The Formation and Decay of Free Radicals Trapped in Photopolymerized Methyl Methacrylate*

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Radicals trapped in poly(methyl methacrylate) gels were produced by direct ultraviolet irradiation (2537 Å) of pure monomer and by photodecomposition (3650 Å) of azobisisobutyronitrile dissolved in pure monomer. It was shown by computer simulation of the resulting e.s.r. spectra that two types of radical, the propagating radical and an allyl-type radical, were present in both cases. The thermal decay curves for both types of radical were derived, and the relative contribution of the allyl radical to the overall spectrum was found to increase during decay. It is proposed that allyl radicals can be produced both by photodegradation of the polymer and by reactions of other radicals with the unsaturated ends of polymer chains.

From the computer-simulated spectra of *Iwasaki* and *Sakai* [1] it is known that the propagating radical $-CH_2\dot{C}(CH_3)CO_2CH_3$, of poly(methyl methacrylate) (PMMA) can give rise to a nine-line e.s.r. spectrum in the polymeric glass. Photopolymerization of MMA or irradiation of PMMA produce nine-line spectra. On heating, however, the observed nine-line spectrum decays to a four-line spectrum [2] and it has not been established unequivocally whether the radical which gives rise to this four-line spectrum is present in the initial polymer glass or whether it is formed only as a decay product of the propagating radical.

In this paper we describe how combinations of computer-synthesized nine- and four-line spectra can be used to improve the simulation of observed spectra of initial and partially decayed samples of photopolymerized MMA. By combining the simulation technique with spin concentration measurements the separate decay curves for the four- and nine--line spectra are deduced.

Experimental

Radicals trapped in PMMA glasses were produced by irradiating pure air-free monomer in silica tubes with 2537 Å radiation, or by photodecomposition of azobisisobutyronitrile (AZBN) dissolved in pure MMA (0.5 mole l^{-1}) in pyrex tubes with 3650 Å radiation. Samples were produced in duplicate after 20 hours irradiation at room temperature. After recording the initial spectra the samples were heated in a thermostatted oil bath at 80.5, 90.0, 95.0 and 100°C. At each temperature the samples were removed periodically and the e.s.r. spectra recorded.

The spectrometer was a Decca X3 instrument operating at 9.27 GHz with 100 kHz modulation. The low incident power level of 1mW in the sample cavity avoided saturation effects. The g-values of the initial spectra were obtained by simultaneously recording the spectrum of Fremy's salt ($g = 2.005537$) [3]. Powdered coal samples, calibrated against the primary standard diphenylpicrylhydrazyl in benzene solution, were used (diluted with chalk) as standards for spin concentration measurements.

Spectral simulations

On heating the PMMA glasses until no further changes could be observed spectra typified by Fig. 1a were obtained. It has been shown previously that this spectrum could derive from an allyl-type radical [2]. In this work such spectra were simulated on an allyl model having three magnetically equivalent protons producing four broad, overlapping absorption lines. Fig. 1b shows a simulated spectrum, matching closely that in Fig. 1a, obtained by synthesizing four Gaussian lines with a hyperfine splitting of 12.8 G, a line width of 13.8 G, and intensity ratio $1:3:3:1$.

The initial nine-line spectra of the trapped radicals were simulated quite well on the Iwasaki—Sakai model [1] which involves a distribution of tilted conformations of the β-protons. Interactions of the β-protons with the unpaired electron are given by

$$a_{\beta H} = B_0 + B_1 \cos^2 \Theta, \tag{1}$$

where $a_{\beta H}$ is the total β-proton coupling and B_0 the small coupling due to spin polarization. The second term arises from hyperconjugative interaction. Θ is defined in Fig. 2. For the rapidly rotating methyl protons equation (1) reduces to

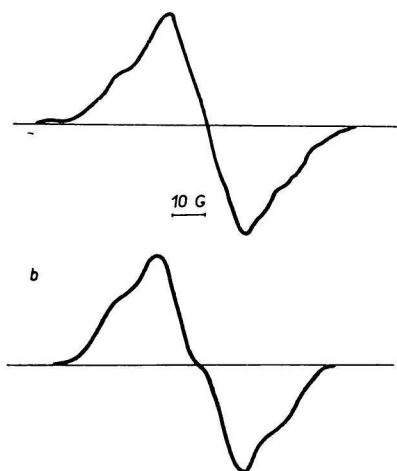$$a_{\beta H} = B_0 + \tfrac{1}{2}B_1. \tag{2}$$

Fig. 1. a) Spectrum of PMMA sample after heating until no further change was observed. *b*) Simulated spectrum of allyl radical.
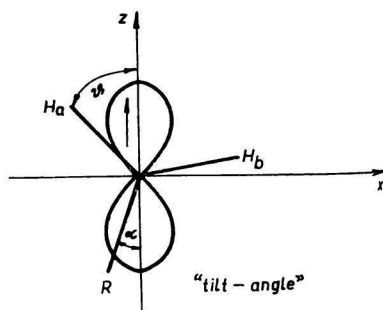
Fig. 2. Hyperfine coupling to β-protons. H_a and H_b on propagating radical of PMMA: definition of α and Θ.

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Good simulations were obtained assuming a methyl proton splitting of 23 G, a line width of 5.2 G, and values of zero and 46 G respectively for B_0 and B_1. The width of the Gaussian distribution of the tilt angle α (Fig. 2) is characterized by $\Delta_{\frac{1}{2}}$ in the Iwasaki—Sakai treatment. In the present work α was 5° and $\Delta_{\frac{1}{2}}$ 6.5°, although these values are not unique in giving adequate spectral simulation.
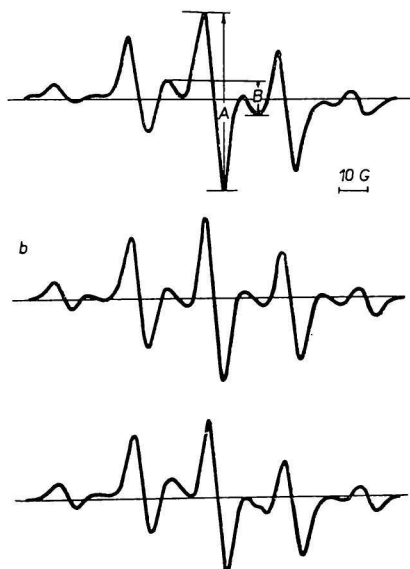

Fig. 3. a) e.s.r. spectrum of unheated PMMA produced by direct photopolymerization of monomer. *b*) Simulation of propagating radical in PMMA according to Iwasaki—Sakai treatment. *c*) Combined simulated spectra of propagating and allyl radicals in ratio 2.2 : 1.

The nine-line spectra produced in this manner were always symmetrical, unlike the observed spectra which always showed a small but well-defined asymmetry. Variation of the programme parameters in the Iwasaki—Sakai model failed to reproduce this asymmetry. A much better fit (see Fig. 3) between simulated and observed spectra was obtained by including in the former a contribution from the four-line allyl spectrum. The simulation of mixed spectra was achieved by use of a computer programme designed to overlap any two simulated spectra with allowance for differing g-values. The same technique was used to simulate experimental spectra recorded at different stages of thermal decay. Fig. 4 shows that the relative contribution from the allyl spectrum increases with time of heating.

Since there is no central line in the allyl spectrum and since the propagating radical spectrum has much sharper lines the g-value for the propagating radical can be obtained from the unheated sample spectra. In all cases g was 2.0029 $\pm$ 0.0001. For the allyl spectrum the g-value cannot be obtained directly since, even after prolonged heating, vestiges of the nine-line spectrum remain. To obtain satisfactory simulation of composite spectra, however, the allyl spectrum had to be centred 0.8 $\pm$ 0.2 G downfield from the nine-line centre. Thus the g-value for the allyl spectrum is 2.0034 $\pm$ 0.0002. These g-values agree well with those deduced by *Griffiths* and *Sutcliffe* [4].
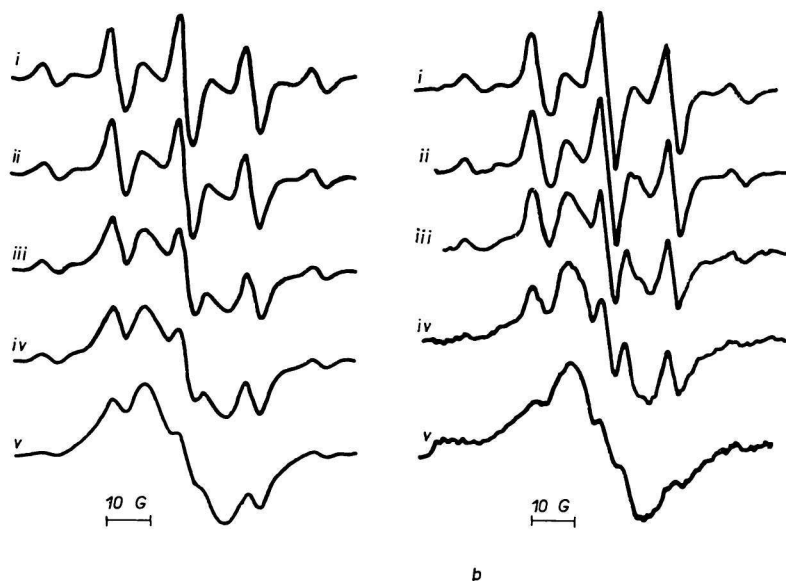
Fig. 4. a) Combined simulated spectra of propagating and allyl radicals in ratios:
(i) 2.2 : 1, (ii) 0.816 : 1, (iii) 0.278 : 1, (iv) 0.151 : 1, (v) 0.0603 : 1.
b) e.s.r. spectra of PMMA produced by direct photopolymerization after heating at 100°C for:
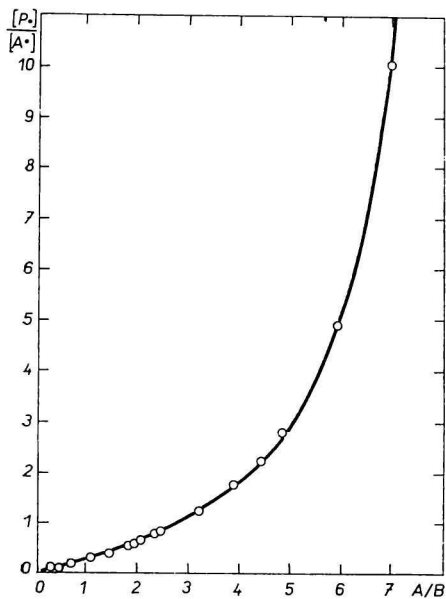(i) 0, (ii) 22, (iii) 62, (iv) 139, (v) 682 minutes.

Fig. 5. Ratio of concentrations of propagating to allyl radical $[P\cdot]/[A\cdot]$ peak-to-peak height ratio A/B from combined simulated spectra. A and B are defined in Fig. 3.

The relative sizes of the peak-to-peak heights A and B in Fig. 3 are determined by the relative contributions of the nine- and four-line spectra. From the simulated combined spectra the ratios of the double integral areas of the two spectra were plotted against the A : B ratio to provide the calibration curve in Fig. 5. Thus from the ratio of A : B in experimental spectra at any stage of heating the ratio of the propagating radical to allyl radical concentrations were obtained. Together with the values of the total radical concentrations this information permits the separate thermal decay curves of the two radicals to be plotted. Typical thermal decay curves for radicals produced both by direct photopolymerization and by polymerization *via* photodecomposition of AZBN, are shown in Figs. 6 and 7. The marked curvature in Fig. 5 shows that the method of taking A and B as direct measures of the relative concentrations of the two radicals cannot be valid. In both samples there is an unexpectedly high proportion of allyl radicals.

Discussion

In the directly photopolymerized sample (Fig. 6) the propagating radical concentration falls rapidly initially, tailing off asymptotically after prolonged heating. The allyl radical concentration, however, shows a short but sharp drop and thereafter increases noticeably before decaying slowly at long heating times. In the AZBN-initiated samples (Fig. 7) the initial spin concentrations are ten to thirty times lower than, and the decay curves quite distinct from, those of the directly photopolymerized samples. The propagating radical concentration decreases in much the same way as before, but after an initial decrease the rise in allyl radical concentration is much more marked than in the corresponding curve in Fig. 6, and in fact causes an increase in total radical concentration. These general types of behaviour were observed during thermal decay experiments at other temperatures. In the directly photopolymerized samples the initial presence of allyl radicals can be accounted for in terms of photo-induced main chain scission and subsequent disproportionation of radical *I* into methyl formate and the allyl radical *II*.
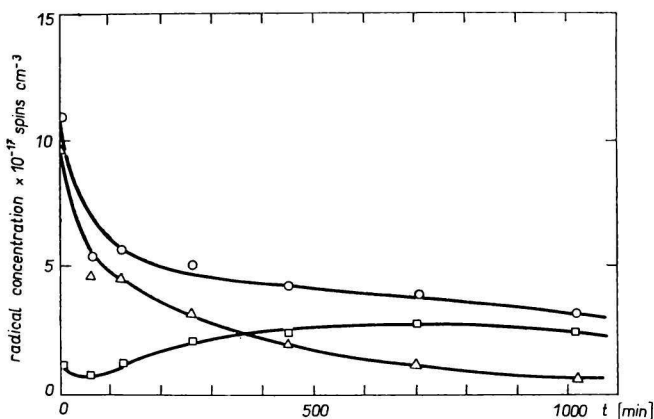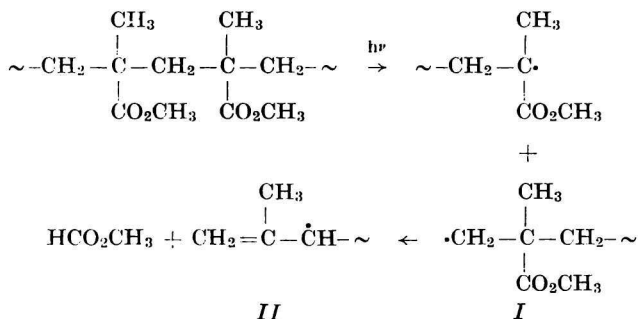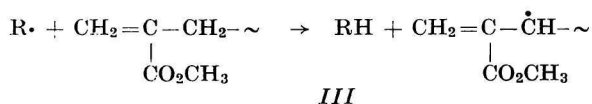

Fig. 6. Decay curves for radicals in directly photopolymerized PMMA heated at 80.5°C.
○ total radical, △ propagating radical, □ allyl radical concentrations.

$$\sim-CH_2-\underset{\underset{CO_2CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CO_2CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\sim \quad \overset{h\nu}{\rightarrow} \quad \sim-CH_2-\underset{\underset{CO_2CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\cdot$$

$$+$$

$$HCO_2CH_3 + CH_2=\underset{}{\overset{\overset{CH_3}{|}}{C}}-\overset{\cdot}{C}H-\sim \quad \leftarrow \quad \cdot CH_2-\underset{\underset{CO_2CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\sim$$

$$II \qquad\qquad\qquad\qquad I$$

This type of reaction cannot account for allyl radicals in AZBN-initiated samples since radiation of 3650 Å wavelength has no effect on PMMA. In this case allyl radicals are probably formed by attack of another radical at a terminal double bond of a dead chain.

$$R\cdot + CH_2=\underset{\underset{CO_2CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\sim \quad \rightarrow \quad RH + CH_2=\underset{\underset{CO_2CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\cdot}{C}H-\sim$$

$$III$$

R· may be a propagating radical or an AZBN fragment. Homolytic decomposition of unphotolyzed AZBN during thermal treatment probably causes the rise in total and allyl radical concentrations shown in Fig. 7 by this means. This type of reaction also explains how allyl radicals are formed as decay products from propagating radicals during heat treatment of directly photopolymerized samples.

The allyl radicals II and III differ in the substituents attached to the central carbon atom. In a polymer matrix they cannot be differentiated by e.s.r. The small spin density
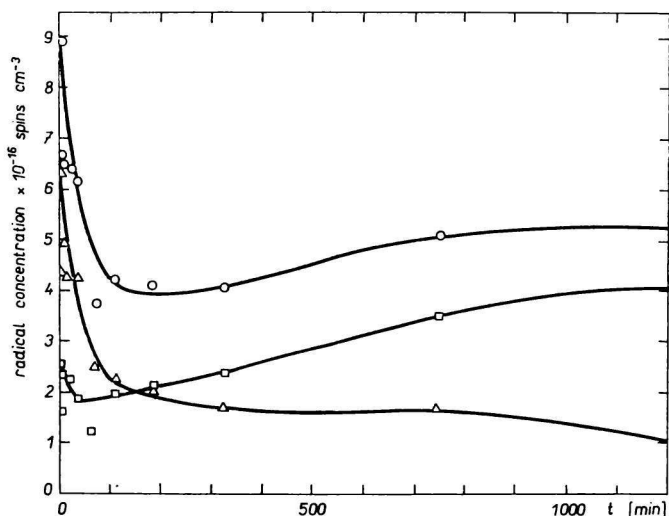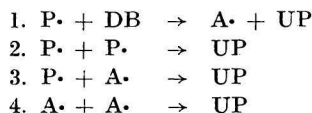

Fig. 7. Decay curves for radicals in AZBN-initiated PMMA heated at 90.0°C.
○ total radical, △ propagating radical, □ allyl radical concentrations.

on the central carbon atom together with the large line widths prevents the methyl protons in *II* from showing resolved splittings.

The main reactions occurring during heat treatment of trapped radicals may be summarized as:

$$
\begin{array}{lll}
1. & P\cdot + DB & \rightarrow \quad A\cdot + UP \\
2. & P\cdot + P\cdot & \rightarrow \quad UP \\
3. & P\cdot + A\cdot & \rightarrow \quad UP \\
4. & A\cdot + A\cdot & \rightarrow \quad UP
\end{array}
$$

where P· represents a propagating or alkyl radical, A· an allyl radical, UP unreactive products, and DB an unsaturated chain end. For a complete kinetic analysis these equations are applicable only to the phase of reaction beyond the initial rapid decay when radicals may be safely assumed to have a homogeneous distribution throughout the sample. Unfortunately this part of the decay curves is rather ill-defined and these equations cannot be verified with the present data. It is clear, however, that the complete experimental curves of radical decay cannot be analyzed in terms of any simple kinetic scheme. Our results do not support the conclusion of *Griffiths* and *Sutcliffe* [4] that the decay of these radicals follows second order kinetics, or that decay is a consequence of diffusion of impurities through the polymer matrix as proposed by *Michel et al.* [5].

References

1. Iwasaki M., Sakai Y., *J. Polym. Sci. A-1*, **7**, 1537 (1969).
2. Bullock A. T., Sutcliffe L. H., *Trans. Faraday Soc.* **60**, 625 (1964).
3. Kerr C. M. L., *Ph. D. Thesis*. Aberdeen University, 1970.
4. Griffiths W. E., Sutcliffe L. H., *Trans. Faraday Soc.* **62**, 2837 (1966).
5. Michel R., Chapman F. W., Mao T. J., *J. Polym. Sci. A-1*, **5**, 677 (1967).