The Radiation Chemistry of Polyethylene. IX. Temperature Coefficient of Cross-Linking and Other Effects[1]

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Abstract: A study has been made of the temperature coefficient over the range 35–120° of the following radiation chemical processes that occur during the γ-ray irradiation of polyethylene: hydrogen evolution, formation of cross-links, chain scission, vinylene double-bond and conjugated-diene formation, and vinyl decay. To calculate cross-links from gel–dose data, use has been made of the Charlesby–Pinner function as modified for a Wesslau molecular weight distribution. Good agreement of the data with the resulting equations is obtained in the case of the initial slope and general shape of the $s + s^{1/2}$ *vs.* dose curve. Deviations at high doses are shown quantitatively to be related to vinylene decay; thus for the first time definite evidence of change of $G(\mathrm{X})$ with dose has been obtained. $G(\mathrm{X})$ at zero dose is almost independent of temperature, but at the highest dose studied, 27 Mrads, $G(\mathrm{X})$ increases significantly with temperature. Hydrogen yields increase slightly with temperature, but at the highest temperature, 120°, $G(\mathrm{H_2})$ is practically independent of dose. Material balance is realized to ±0.2 G unit at 35° and to ±0.1 at 120° both at zero and 27-Mrad dose. However, to obtain material balance, it is necessary to consider diene G values and their variation with dose. G values for both diene and vinylene unsaturation are independent of temperature. It is shown that conflicting results of earlier wokers are due to failure to extract completely the soluble fraction of the irradiated sample and to oxidative chain degradation occurring subsequent to the irradiation because of the presence on exposure to air of unreacted free radicals.

Recently there has been a renewed interest in the temperature coefficient of radiation effects in polyethylene. Turner[3] measured the extent of gel formed in Marlex-50 polyethylene at various doses of electron-beam irradiation at 25 and −196° and concluded from parallel plots of the Charlesby–Pinner[4] function, $s + s^{1/2}$, as a function of reciprocal dose where s is the fraction of sol content that the cross-linking efficiency was nearly the same at the two temperatures. This was a rather surprising result inasmuch as in his review of earlier work Chapiro[5] pointed out that below −50° $G(\mathrm{X})$ was constant with temperature, but above −50° the yield of cross-links rose steadily with temperature. $G(\mathrm{X})$ is the number of cross-links produced per 100 ev of energy absorbed. A more extensive study of the temperature coefficient of the irradiation cross-linking of polyethylene in various physical states has been carried out by Kitamaru and Mandelkern[6,7] and the latter authors with Fatou.[8] They concluded that at room temperature and up to 90° cross-linking is more efficient in the noncrystalline state, but that at 90 to 100° a drastic change occurs and cross-linking becomes more efficient in the crystalline than in the amorphous state by about a factor of 2. In the low-temperature range, *i.e.*, below 70°, they found a decreased efficiency of cross-linking in oriented (fibrous) samples as compared to bulk polyethylene. Their results for all solid samples showed an increase of $G(\mathrm{X})$ with temperature. In a related investigation Salovey and Falconer[9] studied the products produced by both electron-beam and γ-ray irradiation of *n*-hexadecane in the solid state at 4° and the liquid state at 19°. Lowering the temperature of the solid to −80 and −196° decreased G(dimer) from 2.30 at 4° to 2.01 and 1.23, respectively. In the liquid state G(dimer) was 2.60, slightly greater than in the solid. Product molecules of lower molecular weight than the parent were twice as abundant for the liquid irradiation than for irradiation of solid *n*-hexane, thus demonstrating that chain scission was more pronounced in the liquid than in the solid state. In Turner's work mentioned above,[3] there seemed to be more chain scission in the case of irradiation at −196° than at room temperature.

With all of these rather diverse results it appeared worthwhile to reinvestigate cross-linking in polyethylene, especially over the temperature range room temperature to 140°. However, to determine reliable cross-linking yields it is necessary to adopt sound experimental techniques and to develop and use theoretically valid equations in the calculations. The major experimental difficulties which have not always been recognized or overcome in the past are chain degradation due to postirradiation oxidation and failure to remove completely sol from gel when the gel method is used to determine $G(\mathrm{X})$. Theoretical difficulties are also twofold: namely, the necessity of correcting for chain scission and the requirement of knowing the initial molecular weight distribution. As explained below we have used in this work new theoretical expressions based on the Wesslau[10] molecular weight distribution equation which enable us to determine simultaneously $G(\mathrm{X})$ and $G(\mathrm{S})$, the G value for scissions. In addition, several crucial steps in the experimental techniques have been carefully verified.

With regard to increased degradation due to postirradiation oxidation and the concomitant increase of

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[1] Paper VIII of this series: D. M. Bodily and M. Dole, *J. Chem. Phys.*, **45**, 1433 (1966).

[2] On leave from the Department of Mathematics, Faculty of Engineering, Chuo University, Tokyo, Japan.

[3] D. T. Turner, *J. Polymer Sci.*, **B1**, 101 (1962).

[4] A. Charlesby and S. H. Pinner, *Proc. Roy. Soc.* (London), **A269**, 367 (1959).

[5] A. Chapiro, "Radiation Chemistry of Polymeric Systems," Interscience Publishers, Inc., New York, N. Y., 1962, p 418.

[6] R. Kitamaru and L. Mandelkern, *J. Polymer Sci.*, **B2**, 1019 (1964).

[7] R. Kitamaru and L. Mandelkern, *J. Am. Chem. Soc.*, **86**, 3529 (1964).

[8] R. Kitamaru, L. Mandelkern, and J. Fatou, *J. Polmer Sci.*, **B2**, 511 (1964).

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

[10] H. Wesslau, *Makromol. Chem.*, **20**, 111 (1956).

the sol fraction, Chapiro[11] pointed out the necessity of eliminating free radicals that might be trapped in crystalline regions of the irradiated polymer before exposure to air. Oxidation of these free radicals causes chain scission.[12] Turner[3] repeatedly melted his Marlex-50 polyethylene *in vacuo* after irradiation to remove the free radicals. Mandelkern and co-workers[6-8] opened their irradiated samples without annealing to air 24 hr after the irradiation, but, as demonstrated below, this technique leads to more degradation and a lower gel content than if the free radicals are eliminated by annealing *in vacuo* after the irradiation. We believe that radiation–chemical reactions have not terminated until all free radicals have coupled or undergone disproportionation. Such complete termination is especially important in the comparison of cross-linking at different temperatures or between samples of different physical states because the free radicals might react completely, *i.e.*, terminate, in some cases or react with oxygen and produce degradation in others.

In all previous investigations it has been assumed (whenever an assumption was necessary) that the G value for cross-linking was independent of dose. We have found, however, that agreement between experiment and theory is obtained if allowance is made for an increase of G(X) with dose. The latter can be related quantitatively to decay of vinylene unsaturation.

Finally, it should be noted as has been done before that the extent of cross-linking of polyethylene cannot be measured experimentally by any known method presently available at temperatures where the uncross-linked material is insoluble. Thus, samples irradiated at room or liquid nitrogen temperature must be heated to 90° or higher before the extent of cross-linking can be estimated. In this connection it should be pointed out that Yu and Wall[13] studied chain scissions due to irradiations in a 1:1 ethylene–propylene copolymer by measuring stress relaxation at room and higher temperatures. In the case of a strained amorphous network, the stress relaxation depends only on the number of scissions produced by the irradiation and is independent of the number of cross-links introduced into the sample by the irradiation. They demonstrated that the G value for scissions, G(S), was independent of dose and varied little with temperature. However, their estimated value of G(X), 4.70, seems inordinately high and should be confirmed by independent means before the absolute accuracy of the stress relaxation method can be established.

Experimental Section

Materials. Marlex-6002 polyethylene film, 10.5 mils thick, was used as received throughout the course of this work. Its measured density was 0.962 at 15°, crystallinity 75–80%, weight- and number-average molecular weights (as supplied by the manufacturer) 230,000 and 20,000, respectively. The vinylene content was not detectable and the vinyl group concentration was 7.75×10^{-5} mole g^{-1}. The polyethylene also contained a small amount of a phenolic-type antioxidant, but our experience has been that the presence of an antioxidant has a negligible effect on the products of radiolysis. One experiment was done using a carefully annealed sample (see Table I).

Radiation Source and Cell. The radiation source was the same Co^{60} γ-ray source as used in previous studies in this laboratory.[14] The γ-ray intensity as measured by the ferrous sulfate dosimeter was 0.55 and 0.49 Mrad hr^{-1} in the two channels of the irradiation cell. The polyethylene samples were inserted into Pyrex glass tubes and evacuated for 48 hr before sealing. The glass tubes were then placed into the channels of a solid copper block whose temperature was maintained and controlled to ±1° by means of a heater, thermocouple, and a Leeds & Northrup Speedomax H temperature controller.

Table I. Comparison of Gel Fractions Obtained by Different Extraction Methods (Dose 7.3 Mrads)

Sample	Irrad temp,[a] °C	Pre-extraction and annealing treatment	Gel fraction obtained by Soxhlet, 24 hr	Gel fraction obtained by Boiling xylene to const wt
Marlex-6002 6002	RT	Exposed to air for 3 days	0.30	0.31
	RT	140° *in vacuo* for 2 hr	0.53	0.42
	120	Exposed to air for 3 days	0.57	0.49
	120	140° *in vacuo* for 2 hr	0.57	0.50
Preannealed[b] Marlex-6002	RT	Exposed to air for 3 days	0.10	0.03
	RT	140° *in vacuo* for 2 hr	0.43	0.35
	120	Exposed to air for 3 days	0.60	0.52

[a] RT = room temperature. [b] Sample was annealed before irradiation as follows: heated to 140° for 1 day then cooled at the rate of 10°/day until it reached 30°.

Hydrogen Yields. After irradiation and before annealing, the gaseous product was pumped off of the sample and measured in a Toepler–McLeod combination pump and gauge. A cold finger at −196° was used to trap out hydrocarbon products before measuring the hydrogen yield.

Oxidation Products. Oxidation of the polyethylene on exposure to air after the irradiations was monitored qualitatively by observing the growth or absence of the infrared absorption band at 1725 cm^{-1}.

Vinylene Growth and Vinyl Decay. Changes in the vinylene and vinyl double-bond concentrations were measured by infrared techniques[15] as described before. The films were given the post-irradiation annealing before the infrared spectra were taken.

Determination of Diene Yields. Conjugated diene unsaturation was calculated from the measured absorption at 236-mμ wavelength as previously described by Fallgatter and Dole.[14]

Determination of Gel Content. Inasmuch as correct gel data are essential for a reliable discussion of cross-linking, we shall describe here in some detail the techniques which we have used to measure the gel content. The residual soluble component of the irradiated polymer was extracted by immersing the sample in boiling xylene with the polymer held in a 100-mesh stainless-steel basket. The boiling xylene contained 0.5 to 1% of 2,6-di-*t*-butyl-*p*-cresol as antioxidant. The procedure adopted by us was to extract for 24 hr, dry under vacuum for 12 to 18 hr, weigh, extract in fresh solvent for 12 hr, dry for 12 to 18 hr, weigh, and repeat this process until the weight became constant. Tests showed that after a 12-hr drying period further drying produced no change of weight. Our data also indicated that for samples containing a high gel content a 24-hr extraction time was insufficient to remove all of the sol especially when the polymer samples were immersed in liquid xylene condensate of a Soxhlet extractor.[6] We have found that the temperature of the liquid xylene condensate is only about 90°; thus there is considerable doubt whether or not 24 hr of extraction time is sufficient. The data of Table I demonstrate that less sol was extracted by the 24-hr Soxhlet method than by the method of extracting until a constant residual weight was attained.

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(11) See ref 5, p 417.

(12) H. Fischer, *J. Polymer Sci.*, **A1**, 2109 (1963).

(13) H. Yu and L. A. Wall, *J. Phys. Chem.*, **69**, 2072 (1965).

(14) M. B. Fallgatter and M. Dole, *ibid.*, **68**, 1988 (1964).

(15) M. Dole, D. C. Milner, and T. F. Williams, *J. Am. Chem. Soc.*, **80**, 1580 (1958).

Table II. Effect of Postirradiation Treatment on Measured Gel Fractions

Irrad temp,[a] °C	Dose, Mrads	Annealing conditions Temp, °C	Annealing conditions Time, hr	No. of days 0	1	2	3	4	>10
				Fraction of gel content after exposure to air subsequent to annealing					
RT	7.3	25	0	0.38					0.30
RT	7.3	60	12	0.45					0.40
RT	7.3	80	24	0.45					0.40
RT	7.3	95	24	0.45					0.45
RT	7.3	120	12	0.45					0.45
RT	7.3	140	2	0.45					0.45
RT	7.3	25	2(CH_3SH)	0.37				0.34	
RT	8.7	25	0	0.47	0.44	0.40			0.41
RT	8.7	80	2	0.47	0.45	0.41	0.41		0.41
RT	8.7	110	2	0.57	0.58	0.56	0.56		0.55
RT	8.7	140	2	0.56		0.57			0.57
120	27	25	2(CH_3SH)	0.89				0.88	
120	27	140	2	0.91				0.91	
120	13.5	25	0	0.73				0.71	
120	13.5	25	2(CH_3SH)	0.72				0.71	
120	13.5	140	2	0.75				0.75	

[a] RT = room temperature. When the sample was irradiated at room temperature, it was found that at the end of the irradiation the temperature of the copper block was 35°.

An important problem in gel determination has to do with elimination of free radicals before exposure to air. As the free radicals react, more gel is produced, but, if the free radicals are not eliminated before exposure to air, the resulting oxidation causes chain degradation and less gel. Geymer[16] eliminated free radicals in irradiated polypropylene by exposure of the irradiated sample to methyl mercaptan vapor. We tried this technique with polyethylene, but without success (see Table II), probably because of the high crystallinity of the sample. In Table II, the symbol 2(CH_3SH) stands for 2-hr exposure to methyl mercaptan vapor at 1 atm pressure. The methyl mercaptan treatment did not eliminate the oxidative degradation of the polyethylene on exposure of the irradiated sample to air. In the case of all of the samples of Table II in which the gel content decreased on exposure to air, infrared measurements confirmed our conclusion that postirradiation oxidation had occurred.

The data of Table II demonstrate that annealing the irradiated sample *in vacuo* at 140° or irradiation at 120° eliminated the subsequent reduction in gel content on exposure to air at room temperature. Infrared measurements also verified the fact that no postirradiation oxidation had occurred in these cases. We believe that to obtain meaningful comparison of the effect of irradiation temperature on cross-linking, as measured by gel fraction determinations, it is essential that all free radicals be eliminated by annealing *in vacuo* before exposure to air and before making the gel measurements. Otherwise postirradiation chain degradation will occur in the case of the low-temperature irradiations but not in the case of irradiations carried out at higher temperatures, and a false conclusion of more efficient cross-linking at the higher temperatures would be deduced.

Results

A. Hydrogen Yield. The $G(H_2)$ values at different irradiation temperatures and different doses are tabulated in Table III. As can be seen from the data in the table and from Figure 1a, $G(H_2)$ increases gradually with temperature from 35 to 120°. A large increase in $G(H_2)$ occurs on passing to the liquid state at 140°. Previously[17] we had observed that in the case of Marlex-50 polyethylene $G(H_2)$ decreased with an increase of dose for irradiations at room temperature. This observation was confirmed by the present work (Figure 1b), but the effect becomes smaller the higher the irradiation temperature. At 120° $G(H_2)$ is practically constant with dose (Figure 1b). The data plotted in Figure 1a are $G(H_2)$ values extrapolated to zero dose.

Table III. The Effect of Irradiation Temperature on the $G(H_2)$ Values of Marlex-6002 Polyethylene G Values[a]

Dose, Mrads	$G(H_2)$ values at irradiation temperature RT	60°	80°	100°	120°
0	(3.68)	(3.73)	(3.81)	(4.05)	(4.11)
0.5	3.69	3.70	3.95	4.04	4.14
1.5	...	...	...	4.02	4.10
2.5	3.50	3.69	3.73	4.02	4.06
3.7	3.51	3.69	3.78	4.05	4.09
5.0	3.50	3.67	3.76	4.06	4.10
6.1	3.36	...	3.68	...	...
7.5	3.47	3.51	3.68	4.02	4.06
12.5	3.26	3.52	3.68	4.01	4.08
25.0	3.27	3.44	3.53	3.94	4.01

[a] The G values are average values of two to four determinations. Values in parentheses are values estimated for zero dose.

B. Vinyl Decay. Decay of vinyl unsaturation (Vi), as a function of dose at different irradiation temperatures, is plotted in Figure 2 according to a first-order decay law, and the first-order decay constants are tabulated in Table IV. The value of k_1 at 35° can be compared with 1.6×10^{-21} g ev^{-1} found by Williams and Dole[18] for room-temperature irradiations and the value at 120°, 1.7×10^{-21}, with Williams and Dole's value of 2.1×10^{-21} g ev^{-1} for irradiations at 142° in the liquid state.

Table IV. First-Order Decay Constants k_1 and G Values Extrapolated to Zero Dose for Vinyl Decay and Doses to the Gel Point

Irrad Temp, °C	k_1, g ev^{-1} $\times 10^{21}$	$G°(-Vi)$	r_g, Mrads, from Figure 4	r_g, Mrads, from Figure 5
35	1.3	6.1	2.65	2.59
80	1.5	7.0	2.40	2.45
100	1.7	7.9	2.30	2.38
120	1.7	7.9	2.20	2.20

C. Vinylene Unsaturation. Changes in *trans*-vinylene (Vl) concentration are plotted in Figure 3 according to the zero-order growth and first-order decay law

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(16) D. O. Geymer, *Makromol. Chem.*, **100**, 186 (1967).

(17) M. Dole, F. Williams, and A. J. Arvia, *Proc. U. N. Intern. Conf. Peaceful Uses At. Energy, 2nd, Geneva*, **1958**, 29, 171 (1958).

(18) F. Williams and M. Dole, *J. Am. Chem. Soc.*, **81**, 2919 (1959).

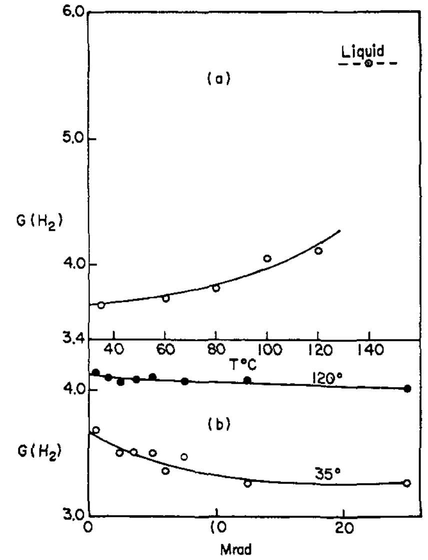

Figure 1. (a) Hydrogen G values as a function of temperature and at zero dose. (b) Hydrogen G values as a function of dose at 35 and 120°.

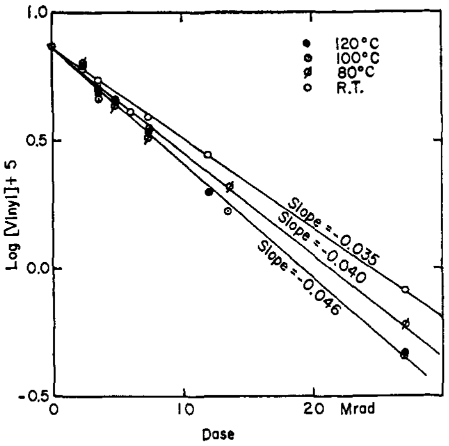

Figure 2. First-order plot of vinyl decay at different temperatures.

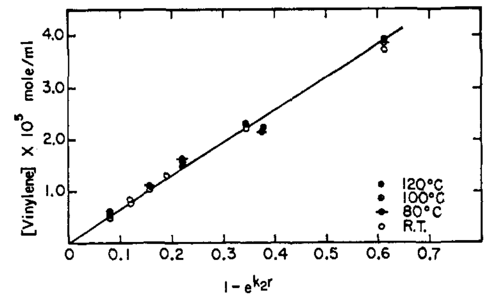

Figure 3. Zero-order vinylene growth and first-order vinylene decay law[15] at different temperatures.

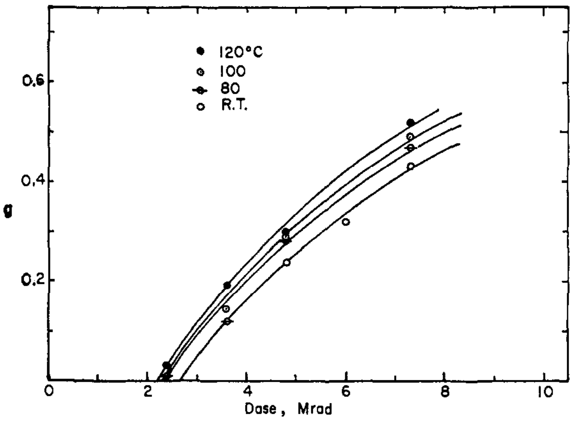

Figure 4. Gel-dose curves at different temperatures.

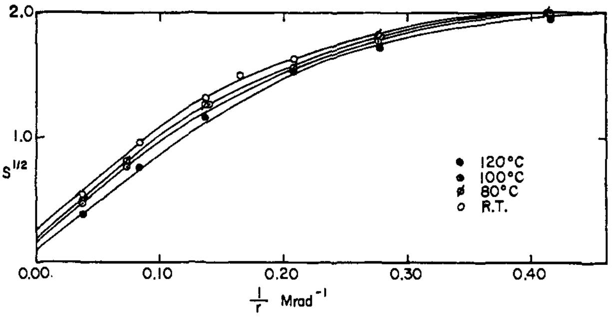

Figure 5. Charlesby-Pinner function for polyethylene at different temperatures plotted as a function of reciprocal dose.

previously found by Dole, Milner, and Williams[15] to be valid for the formation and destruction by irradiation of the vinylene groups in polyethylene.

Within the accuracy of the experiments the linear law seems to be valid at all temperatures studied with growth and decay constants independent of temperature. The first-order decay constant was calculated to be 0.56×10^{-21} g ev^{-1} compared to 0.52×10^{-21} found by Williams and Dole[18] at room temperature, but the latter result was obtained on unannealed films. Williams and Dole found k_2 to be 0.64×10^{-21} for irradiations in the liquid state at 142°. The G value for vinylene formation extrapolated to zero dose is 2.4 at all temperatures in the solid state. Others have found G(Vl) to be independent of temperature.[19]

D. Cross-Linking. Gel data at low doses at different temperatures are plotted in Figure 4 where the effect of temperature on the dose to the gel point, r_g, can be readily seen. The intercept on the abscissa at zero gel is the value of r_g. Another way of determining r_g is to extrapolate the Charlesby-Pinner function,[4] $s + s^{1/2}$, where s is the sol fraction, plotted as a function of reciprocal dose, $1/r$, to a value of $s + s^{1/2}$ equal to 2. Such a plot is shown in Figure 5 where it can be seen that, owing to the small angle with which $s + s^{1/2}$ approaches the value of 2, this method is not very satisfactory. Nevertheless, r_g values estimated by both methods are given in Table IV for comparison.

To calculate G values for cross-linking and scission, it is first necessary to find some theoretical function involving both chain scission and cross-linking yields with which the gel-sol data can be shown to agree. In Figure 6 we have plotted the sol data, as expressed by the Charlesby-Pinner function, in terms of a normalized reciprocal dose, r_g/r, for four different irradiation temperatures. The dotted lines represent the Charlesby-Pinner function as originally derived by these authors[4] for an initial random molecular weight distribution and for a ratio of chain scissions to cross-links, G(S)/G(X) or λ, equal to 0 and 0.2. The solid lines repre-

(19) See ref 5, p 412.

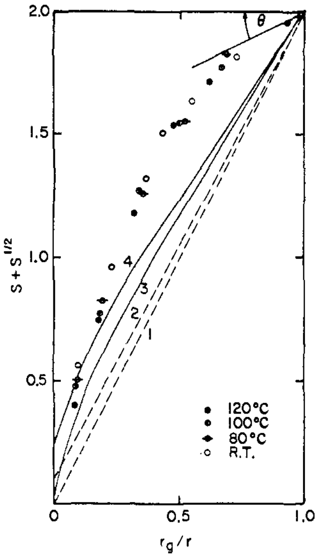

Figure 6. Normalized Charlesby–Pinner plot: curves 1 and 2 for a random molecular weight distribution for λ equal to 0 and 0.2, respectively; curves 3 and 4 for a Schulz–Zimm distribution as derived by Inokuti[20] for λ equal to 0 and 0.5, respectively, and for M_w/M_n equal to 11.5.

sent the Charlesby–Pinner function derived by Inokuti for an initial molecular weight distribution, called by Inokuti[20] a generalized Poisson-type (similar to the distribution of Schulz–Zimm[21,22]), and were calculated for the case of $M_{w,0}/M_{n,0}$ equal to 11.5 and λ equal to 0 and 0.5. Apparently no choice of these parameters would bring about a fit between theory and observation. Accordingly a new theoretical treatment was carried out[23] based on the original work of Saito[24] and similar to that of Inokuti, but using Wesslau's molecular weight distribution function,[10] which is known to give a better description of the molecular weight distribution in linear polyethylene than the generalized Poisson distribution. Wesslau's equation is

$$m(P) = \frac{1}{\beta\sqrt{\pi}P^2}\exp -\frac{1}{\beta^2}\left(\ln\frac{P}{P_0}\right)^2 \qquad (1)$$

where the parameter β is defined by the equation

$$M_{w,0}/M_{n,0} = \exp(\beta^2/2) \qquad (2)$$

$M_{w,0}$ and $M_{n,0}$ are the initial weight- and number-average molecular weights, respectively, and P is the degree of polymerization. $m(P)$, the number of polymer molecules at zero dose per structural unit with degree of polymerization P and P_0, is defined by the expression

$$P_0 = P_n(0)\exp(\beta^2/4) \qquad (3)$$

where $P_n(0)$ is the number-average degree of polymerization at zero dose.

The starting point in the theoretical treatment, details of which will be published later,[23] is the equation

$$g - 1 = \left.\frac{\partial G}{\partial z}\right|_{z = 2gt} \qquad (4)$$

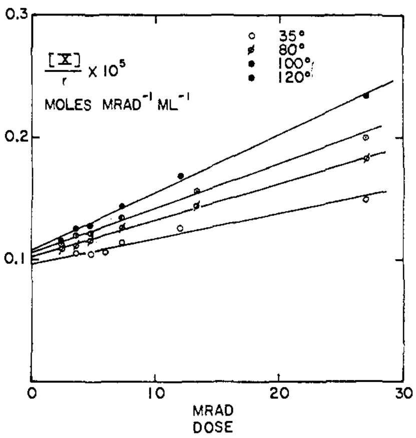

Figure 7. Cross-link–dose ratios as a function of dose at four different temperatures.

where

$$\begin{aligned} G &= \int_0^\infty m(P,\tau)e^{-zP}\,\mathrm{d}P\ (z \geq 0) \\ &= [1/(z+\tau)^2]\{[(2z\tau + \tau^2)/P_n(0)] + \tau^2(z+\tau) + z^2G_0(z+\tau)\} \end{aligned} \qquad (5)$$

G_0 is the Laplace transform of the initial molecular weight distribution, *i.e.*

$$G_0 = \int_0^\infty m(P,0)e^{-zP}\,\mathrm{d}P\ (z \geq 0) \qquad (6)$$

Equation 4 is eq 49 of Saito[24] while eq 6 is eq 45 of Saito. Equation 5 is eq 7 of Inokuti.[20]

In these equations g is the gel fraction, t is the number of cross-links per monomer unit, τ is the number of scissions per monomer unit ($\dot{c}R$ and $\dot{r}R$ in Saito's terminology[24] and $q_0r/2$ and p_0r in Charlesby and Pinner's,[4] respectively).

In terms of the Wesslau distribution, eq 5 becomes

$$\begin{aligned} g - 1 = &-\left(\frac{2g}{2g+\lambda}\right)^2\frac{e^{-\beta^2/4}}{\beta\sqrt{\pi}}\int_0^\infty \exp\left[-\left(\frac{\ln \xi}{\beta}\right)^2 - (2g+\lambda)T\xi\right]\mathrm{d}\xi + \frac{4g\lambda}{(2g+\lambda)^3}\frac{e^{-\beta^2/4}}{T\beta\sqrt{\pi}}\int_0^\infty \frac{1}{\xi} \times \\ &\exp\left[-\left(\frac{\ln \xi}{\beta}\right)^2 - (2g+\lambda)T\xi\right]\mathrm{d}\xi - \frac{4g\lambda e^{-\beta^2/4}}{(2g+\lambda)^3T} - \frac{\lambda^2}{(2g+\lambda)^2} \end{aligned} \qquad (7)$$

where $\xi = [P/P_n(0)]e^{\beta^2/4}$ and $T = y\exp(-\beta^2/4)$. y is the number of cross-links per initial number-average molecule and β has been defined above.

Making use of the experimental value of β equal to 2.2, eq 7 was solved by means of computer programs for a number of g–T pairs and for various values of λ. From these T values the corresponding y's and hence the total cross-links per milliliter could be calculated for the set of different g values. A large scale plot of [X], the cross-links per milliliter, as a function of g was made keeping λ constant, and the values of [X] were read off at the experimentally measured gel fractions. It was found that [X]/r was a linear function of r at the different temperatures as illustrated in Figure 7. On the basis of this treatment, the number of

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(20) M. Inokuti, *J. Chem. Phys.*, **38**, 2999 (1963).
(21) G. V. Schulz, *Z. Physik. Chem.*, **B43**, 25 (1939); **B44**, 227 (1939).
(22) B. H. Zimm, *J. Chem. Phys.*, **16**, 1099 (1948).
(23) O. Saito, H. Y. Kang, and M. Dole, submitted for publication.
(24) O. Saito, *J. Phys. Soc. Japan*, **13**, 198, 1451 (1958).

cross-links formed is a quadratic function of the dose. It turns out that $[X]/r \times 10^6$ is almost exactly equal to $G(X)$ when r is expressed in Mrads; hence the rise of $[X]/r$ with dose illustrates how the G value for cross-linking increases with the dose. The linear relations of Figure 7 can be expressed by an equation of the form

$$[X]/r = a_0 + a_1 r \tag{8}$$

where a_0 and a_1 are empirical constants.

In this calculation, however, there is a serious inconsistency. We have assumed λ, which is $G(S)/G(X)$, to be constant, yet we have just demonstrated that $G(X)$ itself is not constant with dose. There is no reason to believe that $G(S)$ varies with dose; in fact, there is good reason to believe that it may be constant with dose.[13] Hence we must write for λ

$$\lambda = \frac{b_0}{a_0 + a_1 r} \tag{9}$$

where b_0 is an empirical constant.

At low doses λ approaches b_0/a_0, and, if λ and a_0 are known, b_0 can be calculated. We have obtained the best agreement by taking λ to be 0.20 at 35°. Then knowing b_0, a_0, and a_1, λ can be calculated at high doses. With the new value of λ at each dose, a new value of [X] is obtained for each measured gel fraction by means of the master curves mentioned above, and a second $[X]/r$ *vs.* dose plot made. Actually, it is this second approximation which is illustrated in Figure 7. With the new a_0 and a_1 values of the second approximation, b_0 can be calculated again and the whole process repeated. It was found that a third approximation made a negligible change in the calculated cross-link concentrations. We have collected in Table V the finally selected λ values at each dose and temperature.

Table V. Calculated λ Values: $\lambda = G(S)/G(X)$

Dose, Mrads	λ values			
	35°	80°	100°	120°
0 (extrap. values)	0.20	0.24	0.24	0.24
2.4		0.22	0.22	0.22
3.6	0.20	0.21	0.21	0.21
4.8[a]	0.20	0.20	0.20	0.20
6.0	0.20			
7.3	0.19	0.19	0.18	0.18
12	0.17			0.15
13.5		0.16	0.15	
27	0.15	0.15	0.15	0.15

[a] The b_0 value of eq 9 was calculated from λ taken to be 0.20 at a dose of 4.8 Mrads at each temperature.

Table VI contains values for the empirical constants of eq 9 and G values for cross-linking and chain scission extrapolated to zero dose.

Table VI. Empirical Constants of Eq 9 and G values for Cross-Linking and Chain Scission Extrapolated to Zero Dose

Temp, °C	a_0	a_1	$G_0(X)$	$G_0(S)$
35	0.096	0.0021	0.96	0.192
80	0.102	0.003	1.02	0.245
100	0.105	0.0036	1.05	0.252
120	0.108	0.0046	1.08	0.259

Discussion

The first deduction of interest from the new theory is that the slope of the Charlesby–Pinner function, $s + s^{1/2}$, plotted as a function of the normalized dose, r_g/r, at the gel point, $(\tan \theta)_g$, where θ is the angle indicated in Figure 6, is given by the general equation

$$(\tan \theta)_g = \frac{\lambda(4K - 4 + \lambda)}{4(2 - 2K - \lambda)} \tag{10}$$

where

$$K = \int_0^\infty Pm(P, 0)e^{-\lambda t_g P} \mathrm{d}P \tag{11}$$

In the case of a random molecular weight distribution, $M_{w,0}/M_{n,0}$ equal to 2, the Charlesby–Pinner equation yields the simple expression

$$\tan \theta = 2 - (\lambda/2) \tag{12}$$

Incidentally, eq 12 illustrates the well-known deduction[24] that λ cannot be greater than 4 for gel to be formed.

For the Schulz–Zimm distribution

$$K = (1 + \lambda y_g/\sigma)^{-\sigma - 1} \tag{13}$$

where σ is defined by the eq 14

$$\sigma = 1/[(M_{w,0}/M_{n,0}) - 1] \tag{14}$$

and for the Wesslau

$$K = \frac{e^{-\beta^2/4}}{\beta\sqrt{\pi}} \int_0^\infty \exp\,[-(\ln \xi/\beta)^2 - \lambda y_g \xi e^{-\beta^2/4}]\mathrm{d}\xi \tag{15}$$

When λ is equal to zero, the Schulz–Zimm and Wesslau distributions yield the simple expressions

$$\text{Schulz–Zimm:} \quad \tan \theta = 3/(2 - M_{n,0}/M_{w,0}) \tag{16}$$

$$\text{Wesslau:} \quad \tan \theta = 3M_{n,0}/M_{w,0} \tag{17}$$

For the polyethylene samples used in this work, the calculated values of θ for the random Schulz–Zimm and Wesslau distributions are at $\lambda = 0.2$, 62.25, 57.5, and 20.1°, respectively. The observed value was 16° and agrees, therefore, much better with the predictions of the Wesslau distribution than with that of either the Schulz–Zimm or the random distribution. A computer routine was used in making these calculations.

A further test of the new theory can be made by plotting values of the Charlesby–Pinner function, $s + s^{1/2}$, as taken from the values tabulated by Saito and Kang[23] for the case of the Wesslau distribution as a function of the normalized dose, r_g/r, and by comparing the theoretical curves with the experimental. This has been done in Figure 8 where the three theoretical curves are for λ equal to 0, 0.2, and 0.4. It is evident that much better agreement exists between theory and experiment in the case of Figure 8 than in Figure 6. However, the agreement is still not perfect, especially at the higher doses where the experimentally determined gel fractions are higher than theoretically predicted. This observation suggested to us that $G(X)$ was not constant with dose which, indeed, is the conclusion already expressed by eq 8 and Figure 7.

From a chemical standpoint $G(X)$ might also be expected to increase with dose provided that vinylene double bonds decay to form cross-links. A further

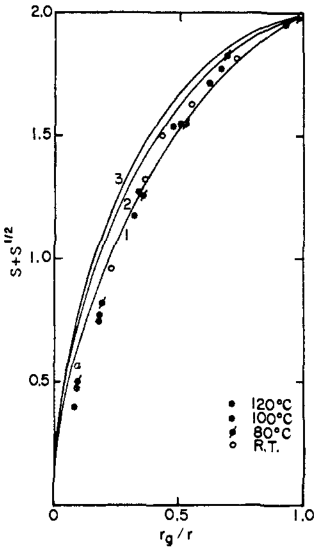

Figure 8. Normalized Charlesby–Pinner plot. Curves 1, 2, and 3 are the theoretical curves based on the Wesslau distribution for λ equal to 0, 0.2, and 0.4, respectively, and for M_w/M_n equal to 11.5.

test of the validity of the calculated $G(X)$ values given in Table VI can be based on the requirements of material balance. Providing that no evolved hydrogen back-reacts with primary free radicals or vinyl groups, that no unmeasured cross-links, *i.e.*, no intramolecular cross-links are formed, and that no residual free radicals remain, the following material balance equation should be valid.

$$G(H_2) = G(X) + G(t\text{-Vl}) + 2G(\text{diene}) \qquad (18)$$

It is assumed that trienes and higher polyenes were negligible at the doses used in this work. Table VII contains values for the right-hand side and left-hand side of eq 18 at two temperatures and at doses of 27 and 0 Mrads. Very good material balance is seen to have been obtained; these results strengthen our conclusion that $G(X)$ increases with dose.

Table VII. Material Balance in the Radiation Chemistry of Polyethylene

Dose, Mrads	$G(X)$	$G(t\text{-Vl})$	$2G$ (diene)	Sum	$G(H_2)$
		At 35°			
0	1.0	2.4	0.5	3.9	3.7
27	1.5	1.4	0.3	3.2	3.3
		At 120°			
0	1.1	2.4	0.5	4.0	4.1
27	2.3	1.4	0.3	4.0	4.0

It is interesting to note that at zero dose there is practically no temperature coefficient of cross-linking. However, at the dose of 27 Mrads, $G(X)$ at 120° is significantly higher than $G(X)$ at 35°. Inasmuch as $G(t\text{-Vl})$ and $G(\text{diene})$ are both independent of temperature, although dependent on the dose (integral G values are tabulated in Table VII), the difference in $G(X)$ at 27 Mrads at 35 and 120° is seen to be due to the decrease in $G(H_2)$ with dose at 35°. As demonstrated by the data of Figure 1, $G(H_2)$ is practically independent of dose at 120°. We can postulate, therefore, that the smaller value of $G(X)$ at 35° as compared to 120° at the dose of 27 Mrads results from a back-reaction of molecular hydrogen with trapped free radicals according to the mechanism

$$R\cdot + H_2 \longrightarrow RH + H \qquad (19)$$

$$R\cdot + H \longrightarrow RH \qquad (20)$$

Dole and Cracco[25,26] demonstrated by means of D–H exchange and esr studies the possibility of reactions 19 and 20. From Table I it will be noted that in the case of the preannealed sample of Marlex-6002 (during the annealing, the film collapsed to a thicker mass) the gel fraction produced at 120° was practically the same as in the case of the original film, 0.52 as compared to 0.50, but that at 35° the gel fraction was lower, 0.35 as compared to 0.42. Presumably the hydrogen could escape less readily from the thicker more crystalline annealed sample, thereby promoting reactions 19 and 20. Williams and Dole[18] found that the hydrogen yield was greatly reduced when the polyethylene film was held strongly between aluminum plates on both sides, but not when it adhered strongly only to one aluminum plate.

The achievement of material balance demonstrates that we now know quantitatively the major chemical events that occur during the γ-ray radiolysis of polyethylene in the solid over the temperature region 35 to 120°. Other chemical events occur, but they apparently have only a minor influence on irradiation intermolecular cross-linking, if any. Such events are the decay of vinyl groups, chain scission, and intramolecular cross-linking (not evident in this work). The mechanism by which diene groups decay is not known, but the total addition to $G(X)$ due to diene decay is only 0.2. This assumes that each diene group decays to two cross-links which are measured as such by the gel measurements. This is probably not strictly true, yet the whole effect is small.

Acknowledgments. This research was supported by the U. S. Atomic Energy Commission and the Advanced Research Projects Agency of the Department of Defense through the Northwestern University Materials Research Center. Thanks are due to Dr. James A. Reid of the Phillips Petroleum Company for the sample of polyethylene used and information on its properties. The A.E.C. Code No. COO-1088-23 is assigned to this paper.

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