

AN ELECTRON SPIN RESONANCE STUDY OF IRRADIATED POLY-4-METHYLPENT-1-ENE

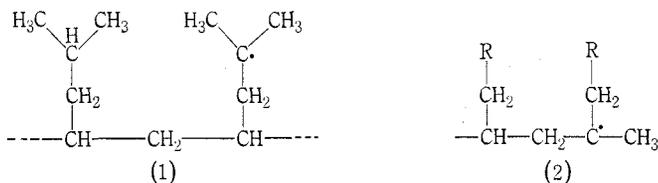
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As part of a programme designed to elucidate the mechanism of deterioration of organic materials, we have been studying the effects of ionizing radiation both on polyolefins and on small molecules.^{1,2} In this communication we report our findings on the nature of those free radicals trapped in irradiated, unstabilized isotactic poly-4-methylpent-1-ene (P4MP1), and identified by electron spin resonance spectroscopy.

The first-derivative e.s.r. spectrum of P4MP1, irradiated and measured at 77°K without warming, Figure 1, consists of eight equally spaced lines, separation $(24 \pm 1) \times 10^{-4}$ Wb m⁻² (1 Wb m⁻² = 10⁴ G), relative intensities (1·2 : 7 : 20 : 35 : 37 : 23 : 7 : 1·3) for which the line-width at half-height for the three outer lines on each side of the centre of the spectrum at $g = 2.003$ is $(7-8) \times 10^{-4}$ Wb m⁻².

This spectrum is consistent with that expected from the free radical (1) trapped in a polycrystalline matrix³ in which the unpaired electron interacts equally with the two methyl groups, which are undergoing relatively free rotation about the CH₃-C axis, and with one of the two protons of the side-chain methylene group. The coupling of the unpaired electron with only one of the methylene β-protons can be explained by restricted rotation about the C-C bond, there being little coupling with the second methylene proton.^{4,5}



The e.s.r. spectrum of P4MP1, irradiated at room temperature or irradiated at 77°K and measured at room temperature, is shown in Figure 2. The spectrum is unchanged when measurements are made on recooling the sample to 77°K; hence, the free radical trapped at room temperature differs from that trapped at 77°K.

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¹ Pinkerton, D. M., *J. Polym. Sci. (A)*, in press.

² Whelan, D. J., *Aust. J. Chem.*, 1970, **23**, 37.

³ Lin, J., and Williams, F., *J. phys. Chem.*, 1968, **72**, 3707.

⁴ Heller, C., and McConnell, H. M., *J. chem. Phys.*, 1960, **32**, 1535.

⁵ Norman, R. O. C., and Gilbert, B. C., *Adv. phys. org. Chem.*, 1967, **5**, 53.

This spectrum consists of an octet, separation $(24 \pm 1) \times 10^{-4} \text{ Wb m}^{-2}$, of doublets, separation $(6 \pm 1) \times 10^{-4} \text{ Wb m}^{-2}$, and we propose that the spectrum arises from the partial structure (2; $R = \text{Pr}^1$), the unpaired electron interacting equally with the seven β -protons. Such an interaction accounts only for the octet structure and we suggest that the doublet splitting seen in each of the peaks arises from an interaction with the isopropyl hydrogen. A similar γ -proton hyperfine coupling has been observed in the neopentyl radical trapped in glassy neopentane at 77°K ,³ though such couplings are not always discernible in polycrystalline and glassy matrices.

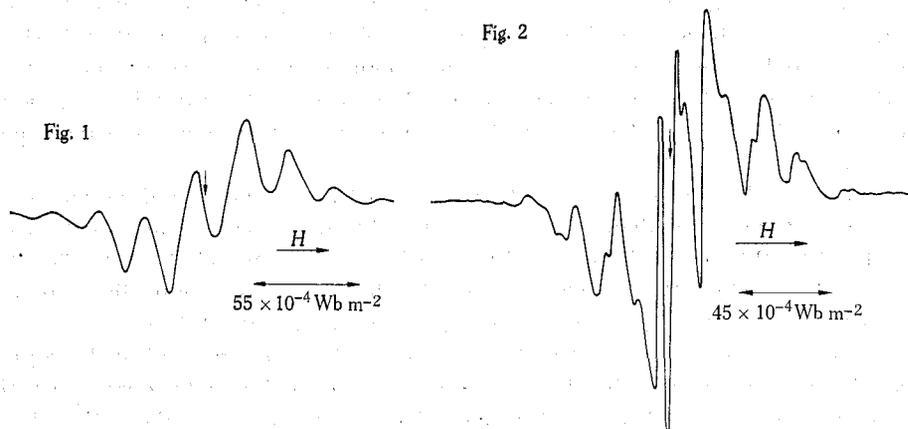


Fig. 1.—First-derivative e.s.r. spectrum of poly-4-methylpent-1-ene, irradiated and measured at 77°K without warming. The arrow head denotes the centre of the signal from the g -marker, DPPH, at $g = 2.0036$.

Fig. 2.—First-derivative e.s.r. spectrum of poly-4-methylpent-1-ene, irradiated at 77°K and measured at room temperature.

The hyperfine splitting pattern of Figure 2 can also be analysed in terms of structure (2) in which there is restricted rotation about two of the C-C axes—but this restriction is not typical in hydrocarbon fragments near room temperature,^{6,7} and we feel that it is not applicable here—more so as the observed intensities of the hyperfine lines fit the pattern of a freely rotating radical (2) better than that expected from a radical centre in which there are rotational barriers.

Actually, our “basic octet” is very similar to the room temperature spectrum from irradiated isotactic polybut-1-ene (PB1).⁸ Accordingly, we suggest that these spectra both arise from the fragments, (2), appropriate to the parent polymer—that from P4MP1 at room temperature having the alkyl structure (2; $R = \text{Pr}^1$).

To support our contention that the free radicals trapped in irradiated P4MP1 and PB1 are alkyl radicals, we note that these radicals decay appreciably on standing under vacuum at room temperature. Similar behaviour has been observed for the

⁶ Fessenden, R. W., and Schuler, R. H., *J. chem. Phys.*, 1963, **39**, 2147.

⁷ Kochi, J. K., and Krusic, P. J., *J. Am. chem. Soc.*, 1969, **91**, 3940.

⁸ Rubin, I. D., and Huber, L. M., *J. Polym. Sci. (B)*, 1966, **4**, 337.

alkyl free radical trapped in isotactic polypropylene (IPP)⁹ and this relative instability contrasts with the known stability of allyl radicals trapped in organic solids.⁹

Our results on irradiated P4MP1 and those of others on irradiated IPP⁹⁻¹² and PB1^{8,10} can be explained by a common process. When these polyolefins and 3-methylpentane,¹³ a model compound incorporating all the features of molecular structure that we note in the polyolefins, are irradiated at 77°K, the free-radical centre is formed on the side-chain and the hydrogen lost is the most acidic one, i.e. tertiary hydrogen is lost in preference to a secondary hydrogen, which, in turn, is lost in preference to a primary hydrogen. This specificity is quite general and most probably arises from the nature of the reactivity of the radical cation¹⁴ formed as a primary product in the irradiation.

When the irradiated polymers are warmed from 77°K to room temperature, the free radicals formed are now centred on the polymer backbone at the tertiary carbon atom. In the case of PB1 and P4MP1, this centre occurs at a chain terminus, though the e.s.r. results alone cannot specify whether this terminus has been formed by chain scission or not. The mechanism of the radical conversion and the macro-molecular effects of radiation on P4MP1 are being investigated.

Experimental

Unstabilized isotactic poly-4-methylpent-1-ene was supplied as a colourless, fine powder from the stock of research material prepared by ICI Ltd, Welwyn Garden City, Herts., England. Samples of the polymer (100 mg) were degassed (10^{-5} torr) for several days before being sealed in quartz-glass e.s.r. tubes. The samples were then irradiated at 77°K with ⁶⁰Co γ -radiation, typical doses being 1.0-1.2 Mrad.

The end of the tube to be inserted into the cavity of the e.s.r. spectrometer was flame-treated after irradiation and then the sample, which was kept at 77°K throughout this treatment, was transferred, by inversion and without warming, to the treated end of the tube which had been recooled back to 77°K.

The e.s.r. measurements were carried out on a JEOL 3BS-X e.s.r. spectrometer, with 100-kHz field modulation, while the amplitude of the sweep modulation was typically $c. 1.5 \times 10^{-4}$ Wb m⁻², peak to peak. For measurements at 77°K, the spectrometer cavity was fitted with an insertion-type Dewar, filled with liquid nitrogen, the detector circuit of the spectrometer operating on a relatively long time-constant.

Those measurements made at room temperature were carried out in the usual way.²

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⁹ Ayscough, P. B., and Munari, S., *J. Polym. Sci. (B)*, 1966, **4**, 503.

¹⁰ Loy, B. L., *J. Polym. Sci. (A)*, 1963, **1**, 2251.

¹¹ Pinkerton, D. M., and Whelan, D. J., unpublished work.

¹² Iwasaki, M., Ichikawa, T., and Toriyama, K., *J. Polym. Sci. (B)*, 1967, **5**, 423.

¹³ Henderson, D. J., and Willard, J. E., *J. Am. chem. Soc.*, 1969, **91**, 3014.

¹⁴ Timm, D., and Willard, J. E., *J. phys. Chem.*, 1969, **73**, 2403.