

# Radiation-Induced Polymerization of Ethylene in Pilot Plant. III. Heavy-Phase Recycling Process

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## Synopsis

Radiation-induced polymerization of ethylene using aqueous *tert*-butyl alcohol as medium was carried out in a large-scale pilot plant with a 50-liter central source-type reactor at a pressure of 105 to 395 kg/cm<sup>2</sup>, temperature of 30° to 80°C, mean dose rate of  $4.5 \times 10^4$  to  $1.9 \times 10^5$  rads/hr, ethylene feed rate of 5.5 to 23.5 kg/hr, and medium feed rate of 21 to 102 l./hr. The space-time yield and molecular weight of the polymer were in the range of 4.7 to 16.8 g/l.-hr and  $1.3 \times 10^4$  to  $8.9 \times 10^4$ , respectively. The space-time yield and molecular weight increased with mean residence time at 30°C, whereas at 80°C they became almost independent of the time. The space-time yield increased with pressure and dose rate, slightly decreased with temperature, and was maximum at ethylene molar fraction of 0.5. The polymer molecular weight increased with pressure and ethylene molar fraction, and decreased with dose rate and temperature. The total amount of deposited polymer on the reactor wall, source case wall, and scraping blades was usually less than 1 kg, which was negligibly small for the analysis of polymerization. Continuous discharge of the polymer slurry and production of fine-powder polyethylene were successfully carried out. In the central source-type reactor, a dose rate of  $1.9 \times 10^5$  rads/hr was obtained with a <sup>60</sup>Co source of ca. 12 kCi.

## INTRODUCTION

A series of engineering studies involving the radiation-induced polymerization of ethylene has been performed at the Takasaki Radiation Chemistry Research Establishment. In the first and second papers,<sup>1,2</sup> we reported the results of pilot-scale experiments of ethylene polymerization in bulk, wet-wall, and heavy-phase recycling processes. In the bulk process, polymer deposit on the reactor wall and agitator blades interfered with a long-period, smooth operation of the plant. In the heavy-phase recycling process, where the reactor wall was covered with dilute aqueous *tert*-butyl alcohol (heavy phase) in equilibrium with the reaction mixture (light phase), the amount of deposited polymer was markedly reduced, and the polymer in the high-pressure system was continuously removed as a slurry.

As a third step of the study, we constructed a large-scale pilot plant with a central-source-type wet-wall reactor 50 liters in capacity in order to evaluate the process. This paper is concerned with the results of the pilot plant operation and the characteristics and feasibility of the process.

## EXPERIMENTAL

## Pilot Plant and Process

A large-scale pilot plant for heavy-phase recycling was constructed based on the development of the wet-wall process<sup>2</sup> in order to study feasibility of the process and to produce enough polyethylene for practical evaluation.

Figure 1 shows a sectional view of the reactor. The 50-liter central source-type reactor with a scraper to prevent polymer deposit and with a jacket for temperature control was designed to be operated at pressures up to 410 kg/cm<sup>2</sup> and at temperatures up to 80°C. The source case, in which the radiation source is inserted, is a concentric cylindrical case and is installed on the top of the vessel. The scraper with streamline blades is connected to a driving shaft at the bottom of the vessel. The shaft with three-stage mechanical seal for high pressure was driven up to 100 rpm with an oil torque motor.

The radiation source is of rod type and consists of four to 12 <sup>60</sup>Co pencils having an activity of ca. 1 kCi each.

Figure 2 shows a flowsheet of the pilot plant consisting of the reactor, two compressors for ethylene feed, three separators, two pressure-reducing devices, recovering systems for ethylene, medium, and polymer, and other utilities.

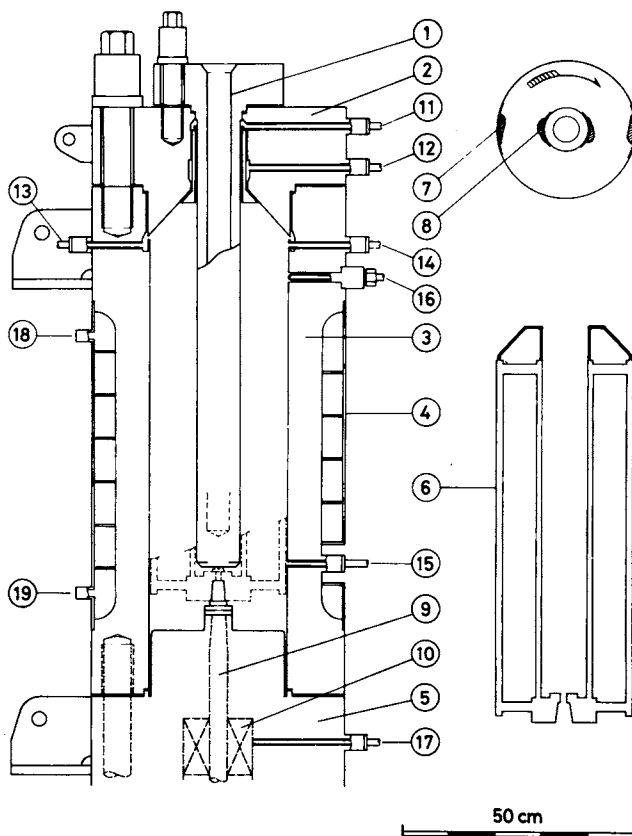


Fig. 1. Sectional view of the reactor: (1) radiation source case; (2) top cover; (3) body; (4) jacket; (5) bottom cover; (6) scraper; (7) outer streamline blade; (8) inner streamline blade; (9) driving shaft; (10) mechanical seal; (11, 12) heavy phase inlet; (13) *t*-BuOH inlet; (14) ethylene inlet; (15) reaction mixture outlet; (16) thermocouple; (17) sealant water inlet; (18) water outlet; (19) water inlet.

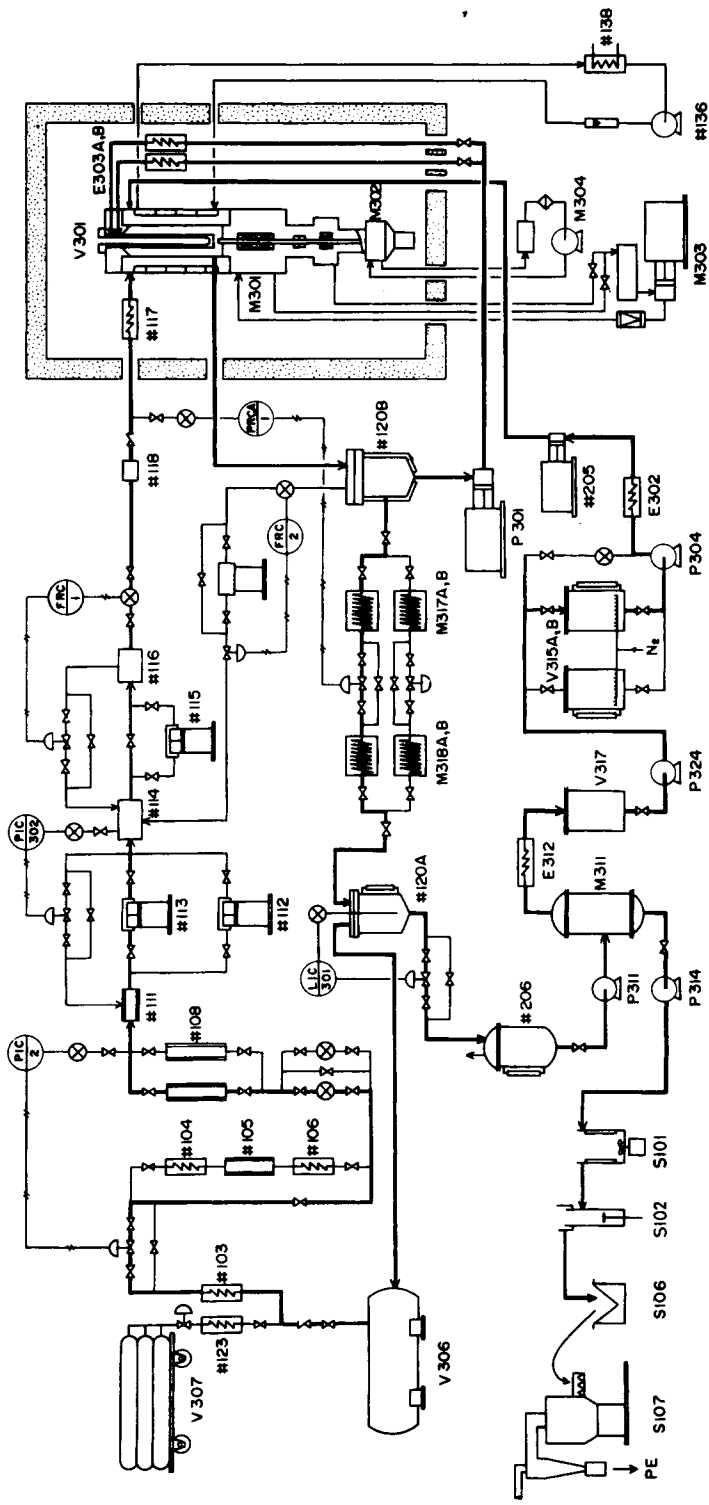


Fig. 2. Flow sheet of the pilot plant. V306, ethylene tank; V307, container for makeup ethylene; #123, #103, #104, ethylene heaters; #105, oxygen remover; #106, ethylene cooler; #108, humidity remover; #111, #114, #116, ethylene buffer tanks; #112, start-up ethylene compressor; #113, makeup ethylene compressor; #115, ethylene recycle pump; #118, flame arrester; #117, ethylene preheater; V301, central source-type wet-wall reactor; #120B, high-pressure separator; P301, heavy-phase recycling pump; E303, heavy-phase cooler; M317, M318, pressure reducing devices; #120A, medium-pressure separator; #206, low-pressure separator; P311, slurry feed pump; M311, pot still; E312, condenser; V317, medium reservoir; P324, medium pump; V315, medium tank; P304, medium recycle pump; E302, medium preheater; #205, medium feed pump; P314, slurry pump; S101, mixer for polymer washing; S102, polymer separator by air flotation; S106, polymer filter; S107, fluidized bed drier; M301, mechanical seal; M302, oil torque motor; M303, sealant pump; M304, oil pump; #136, water pump; #138, water pump; #136, water pump; #138, water pump.

After preparations such as setting up the reactor, gas leakage test, and flushing the system with ethylene, *tert*-butyl alcohol aqueous solution (*t*-BuOHaq) and ethylene were initially charged in the high-pressure system to form the light and heavy phases in equilibrium<sup>2</sup> at the reaction pressure.

The recycled ethylene from the 10-m<sup>3</sup> tank V306 was compressed to the reaction pressure with compressors #112 and #113, heated to the reaction temperature with #117, and fed to the reactor V301. The medium, *t*-BuOHaq, was flushed with high-purity nitrogen in the medium tanks V315A and B to remove the dissolved oxygen, heated to the desired temperature with E302, and then fed to the reactor with pump #205 at a constant flow rate. After stationary feeding of *t*-BuOHaq and ethylene, whose composition was similar to that of the light phase, gamma-ray irradiation was started.

The mixture of ethylene and *t*-BuOHaq in the reactor formed the light phase and a small amount of the heavy phase. Polymerization took place in the light phase, which was mostly composed of ethylene and *t*-BuOH under gamma-ray irradiation. The reaction pressure was automatically controlled with the PRCA-1 instrument. The reaction temperature was controlled by circulating water in the reactor jacket. The mean residence time of the light phase and its composition in the reactor were controlled by changing the feed rates and ratio of ethylene and *t*-BuOHaq according to a phase diagram.<sup>2</sup> The dose rate in the reactor was varied by changing the number of <sup>60</sup>Co pencils inserted in the case.

The mixture of light and heavy phases containing the polymer was transferred to a 45-liter high-pressure separator (#120B) and then separated into two layers. The heavy phase, which is an aqueous solution of ca. 10 wt % *t*-BuOH, was recycled with pump P301 from the bottom of the high-pressure separator to the reactor. A part of the recycled heavy phase flowed down on the wall of the source case and the other part on the reactor wall to prevent polymer deposit. The recycling rate of the heavy phase was changed with plunger stroke speed of the pump. The light phase containing the polymer was removed at the interface of the two layers in the high-pressure separator and transferred through pressure-reducing devices (M317, M318) to a 45-liter medium-pressure separator (#120A) at 20 kg/cm<sup>2</sup>.

In the medium-pressure separator, the light phase containing the polymer was separated into two phases, the gas phase of unreacted ethylene and the liquid phase of *t*-BuOHaq where the polymer was suspended. The unreacted ethylene was transferred to the ethylene tank and reused. Makeup ethylene from a container (V307) was supplied when suction pressure of the compressors was decreased below 20 kg/cm<sup>2</sup>.

The polyethylene slurry in the medium pressure separator was removed at a constant slurry level to a 230-liter low-pressure separator (#206) where the dissolved ethylene was vented.

The slurry was then distilled in a pot still (M311) to recover the *t*-BuOHaq. The coagulated polyethylene in diluted *t*-BuOHaq removed from the bottom was washed in water with a mixer (S101) and separated by air flotation (S102). This procedure was repeated three times to remove the alcohol from the polymer. Washed polymer was filtered with S106 and dried at mild temperature with a fluidized bed drier (S107), and then the fine-powder polyethylene was collected with a cyclone separator.

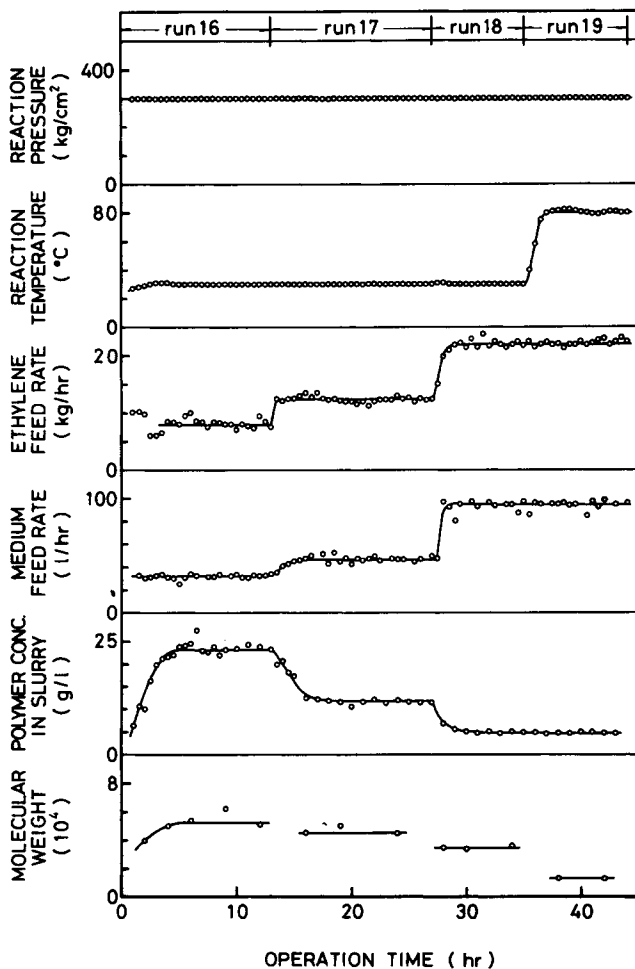


Fig. 3. Time courses of pressure, temperature, ethylene feed rate, medium feed rate, polymer concentration in slurry, and polymer molecular weight for runs 16 to 19.

### Materials

The ethylene used was polymerization grade manufactured by the Maruzen Petrochemical Co., Ltd. Reagent-grade *t*-butyl alcohol was used as received from the Maruzen Oil Co. Ltd. and Dainippon Ink & Chemicals, Inc. Water was purified by ion exchange resins before use.

### Measurement and Analysis

Oxygen in ethylene was measured by a Horiba oxygen analyzer (AE-303). The oxygen contents in both makeup and recycled ethylene were less than 5 ppm. Oxygen in the medium was monitored by a Beckman process oxygen analyzer (Model 778).

The polymer concentration in the slurry removed from the medium pressure separator was measured by gravimetry after drying. The number-average molecular weight of polymer was determined by Tung's equation<sup>3</sup> from its intrinsic viscosity in tetralin at 130°C.

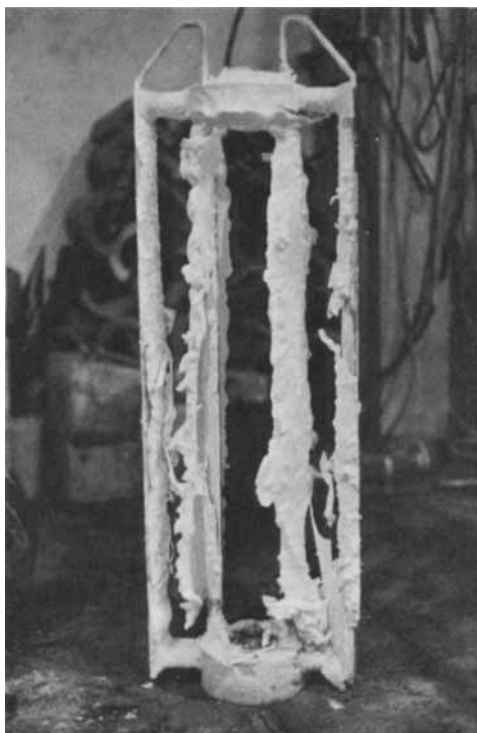


Fig. 4. Appearance of polymer deposit on scraping blades after full two days of normal operation (runs 16–19).

## RESULTS AND DISCUSSION

### Pilot Plant Operation

The operations of the large-scale pilot plant were carried out 19 times in the pressure range of 105 to 395 kg/cm<sup>2</sup>, temperatures of 30° to 80°C, dose rates of  $4.5 \times 10^4$  to  $1.9 \times 10^5$  rads/hr, ethylene feed rates of 5.5 to 23.5 kg/hr, medium feed rates of 21 to 102 l./hr, scraping speeds of 0 to 80 rpm, and heavy-phase recycling rates of 0 to 300 l./hr. Several runs under the various reaction conditions were performed during one operation. Operational results for 40 runs are summarized in Table I together with the reaction conditions.

Figure 3 shows examples for time courses of the polymer concentration in the slurry and the polymer molecular weight in runs 16 to 19 together with reaction conditions. The polymer concentration and molecular weight increased with reaction time and reached a steady state after a period five to eight times longer than the mean residence time of the light phase in the reactor. When the reaction conditions were changed, the polymer concentration and molecular weight shifted to new steady values. The time to reach steady state was almost the same as that in the 10-liter pilot plant of the heavy-phase recycling process.<sup>2</sup>

The reaction conditions in Table I are mean values at the steady state. The space-time yield of polymer was calculated from the polymer concentration and the discharge rate of the slurry, which was almost equal to the medium feed rate. Mean residence time and composition of the light phase in the reactor were calculated from the feed rates of ethylene and *t*-BuOHaq using a phase diagram.<sup>2</sup>



Fig. 5. Appearance of polymer deposit on scraping blades after stopping the recycle of heavy phase (runs 22–24).

The mean dose rate in the reactor was obtained from dosimetry at various positions using clear PMMA plates.<sup>4</sup>

The polymer concentration at steady state was changed from 2.3 to 23.2 g/l. mostly by the medium feed rate. As seen in Table I, the polymers with molecular weights of  $1.3 \times 10^4$  to  $8.9 \times 10^4$  were produced with a space-time yield of 4.7 to 16.8 g/l.-hr.

### Characteristics of the Process

The pilot plant was satisfactorily operated without troubles, and total operation time reached ca. 600 hr producing ca. 300 kg powder polyethylene. Recycled ethylene from the medium-pressure separator containing a small amount of *t*-BuOHaq could be reused without inhibiting the polymerization. *t*-BuOHaq was also repeatedly used after distillation.

The amount of deposited polymer on the reactor wall, source case wall, and scraping blades was less than 1 kg (2% of reactor volume) after a full two days of normal operation, even in the 50-liter reactor. Furthermore, as shown in Figure 4, most of the polymer was deposited on the blade surfaces and not on the walls because of the absence of the recycling heavy phase. When scraping was stopped for 6 hr (run 27) after 18 hr of operation in runs 25 and 26, deposited polymer was scarcely observed on the walls. As shown in Figure 5, a large amount of polymer was deposited on the scraping blades, especially the inner blades, and

TABLE I  
 Operational Results

Run no.	Pressure, kg/cm <sup>2</sup>	Temp., °C	React. time, hr	Dose rate, 10 <sup>6</sup> rads/hr	Feed rate, Ethylene kg/hr	Medium l/hr	BuOH conc. in medium wt%	Mole fraction Ethylene <i>t</i> -BuOH	Residence time, hr	Heavy-phase recycling rate, l/hr	Scraping speed, rpm	Polym. conc. in slurry, g/l.	Space-time yield, g/l. hr	Molecular weight × 10 <sup>-4</sup>
5	200	30	26	1.8	11.5	48.0	75	0.37	0.36	200	30	8.4	8.7	3.0
6	300	30	24	1.8	11.0	43.0	75	0.39	0.35	200	30	13.0	12.6	4.8
7	300	30	7.5	1.8	13.0	35.0	80	0.49	0.33	200	30	17.0	12.8	5.4
8	295	30	11	1.8	17.5	28.0	80	0.64	0.25	200	30	19.5	11.8	5.5
9	300	60	19	1.8	12.0	44.0	75	0.39	0.34	200	30	11.4	10.8	2.0
10	300	80	19	1.8	12.0	47.0	75	0.37	0.34	200	30	10.6	10.7	1.3
11	300	45	24	1.7	11.5	42.0	75	0.41	0.35	200	30	14.5	13.1	4.4
12	300	80	8	1.7	12.0	45.0	75	0.38	0.34	200	30	12.0	11.6	1.5
13	300	80	13	1.7	5.5	23.0	75	0.35	0.34	200	30	23.0	11.4	1.5
14	370	30	31	1.7	13.0	50.0	75	0.39	0.35	200	30	14.4	15.5	5.5
15	300	30	17.5	1.7	22.0	21.0	75	0.77	0.17	200	30	22.5	10.2	6.0
16	300	30	13	1.7	8.0	31.0	75	0.39	0.35	200	30	23.2	15.5	5.3
17	300	30	14	1.7	12.3	46.0	75	0.40	0.35	200	30	12.2	12.1	4.5
18	300	30	8	1.7	22.0	96.0	75	0.35	0.36	200	30	4.7	9.7	3.5
19	300	80	9	1.7	22.2	95.0	75	0.34	0.35	200	30	4.5	9.2	1.3
20	300	30	11	1.7	12.0	45.0	75	0.40	0.35	100	30	14.4	14.0	5.3
21	300	30	11	1.7	12.0	45.0	75	0.40	0.35	200	80	12.6	12.2	4.3



22	300	30	10	1.7	12.2	45.0	75	0.41	0.35	0.73	200	15	14.0	13.6	5.0
23	300	30	10.3	1.7	12.2	45.0	75	0.41	0.35	0.73	0	30	7.0	6.8	2.5
24	300	30	5.3	1.7	12.2	45.0	75	0.41	0.35	0.73	200	30	6.2	6.0	4.2
25	300	30	14.7	1.7	12.2	46.5	75	0.39	0.35	0.71	300	30	12.6	12.0	5.3
26	300	30	3.7	1.7	12.2	46.5	75	0.39	0.35	0.71	50	30	13.5	13.5	5.0
27	300	30	6.3	1.7	12.2	47.1	75	0.39	0.35	0.71	200	0	13.6	13.8	5.3
28	300	30	9.7	1.7	11.4	48.0	75	0.36	0.36	0.72	200	30	13.0	13.4	5.5
29	300	30	11	1.7	11.4	48.0	75	0.36	0.36	0.72	50	30	12.0	12.4	4.9
30	300	30	8	1.7	12.6	102.0	41	0.40	0.36	0.69	200	30	5.2	11.4	4.9
31	300	30	6	1.7	12.6	102.0	41	0.40	0.36	0.69	200	30	5.2	11.4	5.7
32	300	30	9	1.7	12.6	102.0	41	0.40	0.36	0.69	0	30	5.2	11.4	4.7
33	105	30	6.3	1.7	12.3	50.0	75	0.37	0.35	0.63	200	30	5.7	6.1	2.2
34	300	30	7	1.0	23.5	62.0	75	0.51	0.31	0.46	200	30	5.6	7.5	5.7
35	300	30	6	1.0	23.5	92.0	75	0.39	0.35	0.36	200	30	4.0	7.9	5.0
36	300	30	7	1.0	12.0	44.0	75	0.41	0.35	0.74	200	30	10.5	10.0	6.5
37	300	30	7	1.0	7.5	31.0	75	0.37	0.35	1.09	200	30	16.6	11.1	7.3
38	300	30	8	0.45	8.0	32.0	75	0.37	0.35	1.05	200	30	11.0	7.6	8.9
39	300	30	7.5	0.45	11.7	43.0	75	0.41	0.35	0.76	200	30	6.0	5.6	7.0
40	300	30	3.5	0.45	23.0	94.0	75	0.37	0.35	0.36	200	30	2.3	4.7	5.5
41	178	30	15	1.4	12.0	45.0	67	0.51	0.32	0.67	200	30	7.2	7.0	2.4
42	300	30	8	0.55	8.2	28.0	75	0.43	0.34	1.14	200	30	15.0	9.1	5.5
43	395	30	14.6	1.4	12.3	48.0	73	0.39	0.35	0.72	210	30	16.2	16.8	6.4
44	395	30	12	0.40	7.5	32.0	73	0.37	0.35	1.10	210	30	13.0	9.0	6.4

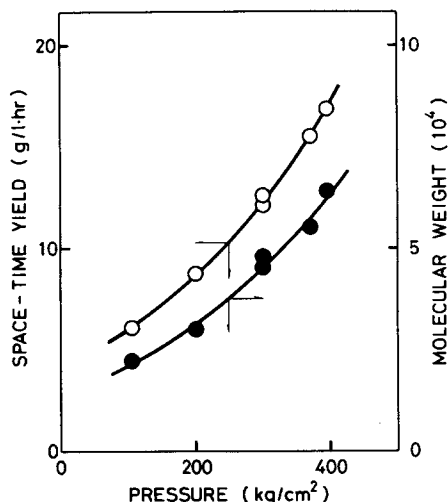


Fig. 6. Effect of reaction pressure on space-time yield and molecular weight of polymer. Reaction conditions: temperature, 30°C; dose rate,  $(1.4 \times 10^5)$ – $(1.8 \times 10^5)$  rads/hr; mean residence time, ca. 0.7 hr; ethylene molar fraction, ca. 0.4.

the deposited amount reached 18 kg by stopping the recycling of the heavy phase for only 10 hr (run 23) during 26 hr of operation (runs 22 to 24). These experiments showed that the recycling of the heavy phase plays an important role in the prevention of polymer deposit in the large-scale pilot plant.

The continuous discharge of the polymer slurry and the production of fine-powder polyethylene were successfully performed in this pilot plant. The unique properties of the polyethylene powder are a large specific surface area of 30 to 100 m<sup>2</sup>/g and a small particle diameter of 8 to 20 microns. A problem in the production of fine-powder polyethylene as polymerized is the formation of a large amount of wastewater containing a small amount of *t*-BuOH.

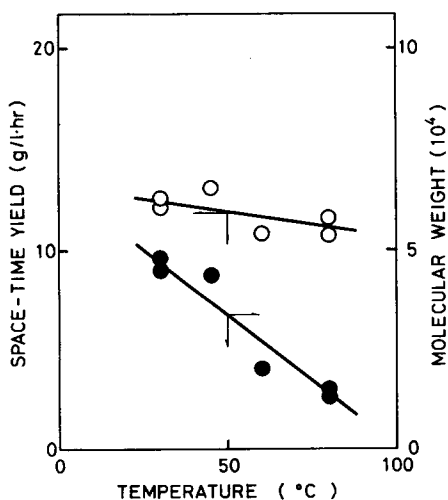


Fig. 7. Effect of reaction temperature on space-time yield and molecular weight. Reaction conditions: pressure, 300 kg/cm<sup>2</sup>; dose rate, ca.  $1.7 \times 10^5$  rads/hr; mean residence time, ca. 0.7 hr; ethylene molar fraction, ca. 0.4.

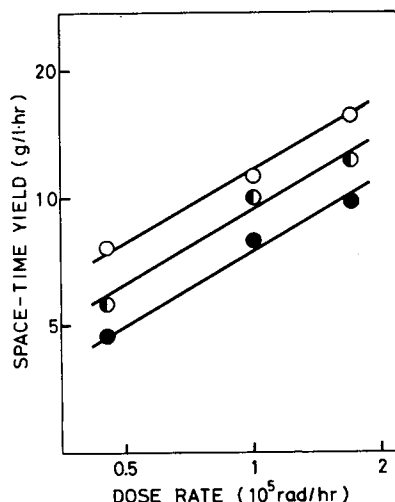


Fig. 8. Effect of dose rate on space-time yield at residence times of 0.36 hr [●], 0.75 hr [◐], and 1.1 hr [○]. Reaction conditions: pressure, 300 kg/cm<sup>2</sup>; temperature, 30°C; ethylene molar fraction, ca. 0.4.

Mean dose rates in the reactor filled with 83 wt % *t*-BuOHaq were  $5.0 \times 10^4$ ,  $1.1 \times 10^5$ , and  $1.9 \times 10^5$  rads/hr for three sources of 3.8, 7.7, and 11.8 kCi, respectively. In the central source-type reactor, the utilization efficiency for radiation energy is much higher than that in the outer source-type reactor,<sup>5</sup> though the dose rate distribution in the radial direction is steeper.

### Polymerization Rate and Polymer Molecular Weight

**Effect of Reaction Pressure.** As shown in Figure 6, both the space-time yield and the molecular weight of the polymer increase with reaction pressure ranging from 105 to 395 kg/cm<sup>2</sup> at 30°C. Accordingly, the number of polymer

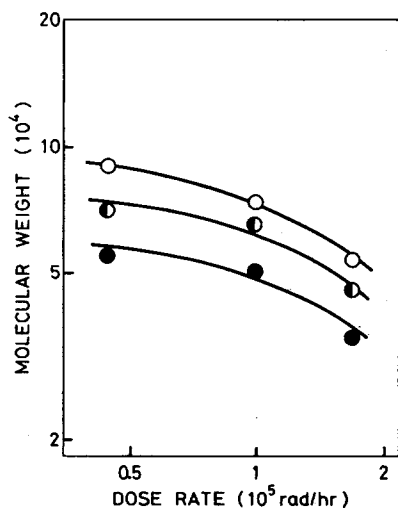


Fig. 9. Effect of dose rate on polymer molecular weight at various residence times. Reaction conditions and symbols are the same as in Figure 8.

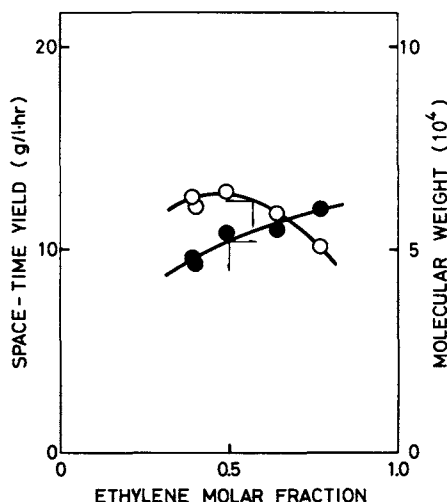


Fig. 10. Effect of ethylene molar fraction in light phase on space-time yield and molecular weight. Reaction conditions: pressure, 300 kg/cm<sup>2</sup>; temperature, 30°C; dose rate,  $1.7 \times 10^5$  rads/hr; mean residence time, ca. 0.7 hr.

chains is almost independent of the pressure. These results are mainly due to the increase in propagation rate with reaction pressure. These results are similar to those in both small-scale batch experiments<sup>6</sup> and 10-liter pilot plant operation.<sup>2</sup>

**Effect of Reaction Temperature.** Figure 7 indicates that the space-time yield slightly decreases, whereas the polymer molecular weight rapidly decreases with reaction temperature at constant pressure. This is because the transfer reaction is more pronounced at higher temperature.

**Effect of Dose Rate.** The space-time yield at various residence times of the

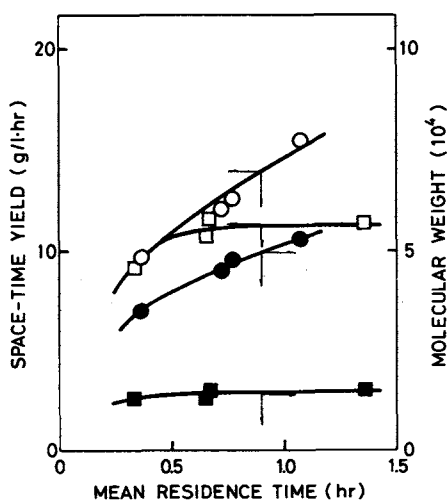


Fig. 11. Effect of mean residence time on space-time yield and molecular weight at 30°C [O, ●] and 80°C [□, ■]. Reaction conditions: pressure, 300 kg/cm<sup>2</sup>; dose rate,  $1.7 \times 10^5$  rads/hr; ethylene molar fraction, ca. 0.4.

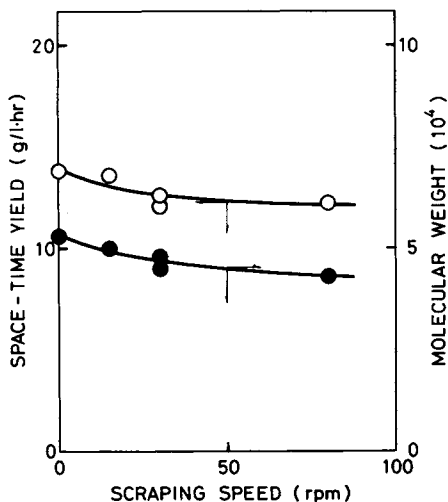


Fig. 12. Effect of scraping speed on space-time yield and molecular weight. Reaction conditions: pressure, 300 kg/cm<sup>2</sup>; temperature, 30°C; dose rate,  $1.7 \times 10^5$  rads/hr; mean residence time, ca. 0.7 hr; ethylene molar fraction, ca. 0.4.

light phase in the reactor increases with dose rate, as shown in Figure 8, simply because the rate of initiation increases with dose rate. Figure 9 indicates that the polymer molecular weight decreases with dose rate as expected from kinetics assuming bimolecular termination.

**Effect of Composition of Light Phase.** With changing light-phase composition, the space-time yield and the molecular weight vary, as shown in Figure 10. The space-time yield is maximum at an ethylene molar fraction of ca. 0.5, whereas the polymer molecular weight monotonously increases with ethylene fraction. These results are similar to those in the 10-liter pilot plant operation<sup>2</sup>

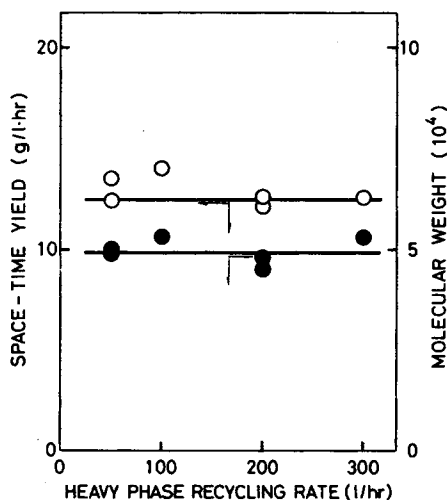


Fig. 13. Effect of heavy-phase recycling rate on space-time yield and molecular weight. Reaction conditions: pressure, 300 kg/cm<sup>2</sup>; temperature, 30°C; dose rate,  $1.7 \times 10^5$  rads/hr; mean residence time, ca. 0.7 hr; ethylene molar fraction, ca. 0.4.

and are explained by the increase in propagation rate and decrease in initiation rate with increase in ethylene fraction.

**Effect of Mean Residence Time.** By changing the feed rates of ethylene and *t*-BuOHaq, the mean residence time of the light phase in the reactor was changed from 0.33 hr to 1.36 hr. If the reaction is carried out at 30°C, as shown in Figure 11, both the space-time yield and the polymer molecular weight increase with residence time, whereas at 80°C they become almost independent of the time. This means that the polymerization proceeds almost steadily at 80°C but nonsteadily at 30°C. This behavior is consistent with that in the batch experiment.<sup>7</sup>

**Effect of Scraping Speed.** While scraping, the light phase is agitated, which probably affects the reaction.<sup>8</sup> As shown in Figure 12, the space-time yield and the polymer molecular weight decrease with scraping speed. The extent of the change is less than that observed in the 10-liter pilot plant operation using a shaftless anchor-type scraper.<sup>2</sup> This is so because the steamline blade brings about less turbulence.

**Effect of Heavy Phase Recycling Rate.** As shown in Figure 13, the space-time yield and the polymer molecular weight are almost independent of the recycling rate in the range of 50 to 300 l./hr.

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