Structure and Properties of Polyethylene Produced by γ-Radiation Polymerization in Flow System

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Synopsis

The radiation-induced polymerization of ethylene was carried out by use of a bench-scale plant with a flow-type reactor of 1 liter capacity under the following conditions: pressure, 200–400 kg/cm^2; temperature, 30–90°C; irradiation intensity, 3.8 × 10^5 rad/hr; and ethylene flow rate, 300–3000 nl/hr. The molecular weight of polymer formed was shown to decrease with increasing reaction temperature and to increase with increasing pressure. When the ethylene flow rate increases, the molecular weight decreases in the polymerization at 30–60°C, but it does not change in the polymerization at 75–90°C. Methyl group content, which is a measure of short-chain branching of the polymer, increases with increasing reaction temperature, i.e., ca. 1 CH$_3$/1000 CH$_2$ at 30°C and ca. 9 CH$_3$/1000 CH$_2$ at 90°C. Methyl content is independent of the ethylene flow rate. The changes in the melt index of polymer with reaction conditions corresponds to the change of the molecular weight. The density, crystallinity, and melting point of polymer decrease with the reaction temperature as the short-chain branching increases, and they are almost independent of ethylene flow rate and pressure.

INTRODUCTION

A series of investigations on the radiation-induced polymerization of ethylene has been carried out in our laboratory.[1–5] These papers were focused mainly on a kinetic study of the polymerization. The physical properties and structure of polyethylene formed in a small-scale batch polymerization induced by γ-radiation were reported by Steinberg et al.[6] and our group.[7]

In addition to the batch experiments, polymerizations in a flow system were carried out with the use of both bench-scale and pilot-scale equipment in our laboratory. Results of the polymerization in the bench-scale flow system were recently reported from a kinetical point of view.[8]

This paper attempts to show the effects of reaction conditions on the structure and properties of the polymer in the bench-scale plant.

EXPERIMENTAL

Apparatus and procedures for the radiation polymerization were described in detail in the previous paper.[8] A schematic diagram of the poly-
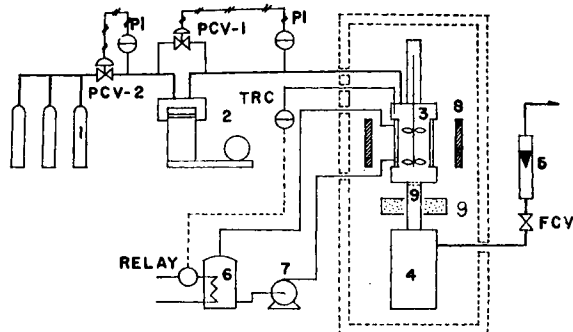
Fig. 1. Flow diagram of polymerization apparatus: (1) ethylene cylinder; (2) compressor; (3) reactor; (4) separator; (5) flowmeter; (6) Dowtherm heater tank; (7) Dowtherm pump; (8) ^{60}Co plate sources; (9) radiation shielding.
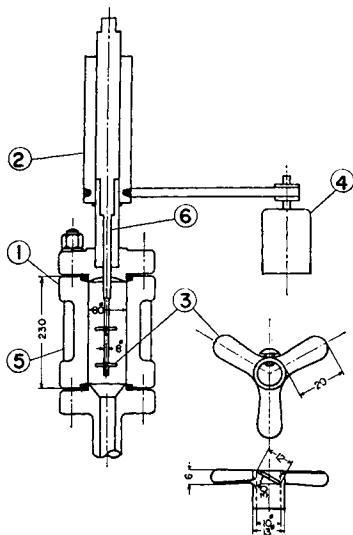
Fig. 2. Reactor system and agitator: (1) reactor; (2) rotor with magnet; (3) impeller; (4) motor for agitation; (5) Dowtherm jacket; (6) stirrer shaft with magnets.

merization apparatus is shown in Figure 1. The reaction vessel, details of which are shown in Figure 2, is of SUS-27 stainless steel and has a capacity of 1 liter. The entire system was evacuated at 0.1 mm Hg at 110°C and was swept out four times with ethylene at 20 kg/cm². Ethylene was then charged at the desired pressure and desired rate by using a diaphragm-type compressor. The radiation source, 54 000-Ci of ^{60}Co, which stored at the bottom of a canal filled with water to a depth of 6 m, was lifted and placed outside the reactor. Powdery polyethylene was produced and carried with the unpolymerized ethylene to a separator of 4 liters capacity, where the polymer was separated from the gas. The polymer accumulated in the separator and unpolymerized ethylene was vented to the atmosphere at

a constant rate. The reaction temperature was controlled automatically by the circulation of Dowtherm in an outer jacket of the reaction vessel. The reaction pressure was measured by a remote Bourdon tube gauge and automatically kept constant by a pneumatic control valve. Agitation of the reaction mixture was carried out by a magnetically driven stirrer with two marine propellers.

The ethylene used was 99.9% pure (free of CO and H_2S), containing less than 5 ppm oxygen and 10 ppm of acetylene.

For the measurements of density and infrared absorption spectra of the polymer, samples were prepared by hot-pressing at 130°C into films ca. 0.2 mm thick and quenching to room temperature for about 10 min. Before the measurement, the samples were kept at room temperature in a desiccator for more than 24 hr. The density was measured in a gradient tube at 25°C with a methanol–water solution.

Infrared absorption spectra were measured with a Japan Spectroscopic Co. Model DS-301 infrared spectrophotometer with NaCl optics. The methyl group content in the polymer was determined from the absorption at 1378 cm^{-1} by the method of Bryant and Voter.[9]

The melting point of the polymer was measured by a differential thermal analysis, melt index by a melt indexer according to ASTM-D-1238, and tensile properties by a Shimadzu Autograph IS-2000 according to ASTM D-638. Number-average molecular weight was determined from viscosity measurements on tetralin solution at 130°C by use of Tung's formula.[10]

RESULTS AND DISCUSSION

The infrared spectrum of the polyethylene produced by radiation polymerization at 30°C is shown in Figure 3. The amount of unsaturation is apparently very small in comparison with that in conventional polyethylene.

The highest rate of unsaturation is vinylidene type at 888 cm^{-1}. The existence of small amount of methyl group is also indicated by a shoulder at 1378 cm^{-1}. The methyl group content, which controls the crystallinity of the polymer, varies with the reaction conditions, as described below. The spectrum of the polymer formed in the flow system is essentially the same as that of the polymer formed in the batch experiment.[7]
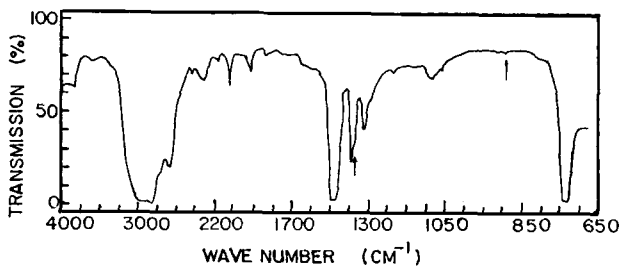

Fig. 3. Infrared spectra of radiation-polymerized polyethylene. Polymerization was carried out at 30°C, 400 kg/cm^2, 3.8 × 10^5 rad/hr.

Effect of Ethylene Flow Rate

Figure 4 shows the effect of ethylene flow rate in the range from 300 to 3000 nl/hr on the polymer molecular weight at various temperatures from 30 to 90°C under a constant pressure of 400 kg/cm². The molecular weight of polymer formed at 30–60°C obviously decreases with increasing ethylene flow rate, which brings about the decrease of the residence time of polymer and monomer in the reactor. This fact is consistent with the fact observed in the batch experiment, i.e., the polymer chain grows successively, and the
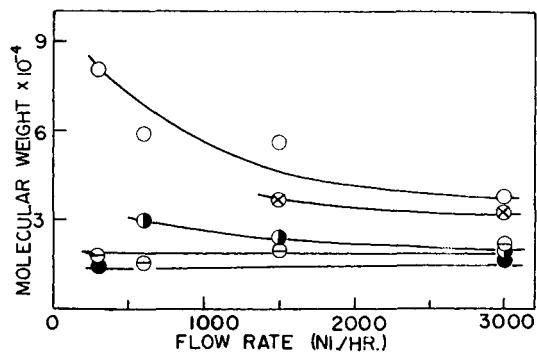

Fig. 4. Effect of ethylene flow rate on the molecular weight of polymer; polymerization was carried out at (O) 30°C, (⊗) 50°C, (◑) 60°C, (⊖) 75°C, and (●) 90°C, at 400 kg/cm² with a dose rate of 3.8 × 10⁵ rad/hr.
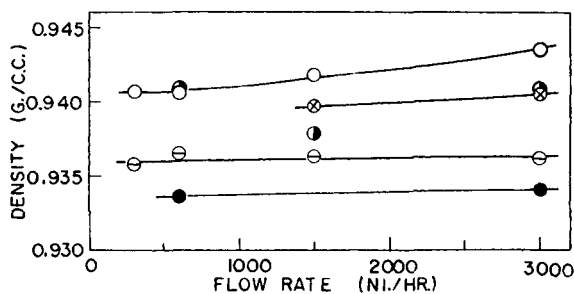

Fig. 5. Effect of ethylene flow rate on the polymer density: reaction conditions and symbols are the same as in Fig. 4.

molecular weight increases continuously with the reaction time in low-temperature polymerization.[1] The dependence of the molecular weight on the ethylene flow rate is also found to decrease with increasing reaction temperature and to vanish above a temperature of 75°C. This agrees with the results of batch experiments, that is, the molecular weight becomes independent of the reaction time at elevated temperatures.[4] A kinetical analysis of these facts leads to the conclusion that the lifetime of growing polymer radicals is rather long at lower temperature, while it is very short at higher temperature.[4]
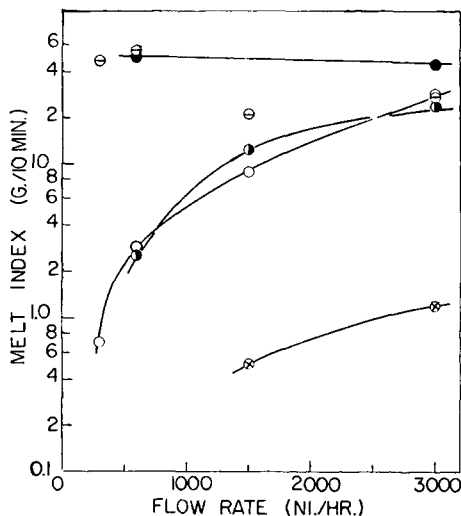
Fig. 6. Effect of ethylene flow rate on the melt index of polymer. For the sample polymerized at 30°C, a high-load melt index is used (measured with the weight of 21.6 kg); reaction conditions and symbols are the same as in Fig. 4.

The methyl group content in the polymer increases slightly with decreasing ethylene flow rate at a given temperature. In other words, the degree of short-chain branching increases to some extent with the residence time of polymer in the reactor.

Figure 5 shows that the density of polymer formed below 60°C increases slightly with the flow rate but, at 75–90°C, the density is independent of the flow rate. This increase of the density is due to the decrease in the branching and molecular weight, which bring about higher crystallinity.[7,11]

The influence of the ethylene flow rate on the polymer melt index is shown in Figure 6. The melt index is observed to increase with the flow rate at temperatures of 30–60°C, while at 75–90°C no dependence on flow rate of the melt index is observed. The melt index of the polymer is controlled by the molecular weight and molecular weight distribution.[7,11]

Effect of Reaction Pressure

As shown in Figure 7, the molecular weight of the polymer increases with increasing pressure, while the methyl group content decreases. The reason for the molecular weight increase is that the pressure dependence of propagation rate is higher than that of initiation rate.[1,2] In addition, the decrease of the methyl group content is ascribed to the fact that the pressure dependence of propagation rate exceeds that of branching formation.[5]

The polymer density and melting point are almost independent of the increasing reaction pressure because the effect of the molecular weight increase on the polymer crystallinity compensates that of the decrease in the degree of short-chain branching.
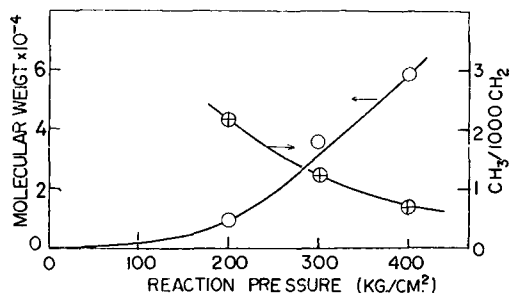
Fig. 7. Effect of reaction pressure on the molecular weight and methyl group content of polymer. Polymerization was carried out at 30°C, 3.8×10^5 rad/hr, ethylene flow rate of 530–600 nl/hr.

Effect of Reaction Temperature

Figure 8 indicates that the molecular weight of polymer markedly decreases with increasing reaction temperature because of the increase of the termination rate.[4] In addition, it can be seen that the temperature dependence of the molecular weight diminishes when the ethylene flow rate increases.

The methyl group content is shown in Figure 9 to increase rapidly as reaction temperature rises. This fact is due to that the temperature dependence of the rate of branching formation is larger than that of the propagation rate. The difference in the activation energy between these two reactions is calculated to be 4.5 kcal/mole.

Since the effect of the temperature on the short branching is the most marked among the reaction conditions, the temperature is an important factor in controlling the physical properties of the polymer. As shown in Figure 10, the crystallinity, the density and the melting point of the polymer decrease when the reaction temperature rises because the short branching increases.
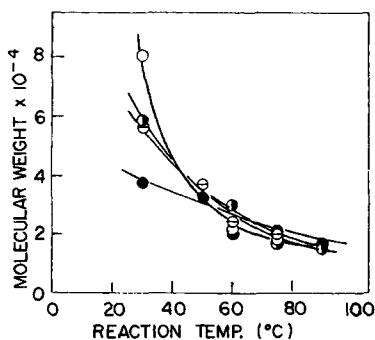

Fig. 8. Effect of reaction temperature on the molecular weight of polymer; polymerization was carried out at various flow rates: (O) 300 nl/hr, (◑) 600 nl/hr, (⊖) 1500 nl/hr, and (●) 3000 nl/hr, at 400 kg/cm² and 3.8×10^5 rad/hr.
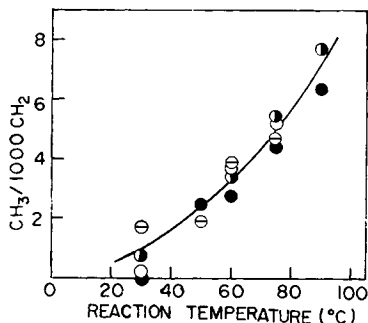
Fig. 9. Effect of reaction temperature on the methyl group content of polymer; reaction conditions and symbols are the same as in Fig. 8.
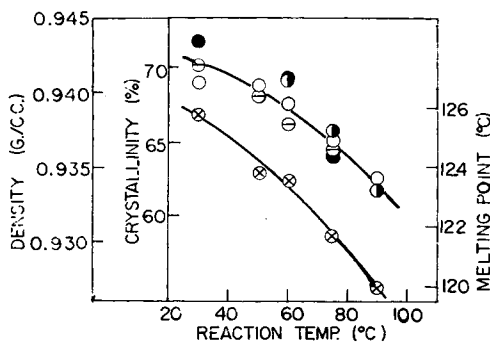

Fig. 10. Effects of reaction temperature on the density, crystallinity, and ⊗ melting point of polymer; reaction conditions and symbols are the same as in Fig. 8.

As shown in Figure 11, the melt index of the polymer increases markedly with increasing reaction temperature because of the molecular weight decrease.

Tensile Properties

The tensile strengths at yield and break and the elongation at break of the polymer are compared in Table I with the properties of the conventional polyethylenes.

TABLE I
Tensile Properties of Radiation-Polymerized Polyethylene[a]

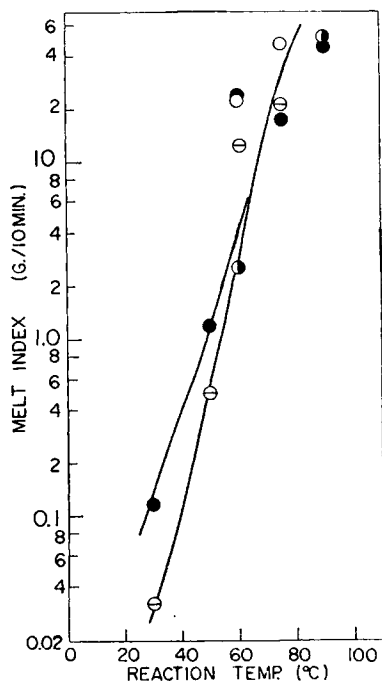| Sample	Density, g/cc	Molecular weight $\overline{M}_n \times 10^{-4}$	Tensile strength, kg/cm² At yield	Tensile strength, kg/cm² At break	Elongation at break, %
Radiation-polymerized PE-1	0.940	19.1	150	131	340
Radiation-polymerized PE-2	0.934	9.6	122	123	340
High-density conventional PE	0.951	5.1	225	188	1250
Low-density conventional PE	0.918	3.0	70	146	550

[a] Strain rate is 10 mm/min.

Fig. 11. Effect of reaction temperature on the melt index of polymer: reaction conditions and symbols are the same as in Fig. 8.

The yield strength of the radiation-polymerized polyethylene of medium density is in a range between that of high-density conventional polyethylene and low-density conventional polymer. This is consistent with the well known fact that for the conventional polyethylene the yield strength is controlled primarily by crystallinity.[11]

Detailed information on the mechanical properties and other properties are being investigated and will be presented in our report on samples produced by the pilot-scale plant whose capacity is ten times that of the bench-scale plant.

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