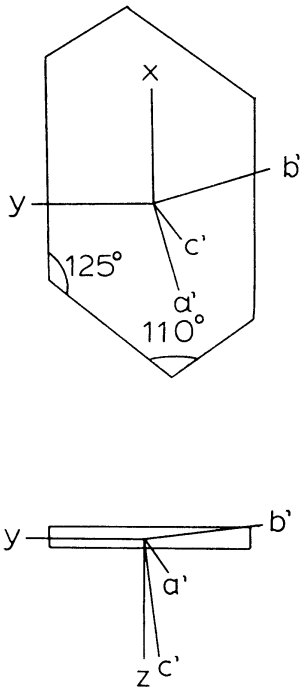

Fig. 1. A single crystal of methacrylamide. x, y, and z are conventional axes selected for the measurements. a', b', and c' are the directions of the principal values of the hyperfine tensors.

solvent of concentrated HCl and ethanol gave, when the solution was warmed to 40°C. and then cooled and evaporated, several satisfying crystals whose shape is shown in Figure 1. The result of an elementary analysis showed that no acid is bonded in the form of hydrochloride.

Crystals were irradiated at 77 and 288°K., the ESR measurements were made at 77, 193, and 293°K., all at a frequency of about 9,400 Mcycles/sec.

The crystal structure and symmetry of this crystal is not known, but a conventional coordinate system was selected as shown in Figure 1. Measurements were made with the magnetic field perpendicular to one of these axes, at 15° intervals, or for 7.5° if necessary, of rotation about this axis.

RESULTS

1. Irradiation at 288°K.

The crystal irradiated with a dose of 3×10^6 r at 288°K. was measured at 293 and 77°K.

A. Spectrum Observed at 293°K. This spectrum is composed of two groups of lines: a quintet and a sextet, as shown in Figure 2. The quintet is isotropic with an equal spacing of 23 gauss and the same nature as already found in irradiated polymethyl-methacrylate.[1-3] The sextet is anisotropic. From the angular dependence of the splitting, it is concluded that there are one nitrogen and one proton coupling with the unpaired electron. The proton interacts isotropically and its splitting factor, A_i, is 28.2 gauss.

TABLE I
Anisotropic Splitting Factors from the Nitrogen Nucleus

I Experimental values			II Principal values			III Direction cosines		
x	y	z	a'	b'	c'	a'	b'	c'
$x+14.0$	-2.6	-0.3	$a'+12.8$	0	0	$x-0.92$	$+0.28$	-0.25
$y-2.6$	$+21.0$	$+1.4$	b' 0	$+22.1$	0	$y-0.23$	-0.94	-0.23
$z-0.3$	$+1.4$	$+12.6$	c' 0	0	$+12.8$	$z-0.29$	-0.14	$+0.94$

The nitrogen interacts anisotropically and its splitting factor, A_a, is shown in Table I.

The term x-x in I denotes the A_{xx} element of the hyperfine tensor, term x-y, the A_{xy} element, etc. In the same way, in II, term a'-a' denotes

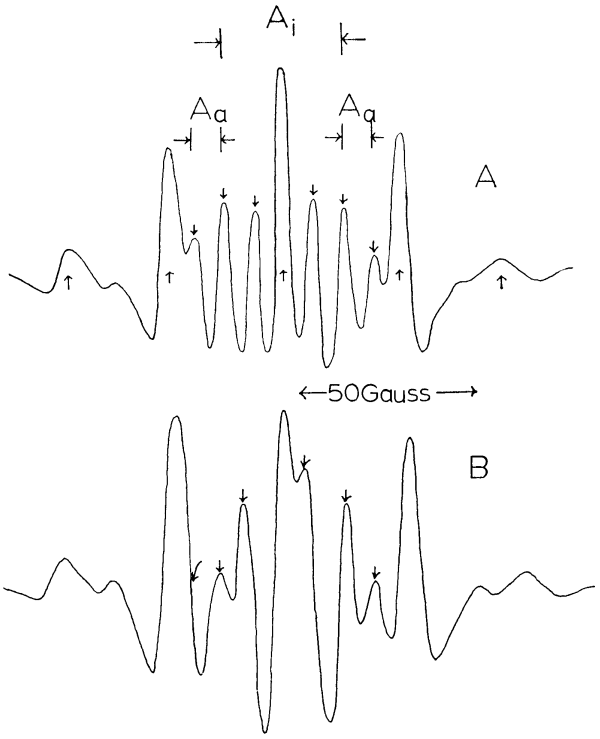

Fig. 2. ESR spectra for the measurements at 293°K.: (A) $\angle$ xH = 90°, $\angle$ yH = 0°; (B) $\angle$ xH = 90°, $\angle$ yH = 45°. A_j indicates the isotropic splitting and A_a indicates the anisotropic splittings.

Fig. 3. Carbon-13 lines of the spectrum obtained from an irradiated single crystal of methacrylamide. $\angle$ xH = 90°, $\angle$ yH = 30°. Only the left half of the spectrum is shown. The ^{13}C splitting constant has been reported as 35 gauss.[4]

one of the principal values $A_{a'a'}$. III shows the direction cosines for the transformation of I into II. These principal values can be divided into two terms, the isotropic and anisotropic terms. The isotropic part is 15.9 gauss while the anisotropic principal values are −3.1, 6.2, and −3.1 gauss for $a'a'$, $b'b'$, and $c'c'$ elements, respectively.

B. Spectra Observed at 77 and 193°K. These are identical with those at 293°K.

C. Spectra from the Crystal with High Dosage. The spectra obtained after irradiation with a dose of 10^8 r at 288°K. showed no anisotropy. This is because the methacrylamide had polymerized completely and was no longer a single crystal. Actually the spectrum was identical with that of polycrystalline material, and the hardness and brittleness of this crystal was different from that of sample irradiated with 3×10^6 r.

D. Carbon-13 Lines. Some anisotropic carbon-13 lines are observed when a strong signal is recorded, as shown in Figure 3.

2. Irradiation at 77°K.

The crystal irradiated with a dose of 3×10^6 r at 77°K. was colored green, while the color of the crystal irradiated at 288°K. is yellow. This crystal was first measured at 77°K., then warmed up to 193°K. and measured,

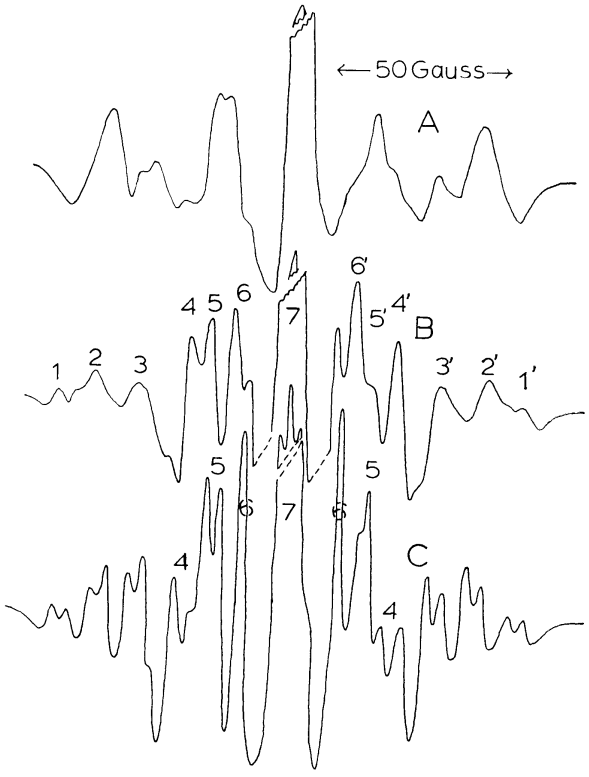

Fig. 4. ESR spectra for the measurements at 77°K. of a crystal irradiated at 77°K., ∠ xH = 90° for all spectra: (A) ∠ yH = 75° with the incident power of 20 mw.; (B) ∠ yH = 165°, the incident power is 1 mw.; (C) ∠ yH = 75°, with the incident power of 1 mw.

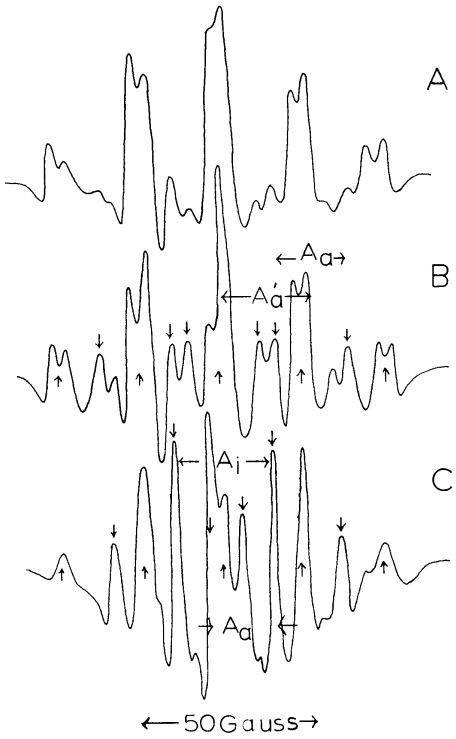

Fig. 5. ESR spectra of the crystal irradiated at 77°K. and then warmed to 193°K., $\angle$ xH = 90° for all spectra: (A) measured at 77°K., $\angle$ yH = 67.5°, the incident power is 20 mw.; (B) at the same orientation and with the same power as in A, but measured at 193°K.; (C) $\angle$ yH = 30°, the incident power is 20 mw., measured at 193°K. A_i indicates the isotropic splitting, and A_a and A_a' indicate the anisotropic splittings, respectively.

then again cooled to 77°K. and measured, and finally rewarmed to 293°K. and measured.

A. Spectra at 77°K. The pattern of the spectra at 77°K. is strongly power-dependent. The spectra at a microwave incident power of about 20 mw. is broadened by power saturation at any orientation in the magnetic field, as shown in Figure 4A. However, when the power is reduced to a few milliwatts, the spectra can be split into about 16 lines, as shown in Figure 4B. When the conventional y-axis is near 90° to the magnetic field, the lines can further be split twice in its number, as shown in Figure 4C. It seems there are too many lines to be interpreted. However, the following analysis seems the most plausible one. There are three components; a sextet (1,3,5,7,5′,3′,1′), a quintet (2,4,7,4′,2′), and a triplet (6,7,6′). If the total intensities of these different components are put as x, $x + y$, y respectively, the intensity of the central line, i.e., the line marked by 7, should be four times as strong as that of the nearest neighbor, 6 or 6′.

B. Spectra After Warming to 193°K. The shape of the spectrum when the crystal irradiated at 77°K. was warmed up to 193°K. and then measured shows far smaller power saturation than that of the crystal before warming.

The spectrum, however, fairly shows power saturation when the crystal is cooled to 77 °K. again, as shown in Figure 5*A*. The spectra has a quintet with the equal splittings of 21.5 gauss, as is clearly seen in the power-saturated spectrum in Figure 5*A*. The other component is an anisotropic double quartet (sometimes double triplet) with an isotropic splitting of 28 gauss, A_i, and with two anisotropic splittings, A_a and $A_{a'}$.

C. Spectrum After Warming to 293°K. The spectrum thus obtained is identical with that obtained by irradiation at 293°K.

DISCUSSION

The number and the spacings of the spectral lines change according to the temperature of irradiation, not of measurement. The spectrum at any condition of measurement has more than two components.

The significant difference of this present compound from other already studied single crystals lies in that it has a C=C double bond, which easily reacts with small fragments produced by the irradiation, e.g., the addition reaction of free radicals.

Abraham and co-workers[2] explained the two species in irradiated PMMA on the basis of configurational isomerism. If the two components of a spectrum are to be explained in that way in this case, they must have at least one common spacing in each of the spectra. In the present case no such common splitting was found.

The quintet of lines is found only in irradiated methyl-substituted vinyl

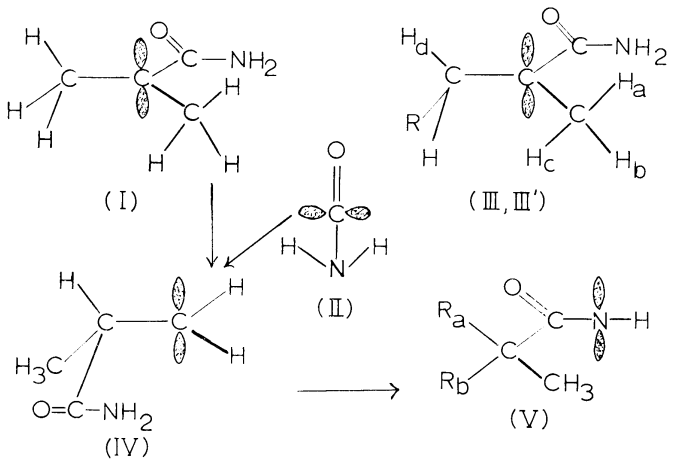

Fig. 6. The scheme of radiation decomposition of methacrylamide. At 77°K., (I), (II), and (III) are observed after irradiation, (I) and (II) change to (IV) between 77 and 193°K. Then at 193°K., both (III) and (IV) are observed. Between 193 and 293°K., (IV) changes to (V). Then at 293°K., both (III) and (V) are observed. From (V), a spectrum which is strongly anisotropic is expected. However, if there is a large contribution of the resonance structures RĊ(=NH)--O and RC(=NH)O·, the anisotropy will be substantially reduced. R is either [CH_2=C($CONH_2$)CH_2—] in (III) or [CH_2=C(CH_3)—] in (III') groups. In (V), R_a and R_b are H, (—$CONH_2$), and/or several monomer units. The figure (IV) shows only the species which is formed from (II); (IV') referred to in the text is formed from (I).

monomers and polymers. Therefore, it is clear that two or three of the coupling protons for the quintet of lines are from this methyl group. If the methyl group is rotating at 293°K. and not rotating at 77°K., the spectrum of the crystal irradiated at 288°K. and measured at 77°K. must show great difference from that measured at 293°K. In the present case they are the same.

From these facts, the difference in the present spectra at different conditions is to be interpreted by chemical changes in the structures of the free radicals. The fact that the crystal irradiated at 77°K. gives the same spectrum as that of the crystal irradiated at 293°K. when the former is measured also at 293°K. shows that the radiation damage caused at 77°K. is the more original process. As a matter of possibility several different bond scissions are expected at 77°K. However, only two types of bond scissions were observed in this study.

As the sextet of lines has equal spacings and an approximate intensity ratios of 1:6:15:20:15:6:1, there should be six equally coupling protons. Such spectrum can only be explained by the species I in Figure 6. It should be assumed that two methyl groups are rotating. The species I is formed by an addition of an emitted hydrogen atom from methacrylamide (M).

$$\begin{aligned} \mathrm{M} &\rightarrow \mathrm{H}\cdot + \mathrm{CH_2{=}C(CONH_2)\dot{C}H_2} \\ \mathrm{H}\cdot + \mathrm{M} &\rightarrow \mathrm{(CH_3)_2\dot{C}CONH_2} \end{aligned} \qquad (1)$$

This species $CH_2{=}C(CONH_2)\dot{C}H_2$ was not observed in this experiment. This is interpreted in the way that this species adds to M and forms a free radical, III. The species III gives a quintet by an equal interaction of the unpaired electron with the four protons H_a, H_b, H_c, and H_d, assuming the methyl protons and the proton H_d are identical. On the other hand, the triplet is to be explained by a species as shown in II. The ESR spectra of species II might show anisotropy; however, a tumbling motion of this species in the crystal lattice will cancel it. Actually, the width of the triplet is smaller than the other lines, as shown in Figure 4. The species II is formed by a C—C scission of M, and the expected counter fragment is $CH_2{=}\dot{C}(CH_3)$. This latter species was not observed in this experiment, either. This is interpreted as follows: this species is too reactive to exist, and adds to M, forming III′, which also gives a quintet. Therefore, the primary radiation damage of M is formulated as:

$$(x + y)\mathrm{M} \rightarrow x\mathrm{CH_2{=}C(CONH_2)\dot{C}H_2} + x\dot{\mathrm{H}} + y\dot{\mathrm{C}}\mathrm{ONH_2} + y\mathrm{CH_2{=}\dot{C}(CH_3)}$$

The ratio of C—H scissions to C—C scissions is $x:y$ and equals to the intensity ratio of the lines from the species I and II, and is 3:2.

One component of the spectra observed at 193°K. (Fig. 5) is a quintet. This is to be assigned to the species III and III′, because these two fragments gave a quintent at 77°K. The spacings have changed from 27 gauss to 21.5 gauss. There will be some difference in the configuration of the free radical between 77°K. and 193°K. The other component is an anisotropic octet. This latter spectrum shows that there is one proton in-

teracting isotropically and two protons equally and anisotropically. The expected structure for this fragment is IV. The species I and II have disappeared on raising of the temperature of the crystal from 77°K. to 193°K., and the species V has appeared instead. The reactions;

$$(CH_3)_2\dot{C}CONH_2 \rightarrow CH_2{=}C(CH_3)CONH + H$$
$$\dot{C}ONH_2 \rightarrow O{=}C{=}NH + H$$
$$H + M \rightarrow \dot{C}H_2{-}CH(CH_3)CONH_2 \qquad (2)$$

are expected between 77°K. and 193°K. The reaction (H + M) was like reaction (1) when it proceeded under irradiation at 77°K., but at 193°K. it is like reaction (2). This difference in the adding sides of the carbon atoms of a bouble bond, when a hydrogen atom adds to it, will be explained as a thermal effect.

The angle between the direction of the unpaired electron and the direction of the C—H bond interacting isotropically with this electron is calculated from the isotropic splitting of 28 gauss and is about 36°.

After the crystal was warmed to room temperature, the free radical giving rise to the quintet was still present, with four equal spacings of 23 gauss. However, the free radical which gave the octet at 193°K. decayed somewhere below room temperature and instead the double triplet appeared. This double triplet indicates that there is one nitrogen nucleus and one isotropically interacting proton. The free radical as shown in V of Figure 6 will give the double triplet lines. Because the isotropic 28.2 gauss splitting seems a reasonable value for the N—H proton if a contribution of the structures R—C(=NH)—O· and R—Ċ(=NH)--O to the species V is not small. The isotropic splitting of 15.9 gauss of the each triplet is also very probable as a nitrogen splitting. Then, the free radical change is:

$$CH_3CH(CONH_2)\dot{C}H_2 + CH_2{=}C(CH_3)CONH_2 \rightarrow$$
$$[CH_2{=}C(CH_3)CONH]\cdot + CH_3CH(CONH_2)CH_3$$

This indicates that the $RCH_2\cdot$ type free radical is not stable at room temperature, perhaps because of its larger mobility than that of R—CH—R′ type radical, in which both sides of the free radical carbon atom is more or less fixed. Methacrylamide polymerizes with two different mechanisms.[5] The one is thermal polymerization occurring above 150°C. and the other is free radical polymerization occurring near 100°C. In the spectrum obtained from polycrystalline methacrylamide the double triplet component disappears after the free radical polymerization has started. This indicates that the free radical V has started another polymerization chain. This alternatively can be described that the free radical V has been transformed into a polymerization end type radical $RCH_2\dot{C}(CONH_2)CH_3$. However, when the crystal is further heated, all the polymerization end is terminated by a chain transfer process to the amino group, leaving the free radical V, which cannot be further transformed because there is no monomer at this stage of the polymerization. Thus, the resulting spectrum is structureless when observed in the polycrystalline state on account of its anisotropy.[5]

From the polycrystalline study, it was shown that the free radicals stable at room temperatures begin to change their configuration near the melting point. However, the structures of the free radicals change very drastically at a far lower temperature.

Many experimental results have shown that polymethyl methacrylate undergoes C—C scission when irradiated. By a C—C scission, two different fragments can be formed; however, only one of the fragments, $R\dot{C}(CH_3)COCH_3$ has been observed.[1-3] Considering that the free radical IV is not stable at room temperature, the unobserved free radical $RCH_2\cdot$ will exist in the transient state and will decompose immediately after its formation at room temperature.

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Résumé

On a étudié par résonance de spin électronique des cristaux simples de méthacrylamide irradiés. Les irradiations ont été effectuées à 77 et 288° K et les mesures effectuées à 77, 193 et 293°K. Ces spectres s'expliquent uniquement par des changements chimiques. La scission originale est la rupture C—C entre ($CONH_2$) et $CH_2{=}C(CH_3)$—, et la rupture C—H entre $CH_2{=}C$—($CONH_2$)CH_2— et H; ces petits fragments réagissent avec le méthacrylamide et finalement produisent deux radicaux libres à température de chambre. Ces deux radicaux libres sont ceux qui propagent ou terminent la polymérisation. La transformation du radical libre à la période finale de la polymérisation est:

$$RCH_2(CH_3)CONH_2 \rightarrow R'R''C(CH_3)CONH\cdot$$

Zusammenfassung

Es wurden Elektronspinresonanzuntersuchungen an bestrahlten Methacrylamid-Einkristallen durchgeführt. Die Bestrahlung erfolgte bei 77°K und 288°K, die Messungen bei 77°K, 193°K und 293°K. Eine Deutung der Spektren ist nur unter der Annahme chemischer Veränderungen möglich. Die ursprüngliche Spaltung besteht in einer C—C—Spaltung zwischen ($CONH_2$) und $CH_2{=}C(CH_3)$— und einer C—H—Spaltung zwischen $CH_2{=}C(CONH_2)CH_2$— und H. Die dabei gebildeten kleinen Bruchstücke reagieren bei Raumtemperatur mit Methacrylamid unter Bildung zweier Radikale. Diese beiden Radikale sind von der Art der am Wachstum oder Abbruch der Polymerisation beteiligten Radikale. Man nimmt an, dass im letzten Schritt der Polymerisation folgende Radikalumwandlung vor sich geht:

$$RCH_2(CH_3)CONH_2 \rightarrow R'R''C(CH_3)CONH\cdot$$

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