

## ESR SPECTRA OF IRRADIATED POLYACRYLIC ACID

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**Abstract**—In view of the interest in acrylic acid co-polymerized with other polymers by radiation to promote enhanced crosslinking, a knowledge of the intermediate reaction products is highly desirable. ESR techniques have been used to study the nature and stability of the radicals formed. Acrylic acid was polymerized by exposure to gamma radiation; the nature of the radicals, their decay at various temperatures, and the effect of inhibitors were investigated.

The ESR spectrum at room temperature is similar to that described by earlier workers; its dependence on temperature and impurities, as well as its decay, were investigated. From this work, there is reason to believe that the described triplet also contains a central singlet of  $\Delta H_{msl} 9$  G; the addition of impurities to the acrylic acid causes the triplet to decay more rapidly, thus leaving the predominant singlet mentioned above. It was also found that the lines in the outer "wings" of the irradiated specimen disappear on heating; at the same time a new line, possibly a singlet of  $\Delta H_{msl} 31$  G, either became more intense or more obvious. Some tentative explanations of this behaviour are advanced.

### INTRODUCTION

Acrylic acid is playing an increasingly important role as a grafting material in polymer systems and there is a great deal of current research to determine the reaction mechanisms.

The electron spin resonance (ESR) spectra of radicals trapped in irradiated poly(acrylic acid) has been examined by previous workers [1, 2] who assign the triplet spectrum to a single radical. We have examined the spectrum in greater detail and find that this triplet can be resolved into two components, a doublet or triplet, and a singlet; this work also provides evidence of secondary radical formation and reactions on heating.

Commercial acrylic acid contains 0.05 per cent of *p*-methoxy phenol as an inhibitor to prevent polymer formation by sunlight, etc. Using ESR techniques, we have examined the role played by the inhibitor in affecting radical formation and decay.

### EXPERIMENTAL

Acrylic acid "puriss" and *p*-methoxy phenol were obtained from Koch Light Laboratories Ltd. and BDH, respectively. The acrylic acid was further purified by triple partial crystallization at low temperatures; the melting points of standard and purified material obtained from a differential scanning calorimeter showed a very significant sharpening in melting temperature for the purified material. Samples of poly(acrylic acid) were made by gamma irradiation of the monomer between 273 and 297° K. Those irradiated in vacuum were prepared in Spectrosil quartz tubes by the freeze/thaw method and evacuated to a pressure of 10 mN/m<sup>2</sup>.

All ESR spectra were taken, except where otherwise stated, on a 9300 Hz transmission spectrometer working at

0.5 mW. The spectrometer was calibrated in the usual way; line widths were measured by using a di-phenyl picryl hydrazyl (DPPH)/ultra marine standard and radical concentration measurements were made using coal standards calibrated against a solution of DPPH in benzene. The absorptions are displayed as the first derivative.

The <sup>60</sup>Co gamma irradiation facility was a nominal 9.2 kCi giving a maximum central dose rate of 3 Mrad/hr measured by ferrous sulphate dosimetry.

The polymer was prepared, in all cases, by irradiation of the monomer; the monomer was irradiated in both solid and liquid phase but no significant difference in polymer spectra was noted. The poly(acrylic acid) was coloured amber by radiation, the intensity increasing with dose; this colouration could be removed, like the radicals, by annealing the material for a few minutes at 400°K.

Quantitative measurements of free radical concentration were made by double integration with a second moment balance. The principle and accuracy of this are described elsewhere [10, 11].

Temperatures were measured by means of mercury in glass and copper-constantin thermometry; the sweep unit used in the ESR spectrometer had a linearity of  $\pm 2$  per cent.

### RESULTS

#### I. Pure poly(acrylic acid)

(a) *Heat treatment and radical decay.* The radicals trapped in poly(acrylic acid), formed by exposure of the monomer to u.v. radiation at 0.3  $\mu$ m or to <sup>60</sup>Co gamma radiation, were found to be fairly stable up to 350°K, but above 390°K complete annealing took place very quickly (< 5 min). Figure 1 shows the effect of heating the irradiated monomer at 373°K; the subsequent measurements were taken at room temperature.

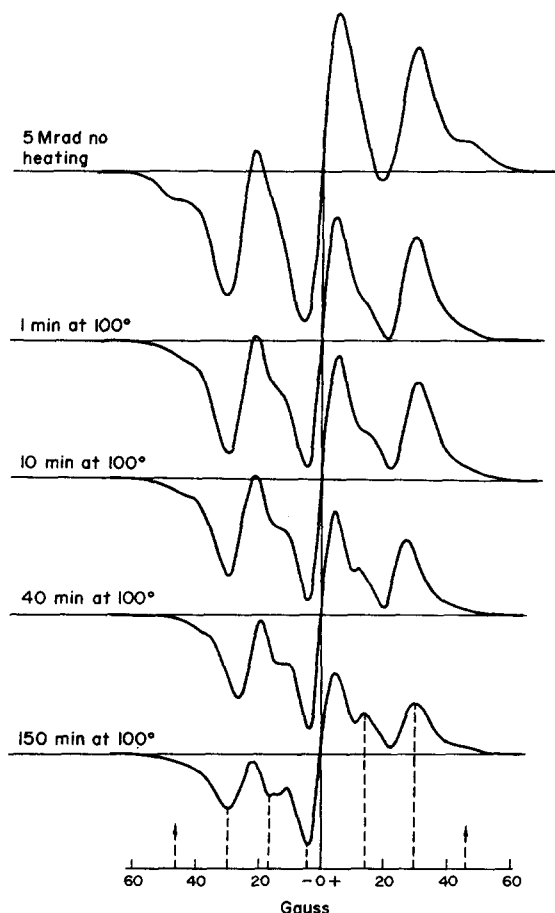


Fig. 1. Purified acrylic acid irradiated to 5 Mrad in vacuum at 273°K and measured at room temperature at constant gain—effect of heating at 373°K.

From Fig. 1 it is evident that a secondary reaction is taking place in the first few minutes of heating; absorptions at  $\pm 46$  G decrease rapidly while absorptions at  $-17$  G and  $+14$  G tend either to increase or to become more highly resolved.

There are also signs of a differential decay between the main lines at  $\pm 4.5$  G and  $\pm 30$  G. Table 1 shows

Table 1. Amplitude ratio of centre line at  $+4.5$  G to outer lines at  $+30$  G acrylic acid irradiated to 5 Mrads at 273°K

| Heat treatment<br>at 373°K | Ratio  |      |
|----------------------------|--------|------|
|                            | Vacuum | Air  |
| Nil                        | 1.25   | 1.43 |
| 1 min                      | 1.17   | 1.30 |
| 4 min                      | 1.21   | 1.40 |
| 10                         | 1.26   | 1.46 |
| 20                         | 1.31   |      |
| 40-45                      | 1.38   | 1.62 |
| 120                        |        | 1.73 |
| 150                        | 1.65   |      |

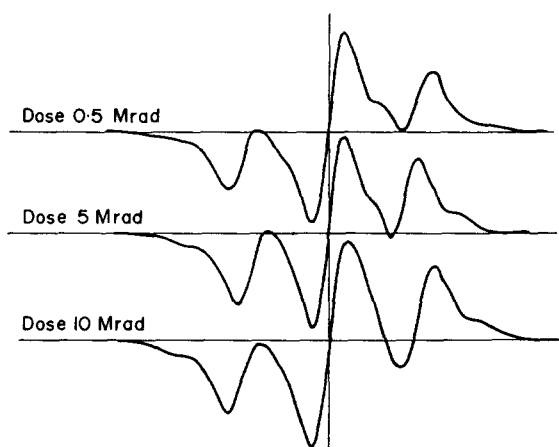


Fig. 2. Unpurified acrylic acid irradiated at room temperature in air to various doses.

the ratio of these peaks as a function of heating time at 373°K. No consistent difference was found between the radical formation, or decay rates, either quantitatively or qualitatively, for samples irradiated in air, argon, hydrogen or vacuum. It was noted, even with similar samples and identical treatment, that a small inconsistency did occur in the ratios of the lines formed initially. The  $G$  value (total number of radicals trapped per 100 eV of absorbed energy) was calculated and found to be  $3.6 \pm 0.8$  at 5 Mrad.

Figure 2 shows the spectra from the unpurified material after irradiation and Fig. 3 shows the effect of heating the irradiated samples at 373°K. The samples were irradiated in air at room temperature for various doses, measured at room temperature, heated for 2 hr at 373°K and re-measured at room temperature. They indicate little change in spectrum with a 20-fold increase in dose; the effect of heating is also very similar for all three doses.

The  $g$  (spectroscopic or "Lande" splitting factor) value was found to be  $2.0031 \pm 0.0001$ . This was derived by inserting a DPPH marker into the cavity and

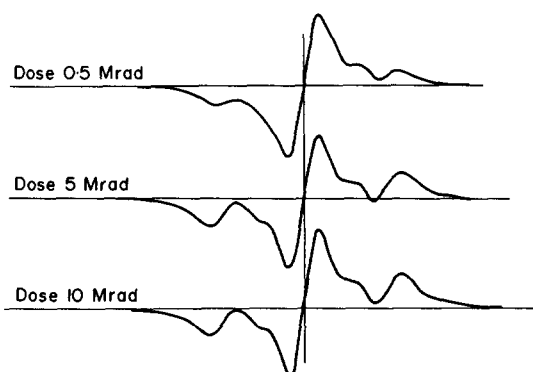


Fig. 3. Unpurified acrylic acid irradiated at room temperature in air to various doses—heated for 2 hr at 373°K.

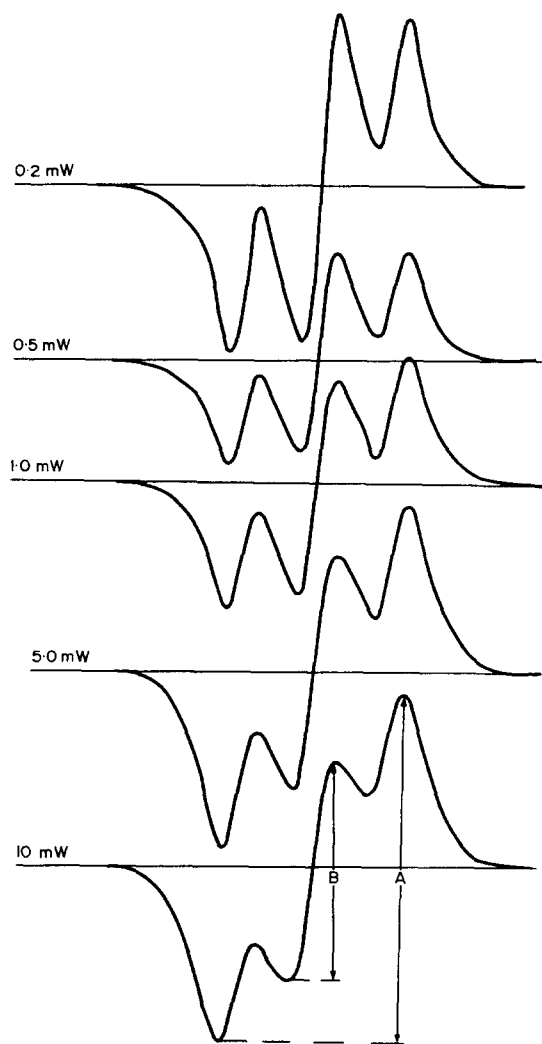


Fig. 4. Acrylic acid irradiated at room temperature—power saturation at 77°K.

measuring the centre line separation on an expanded scale ( $g$  for DPPH was taken as 2.0036).

(b) *Power saturation measurements.* Power saturation measurements were carried out to confirm the presence of two main radicals. These spectra, shown in Fig. 4, were taken at 77 K on a reflection type spectrometer working at 9200 Hz: the ratio of the peak heights against power level is shown in Fig. 5.

Figures 4 and 5 indicate that the centre line of the spectrum is being power saturated at a lower level than the outer lines. It is therefore reasonable to assume that the central part of the spectra contains an absorption line which is not associated with the outer lines and hence indicating the presence of two or more radicals.

(c) *Irradiation at 77°K.* A sample of acrylic acid was polymerized by irradiating the monomer at room temperature to a dose of 4.0 Mrad. The specimen was then annealed at 400°K to remove the free radicals and re-irradiated at 77 K. The spectrum at 77 K is shown in Fig. 6, together with a spectrum, measured at 77°K, of the same specimen after it had been warmed to room temperature. The predominant nature of the singlet at 77°K, prior to warming, and its subsequent weakening on warming are clearly seen.

## II. Effect of the inhibitor—*p*-methoxy phenol $\text{CH}_3\text{O}$ $\text{C}_6\text{H}_4\text{OH}$

(a) *Heat-treatment and radical decay.* Experiments were carried out whereby the stabilizer concentration in the manufacturer's material, containing a stated 0.05 per cent of *p*-methoxy phenol, was increased in stages to 0.5 per cent. One sample was prepared in vacuum with 0.04 per cent of inhibitor added, all other samples were irradiated in air at room temperature to a dose of 5 Mrad. The spectrum was found to be qualitatively identical with that obtained from the inhibitor free material, shown in Fig. 1. However, heating the samples at 373 K caused a much more rapid radical decay, especially of the absorption lines at  $\pm 25$  G, than was seen in the purified material. No difference was found

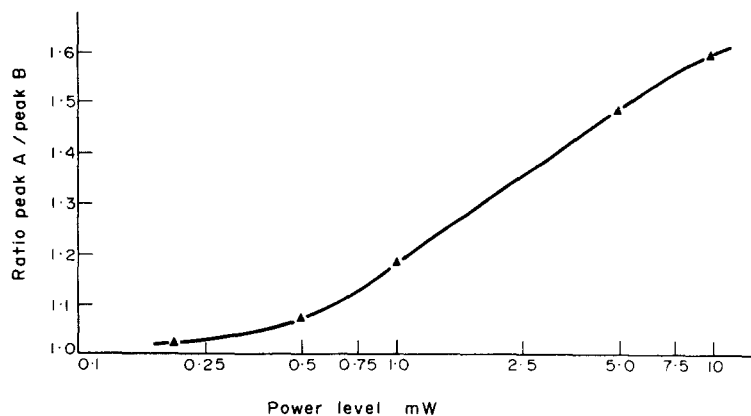


Fig. 5. Acrylic acid irradiated to 4 Mrad in air at room temperature and measured at 77°K.—ratio of the two main peak heights with power level.

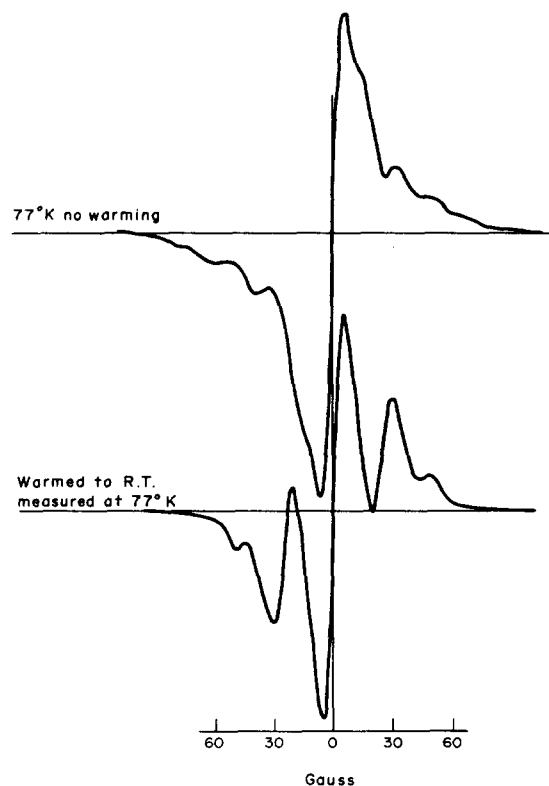


Fig. 6. Poly acrylic acid—annealed and re-irradiated at 77°K.

between the sample prepared in vacuum and a similar sample prepared in air. A series of decay spectra are shown in Fig. 7; this relates to a sample containing 0.35 per cent of inhibitor, irradiated in air to 5 Mrad and then heated at 373°K before measurement at room temperature. It is apparent from these spectra that the lines at  $\pm 30$  G and the secondary reaction radical, formed after heating, at  $-17$  G and  $+14$  G have decayed much more rapidly than the centre line at  $\pm 4.5$  G. Initial radical concentrations are similar for between 0 and 0.35 per cent of inhibitor concentration (Table 2).

(b) *Radical saturation experiments.* Further experiments were carried out with the manufacturer's acrylic acid containing a stated 0.05 per cent, or  $2.5 \times 10^{18}$  molecules/g of inhibitor. From our experiments, it is evident that a radiation dose of about 1.25 Mrad

Table 2. Initial radical concentration

| Sample                        | (R')/g               |
|-------------------------------|----------------------|
| No Inhibitor—5 Mrad in vacuum | $1.1 \times 10^{19}$ |
| No Inhibitor—5 Mrad in air    | $1.1 \times 10^{19}$ |
| 0.11% Inhibitor—5 Mrad in air | $1.1 \times 10^{19}$ |
| 0.35% Inhibitor—5 Mrad in air | $1.1 \times 10^{19}$ |
| 0.5% Inhibitor—5 Mrad in air  | $4.5 \times 10^{18}$ |

would produce a total spin concentration of  $2.6 \times 10^{18}$  radicals/g. To reduce any inhibitor effect, a sample was irradiated in air at 273 K to a dose of 50 Mrad, producing approximately  $4 \times 10^{19}$  radicals/g; this sample was then heated in stages for a total of 8 hr and the radical concentration was reduced to about  $10^{17}$  spins/g. The same sample was then re-irradiated under the same conditions to a dose 12 Mrad and heated, as before, at 373°K. Figures 8 and 9 show the spectra and reaction rates, respectively. It is evident that re-irradiation is causing a more rapid radical decay rather than a slower one due to a reduced inhibitor concentration caused by inhibitor reaction. The position of the peaks, but not their intensity, is unaffected by the large predose.

### III. Effect of water

The addition of 0.5 per cent of water to a sample of pure acrylic acid and gamma irradiation at room temperature produced the typical poly(acrylic acid) spectrum. Heating the sample at 373°K produced a series

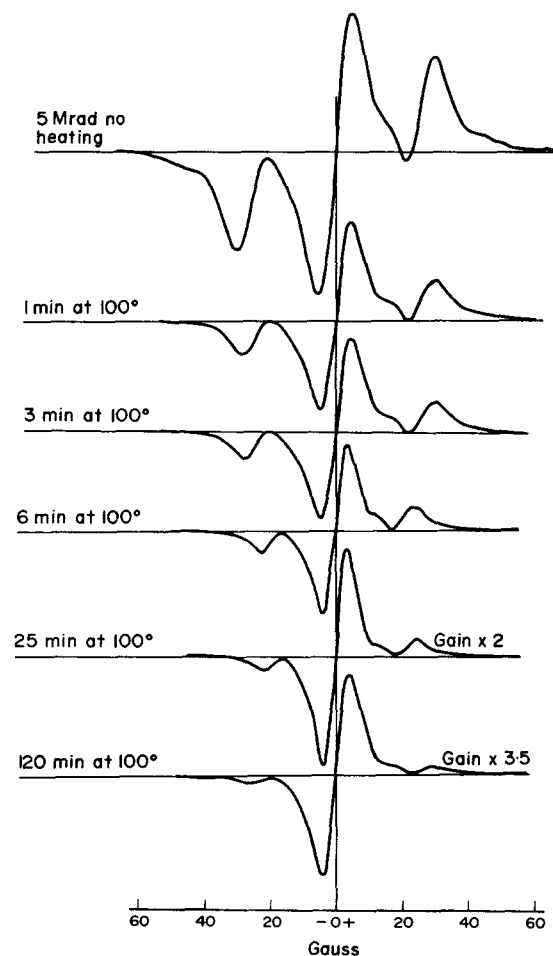


Fig. 7. Acrylic acid + 0.35 per cent *p*-methoxy phenol irradiated to 5 Mrad in air at room temperature—decay at 373°K.

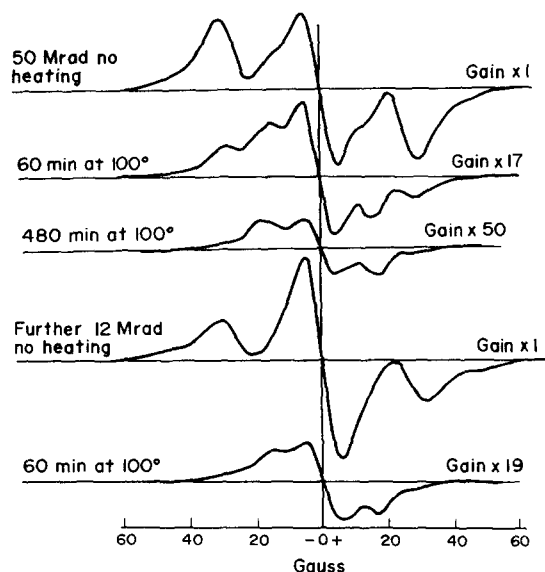


Fig. 8. Unpurified acrylic acid—decay at 373°K after 50 Mrad at 273°K in air then further 12 Mrad at 273°K in air then decay at 373°K.

of decay spectra (Fig. 10) very similar to those for a specimen containing 0.35 per cent of *p*-methoxy phenol.

#### DISCUSSION

During the discussion, it should be borne in mind that no differences were observed between samples irradiated in vacuum or in various gases. This phenomenon is quite likely to be an indication of negligible gaseous diffusion into poly(acrylic acid) rather than a lack of reactive species in the bulk of the material.

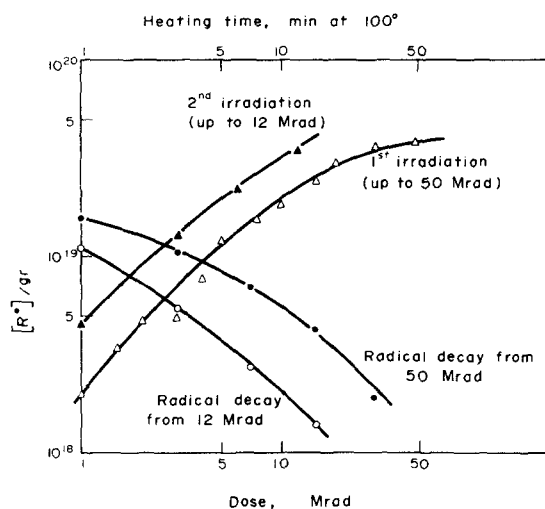


Fig. 9. Acrylic acid irradiated in air at room temperature—radical yield and decay on initial and re-irradiation.

Shiogi *et al.* [2], working at 77°K, suggest that a triplet spectrum is formed as a result of main chain scission and has the form  $\text{—CH}_2\text{—}\dot{\text{C}}\text{H—(COOH)}$ , this being stable at room temperature. They do not, however, observe the  $\text{CH}_2\text{—}\dot{\text{C}}\text{H—CH}_2\text{—}$  radical which



should be correspondingly scissioned, neither do they observe the singlets which we have seen.

Our results indicate the presence of two high *G* value radicals and one low *G* value radical. The low *G* value radical appears in the first instance at approximately  $\pm 47$  G in Fig. 1 and then, on heating at 373°K, decays; at the same time a new absorption line at approximately  $\pm 15$  G becomes more apparent. The relatively low intensity of the initial radical at  $\pm 47$  G prevented accurate measurements but it appears from Figs. 1, 2, 3 and 8 that:

- The radical at  $\pm 47$  G is formed after an initial delay period corresponding to about 0.5 Mrad.
- It reacts on heating to give a different spectrum at  $\pm 15$  G.
- In the pure acrylic acid, the radical at  $\pm 15$  G is more stable than its partners and appears to be a broad singlet with a  $\Delta H_{\text{msl}}$  value of about 31 G.
- A slight anisotropy from the main centre line indicates that the *g* value is about 2.0046.

The fact that radical formation occurs well after the acrylic acid has been polymerized indicates that the radical is not a "propagating chain" radical; the delay period substantiates this.

This radical appears very similar to the polyenyl radicals investigated by Ohnishi *et al.* [3], where the unpaired electron delocalizes and is stabilized by bond

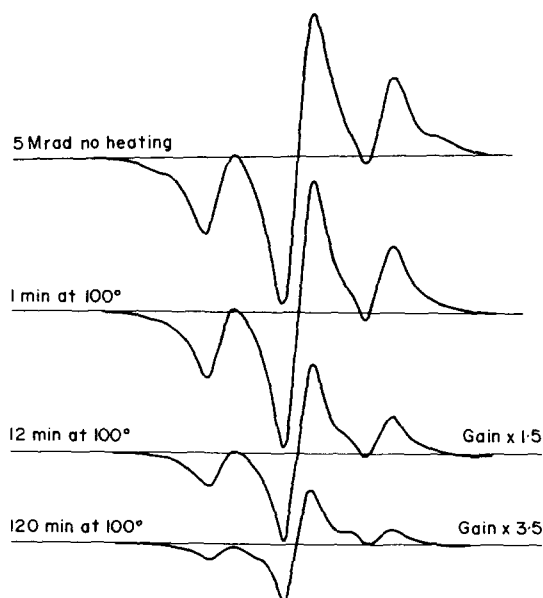


Fig. 10. Purified acrylic acid + 0.5 per cent water and irradiated to 5 Mrad at room temperature—decay at 373°K.

resonance; the effect of the delocalization is to narrow the hyperfine splittings to such an extent that overlapping occurs and eventually a broad singlet is formed. For PVC irradiated to 5 Mrad, they observed:

- (a) A singlet of  $\Delta H_{msl}$  about 34 G;
- (b) A dark brown colouration in the polymer;
- (c) Extremely high temperature stability ( $>420^\circ\text{K}$  to completely anneal the radicals).

Ohnishi *et al.* concluded that this type of radical was characteristic of radiation induced conjugated double bonds; in the case of PVC, they suggested a polyenyl radical of the form



and that as the conjugated region  $n$  becomes larger so the line width is decreased and the temperature stability is increased.

It should be noted that in our system irradiating to higher doses ( $\geq 100$  Mrad) does not decrease the line width to approximately 17 G as observed in PVC. The inference is that the conjugated regions must be limited by some mechanism.

It has been reported by Kambara *et al.* [4] that polyacetylene, having a structure of linear conjugated double bonds, gives a singlet spectrum of  $\Delta H_{msl}$  8.9 G.

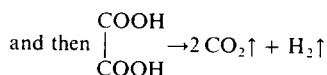
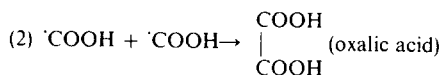
It is difficult to envisage a system in poly(acrylic acid) with such a highly conjugated region and we cannot therefore explain our main singlet spectrum ( $\Delta H_{msl}$  9 G) in this fashion; also, such a narrow line would involve a higher temperature stability than is observed in this case. The singlet could be considered as a chemically trapped species as observed by Alfimov *et al.* [5], but our results may disprove this idea, for the following reasons.

- (a) We have seen that varying the concentration of either water or *p*-methoxy-phenol in the poly(acrylic acid) does not cause an increase in the intensity of any of the radicals formed.
- (b) The singlet, although most apparent in poly(acrylic acid) irradiated at  $77^\circ\text{K}$ , is far too stable at elevated temperatures to be considered as a trapped electron.

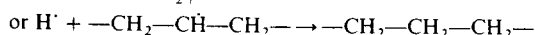
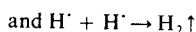
Smith *et al.* [6] have examined the radicals formed in carboxylic compounds and find, together with other workers [7, 8] that singlet spectra can arise from radicals which have their unpaired spin densities localized in oxygen. Our work suggests that the carboxyl group is being scissioned from the main chain to produce the 9 G singlet spectrum, which, very much in evidence at  $77^\circ\text{K}$ , partially reacts on irradiation at room temperature but a proportion is either trapped or stabilized to leave the observed singlet spectrum. Possible decay

systems are:

- (1) recombination with the correspondingly scissioned radical

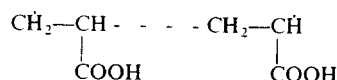


- (3)  $\cdot\text{COOH} \rightarrow \text{CO}_2\uparrow + \text{H}\cdot$



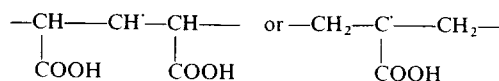
Either of the two latter systems could account for the carbon dioxide spectrum observed in the i.r. analysis of poly(acrylic acid),\* and it seems likely that both (2) and (3) could occur in such a way as to cause partial decay of the spectrum, but (1) would involve the simultaneous decay of both triplet and singlet and (3) would involve some form of stabilization or trapping of the  $\cdot\text{COOH}$  radical; therefore (2) seems most likely.

The formation of a conjugated double bond system in poly(acrylic acid) could involve some form of hydrogen abstraction in the chain. It is interesting to note that the radical responsible for the outer lines at  $\pm 47$  G in the poly(acrylic acid) spectrum do not appear immediately; but presumably, when polymerization is complete. It is likely that a nascent poly(acrylic acid) chain has the form



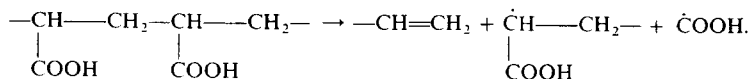
and that any form of hydrogen abstraction on the growing chain would result in branch chain formation from the point of abstraction.

When polymerization is complete, further hydrogen abstraction could result in



radicals being formed. These would be expected to give 4 and 5 line spectra, respectively, unless, as discussed earlier, the unpaired electron was delocalized in a conjugated region. Similarly, carboxyl scission would be expected to leave a  $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2-$  radical on the chain, giving a six line spectrum.

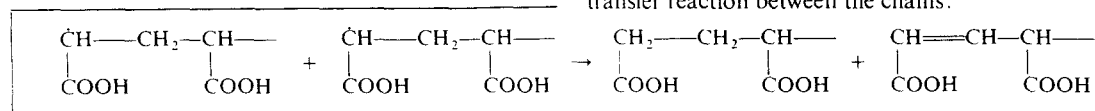
If chain and carboxyl scission occur adjacently, then double bond formation is probable, together with the formation of a radical likely to give the triplet spectrum suggested by other workers [2, 9].



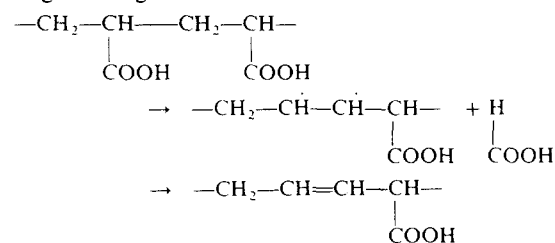
\* Unpublished work.

This would account for the main triplet/singlet spectrum of poly(acrylic acid).

Formation of a double bond system in the poly acrylic acid chain must involve the simultaneous abstraction of a hydrogen atom and carboxyl group from



neighbouring carbon atoms



and a conjugated region could result from a succession of these scissions.

The preferential decay of the  $\text{CH} - \text{CH}_2 -$  radical



producing the triplet spectrum and the role of the additives in enhancing this are more difficult to explain. Poly(acrylic acid) is not very sensitive to crosslinking by radiation (as shown by the equal swelling of irradiated samples placed in water or water-ethanol mixtures—no difference was observed for samples irradiated from 0.5 Mrad up to 50 Mrad) and therefore

mutual combination of the  $\text{CH}(\text{COOH})\text{CH}_2 -$  radical can be ruled out. A possible explanation for the decay is that the additives are promoting a hydrogen transfer reaction between the chains:

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