

Characterization Studies for Polyethylene Formed by Co^{60} γ -Radiation under Constant Conditions in a Nonflow System

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Synopsis

Several properties of polyethylene, synthesized by Co^{60} gamma radiation have been investigated. The polymerization reactions were carried out in static experiments over a wide range of conditions. Measurements include molecular weight, molecular weight distribution, density, methyl group content, crystalline melting point, and melt index. The density of polyethylene formed at 20°C. was found to be 0.94 g./cc. This value appears to be independent of pressure from 170 to 1700 atm. and radiation intensity from 0.58×10^6 to 4.7×10^6 rads./hr. Increasing temperature results in increasing methyl group content and a decrease in density to 0.91 g./cc. at 200°C. The polymers formed, over the entire range of experimental conditions, were completely soluble in *o*-dichlorobenzene at 135°C. Intrinsic viscosities were determined and their dependence on temperature, pressure, intensity, and radiation dose are shown. An attempt was made to correlate melt index to molecular weight and molecular weight distribution.

In recent years much attention has been given to the kinetics of γ -radiation-induced polymerization of ethylene. Generally very little information has been reported on the properties of polyethylene formed by γ -radiation. This paper attempts to correlate some of the properties of polyethylene formed by γ -radiation as a function of the experimental parameters over a wide range of conditions. Recent reports^{1,2} describing other phases of this study which include the kinetics of the radiation-induced ethylene polymerization have been published elsewhere.

The reaction vessel, shown in Figure 1, is of 316 stainless steel and is 1 in. in i.d. and 2.5 in. in o.d., with an internal length of ≈ 8 in. The internal volume of the vessel is 100 cc. The bottom assembly contains a thermocouple well for measuring reaction temperature, and the upper assembly contains a rupture disk and a closure valve. A more detailed description of the experimental apparatus is given in another report.² For experiments with the above vessel, the polymer remained in the radiation field for the duration of the experiment.

Another series of experiments was carried out in an elongated or "fall-through" vessel shown in Figure 2. This type of reaction vessel has an internal volume of 420 cc. and a length of 30 in. The lower part of the

vessel is inserted in a lead shielding cask so that only the top 6 in. (120 cc. volume) is subjected to radiation. The purpose of the elongated vessel was to allow the polymer to fall out of the radiation field as it formed.

Polymer characterization data are presented in two parts. In Part I, the data are given for experiments conducted in the 100-cc. capsule reac-

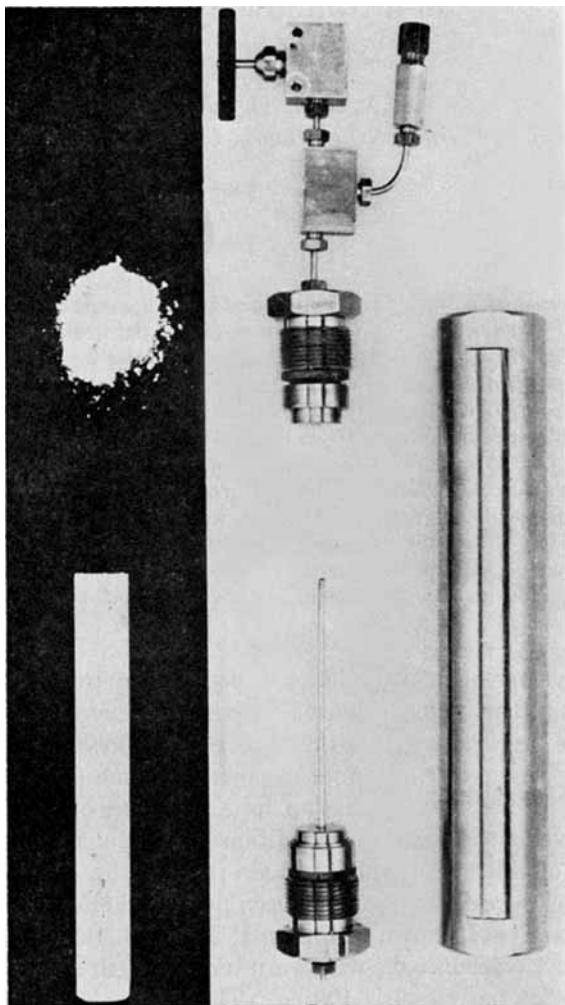


Fig. 1. Reaction vessel and assemblies for Co^{60} γ -radiation polymerization of ethylene.

tion vessel. These data are reviewed in Figures 3–11. Part II reviews the data obtained for experiments performed in the elongated vessel, shown in Figures 12–20. All irradiations were conducted in the water tank-type facility in the High Pressure Gamma Laboratory at Brookhaven National Laboratory.

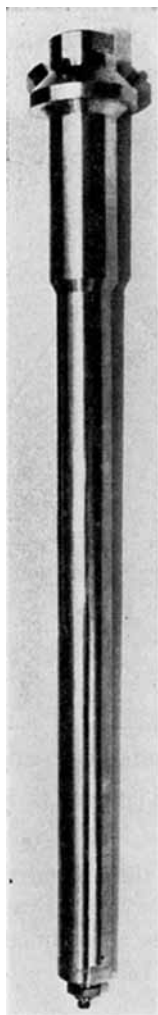


Fig. 2. "Fall-through" reactor vessel for Co^{60} γ -radiation polymerization of ethylene.

PART I

The following information was obtained with the 100-cc. capsule reaction vessel in which the polymer formed remained in the radiation field for the duration of the experiment.

Effect of Radiation Intensity on Molecular Weight

Figure 3 shows the effect of intensities ranging from 0.58×10^5 to 4.7×10^5 rad/hr. on the intrinsic viscosity $[\eta]$ for experiments conducted at pressures of 10,000 and 5000 psi, respectively. Each experiment was irradiated for a total dose of 1.0×10^6 rad at ambient pool temperature (20°C). At the conditions indicated, the intrinsic viscosity is inversely proportional to the radiation intensity.

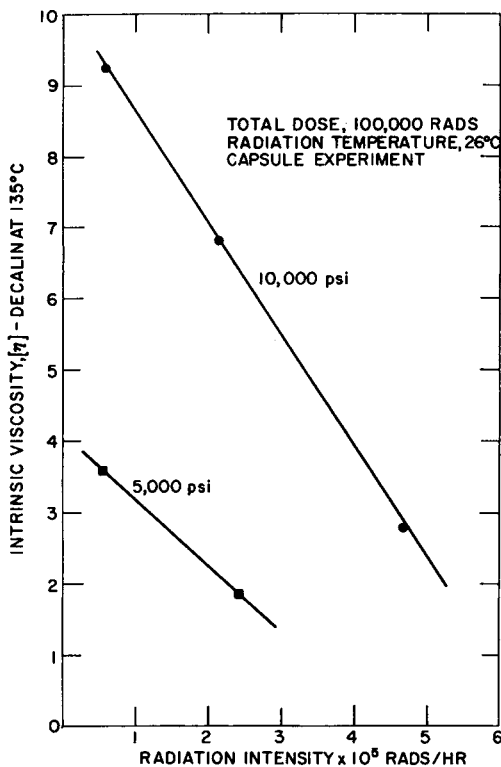


Fig. 3. Radiation intensity vs. intrinsic viscosity.

The polymer formed under these conditions was completely soluble in Decalin at 135°C. Intrinsic viscosities were calculated from dilute solution viscosities measured with a modified Ubbelohde viscometer, with Decalin used as the solvent at 135°C.

Effect of Radiation Dose on Molecular Weight

The effect of total dose or radiation time on intrinsic viscosity, shown in Figure 4, was studied for polyethylene formed at pressures of 2500–10,000 psi. In this series of experiments the reactions were conducted at 20°C. with a radiation intensity of 4.7×10^5 rad/hr.

Extrapolation of the data to zero radiation dose shows that the intrinsic viscosity initially increases very rapidly with dose and then shows a leveling-off effect. The methyl group content over the entire range of pressure and radiation dose was measured to be between 0.5 and 0.7 $\text{CH}_3/100$ carbon atoms. This indicates that the effect of radiation on the residual polymer over the range of conditions used is not appreciable, and that the leveling-off effect is an indication of an approaching steady-state condition.

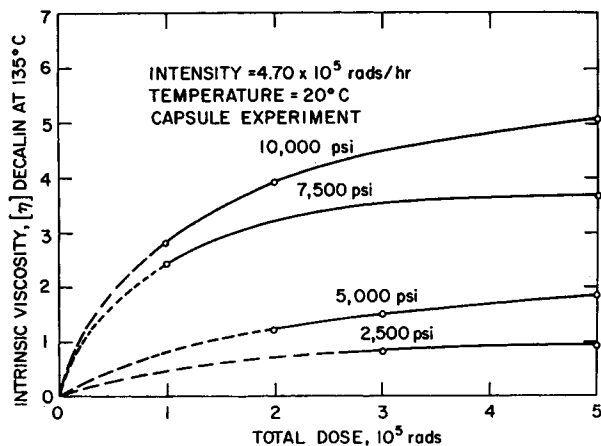


Fig. 4. Intrinsic viscosity vs. total dose.

Effect of Pressure on Molecular Weight

At the constant conditions given in Figure 5, the weight-average molecular weight, denoted by the solid line, appears to be approximately proportional to the pressure in the range 2500–10,000 psi. Weight-average molecular weights were calculated from the molecular weight distribution curves measured by a Water's gel permeation chromatograph, with trichlorobenzene at 130°C. used as the solvent.

The lower curve in Figure 5 represents values of intrinsic viscosity for the same series of samples. These values were used to calculate molecular weight by using the Atkins equation relating $[\eta]$ and \bar{M}_w . The calculated \bar{M}_w values indicated by the dashed line are in reasonably good agreement with the \bar{M}_w values obtained from the distribution curves.

Effect of Pressure on Density and Melting Point

The densities for polyethylene formed over a wide range of conditions at $\approx 20^\circ\text{C}$. are shown in Figure 6. Experimental conditions were radiation intensities from 0.58×10^5 to 4.7×10^5 rad/hr., radiation doses between 1.0×10^5 and 5.0×10^5 rad, and pressures ranging from 2500 to 25,000 psi.

The data indicate that over this range of conditions the density remains essentially constant. A further indication is given by the methyl group content, which is between 0.5 and 0.75 per 100 carbon atoms over the entire range. Points shown are averages of several samples formed under the same conditions.

A variation of melting point with pressure is indicated in Figure 6. One significant difference in the properties of polyethylene as a result of increasing pressure is in the molecular weight. For experiments conducted at room temperature, the molecular weight at pressures $>10,000$ psi is estimated to be of the order of several million. The increase in melting

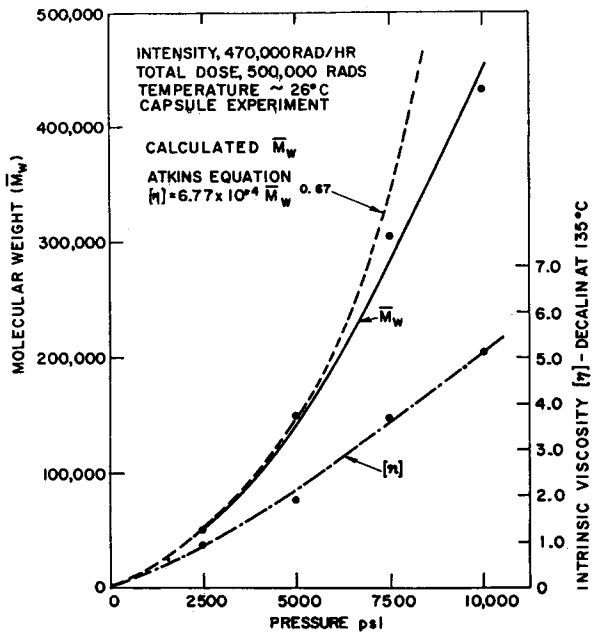


Fig. 5. Polymerization pressure vs. molecular weight.

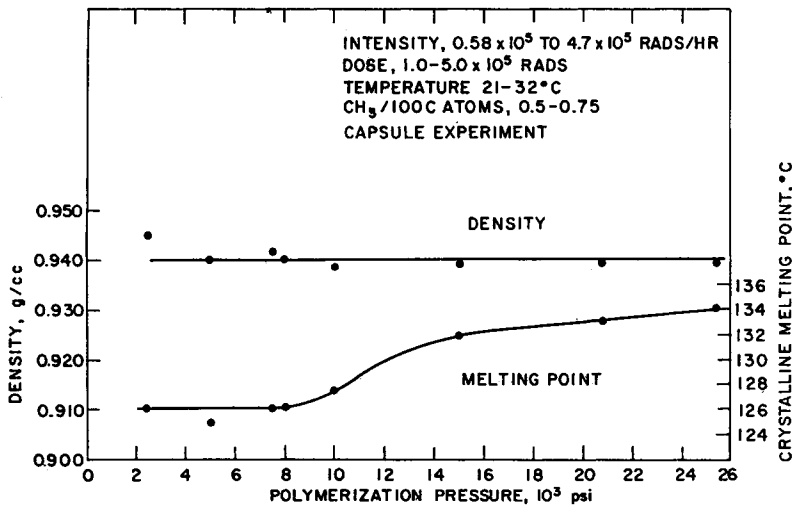


Fig. 6. Polymerization pressure vs. density and crystalline melting point.

point with pressure above $\approx 10,000$ psi for material having the same density indicated above is probably due to molecular weight.

Density was measured by the gradient column method at 23°C. Samples were prepared by pressing powder into film specimens on a Carver press at 165°C. These samples were not annealed prior to measurement.

Melting points were determined with a Perkin-Elmer differential scanning calorimeter calibrated at a scan speed of 10°C./min. Film specimens for determining melting points were prepared in the same manner as for the density measurements.

Effect of Temperature on Density and Methyl Group Content

Increasing the reaction temperature from 26 to 120°C. has a pronounced effect on the density of the polymer, as shown in Figure 7.

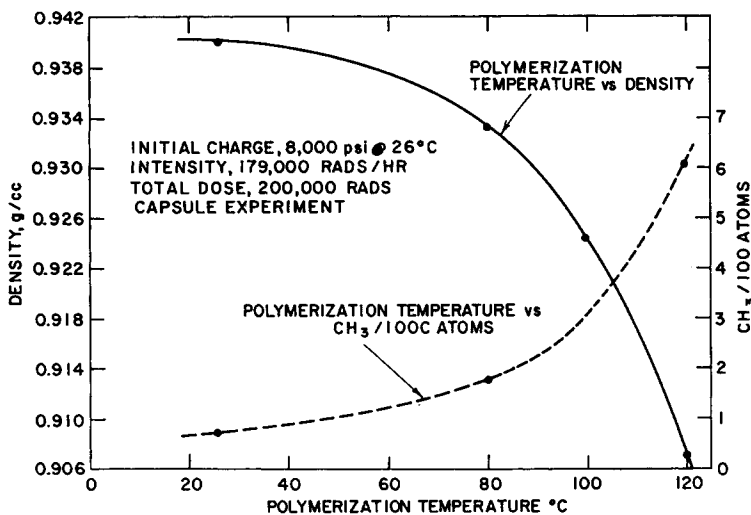


Fig. 7. Polymerization temperature vs. density and methyl groups.

A rapid decrease in density from 0.94 to 0.907 g./cc. occurs with increasing temperature in the range indicated. The methyl group content increases rapidly from 0.7 to 6.0 $\text{CH}_3/100$ carbon atoms as the temperature increases from 26 to 120°C.

This series of experiments was of the static, falling-pressure type, carried out to low conversions. Each vessel was initially charged to 8000 psi at 26°C. and preheated to the desired temperature prior to irradiation. This resulted in the experiments' being carried out at the same initial mass concentration but at different pressures.

Effect of Temperature on Melting Point

The melting points for polyethylene formed under the conditions described in Figure 7 are shown in Figure 8.

A rapid decrease in melting point from 126 to 96°C. is observed as the reaction temperature is increased from 26 to 120°C.

Effect of Pressure on Molecular Weight Distribution

The effect of pressure on the molecular weight distribution is shown in Figure 9 for polyethylene formed at pressures of 2500 and 10,000 psi.

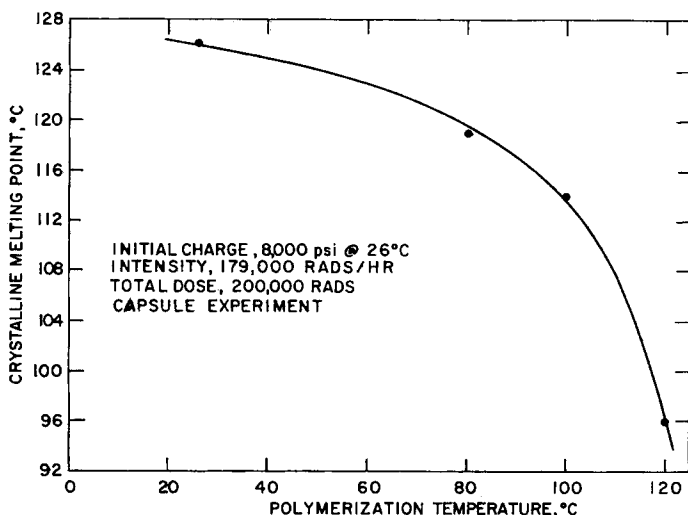


Fig. 8. Polymerization temperature vs. crystalline melting point.

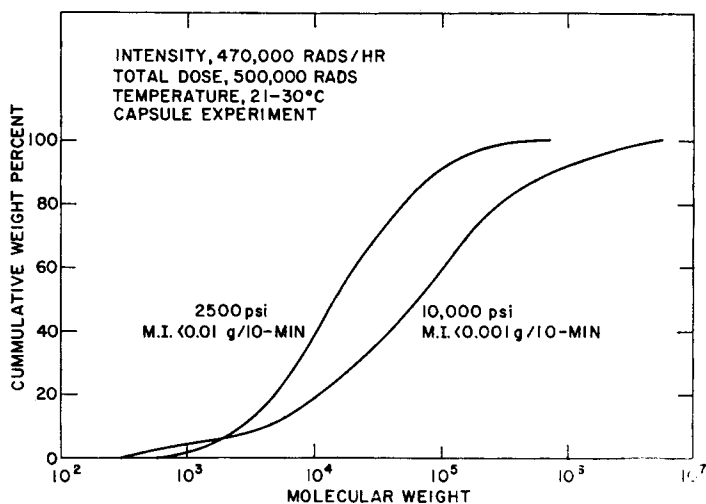


Fig. 9. Polymerization pressure effects on the molecular weight distribution.

Both samples were formed at the intensity, dose, and temperature indicated in the figure. Since each sample received the same radiation dose the per cent conversion, which varies with pressure, was different for each experiment. Conversions were 2% for the 2500-psi run and 16% for the 10,000-psi run. The molecular weights for polymer formed at the higher pressure vary over a range which is wider than that for the lower pressure material. The weight-average molecular weights for the polymers formed at 2500 and 10,000 psi were 49,000 and 433,000, respectively. The melt indices are both low, as indicated in Figure 9. Melt indices for poly-

ethylene formed under a variety of experimental conditions at room temperature did not exceed 0.06 g./10 min.

Measurements for melt indices were made according to the method described in ASTM D1238-62T condition E. Molecular weight distribution curves were obtained with a Water's gel permeation chromatograph. The solvent used was trichlorobenzene at 130°C.

Typical Molecular Weight Distribution Curves for Radiation-Produced Polyethylene

Figure 10 shows typical molecular weight distribution curves for radiation-produced polyethylene formed at temperatures from 20 to 120°C. Data for a commercial high-pressure polyethylene have been obtained and are also presented in the figure for comparison. The curves for Gamma-thene indicate that the highest fraction of polymer is at the high molecular weight end. The data also indicate that a narrower molecular weight distribution is obtained with increasing temperature. The apparent differences in molecular weight distribution and weight-average molecular weight probably account for the measured melt index of 22 g./10 min. for the commercial polyethylene as compared to 0.06 g./10 min. for Gamma-thene formed below 100°C.

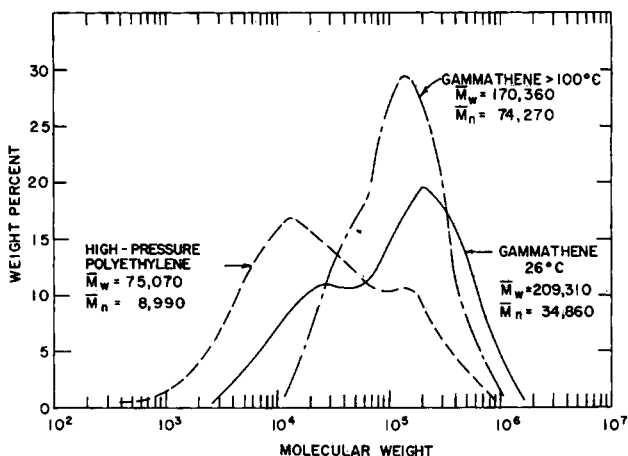


Fig. 10. Typical molecular weight distribution curves in Co^{60} γ -radiation polymerization of ethylene.

Infrared Spectrum for Radiation-Produced Polyethylene

The infrared spectrum shown in Figure 11 is typical of all radiation-produced polyethylene at 20°C. It appears that very little unsaturation is incorporated in the chain or at the chain ends, as indicated by the *trans* and vinyl unsaturation groups at 10.35 and 11.0 μ . The highest proportion of unsaturation is apparently the pendent methylene groups at

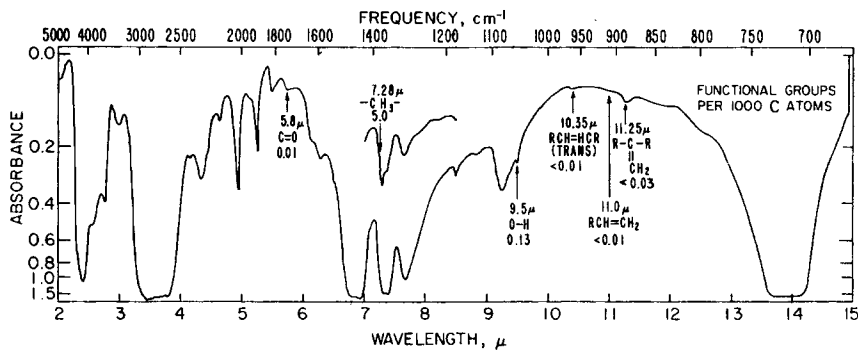


Fig. 11. Typical polyethylene infrared spectrum of Co^{60} γ -radiation polymerization of ethylene.

11.25 μ . A comparison of these data with those for polyethylene formed at 200°C. in a radiation field is given in Table I.

The presence of oxygen, as indicated by the carbonyl group at 5.8 μ in Figure 11, can be due to the oxygen impurity in the ethylene gas which contained <5 ppm O_2 , or possibly to the fact that at the low temperature there may be entrapped radicals in the polymer which react when exposed to atmospheric oxygen.

TABLE I

Radiation temperature, °C.	Unsaturation/1000 C atoms			Mol wt., \bar{M}_w
	$\text{R}_1\text{CH} = \text{CHR}_2$	$\text{RCH} = \text{CH}_2$	$\text{R}_1\text{R}_2\text{C} = \text{CH}_2$	
20	<0.01	<0.01	<0.03	350,000
200	<0.08	<0.01	<0.06	45,400

Another possible explanation is the fact that in the preparation of film specimens no precaution was taken to exclude atmospheric air. This may also account for the hydroxyl group at 9.5 μ .

PART II

The following information was obtained from experiments performed in the elongated or fall-through type of reactor described earlier. The analytical techniques used were the same as those previously described.

Effect of Temperature on Density and Methyl Group Content

The effect of temperature on density and methyl group content, as shown in Figure 12, is not as pronounced for the fall-through type experiments as it is for the 100-cc. capsule-type experiments shown in Figure 7. A comparison of the densities obtained at 120°C. indicates a density of 0.91 g./cc. for the capsule experiment and a value of 0.93 g./cc. for the fall-through experiment,

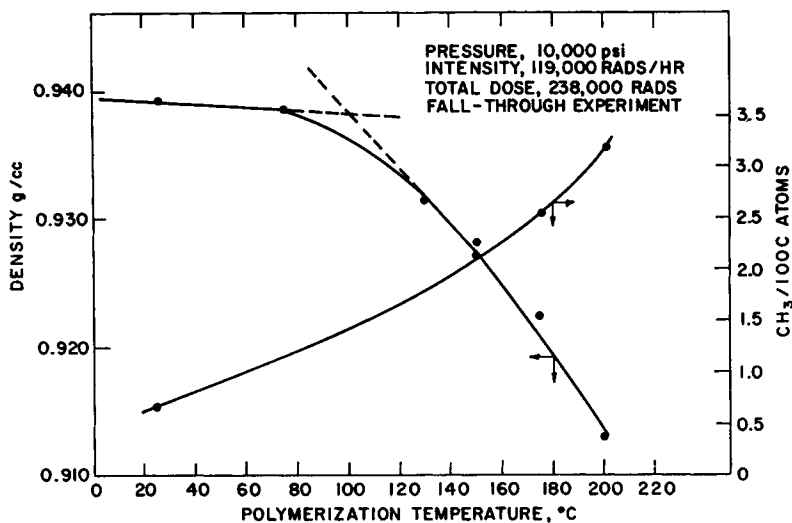


Fig. 12. Polymerization temperature vs. density and methyl groups.

The methyl group content in the same temperature range is higher for the capsule-type experiments (Fig. 7) than for the fall-through experiment (Fig. 12). This implies that removal of the polymer from the radiation field results in higher density material in the range of temperatures given.

Effect of Temperature on Crystalline Melting Point

Melting points (Fig. 13) for the same polyethylene samples used to obtain the density measurements shown in Figure 12 indicate a linear decrease from 128 to 108°C. with increasing reaction temperature from 26 to 200°C.

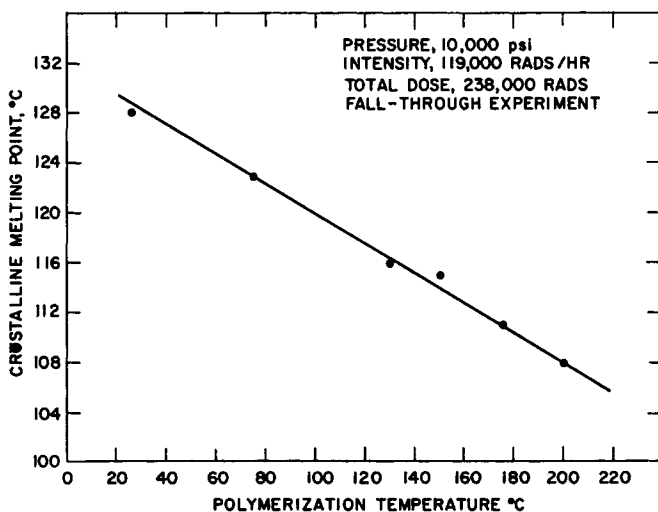


Fig. 13. Polymerization temperature vs. crystalline melting point.

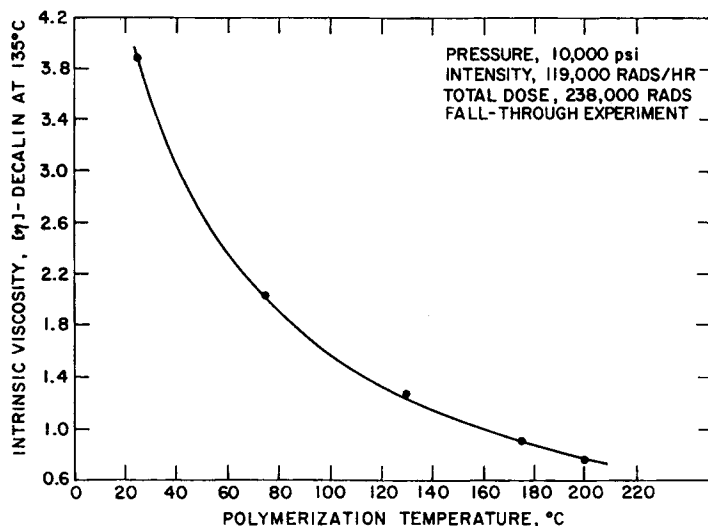


Fig. 14. Polymerization temperature vs. intrinsic viscosity.

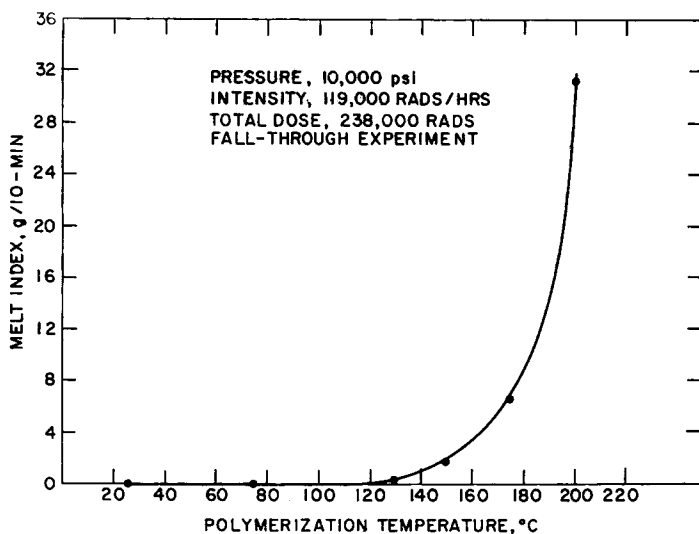


Fig. 15. Polymerization temperature vs. melt index.

Effect of Reaction Temperature on Intrinsic Viscosity

Intrinsic viscosity measurements for the same polyethylene samples used in Figures 12 and 13 are shown in Figure 14 as a function of temperature. The same total irradiation dose was used for each sample, and therefore the per cent conversion varied greatly with temperature. A rapid decrease in $[\eta]$, from 3.9 to 0.7, results with increasing reaction temperature in the range of 26–200°C.

Effect of Reaction Temperature on Melt Index

Under the experimental conditions of pressure, radiation intensity, and dose given in Figure 15, the melt indices for polyethylene formed at temperatures up to $\approx 130^\circ\text{C}$. are extremely low and in most cases could not be measured by the method described earlier. Above 130°C . the melt index increases rapidly with temperature to a value of 31 g./10 min. at 200°C .

Effect of Pressure on Melt Index

Pressure, as indicated in Figure 16, has an appreciable effect on the melt index. The data shown were obtained at 200°C . and at constant radiation intensity and dose. Over the range of pressure shown (7500–14,500 psi), the melt index decreases rapidly with increasing pressure from 100 to 0.2 g./10 min.

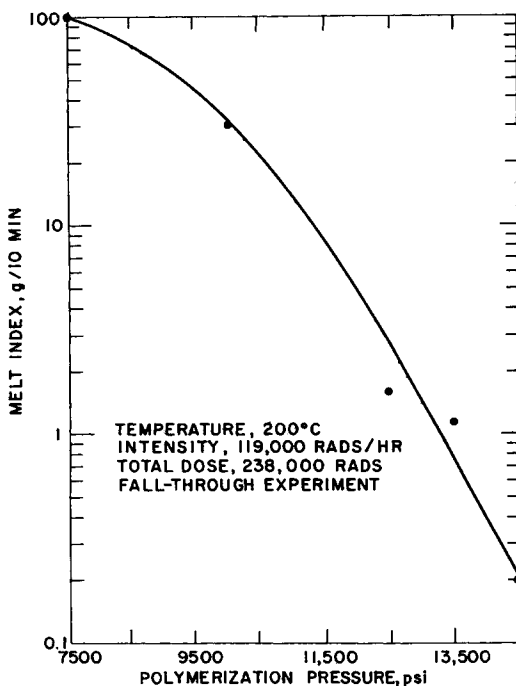


Fig. 16. Polymerization pressure vs. melt index.

Below a pressure of 7500 psi and under the same experimental conditions as above, the melt index was too high to measure by the method employed.

Effect of Pressure on Density and Melting Point

The density for polyethylene formed at 200°C . and under the conditions indicated in Figure 17 appears to remain essentially constant in the range of

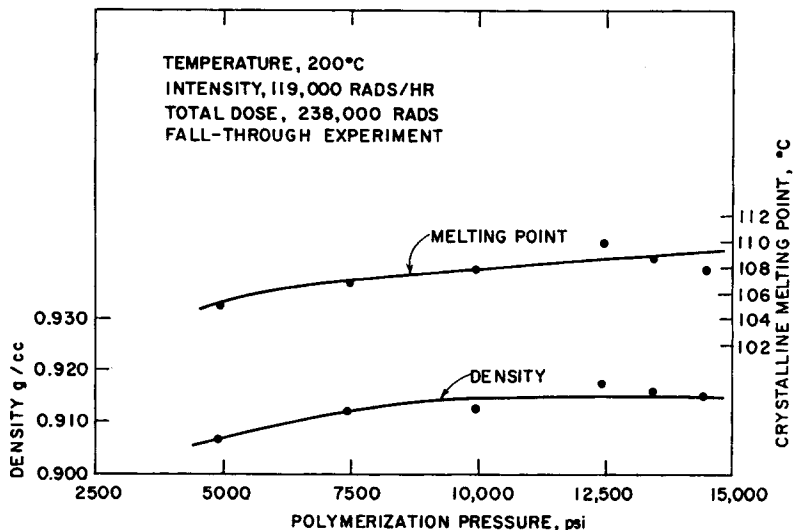


Fig. 17. Polymerization pressure vs. density and crystalline melting point.

pressure from 7500 to 14,500 psi. The lower density value obtained at 5000 psi is for a waxy, low molecular weight polyethylene formed under these conditions.

The melting points obtained for the same polyethylene samples increase slowly from 105 to 109°C. with increasing pressure from 5000 to 14,500 psi, as shown in Figure 17.

Effect of Reaction Temperature on Molecular Weight Distribution

Molecular weight distribution curves are shown in Figure 18 for polyethylene formed at 26, 150, and 200°C. under the conditions of pressure, radiation intensity, and dose indicated in the figure.

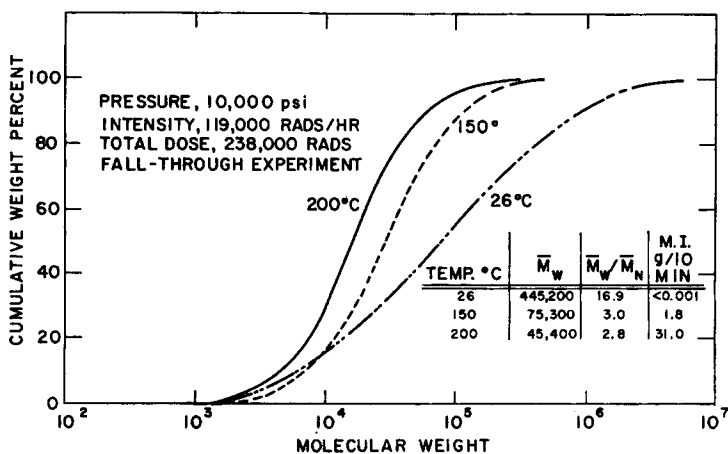


Fig. 18. Polymerization temperature and its effect on molecular weight distribution.

The curves show that as the temperature is increased from 26 to 200°C., the distribution becomes narrower. This is also indicated by the ratio of the weight-average molecular weight to the number-average molecular weight. A small difference in \bar{M}_w/\bar{M}_n is shown for samples formed at 150 and 200°C. as compared to the ratio obtained at 26°C.

Temperature also has a strong effect on \bar{M}_w and on the melt index, as shown in Figure 18. Molecular weights for polymers produced at 26 and 200°C. differ by an order of magnitude. The melt index appears to be a function of molecular weight, increasing rapidly with decreasing \bar{M}_w .

Effect of Pressure on Molecular Weight Distribution

Figure 19 shows the molecular weight distribution curves for polyethylene formed at 200°C. and at pressures of 10,000 and 14,500 psi. Both polymers were formed at the same radiation intensity and total dose. As indicated

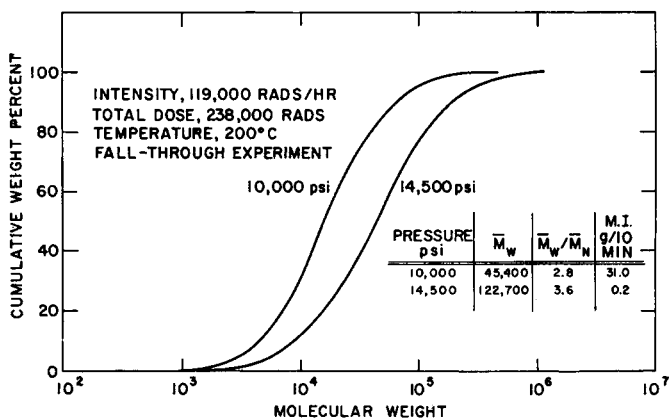


Fig. 19. Polymerization pressure and its effect on molecular weight distribution.

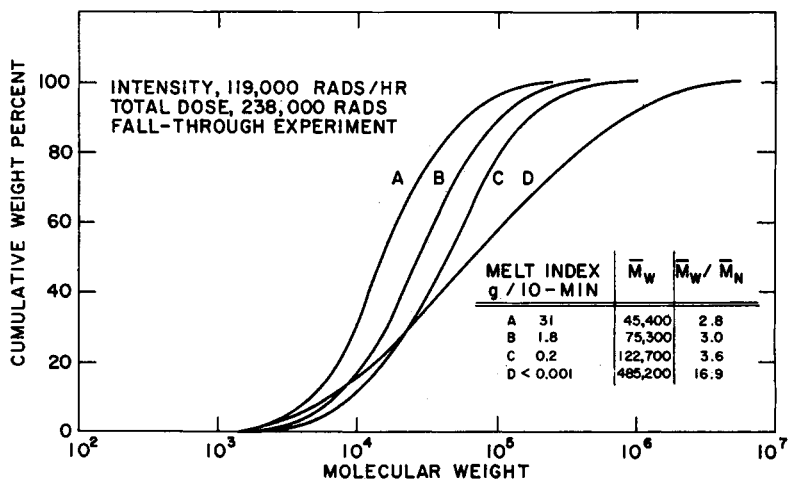


Fig. 20. Molecular weight distribution and its relation to melt index.

by the slopes of the curves and by the \bar{M}_w/\bar{M}_n ratios, both polymers have narrow molecular weight distributions. An appreciable difference in \bar{M}_w , increasing from 45,400 to 122,700 with increasing pressure from 10,000 to 14,500 psi, is indicated in the data. The melt index of 31.0 g./10 min. at 10,000 psi decreases rapidly to a value of 0.2 g./10 min. at 14,500 psi.

Figure 20 is a composite of the molecular weight distribution curves shown in Figures 18 and 19.

It is evident from Figure 20 that the melt index is an inverse function of \bar{M}_w . The distribution appears to be narrower for the polymers of low molecular weight and high melt index.

The broad distribution of sample D, together with its very low melt index, indicates that the polymer is essentially free of long-chain branching. Therefore, the methyl content of 0.7 CH₃/100 C atoms for sample D consists predominantly of short (2–4 carbon atoms in length) side chains.

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Résumé

On a étudié plusieurs propriétés du polyéthylène synthétisé par les radiations γ émises par le Co⁶⁰. Les réactions de polymérisation ont été réalisées en essais statiques dans un large domaine de conditions. Les mesures comprennent le poids moléculaire, la distribution des poids moléculaires, la densité, la teneur en groupe méthyle, le point de fusion cristallin et le point de fusion. On a trouvé que la densité du polyéthylène formé à 20°C est de 0.94 g/cc. Cette valeur est indépendante de la pression entre 170 et 1700 atmosphères, et de l'intensité des radiations entre 0.58×10^{-5} et 4.7×10^{-5} rads/hr. Une élévation de la température augmente le contenu en groupe méthyle et diminue la densité jusqu'à 0.91 g/cc à 20°C. Dans tout le spectre de conditions expérimentales, les polymères formés sont complètement solubles dans l'orthodichlorobenzène à 135°C. On a déterminé la viscosité intrinsèque et on a montré sa dépendance vis à vis de la température, de la pression, de l'intensité, et de la dose de radiations. On a essayé de relier l'indice de fusion avec le poids moléculaire et la distribution des poids moléculaires.

Zusammenfassung

Einige Eigenschaften von Polyäthylen, das mittels Co⁶⁰-Gammastrahlung synthetisiert wurde, wurden untersucht. Die Polymerisationsreaktion wurde in statischen Versuchen in einem weiten Bereich von Versuchsbedingungen ausgeführt. Gemessen wurden Molekulargewicht, Molekulargewichtsverteilung, Dichte, Methylgruppengehalt, kristalliner Schmelzpunkt und Schmelzindex. Die Dichte des bei 20°C gebildeten Polyäthylens betrug 0.94 g/cc. Dieser Wert scheint von 170 bis 1700 at vom Druck und vom 0.58×10^6 bis 4.7×10^6 rad/h von der Strahlungsintensität unabhängig zu sein. Steigende Temperatur führt zu einer Zunahme des Methylgruppengehalts und

einer Abnahme der Dichte auf 0.91 g/cc bei 200°C. Im gesamten Bereich der Versuchsbedingungen waren die gebildeten Polymeren in *o*-Dichlorobenzol bei 135°C vollständig löslich. Viskositätszahlen wurden bestimmt, und ihre Abhängigkeit von Temperatur, Druck, Intensität und Strahlungsdosis wird angegeben. Es wurde versucht eine Korrelation zwischen Schmelzindex und Molekulargewicht sowie Molekulargewichtsverteilung herzustellen.

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