

Radiation-Induced Polymerization of Ethylene in Pilot Plant. V. Molecular Weight Distribution of Polyethylene

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Synopsis

The molecular weight distribution of the polyethylene produced by radiation in a large-scale pilot plant at pressures of 105–395 kg/cm² and temperatures of 30–80°C was determined by gel permeation chromatography and discussed in connection with the polymerization conditions. The bimodal molecular weight distribution was observed in most of polymers. The number-average molecular weight at two peaks are 10⁴ and 10⁵, respectively. The fraction of the peak at higher molecular weight increased with pressure and mean residence time, and with decreasing dose rate and temperature. The distribution was unimodal in the early stage of the operation and became bimodal, remaining unchanged in the later stage. The distribution also changed from bimodal to unimodal with rising temperature. These results were consistent with those in static batch experiments and well explained by the polymerization scheme assuming two physical states to be different in polymer mobility.

INTRODUCTION

In a series of investigations on the radiation-induced polymerization of ethylene,^{1–4} we described the correlations between the average molecular weight and operation conditions of the pilot plant, such as reaction pressure, reaction temperature, dose rate, and others. The average molecular weight of the polymer produced in the presence of an aqueous solution of *tert*-butyl alcohol is in the range $(1.3\text{--}8.9) \times 10^4$ under experimental conditions.³ It increases with reaction pressure and mean residence time, and with decreasing reaction temperature and dose rate.

Kinetics of polymerization has also been reported in a previous article.⁴ In this article, the molecular weight distribution of polyethylene produced in large-scale pilot plant by radiation is discussed in connection with the polymerization conditions. The molecular weight distribution is one of the important factors determining physical properties, and it also reflects the polymerization kinetics.

EXPERIMENTAL

Preparation of the polyethylene sample was carried out in pilot plant with a 50-liter reactor; ethylene was polymerized in the presence of *tert*-butyl alcohol aqueous solution (*t*-BuOHaq) with γ -ray irradiation from ⁶⁰Co. The details of the large-scale pilot plant and the method of polymerization were described in a previous article.³

The molecular weight distribution of the polyethylene was determined by gel permeation chromatography (GPC). GPC measurements were carried out with the GPC model 1A manufactured by Shimadzu, with a five-column series of nominal pore sizes: 1×10^3 , 10^4 , 10^5 , 10^6 , and 10^7 Å. It was operated at 130°C with 1,2,4-trichlorobenzene (TCB) as the solvent at a flow rate of 1 ml/min. The GPC calibration curve was obtained with standard polystyrene.

RESULTS AND DISCUSSION

Figure 1 shows GPC curves of polyethylene produced in the pilot plant at various pressures. The molecular-weight-distribution curve of the polymer was found to be shouldered or bimodal. The molecular weight at the peak of curves changed from about 1×10^4 to 1×10^5 with increase in the reaction pressure from 105 to 395 kg/cm². The lower-molecular-weight peak decreased and shifted slightly toward a higher molecular weight with increasing reaction pressure, whereas the shoulder at higher molecular weight increased with pressure and became a main peak. The ratio of the weight-average to the number-average molecular weight \bar{M}_w/\bar{M}_n was 5 to 7, which was independent of the reaction pressure.

The GPC curves of the polymer were changed with reaction temperature from 30 to 80°C , as shown in Figure 2. The curve was also shouldered or bimodal. The peak or shoulder at higher molecular weight decreased and the peak at lower molecular weight increased with the reaction temperature. These results are similar to those in small-scale batch experiments.⁵ A remarkable difference appears between the polymers polymerized at 30°C and at higher than 45°C . The molecular weight distributions of the polymer produced above 45°C are sharp and nearly unimodal. The molecular weight at the peak is 1.4×10^4 , being independent of the reaction temperature.

Figure 3 shows the effect of dose rate on the molecular weight distribution. The peak at lower molecular weight shifted slightly to a lower molecular weight with a change of dose rate from 4.5×10^4 to 1.8×10^5 rad/hr.

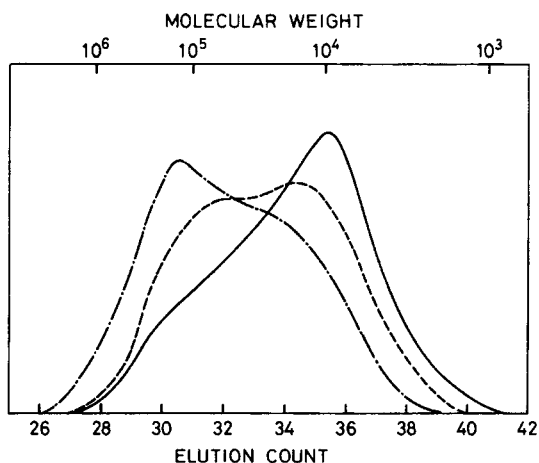


Fig. 1. GPC curves for polyethylene formed at various pressures (kg/cm²): (—), 105; (---), 300; (-·-·), 395. Reaction conditions: temperature, 30°C ; mean residence time, 0.7 hr; dose rate, 1.7×10^5 rad/hr, ethylene mole fraction in reaction mixture, 0.37–0.39.

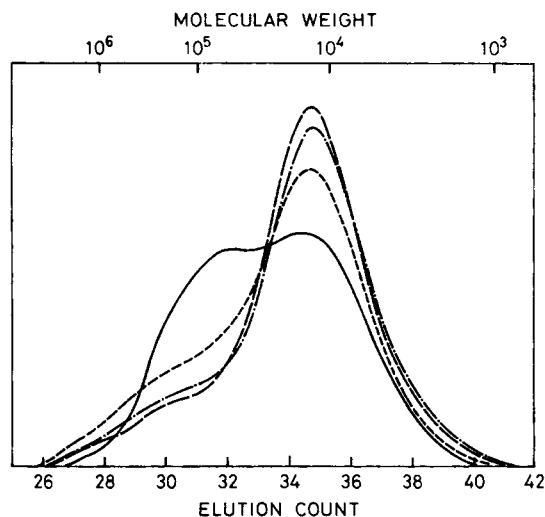


Fig. 2. GPC curves for polyethylene formed at various temperatures ($^{\circ}\text{C}$): (—), 30; (---), 45; (---), 60; (—), 80. Reaction conditions: pressure, 300 kg/cm^2 ; mean residence time, 0.7 hr; dose rate, $1.7 \times 10^5\text{ rad/hr}$; ethylene mole fraction, 0.38–0.41.

The mean residence time of the reaction mixture in the reactor was varied from 0.33 to 1.36 hr with change in the feed rates of ethylene and *t*-BuOHaq. Figure 4 shows the effect of mean residence time on the molecular weight distribution. The curves are bimodal in the experimental range. The fraction of the higher-molecular-weight peak increased with mean residence time.

The change in the molecular-weight-distribution curves of the polymer with time and after the start of irradiation is shown in Figure 5. The molecular weight distribution of the polymer after 1 hr operation is narrow and unimodal. The molecular weight at the main peak is about 1×10^4 and shifts slightly to a higher molecular weight with increase in the operation time. The distribution changes to a bimodal one because of an appearance of a high-molecular-weight peak at

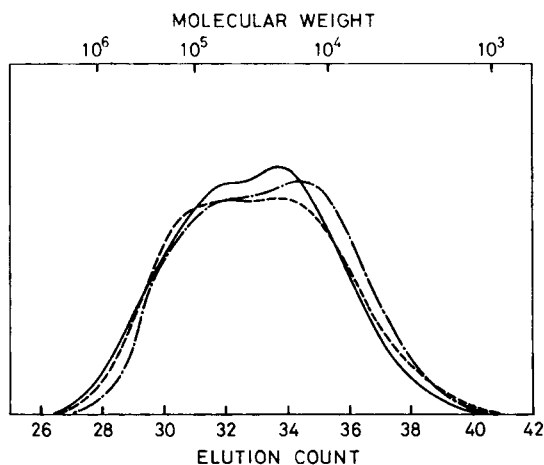


Fig. 3. GPC curves for polyethylene formed at various dose rates (rad/hr): (—), 4.5×10^4 ; (---), 1.0×10^5 ; (---), 1.8×10^5 . Reaction conditions: pressure, 300 kg/cm^2 ; temperature, 30°C ; mean residence time, 0.7 hr; ethylene mole fraction, 0.39–0.41.

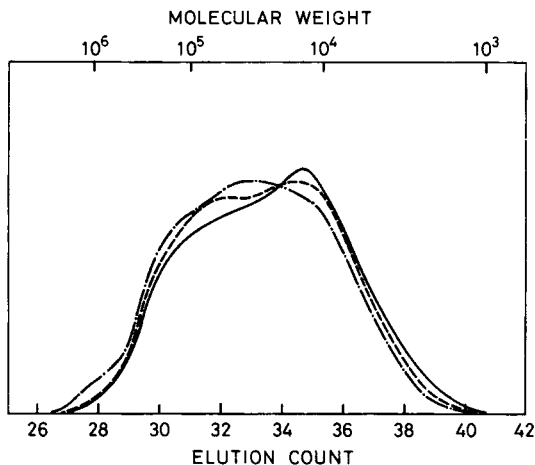


Fig. 4. GPC curves for polyethylene formed at various mean residence times (hr): (—), 0.36; (---), 0.77; (-·-·), 1.07. Reaction conditions: pressure, 300 kg/cm²; temperature, 30°C; dose rate, 1.7×10^5 rad/hr; ethylene mole fraction, 0.35–0.39.

about 1×10^5 after 2.5 hr of operation, but it scarcely changes after 4.5 hr of operation. These results suggest that the polymerization in this pilot plant reaches to steady state at around 4.5 hr, three times the mean residence time.

The bimodal molecular weight distribution was observed in most of the polymers produced in the pilot scale experiments except in the early stage of operation and at high temperature. The bimodal curve of the molecular weight distribution was also observed in the small-scale batch experiments.^{5,6} The batch reaction conditions in which the polymer with bimodal molecular weight distribution is produced differ from those in the pilot scale experiments; however, the molecular weights at two peaks are almost the same as the polymers produced in batch and pilot scale flow experiments.

In the heterogeneous polymerization of ethylene, it is assumed that the physical state of propagating chains plays an important role in the determination of the polymer molecular weight. The formation of the polymer with a different molecular weight is explained by the assumption that polymerization proceeds through the propagating chains in two different physical states: a loose state and a rigid one, where the mobility of the propagating chains is different.⁶

A reaction scheme, as shown in Figure 6, has been proposed for the heterogeneous polymerization of ethylene.⁶ A primary radical produced by radiation grows into propagating chains. Some of the mobile propagating chains in the loose state are deactivated by mutual recombination or by radical transfer to the monomer and the solvent to produce a lower-molecular-weight polymer, and the others grow to high-molecular-weight chains in which their mobilities are reduced as a result of precipitation and crystallization.

The precipitated propagating chains are in a physical state where the mobilities of the chains are poor. They are deactivated to high-molecular-weight polymers by recombination with mobile polymer radicals and by radical occlusion. Mutual termination and transfer reactions of rigid polymer radicals are negligible at the ambient temperature.⁷ Second-order termination by mutual recombination of mobile radicals is predominant in the loose state, and first-order termination by radical occlusion is predominant in the rigid state.

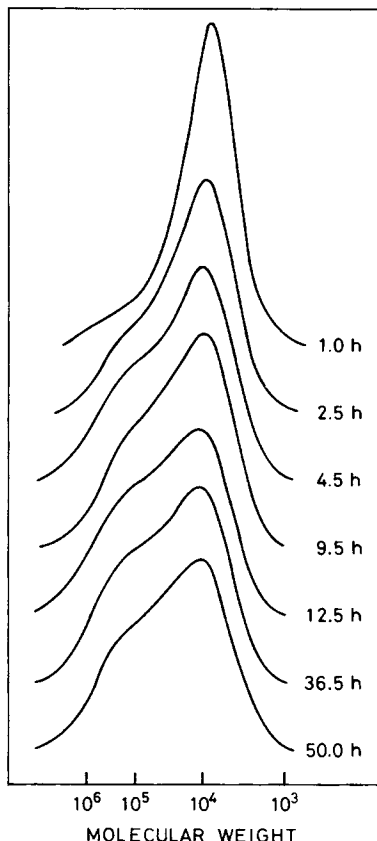


Fig. 5. GPC curves for polyethylene formed at various operation times. Reaction conditions: pressure, 200 kg/cm²; temperature, 30°C; mean residence time, 1.25 hr; dose rate, 1.9×10^5 rad/hr; ethylene mole fraction, 0.34.

At the early stage of operation, polymerization proceeds mainly in the loose state, so that the low-molecular-weight polymer with unimodal distribution is obtained. With the lapse of operation time, polymer chains grow and precipitate. When the deactivation rate of propagating radicals in the rigid state is equal to

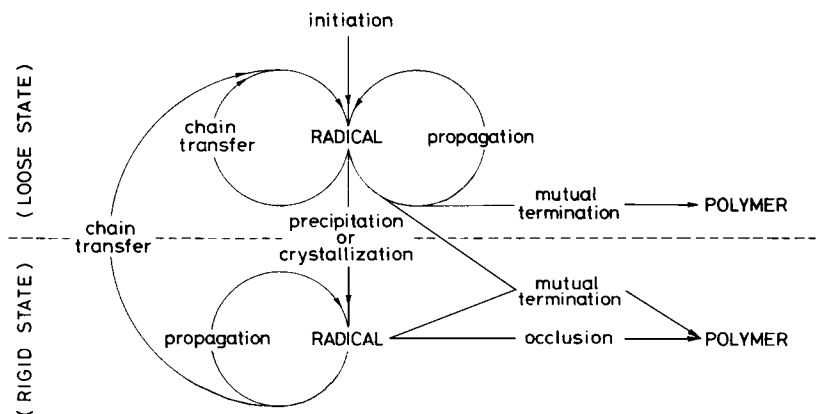


Fig. 6. Reaction scheme of heterogeneous polymerization of ethylene.

the rate of formation of immobile polymer radicals, the steady bimodal molecular weight distribution must be obtained. The results in Figure 5 show that dynamic equilibrium is realized in the flow polymerization.

Pressure dependence of the molecular weight distribution is also explained by considering that the fraction of propagating radicals in the rigid state is increased with pressure because of the increase of the propagation rate with monomer concentration.

The rise of the reaction temperature brings about the increase of polymer mobility and transfer reaction rate, so that the polymerization proceeds mainly in the loose state. The results shown in Figure 2 indicate that the polymerization in the loose state is predominant when the reaction temperature exceeds 45°C. On the other hand, the polymer with bimodal molecular weight distribution was obtained even at 60°C in the static batch experiments.⁵ This difference in temperature effects on the distribution is due to the turbulence in reaction mixture by agitation and the short mean residence time in flow experiments. Increase in the fraction of a radical in the loose state brings about a large rate constant of second-order termination as described in a previous article.⁴

The polymer obtained in the batch experiments at 60°C in short reaction time (0.25 hr) gives a unimodal molecular weight distribution, and a new peak at higher molecular weight appears and increases with the reaction time (1.5–3.0 hr).⁶ The experimental results shown in Figure 4 indicate the same tendency with the batch experiments that the fraction of the peak at higher molecular weight increases with mean residence time. The fact is also explained by the fraction of propagating radicals in the rigid state increase with mean residence time.

The dose rate effects on the molecular weight distribution shown in Figure 3 are due to the fact that the polymerization in the loose state becomes predominant by increasing the low-molecular-weight radicals at higher dose rates.

The changes of fractions in high- and low-molecular-weight polymers by the polymerization conditions in pilot scale experiments are consistent with those in static batch experiments and are well explained by the polymerization scheme assuming two physical states to be different in polymer mobility.

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