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Irradiation of Polyethylene. III. Influence of Temperature and Phase¹

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γ -Ray irradiation of the linear polyethylene, Marlex-50, above the melting point yields a higher evolution of hydrogen, a greater degree of crosslinking and of vinylene double bond production than irradiation at room temperature. The infrared band at 10.1 μ is missing in the case of the 142° irradiated polyethylene, and the crystallization ability is reduced. Vinyl and vinylene double bond decay constants are increased at the upper temperature, but not markedly so. G -Values for vinylene decay in the case of Marlex-50 containing 5% of *trans*-1,4-poly-(butadiene) are as high as 50.6 groups decayed per 100 e.v. of energy absorbed in the whole sample, but gel formation remains unchanged, leading to the postulate of vinylene decay in this mixture by intramolecular coupling. Material balance between hydrogen evolution, crosslinking and double bond formation is approached in the case of Marlex-50 at both 25 and 142° by allowing for a calculated increase in the weight average molecular weight due to endlinking. It is concluded that both M_n and M_w increase by the factor $[Vi]^0/[Vi]$ as endlinking occurs. Material balance is not achieved in the case of a low density polyethylene. At the gel point of the latter the decrease in vinylidene unsaturation is estimated to be almost four times as great as cross-links produced, a fact which suggests that vinylidene groups are located near the ends of the molecules. A post-irradiation fusion of vacuum irradiated Marlex-50 causes a greater vinyl decay, increased vinylene group formation and a greater G -value for crosslinking. These facts suggest strongly that crosslinking can occur by rearrangement of segments containing free radicals as well as by C-C bond formation during the radiolytic detachment of hydrogen. The *trans*-1,4-poly-(butadiene) lowers $G(H_2)$ and $G(-Vi)$ at 142°, but the latter more than the former; *cis*-1,4-poly-(butadiene) has a smaller effect. At room temperature the protective action of the poly-(butadiene) seems to be much less, probably because of non-uniform mixing in the solid state.

Introduction

In the previous paper of this series³ it was demonstrated that when the linear polyethylene, Marlex-50, was irradiated *in vacuo* at room temperature with γ -rays from a Co-60 source, the vinyl groups in the polyethylene decayed according to a first-order law until half of them had disappeared. The relationship of this observation to the "target" theory of Lea⁴ has been discussed by Dole, Williams and Arvia.⁵ Furthermore, the first-order decay law was also shown to be valid for vinylene and vinylidene decay as well as for vinyl group disappearance.

Because the first-order rate constant k_1 was independent of the vinyl group concentration, the G -value for vinyl decay $G(-Vi)$ in units of double bonds disappearing per 100 e.v. could be calculated from the equation

$$G(-Vi) = 100 k_1 [Vi] N \quad (1)$$

where N is Avogadro's number, $[Vi]$ is concentration in units of moles g^{-1} and k_1 has the units $g.(e.v.)^{-1}$. One of the purposes of the present work was to test the effect of rise of temperature and decrease of crystallinity on k_1 which, being independent of concentration, is a more fundamental quantity than the G -value.

In the previous work the failure of the first-order law to hold for vinyl decay at the higher doses was interpreted in terms of a protective action on the vinyl groups by vinylene double bonds produced in the Marlex-50 by the irradiation. It was decided to test this hypothesis by incorporating vinylene groups before the irradiation into the solid polymer in the form of *trans*-1,4-poly-(butadiene), (*trans*-PB), although it was realized that the use of *trans*-PB could not produce a random distri-

(1) Some of this material was presented at the 133rd National Meeting of the A.C.S., San Francisco, California, April, 1958, and at the International Congress of Radiation Research, Burlington, Vermont, August, 1958.

(2) On leave from A.E.R.E., Harwell, England.

(3) M. Dole, D. C. Milner and T. F. Williams, *THIS JOURNAL*, **80**, 1580 (1958).

(4) D. E. Lea, "Actions of Radiations on Living Cells," 2nd Ed. Cambridge Univ. Press, 1954.

(5) M. Dole, T. F. Williams and A. J. Arvia, paper to appear in the Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958.

bution of vinylene groups and that the *trans*-PB would not be incorporated into the crystalline regions of the Marlex-50. However, the use of the *trans*-PB made it possible to study the effect of the irradiation at vinylene concentrations much higher than either the vinyl or vinylene concentrations of the previous paper.³

The present work also contains information on the effect of temperature and change of phase on $G(\text{H}_2)$, ring-link⁶ formation, gel formation and reduction in crystallinity.⁷

Influence of the presence of molecular hydrogen on the observed phenomena has also been studied, but most of the results relating $G(\text{H}_2)$ to hydrogen pressure⁸ will be given in another publication.

Experimental

A. Radiation Source and Cells.—The radiation source, Co-60, was the same as that described previously.³ For irradiations at 142°, above the maximum melting point of Marlex-50, a special irradiation cell and support for the polyethylene film were designed. It was found that Marlex-50 film could be held mechanically between two aluminum plates, which were themselves supported by electrical leads in the vacuum space of a glass cell, and heated to 142° without flow taking place, and that after many hours of irradiation at 142°, the cell could be cooled down and the film recovered intact for infrared measurements. The aluminum plates were heated electrically, the temperature recorded and automatically maintained constant at $142 \pm 2^\circ$ by means of an alumel-chromel thermocouple, hard soldered to a silver sheet pressed against an aluminum plate and associated electrical control system. The nichrome heating tape was covered with glass insulation. As the irradiations began with a vacuum in the cell and as the thermal conductance of the gaseous phase gradually increased due to accumulation of hydrogen, it was necessary occasionally to adjust the automatic temperature control and heating rate.

The longer the films remained between the aluminum plates at 142°, the more strongly the polyethylene seemed to adhere to the aluminum on cooling to room temperature. To extract the films without stretching or damaging them, it was found necessary to heat the aluminum plate holder with film in boiling water from 0.5 to 1 hr. and then gently to pry the plates apart. In this way the films could be recovered in excellent condition.

B. Calibration of Radiation Cell.—Inasmuch as it was not convenient to measure the radiation intensity between the aluminum plates by the usual ferrous sulfate technique, some eight irradiations were carried out at room temperature with Marlex-50 in the cell, and the hydrogen gas yields and vinyl decay rate then used as the reference standards. G -values at 142° also could be calculated taking the data of our previous publication³ as standards.

C. Materials.—As in the previous work Marlex-50 containing a small amount of antioxidant was used as received from the manufacturer. In addition the manufacturer prepared for us a 1.5 and 5% mixture of 90% *trans*-1,4-poly-(butadiene) in Marlex-50 by blending the polymers on a hot roll mill and subsequently converting to film two mils thick. For films of other thicknesses an appropriate number of sheets could be placed in the aluminum cell, and carefully heated for a few minutes (in air for the room temperature runs and *in vacuo* for the high temperature experiments). By combining in this way a sheet of the 1.5% *trans*-PB film with a sheet of the 5%, a sample of 3.25% *trans*-PB in Marlex-50 was prepared. Experiments were also done on a film containing 95% antioxidant free Marlex-50 plus 5% of 95% *cis*-1,4-poly-(butadiene) containing antioxidant. Irradiation of Marlex-50 without antioxidant yielded the same results with respect to vinyl decay as the experiments on Marlex-50 containing antioxidant.

D. Measurement of Gas Yields.—By mass spectrometric analysis the gas from the γ -ray irradiation of Marlex-50 was shown to be 99.7% hydrogen. The hydrogen yield

was measured directly by means of a Toepler pump after freezing out any condensable gas at -196° .

E. Measurement of Solubility.—In order to calculate the G -value for crosslinking, solubility measurements of polyethylene were carried out by suspending sections of the irradiated film in a stainless steel mesh basket in boiling toluene for about 100 hr. until the insoluble fraction became constant in weight.

Results and Interpretation

A. Marlex-50 at 142°.—The influence of temperature and change of phase on radiation effects in pure Marlex-50 will first be considered. From Fig. 1 it can be seen that the rate of vinyl decay was greater at 142° than at room temperature and that the first-order decay law was followed to higher doses. It should be noted that when the vinyl concentration had been reduced to 0.1 of its initial value, accurate concentration measurements became difficult. Nevertheless a definite trend away from the first-order curve is evident. This first-order law failure might be due partially to a small rate of production of vinyl unsaturation by the irradiation. The latter is known to occur in low density polyethylene.⁹ In the previous work³ it was postulated that the *trans*-vinylene groups, produced by the irradiation, exerted a protective action over the vinyl, but there seems to be no indication of this in the present data. If such a postulate of protective action is correct, it would mean that energy transfer from activated vinyl to vinylene groups does not take place or occurs only with difficulty in the molten state. In the previous work³ the lack of vinylene protection on vinylidene decay was also evident and could be attributed to the high amorphous content of the low density polyethylene.

From the first-order vinyl decay constant k_1 of Table I at the two temperatures, an activation

TABLE I
DECAY CONSTANTS AND G -VALUES FOR INITIAL VINYL GROUP DECAY

Polymer	Temperature					
	25°			142°		
	$[\text{Vi}]_0$, moles/g. $\times 10^4$	k_1 , g./e.v. $\times 10^{21}$	G_0 , mole- cules/ 100 e.v.	$[\text{Vi}]_0$, moles/g. $\times 10^4$	k_1 , g./e.v. $\times 10^{21}$	G_0 , mole- cules/ 100 e.v.
Marlex-50	0.99	1.61	9.6	2.09	12.5	
Marlex-50 + 1.5% <i>trans</i> -PB	0.93	~1.6	~9.6	1.67	9.4	
Marlex-50 + 5% <i>trans</i> -PB	1.01			1.42	6.1	

energy equal to 0.66 kcal./mole was calculated. This activation energy is the same order of magnitude as the value 0.8 kcal./mole given by Steacie¹⁰ for the disproportionation reaction in which



hydrogen atom transfer is followed by C-C bond formation¹¹ similar to the endlinking reaction postulated³ for the vinyl decay.

Figure 2 illustrates the applicability of the zero-order growth and first-order decay law³ for the

(9) M. Dole, C. D. Keeling and D. G. Rose, *THIS JOURNAL*, **76**, 4304 (1954).

(6) M. Dole, D. C. Milner and T. F. Williams, *THIS JOURNAL*, **79**, 4809 (1957).

(7) T. F. Williams, H. Matsuo and M. Dole, *ibid.*, **80**, 2595 (1958).

(8) A. J. Arvia and M. Dole, unpublished except in part.³

(10) E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. II, 2nd. Ed., Reinhold Publ. Corp., New York, N. Y., 1954, p. 576.

(11) Really completion of a C=C bond.

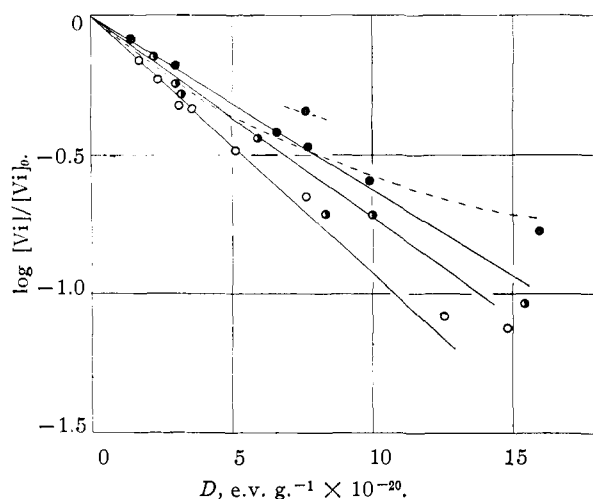


Fig. 1.—The three solid lines represent the decay of vinyl unsaturation at 142° in Marlex-50; containing no *trans*-1,4-poly-(butadiene), bottom curve (open circles); 1.5% *trans*-PB, middle curve (half-shaded circles); 5% *trans*-PB, top curve (solid circles). The dotted line represents the data for pure Marlex-50 at room temperature, while the single solid circle, 5% *trans*-PB at room temperature.

trans-vinylene groups at 142° in the case of pure Marlex-50. From the slope and intercept of the curve at infinite dose, the vinylene growth rate, $G_0(VI)$, and the first-order vinylene decay constant k_2 can be calculated. These results are given in Table II. The activation energy for vinylene de-

TABLE II
INITIAL GROWTH AND DECAY CONSTANTS FOR *trans*-VINYLENE GROUPS

Polymer	Temperature				
	25°		142°		
	$[VI]_0$, moles/ g. × 10 ⁴	k_2 , g./e.v. × 10 ²¹	$G_0(VI)$, mole- cules/ 100 e.v.	k_2 , g./e.v. × 10 ²¹	$G_0(VI)$, molecules/ 100 e.v.
Marlex-50	0.058	0.52	2.4 ^a	0.64	3.1 ^a
Marlex-50 + 1.5% <i>trans</i> -PB	2.1			1.5, ^a 1.4 ^b	-19 ^a -18 ^b
Marlex-50 + 5% <i>trans</i> -PB	7.0			1.2 ^a	-50.6 ^a

^a Calculated from a first-order decay law after correcting for vinylene produced in the Marlex-50 assuming a rate of production equal to that of pure Marlex-50. ^b Assuming that the rate of production of vinylene in the Marlex-50 has been reduced by the *trans*-PB in the same ratio as the reduction in $G(H_2)$ by the *trans*-PB. ^c Corrected for the decay of vinylene initially present (see ref. 3).

calculated from the ratio of k_2 at 142 and 25° is 0.51 kcal./mole, again a very small value. The almost zero dependence of the *trans*-vinylene yield on the temperature agrees with the earlier conclusion of Charlesby and Davison¹² and of Lawton, Balwit and Powell.¹³ In our previous work³ the differences between the rates of *trans*-vinylene production for three different types of polyethylene were attributed to differences in crystallinity. Inasmuch as the formation of vinylene groups in

(12) A. Charlesby and W. H. T. Davison, *Chemistry and Industry*, 232 (1957).

(13) E. J. Lawton, J. S. Balwit and R. S. Powell, *J. Polymer Sci.*, **32**, 257 (1958).

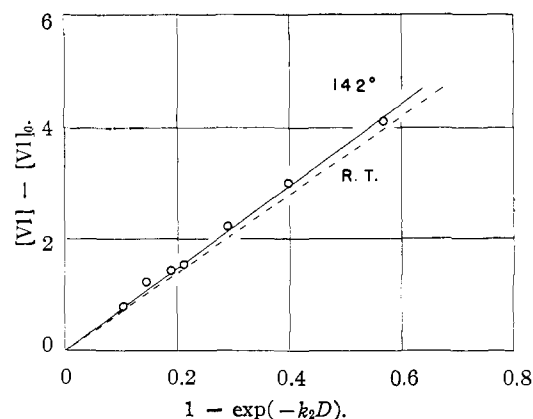


Fig. 2.—Zero-order growth and first-order decay law for *trans*-vinylene unsaturation in Marlex-50.

molten Marlex-50 occurs at a slightly greater rate than in crystalline, the previously observed differences, if real, can be concluded to be the result of the presence of different numbers of branch points along the chains. Although Lawton, Balwit and Powell¹³ state that the *trans*-vinylene yield was unaffected by branching or physical state, Dewhurst¹⁴ found that the presence of branches in the hexane isomers did lower the vinylene yield and in some cases the total yield of unsaturated products.

Charlesby and Davison¹² found that in the case of a low density polyethylene, Alkathene (Marlex-50 results were qualitatively similar), the vinylene and hydrogen yields were independent of temperature while the crosslinking yield increased sharply from -80° up through the maximum melting point. They had no explanation for this discrepancy in the "intuitive" material balance equation

$$G(H_2) = G(VI) + G(X) \quad (2)$$

where $G(X)$ represents crosslinks produced per 100 e.v. of energy absorbed. It is not known exactly how Charlesby and Davison determined $G(H_2)$, but in the present work a marked increase of $G_0(H_2)$ from 3.8 at room temperature at 6.0 at 142° was observed. These are initial G -values, and decline with rise of ambient hydrogen pressure, at least at room temperature, as will be described more completely in a future publication.⁸ Lawton, Balwit and Powell¹³ also failed to confirm the observation of Charlesby and Davison with respect to the constancy of $G(H_2)$ with temperature.

By extrapolating the gel *versus* dose curves back to the dose at incipient gelation, G_{Gel} , the latter can be determined and $G(X)$ calculated as in previous publications⁹ from the equation

$$G(X) = \frac{100N}{2M_w D_{Gel}} \quad (3)$$

where \bar{M}_w is the weight average molecular weight¹⁵ corrected as described below. $G(X)$ at room temperature (with no annealing) is estimated to be 1.6 ± 0.4 , and at 142°, 2.9 ± 0.4 . Equation 3 is essentially the same as eq. 4 used by Dole, Keeling and Rose.⁹ Figure 3 illustrates the increase of gel content with dose. When Marlex-50, irradiated at room temperature, was annealed at

(14) H. A. Dewhurst, *THIS JOURNAL*, **80**, 5607 (1958).

(15) L. H. Tung, *J. Polymer Sci.*, **24**, 333 (1957).

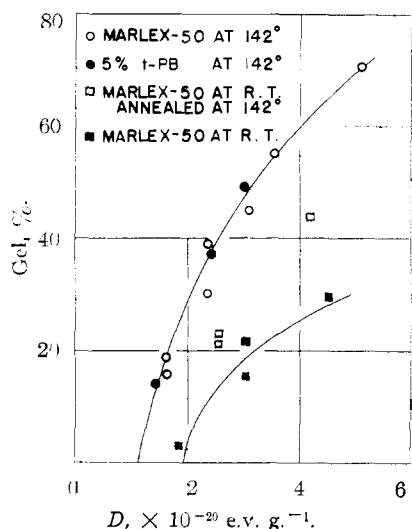


Fig. 3.—Gel formation as a function of dose. All points are for Marlex-50 except the solid circles which represent gel formation in Marlex-50 containing 5% of *trans*-1,4-poly-(butadiene).

142° after the irradiation, but before exposure to oxygen of the air, the data shown in Fig. 3 by the open squares were obtained. The increase in gel content due to annealing is due to free radicals¹³ trapped in the Marlex-50 by the room temperature irradiation. By annealing, further crosslinking reactions occur between the free radicals; furthermore, if the free radicals are not removed by annealing, they will react slowly with oxygen on exposure to air. This oxidation¹⁶ eventually results in degradation¹⁷ and lowers the gel content. Thus it is essential to make the solubility measurements as soon as possible after opening the irradiation cells to air. This was done in the case of the data shown in Fig. 3.

More nearly complete material balance equation, which ignores chain scission, has been given by Dole, Milner and Williams⁶ in the form (4) where $G(H_2) + G(-Vi) = G(X) + G(Vi) + G(E.L.) + G(R.L.) + \frac{1}{2}G(R\cdot)$ (4)

E.L., R.L. and R· signify end-links, ring-links and free radicals, respectively. In the molten state no infrared absorption at 10.1 μ , which we have attributed⁶ to ring-links,¹⁸ was measured in agreement with the previous observation⁶ that this absorption could not be observed in low density polyethylene of about 54% crystallinity. Free radicals also do not exist in the liquid state after the irradiation, so eq. 4 is simplified by the elimination of $G(R.L.)$

(16) Oxidation studies on polyethylene during irradiation will be published later.

(17) A. Chapiro, *J. chim. phys.*, **52**, 246 (1955).

(18) Since our publication of this interpretation of the infrared spectrum, it has been suggested to us that the absorption at 10.1 μ might be due to (a) unstable species, (b) *cis*-vinylene groups or (c) conjugated double bonds. Possibility (a) is eliminated by the fact that the absorption does not disappear on fusion and resolidification of the polymer. Possibility (b) is eliminated as this absorption increases in intensity during irradiation as the *cis*-vinylene absorption at $\sim 13.5 \mu$ decreases. Possibility (c) probably can be eliminated also inasmuch as E. R. Blout, M. Fields and R. Karplus, *THIS JOURNAL*, **70**, 194 (1948), in their infrared study of compounds containing conjugated double bonds did not mention any absorption bands characteristic of these compounds in the range 900–1000 cm^{-1} .

and $G(R\cdot)$. The material balance becomes, then, at 142° and at zero dose

$$6.0 + 12.5 = 2.9 + 2.9 + G(E.L.)$$

By difference $G(E.L.)$ is calculated to be 12.7; as it would be expected to equal $G(-Vi)$ or 12.5 the agreement is satisfactory. At room temperature a corresponding material balance equation can be written

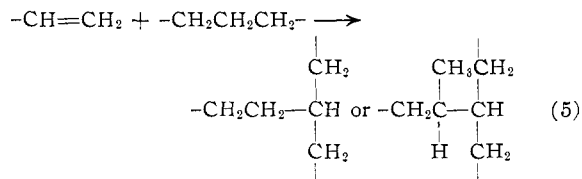
$$3.8 + 9.6 = 1.6 + 2.2 + G(E.L.)$$

In this case $G(E.L.)$ equals 9.6 in exact agreement with $G(-Vi)$. Such agreement is, of course, fortuitous; in fact, a discrepancy to allow for cyclization and residual free radicals should exist (although the latter probably largely disappear during the toluene extraction).

It is next of interest to consider energy balance as well as material balance. To break a C–H bond requires 4.2 e.v. of energy and to activate a vinyl group electronically¹⁹ about 6.5 e.v. After one C–H bond has been broken, H_2 and a cross-link or vinylenic group can be formed exothermally, hence no additional energy is needed, nor is any needed for the reaction of an electronically excited vinyl group to form an end link. The energy balance becomes, then

$$(6.0)(4.2) + (12.5)(6.5) = 106.6$$

This is slightly more than the 100 e.v. of energy absorbed. However, if the excitation of the vinyl group is to a low lying triplet state²⁰ of energy of the order 3.2 e.v. (assuming no change in configuration), then the energy calculation becomes $(12.5)(3.2)$ or 40 e.v. and gives a total energy requirement of 65.2 e.v., well below the 100 e.v. absorbed. The minimum energy requirements are, of course, much less than this. Thus the end linking reaction is exothermic²¹ to the extent of



about 1.1 e.v./molecule while elimination of molecular hydrogen and formation of a vinylenic group requires only about 1.3 e.v./molecule.

It might be asked if the vinyl decay could follow a chain mechanism. This seems unlikely for the solid state because of the high rigidity of the solid and also unlikely for the liquid state because the first-order decay constant k_1 does not change appreciably as the Marlex-50 passes from the crystalline to the amorphous phase.

It is interesting to note that both $G(H_2)$ and $G(-Vi)$ increase with temperature from 25 to 142°. This precludes the possibility that the major decay of vinyl groups is by reaction with hydrogen, either atomic or molecular, because if the greater decay of vinyl groups at 142° were due to a greater

(19) E. P. Carr and H. Stücklen, *J. Chem. Phys.*, **4**, 760 (1936); *THIS JOURNAL*, **59**, 2138 (1937).

(20) For a discussion of the energy of the triplet state of olefins see K. J. Laidler "The Chemical Kinetics of Excited States," Oxford, 1955, p. 95.

(21) The energy relationships in these reactions were estimated from the bond energies given by M. Szwarc, *Chem. Revs.*, **47**, 76 (1950).

scavenging action of the hydrogen, the hydrogen yield would be expected to decrease. Nevertheless, the following experiments suggest that under certain special conditions part of the vinyl decay is by reaction with hydrogen, possibly atomic.

It was found that when the Marlex-50 film was melted between two aluminum plates and the system cooled down, the polyethylene adhered strongly to the aluminum. Under this condition, the hydrogen evolved during the irradiation was unable to escape readily. Its concentration in the polyethylene must have greatly increased. The observed integral $G(H_2)$ fell from 3.8 to 1.6. In this measurement, using a Toepler pump, the polyethylene was melted to allow the complete removal of hydrogen; condensable gases, which seemed to be much more abundant than normally, were frozen out in a liquid nitrogen trap. Figure 4 illustrates the effect of the dissolved hydrogen on

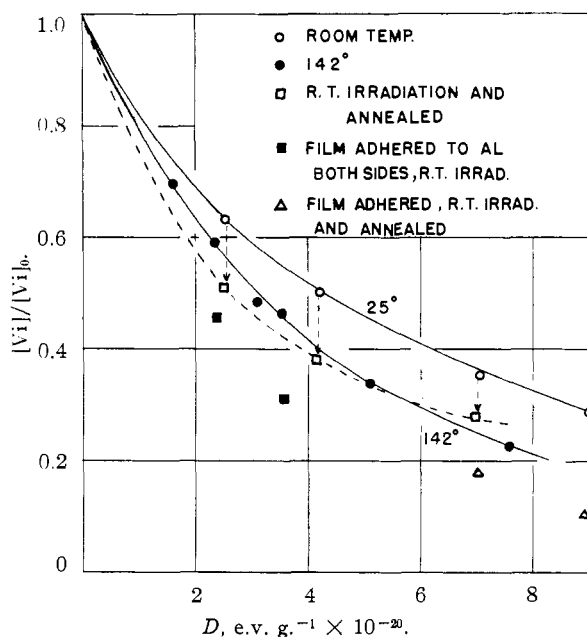


Fig. 4.—Decay of vinyl unsaturation under different conditions.

the vinyl decay rate as well as the effect of post-irradiation annealing of the polyethylene (before exposure to air). The top two curves represent the normal vinyl decay rate at room temperature and at 142° , respectively. The dotted arrows indicate the increase in the vinyl group disappearance on annealing. Note that the annealing has a relatively greater effect at the lower doses than at the high; annealing a sample irradiated to 20×10^{20} e.v. g^{-1} produced no additional vinyl decay. The solid squares represent the vinyl concentration after an irradiation with the polyethylene strongly adhered to the aluminum plates, and the triangles, the same but with a post-irradiation annealing. Probably the solid squares and triangles would fall on the same curve. It also was found that the *trans*-vinylene group decay was greater in the experiments with the polyethylene strongly adhered. The above effects were not due to any catalytic effect of the aluminum oxide coated plates because

none of these effects was observed when the polyethylene adhered strongly to only one plate. Similarly, during the 142° irradiations with the polyethylene in the molten state, where the diffusibility of the hydrogen is increased and the solubility lowered, there was no reduction in $G(H_2)$, but actually a marked increase to 6.0.

As mentioned above, the effect of increased vinyl decay on annealing is probably the result of trapped free radicals remaining in the solid after the irradiation and before exposure to air. Smaller and Matheson²² have recently published evidence from electron spin resonance studies for the existence of the free radical $-\dot{C}H_2\dot{C}HCH_2-$ in Marlex-50 irradiated at liquid nitrogen temperature. The present work coupled with post-irradiation oxidation studies¹⁶ indicates the presence of free radicals after irradiation at room temperature. None can be detected, however, after annealing the irradiated Marlex-50 to 142° .

B. Marlex-50-*trans*-1,4-Poly-(butadiene) Mixtures.—We turn now to a consideration of the results observed in the case of Marlex-50 containing 1.5 and 5% *trans*-1,4-poly-(butadiene). As can be seen from Fig. 1 the decay of vinyl unsaturation was less in the presence of the poly-(butadiene) than in its absence. Figure 5 illustrates the influence at

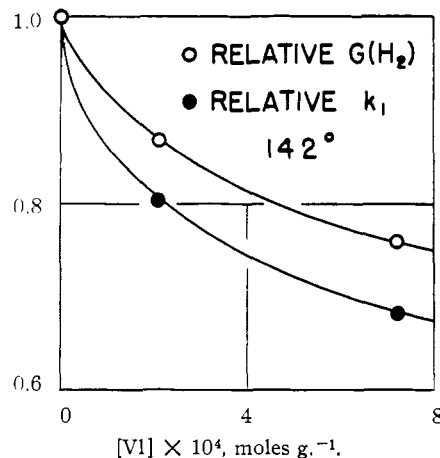


Fig. 5.—The protective action of vinylene groups in *trans*-1,4-poly-(butadiene) on hydrogen yields and vinyl decay constants at 142° .

142° of the poly-(butadiene) on $G(H_2)$ and k_1 as a function of the initial *trans*-vinylene concentration. The data demonstrate that the initial presence of the *trans*-vinylene groups has a relatively greater effect at low concentration of these groups and has a greater effect on the vinyl decay than on the hydrogen yield. The curves of Fig. 5 are similar to many obtained by others in studying the protective effect of one substance on the radiolysis of other substances²³ in solution.

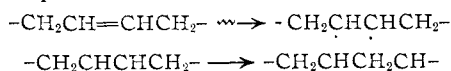
The data of Fig. 3 demonstrate that gel formation at 142° in the presence of the poly-(butadiene) cannot be distinguished from the gel formation in its absence. This negligible influence of the PB is

(22) B. Smaller and M. S. Matheson, *J. Chem. Phys.*, **28**, 1169 (1958); see also, E. J. Lawton, R. S. Powell and J. S. Balwit, *J. Polymer Sci.*, **32**, 277 (1958).

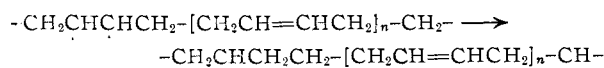
(23) See, for example, M. Burton, J. Chang, S. Lipsky and M. P. Reddy, *Radiation Research*, **8**, 203 (1958).

surprising as the very large G -values for vinylene decay, Table II, might be expected to yield a larger $G(X)$. It should be emphasized that the calculation of the $G(VI)$ values given in Table II were based on the energy absorbed in the whole sample. If the calculation were changed to a basis of the energy absorbed only in the *trans*-PB, assuming an equal rate of energy absorption per gram in the Marlex-50 and *trans*-PB, then the $G(VI)$ values would have been 20 fold more negative in the case of the 5% *trans*-PB and 67 fold more negative in the case of the 1.5% *trans*-PB. The $G(VI)$ values would then have been of the order of -1000 .

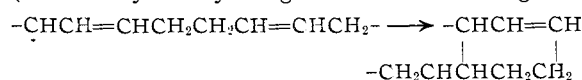
The decay constants for the *trans*-vinylene groups in the mixed polymer at 142° given in Table II are about 2 to 2.5-fold greater than k_2 in pure Marlex-50. It should be noted that all the methylene group hydrogens in poly-(butadiene) are allylic hydrogens and, consequently, the poly-(butadiene) would be expected to be more reactive with respect to hydrogen abstraction reactions than polyethylene. In this connection Snow and Moyer²⁴ have made the significant observation that dimers or higher polymers produced in the irradiation of solid C_{27} paraffins contain a considerably higher concentration of double bonds per 27 C-atoms than the fraction of monomer remaining unpolymerized. They suggest that because the allylic free radical, $-\dot{C}HCH=CH-$, is more stable than others, polymerization occurs preferentially through the participation of this free radical. If this is also true for poly-(butadiene), the higher decay constant for the vinylene groups in the poly-(butadiene)-Marlex-50 mixture is understood, and the negligible effect of the *trans*-PB on the gel yield can be explained on the postulate that *trans*-PB molecules tend to become intramolecularly linked rather than cross linked to other *trans*-PB or polyethylene molecules. Chain coiling of the poly-(butadiene) molecules and their dilution by polyethylene would also tend to promote intramolecular linking. In other words $G(VI)$ in the 1.5 and 5% *trans*-PB-Marlex-50 mixtures (negative in this case) must be largely compensated for by $G(R.L.)$ in the material balance eq. 4. Possible reactions involving the vinylene decay in the *trans*-PB part of the mixture can be written as



or



(here n may be any integral number including zero).



This mechanism bears a considerable resemblance to part of the processes involved in the vulcanization of rubber.²⁵

(24) A. I. Snow and H. C. Moyer, *J. Chem. Phys.*, **27**, 1222 (1957).

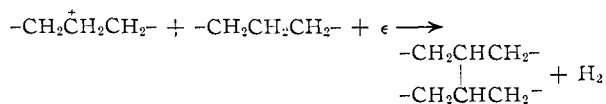
(25) See, for example, the discussion by P. J. Flory, "Principles of Polymer Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, p. 455.

In the previous paper of this series³ it was suggested that the vinylene groups randomly produced in the polyethylene at room temperature exerted a protective action over the vinyl groups and an empirical equation, based on this idea, was found to be accurately valid. In the present work, however, it is clear that, despite the high vinylene concentration in the polybutadiene, vinyl decay was almost unaffected. This lack of protective action at room temperature in the presence of concentrations of *trans*-PB below 5% probably can be attributed to the non-homogeneous nature of the mixture with consequent inhibition of energy transfer from crystalline polyethylene to amorphous polybutadiene.

C. Marlex-50-*cis*-1,4-Poly-(butadiene) Mixtures.—A few irradiations of Marlex-50 mixed with 5% *cis*-1,4-poly-(butadiene), *cis*-PB, were carried out. These experiments revealed a smaller effect of the *cis*-PB on the radiation chemistry of polyethylene than that of the *trans*-PB. At 142° , for example, $G(H_2)$ was reduced by 0.5 unit by the presence of the 5% *cis*-PB as compared to a reduction of $G(H_2)$ by 5% *trans*-PB of 1.4 units. Similarly k_1 was affected less by the *cis*-PB. From the narrowing of the infrared band at $\sim 13.5\mu$ and the decrease in the C=C stretching band at 6.05μ , it was evident that the *cis*-vinylene concentration decreased with a high G -value, but it was impossible to determine $G(\textit{cis-vinylene})$ accurately.

The increase in *trans*-vinylene concentration after a dose of 12×10^{20} e.v. g.⁻¹ at 142° was 2.4 times as great as in Marlex-50, thus demonstrating the isomerization of *cis* to *trans*-PB.

D. Mechanism of Reactions Leading to Gel Formation.—In the early work on the pile irradiation of polyethylene²⁶ a reaction was proposed for the crosslinking mechanism



In the ten years that have elapsed since then, much more information about the crosslinking of polyethylene and other irradiation effects has been obtained, so that additional mechanisms must be postulated. The pertinent new evidence may be listed as follows.

1. Decay of Vinylidene Unsaturation in Low Density Polyethylene during Irradiation.²⁷—Dole, Keeling and Rose⁹ postulated that the vinylidene groups decayed by forming crosslinks. Their evidence indicated that initially the number of crosslinks formed equalled the number of vinylidene groups consumed. The more accurate data of this paper, Table III, yield for the polyethylene, B-3125, at the gel point 7.3×10^{-6} mole of vinylidene decayed per gram while only 1.9×10^{-6} mole of cross-links per gram was formed. If the vinylidene groups exist near the end of the molecular chains, their reaction with a neighboring chain of methylene groups would be more akin to endlinking than to crosslinking. If this is so, the

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

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

$G(X)$ for B-3125 should be reduced from 0.87 to 0.72. As $G(VI)$ was only 1.5, but $G(H_2)$ 3.8, a serious discrepancy in the material balance equation exists. Busse and Bowers²⁸ have already pointed this out in the case of low density polyethylenes.

2. Decay of Vinylene Unsaturation.^{3,29}—At the gel point, the decay of vinylene unsaturation in the case of Marlex-50 amounted to 0.10×10^{-5} mole g^{-1} of vinylene groups, whereas the crosslinks were estimated to be about 0.47×10^{-5} mole g^{-1} . Put into other words, the vinylene decay produced 21% of the crosslinking up to the gel point. The data for 142° also yielded the same result. In the case of the low density polyethylene B-3125, the total number of vinylene groups decayed per gram at the gel point was about the same as in the case of Marlex-50, but because of the smaller number of cross-links, the fraction of cross-links due to vinylene decay amounted to about 60%.

3. Decay of Vinyl Unsaturation.^{3,14}—In this and the previous paper,³ vinyl group disappearance is assumed to occur by the groups first becoming activated by the radiation and then reacting with adjacent molecular chains to form end-links. This means that to calculate $G(X)$ from eq. 3 account must be taken of the increase in the weight average molecular weight due to the endlinking reaction. As pointed out by Charlesby³⁰ endlinking of itself cannot produce an infinite network. Nevertheless, it is reasonable to suppose that as endlinking occurs, \bar{M}_w will increase and the dose required for incipient gelation will decrease. An approximate estimate of the effect of endlinking on the irradiation dose required for gelation can be gained from the following treatment.

The molecular picture assumed is that the vinyl group of molecule A can become endlinked to molecule B at any point along the molecular chain of B; thus, the probability of B having a molecule endlinked to it will be proportional to the weight fraction of B. Imagine the polyethylene to be divided into a number of sections, homogeneous in molecular weight and identified by the vinyl groups in that section. Let each section be designated by the subscript x , and let the initial vinyl group concentration, weight fraction and molecular weight be $[Vi]_x^0$, W_x^0 and M_x^0 . It is assumed that at the gel point the number of vinyl groups decayed in any section will be proportional to the fraction of total vinyl groups decayed at the gel point, f_{gel} , where

$$\frac{[Vi]_{gel}}{[Vi]^0} = 1 - f_{gel}$$

By virtue of the molecular model adopted above, the fraction of all the molecules, whose vinyl groups decay, which are captured by the molecules of section x will be equal to the weight fraction of x . The number of moles captured by section x is,

(28) W. F. Busse and G. H. Bowers, *J. Polymer Sci.*, **31**, 252 (1958).

(29) Mechanisms for the decay of vinylene unsaturation were first given by R. Simha and I. A. Wall, *J. Phys. Chem.*, **61**, 425 (1957), and by R. W. Pearson, *Chemistry & Industry*, 903 (1956); 209 (1957); *J. Polymer Sci.*, **25**, 189 (1957).

(30) A. Charlesby, *Proc. Roy. Soc. (London)*, **231A**, 521 (1955). Charlesby's endlinking mechanism involves main chain fracture and thus is different from the endlinking mechanism postulated here to explain vinyl decay.

therefore, $([Vi]^0 - [Vi]_{gel})W_x$. It is further assumed that the average molecular weight of all molecules captured by the molecules of section x will be equal to the initial number average molecular weight, \bar{M}_n^0 .

Obviously, the number of molecules in section x is not altered by having chains from other sections endlinked to chains of molecules in section x , but the number is decreased by vinyl groups of section x decaying (endlinking of molecules of section x to other molecules). After the dose D_{gel} , the net number of molecules in section x in units of moles per gram is

$$[Vi]_x^0 - [Vi]_x^0 \cdot f_{gel}$$

or

$$[Vi]_x^0 \cdot \frac{[Vi]_{gel}}{[Vi]^0}$$

The number average molecular weight is equal to the reciprocal of the total number of moles per gram. Assuming one vinyl group per molecule

$$M_{n, gel} = \frac{1}{\sum_x [Vi]_x^0 \cdot [Vi]_{gel}/[Vi]^0}$$

or

$$\bar{M}_{n, gel} = \bar{M}_n^0 \frac{[Vi]^0}{[Vi]_{gel}} \quad (6)$$

Eq. 6 is exact if the assumption of one vinyl group per molecule is correct. As far as endlinking is concerned, this is true if true initially.

The weight increase of section x after dose D_{gel} is given by the increase of weight due to molecules of molecular weight \bar{M}_n^0 becoming endlinked to molecules in the section

$$W_x^0([Vi]^0 - [Vi]_{gel}) \cdot \bar{M}_n^0$$

and by the decrease of weight due to some of the initial molecules of section x becoming endlinked to molecules in other sections

$$\frac{[Vi]_x^0}{[Vi]^0} ([Vi]^0 - [Vi]_{gel}) \cdot M_x^0$$

It is not necessary to consider endlinking of molecules in fraction x with other molecules of fraction x as such endlinking would produce no change in the weight of fraction x .

But the two changes of weight given above are equal; hence, in this model the weight of fraction x as identified through the vinyl groups suffers no change due to the endlinking reaction. This conclusion simplifies the treatment and enables us to write the equations

$$\begin{aligned} M_x &= \frac{W_x^0}{[Vi]_{x, gel}} = \frac{W_x^0 [Vi]^0}{[Vi]_x^0 [Vi]_{gel}} \\ &= M_x^0 \frac{[Vi]^0}{[Vi]_{gel}} \\ M_{w, gel} &= M_w^0 \frac{[Vi]^0}{[Vi]_{gel}} \quad (7) \end{aligned}$$

Thus, according to the physical picture of the endlinking process adopted here, both the weight and number average molecular weights increase in the same ratio. In the case of unannealed Marlex-50 irradiated at room temperature, $[Vi]^0/[Vi]$ at the gel point was 1.40; thus the weight average molecular weight used in eq. 3 to calculate $G(X)$ was (1.40)(74,900) or 104,800. Data for $G(X)$ are given in Table III.

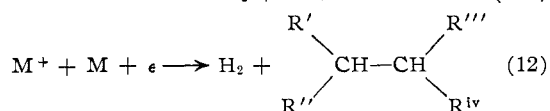
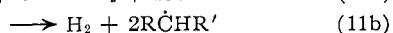
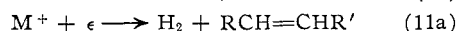
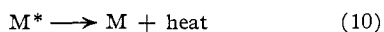
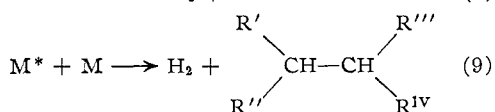
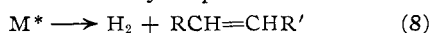
4. Growth of Gel Content on Annealing.—

The data of Fig. 3 demonstrate that crosslinking reactions occur in the polyethylene on annealing to 142° (in the absence of air) subsequent to the irradiation. Inasmuch as the polyethylene was heated to 110° in boiling toluene during the solubility measurements, the effect shown in Fig. 3 might have been even more pronounced had the gel or cross-link concentration been determined at room temperature. This increase in gel content on annealing probably is not the result of ion-molecule reactions but should be explained on the basis of the combination of residual free radicals and additional vinyl and vinylene decay.

5. Measurement of $G(X)$ after Irradiation in the Liquid State.—As $G(H_2)$ increases from about 3.8 to 6.0 or by 2.2 units on increasing the temperature from 25 to 142° and as $G(VI)$ increases only by 0.7, the difference between 2.2 and 0.7 or 1.5 should be due to the increase in $G(X)$. The latter is 1.3, but these numbers agree within the experimental uncertainties. Thus, on melting, the increase in hydrogen evolution on irradiation is due more to the increase in cross-linking than to increase in vinylene formation.

Weiss³¹ has stressed the necessity of the carbon atoms in adjacent chains approaching near to the covalent C-C bond distance of 1.54 Å. in order to form a cross-link. As the nearest C-C distance between carbon atoms of nearest neighbor chains in crystalline polyethylene is about 4.5 Å., it might be expected that the greater the crystallinity of the polyethylene, the less $G(X)$. The results of this research bear out this prediction, as can be seen by comparing the room temperature and 142° data. However, the prediction is not verified on comparing $G(X)$ for highly crystalline Marlex-50 and B-3125 given in Table III. Inasmuch as material balance was not obtained in the case of B-3125, the cross-linking estimate may be incorrect.

The primary act of energy absorption results in ionization and excitation of the hydrocarbon chain. Subsequent reactions may be postulated as



where M, M* and M⁺ represent the normal, excited and ionized hydrocarbon chain, respectively. Reaction 10 represents deactivation of any type leading to the degradation of the energy of radiation to heat. The lower $G(H_2)$ and $G(X)$ values at room

(31) J. Weiss, *J. Polymer Sci.*, **29**, 425 (1958).

TABLE III
DATA FOR CROSSLINKING ESTIMATES
 $G(X)$ Cross-links formed per 100 e.v.

Temp.	25°	142°
Material		
Marlex-50	1.6 ± 0.4	2.9 ± 0.4
B-3125	0.8	

temperature compared to 142° indicate that reaction 10 is probably more efficient in the solid than in the liquid state. As reaction 10 increases in rate relative to all other reactions, the yields of hydrogen and cross-links will be decreased. As no free radicals remain in the solid at room temperature after irradiation at 142°, either reaction 11b does not occur at 142° or if free radicals are produced, they react so quickly that they cannot be detected. Reactions 9 and 12 are more efficient at 142°, probably because of the greater mobility of the hydrocarbon chains.

To conclude, the evidence seems to indicate that crosslinking can occur (1) by vinylene decay, (2) by radiolytic detachment of hydrogen and (3) by the rearrangement and combination of free radicals subsequent to hydrogen detachment. Decay of vinyl and vinylidene groups promotes gelation by increase of \bar{M}_w .

The much larger decrease in vinylidene groups than crosslinks formed in low density polyethylene is a strong indication that these groups occur near the end of the hydrocarbon chains.

E. Comparison with Results of Others.—Considering that Lawton, Balwit and Powell¹³ apparently pre-irradiated their polyethylene samples lightly before beginning their irradiation experiments and neglected changes in vinyl group concentration, their results are in reasonable agreement with those of this paper wherever comparable. An extensive investigation of the radiolysis of polyethylene also was carried out by Schumacher³² at 10 and 80°. His $G(H_2)$ and $G(VI)$ values, 2.5 and 1.25, are smaller than those reported here, probably due to the difficult dosimetry method used by him.

After this paper had been accepted, Dr. W. B. Reynolds of the Phillips Petroleum Co. kindly sent to us their estimate of the weight average molecular weight for the sample of Marlex-50 used in our research (their designation, Marlex 6000 Type 9). Their value of 156,000 for \bar{M}_w is about twice the value of Tung used above, and when used to calculate $G(X)$ gave 0.5 and 1.2 at room temperature and 142° respectively. As a consequence, material balance no longer exists and no difference in this respect can now be seen between the linear and branched polyethylenes. We must assume, therefore, that intramolecular as well as intermolecular bonds formed during the irradiation, and to a greater extent at 142° than at room temperature, $G(R.L.)$ being 1.9 and 1.1 as calculated by difference at the two temperatures in the case of Marlex-50. This is reasonable.

Acknowledgments.—This research was supported by the U. S. Atomic Energy Commission. We are grateful to the Phillips Petroleum Co. for the continued gift of materials.

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(32) K. Schumacher, *Kolloid Z.*, **157** 16 (1958).