[Contribution from the Department of Chemistry, Northwestern University]

The Pile Irradiation of Polyethylene

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Polyethylene in the form of films and granules was irradiated in the heavy water pile of the Argonne National Laboratory, both in a vacuum and in the presence of air. The composition of the evolved gas, stress–strain relations and tensile strength were determined for one period of irradiation. Bromine absorption, infrared absorption spectra, extent of gel formation and viscosity of solutions were measured as a function of the duration of irradiation. The most detailed studies were made of the vacuum irradiated samples. The first noticeable change in the composition of the film was the disappearance of the vinylidene group as hydrogen was evolved. This decrease in unsaturation was more than compensated for by the formation of the vinylene group. The bromine absorption studies demonstrated that 70 to 80% of the hydrogen evolution produced unsaturation, the remaining 20 to 30% cross linkages. From the composition of the evolved gas, it was estimated that C–C bonds along the side chains were ruptured about half as frequently as C–H bonds, but much more frequently than C–C bonds along the main hydrocarbon chain. The viscosity average molecular weight of the soluble fraction at first increased slightly, but then decreased to one third its original value. The cross-linking produced marked changes in the stress–strain characteristics without, however, greatly affecting the tensile strength when the irradiation was carried out in a vacuum. A postulate of long range migration of chemically active centers is proposed to explain the initial rapid decrease in the vinylidene concentration.

I. Introduction

Polyethylene was chosen as the polymer to investigate in the heavy water pile because of the simplicity of its chemical structure, and because it is important to understand the behavior of solids such as polyethylene under high energy irradiation.

The first part of this research(1) was published in a report to the Technical Command, Army Chemical Center.(2) In this report data were given indicating that high energy irradiation produces both unsaturation and cross-linking in the absence of air and considerable oxidation as well as unsaturation and cross-linking in the presence of air. Polyethylene was studied chiefly in the form of films so that infrared studies could be made of chemical changes, so that unsaturation could be quantitatively measured by means of weight increases during the absorption of bromine vapor and so that stress–strain curves could be obtained using thin strips of the film.

During the last few years Charlesby(3–6) and coworkers have also been investigating the effect of pile irradiation on polyethylene using bulk polyethylene. They measured and observed changes of weight, density, color, solubility and melting point. It was concluded that the production of unsaturation was negligible, and they attributed all of the observed effects to cross-linking. The authors of this paper have come to quite different conclusions from those of Charlesby,(3) as will be explained in detail in the theoretical section.

Lasday(7) has measured the total neutron cross section for polyethylene.

Mayburg and Lawrence(8) studied the change in conductance of polyethylene during γ-irradiation, and from the temperature coefficient of the conductance increment reached the tentative conclusion that the conduction was ionic, not electronic. Lawton, Bueche and Balwit(9) irradiated many types of plastics including polyethylene with high energy electrons. Cross-linking efficiencies varied widely from polymer to polymer, but change of temperature from −74 to 193° and increase in intensity of radiation had no effect on the cross-linking efficiency. Little(10) has given a general discussion of the effects of the irradiation of linear high polymers. Charlesby(11) has also studied the solubility and swelling of cross-linked polystyrene.

II. Experimental

A. **Materials Used.**—The early part of this research(1) made use of polyethylene film kindly donated by the Visking Corporation. All films were about 0.003 inch in thickness and were made of du Pont polyethylene, PM-1, extruded from the melt as endless tubing into air (regular production) or into a water-bath at 0° (shock-cooled). More recently film was received from E. I. du Pont de Nemours and Company(12) characterized as follows

Code No. B-3046

Thickness, in.	0.0017
Wt. av. mol. wt. (M_w)	310,000
No. av. mol. wt. (M_n)	32,000
Long chain branching index	7.9
Density	0.9142

In Section III are given the results of infrared studies of these films where additional information concerning their constitution can be obtained.

B. **Details of the Irradiations.**—The irradiations were all carried out using aluminum cans supplied by the Argonne National Laboratory. For the vacuum irradiations the polyethylene film was sealed up in a quartz tube after evacuation with a "break-off" capillary tip on one end and the whole placed in an aluminum can. One of the aluminum cans was perforated with many holes to allow free circulation of air for the irradiations in air. For the first irradiations,(1) the can was lowered into the bottom of the thimble at the center of the heavy water pile of the Argonne National Laboratory. At this point the neutron flux was estimated to be in the neighborhood of 10^{12} thermal neutrons per sq. cm. per sec. In the more recent irradiations, one of the samples was irradiated 55 hours in the central thimble of the pile at a flux of 3×10^{12} thermal neutrons and 8×10^{11}

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(1) Master's Thesis, Northwestern University, 1948, by D. G. Rose. Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Portland, Oregon, Sept., 1948.

(2) Report of *Symposium IV.* "Chemistry and Physics of Radiation Dosimetry," Army Chemical Center, Md., 1950, p. 120.

(3) A. Charlesby, *Proc. Roy. Soc.* (*London*), **215A**, 187 (1952).

(4) A. Charlesby and M. Ross, *ibid.*, **217A**, 122 (1953).

(5) A. Charlesby and N. H. Hancock, *ibid.*, **218A**, 245 (1953).

(6) A. Charlesby, *J. Polymer Sci.*, **10**, 201 (1953).

(7) A. H. Lasday, *Phys. Rev.*, **81**, 139 (1951).

(8) S. Mayburg and W. L. Lawrence, *J. Applied Phys.*, **23**, 1006 (1952).

(9) E. J. Lawton, A. M. Bueche and J. S. Balwit, *Nature*, **172**, 76 (1953).

(10) K. Little, *ibid.*, **170**, 1075 (1952).

(11) A. Charlesby, *J. Polymer Sci.*, **11**, 513, 521 (1953); *Proc. Roy. Soc.*, **222A**, 60 (1954).

(12) The film and information were kindly sent to us by Dr. F. W. Billmeyer, Jr., Polychemicals Department, Experiment Station, E. I. du Pont de Nemours and Company.

fast neutrons per sq. cm. per sec. and the remainder over periods from 5 minutes to 123 hours in a side compartment (called the "goat hole") where the thermal neutron flux was estimated to be 2×10^{11} and the fast neutron flux about 1×10^{10} neutrons per sq. cm. per sec. Extensive γ-radiation accompanied the neutron radiation.

C. Infrared Absorption Spectrum Measurements.—The first infrared absorption studies[1] were made using a Beckman Model IR-2 infrared spectrophotometer, and the more recent studies using an automatic recording Beckman Model IR-2T. In the early work the films were held in place in the cell with adhesive tape and compared against air. This method failed to produce satisfactory spectra using the IR-2T instrument, as interference bands, which varied with the position of the sample in the light beam, appeared. This difficulty was overcome in the 11 micron region by pressing the film between salt plates with a thin layer of paraffin oil between the film and the plates on both sides. Spectra were run in this region against the paraffin oil as standard. The oil was fairly transparent and its absorption did not interfere with the absorption due to olefinic groups in the polyethylene.

D. Bromine Absorption Measurements.—In order to measure quantitatively the extent of unsaturation produced by the irradiation, the method of Rossmann[13] was adopted. This method is based on the measurement of the weight increase in the film when exposed to bromine vapor in the dark. For every double bond in the film one molecule of bromine should be absorbed. The high molecular weight of bromine affords high sensitivity to the method. The apparatus consisted of a bottle containing liquid bromine at room temperature attached to a vacuum line. The vacuum line included a bromination chamber covered with black cloth, a "photon trap" to prevent light from being carried into the chamber along the Pyrex glass, and a Dry Ice trap to freeze out the bromine.

The technique consisted in exposing 100–200 mg. of a previously weighed film to the bromine vapor for one to five hours after evacuating the system to pressures of about one micron of mercury. After pumping out the excess bromine, after each exposure to bromine, through the Dry Ice trap, the film was then weighed and the process repeated for progressively longer periods until a linear increase of weight of the film with time of exposure to bromine was obtained. Figure 1 illustrates a typical set of bromination curves. The linear rise of weight after the initial rapid increase must have been due to the slow substitution of bromine. The set of curves given in Fig. 2 for the infrared absorption at 11.2 μ demonstrates rather conclusively that the bromine vapor reacts quickly with the double bonds present to eliminate the vinylidene unsaturation. The relative errors in the bromine absorption studies lay in the uncertainty (1) of the initial weighing of the film which was difficult to carry out because of the ease with which pure polyethylene films pick up static charges and (2) of the exact chemical reaction between bromine vapor and the film. This point is discussed further below.

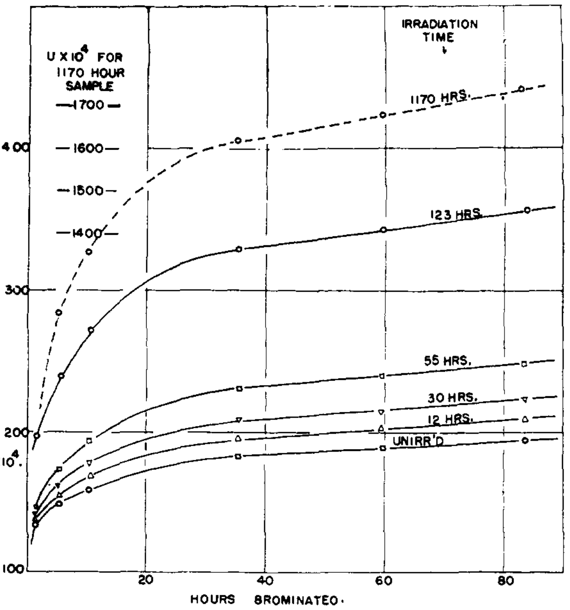

Fig. 1.—Fractional increase in weight of polyethylene film on bromination.

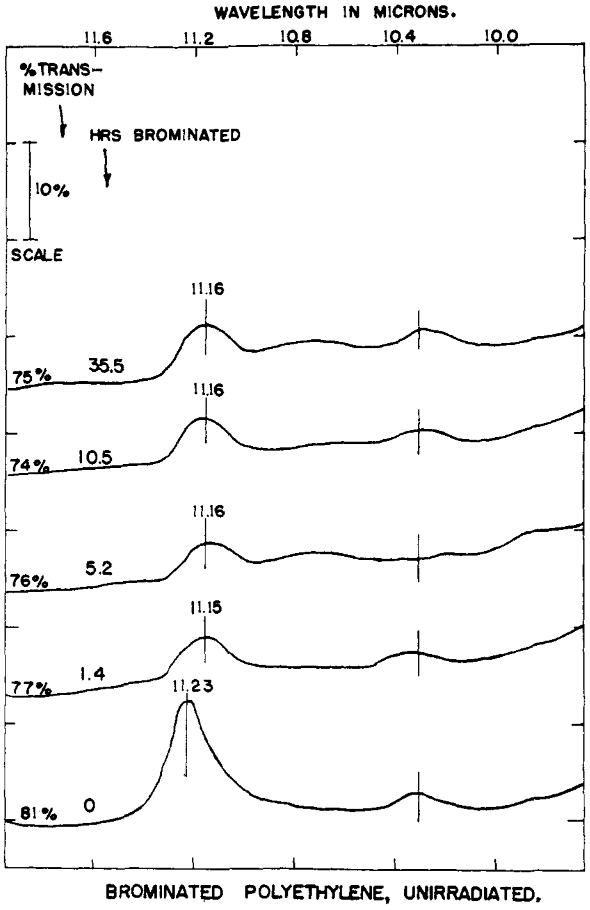

Fig. 2.—Change in infrared absorbance at 11.26 μ on bromination of unirradiated polyethylene film.

E. Measurement and Analysis of Evolved Gas.—During the vacuum irradiation a considerable amount of hydrogen and lower molecular weight hydrocarbon gases was evolved. In the early work[1] a mass spectrometric analysis of the gas whose volume was always measured was kindly performed at the Research Laboratory of the Universal Oil Products Company and in the more recent work by the Analytical Service of the Consolidated Engineering Corporation at Pasadena, California.

F. Measurement of Extent of Gel Formation.—A small tubular shaped basket was made of 200-mesh stainless steel gauze. A solid plug of stainless steel served as a cap for the basket. The basket was weighed empty, with the original sample in the basket and after the toluene extraction. From these weights the amount of gel formation could be estimated. In this work gel is defined as that fraction of the initial polyethylene (0.1 to 0.3 g.) which failed to dissolve in 100 to 130 ml. of boiling toluene during a single treatment of six or more hours.

G. Viscosity Measurements.—A new type of viscometer[14] especially adapted for high polymers was developed and used in this research.

H. Stress–Strain Measurements.—Stress–strain curves and tensile strengths were determined on a Scott IF-4 Inclined Plane tensile test machine[15] which automatically

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(13) E. Rossmann, *Ber.*, **65B**, 1847 (1932); Rossmann's method followed that of P. Becker, *Analyst*, **20**, 49 (1895).

(14) C. D. Keeling and M. Dole, *J. Polymer Chem.*, in press.

(15) These experiments were performed in the laboratory of the Visking Corporation through the courtesy of Dr. C. J. B. Thor.

draws a graph of the stress applied to the sample as a function of the elongation of the sample. The machine determines the tensile strength at the moment of break for a constant rate of loading.

As the tensile strength measurement destroys the strip of film being measured, it was necessary to run samples of unirradiated and irradiated polythene from different sections of film, but the samples were taken as close together as possible. Whenever enough material was available, ten measurements of each sample were taken and the average of these measurements calculated using only values acceptable on the basis of Chauvenet's criterion.[16] In the tensile strength measurements the samples of polyethylene film used were 7.5 cm. long, 0.60 ± 0.03 cm. wide, and the thickness was measured to 5×10^{-5} cm. with a thickness gage (the thickness was measured at five points along the strip and the average taken). The applied stress at moment of break was read off the chart, and knowing this and the weight of the movable carriage the tensile strength at moment of break could be calculated. Measurements were made on the films both in the direction of extrusion (machine direction—M.D.) and in the transverse direction (T.D.). The basic rate of loading was 3300 lb./sq. in. per 0.5 minute, and the calculations followed the recommended ASTM method D-882-49 T.[17]

III. Experimental Results and Theoretical Interpretations

A. Introduction.—The irradiation may be classified roughly into two stages: first, the initial stage of ionization or molecular excitation and second, the resulting stage which includes neutralization of any ions formed, the formation of free radicals, double bonds and cross linkages, chain rupture, double decomposition, or simply the dissipation of the excitation energy in the form of radiant energy or heat.

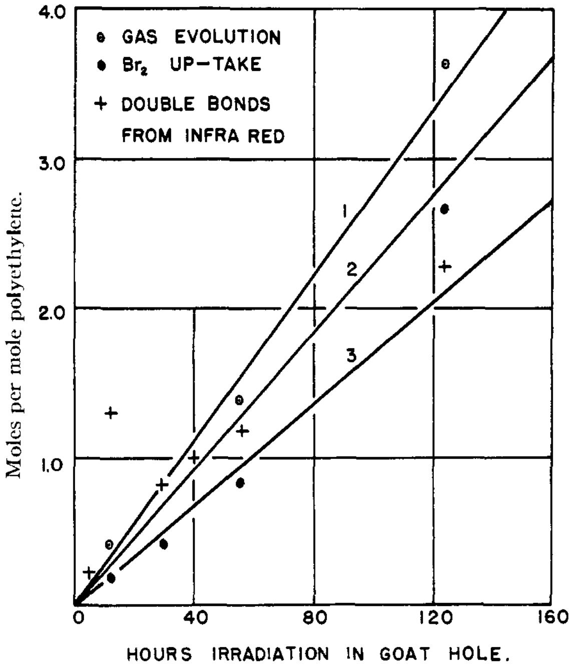

Fig. 3.—Curve 1, moles of gas evolved per mole of polyethylene as a function of hours of irradiation in the goat hole; curve 2, moles of double bonds produced per mole of polyethylene as determined by bromine vapor up-take; curve 3, moles of double bonds per mole of polyethylene as determined by infrared absorbance. The straight lines have been drawn to agree with the data for the 1170 hours irradiated sample.

The end chemical effects of irradiation are entirely different from those produced by thermal degradation. Oakes and Richards[18] thermally-degraded polyethylene, obtaining a continual decrease in the molecular weight as the degradation proceeded with formation of olefinic hydrocarbons chiefly of the $RCH{=}CH_2$ type. In the case of a normal paraffin such as cetane, the chief product of thermal degradation according to both the free radical theory of Kossiakoff and Rice[19] and to the experimental results of Greensfelder, Voge and Good[20] was ethylene with smaller amounts of methane and propylene and even smaller amounts of higher molecular weight olefins.

B. Hydrogen Evolution.—Figure 3 illustrates the evolution of gas as a linear function of time when polythene was irradiated *in vacuo*. This gas was mostly hydrogen as the data of Table I indicate. Breger[21] obtained similar results in the case of the alpha particle bombardment of liquid hexadecane.

Table I

Mass Spectrographic Analysis of Gas Liberated on Irradiation in the Absence of Oxygen

	% by vol. pile irradiation 55 hr.	% by vol. in thimble 45 hr.
H_2	98.6	96.0
CH_4	0.2	0.4
C_2H_6	.7	.9
C_3H_8	.1	.2
C_3H_6	.05	.2
n-C_4H_{10}	.3	.7
i-C_4H_{10}	.05	.3
C_4H_8		.2
N_2		1.1
Total	100.0	100.0

For the polyethylene irradiation of this research the rate of gas evolution was 8.7×10^{-7} mole of gas per gram per hour of radiation in the goat hole. From the amount of gas liberated during the irradiation in the thimble, it can be calculated that 1170 hours of goat hole irradiation were equivalent to 55 hours of thimble irradiation. All of the results of this paper will be expressed in terms of hours of goat hole irradiation. They can be readily expressed in units of gas evolved by the above factor. From the amount of gas evolved in Charlesby's experiments[3] his unit dose can be calculated to be equivalent to 974 hours of irradiation in the goat hole.

Although the effect of γ-radiation was probably the major effect in the pile irradiation, it is interesting to note that the ratio of gas evolved per sec. per gram of polyethylene in the thimble as compared to the goat hole, 21.2, was approximately

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[16] J. W. Mellor, "Higher Mathematics for Students of Chemistry and Physics," Longmans, Green and Co., London, 1926, p. 563.

[17] "1949 Book of A.S.T.M. Standards," Vol. 6, 1950, p. 598.

[18] W. G. Oakes and R. B. Richards, *J. Chem. Soc.*, 2929 (1949).

[19] A. Kossiakoff and F. O. Rice, This Journal, **65**, 590 (1943).

[20] B. S. Greensfelder, H. H. Voge and G. M. Good, *Ind. Eng. Chem.*, **41**, 2573 (1949).

[21] I. A. Breger, *J. Phys. Colloid Chem.*, **52**, 551 (1947); R. E. Honig and C. W. Sheppard, *J. Phys. Chem.*, **50**, 119 (1946), demonstrated that alpha particle and deuteron bombardment of butane produced the same chemical effects.

TABLE II

MOLAR EXTINCTION COEFFICIENTS AND OLEFINIC CONCENTRATIONS FROM INFRARED AND BROMINATION DATA

Absorbing group	Wave length, μ	Molar[a] extinction coefficient	Double bonds per molecule from infrared data						
Hr. of irradiation in "goat-hole"	...	...	0	6	12	30	55	123	1170
$RR'C{=}CH_2$	11.27	103.4	1.0	1.1	0.99	0.83	0.61	0.10	0
$RCH{=}CHR'$ (*trans*)	10.37	85.4	0.03	0.23	0.69	0.50	0.81	1.63	10.2
$RCH{=}CH_2$	11.00	121.0	negligible						0.5
Total net increase in unsaturation from infrared[b]			0	0.50	1.3	0.83	1.2	2.30	19.9
Double bonds per molecule from bromination exps.			0		0.2	0.45	0.86	2.66	26.8
No. of H_2 molecules evolved per molecule of polyethylene			0		0.41	0.68	1.38	3.58	32.2

[a] Molar extinction coefficient, $\epsilon = (M/Cl) \log I_0/I$ where M is the molecular weight of the olefinic group (24 for C=C), C is the concentration of the group in g./l. and l is the cell thickness in cm. [b] Assuming the *cis*-vinylene concentration to be equal to the *trans*-vinylene concentration.

equal to the ratio[22] of the fast neutron flux in the thimble to that of the goat hole, or 17.

Charlesby[3] estimated that the number of molecules of hydrogen liberated was about 5000 times as great as the number of primary events involving fast neutrons. However, there is so much uncertainty concerning the energy distribution in the fast neutrons as well as concerning the γ-ray flux, that energy absorption calculations will not be attempted in this paper.

Hydrogen atoms not produced directly or indirectly by neutron action must have resulted from the production of ions during Compton scattering of γ-rays, followed by neutralization according to the reactions

$$\text{—}CH_2CH_2CH_2CH_2\text{—} + \gamma\text{-rays} \longrightarrow \text{—}CH_2\overset{+}{C}H_2CH_2CH_2\text{—} + \epsilon^- \quad (1)$$

$$\text{—}CH_2\overset{+}{C}H_2CH_2CH_2 + \epsilon^- \longrightarrow \text{—}CH_2\dot{C}HCH_2CH_2\text{—} + H \quad (2)$$

Ionization could also occur due to high velocity protons produced by collision of fast neutrons with the hydrogen atoms of polyethylene. From the work of Mayburg and Lawrence[8] cited above, it is clear that considerable ionization was produced in the solid polyethylene.

Atomic hydrogen must next have abstracted more hydrogen according to the energetically favorable reaction[23]

$$H\cdot + \text{—}CH_2CH_2CH_2CH_2\text{—} \longrightarrow H_2 + \text{—}CH_2\dot{C}HCH_2CH_2\text{—} \quad (3)$$

Thus the production of large amounts of hydrogen is readily understood.

On evolution of hydrogen either cross linkages between hydrocarbon chains or olefinic groups must have been produced. Before calculating the number of cross linkages formed per gram per sec. it is necessary to estimate the number of double bonds formed per gram per sec., as the most reliable method of determining the number of cross linkages is based on the calculation of the difference between the number of hydrogen molecules evolved and the number of double bonds formed.

C. Double Bond Formation.—Data for the number of double bonds formed per molecule of polyethylene as a function of the time of irradiation *in vacuo* in the goat hole are given in Table II. The data obtained from the bromination experiments were calculated by extrapolating the straight lines of Fig. 1 to zero time and then subtracting the value for the unirradiated polyethylene. This method of estimating the double bonds probably yields too large a number of double bonds inasmuch as the irradiation may produce a certain number of "active" hydrogen atoms attached to the hydrocarbon chains which bromine can displace by substitution. In the case of the unirradiated polyethylene, 3.7 double bonds per polyethylene molecule were found by the bromine method and 1.02 double bonds per molecule by infrared absorbance at the wave length characteristic of the vinylidene group. The increase in double bonds estimated by the bromine method, however, parallels fairly well the increase in unsaturation determined by the infrared method as can be seen from Fig. 3 where the data obtained by the two methods are compared. The molar extinction coefficients[24] used in the infrared method are collected in Table II.

The absorption at 11.27 μ due to the vinylidene group was corrected for the absorption due to the ethyl group whose maximum absorption occurs at 11.18 μ. The increase in unsaturation due to the *trans*-vinylene group has been multiplied by two in computing the total increase in unsaturation to allow for formation of *cis*-vinylene groups.

Charlesby[3] assumed that the pile irradiation of polyethylene caused the formation of no olefinic groups, but he made no attempt to detect unsaturation experimentally. His estimates of the extent of cross-linking must necessarily be considerably in error for this reason.

Assuming that the bromine absorption data give the correct extent of unsaturation, the fraction of evolved hydrogen molecules resulting in cross-linking is given in Table III.

If the unsaturation determined by the infrared method is used in the calculation of the extent of cross-linking, the data in the next to the last row of Table III are obtained.

The unsaturation produced in the 55 hour irradiated (thimble) sample is clearly illustrated in Fig.

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[22] This ratio was kindly supplied by Dr. W. H. McCorkle of the Argonne National Laboratory.

[23] In his most recent paper, A. Charlesby, *Proc. Roy. Soc.* (*London*), **222A**, 60 (1954), neglected the possibility of reaction (3).

[24] The molar extinction coefficients were calculated by L. H. Cross, R. B. Richards and H. A. Willis, *Discs. Faraday Soc.*, **9**, 235 (1950), from the data of J. A. Anderson and W. D. Seyfried, *Ann. Chem.*, **20**, 998 (1948). W. M. D. Bryant and R. C. Voter have tabulated wave lengths of the absorbing groups in polyethylene, THIS JOURNAL, **75**, 6113 (1953).

Table III

Estimates of the Extent of Cross-Linking of Polyethylene Produced by Irradiation

Hr. irradiation in goat hole	12	30	55	123	1170
	Fraction of molecules of hydrogen evolved resulting in cross-linking				
From Br_2 uptake	0.51	.34	.38	.26	.17
From infrared	0	0	.13	.36	.38
	% of Insoluble Product				
	14	40	58	80	

4 where the pronounced absorption at 10.37 μ due to the vinylene group, RCH=CHR may be seen.

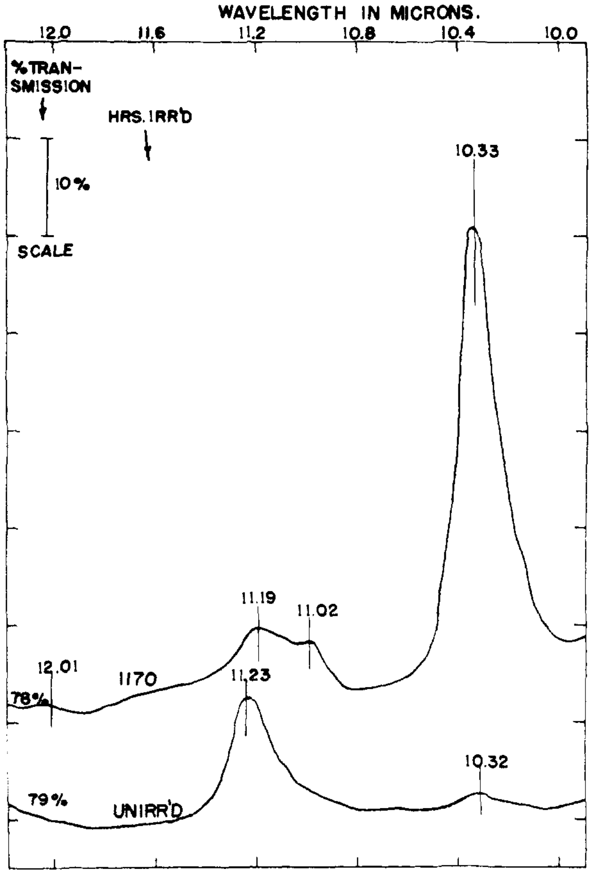

Fig. 4.—Infrared absorption by polyethylene after 55 hours of irradiation in the thimble (equivalent to 1170 hours in the goat hole).

D. Extent of Cross-Linking.—Comparison of the stress–strain curve of Fig. 5 for the unirradiated polyethylene with that of polyethylene irradiated for 45 hours *in vacuo* in the thimble demonstrated that irradiation eliminated all of the cold-drawing properties of the polyethylene, made it more brittle and more like a three-dimensional polymer. This result was immediately interpreted as due to cross-linking.[1,2]

A determination of the tensile strength at break demonstrated that the vacuum irradiation did not affect the tensile strength significantly, although the standard deviation was increased. Irradiation in the presence of air considerably reduced the tensile strength, however, see Table IV.

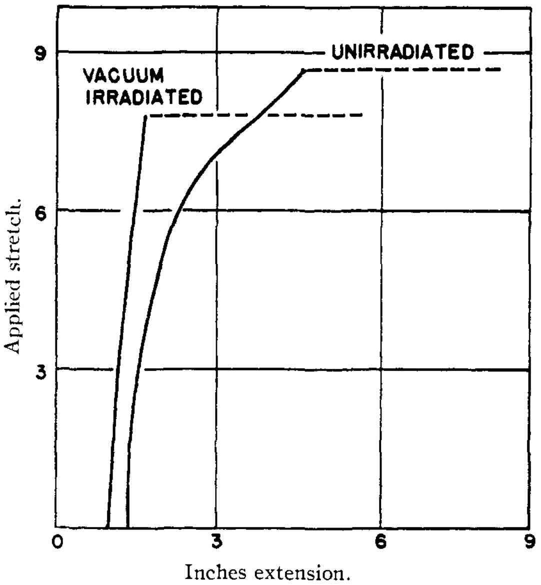

Fig. 5.—Stress–strain curve for shock-cooled Visking film before and after irradiation in vacuum. The units of the ordinate are arbitrary and different for the two curves.

Solubility measurements of irradiated polyethylene were made during attempts to dissolve the material for viscosity studies. Table III contains the solubility data. If the polyethylene had a known molecular weight distribution such as initial chains of uniform length or a most probable distribution it would be possible to estimate the extent of cross-linking from the known fraction of insoluble material by means of the Flory[25] theory of gelation. Unfortunately, the exact molecular weight distribution in polyethylene is unknown, but the weight average to number average molecular weight ratio for the sample used in this research was known. Charlesby[26] has recently shown how Flory's cross-linking index γ, defined as the number of structural units cross-linked per chain, can be related at the gel point to the weight to number average molecular weight ratio regardless of the molecular weight distribution. His equation is (valid only for the gel point)

$$\gamma = \frac{M_n}{M_w} \tag{4}$$

where M_n and M_w are the number and weight average molecular weights of the polyethylene before irradiation. From (4) γ was calculated to be 0.103. The gel point was estimated from the maximum in the intrinsic viscosity–hours of irradiation curve to occur at 6 hours of irradiation. From the estimated amount of hydrogen evolved, the fraction of evolved hydrogen resulting in cross-linking was calculated to be 30%. This agrees well with the other estimates given in Table III.

We conclude that the fraction of liberated hydro-

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(25) P. J. Flory, This Journal., **63**, 3083, 3091, 3096 (1941); **69**, 30 (1947). See also, W. H. Stockmayer, *J. Chem. Phys.*, **12**, 125 (1944).

(26) A. Charlesby, British Atomic Energy Research Establishment Report, M/R 1034, 18 Nov. 1952, *J. Polymer Sci.*, **11**, 513 (1953); *Proc. Roy. Soc. (London)*, **222A**, 542 (1954)

TABLE IV

TENSILE STRENGTH AT BREAK IN LB./SQ. IN.

Material T.D.—Transverse direction M.D.—Machine direction	Time of irradiation in thimble: 45 hr.				90 hr.			
	Tensile strength		Standard deviation		Tensile strength		Standard dev.	
	Control	Irradiated	Control	Irradiated	Control	Irradiated	Control	Irradiated
Visking shock cooled—M.D.	3602	1653	138	17	3364	1471	89	13
Ventilated can	3594	1554	43	11				
Vacuum	3192	3298	29	198				
Visking shock cooled—T.D.	2182	1276	44	6	1619	1180	97	24
Visking regular product—M.D.	3069	1591	53	27	2771	1636	49	10
Ventilated can	1523	1614	24	16				
Vacuum	3245	3201	110	163				
Visking regular product—T.D.	1918	1384	129	12	1525	1642	6	34

gen resulting in cross-linking is in the range 20–40%. There seems to be no basis for Charlesby's contention[3] that the amount of unsaturation produced is negligible.

E. Carbon–Carbon Bond Scission.—If the irradiation breaks C–H bonds, the possibility also exists for the scission of the C–C bond. On the other hand, one might expect that the cage effect would promote rapid recombination. The cage effect in the case of solid polyethylene would be expected to be especially strong inasmuch as the mobility of the long hydrocarbon fragments produced by C–C bond scission is probably many factors of 10 greater in the solid at room temperature than in the liquid above the melting point. The mobility of atomic hydrogen produced by the C–H bond rupture would be far greater although no data exist at the present time from which the mobilities might be estimated. Intrinsic (kinematic) viscosity measurements were made by a method already published[14] to determine the number average molecular weight, M_n, of the soluble fraction of the irradiated polyethylene, and thus to obtain some indication of C–C bond scission.

The structure of polyethylene is such that number average molecular weights can be calculated from intrinsic viscosities.[27,28] Harris's equation for the relationship between the number average molecular weight, M_n, and intrinsic viscosities $[\eta]$ measured in xylene at 75° is

$$[\eta] = 1.35 \times 10^{-3} M_n^{0.63} \qquad (5)$$

For toluene as a solvent at 75° the following expression was computed on the basis of a comparison of measurements in tetralin and toluene and using an equation for polyethylene in tetralin at 75° due to Richards.[29] The equation selected for toluene was

$$[\eta] = 1.05 \times 10^{-3} M_n^{0.65} \qquad (6)$$

Results of the molecular weight calculations for the unirradiated polyethylene film used in this research are given in Table V. The three results are in good agreement.

TABLE V

NUMBER AVERAGE MOLECULAR WEIGHT OF UNIRRADIATED POLYETHYLENE

	Eq. 5	Eq. 6	Vinylidene absorption
M_n	32,000	32,900	31,300

Number average molecular weights of the soluble fraction of the polyethylene calculated from the intrinsic viscosities using eq. 6 are given in Table VI. It is well known that intrinsic viscosity values depend upon the molecular shape as well as molecular weight.[28,30] An attempt was made by the methods of Thurmond and Zimm,[31] and Zimm and Stockmayer[32] to correct the viscosity data for branching. However, the change in the calculated molecular weight was so slight and the uncertainty in the number of branch points per molecule so relatively great that the detailed calculations will not be discussed here. Inasmuch as the major weight fraction of the polyethylene consisted of molecules of very large molecular weight which were the first to become cross-linked and insoluble, the shape of the remaining soluble molecules probably was not altered significantly by the irradiation, at least in the early stages of irradiation.

If the weight of the soluble fraction is divided by the number average molecular weight, the number of moles of soluble polyethylene per 100 g. of initial sample, n_s, is obtained. One would not expect this number to change very much on irradiation because of the unusual molecular weight distribution. Thus the very large molecules undoubtedly became insoluble due to cross-linking before the smaller molecules, and as the relative number of large molecules was small, the net number of soluble molecules should not have changed significantly. The data of Table VI bear out this expectation.

TABLE VI

CALCULATION OF THE NUMBER OF MOLES IN THE SOLUBLE FRACTION OF IRRADIATED POLYETHYLENE

Irradiated in "goat hole," hr.	Soluble material per 100 g., W_s	M_n	n_s	$n_c \times 10^3$	n_r
0	99.4	32,900	3.0	0.002	0
2	98.5	32,900	3.0	.005	0
6	89	35,500	2.5	.035	−0.44
12	86.3	27,700	3.1	.04	+ .14
30	60	15,700	3.8	.13	+ .9
55	40	11,400	3.5	.19	+ .7

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(27) I. Harris, *J. Polymer Sci.*, **8**, 353 (1952).

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(29) R. B. Richards, private communication.

(30) M. L. Huggins, THIS JOURNAL, **64**, 2716 (1942).

(31) C. D. Thurmond and B. H. Zimm, *J. Polymer Sci.*, **8**, 447 (1952).

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These ideas may be made more quantitative by the following calculation: Let n_0 be the original moles of molecules, n_c the moles of molecules rendered insoluble by cross-linking, n_r the moles formed because of C–C bond rupture, and n_s the moles of soluble molecules, all per 100 g. of initial sample. Then

$$n_s = n_0 + n_r - n_c \qquad (7)$$

Table VI gives the values of n_0, n_s, n_c and n_r. The moles of molecules eliminated by cross-linking can be roughly estimated by dividing the weight of the insoluble portion by the weight average molecular weight 310,000. This calculation yielded the values given in Table VI under the heading n_c. By difference using eq. 7 the moles of bonds ruptured per 100 g. of polyethylene, n_r, can be calculated. The last column gives this estimate. There is a slight indication that rupture has occurred, but the data are not accurate enough for a precise estimate.

Another method of estimating C–C bond rupture is to assume that the hydrocarbon gases listed in Table No. I come from rupture of C–C bonds on the short side chains of 4 carbon atoms in length[33] which exist to the extent of 3.26 per 100 C-atoms[34] in the sample of polyethylene used in this research. Thus the moles of C–C bonds in 100 g. of polyethylene is 100/14 or 7.1. Of these 4(3.26/100) (7.1) represent moles of side chain bonds or 0.92. There are 2(7.1) or 14.2 moles of CH bonds; hence the ratio of moles of hydrocarbon gases to hydrogen gas evolved should be 0.92/14.2 or 0.065. The observed ratio was 0.014, taking the data of the 55 hr. thimble irradiation in Table I for the volumes of hydrocarbon and hydrogen gas produced. Actually some of the hydrocarbon gases remained dissolved in the polyethylene during the volume measurements. Weight measurement on prolonged evacuation showed the dissolved gases to be 46% by weight of the initially measured gas which was 17% by weight hydrocarbons. The estimate of 0.014 should be increased to 0.04 if the dissolved gas had the same hydrocarbon composition as the gas whose volume was measured. Thus the C–C bonds on the side chains seemed to have been ruptured about half as frequently as C–H bonds. Referring again to Table VI and using data calculated from Table II, the ratio of C–C bonds to C–H bonds ruptured along the main chains can be estimated to be $0.7 \times 10^{-3}/4.3 \times 10^{-3}$ or 0.16 taking the data for the 55 hour goat hole irradiated sample. If this estimate is correct, the molecular weight would have been reduced by the factor $1/[1 + (0.16)\,(1.38)]$ or $1/1.22$, to 27,000. The actual reduction was to 11,400; hence the chief cause of the decrease in the molecular weight of the soluble fraction seems to have been production of insoluble polyethylene rather than C–C bond rupture. By C–H bond rupture we mean the initial rupture due to the incident radiation. Ruptures of C–H bonds by reaction (3) are not counted; thus, the production of one molecule of hydrogen has been interpreted as due to the rupture of one C–H bond.

Another method of estimating the number of C–C bonds ruptured is based on an estimate of the $RCH{=}CH_2$ groups formed, see Table II. Assuming the formation of one such group per C–C bond rupture, the ratio of C–C bonds ruptured to C–H bonds ruptured is 0.5/32.2 or 0.016. This is somewhat less than the fraction of bonds ruptured on the side chains although of the same order of magnitude. Some of the $RCH{=}CH_2$ groups formed may have been on the butyl side chains; hence a calculation of the reduction in molecular weight from this calculation of the C–C bonds ruptured is not possible.

F. Disappearance of Vinylidene Unsaturation.—One of the most notable aspects of the high energy irradiation of polyethylene was the initial rapid disappearance[35] of the vinylidene olefinic groups concomitant with the production of vinylene unsaturation (see Table II). As there were 2300 CH_2 groups per molecule on the average and only two carbon atoms in the vinylidene group, the statistical chance of the vinylidene group being affected by incident irradiation was only about one in a thousand in order of magnitude. Yet the data demonstrate that by the time all of the vinylidene group had disappeared only 3.6 molecules of hydrogen had been evolved. To account for this nonrandom behavior, the postulate of the long range migration of chemical activity in the solid state was advanced.[35] Thus, along the path of ion pair formation produced by the incident irradiation, electrons, molecule ions, carbonium ions, free radicals and atomic hydrogen centers might have existed. Any of these highly active units could possibly have migrated through the polyethylene (the free radical centers by migration of hydrogen atoms attached to the chains) either along or across the chains, until the vinylidene groups were reached when the latter would have become chemically activated and taken part in the formation of cross linkages.

The reaction of atomic hydrogen with a saturated hydrocarbon chain to form molecular hydrogen and a hydrocarbon free radical is energetically favorable by about 15 kcal./mole as estimated from bond energies tabulated by Szwarc.[36] For this estimate the assumption has to be made that the bond energies given by Szwarc are applicable to the solid state. The large production of molecular hydrogen is evidence for the predominance of this reaction. Atomic hydrogen also reacts rapidly with olefinic groups with very small[37] activation energies. Darwent and Roberts[38] quote the activation energy for removal of H to form molecular hydrogen as about 7 kcal./mole for *n*-butane and 5.0 for *s*-butene. The activation energy for addition of atomic hydrogen to the double bond is about[37] 2.1 kcal./mole. However, the rate of addition of atomic hydrogen to the olefinic groups in polyethylene is limited by its rate of diffusion through the solid. Indications that the reduction of the double bonds by atomic hydrogen is not significant are the follow-

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(33) M. J. Roedel, THIS JOURNAL, **75**, 6110 (1953).

(34) As calculated using eq. 2 of the paper of C. A. Sperati W. A. Franta and H. W. Starkweather, Jr., *ibid.*, **75**, 6127 (1953).

(35) M. Dole and C. D. Keeling, THIS JOURNAL, **75**, 6082 (1953).

(36) M. Szwarc, *Chem. Revs.*, **47**, 75 (1950).

(37) H. W. Melville and J. C. Robb, *Proc. Roy. Soc.* (*London*), **196A**, 445, 466, 479, 494 (1949).

(38) B. De B. Darwent and R. Roberts, *Discs. Faraday Soc.*, **14**, 55 (1953).

ing: (1) Very little unsaturation, if any, could be produced if reduction by atomic hydrogen was important; (2) V. L. Burton[39] bombarded oleic acid with deuterons and obtained about $^1/_2$ mole of hydrogen per mole of oleic acid converted while only 2% of the oleic acid was reduced to stearic acid.

Turning now to the possibility that the positive ions, either molecule-ions or carbonium ions, were the chemically active centers that migrated to the vinylidene groups, the problem becomes more difficult. Although it can be estimated that the positive charge of the molecule ion has an energy state at the vinylidene group about 20 kcal./mole lower than along the main chain, if the ionization potential data for gaseous *n*-butane and butylene-1 given by Mitchell and Coleman[40] can be applied to solid polyethylene, the ions were probably not responsible for the disappearance of the vinylidene groups for the following reasons: the lifetime of ions is extremely short. Richards[41] estimated 10^{-7} sec. from experiments on the α-particle bombardment of liquids. Samuel and Magee[42] calculated that ions in water persisted for even shorter half-lives, of the order of 10^{-13} sec. or shorter (the time calculated for an electron to return to a positive ion). Prevost-Bérnes, Chapiro, Cousin, Landler and Magat[43] could find no evidence for an ionic mechanism of the observed effects in their studies of the irradiation of many organic liquids including heptane and octane.

The available evidence seems to indicate that free radicals are the chemically active centers whose positions migrate in solid polyethylene (due to jumps of hydrogen atoms from one bond to another). Free radicals may have a very long lifetime. Schmitz and Lawton[44] irradiated monomeric tetraethylene glycol dimethacrylate (TEGMA) and obtained free-radical induced polymerization. At temperatures below −55° where TEGMA becomes glassy, the polymerization ceased, but on warming up to room temperature polymerization was initiated in the absence of irradiation even after storage at Dry Ice temperatures for several days.

Inasmuch as the heat of the reaction

$$CH_2{=}CHCH_3 + CH_3\dot{C}HCH_3 \longrightarrow CH_3CH_2CH_3 + CH_2{=}\dot{C}HCH_2 \qquad (9)$$

is approximately −11 kcal./mole as estimated from bond strengths,[36] the location of the free radical center at the vinylidene groups is energetically more stable than along the hydrocarbon chain. The postulate which we wish to present, therefore, is that a free radical center can migrate for relatively long distances through the solid polyethylene until it meets a vinylidene group at which point it will be stabilized and remain until cross-linking occurs. Migration across the chains may be easier than along the chains. Slight stabilization at a branch point might occur as energy calculations yield a small value of −3 kcal./mole for the difference in energy of the free radical center along the main chain and attached to a branch point.

It is interesting to note that at the end of 123 hours of irradiation when the vinylidene groups had largely disappeared, (Table II), the number of cross linkages formed per molecule (Table III) or (3.58) (0.31) is practically equal to the number of vinylidene groups per molecule initially present in the polyethylene. The value 0.31 selected for this calculation is the average of the values given in Table III as calculated from the bromine up-take and the infrared absorption.

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