

Physical Properties and Structure of the Polyethylene Produced by γ -Radiation Polymerization

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Synopsis

Polyethylene produced by γ -radiation had short-chain branching to some extent and a small amount of vinylidene unsaturation. An OH group was found in polyethylene produced in the presence of methanol. The properties and structure of the polymer were found to vary widely with changes in the reaction condition, such as ethylene pressure, reaction temperature, time, and dose rate. Polymer density, an important property, varied from 0.88 to 0.96 g./cc. and crystallinity from 40 to 80%, depending on the reaction conditions. Polyethylene polymerized at room temperature at a pressure of 300–400 kg./cm.² was shown to have an extremely high molecular weight (up to 300,000) and low methyl content (below 0.5CH₃/100C). Density depends solely on the crystallinity of the polymer, which was found to be determined by the degree of short-chain branching and molecular weight. Quantitative relationships between them were obtained. The use of methanol as a solvent was found to have no effect on short-chain branching but have a marked effect on molecular weight; hence, high-density polyethylene could be obtained with the use of methanol solvent. Polyethylenes with a high molecular weight (above 100,000) had a higher melting point than high-pressure polyethylene. The quantitative correlation between molecular weight and melt index was also determined and found to be similar to that of Sperati. Some mechanical properties were also measured.

INTRODUCTION

The properties and structure of conventional polyethylene produced by both free radical-initiated and ionic polymerization have been widely investigated, while those of polyethylene produced by radiation polymerization have not been studied extensively to date, though some data have been reported.¹⁻³ Since radiation polymerization is expected to be a useful commercial polyethylene process, it is very important to elucidate the structure and properties of this polyethylene.

A study of the influence of reaction conditions on chain branching, which has a marked effect on polymer properties, was reported previously.⁴

The purpose of this study is to elucidate the properties and structure and the correlations between them in polyethylene produced by γ -irradiation.

EXPERIMENTAL

Polymerization Procedure

The equipment and procedure for polymerization were almost the same as described in the previous paper.⁵ The procedure is, therefore, described here briefly. The ethylene used was 99.9% pure (free of CO and H₂S), containing 48 ppm acetylene and 3 ppm oxygen. Alcohol used as solvent was a commercially guaranteed grade. A 100-cc. stainless-steel high-pressure reaction vessel was thoroughly cleaned, evacuated, and flushed three times with monomer before being filled with ethylene. The polymerizations were carried out under various reaction conditions at pressures of 70–400 kg./cm.² at 20–30°C. and at dose rates of 5×10^3 – 4.3×10^5 rad/hr., and Co⁶⁰ was used as the radiation source. Most of the experiments were carried out without solvent, but several experiments were performed in the presence of alcohol.

Evaluation Procedure

For density measurement and infrared analysis, the sample was prepared by hot pressing at 130°C. into films of ca. 0.2 mm. thickness and quenching to room temperature for 15 min. Before measurement, the sample was kept at room temperature in a desiccator for more than 24 hr.

The density was determined by the gradient tube method at 23°C., with the use of a water-methanol mixed solution. The density determination itself had a standard deviation of about 0.0002 g./cc.

Infrared absorption spectra were measured with a Nippon-bunko Model DS 301 infrared spectrophotometer using NaCl optics. The concentration of methyl groups in polyethylene was determined from the peak at 1378 cm.⁻¹ by the method of Bryant and Voter.⁶ The contents of various types of unsaturation, i.e., terminal vinyl, *trans*-vinylene, and vinylidene, were determined from the peaks at 908, 964, and 888 cm.⁻¹ respectively, according to Cross⁷ and Cernia.⁸

The degree of crystallinity was obtained by an x-ray method.⁹

The melting point of polyethylene was measured by Rigakudenki Model VKP-32 differential thermal analysis (DTA), and the melt index was determined by a melt-indexer according to the procedure of ASTM D 1283-52T.

Number-average molecular weights were determined from the viscosity measurement of tetralin solutions at 130°C. by use of Tung's formula.¹⁶

$$[\eta] = 5.1 \times 10^{-4} \bar{M}_n^{0.725}$$

RESULTS AND DISCUSSION

Molecular Structure Determined from the Infrared Spectrum

Branched Structure. Infrared spectra show that the radiation-polymerized polyethylene has several short-chain branchings, like high-pressure

TABLE I
Molecular Structure of Polyethylene

	\bar{M}_n	Density, g./cc.	Crystal- linity, %	Methyl content, CH ₃ /1000C	Double bonds/1000C		
					RRC=CH ₂	RCH=CHR	RCH=CH ₂
γ -Radiation polymerized ^a	223,000	0.938	70	4.4	0.037	0	0
Sumikathene F-70	28,000	0.915	—	28.6	0.377	0.063	0.046
Marlex 35	—	0.96	—	0	0.029	0	1.77

^a Polymerization conditions: pressure, 150 (initial) to 106 (final) kg./cm.²; temperature, 26 \pm 1°C.; dose rate, 2.5 \times 10⁴ rad/hr.; time, 20.3 hr.

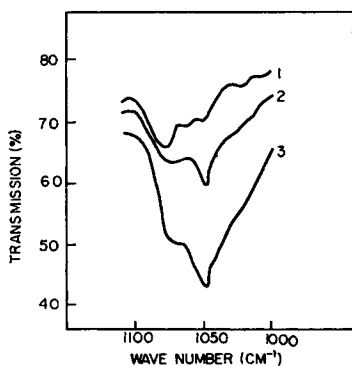


Fig. 1. Infrared spectra at 1050 cm.^{-1} of polyethylenes produced by radiation: (1) polymerized without methanol; (2) polymerized in the presence of 50 ml. methanol; (3) polymerized in the presence of 75 ml. methanol. Reaction pressure, 300 kg./cm.^2 ; temperature, $22 \pm 1^\circ\text{C.}$; dose rate, $2.5 \times 10^4\text{ rad/hr.}$; time, 5 hr.

polyethylene. The concentration of methyl groups, which corresponds to the degree of short-chain branching, varies widely, i.e., from 1 to $70\text{ CH}_3/1000\text{C.}$ The methyl content was found to increase with the reaction temperature and decrease with the pressure as was reported previously.⁴ As shown in Table I, the methyl content of the sample polymerized by radiation at 26°C. and 150 kg./cm.^2 is $4.4\text{ CH}_3/1000\text{C.}$ It is to be noted that this value is much smaller than that of a conventional high-pressure polyethylene polymerized by a radical initiator. The reason for this seems to be attributable to the difference in the reaction temperature. It is an important characteristic of the radiation polymerization that the ethylene easily polymerizes, even at room temperature, to a polymer with high molecular weight and very low methyl content. Our radiation-polymerized polyethylene was shown to have little crosslinking from the fact that the sample was completely soluble in hot tetralin, and the correlation between specific gravity and crystallinity is almost the same as that for conventional high-pressure polyethylene.

From these results, it may be concluded that almost no radiation-induced crosslinking takes place in these experiments.

Unsaturation. Conventional polyethylene (e.g., Sumikathene F-70) has various types of unsaturation (Table I), while, radiation-polymerized polyethylene lacks both terminal vinyl and *trans*-vinylene types, and has only a small amount of vinylidene unsaturation. The fact that the vinylidene is almost the sole unsaturation in both radical-initiated and γ -radiation polyethylene, suggests a similarity in the polymerization mechanism. Reaction conditions such as temperature, pressure, and dose rate have no considerable effect on the unsaturation content.

Hydroxyl Group. As shown in Figure 1, the presence of the hydroxyl group ($-\text{OH}$) is clearly indicated by the 1050 cm.^{-1} band in the infrared spectrum of polymer produced in the presence of methanol (Fig. 1). The hydroxyl group has never been observed in conventional polyethylene. It

is also shown that the content of OH group increases with the amount of methanol added. Details of this phenomenon will be reported in a subsequent report. This OH group has no effect on physical properties such as density, crystallinity and melt index.

Physical Properties

Density and Crystallinity. Various polyethylenes with the densities of 0.88–0.96 g./cc. and the crystallinities of 40–80% were obtained depending on the reaction conditions. It was recognized early that density depended solely upon the crystallinity of polymer, and a correlation between these properties was given by Sperati¹⁰ for high-pressure polyethylene.

Plots of the density d against crystallinity X as determined by x-ray are shown in Figure 2, from which following quantitative relationship is obtained:

$$d = 2.0 \times 10^{-3}X + 0.803 \quad (1)$$

where, d represents density and X is per cent crystallinity. This formula was found to be exactly the same as that of Sperati.

In addition, the theoretical equation, eq. (2), relating the specific volume of the amorphous and crystalline parts of the solid polyethylene

$$V = V_a(1 - X_m) + V_cX_m \quad (2)$$

was applied, where, V , V_a , and V_c represent the specific volume of the entire sample, amorphous part, and the crystalline part, respectively, and X_m is the weight fraction crystallinity. The data were plotted again in Figure 3, from which V_a and V_c are obtained as 0.992 and 1.225 cc./g., respectively. These values are almost the same as for conventional polyethylene.¹¹

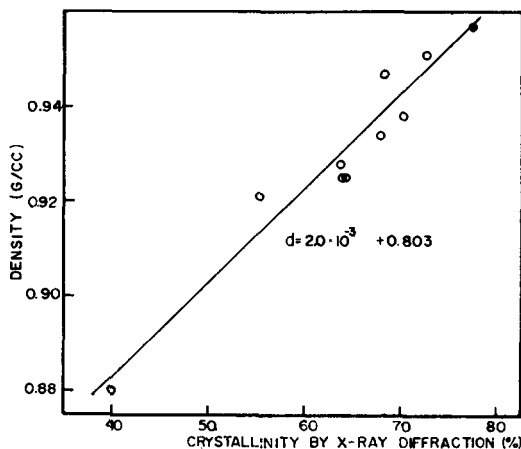


Fig. 2. Relation between density and crystallinity: (O) samples polymerized without solvent; (●) samples polymerized in the presence of methanol.

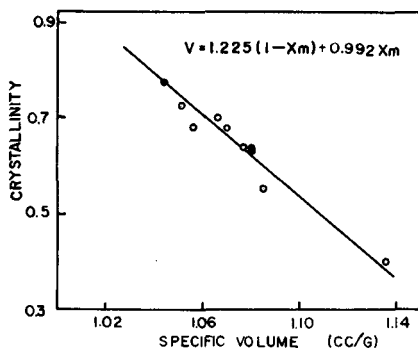


Fig. 3. Relation between crystallinity and specific volume: (O) samples polymerized without solvent; (●) sample polymerized in the presence of methanol.

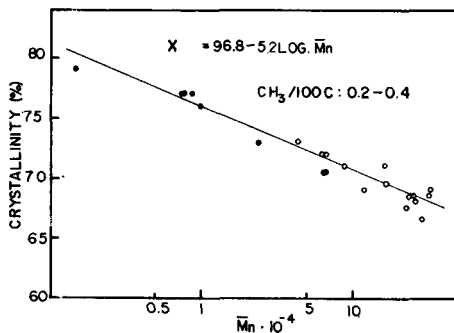


Fig. 4. Relation between crystallinity and molecular weight: (O) samples polymerized without solvent; (●) samples polymerized in the presence of methanol.

Effect of Molecular Weight on Crystallinity. In order to elucidate the factors which affect density and crystallinity, several studies^{10,12-14} were made. Even though it was soon shown that high-pressure polyethylene had a branched structure which interrupted crystallization and reduced density, the effect of molecular weight on density has often been overlooked, except at much lower molecular weight.¹³ More recently, however, it was clearly shown¹⁵ that molecular weight has an important effect on density up to $\bar{M}_n = 50,000$ for high-pressure polyethylene. The density increases as the molecular weight decreases. For these polyethylenes, the effect of molecular weight on density is shown in Figure 4 up to much higher molecular weight, i.e., from 1,500 to 400,000. The samples in Figure 4 have almost the same methyl content. Therefore, the change in density must be ascribed to a change in molecular weight. This effect of molecular weight seems to indicate that the shorter polymer chain orients more easily in the crystalline regions.

In addition, it should be noted that the samples polymerized in the presence of methanol have greater density than those obtained without methanol. This fact may indicate that methanol decreases the molecular weight of polymer without changing methyl content.

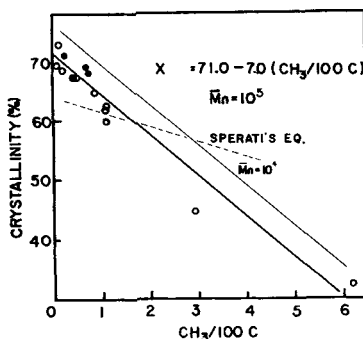


Fig. 5. Relation between crystallinity and methyl content: (O) samples polymerized without solvent; (●) samples polymerized in the presence of methanol.

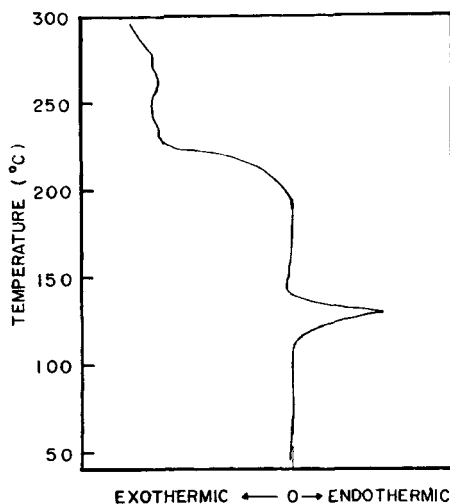


Fig. 6. Differential thermal analysis diagram for radiation-polymerized polyethylene having $\bar{M}_n = 223,000$ and 70% crystallinity. Rate of temperature increase is 2.5°C./min.

Effect of Short-Chain Branching on Crystallinity. It was reported by Sperati et al.¹⁰ and other workers that as the short-chain branching in high-pressure polyethylene increases, the polymer density and crystallinity decrease markedly.

The quantitative effect of short-chain branching is illustrated in Figure 5, from which eq. (3) was obtained for radiation-polymerized polyethylene of $\bar{M}_n = 100,000$

$$X = 71.0 - 7.0(\text{CH}_3/100\text{C}) \quad (3)$$

where X represents per cent crystallinity, and $\text{CH}_3/100\text{C}$ is the number of methyl group (except terminal) per 100 carbon atoms.

Melting Point and Melt Index. A typical DTA diagram of a polymer with \bar{M}_n 223,000 and 70% crystallinity is shown in Figure 6. An endo-

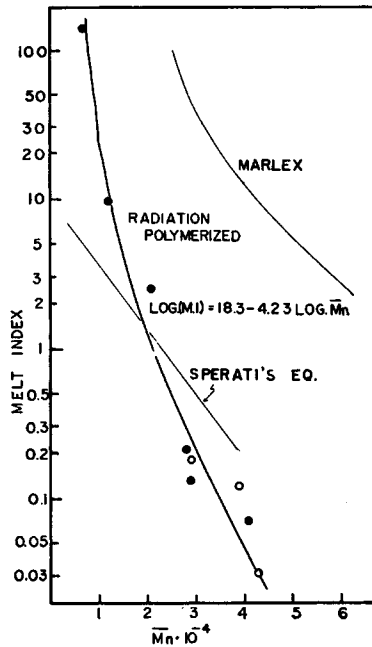


Fig. 7. Relation between melt index and molecular weight: (O) samples polymerized without solvent; (●) samples polymerized in the presence of methanol.

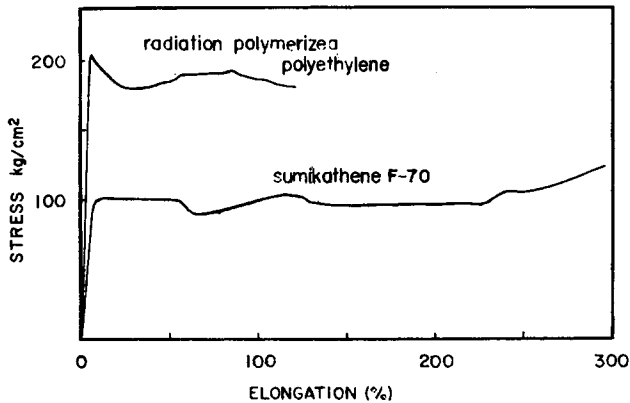


Fig. 8. Stress-strain curve of radiation-polymerized polyethylene and high-pressure polyethylene (Sumikathene F-70) Specimens were prepared by hot compression molding; thickness 0.5 mm. for radiation-polymerized sample and 0.2 mm. for Sumikathene. Strain rate, 500 mm./min.

thermic peak is clearly observed at about 130°C.; i.e., melting of the sample begins at 117°C. and ends at 140°C. A sample with $\bar{M}_n = 29,000$ and 64.1% crystallinity melts at a lower temperature (108–123°C.). The melting point of the polymer may depend mainly on the crystallinity and

molecular weight. In addition, Figure 6 also indicates the exothermic peak caused by the oxidation of sample at 200–230°C.

Melt index MI, one of the important properties in the practical performance of the polymer, depends mainly on molecular weight. The effect of \bar{M}_n on melt index is shown in Figure 7, from which the relationship of eq. (4) was obtained:

$$\log \text{MI} = 18.3 - 4.23 \log \bar{M}_n \quad (4)$$

There is no large deviation from Sperati's equation for high-pressure polyethylene. The melt index of radiation-polymerized polyethylene is much higher than that of Marlex (Phillips polyethylene) with same molecular weight. The reason for this difference is not clear, but it may be due to the difference in the molecular weight distribution and in the degree of long and short branching.

Mechanical Properties. Typical stress-strain curves of a radiation-polymerized polyethylene with $\bar{M}_n = 232,000$, 68.6% crystallinity and of Sumikathene F-70 (high-pressure polyethylene with $\bar{M}_n = 28,000$) are shown in Figure 8. These curves were obtained from the results tests repeated seven times. The numerical values are summarized in Table II.

TABLE II
Mechanical Properties of Polyethylene

Property	Radiation-polymerized polyethylene ^a	High-pressure polyethylene (Sumikathene F-70)
Tensile strength, kg./cm. ²		
At fracture	180	99.5
At upper yield	204	123
Elongation, %	122	295

^a Polymerization conditions: pressure, 203 (initial) to 113 (final) kg./cm.²; temperature, 28 ± 1°C; dose rate, 2.5 × 10⁴ rad/hr.; time, 20 hr.

It is apparent that the radiation-polymerized polyethylene has considerably higher tensile strength and lower elongation than the high-pressure polyethylene. These differences may be due to the difference in molecular weight.

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Résumé

Le polyéthylène produit au moyen des rayons gamma possède des courtes chaînes ramifiées et une petite quantité d'insaturation vinyldénique. On a trouvé que l'existence de groupement OH dans le polyéthylène se produisait en présence de méthanol. On a trouvé que les propriétés et la structure du polymère changeaient fortement lorsqu'on changeait les conditions de réaction telles que la pression d'éthylène, la température de réaction, la durée et la vitesse de dose. La densité du polymère, qui est une propriété importante, varie de 0,88 à 0,96 (g/cc) et la cristallinité de 40 à 80% suivant les conditions de réaction. Le polyéthylène, polymérisé à température de chambre à des pressions de 300 à 400 kg/cm², possède un poids moléculaire extrêmement élevé, pouvant aller jusqu'à 300.000, et une faible teneur en méthyle, en-dessous de 0,5CH₃/100 C. La densité dépend exclusivement de la cristallinité du polymère, lequel est déterminé par le degré de ramification en courtes chaînes et par le poids moléculaire. On a obtenu des relations quantitatives entre ces valeurs. On a trouvé que le méthanol employé comme solvant n'avait pas d'influence sur la ramification à chaînes courtes, mais avait une influence considérable sur le poids moléculaire; en conséquence, du polyéthylène de haute densité pourrait être obtenu en employant le méthanol comme solvant. Le polyéthylène possédant un poids moléculaire supérieur à 100.000 possède un point de fusion plus élevé que celui du polyéthylène haute-pression. On a également déterminé la relation quantitative qui existe entre le poids moléculaire et l'indice de fusion et elle est semblable à celle de Sperati. On a également mesuré certaines propriétés mécaniques.

Zusammenfassung

Durch γ -Strahlung erzeugtes Polyäthylen besitzt ein gewisses Ausmass an Kurzkettenverzweigung und eine geringe Menge an Vinyldendoppelbindungen. In Gegenwart von Methanol erzeugtes Polyäthylen weist OH-Gruppen auf. Eigenschaften und Struktur des Polymeren hängen in hohem Grad von den Reaktionsbedingungen, wie Äthylendruck, Reaktionstemperatur, Dauer und Dosisleistung ab. Die Polymerdichte, eine wichtige Eigenschaft, variiert in Abhängigkeit von den Reaktionsbedingungen von 0,88 bis 0,96 g/cc und die Kristallinität von 40–80%. Bei Raumtemperatur unter einem Druck von 300 bis 400 kg/cm² polymerisiertes Polyäthylen besass ein extrem hohes Molekulargewicht bis zu 300.000 und einen niedrigen Methylgehalt unterhalb 0,5 CH₃/100 C. Die Dichte hängt nur von der Kristallinität des Polymeren ab, welche ihrerseits durch den Grad der Kurzkettenverzweigung und das Molekulargewicht bestimmt ist. Die quantitative Beziehung zwischen diesen Grössen wurde aufgestellt. Die Verwendung von Methanol als Lösungsmittel hat keinen Einfluss auf die Kurzkettenverzweigung, jedoch einen beträchtlichen Einfluss auf das Molekulargewicht; durch die Verwendung von Methanol als Lösungsmittel konnte daher Polyäthylen

hoher Dichte erhalten werden. Polyäthylen mit einem Molekulargewicht oberhalb 100.000 besass einen höheren Schmelzpunkt als Hochdruck-Polyäthylen. Weiters wurde die quantitative Korrelation zwischen Molekulargewicht und Schmelzindex bestimmt, die Ähnlichkeit mit der von Sperati aufgestellten aufweist. Schliesslich wurden einige mechanische Eigenschaften gemessen.

Received February 5, 1965