

The Effect of Radiation on the Melt Index of Polyethylene.

II. Effect of Initial Polyethylene Properties*

B. G. HARPER

Organic Basic Research Department, The Dow Chemical Company, Freeport, Texas

INTRODUCTION

The effect of electron irradiation on the melt index of polyethylene was investigated and reported previously.¹ It was found that for a number of different types of polyethylene the melt index changes uniformly with radiation dose and that this change can be represented by the following equation:

$$D = \frac{a+b}{k}x - \frac{b}{2k}x^2 + \frac{2.303}{k} \log \frac{1}{1-x} \quad (1)$$

where D is the radiation dose in Mrad., k , a , and b are constants, and $x = (MI_0 - MI)/MI_0$ represents the degree of change in the melt index. MI_0 is the initial melt index and MI is the melt index at dose D .

The initial properties of polyethylene are reported to influence the nature of the irradiation reaction products. Lawton, Balwit, and Bueche² described the effect of initial molecular weight and found that the higher the molecular weight the lower the dose necessary to produce incipient gelation. Charlesby³ and Baskett⁴ both showed that the initial molecular weight distribution of polyethylene also influences the type of product resulting from irradiation. Lawton, Balwit, and Powell⁵ studied the effect of crystallinity on the properties of irradiated polyethylene and concluded that crosslinking occurs more readily in amorphous polyethylene than in the crystalline polymer. Charlesby, Von Arnin, and Callaghan⁶ also reported on the effect of crystallinity on the radiation effects in polyethylene. They found that the G value for crosslinking is approximately the same in the crystalline as in the amorphous regions of poly-

ethylene. They further concluded that the lower gel dose for the low density amorphous polymer is due to its higher weight-average molecular weight.

It was thought that the effects of some of these initial properties on the crosslinking of polyethylene might be observed from the shapes of melt index-dose curves. The work reported earlier¹ was continued in an effort to see whether this is true.

EXPERIMENTAL

Irradiation

High pressure polyethylene was irradiated in the form of pellets. The pellets were vibrator-fed onto a moving conveyor belt and carried through the electron beam of a General Electric Company resonant transformer electron-beam generator. Both the depth of the layer of pellets and the irradiation dose per pass through the beam could be controlled by adjusting the vibrator feeder and the conveyor rate. In these experiments the depth of the pellet layer was adjusted so that the beam would just penetrate the entire layer. By passing the pellets rapidly through the electron beam and stirring after each pass, the small temperature rise that accompanies radiation was minimized and each pellet received approximately the same uniform dose.

The resonant transformer was operated at 1050 kv. (peak) and 1.0 ma. A description of this radiation equipment appeared in an article in 1953 by Knowlton, Ranftl, and Mahn.⁷

Dose and Melt Index Determinations

Cellophane dye dosimetry was used to determine the dose according to procedures described previously.¹

The melt indices were determined in duplicate according to ASTM Standard D 1238-52T.

* Presented, in abbreviated form, at the Southwest Regional Meeting of the American Chemical Society, December 1960.

Materials

The high pressure polyethylenes used in these experiments were products of The Dow Chemical Company. The types used, along with their initial melt indices and molecular weights, are given in Table I.

TABLE I
Polyethylene Properties

Sample	MI_0	\bar{M}_v	\bar{M}_w^a
410M	1.45	42,400	Not available
510E	1.98	31,200	1,500,000
610M	5.28	27,400	918,000
500E	2.24	33,900	760,000
700M	7.09	29,500	600,000
900M	19.23	24,100	630,000
550E	1.96	26,800	270,000
770M	8.04	24,600	230,000
990M	17.70	21,500	154,000

^a Typical values from light scattering.

RESULTS AND DISCUSSION

Nine different types of high pressure polyethylene were irradiated, each at various doses, and their melt indices determined as a function of dose. The curves obtained by plotting melt index versus dose are of the same general form as those reported earlier.¹ A typical melt index-dose curve is shown in Figure 1. Equation (1) fits the data for all of these different types of polyethylene. The constants for these equations were determined with the use of an IBM 650 computer and are given in Table II.

In Figure 2 are shown the changes in $(MI_0 - MI)/MI_0$ with dose for all nine types of polyethylene, and the agreement between the data points and the calculated curves.

It is obvious from the curves in Figure 2 and from the molecular weight data in Table I that the melt index changes more rapidly with radiation dose for high molecular weight than for the low molecular

TABLE II
Constants of Equation (1)

Sample	k	a	b
410M	0.944	-1.876	1.912
510E	0.445	-2.865	2.704
610M	0.763	-2.925	4.214
500E	1.219	-0.695	2.600
700M	0.962	-2.726	5.239
900M	0.846	-2.182	5.361
550E	0.388	-2.379	3.268
770M	1.045	1.039	4.023
990M	0.493	-1.334	4.298

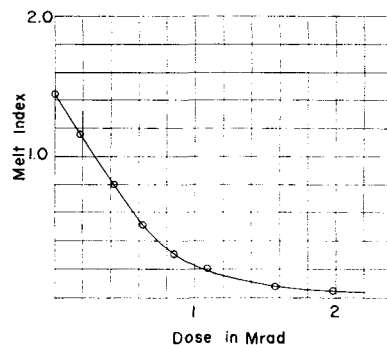


Fig. 1. Typical curve of melt index vs. dose for high pressure polyethylene.

weight samples. It is not apparent, however, whether any quantitative relationship exists between these factors.

The initial slope of either the MI -dose curve or the curve of $(MI_0 - MI)/MI_0$ versus dose, however, can be quantitatively related to the initial properties of the polyethylene, and is easy to determine.

The initial slope of the MI -dose curve may be derived as follows. The differential form of eq. (1) is

$$\frac{dx}{dD} = \frac{k(1-x)}{1+a(1-x)+b(1-x)^2} \quad (2)$$

where

$$x = (MI_0 - MI)/MI_0 = 1 - (MI/MI_0)$$

so that

$$\begin{aligned} \frac{dMI}{dD} &= \frac{-dMI}{MI_0 dD} \\ &= \frac{k(MI/MI_0)}{1+a(MI/MI_0)+b(MI/MI_0)^2} \end{aligned}$$

or

$$\frac{dMI}{dD} = \frac{k(MI)}{1+a(MI/MI_0)+b(MI/MI_0)^2}$$

Thus at $D = 0$, $MI = MI_0$, and

$$\frac{dMI}{dD} = \frac{k(MI_0)}{1+a+b} \quad (3)$$

For the curve of $(MI_0 - MI)/MI_0$ versus dose, the initial slope from eq. (2) is

$$dx/dD = k/(1+a+b) \quad (4)$$

Attempts were made to relate the initial slope of the MI -dose curve to the initial molecular

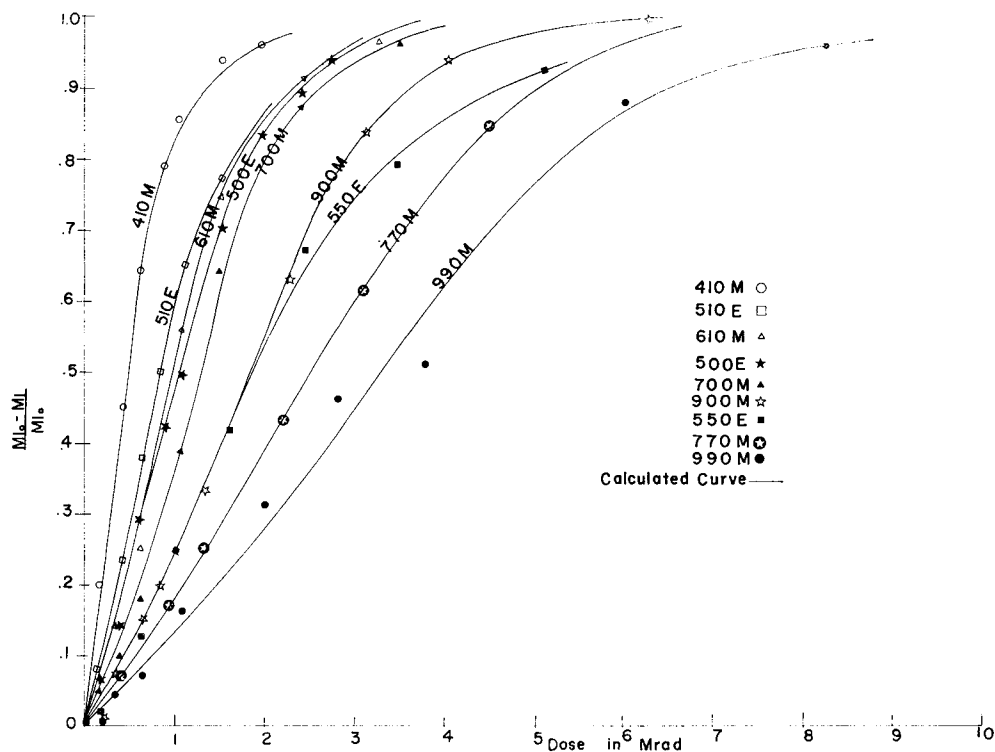


Fig. 2. $(MI_0 - MI)/MI_0$ vs. dose for nine types of high pressure polyethylene.

weight of the polyethylene. No relationship was found. This is not surprising since the expression (3) for the initial slope includes the initial melt index term.

It was found, however, that the initial slope of the curves of $(MI_0 - MI)/MI_0$ versus dose is related to both the weight-average and the viscosity-average molecular weights. Table III gives the initial slope of these curves for each type of polyethylene. Figures 3 and 4 show these slopes plotted versus viscosity-average and weight-average molecular weights, respectively.

It is apparent from these curves that the shape of the melt index-dose curves is controlled to some

extent by initial molecular weight of the polyethylene being irradiated. There is, however, considerable scatter in the points on the curves, which makes the curves of limited usefulness in predicting molecular weight. All the samples used in these experiments are high pressure polyethylene prepared by very similar processes. They were so chosen in the hopes that they would have similar molecular weight distributions. It is unlikely, however, that the distributions would be identical, and perhaps the scatter in these points is due to differences in molecular weight distributions.

The crystallinities of these samples, as determined by x-ray diffraction, are listed in Table IV.

TABLE III
Initial Slopes of Curves in Figure 2

Sample	$k/(1 + a + b)$
410M	0.91
510E	0.44
610M	0.33
500E	0.42
700M	0.27
900M	0.20
550E	0.21
770M	0.17
990M	0.12

TABLE IV
Crystallinity of Polyethylene Samples

Sample	Crystallinity, %
410M	67.7
510E	68.5
610M	68.9
500E	69.3
700M	70.1
900M	70.3
550E	72.0
770M	71.5
990M	72.6

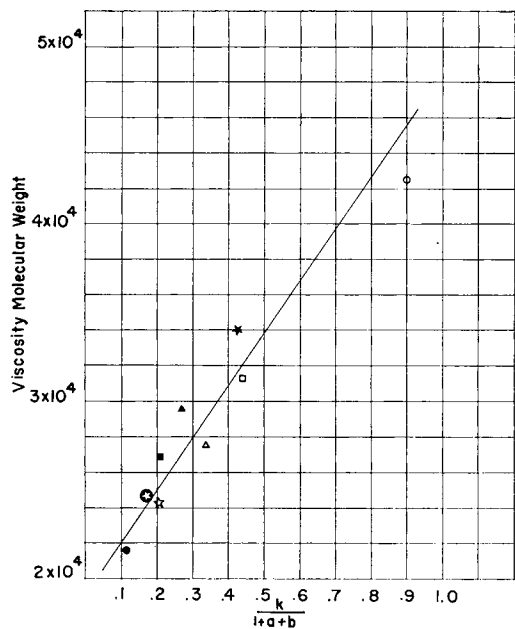


Fig. 3. Relationship between the initial viscosity-average molecular weight and the initial slope of the curve of $(MI_0 - MI)/MI_0$ versus dose.

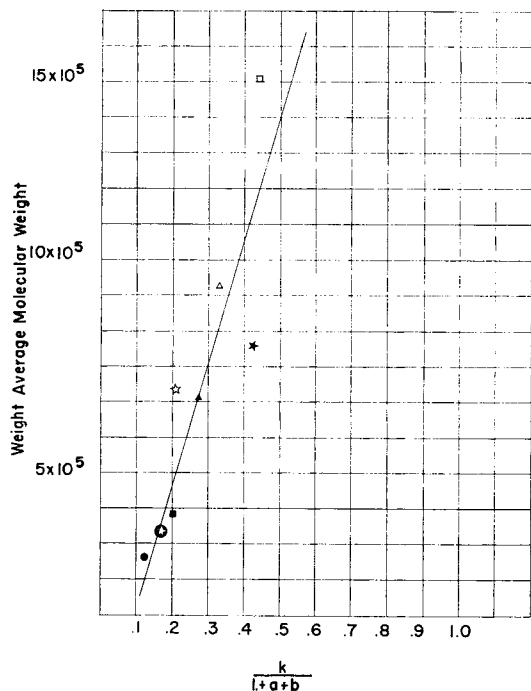


Fig. 4. Relationship between the initial weight-average molecular weight and the initial slope of the curve of $(MI_c - MI)/MI_0$ versus dose.

Crystallinity was found to vary uniformly with the initial slope of the curve of $(MI_0 - MI)/MI_0$ versus dose. A plot of the reciprocal of the initial slopes versus crystallinity is shown in Figure 5.

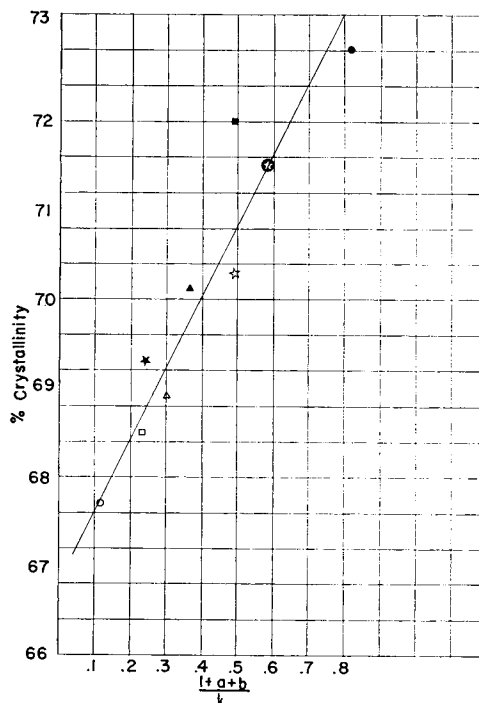


Fig. 5. Relationship between the initial crystallinity and the initial slope of the curve of $(MI_0 - MI)/MI_0$ versus dose.

The crystallinities of these samples were not determined until late in this investigation, and much to our chagrin we found them to vary approximately inversely with the molecular weight.

CONCLUSIONS

These results show that the melt index of polyethylene is lowered uniformly by increasing irradiation doses. This effect can be defined by a single equation for all types of polyethylene studied. The properties of the polyethylene influence the shape of these curves such that the initial slope of the curve of $(MI_0 - MI)/MI_0$ versus dose is proportional to either the molecular weight or the crystallinity of high pressure polyethylene. Because of an approximately inverse relationship between the molecular weight and the crystallinity of the samples studied, it was not possible to conclude at present which property has the controlling influence.

Thanks are due to J. H. Brown, Jr., Director of this Laboratory, for his suggestions and advice. Thanks are also due to E. F. Sablatura for the melt index determinations, and to D. R. Peterson for crystallinity determinations.

References

1. Harper, B. G., *J. Appl. Polymer Sci.*, **2**, 363 (1959).
2. Lawton, E. J., J. S. Balwit, and J. A. M. Bueche, *Ind. Eng. Chem.*, **32**, 1703 (1954).
3. Charlesby, A., talk delivered to the Royal Society of London, February 4, 1954.
4. Baskett, A. C., *Ricerca Sci.*, **25A**, 379 (1955).
5. Lawton, E. J., J. S. Balwit, and R. S. Powell, *J. Polymer Sci.*, **32**, 257 (1958).
6. Charlesby, A., F. Von Arnin, and J. L. Callaghan, *Intern. J. Appl. Radiation and Isotopes*, **3**, 226 (1958).
7. Knowlton, J. A., G. R. Mahn, and J. W. Ranftl, *Nucleonics*, **11**, 64 (1953).

Synopsis

Nine different types of polyethylene were irradiated in air and their melt indices determined as a function of radiation dose. Equations were derived which relate the melt index to the dose. The initial slopes of the curves represented by these equations were found to be related to the initial molecular weight and/or the initial crystallinity of the polyethylenes studied. A 1-M.e.v. resonant transformer electron-beam generator was used as a source of radiation and cellophane dye dosimetry was used to determine the radiation dose.

Résumé

9 types différents de polyéthylène ont été irradiés à l'air et leurs indices de fusion ont été déterminés en fonction de la dose d'irradiation. Il en est résulté des équations qui mettent en relation le point de fusion et la dose d'irradiation. On a trouvé que l'inclinaison initiale des courbes représentées par ces équations est fonction du poids moléculaire initial, de la cristallinité initiale des polyéthylènes étudiés, ou des deux à la fois. Un générateur électronique de 1 m.e.v. a été utilisé comme source d'irradiation et la dosimétrie par teinture de cellophane a été employée pour déterminer la dose d'irradiation.

Zusammenfassung

Neun verschiedene Typen von Polyäthylen wurden in Luft bestrahlt und ihre Schmelzindices als Funktion der Bestrahlungsdosis bestimmt. Es wurden Gleichungen für die Beziehung zwischen dem Schmelzindex und der Bestrahlungsdosis abgeleitet. Die Anfangsneigung der durch diese Gleichungen dargestellten Kurven steht im Zusammenhang mit dem Anfangsmolekulargewicht und bzw. oder mit der Anfangskristallinität des untersuchten Polyäthylens. Als Strahlungsquelle wurde ein 1 Mev Resonanztransformator-Elektronenstrahlgenerator und zur Bestimmung der Strahlungsdosis die Cellophanfarbstoffdosimetrie verwendet.