

THE DECAY OF IRRADIATION DEFECTS IN POLYMETHYL METHACRYLATE

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Summary

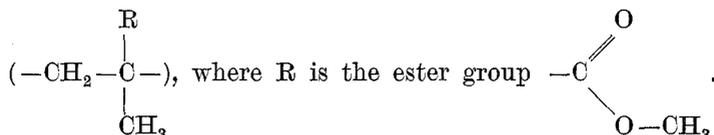
The decay of defects in polymethyl methacrylate caused by γ -irradiation has been followed by electron-spin resonance. The samples were irradiated at room temperature and annealed at 80, 90, and 100 °C. Two radical species can be recognized by their different modes of decay. Some attempt is made to identify the chemical groups involved and to explain the decay mechanism.

I. INTRODUCTION

The effect of radiation on the structure of various plastics has been intensively studied from a chemical point of view and much information derived regarding the processes of chain scission and cross linking (Charlesby 1960). About 10 years ago the technique of electron-spin resonance (e.s.r.) was used to show the presence of broken bonds in various plastics which had been γ -irradiated. One of the first was polymethyl methacrylate (PMMA), a substance which gives a symmetrical e.s.r. pattern consisting of interleaved four- and five-line spectra. (A typical trace of the derivative of the e.s.r. absorption signal against magnetic field is shown in Figure 1.) It has also been observed (Boag, Dolphin, and Rotblat 1958) that the optical absorption spectrum of PMMA changes appreciably under irradiation. This effect can be enhanced by incorporating a red dye into the plastic during manufacture. The colour change, from a bright red to a dull, dark red, is used as a method of radiation dosimetry in the megarad region.

The investigations reported here were prompted firstly by a desire to consider in more detail the origin of the e.s.r. signal of irradiated PMMA. And secondly, we wished to investigate the possibilities of using the intensity of the e.s.r. signal for dosimetry.

A review of e.s.r. work in this field prior to 1958 is contained in the paper by Abraham *et al.* (1958). Subsequent work reported by other authors has not seriously modified the situation. The polymer chain of PMMA has the formula



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II. EXPERIMENTAL RESULTS

(a) *Annealing at Elevated Temperatures*

In an endeavour to study the process further it was decided to follow the change in the e.s.r. spectrum of γ -irradiated PMMA as the sample was held at a fixed temperature near the melting point.

The e.s.r. spectrometer was of standard design (Ingram 1958) and constructed in our laboratories. A transmission cavity, operating in the rectangular H_{012} mode, was formed from standard X band waveguide. Halfway along the cavity was a $\frac{1}{2}$ in. quartz tube in which the sample under test was mounted. The tube formed a sleeve through which air preheated to a definite temperature, was passed. Thus a sample could be maintained at a fixed temperature while its e.s.r. signal was recorded. The main magnetic field, of about 3300 gauss, was provided by an electromagnet having 4 in. diameter pole faces with Rose shims. The e.s.r. absorption was modulated at 100 kc/s by a hairpin loop within the cavity. The samples were cut as strips from a $\frac{3}{16}$ in. sheet of the commercial plastic (standard Perspex made by Imperial Chemical Industries, U.K.). The strips were rounded and formed into rods about 4 in. long. The samples were then placed near a ^{60}Co source for 12 hr and received at room temperature about a megarad of γ -radiation.

Each sample was then placed in turn in the resonant cavity of the e.s.r. spectrometer and warm air blown over it while its spectrum was recorded. Three temperatures were chosen, 80, 90, and 100 °C. A typical set of spectra is shown in Figure 1 for a sample held at 80 °C. It is noticeable that the strong five-line spectrum decays faster than the initially weaker four-line spectrum until eventually they become comparable in height. This is shown in Figure 2, a plot of line height with time. (The various lines of the spectrum have been assigned the letters *a*, *b*, *c*, etc.; and only the heights of the three largest plotted.) These values have been replotted in Figure 3 against the square root of the time. It is seen that the major lines of the five-line spectrum decay very nearly as $\exp[-\sqrt{t/t_0}]$ while the four-line spectrum decays more slowly. This behaviour is common to all the samples of PMMA which we have investigated. The values of t_0 were 24, 11, and 3 min for annealing at 80, 90, and 100 °C respectively for this group of samples.

In order to test for any possible effect due to atmospheric oxygen the experiment was repeated with the plastic samples sealed in glass tubes, some containing oxygen and others nitrogen. Furthermore half of these samples, together with some unsealed ones, were baked at 110 °C for 1 hr before irradiation. This was intended to show up any effect due to unreacted monomer. All samples were then irradiated. Before being placed in the spectrometer one end of each glass sample tube was heated till the radiation defects in the glass there had been annealed out. Precautions were taken to ensure that the plastic sample was unaffected while this took place. Thus the e.s.r. signal finally observed was due to the plastic alone. The result of this systematic series of tests was negative, that is, all samples showed essentially the same decay behaviour while they were annealed at 80 °C. The decay time t_0 for all samples lay between 12.2 and 13.3 min with the exception of an unbaked unsealed sample with a decay time

of 16.8 min. This exception may be due to instrumental errors. In addition, one sample was annealed at 90 °C and another at 100 °C. The decay behaviour was similar to the decay at 80 °C, but the decay times t_0 were 6.5 and 4.0 min respectively. This group of samples was cut from a different sheet of the plastic which probably accounts for the smaller variation of t_0 with temperature compared with the variation of the original group.

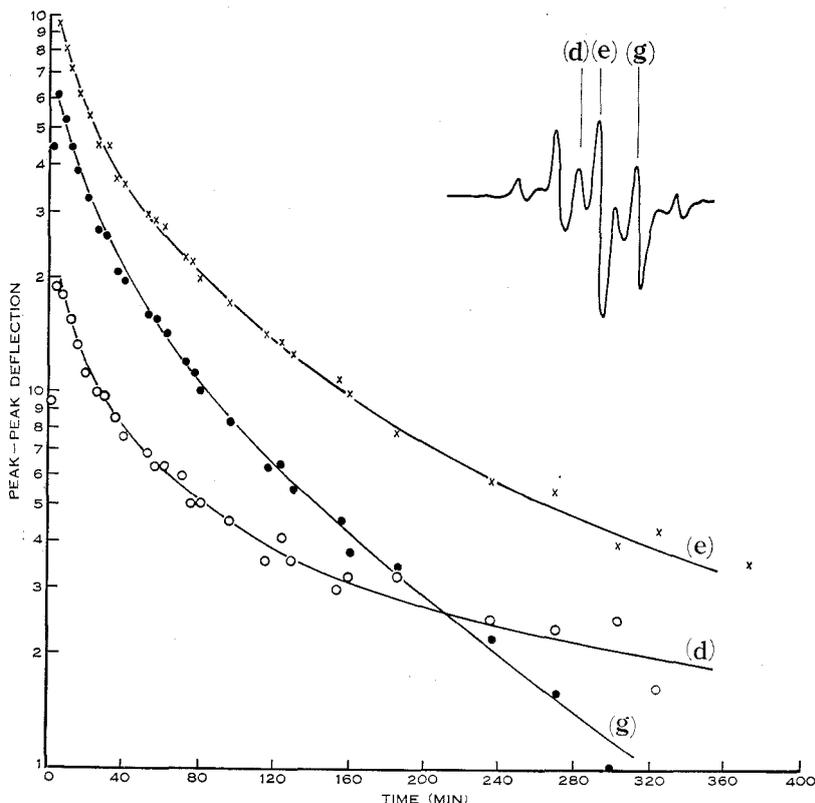


Fig. 2.—Decay of e.s.r. spectrum of γ -irradiated polymethyl methacrylate annealed at 80 °C.

(b) *Annealing at Room Temperature*

In order to investigate the dependence of the radiation induced e.s.r. signal of PMMA on the integrated radiation dose, a set of five samples cut from the original sheet received in turn 0.11, 0.32, 0.8, 2.5, and 8.8 megarads over a 12 hr exposure period. The three samples which received the lowest doses gave the familiar superposed four and five-line spectra. However, the 8.8 megarad sample gave a line shape almost exactly like that labelled 180 min of Figure 1, where the four-line spectrum is prominent. The 2.5 megarad sample gave a similar but not quite so distorted pattern. The reason for this divergence of the behaviour of the e.s.r. pattern at large doses is not known. Possibly these samples became partly annealed during the irradiation process by being heated

internally by the absorption of the radiation. Alternatively the change in line shape may be an e.s.r. saturation effect associated with spin-spin interactions.

Excluding these two heavily irradiated samples, the spectra of the remaining three showed a linear dependence of peak-to-peak deflection on dose. Over a period of 36 days these samples were allowed to decay at room temperature. The observed law of decay of the spin density was exponential with respect to

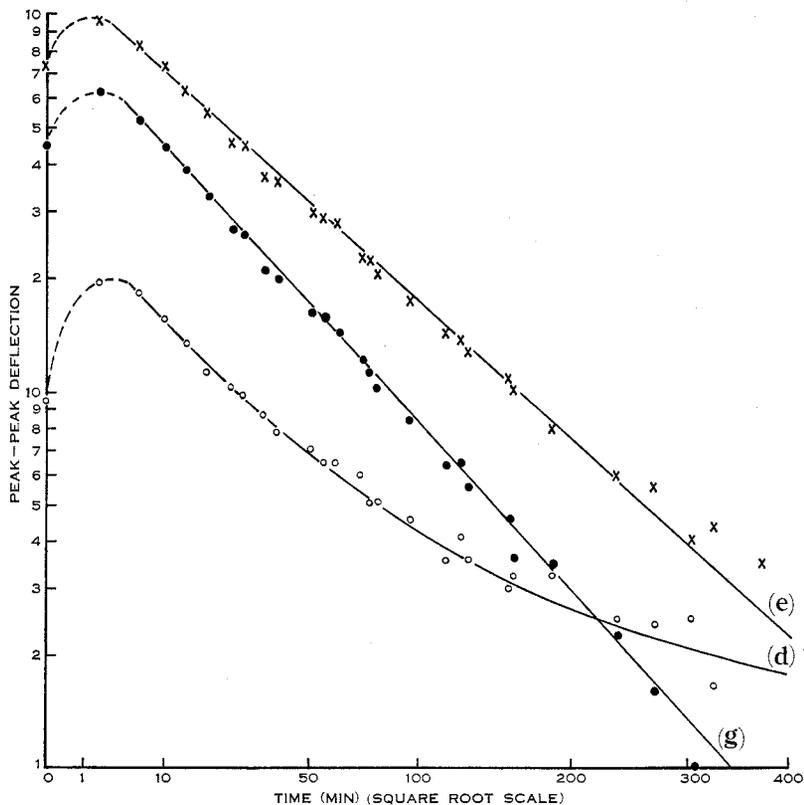


Fig. 3.—Decay of e.s.r. spectrum of γ -irradiated polymethyl methacrylate annealed at 80°C.

the square root of the time, that is, $\exp[-\sqrt{t/t_0}]$, and was thus the same as for samples decaying at higher temperatures. Furthermore the constant t_0 was independent of the integrated dose, and had the value of about 36 days.

The behaviour of the peak-to-peak deflection of the two most heavily irradiated samples was similar, but showed a more rapid decay. The value of t_0 was approximately 10 days.

III. DISCUSSION

(a) Decomposition of the Spectrum

A reasonable deduction to be made from the results described above is that the e.s.r. signal obtained from γ -irradiated PMMA is composed of two separate components. One component gives the comparatively quickly decaying five-line spectrum, while the other gives the more slowly decaying four-line spectrum.

The relative intensities of these two components change as the annealing process proceeds until eventually the four-line spectrum becomes comparable in intensity to the five-line spectrum. As mentioned above this behaviour was common to all PMMA samples observed by us, regardless of the temperature at which they were held during annealing. The simplest explanation for the origin of the pattern is to postulate the existence of two separate chemical free radical species which decay at different rates. It seems impossible to hold to the "alternative structure" explanation mentioned in the introduction unless it is supposed that the probability of one structure relative to the other changes slowly with time. But this is impossible in what must be for any individual free radical a steady-state regime until it is annihilated in a catastrophic act.

An observation similar to ours has been made by Piette (1960), although in his experiment the sample was not held at a fixed temperature during the annealing process. Bresler, Kazbekov, and Saminskii (1959) have also observed the decay of the PMMA spectrum and commented on the change in the shape of the spectrum.

(b) *The Five-line Spectrum*

The actual mode of decay of the two free-radical species is seen to be different. As mentioned above, the initially strong five-line spectrum decays as

$$N = N_0 \exp [-\sqrt{t/t_0}],$$

where N_0 is the initial number of free radicals of this kind and t_0 is a characteristic time describing the decay rate. This expression for N satisfies the differential equation

$$\frac{dN}{dt} = -\frac{1}{2} \left[\frac{N}{\sqrt{t_0 t}} \right].$$

The presence of the square-root term strongly suggests that an explanation based on diffusion be sought, and indeed such an explanation can be given as follows. Each free radical responsible for the five-line spectrum, regarded as one of a set of particles A , is supposed to be surrounded by a sphere of influence. Outside this sphere, in the surrounding material there is a fine dispersion of particles B each of which is capable of reacting instantly with the free-radical A once it has diffused over the surface of the sphere of influence. This situation has been discussed by Chandrasekhar (1943), by Collins and Kimball (1949), and more generally by Waite (1958). These authors show that the rate of accumulation of the particles B into a sphere of influence of radius R is

$$4\pi RC_B D [1 + R/\sqrt{(\pi Dt)}],$$

where C_B is the initial concentration of the B particles, D their coefficient of diffusion through the plastic medium, and t the time. If R is large or D small the differential equation governing this diffusion-controlled reaction between the particles A and B is then

$$\frac{dC_A}{dt} = -4C_A C_B R^2 \sqrt{(\pi D/t)}.$$

The constant t_0 is this given by

$$t_0 = 1/(16\pi DC_B^2 R^4).$$

It is interesting to consider how this expression for t_0 depends on temperature. In the physical circumstances in which the experiment was conducted the plastic was near its melting point and one can expect rapid changes in D as the temperature is changed. The concentration C_B is a constant by definition. The dependence of the radius of the sphere of influence, R , on temperature is unknown. If R is determined by steric considerations it will probably not change rapidly with temperature. It is usual however to assume that the diffusion coefficient D can be described by an Arrhenius relationship (cf. Barker and Moulton 1960), and, bearing in mind the behaviour of the other factors in the above expression for t_0 , it is expected that

$$t_0 = \tau_0 \exp (+E/kT).$$

A plot of the logarithm of t_0 against the reciprocal of the absolute temperature T yields a value for E of 1.2 eV for samples cut from the original sheet of plastic and 0.66 eV for samples cut from the second sheet. The value 1.2 eV is consistent with the decay time of 36 days for samples held at room temperature. These values are of the same order of magnitude as the value 0.31 eV obtained by Barker and Moulton (1960) under somewhat similar circumstances for the plastic lexan.

The nature of the dispersed reactant B has not been determined but in all probability it is molecular oxygen loosely held in the body of the plastic. It could be present due to decomposed initiator or have been absorbed slowly since manufacture if the sample sheets had been stored open to the air. Evidence for this absorption is given by Boag, Dolphin, and Rotblat (1958), who studied the optical changes produced in clear PMMA by irradiation. They observed the steady elimination of a yellow tint as oxygen diffused from the surrounding air into the body of their samples. Furthermore, both this observation and a variety of e.s.r. experiments (Ingram 1958; Barker and Moulton 1960) show that oxygen if present will combine with free radicals, greatly modifying or even removing their e.s.r. spectrum.

It is interesting that the decay of the free radical density measured by Hukuda (1960) in γ -irradiated PMMA also obeys the above law, as can be seen by replotting the results given in Figure 10 of Hukuda's paper. The value of t_0 is 4 days at 25 °C.

(c) *The Four-line Spectrum*

Turning now to the other, initially weaker, four-line spectrum, reference to Figure 3 shows that its mode of decay is quite different. Plotting the logarithm of the signal strength against the square root of the time gives no simple functional relationship. However, some analogy may be drawn with the work of Fletcher and Brown (1953) who discuss the annealing of interstitial atoms and vacancies produced by the irradiation of various substances. Their mathematical model may be interpreted in the present case as follows. Free radicals are created in the PMMA in pairs, such that after some initial chemical reactions involving possibly the transfer of an unpaired electron to a neighbouring molecule the average distance apart of the two components is R' . Further it is supposed that one component is relatively immobile, but is surrounded by a sphere of

influence, of radius R . The second component can diffuse towards its mate and be captured when it is closer than R . The pair is then annihilated. Alternatively the second component can diffuse away. It can be shown that the number of pairs N remaining after a time t is

$$N = N_0 \{ (1 - R/R') + (R/R') \operatorname{erf} [(R' - R)/\sqrt{(4Dt)}] \},$$

where D is a diffusion constant. This expression gives a value of N_0 for N initially, and as t tends to infinity N tends to $N_0(1 - R/R')$. If one wishes to fit this expression to the decay of the four-line spectrum it is easily seen that since

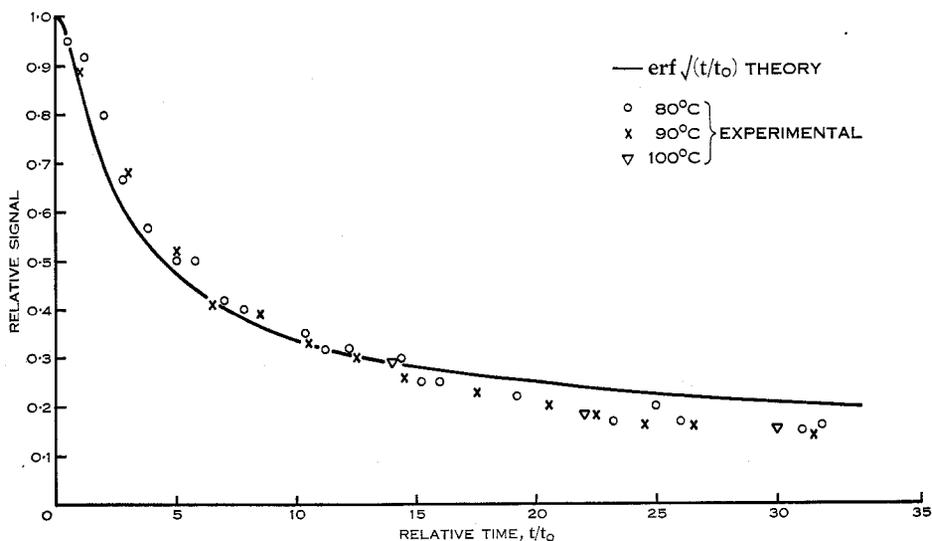


Fig. 4.—Decay of the four-line spectrum of γ -irradiated polymethyl acrylate at various temperatures.

our observed N becomes quite small with increasing time then R' must be only slightly larger than R . If one writes $R(1 + \epsilon)$ for R' then he obtains

$$N = N_0 \operatorname{erf} [\epsilon R/\sqrt{(4Dt)}]$$

approximately, provided ϵ is small and t not too large. The solid line in Figure 4 shows a plot of $\operatorname{erf} \sqrt{(t_0/t)}$ against (t/t_0) . The plotted points give the value of the height of the "d" line derived from the annealing of the original set of samples at 80, 90, and 100 °C. The time scale has been adjusted in each case to give reasonable correlation with the solid line, the values of t_0 being 5, 2, and 0.5 min respectively. In effect, allowance has been made for the variation of the diffusion coefficient with temperature, assuming that the other parameters in the annealing process are independent of temperature. The ratios of the scaling factors obey an Arrhenius relationship yielding an activation energy of 1.3 eV. This is almost the same as the activation energy, 1.2 eV controlling the annealing of the five-line spectrum in the same set of samples.

The general form of the theoretical expression for the number of free radicals left after a time t is seen to describe the decay of the four-line spectrum in broad outline; but fails during the start of the annealing process and again after the

process has been in operation for some time. The first few minutes of the annealing are confused experimentally by the initial heating of the sample from room temperature to the temperature decided upon for the experiment. During this time the e.s.r. signal invariably increases by about 10%. This may be a process akin to "motional narrowing" although there seems to be no detectable difference in line width on the recorded traces at the two temperatures. Alternatively the increase may be due to thermal degradation of weakly bonded peroxides formed during the irradiation.

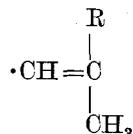
The disagreement between the theoretical expression and the measured values for later times can be explained by the process of interdiffusion between pairs of free radicals. This process must occur when sufficient time has elapsed for those radicals which, having diffused away from their original mates, are in the vicinity of other uncombined pairs. The subsequent combinations will reduce still further the number of radicals surviving at any given time. Thus the observed number of radicals will be smaller than predicted by the $\text{erf } \sqrt{(t_0/t)}$ relationship.

(d) Identification of the Radicals

The identification of the actual radicals responsible for the spectra observed is uncertain but some plausible suggestions can be made. It seems that one of the primary effects of γ -radiation of polymethyl methacrylate is to cause scission of the polymer chain rather than cross linking. Initially a pair of radicals will be formed.

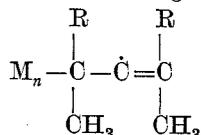
Many of these pairs will recombine and the effect of the irradiation be immediately nullified. However it seems likely that the plastic will contain some unreacted monomer molecules, these being either unused in the original polymerization of the material or formed during the experiment by thermal degradation. The unpaired electron could thus transfer to the monomer and the reactive chain terminate by acquiring a hydrogen atom. (This is one of the possible chain terminating processes occurring during ordinary polymerization.) If so then the radical, that is shown on the right, is formed.

Here there are four protons available to give the five-line spectrum, due to their interaction with the orbit of the unpaired electron.



Alternatively, as Bresler, Kazbekov, and Saminskii (1959) point out, either of the original free radicals could transfer to the end of a polymer already terminated by disproportionation. The radical shown on the lower right then results:

(Transfer to the other polymer of the disproportionation merely repeats the scission radical.)



The electron here will associate unequally with the two CH_3 groups. It seems likely that the group joined by the double bond will be preferred. If this is so we expect a spectrum of four lines like the one observed.

The same e.s.r. spectrum has been observed by Ingram, Simons, and Townsend (1958) for a variety of initiating agents. This fact rules out an

explanation based on unreacted initiator or on transfer to that end of a polymer chain occupied by the initiating agent.

Finally, one has to explain how these chemical free radicals become annealed. It follows from what has been said above that the most probable explanation for the decay of the five-line spectrum concerns the diffusion of molecular oxygen within the body of the plastic and its combination with the monomer radical. Combination of oxygen with the terminated polymer radical apparently is not favoured. And further, the monomer radical, being smaller, would be expected to be more mobile than the polymer and thus be more likely to collide with the oxygen.

The mode of decay of the four-line spectrum suggests the recombination of two radicals produced as a pair, as discussed above. Evidently this is the favoured mode of decay of the polymer radical, one such radical combining with another. It is not unlikely that a polymer radical will combine with a monomer, but to what extent this occurs is not revealed by our experimental results. At best the above considerations can be only tentative.

IV. CONCLUSIONS

The decay of defects in polymethyl methacrylate caused by gamma irradiation has been observed by electron spin resonance. Two radical species can be recognized, which anneal differently with time. One species decays as $\exp[-\sqrt{(t/t_0)}]$ which is characteristic of a diffusion process associated with, probably, oxygen molecules distributed uniformly within the plastic sample. The second species decays as $\text{erf} \sqrt{(t_0/t)}$ which suggests the mutual annihilation of defect pairs. Some attempt is made to identify the chemical groups involved.

The defect density induced by the radiation was shown to be linear with integrated dose in the range 0.1 to 0.8 megarad, received over a 12-hr exposure. Thus there is the possibility of using the e.s.r. signal as a method of dosimetry. Corrections would have to be made to allow for the inevitable slow decay of the signal at room temperature.

V. ACKNOWLEDGMENTS

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VI. REFERENCES

- ABRAHAM, R. J., MELVILLE, H. W., OVENALL, D. W., and WHIFFEN, D. H. (1958).—*Trans. Faraday Soc.* **54**: 1133.
- ALEXANDER, P., CHARLESBY, A., and ROSS, M. (1954).—*Proc. Roy. Soc. A* **223**: 392.
- BARKER, R. E., and MOULTON, W. G. (1960).—*J. Polymer Sci.* **47**: 175.
- BOAG, J. W., DOLPHIN, G. W., and ROTBLAT, J. (1958).—*Radiation Res.* **9**: 589.
- BRESLER, S. E., KAZBEKOV, E. N., and SAMINSKII, E. M. (1959).—*Vysokomolekularnye Soedinenia* **1**: 132.
- CHARLESBY, A. (1960).—“Atomic Radiation and Polymers.” (Pergamon Press: Oxford.)
- CHANDRASEKHAR, S. (1943).—*Rev. Mod. Phys.* **15**: 1.
- COLLINS, F. C., and KIMBALL, G. E. (1949).—*J. Colloid Sci.* **4**: 425.

- FLETCHER, R. C., and BROWN, W. L. (1953).—*Phys. Rev.* **92**: 585.
- HUKUDA, K. (1960).—*Mem. Fac. Sci. Kyūsyū Univ.* B **3**: 41.
- INGRAM, D. J. E. (1958).—"Free Radicals." p. 81. (Butterworths Scientific Publications: London.)
- INGRAM, D. J. E., SYMONS, M. C. R., and TOWNSEND, M. G. (1958).—*Trans. Faraday Soc.* **54**: 409.
- PIETTE, L. H. (1960).—"NMR and EPR Spectroscopy." p. 217. (Pergamon Press: Oxford.)
- WAITE, T. R. (1958).—*J. Chem. Phys.* **28**: 103.
- WALL, L. A., and BROWN, D. W. (1957).—*J. Phys. Chem.* **61**: 129.