

Unsaturation in Irradiated Marlex 50 Polyethylene: Dose Rate and Post-Irradiation Effects

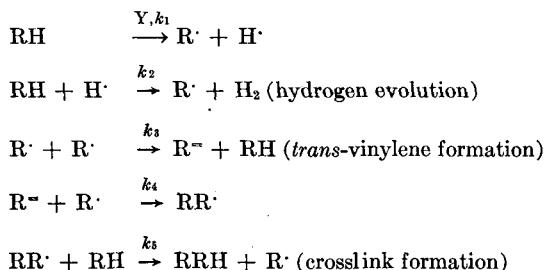
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A previous paper by one of the authors¹ described the known effects of irradiation on polyethylene in terms of the primary formation of free radicals.



Y is a factor dependant on the dose rate and the primary act, R[·] is a chain radical, and R⁻ represents a *trans*-vinylene group. The concentration of *trans*-vinylene double bonds, [R⁻], is dose rate dependant according to this mechanism. The relationship between the dose rate factor Y, the concentration of double bonds [R⁻], and the total dose r, may be derived from the equations in the previous paper.¹

$$[\text{R}^-]/K_1 = Y^{1/2}(1 - \exp\{-K_2 r/Y^{1/2}\})$$

where

$$K_1 = (k_1 k_3 [\text{RH}])^{1/2} / k_4$$

and

$$K_2 = k_4 \left[\frac{k_1 [\text{RH}]}{k_3} \right]^{1/2}$$

This relationship is illustrated in Figure 1. It is apparent that, except at the lowest dose rates, experimental errors may obscure the comparatively small dose rate dependance of *trans*-vinylene unsaturation.

In the work described here, care was taken to eliminate experimental error by determining the infrared absorbance for *trans*-vinylene at 965 cm.⁻¹ immediately after irradiation, and by standardizing the instrumental technique.

Antioxidant-free Marlex 50 powder was molded to a sheet of 0.4 mm. thickness between photographic glazing plates at 140°C. in a hydraulic press. This thickness was most suitable for the determination of amorphous content. By superimposition, thicknesses of 0.8 mm. for *trans*-vinylene, and 1.6 mm. for carbonyl, measurements could be obtained. Strips of this polymer were sealed in glass tubes of 1 mm. wall thickness at a pressure of 10⁻³ mm. of mercury pressure. One such sample was retained as a control specimen for the complete series of experiments.

Samples received a range of doses of electron or gamma irradiation. The Spent Fuel Rod Assembly at A.E.R.E. Harwell provided continuous gamma irradiation at 1 Mrad/hr. The 4 mev linear accelerator at this laboratory, when equipped with a platinum target, provided 2.5 μsec. pulses of gamma radiation at 600 pulses/sec. at a dose rate of 6 Mrad/hr. Without the target the accelerator provided pulsed electron radiation at 1, 5, or 20 Mrad/min. Ferrous dosimetry was used to determine gamma ray dose rates, while a water calorimeter, calibrated against ferrous sulfate dosimetry at low dose rates, was used for electron radiation.

All samples were irradiated at temperatures between 18 and 25°C., those irradiated at 20 Mrad/min. being cooled with a water jet.

The infrared absorption spectra were recorded on a Unicam S.P.100 spectrophotometer incorporating a grating monochromator and operated under

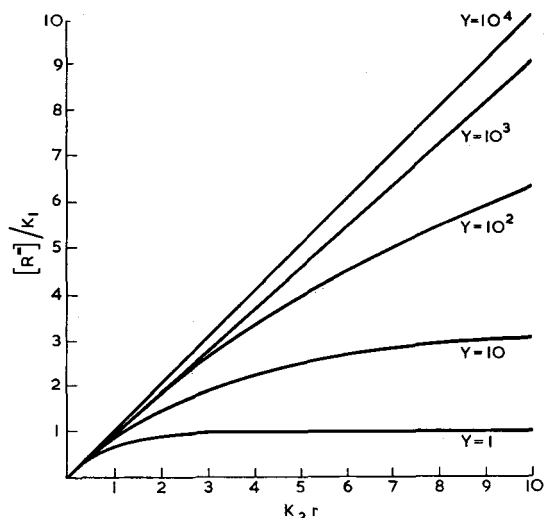


Fig. 1. Theoretical relationship between *trans*-vinylene unsaturation $[R^-]$ and radiation dose, r , at various dose rates, $Y = 1, 10, 10^2, 10^3,$ and 10^4 . The graph for $Y = 10^4$ also corresponds to the rate of hydrogen evolution on this scale.

vacuum (8×10^{-3} mm.) as a double beam instrument. On opening the evacuated tubes, the specimens were cut into two strips which were superimposed, the pathlength determined as the average of six readings on a Mercer thickness gage over the area of the Nernst image, and the specimen then immersed in Nujol as a protection against attack by atmospheric oxygen. The oil also served as an ideal immersion liquid to avoid interference bands arising from surface reflections from the superimposed polymer sheets. The instrument slit width was checked at a constant 0.6 mm. over the relevant spectral range and a spectrum of the control specimen obtained prior to each set of determinations. The 909 cm.^{-1} absorbance* of this control specimen was used as a measure of instrumental variation. Fifteen determinations of the absorption at 909 cm.^{-1} on a separate control specimen, over a period of 7 months, varied between 25.0 and 25.4 absorbance units.

Previous workers² have drawn attention to the crystallinity dependance of the unsaturation bands of polyethylene. As a precautionary measure the value for amorphous content of our specimens was determined using the band at 1305 cm.^{-1} .³ The amorphous content of all specimens varied only between 14.7 and 15.3%. From measurement of the absorbance at 965 cm.^{-1} at temperatures between 23 and 200°C. , it was deduced that this variation in amorphous content would effect the

* Absorbance is defined as the optical density for a pathlength of 1 cm.

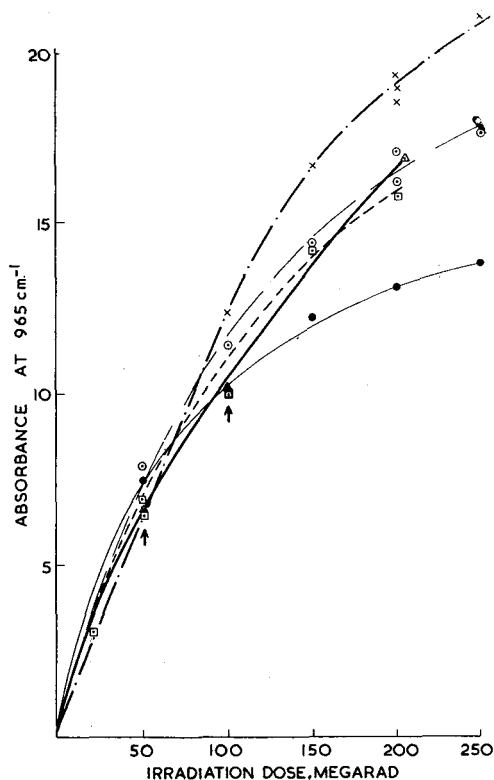


Fig. 2. Variation of *trans*-vinylene absorbance (965 cm.^{-1}) with radiation dose at the following dose rates: (\times) Mrad/min. (electron); (\circ) 5 Mrad/min. (electron); (\bullet) 20 Mrad/min. (electron); (Δ) 1 Mrad/hr. (gamma); (\square) 6 Mrad/hr. (gamma). Arrows denote dual determinations.

trans-vinylene absorbance, determined at room temperature, by less than 0.2%.

Examination of the spectrum of all samples for carbonyl absorption near 1700 cm.^{-1} showed that no oxidation had occurred either during or after irradiation.

The dose rate dependance of *trans*-vinylene double bonds as a function of dose is illustrated in Figure 2. There is a superficial resemblance to the theoretical graphs (Fig. 1). Little difference was observed in our experiments between continuous gamma irradiation at 1 Mrad/hr. and the pulsed gamma irradiation at 6 Mrad/hr. At an electron dose rate of 1 Mrad/min., however, there is a definite increase in *trans*-vinylene unsaturation at doses above 100 Mrad, compared with the lower dose rates. At 5 and 20 Mrad/min., the tendency is for *trans*-vinylene absorbance to decrease with increasing dose rate. At doses below 100 Mrad, there is no significant dose rate dependance over the range 1 Mrad/hr. to 20 Mrad/min.

Wide variation in the *trans*-vinylene absorbance was noted in early experiments when the specimens

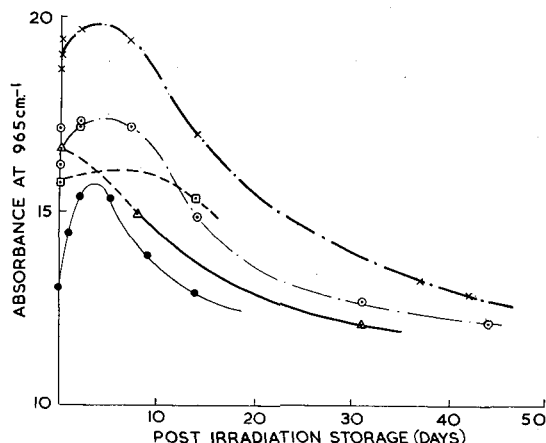


Fig. 3. Variation of *trans*-vinylene absorbance (965 cm^{-1}) with storage time in vacuum after a radiation dose of 200 Mrad. Symbols correspond to the dose rates listed in Fig. 2.

were not examined immediately after irradiation. A systematic study of the effect of storage is illustrated in Figure 3. Specimens irradiated to 200 Mrad and then stored in their vacuum envelopes were examined after known periods up to 42 days. *trans*-Vinylene absorbance was generally observed to increase to a maximum value within 4 days and then to decrease to a value well below that recorded immediately after irradiation. The relative increase in *trans*-vinylene unsaturation was greater at the higher dose rates.

The dose rate dependence of *trans*-vinylene concentration in the polymer is sufficiently well established by these experiments, and confirmatory determinations are shown on three of the graphs in Figure 2. This supports the original theory¹ that *trans*-vinylene groups result from the interaction of radiation-induced radicals, but the trend to lower unsaturation values at high dose rates cannot be explained solely on this basis.

Koritski and his co-workers,⁴ as a result of E.S.R. studies, have recently reported the presence of two types of radical in irradiated polyethylene. One of these is the alkyl radical mentioned by previous workers,⁵ which was observed to react rapidly at room temperature. The other is a longer-lived radical observable many days after irradiation, and to which Koritski ascribes an allylic structure. The possibility of two or more types of radical, with different reactivities and mobilities in the crystalline and amorphous regions of the polymer, has not yet been considered in kinetic theories. It is possible that the more rapid change in *trans*-vinylene groups, observed after irradiation at high dose

rates, reflects a higher initial concentration of trapped radicals (Fig. 3). If this is correct, the reduction in vinylene concentration at high dose rates may be attributed to the failure of some radicals to react within the period of the irradiation. It is evident from Figure 3 that the free radicals remaining in the polymer after irradiation can react initially to form *trans*-vinylene groups and subsequently to cause their disappearance, presumably with the formation of intermolecular crosslinks. Williams and Dole⁶ ascribe the increase in the gel content caused by annealing irradiated Marlex 50 at 142°C . to the reactions of residual free radicals with double bonds.

The dose rate dependence of *trans*-vinylene groups should be accompanied by a reciprocal dependence of radiation induced crosslinks. This, however, is more difficult to evaluate because the methods of estimating the crosslinks—gel fraction, modulus in the rubbery state, and swelling—all involve heating the polymer to elevated temperatures. This would result in accelerated post-irradiation reactions, including oxidation.

We hope to record additional observations made during the course of this work and a more detailed discussion of the theory in a future paper.

We are grateful to Mr. J. McCann for carrying out the linear accelerator irradiations, to Mr. R. G. J. Miller of I.C.I. Plastics Research for polyethylene pressings of known crystallinity for calibration purposes, and to Phillips Petroleum Company for a sample of antioxidant-free Marlex 50. One of the authors (R.W.P.) wishes to thank the Dunlop Rubber Company Ltd. for permission to publish.

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Synopsis

Infrared absorption spectroscopy has been used to demonstrate dose rate dependence of *trans*-vinylene unsaturation in irradiated Marlex 50 polyethylene. When the irradiated polymer is stored in vacuum a decrease is observed in *trans*-vinylene absorbance over a period of several weeks. After high dose rate irradiation the decay is preceded by an initial increase. These phenomena are ascribed to the reaction of "trapped" radicals.

Résumé

On emploie la spectroscopie infra-rouge pour démontrer la dépendance de la non-saturation dans un polyéthylène

Marlex 50 irradié en fonction de la dose d'irradiation. Quand le polymère irradié est placé sous-vide, on observe une diminution de l'absorption *trans*-vinylène sur une période de plusieurs semaines. Après une forte dose d'irradiation, la diminution est précédée par une augmentation initiale. Ces phénomènes sont attribués à la réaction de radicaux occlus.

Zusammenfassung

Infrarotabsorptionsspektroskopie wurde zur Bestimmung der Abhängigkeit der *trans*-Vinylenunsättigung in bestrahl-

tem Marlex-50-Polyäthylen von der Dosisgeschwindigkeit verwendet. Beim Lagern des bestrahlten Polymeren im Vakuum wird während einer Periode von einigen Wochen eine Abnahme der *trans*-Vinylenabsorption beobachtet. Nach Bestrahlung mit hoher Dosisgeschwindigkeit geht der Abnahme eine anfängliche Zunahme voraus. Diese Erscheinungen werden der Reaktion "eingeschlossener" Radikale zugeschrieben.

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