

Radiation-Induced Polymerization of Ethylene in a Pilot Plant. II. Development of Wet-Wall Process

MASAAKI TAKEHISA, HIROMASA WATANABE, HIRONDO KURIHARA, YOSHIO TAKASAKA, YOSHIO MARUYAMA, KAZUKIYO MIYANAGA, TAKESHI SUWA, HAYATO NAKAJIMA, KOUICHI YAMAGUCHI, MASAMICHI TOHEI, WAICHIRO KAWAKAMI, TERUTAKA WATANABE, SHIRO SENRUI, and SUEO MACHI,
Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, Takasaki, Japan

Synopsis

Radiation-induced polymerization of ethylene using *tert*-butyl alcohol aqueous solution as a medium was carried out in a pilot plant with 10 liter reactor at pressures of 100 to 400 kg/cm², ethylene feed rates of 1.2 to 11.8 kg/hr, medium feed rates of 0 to 100 liter/hr, dose rates of 0.6×10^5 to 1.4×10^5 rad/hr, and at room temperature. The space-time yield and molecular weight of polymer were in the range of 1.2 to 16.7 g/liter hr and 6×10^3 to 2×10^5 , respectively. The space-time yield and molecular weight increased with pressure and mean residence time. The space-time yield was the maximum at an ethylene molar fraction of 0.5. The produced polymer was continuously taken out from the high-pressure system as a slurry. The amount of deposited polymer to the reactor wall was markedly decreased, and five full days continuous operation was successfully performed with the space-time yield of 13.5 g/liter hr.

INTRODUCTION

A series of engineering studies involving the radiation-induced polymerization of ethylene have been performed at the Takasaki Radiation Chemistry Research Establishment. In the first paper of the series,¹ we reported the results of pilot scale experiments of bulk polymerization and concluded that the continuous transfer of the produced polyethylene to a receiver was difficult because of the polymer deposit to the reactor wall and agitator blades.

As a second step, in order to minimize the polymer deposit and take out the polymer continuously from the plant, a wet-wall process has been developed where the reactor wall is covered with *tert*-butyl alcohol aqueous solution which does not have a considerable effect on the polymerization reaction.

This paper presents the development procedure and characteristics of preliminary wet-wall process together with the experimental results, and indicates the possibility of continuous long period operation by removing the polyethylene as a slurry.

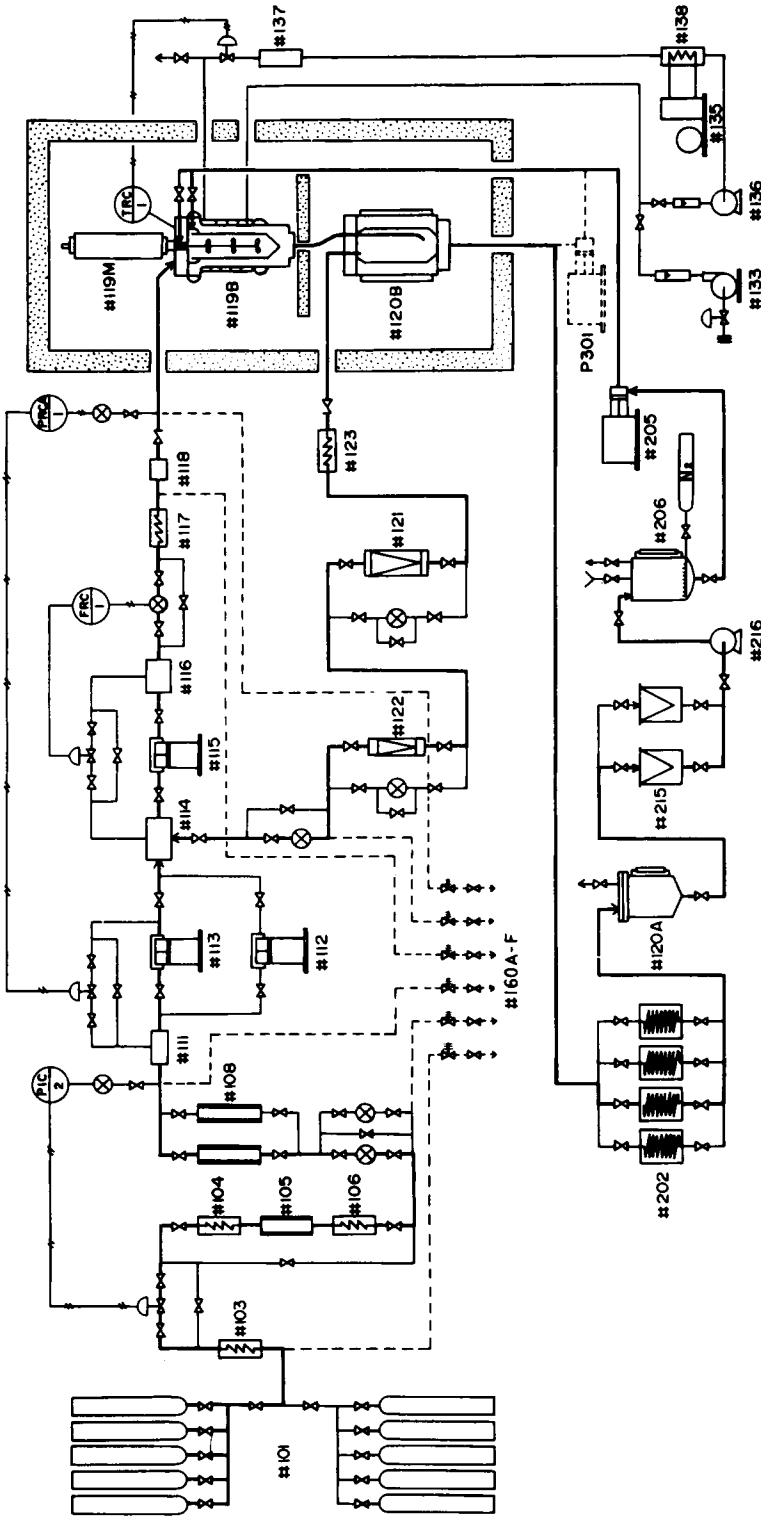


Fig. 1. Flow sheet of the pilot plant for wet-wall process: No. 101, ethylene cylinders; Nos. 103, 104, 117, ethylene heater; No. 105, oxygen remover; Nos. 106, 123, ethylene cooler; No. 108, humidity remover; Nos. 111, 114, 116, ethylene buffer tank; No. 112, start-up ethylene compressor; No. 113, make-up ethylene compressor; No. 115, ethylene recycle pump; No. 118, flame arrester; No. 119B, wet-wall reactor; No. 119M, magnetically driven agitator; No. 120B, high-pressure separator; Nos. 121, 122, filter; No. 202, pressure-reducing device; No. 120A, low-pressure separator; No. 215, bag-filter; No. 216, medium tank; No. 205, medium feed pump; No. 133, air blower; No. 135, refrigerator; No. 136, water pump; No. 138, water chiller; No. 137, head tank; Nos. 160A-160F, sampling port for oxygen analysis; P301, slurry recycle pump used in runs 24 to 29.

DEVELOPMENT OF WET-WALL PROCESS

Experimental Apparatus and Procedure

Modification of the Pilot Plant from Bulk to Wet-Wall Process

It seems possible to prevent the polymer deposit on the reactor wall by isolating it from ethylene and polymer by covering the wall with a liquid. Furthermore, the liquid is useful as a carrying medium for the continuous removal of polyethylene from the reactor.

Based on these ideas and preliminary experiment, the pilot plant of bulk polymerization was modified as follows: (i) replacement of the bulk reactor with a wet-wall one; (ii) addition of a pressure-reducing device for continuous taking out of polyethylene slurry from the high-pressure reaction zone to atmospheric pressure; (iii) addition of a low-pressure separator for dissolved ethylene in the slurry; (iv) addition of two filters for polymer separation from the slurry; and (v) addition of a feed pump and tanks for the medium.

Description of the Pilot Plant of Wet-Wall Process

Figure 1 shows a flow sheet of the pilot plant of the wet-wall process consisting of a 10 liter reactor, two compressors for ethylene feed, two separators, tanks, a pressure-reducing device for polymer removal, filters, and other utilities.

The stainless steel reactor is a cylindrical vessel 150 mm in diameter equipped with a magnetically driven agitator (No. 119M), a overflow weir for uniform covering of the wall with medium, and nozzles for ethylene feed, medium feed, and removal of the mixture of unreacted ethylene, polymer, and medium.

The pressure-reducing device is composed of four coiled tubes of 2 mm bore and 100 m length; the number of tubes used was changed according to the flow rate and polyethylene concentration of the slurry. These tubes are immersed in hot water to prevent the polyethylene slurry from freezing during expansion of high-pressure ethylene gas.

The ethylene from the bank of cylinders (No. 101) was compressed to desired reaction pressure with Nos. 112 and 113. The ethylene, which was mixed with unreacted ethylene from the high-pressure separator (No. 120B), was heated to the desired temperature with No. 117 and fed to the reactor (No. 119B) at controlled pressure and temperature.

The medium, an aqueous solution of *tert*-butyl alcohol, was flushed with high-purity nitrogen in the medium tank (No. 206) to remove the dissolved oxygen which inhibits the polymerization reaction and then fed to the reactor with a plunger pump (No. 205) to cover the reactor wall and agitator. The feed rate of the medium was controlled by adjusting the stroke speed of plungers.

The ethylene was polymerized to fine powder polyethylene by γ -ray irradiation from Co-60 with an intensity of ca. 1.5×10^5 rad/hr. The facilities and method for irradiation are the same as described in the preceding paper.¹

The powder polyethylene produced in the reactor was transferred together with the unreacted ethylene and the carrying medium to the high-pressure separator (No. 120B) which was located under the reactor and shielded from γ rays. Unreacted ethylene was recycled from the high-pressure separator to the reactor with a pump (No. 115).

The polyethylene slurry was continuously transferred from the high-pressure separator to a low-pressure separator (No. 120A) through the pressure-reducing device (No. 202). The level of the slurry in the high-pressure separator was manually controlled with the removal rate of the slurry by changing the number of tubes.

After the dissolved ethylene was vented in the low-pressure separator, the polyethylene slurry was filtered with a bag filter (No. 215). The filtrate was reused as the carrying medium after being adjusted in its composition. The concentrated slurrylike paste was taken out and dried to polyethylene powder.

Tert-Butyl Alcohol Aqueous Solution as the Medium

It is necessary for the medium to satisfy the following properties: (i) polymerization is not retarded with the use of the medium; (ii) the properties of the polymer, such as molecular weight, are not degraded; (iii) surface tension of the medium is low enough to wet the polyethylene and the reactor wall; and (iv) solubility of ethylene in the medium is small under the reaction conditions.

The experiments using a 100 ml autoclave have shown that *tert*-butyl alcohol was the best among various kinds of alcohols for both the polymerization rate and polymer molecular weight.² Water, a poor solvent for ethylene, is cheap and does not affect the polymerization, but unfortunately does not wet the polyethylene and the reactor wall.

The aqueous solution of *tert*-butyl alcohol (*t*-BuOH aq) meets the above-mentioned requirements and was therefore used as the medium.

Materials

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

Measurement and Analysis

Oxygen in ethylene from the bank of cylinders was continuously measured by a Horiba oxygen analyzer. The oxygen content was usually less than 5 ppm. Oxygen in the medium from the medium tank was monitored by a Beckman process oxygen analyzer (Model No. 778).

Polymer concentration in the slurry was measured with the use of a turbidimeter after being diluted with *t*-BuOH aq. A number-average molecular weight of polymer was determined by Tung's equation³ from its intrinsic viscosity in tetralin at 130°C.

Operational Results of the Wet-Wall Process

Operation of the pilot plant by the wet-wall process was carried out 29 times at pressures of 400 kg/cm², temperatures of 11 to 40°C, ethylene feed rates of 1.2 to 11.8 kg/hr, and carrying medium feed rates of 0 to 100 liter/hr; the results are summarized in Table I.

Polymerization Rate

The space-time yield of the polymer shown in Table I was calculated from the polymer yield including the deposited polymer in the reactor.

In several runs, such as run 9, the space-time yield was consistent with small scale experiments⁴; in some runs however, the polymerization reaction was inhibited by a small amount of oxygen in the medium of ethylene, so that the space-time yield was lower than expected.

Polymer Deposit to the Reactor Wall

The amount of polymer deposited on the reactor wall and agitator was smaller than that in bulk process reported in the previous paper,¹ but the polymer deposit was not completely avoided.

Experimental runs 1 to 4 show that the deposited polymer was increased exponentially with operation time similar to bulk polymerization.¹ The amount deposited to the upper part of the reactor was smaller than that to the lower part. The upper part was probably covered with medium.

Runs 6 to 9 were carried out at various compositions of the medium. The amount of polymer deposited was markedly decreased in the medium of 40 wt% *t*-BuOH.

Polymer deposit to the various materials was examined. In run 9, three propellers plated with gold, silver, and enamel were used as agitator blades: the amount of polymer deposited to the gold-plated propeller was the smallest. Three kinds of paddle-type scrapers made of poly(tetrafluoroethylene), polypropylene, and polyethylene were used in run 16: the amount deposited to the polytetrafluoroethylene scraper was the smallest. It was concluded that polymer deposit to any material was not prevented for a long-period operation.

In run 14, a conical copper sleeve was inserted in the reactor in order to increase medium thickness as the medium flowed down along the sleeve. The deposited polymer was decreased with increase of the medium thickness. In run 20, we use a cylindrical copper sleeve with a 25 mm gutter width, where all of the medium flowed down, and no polymer was deposited in the gutter.

By considering that the deposited polymer was easily removed by hand, the experiments were carried out using several kinds of scraping blades, such as the paddle-type phosphor bronze blade (run 18), an anchor-type copper blade (run 12), and a shaftless helical ribbon-type phosphor bronze blade (run 19). In run 18, no polymer deposit was observed on the reactor wall where the blade contacted, but much polymer was deposited on the shaft as shown in Figure 2. There was no deposited polymer on the reactor wall and the helical ribbon blade in run 19 (Fig. 3).

A chemical method for the prevention of polymer deposit was examined in run 22 where water containing 600 ppm sodium chloride (scavenger to H⁺, OH⁻, and e_{aq}⁻) and 100 ppm lauryl alcohol (surfactant) was used as the medium. The amount of deposited polymer was decreased; however, most of polymer coagulated and remained in the reactor and separator because the medium could not disperse the polymer.

In runs 24 to 29, the slurry was recycled with a newly equipped pump (P301 in Fig. 1) at ca. 200 liter/hr from the high-pressure separator to cover the wall, and the feed rate of the fresh medium was reduced. However, prevention of polymer deposit was not satisfactory.

TABLE I
 Operational Results of Wet-Wall Process^a

Run No.	Pressure, kg/cm ²	Temperature, °C	Reaction time, hr	Feed rate		Concentration in medium, wt. %	Type of agitation blade ^b	Agitation speed, rpm	Polymer yield, g	Deposited polymer, g	Space-time yield, g/liter hr	Molecular weight (× 10 ⁴)
				Ethylene, kg/hr	Medium, liter/hr							
1	400	30	1.2	9.4	100	40	A	300	36	0	3.0	1.1
2	400	35	8	2.8	70	40	A	300	480	8	6.0	2.9
3	400	30	4.5	1.2	80	40	N	0	390	2	8.7	5.3
4	400	11	20	1.2	80	40	N	0	260	100	1.3	4.0
5	400	20	8	6.4	63	40	N	0	775	130	9.4	5.8
6	400	19	8	6.5	86	15	N	0	870	180	11	11
7	400	16	8	5.9	75	20	A	300	540	140	6.8	4.5
8	400	20	8	5.3	37	60	A	300	575	20	7.2	3.0
9	400	20	6.7	6.4	35	40	A	300	700	4	12	6.0
10	400	23	20	5.5	70	40	A	300	2640	2600	13	c
11	400	25	30	6.0	90	40	A	300	730	150	2.4	3.1
12	400	20	2.5	5.0	95	40	B	60	230	200	9.3	7.0
13	400	36	9.2	6.6	66	40	N	0	270	20	3.2	3.3
14	400	36	8	8.2	80	40	N	0	135	20	3.1	0.6
15	400	35	8	6.5	75	40	N	0	90	0	1.2	1.8

16	400	30	25	7.1	88	40	C	82	470	9	2.0	2.4
17	400	30	16.7	10.0	80	40	C	90	930	30	6.0	3.7
18	400	30	24	10.6	75	40	C	100	940	450	4.2	2.4
19	400	40	12	11.8	90	36	D	85	565	25	5.1	3.2
20	400	32	12	9.7	78	40	N	0	375	70	3.4	3.6
21	400	30	8	10.2	80	38	N	0	480	50	6.5	3.2
22	400	33	8	2.7	100	0 ^d	N	0	370	410	9.1	20
23	400	35	8	3.5	96	0 ^e	N	0	0	0	0	—
24	400	36	7.5	5.0	0	60	N	0	820	710	12	c
25	400	32	8	0.4	0	60	N	0	855	700	12	c
26	400	33	6	10.0	0	75	N	0	345	300	6.2	5.8
27	400	32	26.5	5.0	14	75	N	0	1230	580	5.0	6.1
28	400	30	9	5.2	14	75	D	60	625	100	7.5	6.3
29	400	30	20	5.7	18	75	D	60	1690	300	9.2	8.4

^a Reaction condition; dose rate is 1.4×10^5 rad/hr.

^b N, none; A, propeller; B, anchor; C, paddle; D, shaftless helical ribbon.

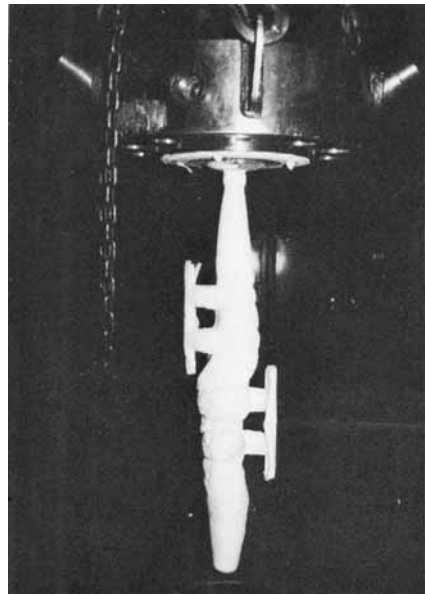
^c Could not be measured because the polymer was not dissolved in hot tetralin.

^d Water containing 100 ppm lauric alcohol and 600 ppm sodium chloride was used as a medium.

^e Water containing 0.25 wt% anionic surfactant and 600 ppm sodium chloride was used as a medium.

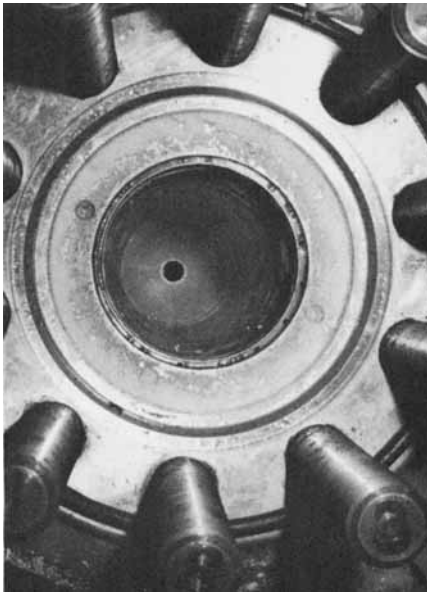


(a)

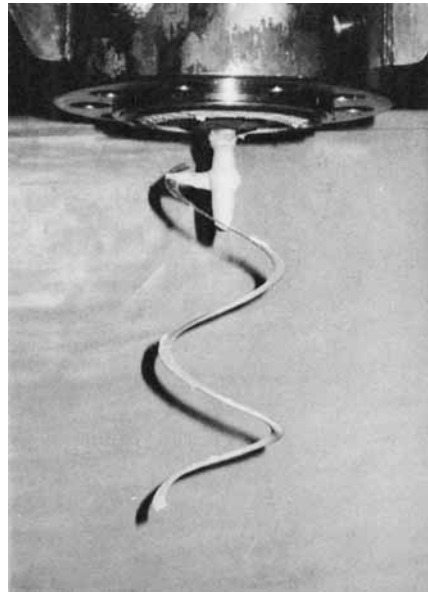


(b)

Fig. 2. Appearance of polymer deposit to reactor wall (a) and scraping blade (b) in run 18.



(a)



(b)

Fig. 3. Appearance of polymer deposit to reactor wall (a) and scraping blade (b) in run 19.

Advantages of this slurry recycling method are to increase the polymer concentration in slurry and to decrease the contamination with oxygen from the medium.

DEVELOPMENT OF THE HEAVY PHASE RECYCLING PROCESS

Experimental Apparatus and Procedure

In the operation of the pilot plant using the wet-wall process, many problems and troubles occurred, such as entrainment of liquid in recycled ethylene gas. Most of these troubles were due to unforeseen composition in equilibrium of the ternary system, ethylene-*t*-BuOH-water, under pressure.

The phase behavior of ethylene and *t*-BuOH aq containing polymer with an ethylene pressure of 400 kg/cm² was examined using a 200 ml autoclave equipped with a pair of quartz windows. The level of solution in the autoclave was observed to decrease by shaking resulting from *t*-BuOH extraction to ethylene, and the polymer homogeneously suspended in the solution was concentrated on the surface of the lower layer (heavy phase).

A heavy phase recycling process has been developed on the basis of these facts.

Phase Equilibrium

The phase equilibrium diagram shown in Figure 4 was obtained in the pressure range of 60 to 300 kg/cm² and at 30 to 75°C. A mutual solubility curve is almost independent of pressure and temperature but tie lines are slightly affected by temperature.

The mixture with composition A in the heterogeneous region is separated into two phases, B and C, along the tie line and the ratio of the two phases corresponds to $\overline{AC}:\overline{AB}$.

Phases B and C denote a light phase and a heavy phase, respectively. The density of the light phase varies from 0.4 to 0.8 g/cm³ depending on the composition, pressure, and temperature. The density of the heavy phase is ca. 1.0 g/cm³ independent of these parameters.

The light phase is rich in ethylene and *t*-BuOH where polymerization takes

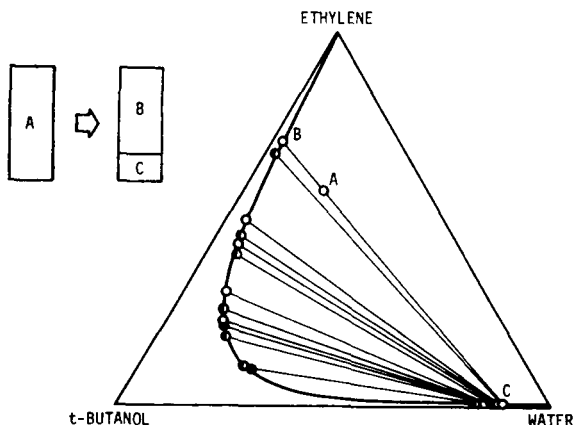


Fig. 4. Phase equilibrium diagram of ethylene-*t*-butyl alcohol-water ternary system at 30°C and at various pressures: [○], 300 kg/cm²; [●], 100 kg/cm²; [●], 60 kg/cm².

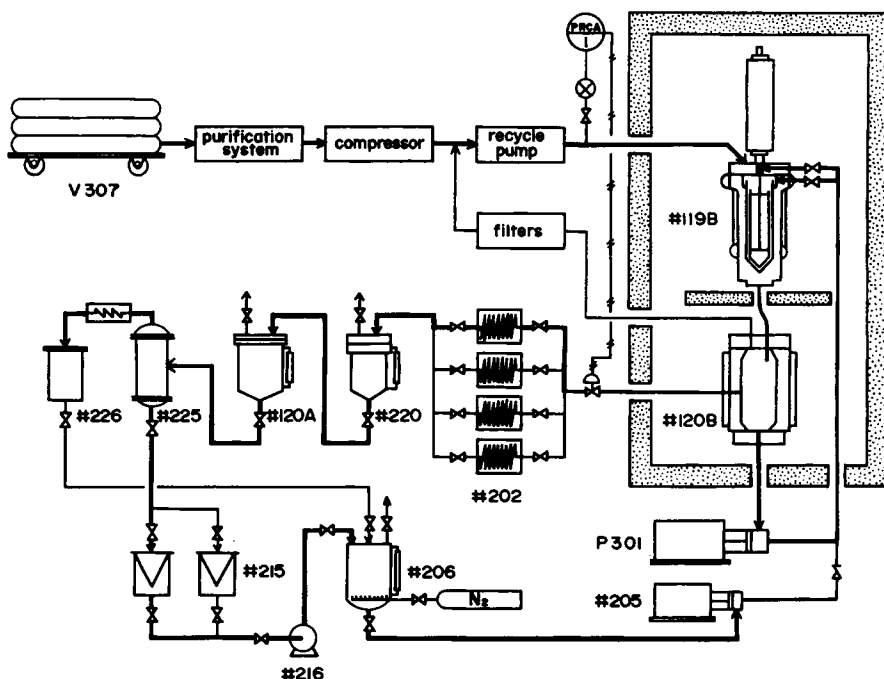


Fig. 5. Flow sheet of the modified pilot plant for heavy phase recycling process: V307, ethylene container; No. 119B, wet-wall reactor; No. 120B, high-pressure separator; No. 202, pressure-reducing device; No. 220, medium-pressure separator; No. 120A, low-pressure separator; No. 224, pot still; No. 225, condenser; No. 226, receiver; No. 215, bag filter; No. 216, medium pump; No. 206, medium tank; No. 205, medium feed pump; P301, recycle pump for heavy phase.

place. The heavy phase, mostly composed of water, can be used as the medium to avoid the polymer deposit because the polymerization rate in this phase is negligibly small.

Modification of the Pilot Plant

The heavy phase recycling process was developed on the basis of the phase equilibrium. Figure 5 shows a flow sheet of the pilot plant modified as follows: (i) a line for removing the polymer in the light phase was added between the middle of the high-pressure separator and the pressure-reducing device; (ii) a pressure control valve was added to the pressure-reducing device; (iii) a 7 liter medium-pressure separator was added between the pressure-reducing device and the low-pressure separator; (iv) a container of 4.1 m³ was equipped for supplying high-purity ethylene for a long period; and (v) a 20 liter pot still was added to recover the medium and to facilitate filtration of the slurry.

Description of the Pilot Plant

Prior to the operation, *t*-BuOH aq and ethylene were charged in the high-pressure system to form the light and heavy phases in equilibrium. The heavy phase in the high-pressure separator was recycled into the reactor to prevent polymer deposit. After the stational feeds of 83 wt% *t*-BuOH aq and ethylene

whose composition was similar to that of light phase, γ -ray irradiation was started.

A mean residence time of the light phase and its composition in the reactor were controlled by the feed rates and ratio of ethylene and medium according to the phase diagram.

The polymer produced in the reactor was transferred to the high-pressure separator with the mixture of light and heavy phases which were then separated. The light phase containing the polymer was taken out at an interface of two phases in the high-pressure separator and transferred to the medium-pressure separator at 20 kg/cm² where the ethylene gas was vented and the slurry was transferred to the low-pressure separator. After the dissolved ethylene was vented, the slurry was distilled in the pot still to recover the *t*-BuOH aq, which was reused as the medium after adjusting the composition. The slurry from the bottom of pot still was filtered to recover the polyethylene.

Operational Results of the Heavy Phase Recycling Process

The operation of the pilot plant by the heavy phase recycling process was carried out 11 times with a pressure range of 100 to 400 kg/cm², a temperature of ca. 25°C, an ethylene feed rate of 1.0 to 7.6 kg/hr, a medium feed rate of 2.0 to 22 liter/hr, and a dose rate of 6×10^4 and 1.2×10^5 rad/hr. Several runs under the various reaction conditions were performed during one operation. Operational results are summarized in Table II together with the reaction conditions.

Polymerization Reaction

The polymer concentration in the slurry increased with the operation time and reached steady state after a period of six to ten times longer than the mean residence time of the light phase in the reactor. The molecular weight of polymer changed with time as did the polymer concentration.

The space-time yield of polymer shown in Table II was calculated from the polymer concentration and the removal rate of slurry at steady state.

The polymerization reaction was scarcely inhibited because oxygen was well removed from the medium whose feed rate was much smaller than that in the wet-wall process.

Continuous Removal of the Polymer

The polymer was well removed from the high-pressure system as a slurry containing polymer up to 40 g/liter. The concentrated slurry above 30 g/liter was diluted with *t*-BuOH aq at inlet of the pressure reducing device to prevent the device from being clogged.

Polymer Deposit to the Reactor Wall

The amount of polymer deposited to the reactor wall was extremely decreased compared with the wet-wall process and a longer operation period was achieved by this process.

TABLE II
 Operational Results of Heavy Phase Recycling Process^a

Run No.	Pressure, kg/cm ²	Temperature, °C	Reaction time, hr	Feed rate		Mole fraction		Residence time, hr	Type of scraping blade ^b	Scraping speed, rpm	Space-time yield, g/liter hr	Molecular weight (× 10 ⁴)
				Ethylene, kg/hr	Medium, liter/hr	Ethylene	<i>t</i> -BuOH					
32-1	150	18-26	20	3.1	14.2	0.31	0.37	0.45	N	0	6.5	3.5
32-2	100	19-26	20	3.1	14.5	0.33	0.38	0.41	N	0	4.1	2.7
33-1	250	17-26	22	3.1	13.2	0.33	0.36	0.48	H.R	c	7.7	6.3
33-2	400	21-28	12	3.1	12.8	0.33	0.36	0.49	H.R	c	16.7	10.6
33-3	300	24-28	8	3.1	12.9	0.33	0.36	0.50	H.R	c	8.5	6.2
33-4	350	26-29	22	3.0	13.0	0.33	0.37	0.50	H.R	c	11.7	6.5
34-1	300	16-26	12	3.1	12.5	0.34	0.36	0.51	H.R	20	12.2	7.2
34-2	300	15-27	8	6.1	24.5	0.34	0.36	0.26	H.R	20	6.1	4.7
34-3	300	19-28	8	2.1	10.5	0.30	0.38	0.65	H.R	20	11.9	4.2
34-4	300	17-25	14	2.0	10.5	0.29	0.39	0.66	H.R	20	6.4	—
35-1	300	29-31	24	3.0	13.3	0.32	0.37	0.49	A	21	12.7	6.4
35-2	300	28-30	24	3.2	13.3	0.33	0.36	0.48	A	21	14.1	6.9
35-3	300	30-31	24	3.0	13.3	0.33	0.36	0.50	A	21	14.1	7.0

35-4	300	28-31	24	3.1	13.6	0.32	0.37	0.48	A	21	13.7	—
35-5	300	28-31	24	3.0	15.0	0.29	0.38	0.46	A	21	9.5	5.4
37-1	300	22-30	18	1.8	9.6	0.28	0.39	0.73	A	20	10.5	5.5
37-2	300	22-30	20	1.3	7.0	0.28	0.39	0.99	A	20	17.3	7.5
38-1	300	25-30	10	4.6	10.0	0.49	0.28	0.48	A	20	11.7	6.7
38-2	300	25-30	14	5.3	7.0	0.61	0.21	0.52	A	20	12.9	8.9
38-3	300	25-30	7	6.4	4.0	0.72	0.13	0.53	A	20	8.9	7.4
38-4	300	28-30	9	7.6	2.0	0.89	0.06	0.51	A	20	4.7	6.3
39-1	300	23	13	3.2	13.0	0.33	0.40	0.50	A	105	9.9	5.7
39-2	300	19	8	3.2	13.0	0.33	0.40	0.50	A	300	2.9	1.5
39-3	300	20	8	3.2	13.0	0.33	0.40	0.50	A	0	8.1	5.1
40-1	300	15-17	7	5.0	21.7	0.33	0.46	0.30	A	20	7.8	3.4
40-2	300	25-26	10	1.5	6.5	0.33	0.46	1.0	A	20	15.8	8.3
40-3	150	28	6	5.9	3.1	0.80	0.10	0.50	A	20	2.8	3.1
40-4	150	27	6	4.1	8.7	0.50	0.30	0.50	A	20	3.7	3.4

^a Reaction conditions; dose rate is 1.2×10^5 rad/hr except for run 34-4 (6×10^4 rad/hr), and concentration of *t*-BuOH aq is 83 wt%.

^b N, none; H,R, shaftless helical ribbon; A, shaftless anchor.

^c The blade was broken during the operation.

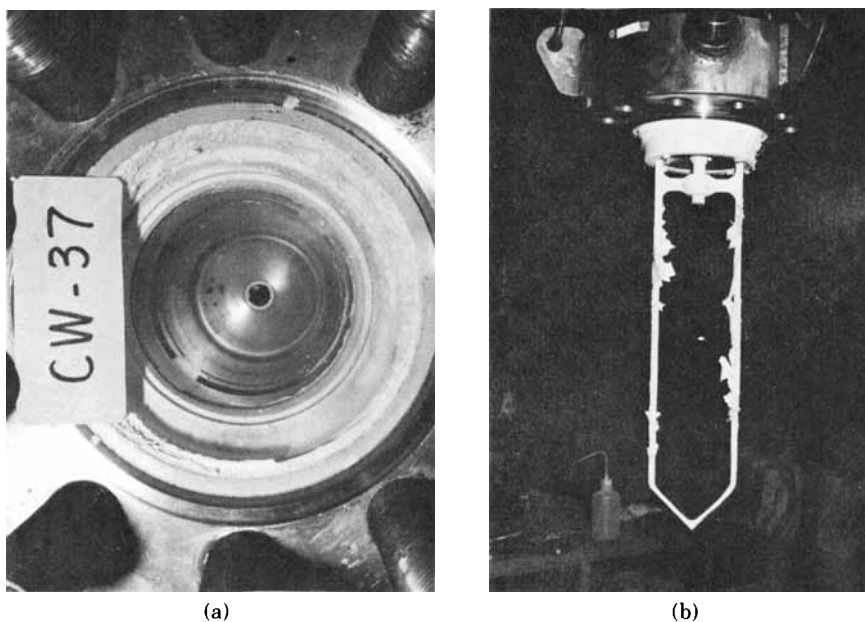


Fig. 6. Appearance of polymer deposit to reactor wall (a) and scraping blade (b) in run 37.

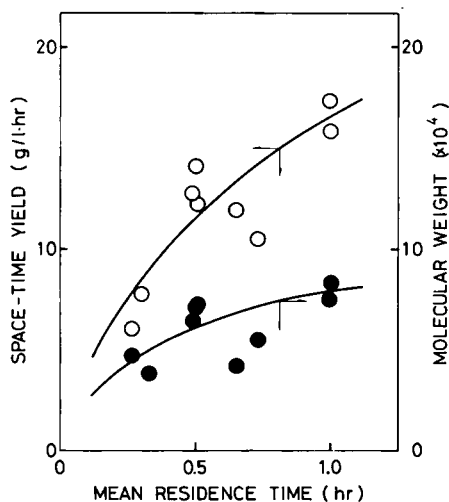


Fig. 7. Effect of mean residence time on space-time yield and polymer molecular weight. Reaction conditions: pressure, 300 kg/cm²; temperature, 15–31°C; dose rate, 1.2×10^5 rad/hr; ethylene molar fraction in light phase, 0.28–0.34.

As shown in Figure 6, the deposited polymer was not observed on the reactor wall even after 38 hr of operation in run 37. A small amount of polymer was deposited to the scraping blade.

In run 35, five full days of operation were successfully performed. A large amount of polyethylene (ca. 15 kg) was produced with a space-time yield of 13.5 g/liter hr. In this operation, the ca. 770 g of polymer deposited around the scraping blade.

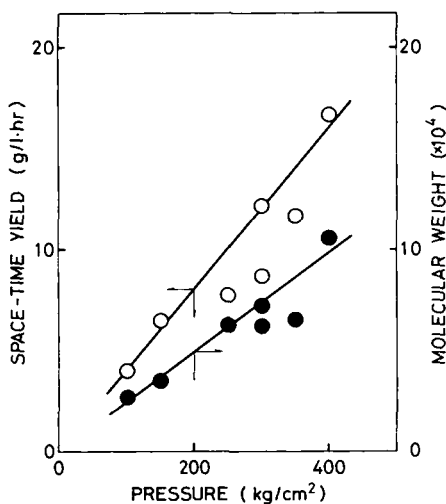


Fig. 8. Effect of pressure on space-time yield and molecular weight. Reaction conditions: temperature, 17–31°C; dose rate, 1.2×10^5 rad/hr; mean residence time, 0.41–0.50 hr; ethylene molar fraction, 0.31–0.33.

In conclusion, scraping the reactor wall is necessary in addition to covering the wall with a heavy phase for smooth long-period operation. The shaftless anchor-type blade was the most suitable for prevention of polymer deposit.

RESULTS AND DISCUSSION

Polymerization Rate and Polymer Molecular Weight

Effect of Mean Residence Time

The space-time yield and the polymer molecular weight were increased with increase in the mean residence time of the light phase in the reactor (Fig. 7). This is explained by the fact that the lifetime of the polymer radical is rather long at low temperature⁴ and the polymerization reaction is therefore nonstational.

Effect of Reaction Pressure

The space time-yield and the molecular weight were increased with the reaction pressure (Fig. 8). The pressure exponents for the space-time yield and the molecular weight are nearly 1.0 and 0.9, respectively. These pressure dependences are lower than those in bulk polymerization.⁵

Effect of Light Phase Composition

Figure 9 shows the effects of molar fraction of ethylene in the light phase on the space-time yield and the molecular weight. The space-time yield has a maximum at an ethylene molar fraction of 0.5, and the molecular weight monotonously increases with the ethylene molar fraction. These phenomena may be explained by the increase in propagation rate and decrease in rate of radical formation mainly from *t*-BuOH with an increase in the ethylene molar fraction.

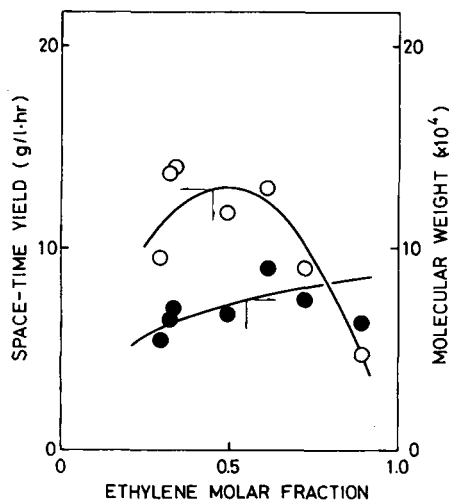


Fig. 9. Effect of ethylene molar fraction on space-time yield and molecular weight. Reaction conditions: Pressure, 300 kg/cm²; temperature, 25–31°C; dose rate, 1.2×10^5 rad/hr; mean residence time, 0.46–0.53 hr.

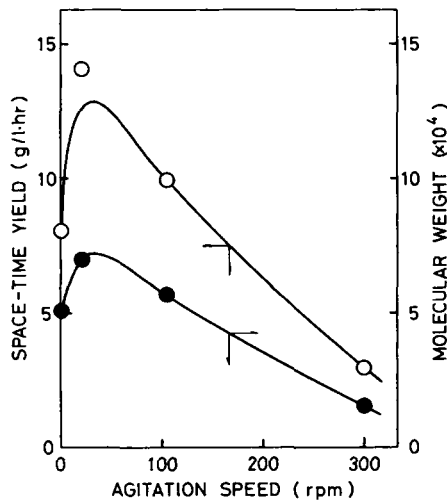


Fig. 10. Effect of agitation speed on space-time yield and molecular weight. Reaction conditions: pressure, 300 kg/cm²; temperature, 19–31°C; dose rate, 1.2×10^5 rad/hr; mean residence time, 0.50 hr; ethylene molar fraction, 0.33.

Effect of Dose Rate

The space-time yield was increased with the dose rate, and its dose rate exponent was nearly 1.0. This indicates that the predominant termination reaction is first order.

Effect of Agitation Speed

As shown in Figure 10, the space-time yield and molecular weight are increased with slow agitation of 20 rpm and then decreased markedly with the increase in the agitation speed. The increases are due to the increase in the diffusion rate of ethylene, and the decreases may be due to the decrease in the propagation rate.⁶

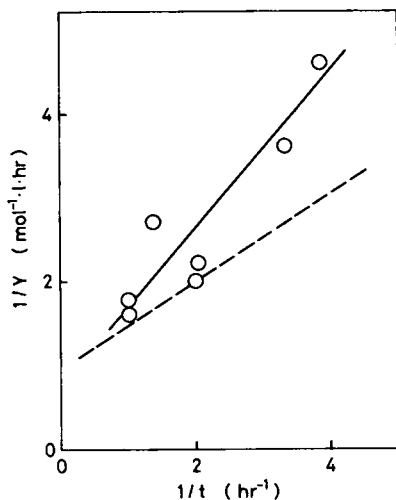


Fig. 11. Reciprocal of space-time yield vs. reciprocal of mean residence time: solid line, this work; broken line, bulk polymerization. Reaction conditions are the same as in Figure 7.

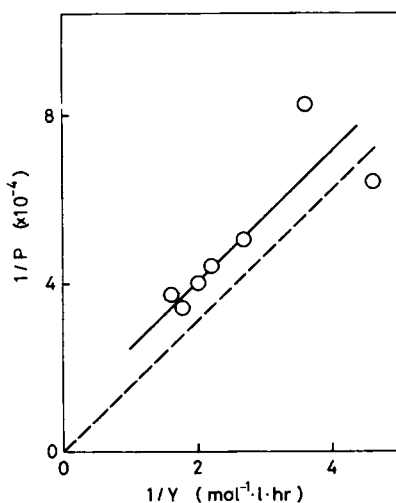
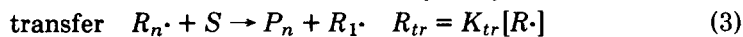
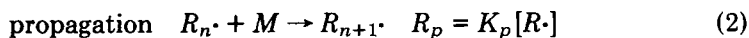
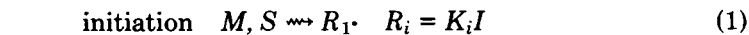


Fig. 12. Reciprocal of degree of polymerization vs. reciprocal of space-time yield: solid line, this work; broken line, bulk polymerization. Reaction conditions are the same as in Figure 7.

Kinetical Consideration

Assuming that elementary reactions are given in eqs. (1) to (4) and that the light phase and polymer in the reactor are in backmix flow, the reciprocals of the space-time yield and degree of polymerization are derived in eqs. (5) and (6):



$$\frac{1}{Y} = \frac{1}{K_p K_i I} \frac{1}{t} + \frac{K_t}{K_p K_i I} \quad (5)$$

$$1/P = K_i I / Y + K_{tr} / K_p \quad (6)$$

where M represents the ethylene monomer, S is the medium (i -BuOH), $R_n\cdot$ is a propagating radical composed of n monomers, Z is the substance by which $R_n\cdot$ is deactivated, and P_n is a dead polymer composed of n monomers; R_i , R_p , R_{tr} , R_t , K_i , K_p , K_{tr} , and K_t are the rates and apparent rate constants of initiation, propagation, transfer, and termination, respectively; $[R\cdot]$ is the total concentration of propagating radicals, I is the dose rate; Y and P are the polymerization rate and degree of polymerization at steady state, respectively, and t is the mean residence time of the light phase in the reactor.

The data from the pilot plant operations of heavy phase recycling process are plotted according to eqs. (5) and (6) in Figures 11 and 12 together with the results of the bulk polymerization.⁷

As shown in Figure 11, the slope that gives $1/K_p K_I I$ is steeper than that for bulk polymerization. Figure 12 shows that $K_i I$ is similar to that for bulk polymerization and the intercept of solid line shows that the transfer reaction occurs.

These results show that K_p is smaller than that for bulk polymerization. The fact that $K_i I$ at ca. 1.2×10^5 rad/hr is almost same as that for bulk polymerization at ca. 3.8×10^5 rad/hr indicates that K_i for this process is three times larger than that for bulk. This is due to the formation of initiating radicals from water and t -butyl alcohol with larger G value than that for ethylene.⁸

We would like to acknowledge our appreciation to members engaged to this project for their helpful discussion and experimental collaborations. We would also like to take this opportunity to thank following private companies for their helpful cooperation: Asahi-Dow Ltd., Idemitsu Kosan Co., Ltd., Maruzen Oil Co., Ltd., Mitsubishi Chemical Industries Ltd., Mitsubishi Petrochemical Co., Ltd., Mitsui Engineering & Shipbuilding Co., Ltd., Mitsui Petrochemical Industries, Ltd., Nippon Shokubai Kagaku Kogyo Co., Ltd., Showa Denko K. K., Sumitomo Chemical Co., Ltd., and Ube Industries, Ltd.

References

1. M. Takehisa, S. Machi, H. Watanabe, T. Ueno, S. Takahashi, R. Tsuchiya, K. Otaguro, I. Motoda, Y. Takasaka, K. Miyanaga, W. Kawakami, K. Yamaguchi, T. Sugo, H. Nakajima, T. Watanabe, and C. Hinachi, preceding paper, *J. Appl. Polym. Sci.*, **24**, 853 (1979).
2. F. Suganuma, S. Machi, H. Mitsui, M. Hagiwara, and T. Kagiya, *J. Polym. Sci., A-1*, **6**, 2069 (1968).
3. L. H. Tung, *J. Polym. Sci.*, **24**, 333 (1957).
4. S. Machi, M. Hagiwara, M. Gotoda, and T. Kagiya, *J. Polym. Sci.*, **A3**, 2931 (1965).
5. S. Machi, M. Hagiwara, M. Gotoda, and T. Kagiya, *Bull. Chem. Soc. Jpn.*, **39**, 675 (1966).
6. W. Kawakami, M. Hagiwara, Y. Hosaki, S. Machi, and T. Kagiya, *Bull. Chem. Soc. Jpn.*, **40**, 2668 (1967).
7. W. Kawakami, Y. Hosaki, M. Hagiwara, S. Machi, and T. Kagiya, *Ind. Eng. Chem.*, **6**, 302 (1967).
8. T. Wada, T. Watanabe, and M. Takehisa, *J. Polym. Sci., A-1*, **10**, 1655 (1972).

Received January 2, 1979