Radiation-Induced Cross-linking of Paraffins[1]

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ABSTRACT: Cross-linked products resulting from the irradiation of long-chain linear paraffins are resolved from parent alkanes and yields determined by gel permeation chromatography. For irradiated solid and liquid *n*-pentatriacontane and solid *n*-hexatriacontane, the *G* values of cross-linking at zero dose are 1.4, 1.8, and 1.1, respectively. Gel permeation chromatograms of irradiated liquid *n*-hexatriacontane indicate an additional product corresponding to 25% of the total dimer area, regardless of dose and further purification.

Gel permeation chromatography is a convenient technique for analyzing cross-linked products ("dimers") from the irradiation of long-chain normal paraffins.[2a] In this method, samples are examined in dilute solution so that the volatilization of high molecular weight materials, necessary for gas chromatography, is obviated. Since elution is in inverse order of molecular size in gel permeation chromatography,[2b] dimers precede and are often resolved from parent paraffins. With appropriate columns, product yields are reproducibly determined even at very small extents of radiolytic cross-linking. The chromatographic separation of cross-linked products may be adequate to indicate the detailed configuration of isomers of dimer and the location of cross-links. Since high molecular weight paraffins are monodisperse analogs of polyethylene, chromatographic studies of their radiolytic products may elucidate radiation-induced reactions in polymers as well as radiochemical processes in general. Since the nature of cross-linking resulting from high energy irradiation depends on physical state,[3] particular attention will be directed to this variable in considering radiation effects.

Experimental Section

n-Pentatriacontane (C_{35}), 99% minimum purity, and *n*-hexatriacontane (C_{36}), 99.5% minimum purity, were obtained from Lachat Chemicals Inc., Chicago Heights. Small amounts of *n*-hexatriacontane were purified further by recrystallization from cyclohexane. Differential scanning calorimetry indicated that the resultant material was of very high purity. Infrared spectra of original and recrystallized *n*-hexatriacontane did not evidence any unsaturation. However, olefin was so detected in the small aliquot rejected on fractional crystallization. Other linear alkanes used for calibration were from Humphrey Chemical Co., North Haven, Conn. *n*-Tetranonacontane (C_{94}) was prepared by Professor J. Dixon, The Pennsylvania State University. The polyethylene sample was Marlex TR-860, a product of Phillips Petroleum Co.

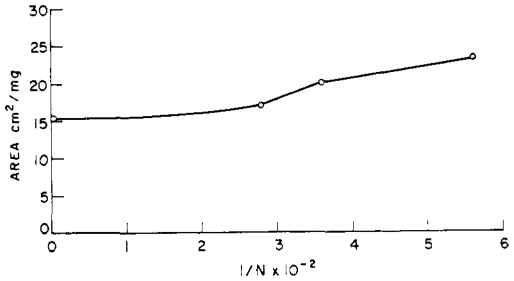

Figure 1. Gel permeation chromatographic response for normal alkanes.

About 0.25 g of paraffin contained in thin-walled (0.5 mm) Pyrex tubes was degassed by repeated melting under vacuum, sealed at 10^{-5} torr and irradiated with 1-MeV electrons from a van de Graaff generator at a dose rate approximating 4 Mrads/min. Calibration of absorbed dose was effected by measuring hydrogen yields from cyclohexane irradiated under the same conditions.[4] Sealed paraffin samples were melted and flattened prior to irradiation in the solid state at 48° or as liquids at 78°. Tubes were thermostated during irradiation on a hollow copper block through which water was circulated at the appropriate temperature. Following irradiation, samples were stored at room temperature and then melted *in vacuo*.

Aliquots of irradiated materials were dissolved in 1,2,4-trichlorobenzene (Dow Chemical Co.) containing antioxidant (Santanox R, Monsanto Chemical Co.) at 140° and injected into a gel permeation chromatograph (Waters Associates). A series of three polystyrene gel columns of "porosity rating" 600, 250 and 60 Å was used at 135° with trichlorobenzene as the mobile phase.

Chromatographic response was calibrated for specific products by interpolating on a graph of area response (square centimeters per milligram injected) against the reciprocal number of carbon atoms in a linear paraffin (Figure 1). All points represent the average of several determinations of area response, three points refer to normal paraffins, the highest molecular weight point is due to a well-characterized polyethylene sample. Areas were measured with a planimeter. Cross-linking yields were determined by measuring the area assigned to cross-linked product and assuming the response to be equal to that of linear dimer. Cross-linking yields are expressed as *G* values, molecules of dimer per 100 eV of absorbed energy.

The elution volume corresponding to maximum deflections of a differential refractometer detector was calibrated for molecular weight (Figure 2). Again, all calibration points refer to linear paraffins, except that for the highest molecular weight, which results from the polyethylene sample. The elution volume for linear C_{72} or C_{70}, which corresponds to cross-linked products of the paraffins studied, is at count 18.0.

Results and Discussion

Radiolytic cross-linking in long chain linear paraffins may be examined by analyzing irradiated alkanes by

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[1] Presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 2, 1968.

[2] (a) R. Salovey, W. E. Falconer, and M. Y. Hellman, *J. Polym. Sci., Part C*, **21**, 183 (1968); (b) K. H. Altgelt and J. C. Moore in "Polymer Fractionation," M. Cantow, Ed., Academic Press, New York, N. Y., 1967, p 123.

[3] R. Salovey and W. E. Falconer, *J. Phys. Chem.*, **69**, 2345 (1965).

[4] W. E. Falconer and R. Salovey, *J. Chem. Phys.*, **44**, 3151 (1966).

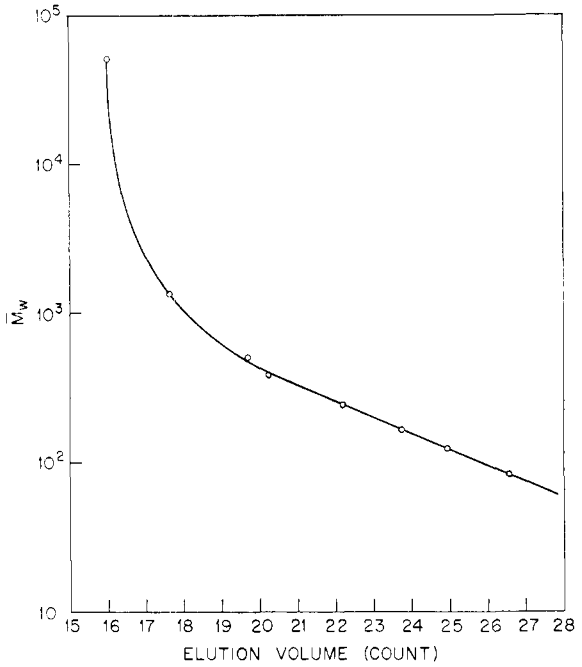

Figure 2. Molecular weight calibration for normal alkanes in gel permeation chromatography.

gel permeation chromatography. Reactants and products are resolved by permeation through a porous polystyrene gel, as molecules of increasing size find less accessible volume in the gel network and elute before smaller molecules. A separation on the basis of hydrodynamic volume in solution is effected with elution volume in inverse order of molecular size.[2b] Eluted materials are detected in a differential refractometer and a continuous record of refractive index difference between eluent and reference solvent stream is obtained. For any given homologous series, refractive index is a function of molecular weight and, particularly in the low molecular weight ranges, chromatographic response must be calibrated for specific products (Figure 1). The appropriate chromatographic response was interpolated neglecting the fact that dimeric products, although of single molecular weight, are polydisperse with respect to branching and differ in refractive index. However, since refractive index varies slightly with molecular weight, particularly at increasing molecular weight, the assumption of a single chromatographic response for all isomers of dimer equal to that for the corresponding linear alkane is not unreasonable.

Although the dependence of refractive index on molecular configuration is slight, the elution volume of isomers of dimer is sensitive to configuration. Figure 3 illustrates a gel permeation chromatogram of *n*-hexatriacontane irradiated to 17 Mrads at 48° in the solid state. A broadened peak preceding the elution of *n*-hexatriacontane corresponds to cross-linked products of irradiation. Since molecular size varies among the branched isomers of C_{72}, the elution pattern of cross-linked products is broadened. Linear C_{72} would give a narrower peak, about two counts wide—as observed with other linear alkanes—centered at 18.0 (Figure 2). The experimental peak is slightly shifted

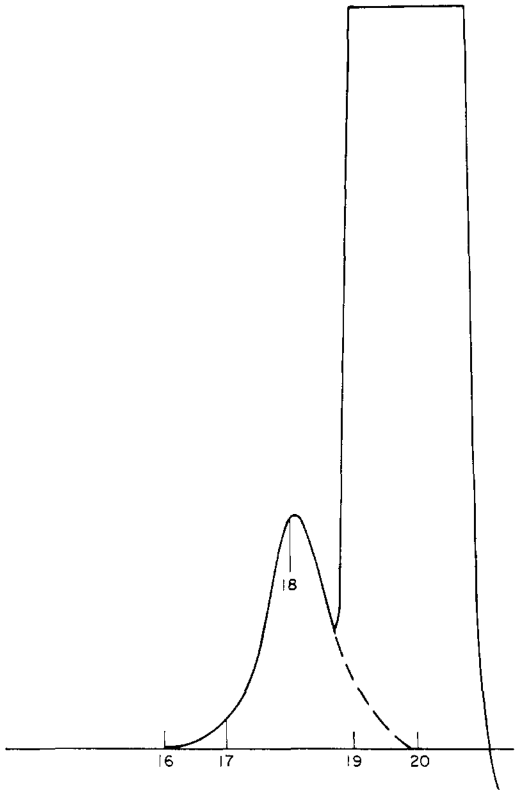

Figure 3. Gel permeation chromatogram of irradiated solid *n*-hexatriacontane, 17 Mrads, 48°.

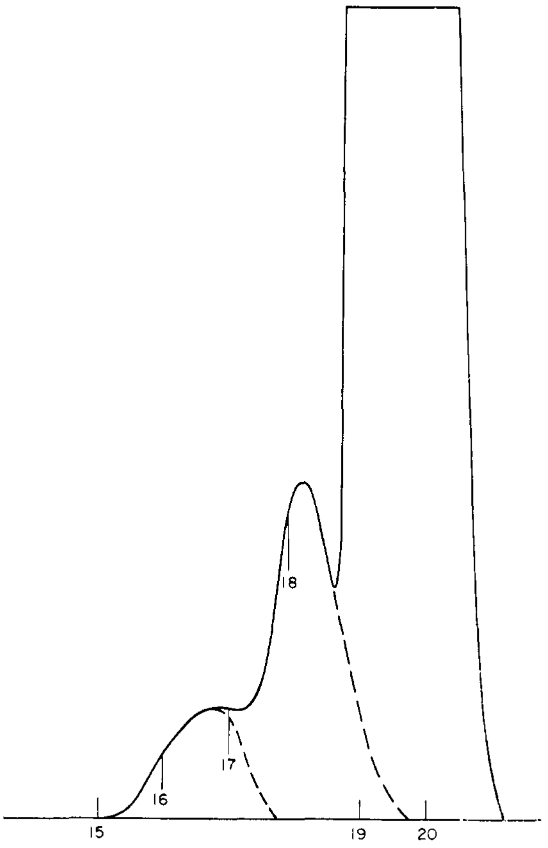

Figure 4. Gel permeation chromatogram of irradiated liquid *n*-hexatriacontane, 51 Mrads, 78°.

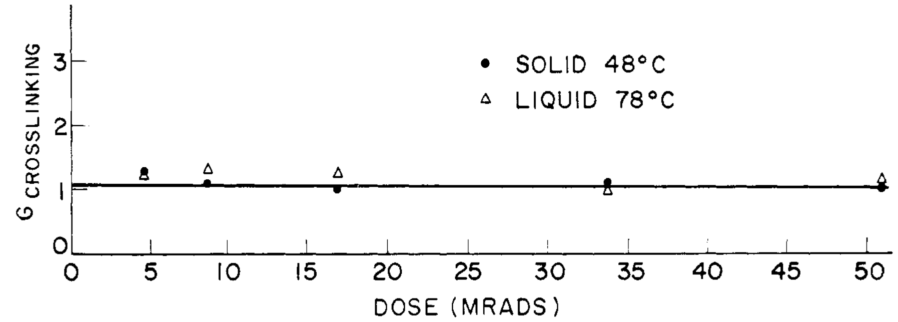

Figure 5. Cross-linking yields in irradiated n-hexatriacontane.

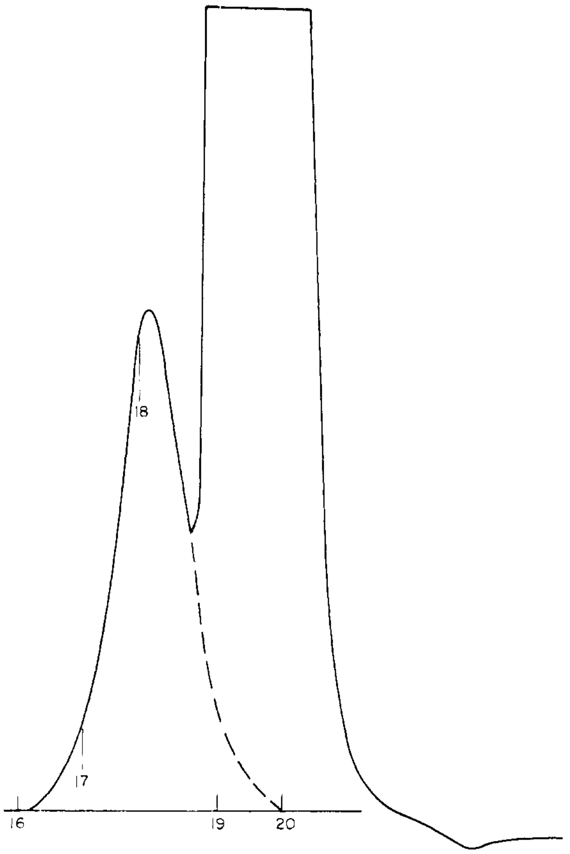

Figure 6. Gel permeation chromatogram of irradiated n-pentatriacontane.

in the direction of decreasing molecular weight because branching decreases the hydrodynamic volume.

The gel permeation chromatogram for n-hexatriacontane irradiated to 51 Mrads in the liquid state (just above the melting point of 76°) is shown in Figure 4. The shape of the peak ascribed to cross-linked products is very different in solid and liquid phase irradiations of n-C$_{36}$ paraffins. Differences in peak shape indicate different cross-linked products in solid and liquid state irradiations. A possibility is that the small peak, arbitrarily sketched in, eluting before the usual product peak, is assigned to linear C$_{72}$. For the liquid phase radiolysis of n-C$_{36}$ paraffin, the "additional" peak corresponds to about 25% of the total product area regardless of irradiation dose. Comparison with the calibration curve (Figure 2) indicates that the small peak elutes at higher molecular weight than linear C$_{72}$ paraffin, and requires more than one cross-link for certain molecules. Since only about 1% of the parent paraffin was linked, it is surprising that 25% of this involves multiple cross-linking. Since this fraction is independent of dose, it would be necessary for a more highly cross-linked product to be formed in a single event by the combination of proximate radicals. Using n-hexatriacontane purified further by recrystallization from cyclohexane, it was found that the "additional" peak was as prominent as usual following liquid state irradiation. It is inferred that the corresponding product is intrinsic to irradiated liquid n-C$_{36}$ paraffin. Radiolytic yields were calculated assuming it to be dimer.

Although distinct product distributions characterize solid and liquid state radiolyses of n-C$_{36}$ paraffin, total cross-linking yields at several doses are very close (Figure 5). The cross-linking yield for the irradiated solid is independent of dose over the dose range studied, with G equal to 1.1 ± 0.1. In the liquid state, cross-linking yields were slightly higher and also independent of dose.

The even–odd alternation in crystallographic properties of solid linear alkanes[5] is often reflected in variations in radiolytic behavior.[6] Since normal C$_{35}$ and C$_{36}$ paraffins assume different crystal modifications,[5,7] diverse cross-linking yields were anticipated. Figure 6 is a typical chromatogram of n-C$_{35}$ paraffin irradiated in either solid or liquid states. (The melting point is 74.6°.[7]) The elution pattern of n-C$_{70}$ paraffin would be centered at 18.0 (Figure 2). The actual product peak is broadened and shifted because of the dispersity in branching among cross-linked products. A common elution pattern for liquid and solid is interpreted in terms of a similar distribution of cross-linked products.

Total yields of radiation-induced cross-linking in n-C$_{35}$ paraffin are plotted in Figure 7. Although the product distribution was independent of phase, cross-linking yields depend on physical state. In the solid, radiolytic cross-linking yields increase from a G value of 1.5 to 1.8 between 4 and 50 Mrads. At an irradiation temperature of 48°, the crystallographic state is orthorhombic for n-C$_{35}$ and monoclinic for n-C$_{36}$[5,7] and differences in cross-linking yields may be attributed to crystal packing. For liquid state irradiation of n-C$_{35}$ at 78°, cross-linking yields increase from 1.8 to 2.2 over the same dose range. The marked difference in cross-linking distribution and yields between liquid

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(5) Yu. V. Mnyukh, *J. Phys. Chem. Solids*, **24**, 631 (1963).

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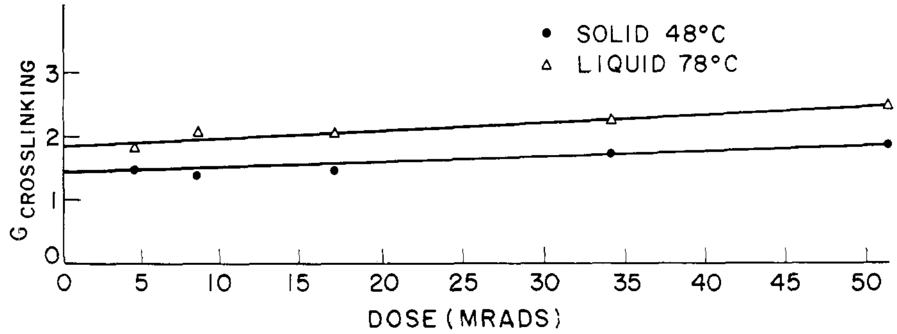

Figure 7. Cross-linking yields in irradiated *n*-pentatriacontane.

paraffins with 35 or 36 carbon atoms suggests that packing of the paraffin molecules may differ in the two linear alkanes just above the melting point.

The variation in total cross-linking yield with phase on irradiation of an orthorhombic long chain paraffin has been reported for *n*-heptadecane (C_{17}) where G_{dimer} equals 1.6 for liquid and 1.1 for solid, as determined by gas phase chromatography.[6] Similarly, cross-linking yields in *n*-eicosane (C_{20}) differ widely in solid and liquid states, both from gas phase and gel permeation chromatographic analyses.[2a]

Conclusions

Cross-linked products resulting from the irradiation of long chain linear paraffins are resolved from parent alkanes and yields determined by gel permeation chromatography. For irradiated solid and liquid *n*-pentatriacontane and solid *n*-hexatriacontane, the *G* values of cross-linking at zero dose are 1.4, 1.8, and 1.1, respectively. Gel permeation chromatograms of irradiated liquid *n*-hexatriacontane indicate an additional, presumably multiply cross-linked, product corresponding to 25% of the total dimer area, regardless of dose. The same product distribution is observed in liquid state radiolyses of *n*-hexatriacontane purified by the removal of an olefinic impurity on recrystallization.

An increase in cross-linking yield with dose observed in irradiated *n*-C_{35} paraffin is reminiscent of a similar effect inferred from solubility studies on irradiated polyethylene.[8] The marked effect of physical state and crystalline packing on cross-linking yields suggests complex cross-linking in polyethylene with regions of varied order and packing.

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Communications to the Editor

The Effect of Oxidation Products on the Photostability of Polypropylene Films

The formation of oxidation products during processing has frequently been cited as a source of the instability of polyolefins to near-ultraviolet radiation.[1,2] A detailed study of the possible photodegradative processes involving these products may lead to improved methods of stabilizing polymers against exposure to sunlight. The recent work of Guillet and Heskins[2] on solutions of ethylene–carbon monoxide copolymers has shown the photolysis of carbonyl groups by a Norrish type II reaction to be a major source of chain scission. This paper is a description of some effects of carbonyl groups on the photostability of polypropylene in the solid phase.

Films of unstabilized, isotactic polypropylene (Hercules Profax 6801) were prepared by heating the resin in air to 225° on a quartz plate for a controlled period (1–5 min) followed by rapid cooling. The oxidized polymer was transferred to a nitrogen atmosphere, and briefly squeezed between quartz plates at 50 psi in a press preheated to 225°. The films were then quenched in a Dry Ice–methanol slurry and stripped from the quartz; samples of controlled, uniform thickness (15–130 μ) and high optical clarity were obtained. The extent of oxidation of each film was determined by infrared (ir) spectrophotometry (*e.g.*, Figure 1), which shows that the products of oxidation at 225° are simple in comparison[3] with the products of low temperature (less than 100°) thermal oxidation or of photooxidation. The ir spectra of films oxidized at 225° showed a relatively sharp ketone carbonyl peak at 1721 cm^{-1} together with some absorption at 1645 cm^{-1}, indicating C–C unsaturation but no detectable absorption at 3560–3370 cm^{-1} for hydroperoxide. The oxi-

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(1) A. W. Pross and R. M. Black, *J. Chem. Soc. Jap., Ind. Chem. Sect.*, **69**, 113 (1950).

(2) M. Heskins and J. E. Guillet, *Amer. Chem. Soc., Div. Polym. Chem., Preprints*, **9**, 370 (1968); *Macromolecules*, **1**, 97 (1968).

(3) Low-temperature oxidation gives a broad carbonyl band, (1675–1790 cm^{-1}, Figure 1) and a large hydroperoxide content. Thermal and photooxidation products are identical, however, under suitably chosen conditions of temperature and irradiation wavelength.