

## Gel Formation in Polymers Undergoing Radiation-Induced Crosslinking and Scission

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### Synopsis

A study was made of the solubility of irradiated polyethylene. The experimental data were treated according to the Saito-Inokuti theory for gel formation in polymers exposed to ionizing radiation. Among other things, this theory is based upon the molecular weight distribution of the unirradiated polymer; in the present work, the actual distributions were determined by high-temperature gel permeation chromatography and corrected for long-chain branching. Under these circumstances, good agreement between theory and experimental data was obtained, which allowed the determination of the radiation yield of main-chain scission and crosslinking.

### INTRODUCTION

Several published papers have discussed theories for describing the formation of three-dimensional networks produced by the effect of ionizing radiation on polymers. It is the purpose of the present paper to interpret these works in the light of new data on polyethylene molecular weight distributions and to test the practical and theoretical value of a model for the radiation crosslinking of polyethylene based on more general molecular weight distribution functions such as the one published by Miltz and Ram.<sup>12</sup>

Prominent among the theories are those advanced by Charlesby,<sup>1</sup> Saito,<sup>2,3</sup> Inokuti,<sup>4,5</sup> and Saito, Kang, and Dole.<sup>6,7,8</sup>

Charlesby developed a theory for the gel formation in a crosslinked polymer as a function of the crosslinking density that should be valid for a polymer that has any molecular weight distribution (MWD) and does not undergo scission. The resulting general equation takes the form of an infinite series but reduces to a simple analytical expression for three distributions: uniform (monodisperse), random, and pseudorandom.

Charlesby and Pinner<sup>1,9</sup> applied this theory to irradiated polymers with an initial random distribution and arrived at the following equation:

$$S + \sqrt{S} = \frac{1}{2P_n r k} + \frac{\lambda}{2}; t = kr \quad (1)$$

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The Charlesby-Pinner plot of  $(S + \sqrt{S})$ , where  $S$  is the soluble fraction, versus the reciprocal of the dose  $r$  in Mrads has an ordinate intercept of  $\lambda/2$ , where  $\lambda$  is the ratio of the probability of scission to that of crosslinking,  $t$  is the number of crosslinks per monomer unit,  $P_n$  is the number-average degree of polymerization, and  $k$  is a proportionality constant. These authors assumed that scission and crosslinking are independent processes and that the probabilities for the two events are constant with dose. At the same time, they assumed that all chain units have the same probability for scission and crosslinking. In developing this formula, they did not take the formation of intramolecular crosslinks and endlinking into account. If  $P_n$  is known, the slope yields the number of crosslinks per monomer unit per Mrad; this is proportional to the radiation yield of crosslinks,  $G(X)$ , the number of crosslinked units per 100 eV of absorbed energy. When combined with  $\lambda$ ,  $G(X)$  can be used to determine  $G(S)$ , which is the number of scissions per 100 eV of absorbed energy.

The computational difficulties associated with the use of the general Charlesby-Pinner equation limited the application of the theory and led to the alternative theory of Saito,<sup>2,3</sup> which has the advantage of greater computational ease.

Inokuti<sup>5</sup> extended the Saito theory to include simultaneous crosslinking and scission. His expression for the sol fraction is given in eq. (2):

$$1 - g = \frac{1}{z^3} \left( \frac{4\tau t g}{P_n} + \tau^2 z - 4t g G_0(z, P) - 4t^2 g^2 z \frac{\delta G_0(z, P)}{\delta(z)} \right) \quad (2)$$

where

$$G_0(z, P) = \int_0^\infty n(P) e^{-zP} dP$$

and

$$z = 2tg + \tau$$

where  $g$  is the gel fraction,  $\tau$  is the number of scissions per monomer unit, and  $P$  is the degree of polymerization of a narrow number fraction,  $n(P)dP$ .

At present, this modification of the Saito equations provides the best basis for the interpretation of gel-dose data, but one must bear in mind that its limitations are the same as those discussed above for the Charlesby-Pinner model.

Inokuti applied his equations to distributions of the generalized Poisson type on the assumption that such distributions are more often encountered in practice than uniform or random ones.

Kang, Saito, and Dole<sup>6</sup> found that this assumption did not lead to satisfactory agreement with results based on a wide range of data on the radiation crosslinking of polyethylene.

They observed that the substitution of the Wesslau molecular weight distribution<sup>10</sup> into Inokuti's equations gave a much better fit to some polyethylene data. The Wesslau distribution is given by the following equation:

$$W(P) = \frac{1}{P\beta\sqrt{\pi}} \exp\left(-\frac{1}{\beta^2} \ln^2 \frac{P}{P_0}\right) \quad (3)$$

where

$$P_0 = \sqrt{P_w P_n} \text{ and } \beta = \sqrt{2 \ln P_w / P_n}$$

They also pointed out that it might be necessary to take into account the change in the radiation yields for crosslinking with changes in dose and temperature, and they provided experimental data for that purpose.

In references 7 and 15, results of their calculations are presented in a table showing the relationship between gel fraction and the density of crosslinks as a function of  $\beta$  and  $\lambda$ . A plot of values from this table is presented in Figure 1, where the gel fraction is plotted versus  $y$ , the number of crosslinks per number-average molecule divided by  $y_g$ , the value of  $y$  at the incipient gel point.

We have extended this work using polyethylene samples whose molecular weight distributions were determined by gel permeation chromatography and by the application of more general distribution functions.

## EXPERIMENTAL

### Characterization of Polymers

Three additive-free low-density polyethylene samples, Alkathene 401 and 334, supplied by Maersk Kemi, Copenhagen, Denmark, and DFDS 6600, supplied by Unifoss, Stenungssund, Sweden, were used in this investigation. Relevant data concerning these polymers are included in Table II.

Molecular weight distributions (MWD) were measured by high-temperature gel permeation chromatography and reduced for long-chain branching following

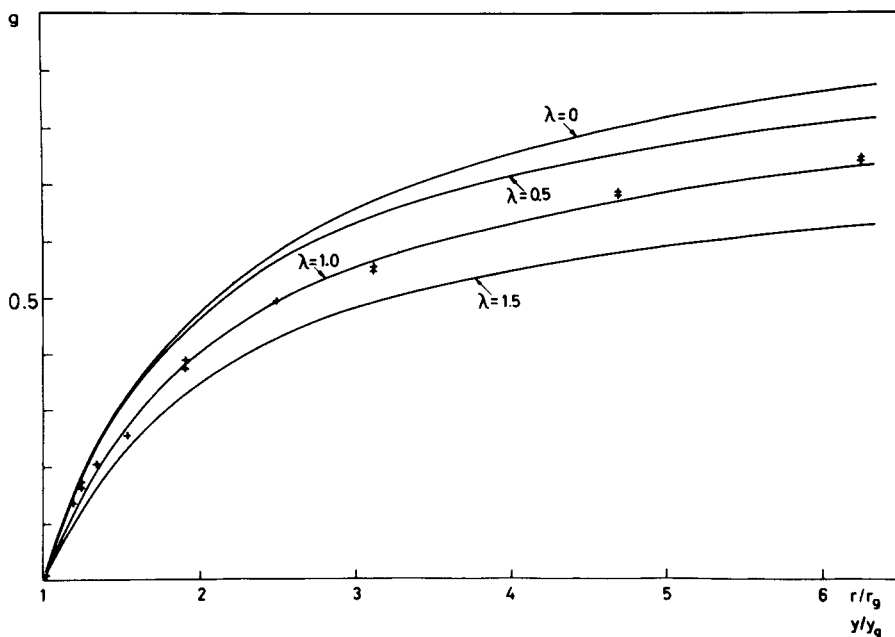


Fig. 1. Solid lines: correlation between  $y$  and  $g$  from table in ref. 7,  $\beta = 1.5$ ; (+) DFDS-6600 experimental values for gel content ( $r_g = 3.2$  Mrad).

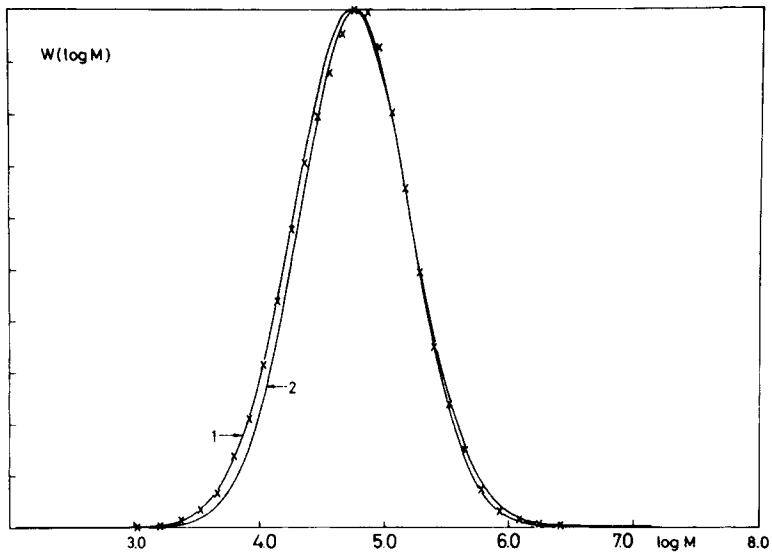


Fig. 2. (x) experimental MWD for DFDS 6600; (1) Wesslau distribution; (2) Miltz-Ram distribution.

the method of Drott and Mendelson.<sup>13,14</sup> The results are presented in Figures 2, 3, and 4. The molecular weight averages are given in Table I. In the case of Alkathene 401,  $M_n$  and  $M_w$  were also determined by cryoscopy and light scattering. The measured values of 30,000 and 500,000 are in good agreement with those obtained from the GPC data.

### Irradiation and Gel Determination

The polymers were irradiated with 10-MeV electrons from a pulsed electron accelerator equipped with a 40-cm scanner; the average dose rate was 1 Mrad/sec.

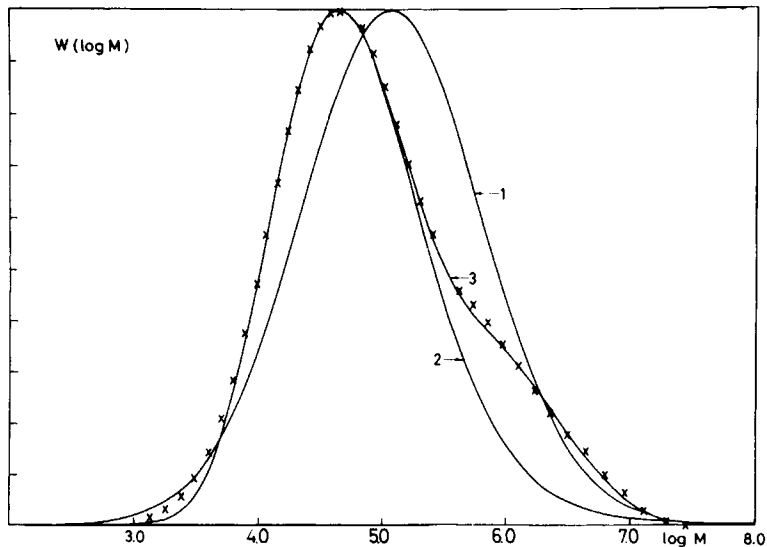


Fig. 3. (x) experimental MWD for Alkathene 401; (1) Wesslau distribution; (2) Miltz-Ram distribution; (3) five-parameter function.

TABLE I  
 $M_n$  and  $M_w$  for Alkathene 401, 334, and DFDS 6600 Determined by GPC, Compared to  $M_n$  and  $M_w$  Calculated from the Fitted Distribution Functions<sup>a</sup>

	Alkathene 401		Alkathene 334		DFDS 6600	
	HT-GPC	Fitted value	HT-GPC	Fitted value	HT-GPC	Fitted value
$M_n$	29.5	31.0	30.3	35.0	31.2	35.1
$M_w$	505	516	251	231	99	96

<sup>a</sup> All values in the table are multiplied by  $10^{-3}$ .

Dosimetry was carried out by calorimetry. The polymers were irradiated as pellets, average diameter 4 mm, supplied by the manufacturer and packed in a nitrogen atmosphere in polyethylene bags. No attempt was made to control the temperature of the samples during irradiation, the increase in temperature being less than 50°C. After irradiation, they were annealed at 100°C for 24 hr under vacuum. No free radicals could be detected by ESR measurements after this treatment.

The gel fraction was determined by Soxhlet extraction in a manner designed to extract all soluble polymer without introducing new scissions into the three-dimensional network. An insulated Soxhlet extractor with a glass filter thimble was used for extraction with boiling xylene. The temperature in the extractor was  $138^\circ \pm 1^\circ\text{C}$ . To prevent oxidative degradation of the polymer, all extractions were carried out in a nitrogen atmosphere. The samples were extracted for 72 hr and then dried at 80°C under vacuum to constant weight.

The experimental gel fraction as function of dose for Alkathene 401 is shown in Figure 5.

## DISCUSSION

The radiation data in Figure 9 are presented as a Charlesby-Pinner plot,  $S + \sqrt{S}$  versus  $r_g/r$ , where  $r_g$  is the dose at incipient gel formation. Under the

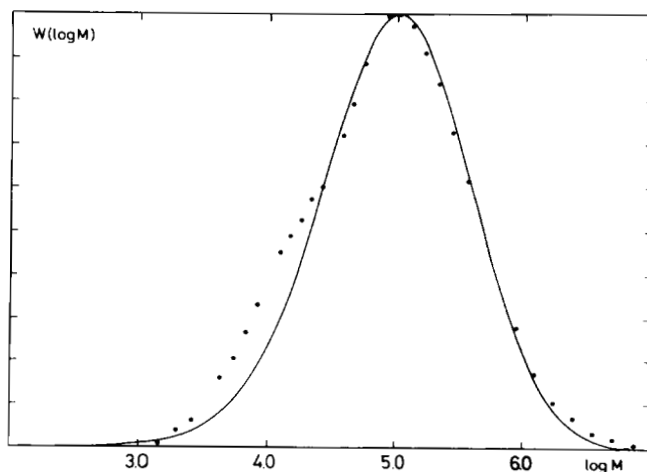


Fig. 4. (•) experimental MWD for Alkathene 334; Solid line, Miltz-Ram distribution.

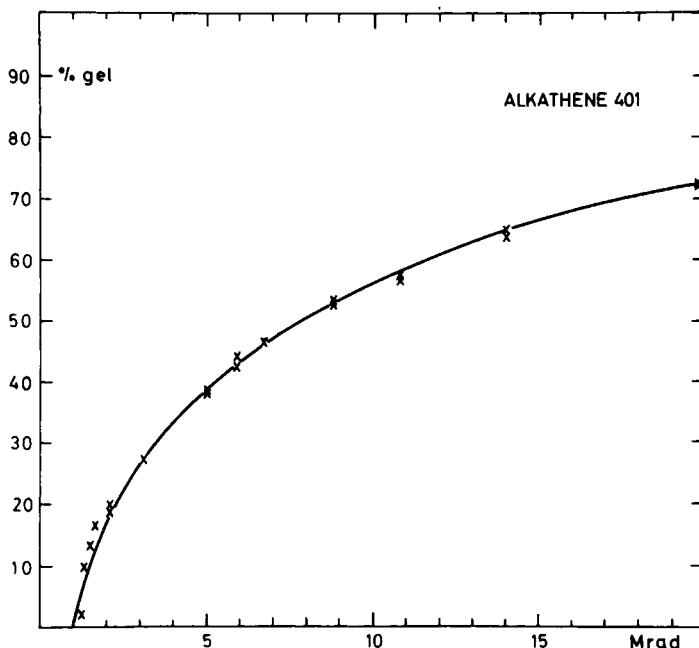


Fig. 5. Gel formation vs. radiation dose for Alkathene 401.

assumptions of the model, the plot should yield a straight line for a polymer with a random MWD. Neither the radiation data for Alkathene 401 nor for DFDS 6600 give a straight line in this plot; in both cases, there is a deviation from the straight line at higher doses. Mitsui et al.<sup>13</sup> suggest that such behavior arises from a system with random MWD which undergoes intramolecular crosslinking, which the Charlesby-Pinner theory does not take into account. However, this explanation seems not to be valid because a formation of intramolecular crosslinks would give less gel than predicted from the Charlesby-Pinner theory, but still not curves shaped like those in Figure 9. It appears that at least one of the principal reasons for the deviation is to be found in the molecular weight distribution.

In Figures 1 and 10, the experimental data are compared with the theory developed by Saito, Kang, and Dole,<sup>7</sup> hereafter referred to as the SKD theory. The correlation between  $g$ , the gel fraction, and  $y$ , the number of crosslinks per number-average molecule, given in reference 7 is used; and  $\beta$ , cf. eq. (3), is chosen in accordance with the GPC data. The solid line represents the SKD values for different values of  $\lambda$ , as indicated. The abscissa is  $r/r_g$  in the case of the experimental values and  $y/y_g$  in the case of the SKD values,  $y_g$  being the value of  $y$  at the gel point. Experimental data for DFDS 6600 are well represented by the SKD theory for  $\lambda = 1$ , and this allows the calculation of  $G(X)$  from the ratio of  $r/r_g$  to  $y/y_g$ ;  $\lambda$  and  $G(X)$  are presented in Table II. In the case of Alkathene 401, no correlation between calculated and experimental values is obtainable with the SKD theory.

The problems associated with the SKD model in the case of Alkathene 401 might arise from the following facts, which are contradictory to the assumption on which the model is based: (1)  $\lambda$  is not independent of dose, and (2) the Wesslau distribution does not fit the experimental MWD.

TABLE II  
Summarized Experimental Data

Polymer	$\lambda$	$G(X)$	$G(S)$	Incipient gel dose, Mrad	$M_w$ $\times$ $10^{-3}$	$M_n$ $\times$ $10^{-3}$	$M_w/M_n$	Density, g/cm <sup>3</sup>	Melt index, min	LCB <sup>a</sup>
Alkathene 401	0-0.05	1.1	<0.05	1.0	505	29.5	17.1	0.916	20	0.009
Alkathene 334	1	1.8	1.8	2.1	251	30.3	8.3	0.921	0.3	0.004
DFDS 6600	1	2.7	2.7	3.2	99	31.2	3.2	0.922	24	0.001

<sup>a</sup> The number of branch points in a molecule divided by the molecular weight of the molecule.

### The Distribution Function

The Wesslau distribution was developed in 1956 to describe the MWD of high-density polyethylenes of the Ziegler type. There is no experimental evidence to suggest that it can fit low-density polyethylene.

Since Wesslau's work, the advent of GPC has given rise to more detailed examinations of polyethylene MWD. Of particular importance to this paper is the work by Miltz and Ram.<sup>14</sup> Their GPC investigations of low-density polyethylene samples led them to propose the following three-parameter weight distribution function:

$$W(M) = AM^a \exp(-b \ln^c M) \quad (4)$$

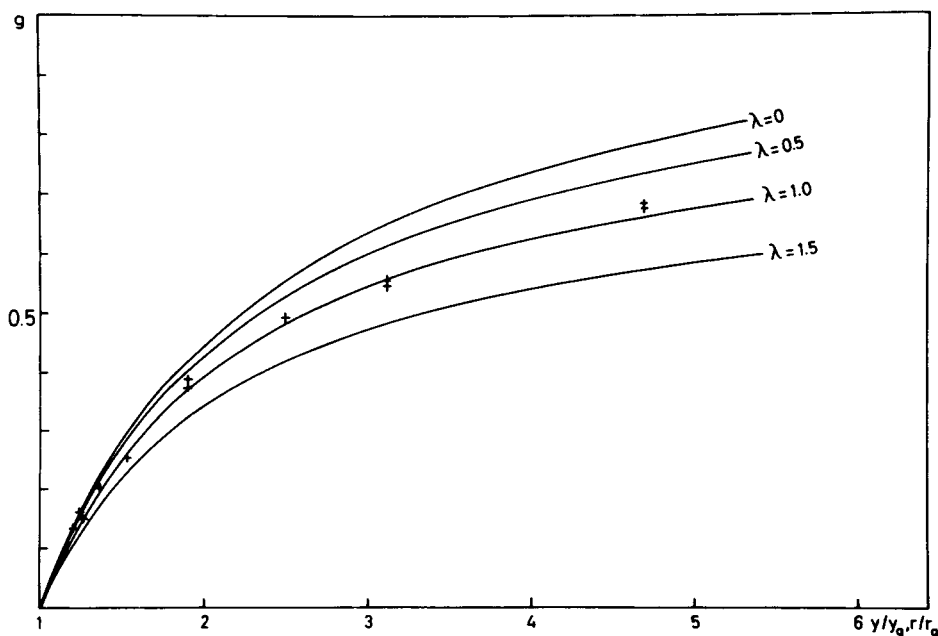


Fig. 6. (+) DFDS 6600, experimental values of gel content ( $r_g = 3.2$  Mrads); solid lines, solution of the Inokuti equation using the five-parameter MWD, for different  $\lambda$  values.

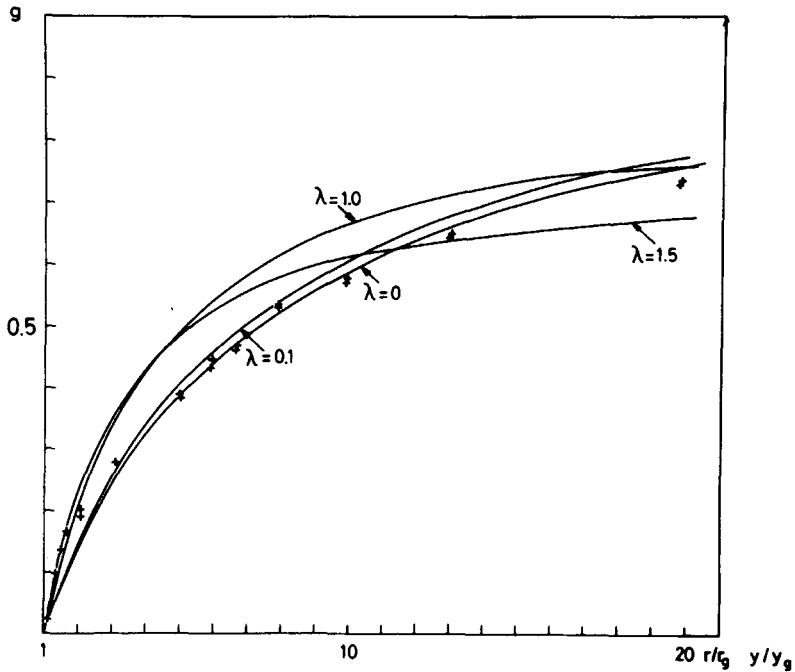


Fig. 7. (+) Alkathene 401, experimental values of gel content ( $r_g = 1.0$  Mrad); solid lines, solution of the Inokuti equation using the five-parameter MWD, for different  $\lambda$  values.

where  $A$  is a normalizing constant and  $M$  is the molecular weight of the weight fraction  $W(M)$ .

An attractive feature of this function is that if  $a = -1$  and  $c = 2$ , it reduces to the Wesslau distribution. Thus, not only does it fit the data for low-density polyethylene, but it may also fit the data for high-density polyethylene as well. If so, it should provide a better basis for the application of the Saito theory as modified by Inokuti.

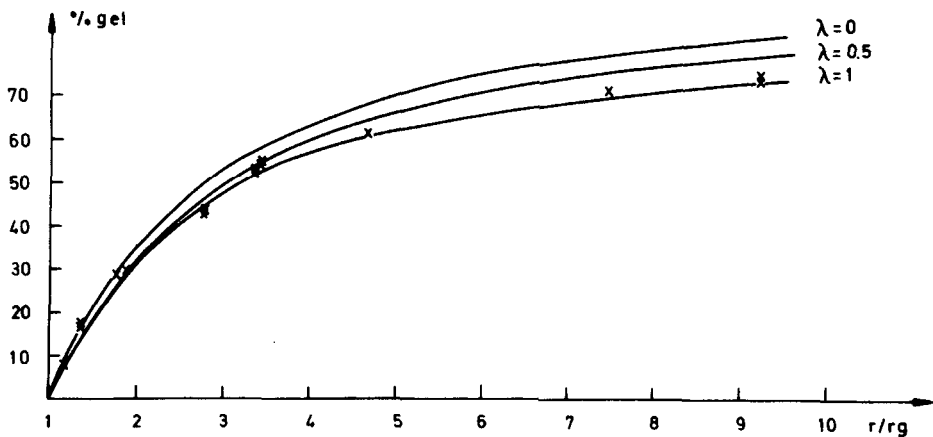


Fig. 8. (X) Alkathene 334, experimental values of gel content ( $r_g = 2.1$  Mrad); solid lines, solution of the Inokuti equation using the Miltz-Ram MWD, for different  $\lambda$  values.



### Theory of Gel-Dose Relationship for Polymers with the Miltz-Ram Distribution

Use of the general expression of Inokuti, eq. (2), on a system undergoing random crosslinking and scission together with the Miltz-Ram MWD leads to the same result as eq. (2), using the following expressions for  $G_0(z,P)$  and  $[\delta G_0(z,P)]/\delta z$ :

$$G_0(z,P) = \int_0^\infty A (28P)^a \exp - [b \ln^c (28P) + zP] dP$$

$$\frac{\delta G_0(z,P)}{\delta z} = - \int_0^\infty AP (28P)^a \exp - [b \ln^c (28P) + zP] dP$$

where  $A$  is determined as  $1/[\delta G_0(z,P)/\delta z]$  for  $z = 0$ , which gives  $G_0(z,P) = -1/P_n$  for  $z = 0$ .

No general numerical solution of eq. (2) could be given in this case because of the complex nature of eq. (4). However, the maximum gel content, i.e., the gel fraction at infinite dose, is independent of the MWD of the unirradiated polymer and depends only on  $\lambda$ , as shown by Inokuti.<sup>4</sup> The relation between the maximum gel content and  $\lambda$  is shown in Figure 11.

### Calculation

In Figures 2, 3, and 4, the MWD based on GPC measurements is compared with the Wesslau and Miltz-Ram distribution function. The plot of  $W(\log M)$

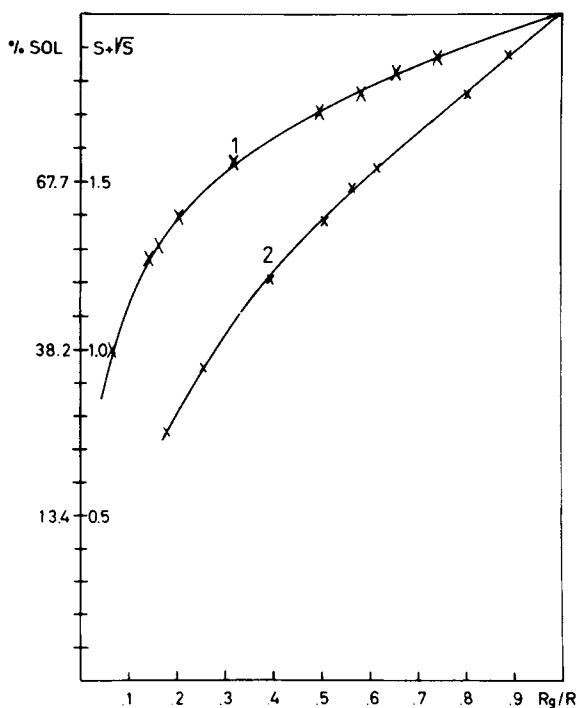


Fig. 9. Charlesby-Pinner plot of gel data for DFDS 6600 (1) and Alkathene 401 (2).

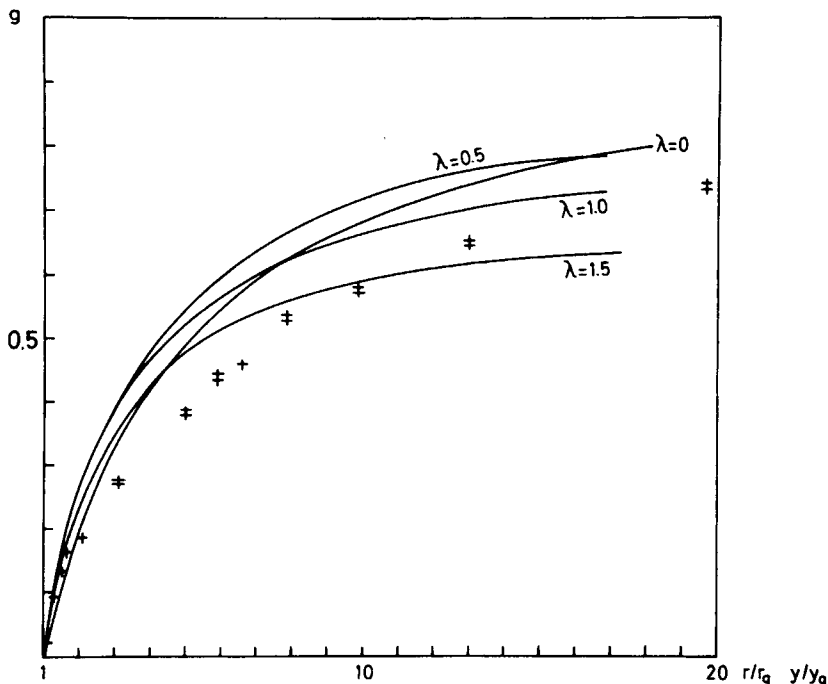


Fig. 10. (+) Alkathene 401, experimental values of gel content ( $r_g = 1.0$  Mrad); solid lines, correlation between  $y$  and  $g$  from table in ref. 7, assuming  $\beta = 2.4$ .

versus  $\log M$  was chosen because of its sensitivity to the high molecular weight fraction, this same sensitivity also being shown by the Inokuti model.

In the case of DFDS 6600 and Alkathene 334, both the Wesslau and the Miltz-Ram distribution functions provide a good fit to the experimental MWD, as shown in Figures 2 and 4. This is not the case with Alkathene 401. Neither the Wesslau nor the Miltz-Ram distribution functions can describe the experimental data. However, as shown in Figure 3, a five-parameter function containing both the Wesslau and the Miltz-Ram expressions can fit the data. This combined MWD was later used to solve eq. (2). Molecular weight averages of these MWD fits are given in Table I.

The mathematical treatment of eq. (2) was carried out as described by Saito, Kang, and Dole,<sup>8</sup> using a Hewlett-Packard 9820 A calculator; calculations were made for different  $\lambda$  values. The result is seen in Figures 6, 7, and 8;  $\lambda$  and  $G(X)$  are assumed to remain constant at radiation doses up to 20 Mrads. Because of the good agreement between gel data and model, this seems to be a valid assumption. This conclusion is in contradiction to that of Kang, Saito, and Dole in reference 6, but the divergence could be due to a difference in the characterization of the unirradiated polymer, as previously mentioned. It should be noted that the calculations described are not only based on the gel formation theory, but include the theory for long-chain branching of PE. The values of  $\lambda$ ,  $G(X)$ , and  $G(S)$  which gave the best fit between the theory and the experimental values of gel fraction versus dose are summarized in Table II together with other pertinent data for the three types of low-density polyethylene investigated here. It seems difficult to establish any conclusive correlations between these data,

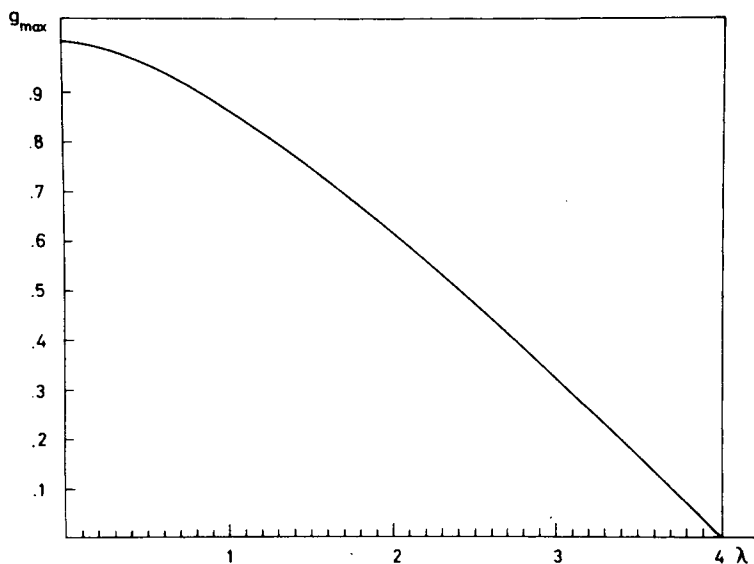


Fig. 11. Maximum gel content  $G_{\max}$ , i.e., the gel fraction at infinite dose, as a function of  $\lambda$ .

except of an expected decrease of the incipient gel dose with an increase of  $M_w$  (or  $M_w/M_n$ ,  $M_n$  being the same for all three samples).

The  $G$  values for crosslinking are rather high compared with most values on the room-temperature irradiation of low-density polyethylene cited in the literature,<sup>9,15</sup> and so are the  $\lambda$  values for Alkathene 334 and DFDS 6600. Also the extremely low value of  $\lambda \leq 0.05$  for Alkathene 401 is remarkable (Table II). This difference may, however, be the result of the way in which similar experimental data previously have been treated in the literature, i.e., mainly according to the Charlesby-Pinner theory, based upon the assumption of a random molecular weight distribution of the polymer. It was shown in this work that this distribution could not describe the actual molecular weight distribution of commercially available polyethylene. There is no reason to believe that the  $G$  values resulting from this investigation should not be correct for the products studied.

## CONCLUSIONS

The apparently good agreement between the experimental data and the modified model presented here leads to the conclusion that the Saito-Inokuti theory for gel formation in polymers exposed to ionizing radiation is useful in its present form for determination of the radiation-chemical yields of crosslinking and scission in commercially available PE, provided the correct MWD of the sample is known.

However, it was impossible to observe any obvious correlation between radiation-chemical data and other available characterizing data concerning the polymers investigated.

Other properties of the polymers, such as degree of unsaturation, short-chain branching, and degree of crystallinity, are known to influence the gel formation and should be included in future investigations.

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