

The Development of Crystallinity and Transparency in Irradiated Polyethylene

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I. INTRODUCTION

Polyethylene is a semicrystalline polymer. Its crystallinity accounts to a large extent for its mechanical strength. Except in the form of very thin films, polyethylene is opaque to light. This opacity is a direct consequence of its crystallinity. For many purposes, it is desirable to obtain transparent polyethylene which retains the good physical properties of ordinary polyethylene. It has been shown that high-energy irradiation of polyethylene reduces the crystallinity and, simultaneously, imparts mechanical properties to the material in some respects that are more desirable.¹ The object of our work was to study the radiation-induced morphological changes in polyethylene which give rise to enhanced transparency.

It has been noted previously^{2,3} that irradiation reduces the opacity of polyethylene. This effect has not been studied in a systematic way except in the work of Rainer et al.;⁴ however, even in this instance only qualitative descriptions were given for the effect of radiation.

The G value for the irradiation crosslinking of polyethylene increases with temperature. Lawton⁵ has given evidence which shows that crosslinks are produced mainly in the amorphous regions. Epstein⁶ and Charlesby⁷ and others, on the other hand, find that the G value for crosslinking is independent of the degree of crystallinity of the irradiated sample. We tend to favor Lawton's arguments. A recent paper by Mandelkern, Roberts, Halpin, and Price⁸ demonstrates the effect of temperature on crosslinking as related to melting point and specific volume. It has been shown by Mandelkern et al., and previously by Hammer et al.,⁹ that the irradiation of polyethylene below the melting point produces a structure which

maintains its spherulite form above the transition temperature. Here it will be shown that, regardless of the mechanism for the increase in G value with temperature, the effect of increasing the irradiation temperature is an increase in the transparency, resulting from changes in the size of the crystallites and spherulites, the rate of crystallization, and also the crystallinity at temperature equilibrium.

The transmission of light through polyethylene films during cooling has been studied by Hawkins and Richards.¹⁰ They related their findings to spherulite formation and the accompanying changes in refractive index. The present paper contains similar studies with the effect of irradiation and final temperature superimposed. Stein¹¹ has measured the temperature dependence of the light-scattering angle during heating and cooling. He found that the size of the scattering center remained constant as the sample was heated from room temperature to temperatures approaching the melting point. The mean square refractive index fluctuation was, however, found to be dependent on the temperature in a manner similar to the dependence of crystallinity on temperature. The scattering center is smaller in size than the spherulite but larger than the crystallite. Baccaredda and Schiavinato¹² have measured the refractive index and degree of crosslinking of pile-irradiated polyethylene. They found that samples irradiated at 140°C. have much lower refractive indices than corresponding specimens irradiated at lower temperature. They attributed this to the fixing action of the radiation on the random configuration of the amorphous phase.

Price¹³ has studied the growth rate of spherulites in Marlex-50 irradiated at 150°C. The melting point of his irradiated samples decreased with increasing dose. The nucleation rate was found to control the growth rate. Equal degrees of

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supercooling resulted in comparable growth rates regardless of dose. Another article by Price¹⁴ shows how a combination of light-scattering and density measurements can yield information concerning size, shape, and number of crystals formed as a function of time during cooling of the polyethylene from above its melting point. The crystallization was stopped at a stage where only 10% of the polymer volume consisted of crystalline material.

Last¹⁵ has shown that marked changes in the transparency of low density polyethylene can be achieved by the use of certain additives (e.g., polypropylene) that serve as nucleating agents. A microscopic examination of the samples with enhanced transparency showed considerably reduced spherulite size as compared to untreated polyethylene. Changes in crystallinity and density were slight. Due to the enhanced nucleation rate, brought about either by addition of nucleating agents, as Last describes, or by a lowering of the crystallization temperature, as found in the present study, the spherulite size is reduced. Last feels that the smaller spherulite size is responsible for the reduction in scattering. Stein¹¹ has found that the low-angle scattering is effected by the spherulites which are several thousand angstroms in diameter and therefore comparable to the wavelength of visible light. For particles small compared with the wavelength of light, the Rayleigh formula is valid and the transmission decreases with the number of scattering centers. For particles with diameters approaching the wavelength of light, the Rayleigh formula is no longer valid. Empirically it is found that a plot of transmission versus particle diameter for ZnO and carbon black samples passes through a minimum at about 0.2μ .¹⁶ A similar effect may be assumed to exist for polyethylene. Evidently under the conditions under which Last performed his experiments on low density polyethylene, the size of the scattering centers achieved by addition of a nucleating agent was on the left side of the minimum. With high density polyethylene the reduction in particle size, by various methods, may result in a reduction in transparency if the final size is on the right side of the minimum ($> \sim 0.2 \mu$).

In the following experimental and discussion sections, it will be shown how particle and spherulite growth from the melt can result in increased transparency. The effect of irradiation and growth temperature on the growth process will also be demonstrated.

II. EXPERIMENTAL PROCEDURE

A. Materials

The polyethylene used in this study consisted for the main part of Marlex 50, series 6000, type-9 5.5-mil film and type-2 20-mil film. The physical and chemical properties of these materials are summarized in a technical information bulletin¹⁷ and in two technical papers.^{18,19} The 5.5-mil Marlex has been found in our laboratory to be about 92% crystalline and to have a crystalline size of 340 Å. The 20-mil material was about 85% crystalline and had a crystalline size of about 240 Å. The specific volumes at 30°C. were 1.046 and 1.056 cm.³/g. for the 5.5-mil and 20-mil material, respectively.

B. Radiation Source and Dosimetry

Electrons with energy of 2 m.e.v. from a Van de Graaff accelerator were used for irradiation of the polyethylene samples. In cases where the samples were about $1/2$ in. diameter, an unfocused beam at a distance of 6 in. was used in order to assure uniform distribution over the stationary sample. When large sheets were irradiated a conveyor was used to pass the sample back and forth under the unfocused scanning electron beam. In both cases, the dose rate was measured by the method of Henley and Richman,²⁰ which makes use of the change in light transmission due to total irradiation dosage impinging on 0.001-in. thick Du Pont MSC-300 light blue cellophane.

C. Light Transmission Measurements

A Bausch and Lomb Spectronic 20 photometer was used in making the light transmission measurements of the polyethylene samples at room temperature. In the preliminary studies the measurements were made at a number of wavelengths covering the visible range of the spectrum.

Measurements were also made at controlled temperatures, in a cell constructed so as to permit observation of the transparency at the temperature of the irradiation, obviating the need to first cool the sample and then subsequently reheat it. With the use of this cell it was possible also to measure (a) the transparency of a sample at any particular temperature as a function of time, and (b) changes in transparency with temperature.

Figure 1 is a schematic diagram of the cell. Sections A, B, and C are copper blocks each of which is separated by transite. The temperature baths D and E serve as heat sinks for sections A and B. Holders F and G carry the polyethylene

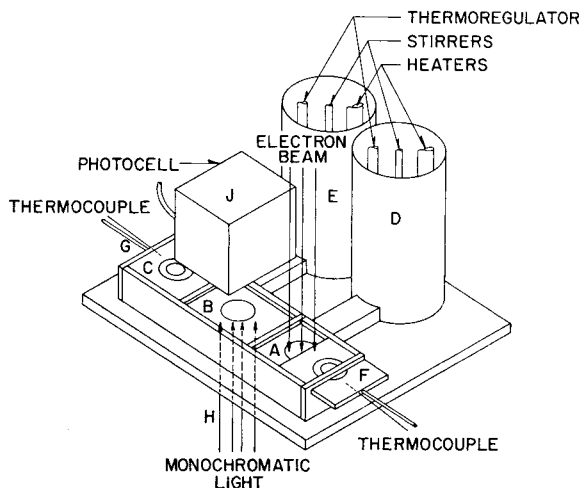


Fig. 1. Irradiation and light transmission apparatus.

samples and slide from A to B and from C to B, respectively. Thermocouples are permanently mounted in F and G and are assumed to give measurements coinciding with the sample temperature. The sample is irradiated in position A at controlled temperature with electrons from a Van de Graaff accelerator. A source of monochromatic light H (modified Bausch and Lomb Spectronic 20) is mounted below B and a photocell J is mounted above. After the irradiation the photocell is placed in position and the spectrometer adjusted for full-scale deflection with no sample in holder G which is dimensionally identical with holder F. The temperature of section B can be held at anywhere from liquid N₂ temperatures to ~150°C., which allow a fair amount of latitude for studying the combined effects of quenching and irradiation on the transparency of the polyethylene. The irradiated sample is then transferred quickly from A to B. The output of the photocell and the thermocouples are recorded automatically, making it convenient to study changes in transparency as functions of time and temperature.

D. Dilatometric Measurements

The measurement of the specific volume of a polyethylene sample over the range between room temperature and well beyond the transition point affords a means of obtaining the melting point and degree of crystallinity of the sample. The average change in specific volume with temperature for a typical sample of polyethylene is 0.002 cm.³/°C. Fairly accurate determinations are therefore required if this technique is to be used to detect

differences in crystallinity due to various irradiation procedures.

The dilatometer consisted of a precision-bore capillary tube with a cup attached at the bottom by means of a ball-and-socket joint. In performing the experiment, a weighed sample was placed in the cup and attached to the vacuum apparatus for degassing for about 24 hr. The sample was heated to and kept in a molten state for 1 hr. during the degassing. Mercury from a reservoir attached to the vacuum system was then allowed to enter the dilatometer through a stopcock to a height slightly above a reference mark on the capillary. (Prior calibration was necessary in order to obtain the volume between the bottom of the cup and the reference mark and also the diameter of the capillary in the undistorted portion above the reference mark.) The dilatometer was then removed from the vacuum system and placed in a controlled-temperature oil bath ($\pm 0.002^\circ\text{C}$.) Changes in height with rise in temperature were measured with a cathetometer reading to ± 0.001 cm. The volume of the cup, ratio of initial weight of Hg to polyethylene, and diameter were chosen so that the increase in height ΔH of the mercury column accompanying a 1°C . change in temperature could be measured by the cathetometer with good accuracy; i.e., in the region of smallest $\Delta V/\Delta T$, $\Delta H/\Delta T = 0.02$ cm./°C. From these measurements of specific volume versus temperature it is possible to determine the crystallinity as a function of temperature. The same apparatus may also be used to study crystallization kinetics at any desired temperature.

E. X-Ray Diffraction

X-ray diffraction measurements were used to measure the degree of crystallinity and the crystallite size in a number of polyethylene samples that had received various radiation doses. The changes in the x-ray patterns during the heating of the samples from room temperature to above the melting point were measured as a function of time, as were the corresponding changes during the cooling cycle. Either North American Philips or General Electric x-ray Geiger tube spectrometers were used.

Prominent crystalline reflections associated with the 110 and 200 indices are observed with polyethylene. In addition, there is a shoulder on the low-angle side of the 110 peak which is associated with the amorphous phase. The method of estimating the crystallinity involves a comparison

of the areas under the 110 and amorphous peaks. The crystallite size is obtained from measurement of the line broadening of the 110 peak. In the x-ray measurements during heating or cooling, the spectrometer was centered on the maximum of the crystalline peak or the amorphous peak, and the changes in reflected intensity measured as a function of time.

F. Stress-Strain Measurements

Stress-strain measurements were performed at room temperature on irradiated 5.5-mil Marlex test specimens 1 in. long. The cross head loading rate was 0.3 in./min.

III. EXPERIMENTAL RESULTS

A. Light Transmission Measurements

1. Effect of Irradiation Dose on Transparency

Prior to the construction of the irradiation photometer described above, a number of preliminary irradiation experiments were performed in an attempt to gain further insight into the nature of the experimental parameters that must be controlled in order to obtain significant experimental results. Experiments were performed on 5.5-mil and 20-mil Marlex at 55, 125, and 145°C. A number of difficulties were encountered in the experiments, the most important of which were browning in the lower temperature irradiations, bubble formation at high temperature, and non-uniform heating of the sample due to the poor heat conductivity of the polyethylene.

To estimate the effect of browning, the transparency was measured immediately after irradiation and again after the samples had been left for about one month at room temperature. The samples irradiated at 55°C. became more transparent with time at room temperature, while the samples irradiated at 125 and 145°C. remained essentially unchanged. The clarification of the 55°C. samples is probably due to the delayed crosslinking by trapped radicals. Better transparency was obtained at the higher temperatures of irradiation.

Figure 2 gives the results of a series of experiments with 20-mil Marlex that was designed to eliminate bubbling during the high temperature irradiation. Each of the samples was first irradiated at 20–40°C. up to 50 Mrad with 2-m.e.v. electrons. (A similar technique has been patented by W. R. Grace Corp.; our procedure was devel-

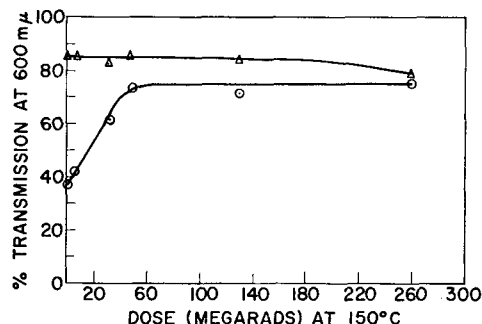


Fig. 2. Per cent transmission vs. irradiation dose for samples of 20-mil Marlex irradiated with 50 Mrad at room temperature followed by doses at 150°C. Transmission measurements at 150°C., (Δ) and room temperature, (\circ).

oped without prior knowledge of the Grace patents.⁴) The transparency of each sample was 16–19% before irradiation, and after irradiation it was 1% lower. All the samples were somewhat browned. Additional irradiation at 150°C. up to 130 Mrad resulted in transparencies of 84 to 86% at 150°C. The transparency at 150°C. after 260 Mrad was somewhat lower. At room temperature after the 150°C. irradiation, the transparency is seen to increase from 37% for no radiation at 150°C. to ~75% for 50 Mrad at 150°C. A very interesting feature of these experiments was that in one sample irradiated at low temperature, heated to 150°C., and subsequently cooled, the transparency increased from 16 to 37%. This was probably due to crosslinking by trapped free radicals which were liberated as the temperature was raised. The maximum effective dose was found to be 50 Mrad at room temperature followed by 50 Mrad at 150°C. A transparency of 85% at room temperature for a 20-mil sample of Marlex appears to be the maximum achievable value, since this is the result obtained at above the transition point. A transmission of 75% is therefore probably very close to the best that can be obtained with samples of the initial smoothness of those used in this study. No bubbling was noted in any of these samples.

2. Effect of Quenching Conditions on Transparency

A number of experiments were performed to show the effect of quenching on transparency. They are not presented here in order to conserve space. Transparency was improved by the use of rapid quenching. The transparency produced by quenching is, however, unstable to temperature cycling. Beneficial results may be obtained by combining irradiation with quenching.

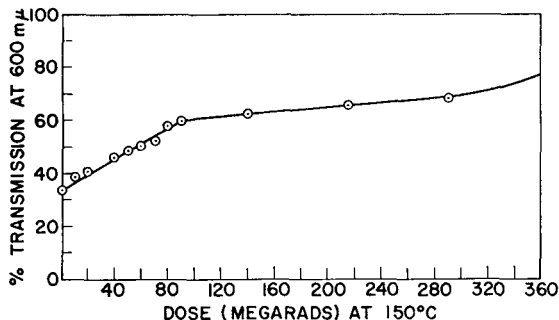
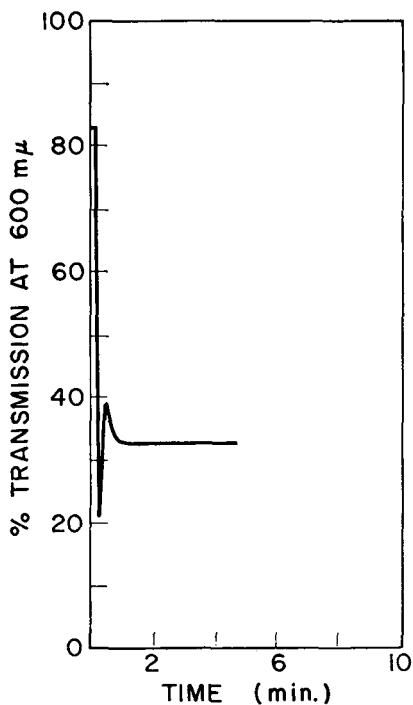


Fig. 3. Per cent transmission at room temperature vs. dose at 150°C. for 20-mil Marlex (sample no. 113). Initial dose at room temperature, 37.5 Mrad.

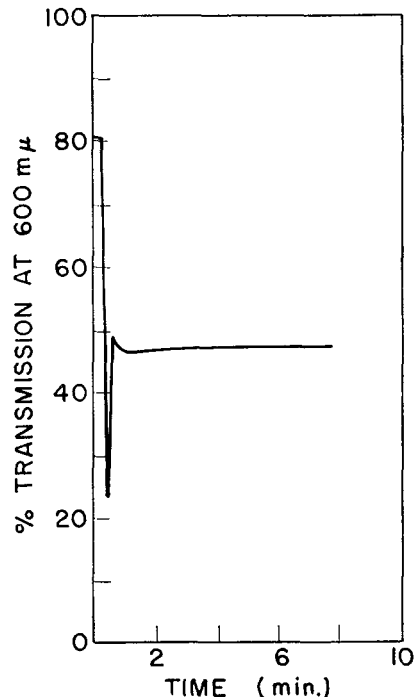


DOSE AT 150°C - 0 mr

Fig. 4. Per cent transmission vs. time for 20-mil Marlex (sample no. 113) irradiated with 37.5 Mrad at room temperature and quenched from 150 to 25°C.

3. The Effect of Radiation Dose on Transparency-Time Curves

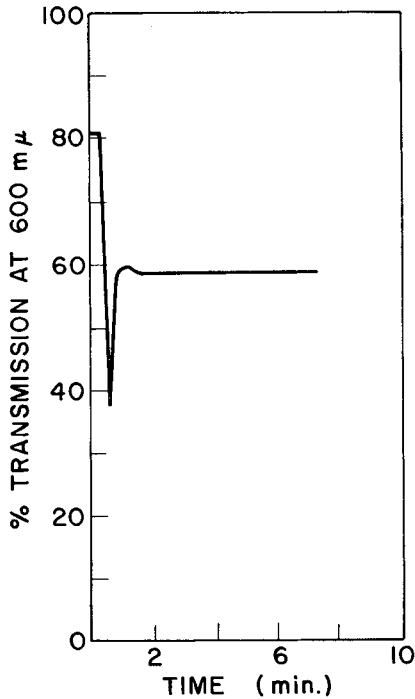
A number of 20-mil samples were irradiated at room temperature and then in some cases at 150°C., above the transition temperature. The irradiation cell and photometer previously described were used in these experiments in observing changes in transparency as a function of time and temperature.



DOSE AT 150°C-50 mr

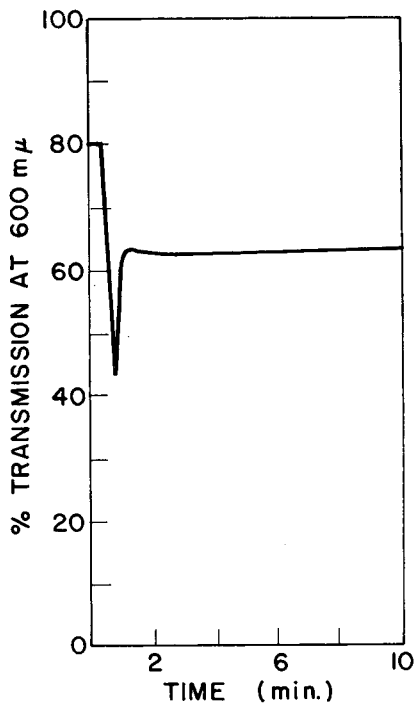
Fig. 5. Per cent transmission vs. time for 20-mil Marlex (sample no. 113) irradiated with 37.5 Mrad at room temperature and various dosages at 150°C., and quenched from 150 to 25°C.

Sample 113 received an initial dose of 37.5 Mrad at room temperature followed by a number of different irradiations at 150°C. After each irradiation the transparency was observed as a function of time as the sample cooled from 150°C. to room temperature. The total dose at 150°C. was 368 Mrad. Figure 3 shows the final transparency after the sample was quenched to room temperature, as a function of dose at 150°C. Figure 4 shows the changes in transparency as a function of time during cooling from 150°C. for the sample after it received a dose of 37.5 Mrad at room temperature. Figure 5 gives the change in transparency with time, after the sample received an additional 50 Mrad at 150°C. At somewhat higher dosage (90 Mrad at 150°C.), the minimum and the equilibrium transparency were increased (Fig. 6). Further increase in dose (up to 140 Mrad at 150°C.) resulted in a gradual decrease in the maximum and its eventual disappearance (Fig. 7). At a dose of 215 Mrad the minimum decreased markedly (Fig. 8). At a dose of about 290 Mrad (Fig. 9) the minimum and maximum were no longer present; the transparency simply



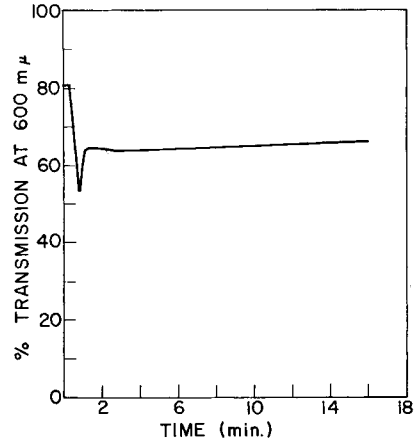
DOSE AT 150°C - 90 mr

Fig. 6. See legend of Figure 5.



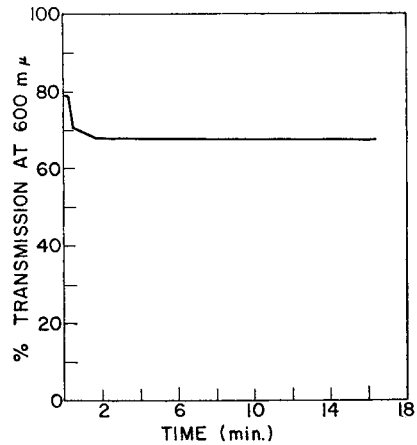
DOSE AT 150°C - 140 mr

Fig. 7. See legend of Figure 5.



DOSE AT 150°C - 215 mr

Fig. 8. See legend of Figure 5.



DOSE AT 150°C - 290 mr

Fig. 9. See legend of Figure 5.

decreased monotonically with time to the equilibrium value, which is appreciably higher than that at lower dosage.

4. The Effect of Quench Temperature on Transparency-Time Curves

For moderate dosage (sample no. 112, 20 mils, 37.5 Mrad at room temperature and 55 Mrad at 150°C.), the curves of transparency versus time for quenching from 150°C. to various temperatures follow the general features given below (see Figs. 10-21). The figures are numbered in the order in which the experiments were performed. These experiments were reproduced with other samples. Similar experiments were performed with samples that were given various irradiation dosages.

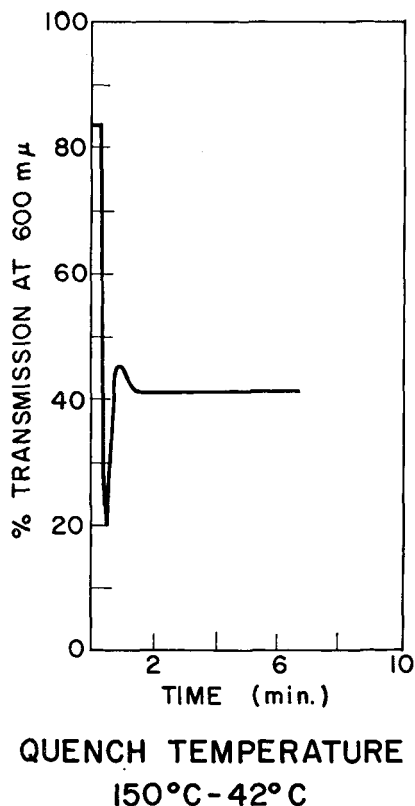


Fig. 10. Per cent transmission vs. time for 20-mil Marlex (sample no. 112) irradiated with 37.5 Mrad at room temperature and 55 Mrad at 150°C., and quenched from 150°C to various temperatures.

In the curves for quench temperatures of about 60°C. or below, the minima and maxima have small half-thicknesses. As the quench temperature is increased, the maximum transparency becomes broader and decreases slightly. At the same time, the minimum becomes slightly deeper. Still further increase in quench temperature results in an increase in the half-thickness of the minimum and in lowering of the maximum and minimum. At about 100°C. the minimum is essentially unchanged but the maximum is no longer present. In the range of about 100–118°C. the process represented by changes in transparency is slowed down to a very considerable extent, with a very slow recovery from the minimum value. The initial drop in transparency is still relatively rapid as compared to the recovery from the minimum. At temperatures above 119°C., there is once again a relatively sharp minimum, but the minimum transparency is increased. At temperatures very close to the melting point, there is a monotonic and slow decrease in transparency with time to a constant value.

Another sample, no. 112, was irradiated with 37.5

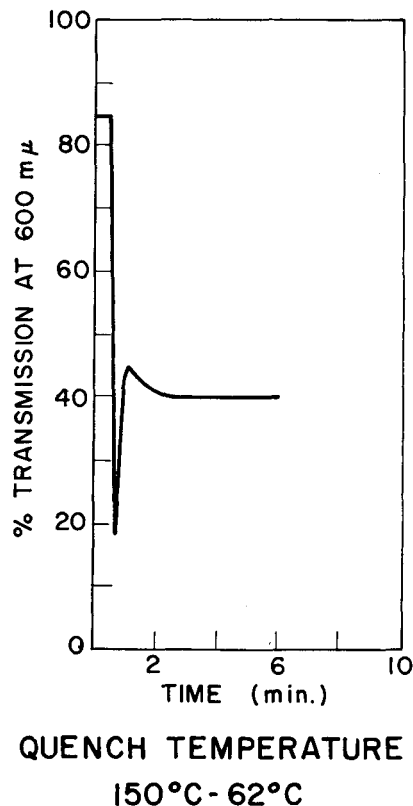


Fig. 11. See legend of Figure 10.

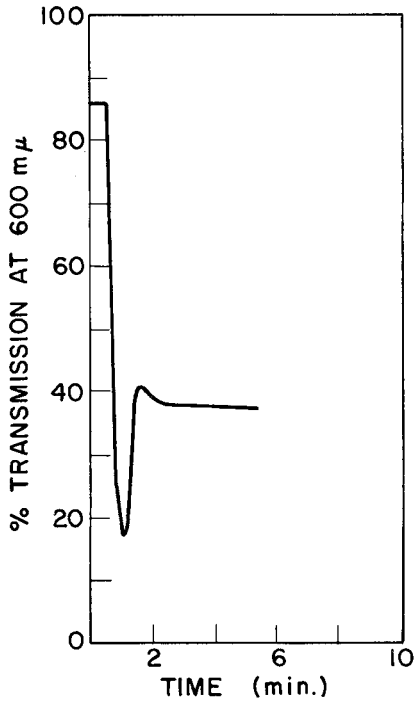
Mrad at room temperature followed by 55 Mrad at 150°C. The sample was then allowed to cool to room temperature and then reheated but only to 135°C., and quenched to 40°C. The transparency-time curve has the following features (Fig. 22): the minimum, ~20%, has very narrow half-width; the maximum is ~46%; the equilibrium value is ~42%. Sample no. 116 (Fig. 23) is a nonirradiated sample that was similarly quenched. Its original transparency of 20% dropped rapidly during the quench to 5% and then increased moderately rapidly to ~8%, the equilibrium value.

A number of 5.5-mil Marlex samples were given doses of 50 Mrad at room temperature followed by doses of up to 110 Mrad at 150°C. The transparencies of each of the samples as a function of time and temperature at various quench temperatures from room temperature to temperature close to the melting point were obtained; they are similar to those obtained for the 20-mil samples.

B. Dilatometric Measurements

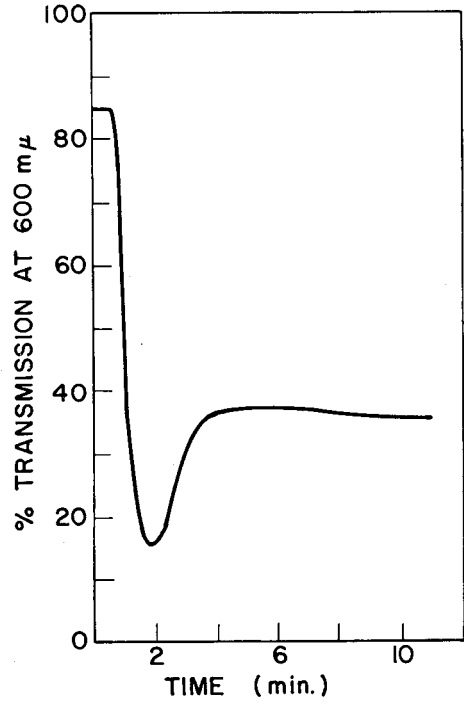
1. Specific Volume-Temperature

The following formula was used to calculate the specific volume of the polyethylene as a function of



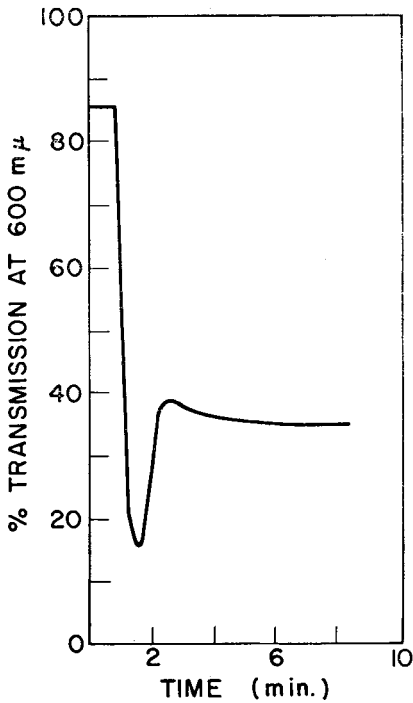
QUENCH TEMPERATURE
150°C - 86°C

Fig. 12. See legend of Figure 10.



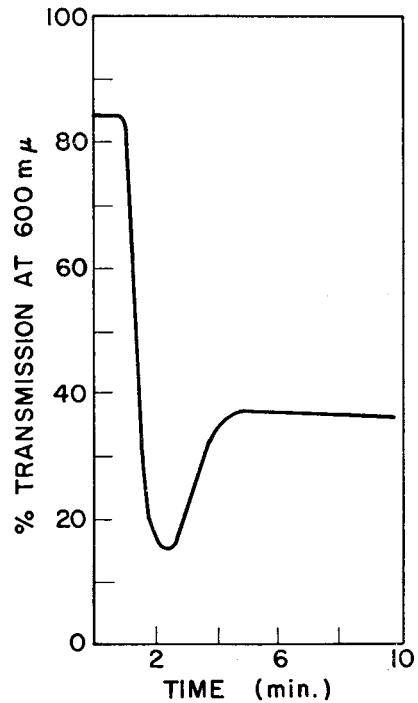
QUENCH TEMPERATURE
150°C ~ 100°C

Fig. 14. See legend of Figure 10.



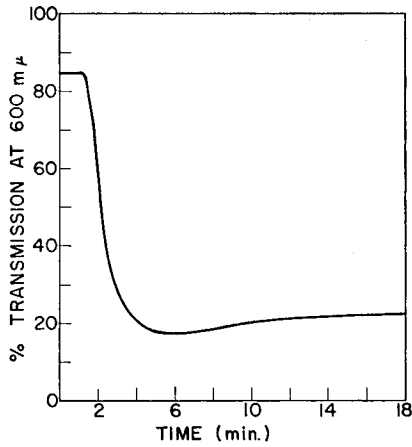
QUENCH TEMPERATURE
150°C - 98°C

Fig. 13. See legend of Figure 10.



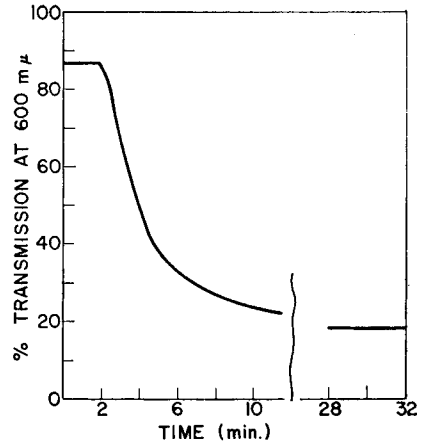
QUENCH TEMPERATURE
150°C - 105°C

Fig. 15. See legend of Figure 10.



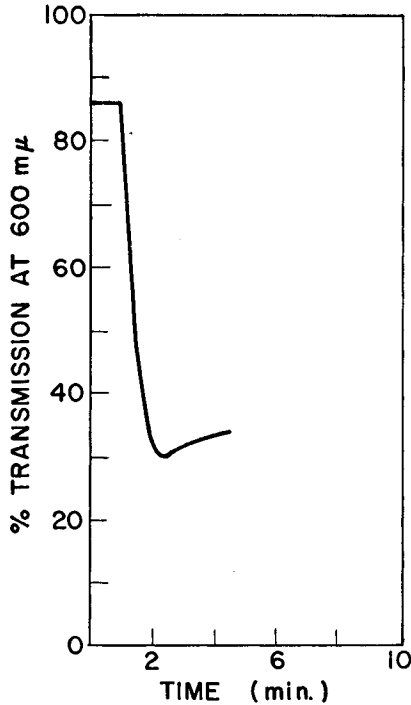
QUENCH TEMPERATURE
150°C - 107°C

Fig. 16. See legend of Figure 10.



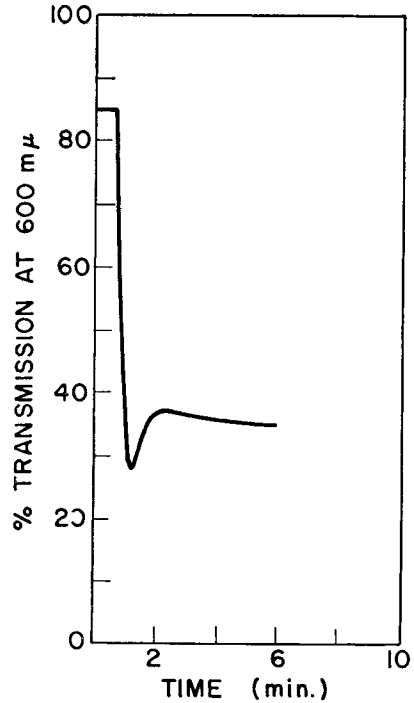
QUENCH TEMPERATURE
150°C - 112°C

Fig. 18. See legend of Figure 10.



QUENCH TEMPERATURE
150°C - 120°C

Fig. 17. See legend of Figure 10.



QUENCH TEMPERATURE
150°C - 119°C

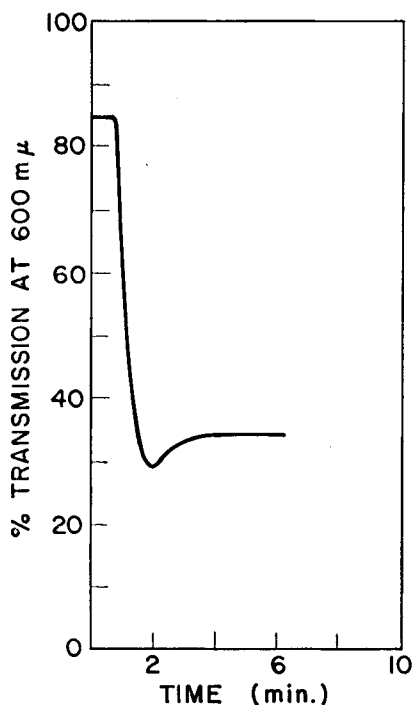
Fig. 19. See legend of Figure 10.

temperature from changes in the height of the mercury column:

$$V_{PE} = \frac{(V_0 + 3\lambda TV_0) + hK - V_{Hg}W_{Hg}}{W_{PE}}$$

where V_{PE} and V_{Hg} are the specific volumes of

polyethylene, and mercury, respectively, in $\text{cm.}^3/\text{g.}$; V_0 is the volume of the dilatometer up to the etch mark, 0.4661 cm.^3 ; λ is the linear thermal expansion coefficient of Pyrex, $3.3 \times 10^{-6} \text{ cm./}^\circ\text{C.}$; K is the cross-sectional area of the capillary, $7.807 \times 10^{-3} \text{ cm.}^2$; and W_{PE} , W_{Hg} are the densi-



**QUENCH TEMPERATURE
150°C - 120°C**

Fig. 20. See legend of Figure 10.

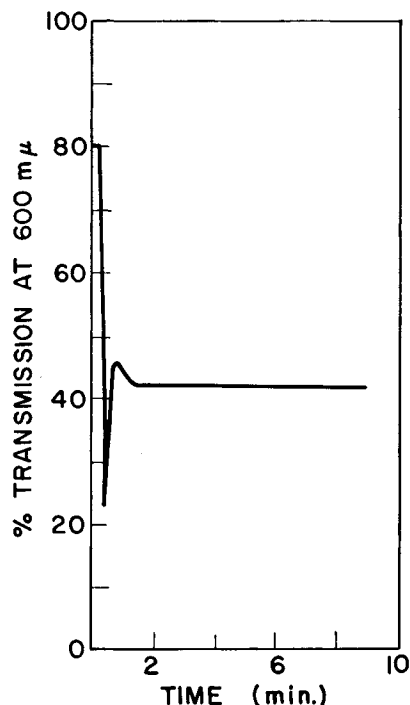
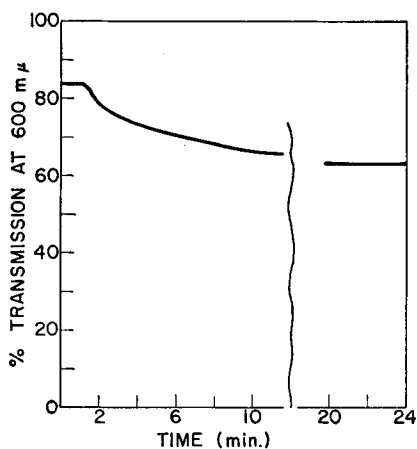


Fig. 22. Per cent transmission vs. time for 20-mil Marlex (sample no. 112) irradiated with 37.5 Mrad at room temperature and 55 Mrad at 150°C., and quenched from 135 to 40°C.



**QUENCH TEMPERATURE
150°C - 130°C**

Fig. 21. See legend of Figure 10.

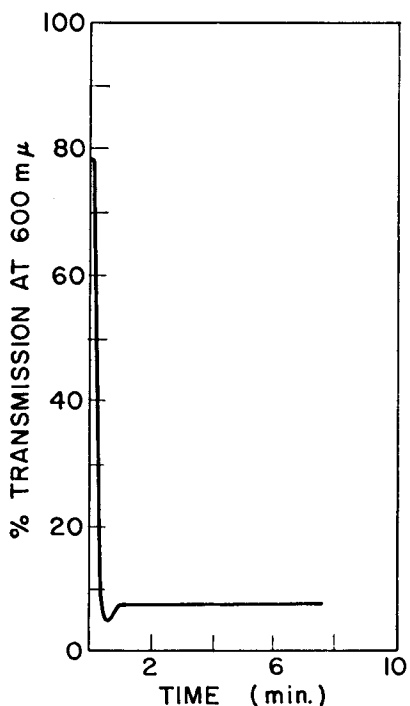


Fig. 23. Per cent transmission vs. time for unirradiated 20-mil Marlex (sample no. 116) quenched from 135 to 40°C.

ties of polyethylene and mercury, g./cm.³ The curves of specific volume versus temperature are not shown in order to conserve space. The melting points obtained from these data are given in Table I.

TABLE I
Effect of Irradiation on Physical Properties of Polyethylene

Marlex sample no.	Thickness, mils	Irradiation dose, Mrad		Melting point, °C.	Crystal- linity, % (x-ray)	Crystallite size A (x-ray)	Total elongation at rupture, %	Tensile strength at rupture, psi
		R. T.	150°C.					
147	5.5	0	0	137.0	92	340	600+	3820
145	5.5	50	0	128.5	79	300	420	3100
140	5.5	50	33	117.0	64	190	160	2440
141	5.5	50	50	116.5	71	200	40	2400
142	5.5	50	110	113.0	31	180	50	1730
148	20	0	0	136.0	85	240	—	—
116	20 ^a	0	0	136.0	85	185	—	—
120	20	54	27	124.0	—	—	—	—
121	20	54	108	106.0	—	—	—	—
25	20	0	172 ^b	114.0	—	—	—	—

^a Quenched material.

^b At 125°C.

2. Crystallinity-Temperature

The following formula was used to calculate the crystallinity at various temperatures from the specific volume data:

$$\% \text{ Crystallinity} = \frac{100(V_a - V_{\text{obs}})}{(V_a - V_c)}$$

where V_{obs} is the observed specific volume at a given temperature; V_a is the specific volume of the amorphous polyethylene at a given temperature, obtained from a linear extrapolation of the specific volume from above the melting point to any temperature below the melting point; and V_c is the specific volume of the crystalline material as calculated according to Nielson²¹ from the formula $V_c = 1.025 + 0.0003T$. Some of these data are placed in Figure 24. It is seen that the crystallinity decreases with increasing radiation dose.

C. Crystallization Kinetics

Curves of the percentage of total possible crystallization,

$$100[(H_0 - H_t)/(H_0 - H_\infty)]$$

as a function of the logarithm of time for various crystallization temperatures for sample no. 145 (50 Mrad at room temperature) are shown in Figure 25. H_0 is the height of mercury in the dilatometer at zero time at the temperature of crystallization, obtained by extrapolation of the column height-time curve to zero time. H_t is the height of the mercury at time t . H_∞ is the height of the mercury at infinite time and is obtained

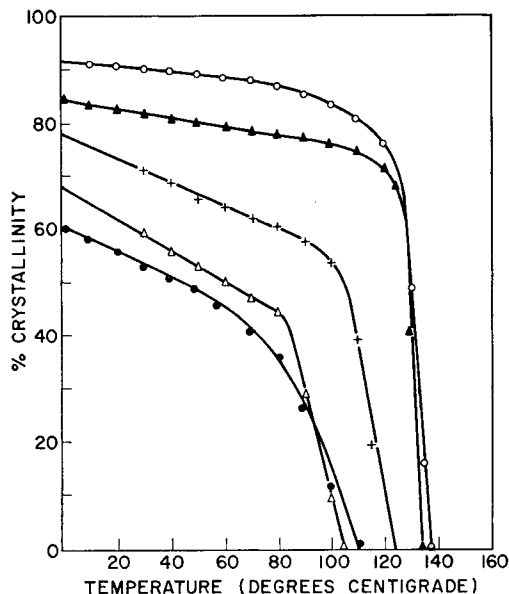


Fig. 24. Per cent crystallinity vs. temperature for (O) unirradiated 5.5-mil Marlex, (▲) unirradiated 20-mil Marlex, (●) 20-mil Marlex (sample no. 25) irradiated with 172 Mrad at 125°C., (+) 20-mil Marlex (sample no. 120) irradiated with 54 Mrad at room temperature and 27 Mrad at 150°C., (Δ) 20-mil Marlex (sample no. 121) irradiated with 56 Mrad at room temperature and 108 Mrad at 150°C.

from a knowledge of the specific volume of polyethylene at the crystallization temperature and the weight of polyethylene and mercury in the dilatometer. The melting point for the irradiated sample was 125.7°C. By comparison with the data of Mandelkern and Quinn²² for unirradiated linear polyethylene, it is seen that the rate of crystallization at a particular temperature is very much re-

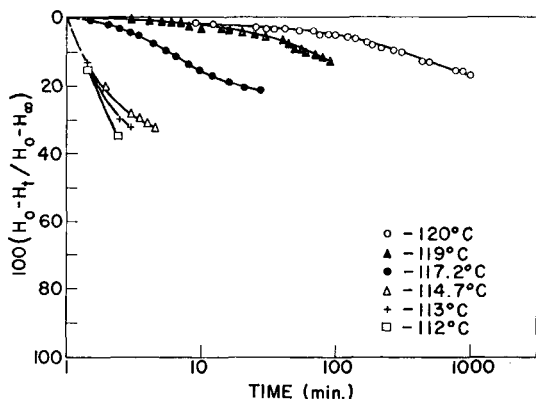


Fig. 25. Rates of crystallization of 5.5-mil Marlex (sample no. 145) irradiated with 50 Mrad at room temperature.

duced by irradiation. On the basis of degree of supercooling, however, the irradiated samples have higher rates of crystallization.

D. X-Ray Diffraction

X-ray diffraction data at room temperature were obtained for each of the 5.5-mil Marlex samples. The crystallinity was estimated from the relative sizes of the areas under the crystalline and amorphous peaks. The half-width of the crystalline peak was used to obtain a measure of the crystallite size. These data are given in Table I.

In order to observe x-ray diffraction during melting and crystallization, an unirradiated sample of 20-mil Marlex 50 was placed in an evacuated x-ray diffraction specimen chamber. It was then quenched slowly from above the transition point to 120°C. Above the transition point, the sample was completely amorphous and also transparent. As temperature dropped to 120°C., the crystalline peaks grew in and the sample became milky white. The crystallinity was estimated to be ~50% of the original value. The sample was then quenched suddenly from 120°C. with liquid N₂. It became translucent, and simultaneously the crystallinity increased. On removal from the vacuum chamber, the sample warmed up and became milky white again. The x-ray spectrum of the sample at this stage gave indication of further crystal growth.

This experiment showed that the amount of amorphous polymer increases with the radiation dose, and that the increase in crystallization and in crystallite size occurs simultaneously with increase in transparency during cooling. These results corroborate our ideas based solely on our observations of transparency versus time described above.

E. Stress-Strain Data

Table I gives the room temperature stress-strain data for the 5.5-mil Marlex samples irradiated with various doses at room temperature and at 150°C.

IV. DISCUSSION

For the purpose of explaining the changes in light transmission as the polyethylene is cooled from above the melting point to the final annealing temperature, it is assumed (1) that irradiation induces crosslinking which puts restraints on the polymer that were not originally present; (2) that crystallization involves the following processes: nucleation, coalescence of nuclei, crystal growth on existing nuclei or particles, and orientation of the crystalline particles to form spherulites, or other shorter order orientation of crystallites. Let us also assume (3) that the curves for rate of nucleation and rate of crystal growth and spherulite growth versus temperature are similar in shape to those shown in Figure 26. These curves will be altered depending on the amount of crosslinking, the major effect being a reduction in rate of nucleation and growth caused by the lowering of the melting point with increase in crosslinking. A similar assumption has been used by Buchdahl, Miller, and Newman²³ in their discussion of the crystallization kinetics and mechanical properties of polyethylene. Hirai's²⁴ theoretical paper on the rate of spherulite growth in polymeric substances substantiates the data of Taksganagi and Kusumoto²⁵ for the temperature dependence of spherulite growth rate in polyethylene succinate and the

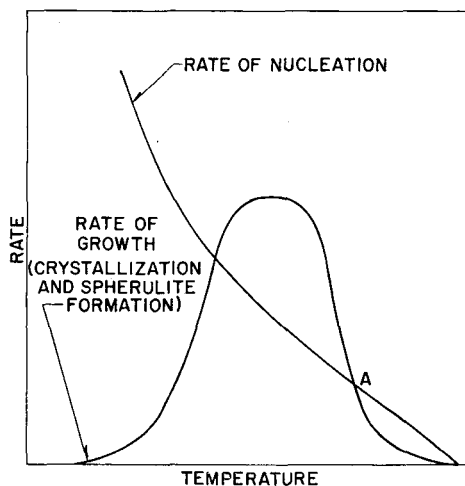


Fig. 26. Rates of nucleation and growth as functions of temperature.

data of Burnett and McDevit²⁶ for nylon 6. The curves given in these references are similar to the growth curve in Figure 26.

A. Rate of Change of Transparency as a Function of Quenching Temperature

Sample no. 112 was quenched from 150°C. to various temperatures (see Figs. 10-21).

(1) When the quench temperature is about 60°C. or lower (Figs. 10-11), the maxima and minima of the transparency-time curves have small half-thicknesses. The rapid initial drop in transparency is thought to be due to very rapid nucleation. The large number of nuclei formed result in poor transparency in this stage of crystallization. During the measurements, the temperature was falling continually from 150°C. to its equilibrium value. The growth rate, which was small at the higher temperatures, passed through a maximum and returned to a fairly low value at the equilibrium temperature (see Fig. 26). The major portion of the growth takes place relatively rapidly. The growth process may involve the coalescence of nuclei and small crystallites as well as the melting of small particles to allow formation of larger ones. Rearrangement of the crystals to form spherulites as well as ordered regions smaller than the spherulites also takes place. These processes cause the transparency to rise from the minimum. Scattering is a result of differences in refractive indices, and the smaller the differences the less the resulting scattering. Crystallization and spherulite growth reduces the number of interfaces between crystalline and amorphous regions. This process continues until the restraints due to crystallization prevent the molecular motion necessary for growth. Nucleation, which takes place simultaneously with growth, can continue after growth is no longer possible. This small amount of residual nucleation is the cause of the decrease following the maximum in the light transmission curve.

(2) For slightly higher end temperatures of quenching (Fig. 11), the increase in growth rate causes a broadening and a slight decrease in magnitude of the maximum transparency. Since as the quench temperature increases the gradient between the starting temperature of 150°C. and the final quench temperature decreases, the sample spends comparatively longer times in the high temperature region where the growth rate is very low and where the nucleation rate is greater. This may be the cause of the lowering of the transparency minimum.

(3) The increase in the half-thickness of the minimum on further increase in the end temperature, first evident in Figure 12, is due to the decrease in the nucleation rate. Growth of overall crystallization involves both the number of nuclei and the rate of growth of an individual crystal or spherulite. Because of this, one obtains a broadening of the minimum and maximum when the nucleation rate decreases, even though the growth rate is increasing.

(4) At an end temperature of about 100°C. (Fig. 14) the growth rate is sufficiently high compared to the nucleation rate to eliminate the residual nucleation that was the cause of the maximum. At these higher temperatures there are fewer restraints due to a lowering of the equilibrium amount of crystallinity, which makes the greater growth rate possible. At this temperature we may be close to the maximum in the growth rate.

(5) The region of end temperatures from about 100 to 118°C. (see Figs. 14-16) is a very interesting one. The very broad minimum contrasts sharply with that found at lower temperatures. Both nucleation and growth are relatively slow.

(6) The return to the relatively sharp minimum at about 119°C. (see Figs. 17, 19) and the increase in transparency over that obtained at an end temperature only a few degrees lower probably indicates that we are on the right-hand side of point A in Figure 26. In this region the growth rate is extremely small and the equilibrium amount of total crystallization is also low (perhaps only 5%). The nucleation rate is still high enough to cause the left side of the minimum to have a relatively steep slope. Let us assume that essentially all of the equilibrium amount of crystallinity has been precipitated in the form of nuclei or very small crystallites. When growth occurs by coalescence or other means, an increase in transparency results since no further nucleation is possible. This process does not require a long time because the total crystallinity is low.

(7) With end temperatures very close to the melting point, the nucleation is slow and rate-controlling. There is only a slight decrease in transparency from that obtained above the melting point, (Fig. 21).

B. Rate of Change of Transparency on Cooling as a Function of Dose at 150°C.

When sample no. 113 (see Figs. 4-9) was given doses of 37.5 Mrad at room temperature followed by 50 Mrad at 150°C. and then cooled to room

temperature, changes in transparency occurred that can be explained in the same way as those in sample no. 112.

With increase in irradiation dose at 150°C. more restraints were placed on the polymer. This resulted in a lower fraction of equilibrium crystallinity. The changes in the initial slope of the curve with increasing dose (Figs. 4-9) indicates a reduction in the rate of formation of nuclei. Successively shallower minima were therefore obtained. The general features of the transparency-time curves remain the same, but at a relatively high dose (150 Mrad at 150°C.) the maximum is no longer found (cf. Fig. 7). To explain this one may imagine that sufficient crosslinking had taken place to appreciably decrease the amount of residual nucleation occurring on the right side of the minimum. It appears from the half-thicknesses of the minima in Figures 4-8, that the rates of nucleation and growth were both reduced with increasing dosages. At still higher dosage (300 Mrad; cf. Fig. 9), crosslinking limits the mobility to such an extent that the minimum due to orientation into larger crystallites and/or spherulites is no longer present. The amount of nucleation is also small, so that the transparency approaches fairly closely that found above the transition temperature.

In the nonirradiated sample (no. 116) with no crosslink restraints, quenching from 135°C. (Fig. 23) resulted in a very large amount of nucleation, as indicated by the sample's transparency of only 5%. There was only a small amount of growth (equilibrium $T = 8\%$) since there was so little room for rearrangement and coalescence. An irradiated sample lightly crosslinked and quenched in the same way (Fig. 22) could not form as many nuclei, so that there was room for rearrangement and growth to proceed. Also, the irradiated sample had a transparency maximum, which indicates that nucleation continued to a small extent after growth had stopped.

The x-ray diffraction data shown in Table I indicate that both the crystallinity and the crystallite size decrease on irradiation.

In the experiment where the changes in crystallinity were followed by observing the intensity of the 110 crystalline peak as a function of time while the sample was cooled slowly from above the melting point to 120°C. and then suddenly quenched from 120°C. to liquid N₂ temperatures, increases in crystallinity and in crystallite size were observed simultaneously with a marked increase in

transparency. This very important observation is interpreted as confirmation of the mechanism described above for the increase in transparency due to rearrangement and growth of nuclei and small particles. An increase in total crystallinity alone would be expected to result in a decrease in transparency.

Hawkins and Richards¹⁰ and Stein¹¹ have observed changes in light transmission with temperature for low density polyethylene similar to those described above. Last,¹⁵ also working with low density polyethylene, found that acceleration of the nucleation rate by the addition of polypropylene resulted in enhanced transparency and reduction of spherulite size. The data presented above for high density polyethylene show that an increase in transparency occurs due to growth and rearrangement. As was pointed out in the introduction, the transmission of light as a function of particle size goes through a minimum at about 0.2 μ . Low density polyethylene generally contains smaller spherulites and crystallites than does the high density material; therefore, provided that the final size of the scattering center is on the left side of the minimum in the transmission-particle size curve, the increase in transparency with enhanced nucleation rate as found by Last may be understood.

The quench and irradiation procedures described in our work result in enhanced transparency and reduction in the final size of the spherulites and crystallites. During the crystallization process, rearrangement and growth of the nuclei are manifested in an increase in transmission from a minimum value. At the minimum in the transparency-time curve, the particles are probably small compared to the wavelength of visible light, so that the Rayleigh formula is valid. As the nuclei and crystals grow and rearrange, the scattering centers pass through the minimum in the transparency-particle size curve. Transparency depends on the total amount of crystallinity and on the size of the scattering centers. Thus, unirradiated 20-mil Marlex cooled slowly from above the melting point (no. 148) is 85% crystalline, has a crystallite size of 240 Å, and is 19% transparent at 600 $m\mu$. A similar sample (sample no. 116) which was quenched rapidly from 135°C. to room temperature is 85% crystalline, has a crystallite size of 185 Å, and is 8% transparent at 600 $m\mu$. This demonstrates the effect of reduction of crystallite size on the transparency of high density polyethylene. The effect of crosslinking can be seen by comparing the above

results with those obtained for sample no. 112 (37.5 Mrad at room temperature, 55 Mrad at 150°C.) quenched from 135°C. to room temperature. It had a final transparency of 42%. Therefore, the increased transparency is probably the result of a lowering of the crystallinity by cross-linking despite the concurrent reduction in crystallite size. The effect of irradiation on reduction of crystallinity and crystallite size of 5.5-mil Marlex is shown in Table I. Microscopic observations of films obtained by evaporation of dilute solutions of polyethylene in xylene and subsequently irradiated, first at room temperature and then at 150°C., show a reduction in spherulite size with increasing irradiation dose.

Tensile measurements of 5.5-mil Marlex samples at room temperature indicate that about 60% of the original strength of the unirradiated material is retained when the sample is given its optimum dose for transparency, 50 Mrad at room temperature followed by 50 Mrad at 150°C. (Table I). The dilatometric measurements show a reduction in melting point with increasing irradiation dose (Table I).

Figure 25 shows data on crystallization versus log time for a 5.5-mil irradiated Marlex sample (no. 145, 50 Mrad at room temperature). The rate of crystallization is considerably slower than that of an unirradiated sample. This is due partially to the reduction in melting point of the irradiated polyethylene. For the same degree of supercooling the rate of crystallization for the irradiated sample is greater than that for the unirradiated material. Price,¹³ in observing the kinetics of spherulite formation in Marlex samples, found a lowering of the melting point with increasing irradiation dose. The rates of spherulite formation were comparable for similar degrees of supercooling. In our case, degradation products or crosslinks may have served as nucleating agents for crystallization. This results in higher rates of crystallization than would be expected on the basis of supercooling alone.

V. SUMMARY

Owing to the complexity of the interrelations between crystallinity, crystallite size, spherulite size, shorter range crystallite orientation, and transparency, it is difficult to devise procedures for achieving transparency which are valid for both high and low density polyethylene. It is possible either by quenching or by other means of increasing the rate of nucleation to obtain material whose scattering centers are small enough to be in the range of increasing transparency with decreasing

size on the transparency-particle size curve. If one is on the right side of the minimum of this curve, however, one obtains a decrease in transparency with reduction in the size of the scattering center. High density polyethylene generally has larger-sized crystallites and spherulites than low density material. It is therefore more difficult to achieve an increase in transparency in the high density material by quenching. For polyethylene of either high or low density, if transparency is achieved by quenching, reheating and then slow cooling will result in increased crystallite and spherulite size with reduction in transparency.

Irradiation of high density polyethylene reduces the crystallite and spherulite size. If this were the only effect of irradiation, there would probably be a reduction in transparency with irradiation. This is not the case, however. The overall amount of crystallinity is reduced by irradiation and it is probably this factor which is primarily responsible for the increased transparency. The reduction of rate of crystallization with irradiation results in larger crystallites and spherulites than could otherwise be obtained, and is one of the factors which favor enhanced transparency. At relatively high doses the final size of the scattering centers may be on the left side of the minimum of the transparency-particle size curve, in which case the enhancement of transparency is the result of the combined effect of reduction in size of the scattering centers and reduction of crystallinity. The transparency achieved by irradiation is not destroyed permanently by reheating, since upon normal cooling the material regains its original crystallinity and size of scattering centers. For Marlex polyethylene the optimum irradiation dose appears to be about 50 Mrad at room temperature followed by about 50 Mrad above the transition temperature. This eliminates problems due to bubbling and produces a material with good transparency as well as mechanical strength.

The author would like to acknowledge the support for this work by the Division of Isotope Development of the Atomic Energy Commission. Numerous discussions with Dr. L. M. Epstein were very helpful and are appreciated. Drs. T. Phillips, E. Halpern, and W. E. Wallace helped in the performance of the x-ray and infrared analyses. J. Kwiecinski and H. W. Weisberg assisted in many of the light transmission and dilatometric determinations.

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Synopsis

A procedure has been developed for producing highly transparent polyethylene by use of high-energy electron

irradiation above the melting point. The polyethylene retains about 60% of its original tensile strength after receiving the optimum irradiation dose of 50 Mrad at room temperature followed by 50 Mrad at 150°C. The transparency of a 0.02 in. sample increases from about 20% to 75% under this treatment. Changes in transparency with time and temperature, during cooling of the polyethylene from 150°C. to various quench temperatures were investigated as a function of irradiation dose. The increase in transparency is a result of reduction in crystallinity, in size of crystallites and spherulites, and in rate of crystallization caused by the restraints imposed by the radiation-induced crosslinking.

Résumé

On a développé une méthode de production de polyéthylène hautement transparent, en employant une irradiation électronique d'énergie élevée et au-dessus du point de fusion. Le polyéthylène tient à peu près 60% de sa force de tension originale après une dose d'irradiation optimum de 50 mégarads à température ambiante, suivi de 50 mégarads à 150°C. La transparence d'un échantillon de 2/100 de pouce augmente d'environ 20% jusqu'à 75% en le traitant de cette façon. Des changements de transparence avec le temps et la température suivant que le polyéthylène tombe de la température de 150°C à différentes températures plus basses ont été étudiés en fonction de la dose d'irradiation. L'augmentation de la transparence est un résultat de la réduction de la cristallinité, de la grandeur des cristallites et des sphérulites et de la vitesse de cristallisation, causés par les rétrécissements entraînés par le pontage produit sous l'influence de la radiation.

Zusammenfassung

Ein Verfahren zur Erzeugung hochgradig transparenten Polyäthylens unter Benützung hochenergetischer Elektronenbestrahlung oberhalb des Schmelzpunktes wurde entwickelt. Das Polyäthylen behält nach der optimalen Bestrahlungsdosis von 50 Megarad bei Raumtemperatur, gefolgt von 50 Megarad bei 150°C, etwa 60% seiner ursprünglichen Zugfestigkeit. Bei dieser Behandlung steigt die Transparenz einer 0,02"-Probe von etwa 20% auf 75%. Die Abhängigkeit der Transparenz von der Zeit und der Temperatur beim Abfall der Temperatur des Polyäthylens von 150°C zu verschiedenen Abschrecktemperaturen wurde als Funktion der Bestrahlungsdosis untersucht. Die Zunahme der Transparenz ist eine Folge des Rückganges der Kristallinität, der Grösse der Kristallite und Sphärolite sowie der Kristallisationsgeschwindigkeit, welcher durch die strahlungsinduzierte Vernetzung zu Stande kommt.

Received September 23, 1960