Nature of trapped free radicals in γ-irradiated poly(vinyl alcohol) films

P. K. Wong
Queensborough Community College, Bayside, New York 11364, USA and Brookhaven National Laboratory, Upton, New York 11973, USA

(Received 9 December 1977; revised 19 December 1977)

The radicals trapped in γ-irradiated poly(vinyl alcohol) films were examined by e.s.r. spectroscopy, with respect to their thermal stability and the effects of foreign materials occluded in the polymer. Two different radicals are observed and their identity discussed.

INTRODUCTION

The trapped radicals in γ-irradiated polyethylene have been extensively studied[1], but e.s.r. studies on irradiated poly(vinyl alcohol) have not received much attention. Abraham and Whiffen[2] examined the e.s.r. spectra of γ-irradiated poly(vinyl alcohol) and found a triplet spectrum, without identifying the radicals. Ogawa[3] compared the e.s.r. spectrum of poly(vinyl alcohol) with that of 2,4-pentanediol, both γ-irradiated, and assigned the observed triplet to the radical species $-CH_2-\dot{C}OH-CH_2-$. Subsequently, Hase and Yamaoka[4] examined the radicals in poly(vinyl alcohol) irradiated at 77K. They found a singlet superimposed on a quintet. Based on the decaying pattern of the radicals, the singlet was attributed to a trapped electron and the quintet to a radical species $-CH_2-CHOH-\dot{C}H-CHOH-$. Both the singlet and quintet are unstable at room temperature. In this paper, we report the finding that the room temperature triplet e.s.r. spectrum observed in γ-irradiated poly(vinyl alcohol) is actually due to two different radicals and that additives in the polymer act as good radical scavengers.

EXPERIMENTAL

Poly(vinyl alcohol) was obtained from Borden Chemical Co. Average molecular weight of the polymer is about 88 000. The polymer powder was dissolved in triple-distilled water. The aqueous solution containing 60% by wt of the polymer was poured into a dish containing clean mercury; the water was allowed to evaporate at room temperature in the dark. The dry film was then lifted from the mercury surface and cut into rectangular pieces. The rectangular film was then rolled up and inserted into a quartz tubing for e.s.r. spectroscopic examination. Before γ-irradiation, the film was evacuated for at least 24 h until the residual pressure was 10^{-4} torr (1.3×10^{-2} N/m^2). The quartz tubing was then sealed off from the vacuum manifold.

Irradiation was carried out in a ^{60}Co γ-ray source at a dose rate of about 0.5 Mrad/h. After irradiation, the quartz tubing was flame-heated to remove paramagnetic centres produced by the irradiation, while the film was at the other end of the sealed tubing. The irradiated polymer was then examined in a Varian 4500 e.s.r. spectrometer, the field dial of which was calibrated by Fremy's salt, g values were obtained by comparing that of DPPH ($g = 2.0037$). Polymer samples were heated by using the variable temperature accessory of Varian Associates. Temperature was measured by a calibrated thermocouple located just below the e.s.r. sample tube.

RESULTS

Radical production with irradiation dosage

Gamma-irradiation of poly(vinyl alcohol) films produces radicals that show a 3-line e.s.r. signal. *Figure 1a* displays a typical spectrum, detected immediately after 0.67 Mrad of irradiation. Since there are reasons to believe that this spectrum is not due to one single radical type (see below) the growth of the three peaks against total irradiation dose was carried out and the results shown in *Figure 2*.

Stability of radicals

On storage at room temperature, the trapped radicals decayed slowly, and the intensity of the e.s.r. lines decreased. *Figure 1b* is the e.s.r. spectrum of the radicals in the same sample 7 days after *Figure 1a* was obtained. Comparing the lines in the two spectra, it is apparent that the central line decayed much more slowly than the two outer lines. Thus the thermal stability of these lines were studied and the data given in *Figure 3*. Samples of poly(vinyl alcohol) films were irradiated to a total dose of about 1 Mrad and then were held at a fixed temperature, while the intensity of the three e.s.r. lines was recorded. For the sample held at 310K, the observation was continued for 5 days; at that time the two outer lines totally disappeared, while the central line still showed 35% of the original signal remaining.

The thermal stability of the three e.s.r. lines also depends on the total γ-dose. *Table 1* shows the intensity of these 3 lines remaining after each irradiated sample was annealed at 350K for 10 min. At 0.7 Mrad, the two outer lines decayed over 90% and the central line decayed 80%; at a higher degree dose (1.4 Mrad), however, the two outer lines decayed over 96%, while the central line decayed only 47%.

Sensitivity of radicals to additives in polymer

The quantity of radicals trapped in the γ-irradiated poly(vinyl alcohol) may be affected by traces of foreign molecules incorporated into the polymer. To investigate this effect on the radicals responsible for the observed e.s.r. sig-

0032–3861/78/1907–0785$01.00

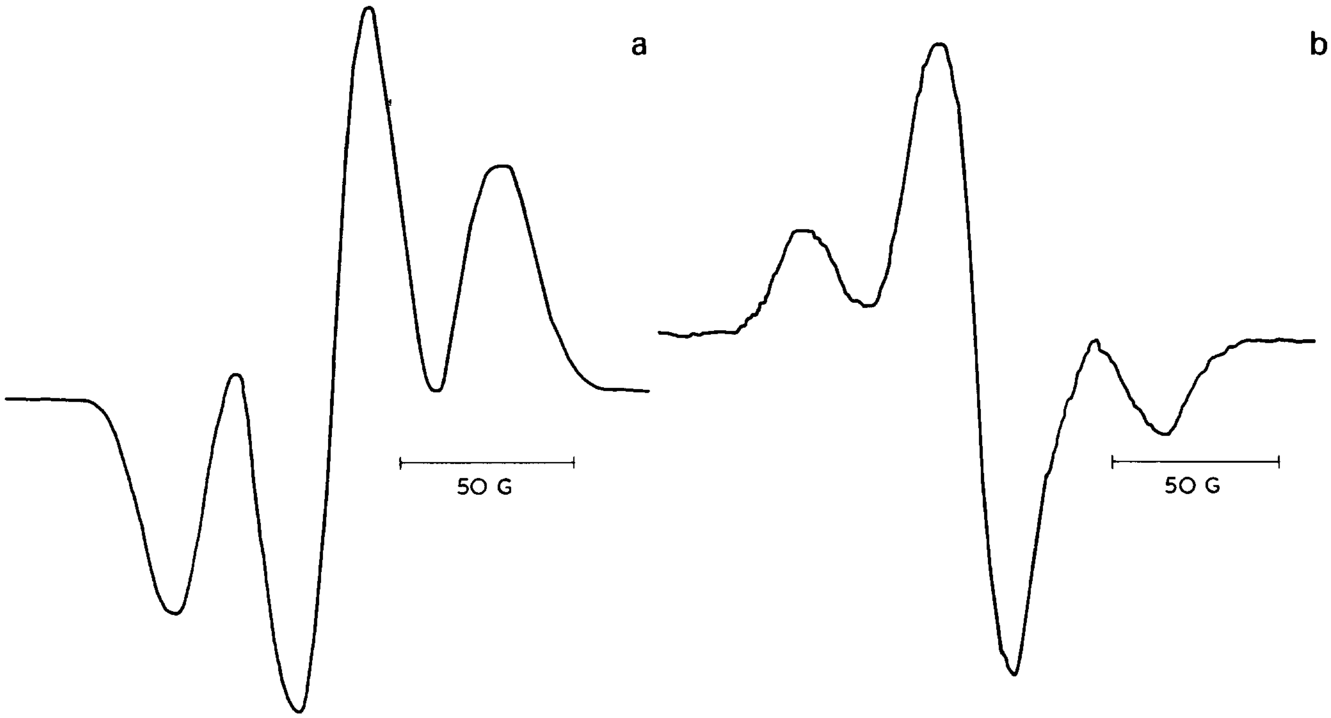


Figure 1 E.s.r. spectrum of γ-irradiated poly(vinyl alcohol) film at 298K. (a) Observed immediately after 0.67 Mrad exposure; s.l. 80. (b) Observed after 7 days; s.l. 250

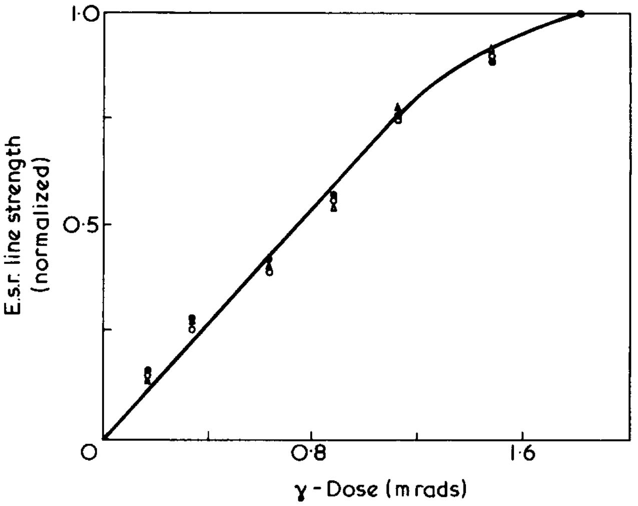


Figure 2 Growth of e.s.r. lines against radiation dosage. ○, First line; ●, second line; ▲, third line

nals, small quantities of water-soluble compounds were added to the aqueous polymer solution. The film was then cast as described before. Irradiation and e.s.r. examination was done following the same procedure.

The effect of $AgClO_4$ incorporated into the polymer on the e.s.r. signal is shown in *Figure 4*. The quantity of added $AgClO_4$ is given as wt % of the polymer. As is clear from *Figure 4*, 5% by wt of $AgClO_4$ incorporated into the polymer reduces the radical production by about 60%.

Similar experiments were carried out with DL-alanine and deoxyadenosine-5-monophosphate (dAmp) and the results are plotted in *Figure 5*. As in the case of $AgClO_4$, addition of alanine and dAmp depresses the formation of trapped radicals.

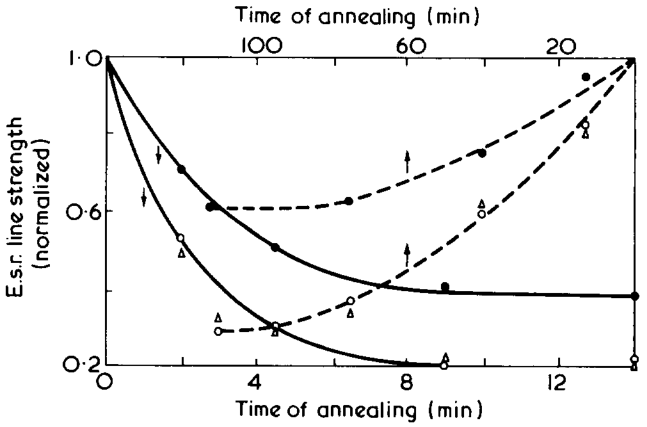


Figure 3 Thermal stability of e.s.r. lines at different temperatures. ○, First line; ●, second line; △, third line; ——, 343K; – – –, 300K

DISCUSSION

γ-Irradiation of poly(vinyl alcohol) produces an e.s.r. quintet at 77K and a triplet at room temperature. The quintet decays on warming to the triplet. The triplet has been interpreted to be radical species $-CH_2-COH-CH_2-CHOH-$[3], which has been generally accepted[4]. However, owing to the anisotropy and the linewidths of these e.s.r. lines, there may be other signals masked by the triplet and not detected; this is especially true if the second radical species shows only a singlet. In *Figure 1a*, the triplet as shown was obtained from room temperature by γ-irradiation of a poly(vinyl alcohol) film. The isotropic *g* value of this spectrum is close to that reported by Abraham and Whiffen[1], and, as suggested by these authors, there may be a singlet superimposed on this triplet spectrum. Since it is not possible to detect the signal of the second radical by spectral analysis, some form of kinetic studies on the trapped radicals may be helpful. If we as-

Table 1 γ-Dose dependency of stability of e.s.r. spectrum in irradiated poly(vinyl alcohol)*

Total dose (Mrad)	E.s.r. signal intensity (%)		
	1st line	2nd line	3rd line
0.7	6	20	9
1.4	2	53	4

* Irradiated samples kept at 350K for 10 min. Measured line intensity normalized to that before annealing

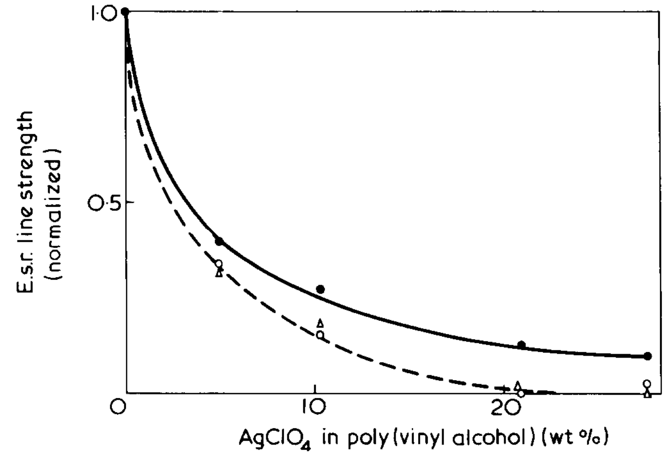


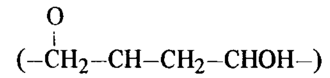
Figure 4 Effect of $AgClO_4$ on the radicals in poly(vinyl alcohol). ○, First line; ●, second line; △, third line

sume that the central line (second line) of the triplet is due to two separate signals from two radical species, whereas the two outer lines (first and third) are part of the triplet, then the central line may behave differently from the two outer lines. *Figure 1b* shows that, after some thermal aging of the irradiated polymer, the two outer lines decayed much faster than the central line, suggesting different thermal stability of the two radicals. Referring to *Figure 3,* we see that at 310K, the two outer lines decay by 75% after approximately 100 min of storage, while the second line only suffers a 40% decay. At a higher annealing temperature (343K), 80% of the two outer lines decays in 9 min, during which the central line only decays by 60%. There is no detectable change in linewidth on warming, and the different decay rates between the outer lines and the central line cannot be due to line-broadening effect. The most likely interpretation is that the central line is a composite of two signals superimposed on each other. One of the lines is part of the triplet, which is assigned to the $-CH_2-COH-CH_2-CHOH-$ radical, and the other is a featureless singlet which has greater thermal stability than the triplet. It is also noteworthy that the decay rate can be separated into two segments; a fast decay which is essentially over at about 80 min at 310K and a very slow decay, which lasts for about 5 days before all the radicals vanish.

In order to investigate the possibility whether the relative concentration of these two radicals can be changed by irradiation dose, the strength of the three e.s.r. lines are plotted against dose in *Figure 2.* It appears that there is no substantial difference in the rate of production of the two species with respect to the amount of irradiation.

It is known that the yield of trapped radicals is sensitive to foreign substances doped into the trapping medium. If the spectra in *Figure 1a* are indeed due to two distinct radicals, the addition of materials may affect their yield or stability. In *Figure 4,* $AgClO_4$ is shown to diminish the radical yield, the effect being more pronounced on the triplet than on the singlet. At about 20 wt % of $AgClO_4$, the triplet is totally removed and only the singlet remains. The introduction of $AgClO_4$ at a relatively high percentage weight probably substantially alters the polymer's structure, decreasing the number of trap sites in the irradiated polymer. On the other hand, a small quantity of alanine or dAmp occluded in the polymer also depresses the radical yield. This is usually called the protective effect of the additive, which is less effective on the triplet than on the singlet. A small amount by weight (6%) of alanine or dAmp incorporated in the polymer prior to irradiation causes an 80% drop in the radical yield of the triplet, but only 25% drop in the radical yield of the singlet.

All the experimental observations reported here indicate that γ-irradiation of poly(vinyl alcohol) produces $-CH_2-COH-CH_2-CHOH-$, responsible for the triplet e.s.r. spectrum; the other radical, which has a singlet line signal, cannot be identified definitely, but is known to be more thermally stable and less sensitive to protective effect than the triplet. Ohnishi and coworkers[5], observed a similar singlet about 17 gauss in width in irradiated poly(vinyl alcohol). γ-irradiation of polystyrene[6] and poly(vinyl chloride)[7] also produces a featureless symmetric e.s.r. line of about 25 gauss in width, similar to the one observed in poly(vinyl alcohol). The radical from these irradiated polymers is thought to be a polyenyl radical, $-CH-(CH{=}CH)_n-$. The radical does not possess a structure in the e.s.r. signal because of the electron delocalization throughout a long chain of conjugated double bonds; this radical is thermally quite stable. Based on the similarity of the e.s.r. singlet in γ-irradiated poly(vinyl alcohol) and poly(vinyl chloride), the singlet we observed is most likely a polyenyl type radical. On the other hand, an alkoxy radical



$$(-\overset{O}{\overset{|}{C}}H_2-CH-CH_2-CHOH-)$$

cannot be strictly excluded as the alternative species showing the e.s.r. singlet. Such a radical may be thermally stable and may also lack fine structure in its spectrum. Weiner and Hammond[8] produced t-butoxy radicals by photolysing di-t-

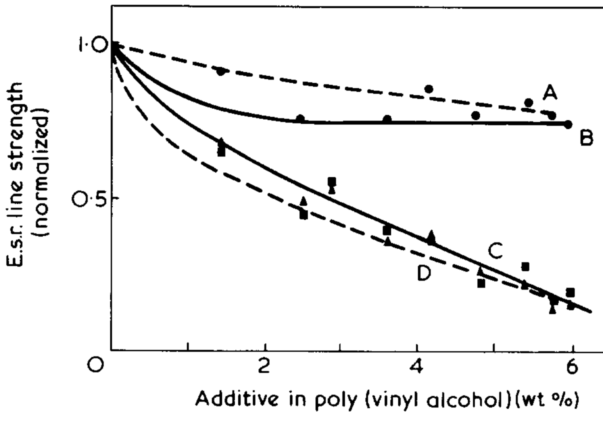


Figure 5 Effect of alanine (A,C) and dAmp (B,D) on the radicals in poly(vinyl alcohol). ■, First line; ●, second line; ▲, third line

butoxide, and they detected a single e.s.r. signal. Sargent and Gardy[9] γ-irradiated carbinols and detected alkoxy radicals by spin-trapping.

It can be concluded that there are at least two radicals in γ-irradiated poly(vinyl alcohol) at room temperature. One of the species, showing an e.s.r. triplet, is a radical produced by the elimination of hydrogen from the hydroxy-carbon; the second radical showing a featureless singlet, is either a polyenyl radical or less likely an alkoxy-radical.

ACKNOWLEDGEMENTS

This research was carried out at Brookhaven National Laboratory under contract with the US Energy Research and Development Administration and supported in part by its Division of Basic Energy Sciences and a grant from the Research Foundation of the State University of New York.

REFERENCES

1 Shimada, S., Masatoshi, M., Yasuro, H. and Hisatsugu, K. *Polymer* 1977, **18**, 19; Dole, M. The Radiation Chemistry of Macromolecules', (Ed. M. Dole), Academic Press, New York, 1972, Vol 1, p 335

2 Abraham, R. J. and Whiffen, D. H. *Trans. Faraday Soc.* 1958, **54**, 1291

3 Ogawa, S. *J. Phys. Soc. Jpn* 1960, **16**, 1488

4 Hase, H. and Yamaoka, H. *Radiat. Eff.* 1973, **19**, 195

5 Ohnishi, S., Ikeda, Y., Sugimoto, S. and Nitta, I. *J. Polym. Sci.* 1960, **47**, 503; Ohishi, S., Kashiwagi, M. and Nitta, I. *Polymer* 1960, **2**, 119

6 Hurrah, L. A. 'Organic Solid State Chemistry', (Ed. G. Adler), Gordon and Breach, New York, 1969, p 197; Dole, M. 'The Radiation Chemistry of Macromolecules', (Ed. M. Dole), Academic Press, New York, 1973, Vol 1, p 335

7 Salovey, R., Luongo, J. P. and Yager, W. A. *Macromolecules* 1969, **2**, 198; Salovey, R. 'The Radiation Chemistry of Macromolecules', (Ed. M. Dole) Academic Press, New York, 1973, Vol 2, p 37

8 Weiner, S. and Hammond, G. S. *J. Am. Chem. Soc.* 1969, **91**, 2182

9 Sargent, F. P. and Gardy, E. M. *Can. J. Chem.* 1974, **52**, 3645