Electron Resonance Spectra of Gamma-Irradiated Polymers: Measurements at 77°K. on Polymethacrylic Acid and Related Compounds*

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INTRODUCTION

Considerable research has been carried out on the changes which take place when polymers are subjected to ionizing radiations.[1,2] Recently, electron resonance measurements have shown that irradiated polymers often contain high concentrations of trapped free radicals[3-5] for which it is sometimes possible to postulate plausible structures. Abraham, Melville, Ovenall, and Whiffen[4] found that the electron resonance spectra given by polymethacrylic acid and its methyl and ethyl esters after gamma-irradiation at 20°C. were identical with the spectra given by radicals trapped in the addition polymerization of methyl methacrylate.[6-8] These spectra have been attributed to trapped propagating radicals.[4,8] However, when these polymers were gamma-irradiated at 90°K. and studied at this temperature without intermediate warming, slightly different spectra were obtained, which changed irreversibly into the usual spectra when the samples were allowed to reach room temperature. Since it appeared that such studies might yield information on the free radical reactions which occur when solid polymers are irradiated, these low temperatures measurements have been extended.

EXPERIMENTAL

Gamma-irradiations were carried out with a 1200-curie Co^{60} source in the form of a hollow cylinder, 1.9 in. internal diameter and 18 in. long, enclosed in a water-cooled lead safe. Samples were placed in an aluminum canister, attached to a lead plug, and lowered into the source by remote control. For low-temperature irradiations, a glass Dewar was constructed to fit inside the canister, and liquid nitrogen was used as refrigerant. The Dewar had a capacity of about 100 ml. and required refilling every 4 hr. The dose rate was approximately 3×10^5 r/hr., and most samples were irradiated for 24 hr. All samples were degassed and sealed off under high

vacuum. Soft glass tubes having little microwave loss were used for measurements at 300°K., while samples to be measured at 77°K. were sealed in thin Pyrex tubes. Up to six of the latter could be irradiated simultaneously at 77°K.

Electron resonance measurements were made with a transmission cavity spectrometer operating near 9.2 kMc/sec., with bolometer detection of the microwave power. Low-amplitude magnetic field modulation was employed with phase detection to give the second derivative of the absorption spectrum on a pen recorder. Some measurements were also made with similar spectrometers operating near 3 and 24 kMc/sec. Hyperfine splittings were estimated by comparison with the spectrum of a sample of manganese ions diluted by zinc sulfide. This has a hyperfine pattern of six sharp lines, with accurately known spacings.[9]

For measurements at 77°K., the unsilvered tip of a Dewar vessel was inserted into the microwave cavity of the 9 kMc/sec. spectrometer. Since the available volume was small, samples were introduced directly into the Dewar flask, in contact with the liquid nitrogen refrigerant. It has been found that atmospheric oxygen will interact with radicals trapped in solid polymers.[5,8,10,11] However, provided samples were cooled to 77°K. before breaking open the tubes, measurable spectra were usually obtained. Since the spectra of the polymers studied here merely decay in air and do not show the effects presumed due to peroxy radicals,[5,10,11] this problem was not serious. To remove noise caused by boiling of the liquid nitrogen, the latter was cooled by exhausting the Dewar for some minutes before inserting it into the spectrometer. In some cases solid nitrogen was formed by this treatment. Thus spectra reported at a nominal temperature of 77°K. were actually observed somewhere in the range 63–77°K. No exact measurements of free radical concentrations were made at 77°K., owing to difficulties introduced by working at low temperatures. All spectra were centered closely on the free electron spin g value of 2.00, although accurate measurements were made in only a few cases. Most significant experiments were carried out at least twice.

RESULTS AND DISCUSSION

Polymethacrylic Acid

Room Temperature Measurements

Polymethacrylic acid samples were prepared by exposing the degassed monomer to sunlight at room temperature. Polymerization took place, giving a white, powdery solid smelling strongly of monomer. After gamma-irradiation *in vacuo* at 300°K., on observation at this temperature at 9.2 kMc/sec., this material gave the spectrum of Figure 1. This consists of five main lines with interline spacings of 22.7 gauss and intensities in approximately the ratio 1:4:6:4:1, with a subsidiary four-line pattern. No lines were observed outside those at ±45.5 gauss, even when the latter
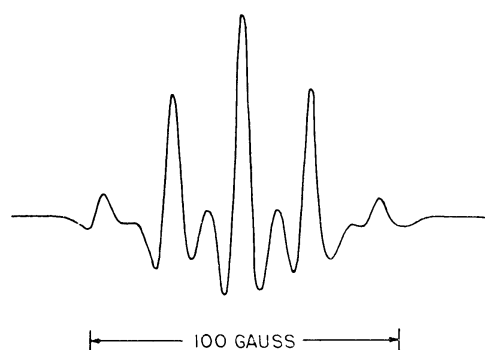
Fig. 1. Electron spin resonance spectrum at 300°K. of polymethacrylic acid after gamma-irradiation at 300°K. (All spectra are second derivatives, with the magnetic field increasing uniformly from left to right.)

were recorded with a signal-to-noise ratio of fifty. This hyperfine pattern is identical with that reported by Abraham, Melville, Ovenall, and Whiffen.[4]

The line spacing is in agreement with the 22.5 gauss reported by Schneider for x-irradiated polymethyl methacrylate,[3] and rather less than the value of 26 gauss formerly reported* for gamma-irradiated polymethacrylic acid and its methyl and ethyl esters.[4]

Similar spectra from methacrylate polymers have been reported and discussed in many papers,[3,4,6-8] but measurements have been confined, with one exception,[3] to the region of 9 kMc/sec. This spectrum was therefore observed at other microwave frequencies to determine if the hyperfine structure was frequency-dependent. Samples gamma-irradiated at 300°K. were examined at frequencies near 3, 9, and 24 kMc/sec., small quantities of diphenyl picryl hydrazyl (DPPH) being used as g markers. In all cases the centers of the spectra coincided with the center of the DPPH resonance within an observational uncertainty of about one gauss. The spectra at 3 and 9 kMc/sec. were identical. The spectrum at 24 kMc/sec. was similar, but the individual lines of the quintet were broader than at the lower frequencies, and the weaker quartet could barely be distinguished. Schneider, using oscilloscope presentation of the absorption curve of x-irradiated polymethyl methacrylate at 23.7 kMc/sec. and room temperature, observed that the quartet was too weak to be resolved.[3] It is likely that an increase in line width, rather than a change in the relative intensities of the lines, is responsible for this difference in the spectra. From these measurements it can be concluded that the two sets of lines arise from groups of protons coupled to electrons with the same g value, which is essentially that for a free electron spin.

Measurements at 77°K.

A sample of polymethacrylic acid which had been gamma-irradiated at 300°K. was examined in the 9 kMc/sec. spectrometer at 77°K. The

* Added in proof: A private communication from Dr. D. H. Whiffen states that the discrepancy is due to a systematic field-sweep calibration such that all splittings given in references 4 and 5 should be reduced by 12%.
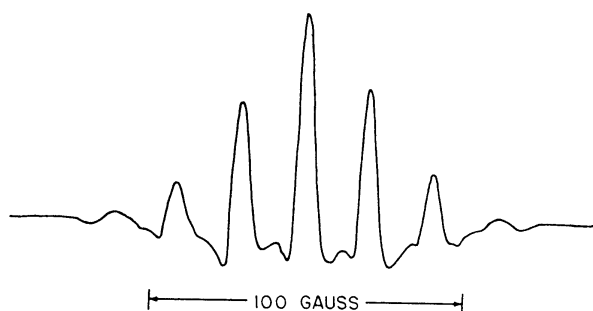
Fig. 2. Electron spin resonance spectrum at 77°K. of polymethacrylic acid after gamma-irradiation at 77°K.

spectrum was identical with that at 300°K. (Fig. 1). However, when samples were irradiated at 77°K. and examined at this temperature without intermediate warming, the spectrum shown in Figure 2 was obtained. This consists of seven lines with interline spacings of 21.5 gauss, the outside pair of lines being clearly visible at high gain. The intermediate pattern of lines is much weaker than that observed for samples irradiated at 300°K. and may be due entirely to overlap of the second derivatives of the seven-line pattern. The region around ±250 gauss from $g = 2.00$ was examined for the presence of the hydrogen atom doublet,[12] but this was not detected, even at high gain settings giving a signal-to-noise ratio of 100 for the central line. When a sample irradiated at 77°K. was allowed to warm up to 300°K., the spectrum given at this temperature was identical with that of Figure 1. No lines were observed outside the quintet, although the outermost lines of the latter were recorded fifty times stronger than the noise level. The spectrum of Figure 1 was also given by a sample irradiated at 77°K., warmed to 300°K. and kept at that temperature for 10 min., and then cooled back to 77°K. for measurement. A sample irradiated at 77°K. was raised to 195°K. for 10 min. by placing it in an acetone/solid carbon dioxide bath. It was then measured at 77°K. The spectrum was similar to that in Figure 1, except that the outer lines of the seven-line pattern (Fig. 2) were visible at ±65 gauss but reduced in relative intensity. Such a spectrum was also given by a sample treated similarly but held at 195°K. for one hour.

Analysis of the Seven-line Spectrum

It will be assumed that angular dependent interactions between the unpaired electron and the protons are small, and give rise to line broadening only. The hyperfine pattern given by n protons equally coupled to the unpaired electron through hyperconjugation or configuration interaction consists of $(n + 1)$ equally spaced lines with intensities proportional to the coefficients in the expansion of $(1 + x)^n$.[13] In Table I, these intensities are given for relevant even numbers of protons, the central line being set at 100 in each case. Since each pattern is symmetrical, only one half is given. Also shown are the relative intensities observed for the seven-line

pattern and for other spectra described in this paper. These were esti-mated from the second-derivative curves and are only approximate. The intensities of lines at equal field splittings from the centers of the patterns have been averaged. It can be seen that the hyperfine pattern for a radical in which the unpaired electron interacts equally with six protons corresponds closely to the seven-line pattern of Figure 2.

The Effect of Monomer on the Low Temperature Spectra

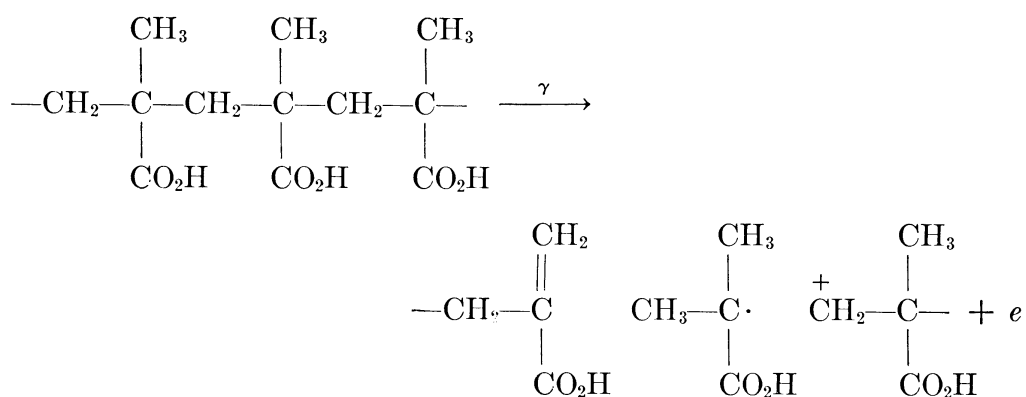The simplest structure which gives the seven-line hyperfine pattern is the dimethyl carboxy methyl radical

$$
\begin{array}{c}
CH_3 \\
\diagdown \\
C\cdot\!-\!CO_2H \\
\diagup \\
CH_3
\end{array}
$$
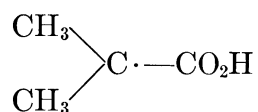
in which the six β protons are equally coupled to the unpaired electron through hyperconjugation. (It is assumed that the methyl groups rotate faster than 10^8 times per second.) Ingram et al.[14] found that photolysis of a mixture of hydrogen peroxide and isopropanol at $110°K$. gave rise to a species with an electron resonance spectrum of seven lines spaced about 20 gauss apart. This spectrum was attributed to the radical

$$
\begin{array}{c}
CH_3 \\
\diagdown \\
C\cdot\!-\!OH \\
\diagup \\
CH_3
\end{array}
$$
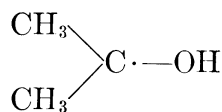
formed by the abstraction of the secondary hydrogen atom by a hydroxyl radical.

The formation of a dimethyl carboxy methyl radical from polymeth-acrylic acid requires the removal of an entire monomer unit from a polymer chain, perhaps by the following process.

$$
\begin{array}{ccccccc}
& CH_3 & & CH_3 & & CH_3 & \\
& | & & | & & | & \\
-CH_2\!-\!C\!-\!CH_2\!-\!C\!-\!CH_2\!-\!C\!-\! &&& \xrightarrow{\ \gamma\ } \\
& | & & | & & | & \\
& CO_2H & & CO_2H & & CO_2H &
\end{array}
$$

$$
\begin{array}{cccccc}
& CH_2 & & CH_3 & & CH_3 \\
& \| & & | & + & | \\
-CH_2\!-\!C & & CH_3\!-\!C\cdot & & CH_2\!-\!C\!- & +\ e \\
& | & & | & & | \\
& CO_2H & & CO_2H & & CO_2H
\end{array}
$$

Since two carbon-carbon bonds must be broken in such a process, this seems unlikely to occur. Successive ionization and breakage of the bonds is improbable.

Alternatively, the radicals might be formed by the addition of hydrogen atoms to residual monomer. To investigate this possibility, a sample of
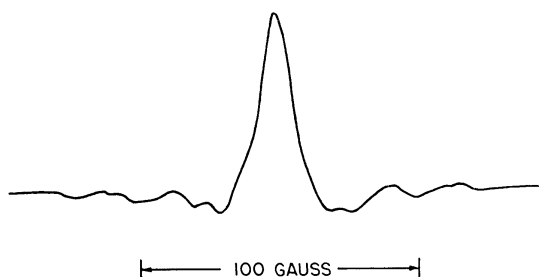
Fig. 3. Electron spin resonance spectrum at 77°K. of polymethacrylic acid freed from monomer after gamma-irradiation at 77°K.

polymethacrylic acid was dissolved in methanol and precipitated by pouring into a large volume of diethyl ether. The polymer was washed with precipitant and freed from volatile matter by heating to 100°C. for twelve hours *in vacuo*. Since methacrylic acid is soluble in both solvent and precipitant, the precipitated polymer should have been largely free from monomer. When samples of this material were irradiated at 77°K. and examined at this temperature without intermediate warming, the electron resonance spectrum was a single line, with some weak hyperfine structure (Fig. 3). No hydrogen atoms were detected. It is apparent that, in most of the radicals formed by this treatment, there is relatively little magnetic interaction between the unpaired electron and protons. Samples irradiated at 77°K. and heated to 300°K. for 10 min. before measurement at 77°K. gave the normal spectrum (Fig. 1).

In a further experiment, the reprecipitated polymer was allowed to absorb about 5% of its weight of monomer in the vapor phase in the absence of air. This material was sealed off and heated to 100°C. for 12 hr. in an

TABLE I

Comparison of Theoretical and Observed Hyperfine Patterns

Number of protons	Intensity of lines					
4	100	67	17	0	0	0
6	100	75	30	5	0	0
8	100	80	40	12	1.4	0
10	100	84	48	18	4.0	0.4
Observed spectra						
Seven-line pattern of Figure 2	100	71	25	4	[a]	
Quintet of Figure 1	100	63	11	[b]		
Quintet of Figure 4	100	66	11.5	[c]		
Seven-line pattern of Figure 5[d]	240	75	25	7	[e]	

[a] No other lines observed above a noise level of one unit.

[b] No other lines observed above a noise level of 0.2 unit.

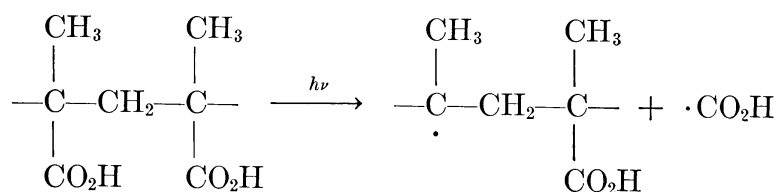[c] No other lines observed above a noise level of 0.5 unit.

[d] This spectrum was fitted by setting the intensity of the lines at ±21 gauss from the center of the pattern at 75 units.

[e] No other lines visible above a noise level of 2 units.

attempt to obtain homogeneity. After irradiation *in vacuo* at 77°K. and measurement at this temperature without intermediate warming, the electron resonance spectrum was that of Figure 2. On warming to 300°K. for 10 min. before measurement at 77°K., the normal spectrum (Fig. 1) was given.

Irradiation Chemistry

Little work has been published on the action of ionizing radiation on solid polymethacrylic acid. Most studies have been confined to aqueous solutions, where the effects are due mainly to radiolysis of the solvent.[15] Miller, Lawton, and Balwit have reported that solid polymethacrylic acid undergoes predominant degradation when irradiated with 800-kv. electrons,[16] and in this respect, it is similar to polymethyl methacrylate. Recently, Baxendale and Thomas have studied the degradation of polymethacrylic acid in aqueous solution under ultraviolet irradiation.[17] These authors consider, by analogy with the photolysis of aliphatic acids, that the primary step in the degradation is probably:

$$\begin{array}{ccccc}
CH_3 & & CH_3 & & \\
| & & | & & \\
-C-CH_2- & C- & \xrightarrow{h\nu} & & \\
| & & | & & \\
CO_2H & & CO_2H & &
\end{array} \quad \begin{array}{ccc}
CH_3 & & CH_3 \\
| & & | \\
-\overset{\bullet}{C}-CH_2- & C- & + \ \cdot CO_2H \\
& & | \\
& & CO_2H
\end{array}$$

This process is then followed by breakage of the polymer backbone.

Extensive studies have been carried out on the irradiation of solid polymethyl methacrylate, and it is possible that there may be similarities in the behavior of these two polymers. Alexander, Charlesby, and Ross,[18] assuming that scission occurs exclusively, found a G value (number of molecular events per 100 e.v. absorbed energy) of 1.6 for main-chain breakage by pile radiation. They analyzed the gases evolved when the
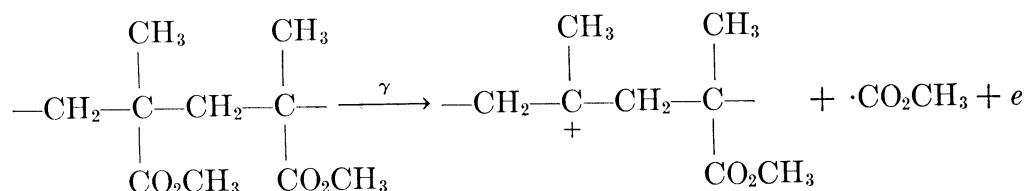
TABLE II
Mass Spectrometric Analyses of Gases Evolved on Irradiation of Polymethyl Methacrylate

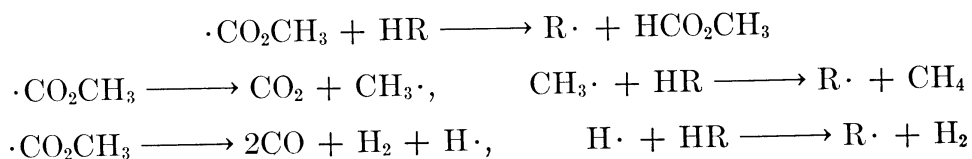| Product	Charlesby et al.[18] Total gas, %	Wall and Brown[19]		
		Moles/10³ kg.[a]	Total gas, %	G values
H_2	44.1	1.37	13.2	0.21
CO_2	18.8	2.07	19.4	0.32
CO	22.8	2.83	27.5	0.44
HCO_2CH_3	nil	0.57	5.5	0.09
CH_4	6.0	3.56	34.2	0.55
Empirical composition of gas	$C_2H_4O_{2.5}$	$C_2H_4O_{1.7}$		0.75

[a] Produced by a dose of 3.9×10^{20} e.v./g.

irradiated polymer was dissolved in chloroform by mass spectrometry. Wall and Brown[19] also used a mass spectrometer to determine the gases evolved by finely divided polymethyl methacrylate upon Co^{60} gamma irradiation. These results are compared in Table II. While the detailed compositions of the evolved gases differ widely, the overall compositions are in fair agreement, and correspond closely to that of methyl formate, $C_2H_4O_2$. From the loss in weight of the polymer Charlesby et al. estimated that the equivalent of one $C_2H_4O_2$ fragment is given off for each main-chain break. The results of Wall and Brown give about half of this if a G value of 1.6 is assumed for scission.
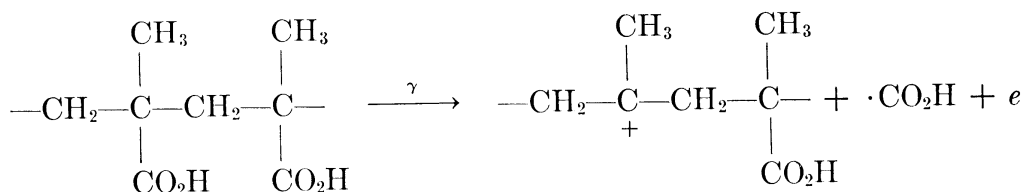
Since scission and side chain breakage occur to about the same extent, it seems likely that they are closely related. The primary effect of the radiation may be to break off the side chain:
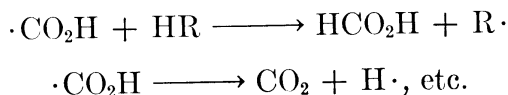
$$\begin{array}{ccccc} & CH_3 & & CH_3 \\ & | & & | \\ -CH_2-C-CH_2-C- & \xrightarrow{\gamma} & -CH_2-\underset{+}{C}-CH_2-C- & + \cdot CO_2CH_3 + e \\ & | & | & & | & | \\ & CO_2CH_3 & CO_2CH_3 & & & CO_2CH_3 \end{array}$$

This may then abstract a hydrogen atom from the polymer, either directly or after being broken into fragments:

$$\cdot CO_2CH_3 + HR \longrightarrow R\cdot + HCO_2CH_3$$

$$\cdot CO_2CH_3 \longrightarrow CO_2 + CH_3\cdot, \qquad CH_3\cdot + HR \longrightarrow R\cdot + CH_4$$

$$\cdot CO_2CH_3 \longrightarrow 2CO + H_2 + H\cdot, \qquad H\cdot + HR \longrightarrow R\cdot + H_2$$

These reactions would explain the various fragments given off on irradiation. Finally, it must be postulated that rearrangement of the backbone, perhaps after abstraction of the hydrogen atom and the return of the electron, results in scission. It is possible that a similar series of reactions takes place when solid polymethacrylic acid is gamma-irradiated, namely:

$$\begin{array}{ccccc} & CH_3 & & CH_3 \\ & | & & | \\ -CH_2-C-CH_2-C- & \xrightarrow{\gamma} & -CH_2-\underset{+}{C}-CH_2-C- & + \cdot CO_2H + e \\ & | & | & & | & | \\ & CO_2H & CO_2H & & & CO_2H \end{array}$$

followed by:

$$\cdot CO_2H + HR \longrightarrow HCO_2H + R\cdot$$

$$\cdot CO_2H \longrightarrow CO_2 + H\cdot, \text{ etc.}$$

Conclusions

The spectrum given by samples of polymethacrylic acid, gamma-irradiated at 300°K. and observed at this temperature and at 77°K., agrees with

that reported for samples irradiated at 300°K. and measured at 300 and 90°K.,[4] except in the exact value of the hyperfine splittings. It seems fairly certain that this spectrum arises from normal propagating radicals with structure

$$
\begin{array}{c}
\quad\quad CH_3 \\
\quad\quad / \\
-CH_2-C\cdot \\
\quad\quad \backslash \\
\quad\quad CO_2H
\end{array}
$$
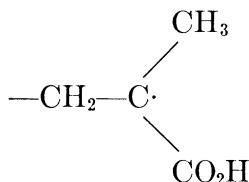
and that either one to two of the five β protons must interact only weakly with the unpaired electron.[4,8] These radicals are probably formed by the addition of monomer to radicals produced by the irradiation. The monomer may be already present or may be produced by depolymerization following scission.[8]

Several conclusions can immediately be drawn from the spectra of samples irradiated at 77°K. The radicals trapped at this temperature probably have a structure in which six protons interact equally with the unpaired electron. When the temperature is raised to 195°K., most of these radicals are irreversibly replaced by trapped propagating radicals, the remainder appearing stable. On raising the temperature to 300°K., this irreversible replacement is complete. The production of these radicals requires the presence of monomer.

The following is put forward as a possible explanation of these phenomena. Following the scheme suggested in the last section, one effect of the gamma-irradiation is the production of $\cdot CO_2H$ radicals. Many of these decompose to give carbon dioxide and hydrogen atoms. When residual monomer is present in the polymer, some hydrogen atoms will add to monomer molecules to give dimethyl carboxy methyl radicals, $(CH_3)_2C\cdot-$ $-CO_2H$, which give rise to the seven-line spectrum. The monomer is held trapped at 77°K., but hydrogen atoms can diffuse through the polymer at this temperature. On warming to 300°K., the monomer becomes free to diffuse, and addition of this to the dimethyl carboxy methyl radicals causes the seven-line spectrum to be replaced by the normal five-plus-four line spectrum. When polymer freed from monomer is irradiated at 77°K., some of the $\cdot CO_2H$ radicals may decompose as before and the hydrogen atoms recombine. However, the remainder of the $.CO_2H$ radicals remains trapped and are responsible for the single-line spectrum. The conversion of this spectrum into the normal room-temperature spectrum, on warming to 300°K., suggests that breakage of the polymer chains is accompanied by the production of monomer.

Polymethyl Methacrylate

Polymethyl methacrylate was prepared by the bulk polymerization of the degassed monomer, azobisisobutyronitrile being used as photoinitiator. This polymer gave the normal spectrum (Fig. 1) when gamma-irradiated

at 300°K. and a rather weak quintet when gamma-irradiated and observed at 77°K.; the latter changed irreversibly into the normal spectrum on warming to 300°K. This behavior is similar to that reported for a sample irradiated at 90°K.[4]

Polyethyl Methacrylate

A commercial sample of polyethyl methacrylate gave essentially the spectrum of Figure 1 when gamma-irradiated and observed at 300°K. and 77°K. When irradiated at 77°K., a broad quintet with interline spacings of about 23 gauss was obtained (Fig. 4). This was not affected by keeping the polymer at 195°K. for one hour, but after warming to 300°K. for 10


$\vdash$————— 100 GAUSS ————$\dashv$
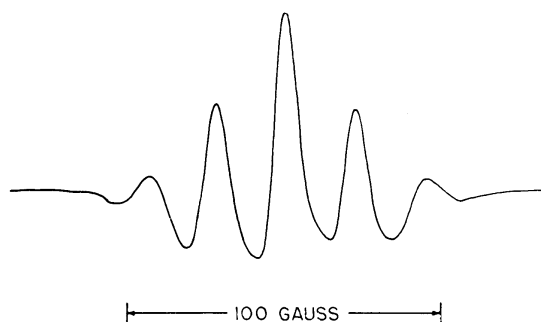
Fig. 4. Electron spin resonance spectrum at 77°K. of polyethyl methacrylate after gamma-irradiation at 77°K.

min. the spectrum was that of Figure 1. The low temperature spectrum was clearly a quintet and not a septet, as can be seen from Table I. No hydrogen atoms were detected at 77°K. It is possible that this spectrum arises from a radical formed by the removal of a hydrogen atom from the ethyl side chain, i.e.,

$$
\begin{array}{c}
CH_3 \\
| \\
-CH_2-C- \\
| \\
CO_2C_2H_4^{\cdot}
\end{array}
$$
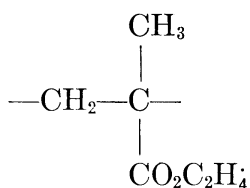
This radical would give a quintet spectrum if the unpaired electron interacted with the α and β protons to approximately the same extent. Equivalent interactions of α and β protons have been proposed to explain the electron spin resonance spectra given by some gamma-irradiated hydrocarbons at low temperatures.[20] The α protons would be expected to give rise to considerable line-broadening through orientation-dependent dipole–dipole interactions.[21] (The radicals postulated to explain the narrower spectra of Figures 1 and 2 contain no α protons.) However, it is not possible to give a similar explanation for the weak quintet given when polymethyl methacrylate is gamma-irradiated at 77°K. As in the cases

of the polymers considered earlier, the room temperature spectrum is probably due to trapped propagating radicals.

Polydimethyl Itaconate

Despite the fact that this polymer gives a strong electron spin resonance spectrum when gamma-irradiated at room temperature,[22] only a very weak asymmetric single line was given at 77°K. by gamma-irradiation at this temperature. This was not affected by heating to 300°K. for 10 min.

Poly n-Butyl Methacrylate and Poly n-Hexyl Methacrylate

These were prepared by polymerization of the degassed monomers, azobisisobutyronitrile being used as photoinitiator. At room temperature, both were rubbery solids, and neither gave a detectable electron resonance spectrum when gamma-irradiated at 300°K. Samples of poly n-butyl methacrylate irradiated at 77°K. gave a spectrum at that temperature consisting of seven lines (Fig. 5), with interline spacings of about 21 gauss.
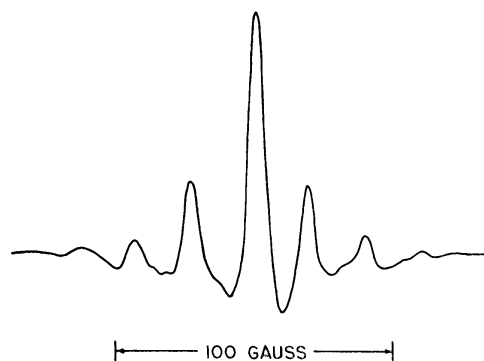

|————— IOO GAUSS —————|

Fig. 5. Electron spin resonance spectrum at 77°K. of poly-n-butyl methacrylate after gamma-irradiation at 77°K.

The central line is considerably more intense than would be expected for the usual gaussian pattern (Table I), and its peak occurs at a slightly higher magnetic field than the center of the rest of the pattern. It seems likely that this spectrum consists of a septet, together with a superimposed single line, the latter having a slightly lower g value. It is possible that radicals of structures, $(CH_3)_2C^{\cdot}$—$CO_2C_4H_9$ and $\cdot CO_2C_4H_9$, are present, being produced by mechanisms similar to those discussed in connection with polymethacrylic acid. However, the seven-line pattern could also be due to a radical formed by the removal of a hydrogen atom from the butyl sidechain, namely: —CH_2—CH_2—$CH^{\cdot}$—CH_3. This radical would give a septet if the coupling coefficients of all the α and β protons were approximately equal.

Poly n-hexyl methacrylate gave a spectrum at 77°K. rather similar to that of the butyl ester but less intense, so that it was not possible to determine if the pattern consisted of five or seven lines.

SUMMARY

It is concluded that when methacrylate polymers are gamma-irradiated at 77°K., the free radicals trapped at this temperature are usually different from those which are trapped when the polymers are irradiated at 300°K. On warming to 300°K., free radical reactions occur, and the electron resonance spectra change into those which would have been observed had the polymers been irradiated at the higher temperature. In the case of polymethacrylic acid, the effect of the presence of monomer on the radicals trapped at 77°K. has been investigated, and it has been possible to advance an explanation for the various spectra. The results given by the other polymers are less clear.

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Synopsis

The electron spin resonance (e.s.r.) spectra of free radicals trapped in some addition polymers after gamma-irradiation at 77°K. are described and discussed. When poly-methacrylic acid is gamma-irradiated at 77°K., the e.s.r. spectrum at this temperature consists of a symmetrical pattern of seven lines which may be due to dimethyl carboxy methyl radicals, $(CH_3)_2C \cdot$—CO_2H. On warming to 300°K. this spectrum is replaced by the normal "five-plus-four line" spectrum, which has been attributed to trapped prop-agating radicals. When polymethacrylic acid freed from monomer is gamma-irradiated at 77°K. the e.s.r. spectrum is a single line, probably arising from trapped $\cdot CO_2H$ radi-cals. A reaction scheme is put forward to account for the production of these radicals. Some observations on polymethyl, polyethyl, poly n-butyl, and poly n-hexyl meth-acrylates and polydimethyl itaconate are also reported.

Résumé

Les spectres de résonance de spin électronique (e.s.r.) ont été décrits et discutés pour des radicaux libres occlus dans certains polymères d'addition après irradiation par des rayons gamma à 77°K. Lorsque l'acide polyméthacrylique est irradié par des rayons gamma à 77°K le spectre de résonance électronique se présente sous un aspect symétrique à sept lignes qui peut être attribué aux radicaux diméthyl carboxy méthyle $(CH_3)_2C \cdot$—CO_2H. Par chauffage à 300°K ce spectre est remplacé par le spectre normal formé de cinq et quatre raies qui peut être attribué aux radicaux propagateurs occlus. Lorsque l'acide polyméthacrylique exempt de monomère est irradié par des rayons gamma à 77°K le spectre de résonance électronique présente une ligne unique, dérivant probable-ment de radicaux $\cdot CO_2H$ occlus. Un schéma réactionnel est proposé pour expliquer la formation de ces radicaux. Quelques observations sur les polyméthacrylates de méthyle, d'éthyle, de n-butyle et de n-hexyle ainsi que sur le polyitaconate de diméthyle sont également signalées.

Zusammenfassung

Die Elektronenspinresonanz-(E.S.R.)-spektren von freien Radikalen, die in manchen Additionspolymeren nach γ-Bestrahlung bei 77°K eingeschlossen bleiben, werden besch-rieben und diskutiert. Bei der γ-Bestrahlung von Polymethacrylsäure bei 77°K besteht das E.S.R.-spektrum bei dieser Temperatur aus einer symmetrischen Anordnung von sieben Linien, die den Dimethylcarboxymethylradikalen, $(CH_3)_2C \cdot$—$COOH$, zuges-chrieben werden können. Beim Erwärmen auf 300°K tritt an Stelle dieses Spektrums das normale "fünf-plus-vier-Linienspektrum" auf, das den eingeschlossenen, wachsenden Radikalen zugeschrieben wurde. Bei der γ-Bestrahlung von monomerfreier Poly-methacrylsäure bei 77°K bildet das E.S.R.-spektrum eine einzelne Linie, die möglicher-weise durch eingeschlossene $\cdot CO_2H$-Radikale erzeugt wird. Ein Reaktionsschema zur Erklärung der Bildung dieser Radikale wird aufgestellt. Über einige Beobachtungen an Polymethyl-, Polyäthyl-, Poly-n-butyl- und Poly-n-hexylmethacrylaten sowie an Polydimethylitaconate wird ebenfalls berichtet.