Radiation-Induced Polymerization of Ethylene in a Pilot Plant. I. Bulk Process

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Synopsis

Radiation-induced bulk polymerization of ethylene was carried out with use of a pilot plant with a 10 liter reactor at pressures of 225–400 kg/cm^2, temperatures of 30–95°C, ethylene feed rates of 5–28 kg/hr, and dose rate of 3.8 × 10^5 rad/hr. Characteristics of the process are mild polymerization conditions and capability of producing medium density polyethylene in powder form. The space-time yield and molecular weight of polymer were in the range of 3.5 to 13.1 g/liter hr and 2.2 × 10^4 to 14 × 10^4, respectively. The space-time yield increased with mean residence time and 2.4 powders of pressure, and decreased with temperature. Molecular weight changed similarly with the reaction conditions. These results were consistent with those of the bench plant experiment and the scale effect was small. Polymer deposit to the reactor wall limited a period of continuous operation of the plant. The amount of deposited polymer was increased with the square of reaction time. The rate of polymer deposit was proportional to polymer concentration and to the cube of pressure. The polymer deposit cannot be solved in the bulk process.

INTRODUCTION

Radiation process has received a great deal of attention as a new process for preparing pure polyethylene without using a catalyst or initiator and with better reaction controllability. Following several basic researches on the radiation-induced polymerization of ethylene in bulk and in solution in the late 1950s to early 1960s,[1-10] the developments of polymerization in flow system were carried out at Brookhaven National Laboratory[11] and at the Japan Atomic Energy Research Institute.

Both developments have aimed at industrialization of the processes. Brookhaven National Laboratory chose the polymerization conditions of high temperatures up to 200°C and pressures up to 1300 atm similar to a commercial high-temperature and pressure process yielding low-density polyethylene. The Japan Atomic Energy Research Institute, on the other hand, chose the polymerization at temperatures lower than the melting point of polyethylene. Characteristics of the latter process are mild polymerization conditions and capability of producing medium-density polyethylene in powder form.

This paper is the first part of a series of summary reports of extensive work which was carried out in pilot plants for eight years, and describes bulk polymerization of ethylene in a semibatch system.

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EXPERIMENTAL APPARATUS AND PROCEDURE

Pilot Plant and Process Description

Figure 1 shows a flow sheet of the pilot plant. Ethylene reserved in the bank of cylinders (No. 101) was heated with No. 103 and reduced to a constant pressure of 20 kg/cm^2. If oxygen content in ethylene was more than several ppm, a purification system was used which consisted of a preheater (No. 104), a catalytic converter using Engerhalt Deoxo catalyst (No. 105), and a cooler (No. 106). After being dried by a molecular sieve column (No. 108), ethylene was compressed with Nos. 112 and 113 up to the desired reaction pressure. The compressors were two-stage Colublin's oilless diaphragm type which had the advantage of eliminating contamination of ethylene. The maximum delivery pressure was 410 kg/cm^2 and capacities were 28 (No. 112) and 6 nm^3/hr (No. 113) at a suction pressure of 20 kg/cm^2. Compressed ethylene at a controlled pressure in the reservoir (No. 114) was transferred with a Colublin's diaphragm pump (No. 115) to the reactor (No. 119) through the preheater (No. 117) and flame arrester (No. 118). The 10 liter reactor was a cylindrical vessel 15 cm in diameter equipped with a magnetically driven agitator. Ethylene was polymerized in the reactor to form powder polyethylene under γ irradiation from Co-60. The reaction temperature was controlled by charged ethylene temperature and by circulating water, air, or steam in the reactor jacket. The produced polymer in the reactor was transferred with unreacted ethylene to one of the 45 liter polymer receivers (Nos. 120A and 120B) through a pneumatic three-way valve. Powder polymers precipitated in the polymer receiver and unreacted ethylene was returned to the diaphragm pump (No. 115) after a small amount of entrained polymers was completely removed with sintered metal filters with 10–50 μm pores (Nos. 121 and 122). The receivers were shielded from radiation by lead blocks in order to minimize radiation effects on the polymer. The dose rate in the receiver was 100 rad/hr.

Prior to operation, the entire system of the plant was pressurized to reaction pressure with nitrogen to detect gas leakage. The reactor was then evacuated at 150°C for several hours to remove contaminants on the reactor wall. The entire system was flushed four times with ethylene at 20 kg/cm^2 to remove oxygen. Oxygen concentration in ethylene was monitored during operation. When the oxygen concentration exceeded 10 ppm, the operation was stopped.

Pressure and flow rate of ethylene were automatically controlled with instruments of PRCA-1 and FRC-1, respectively. After the pressure, temperature, and flow rate were stabilized at reaction conditions, the Co-60 source was transferred to the reactor. After the desired period of time, the polymerization was stopped by removing the radiation source. The unreacted ethylene was purged and the system was swept out with nitrogen until the ethylene concentration was reduced below 2%. The reactor and polymer receivers were then opened to take out the polymer.

Irradiation

A schematic sketch of the radiation source holder together with the reactor is shown (Fig. 2). The 108 kCi Co-60 radiation source consisted of 60 pencils and was constructed as four curved slabs which were safely handled with ma-
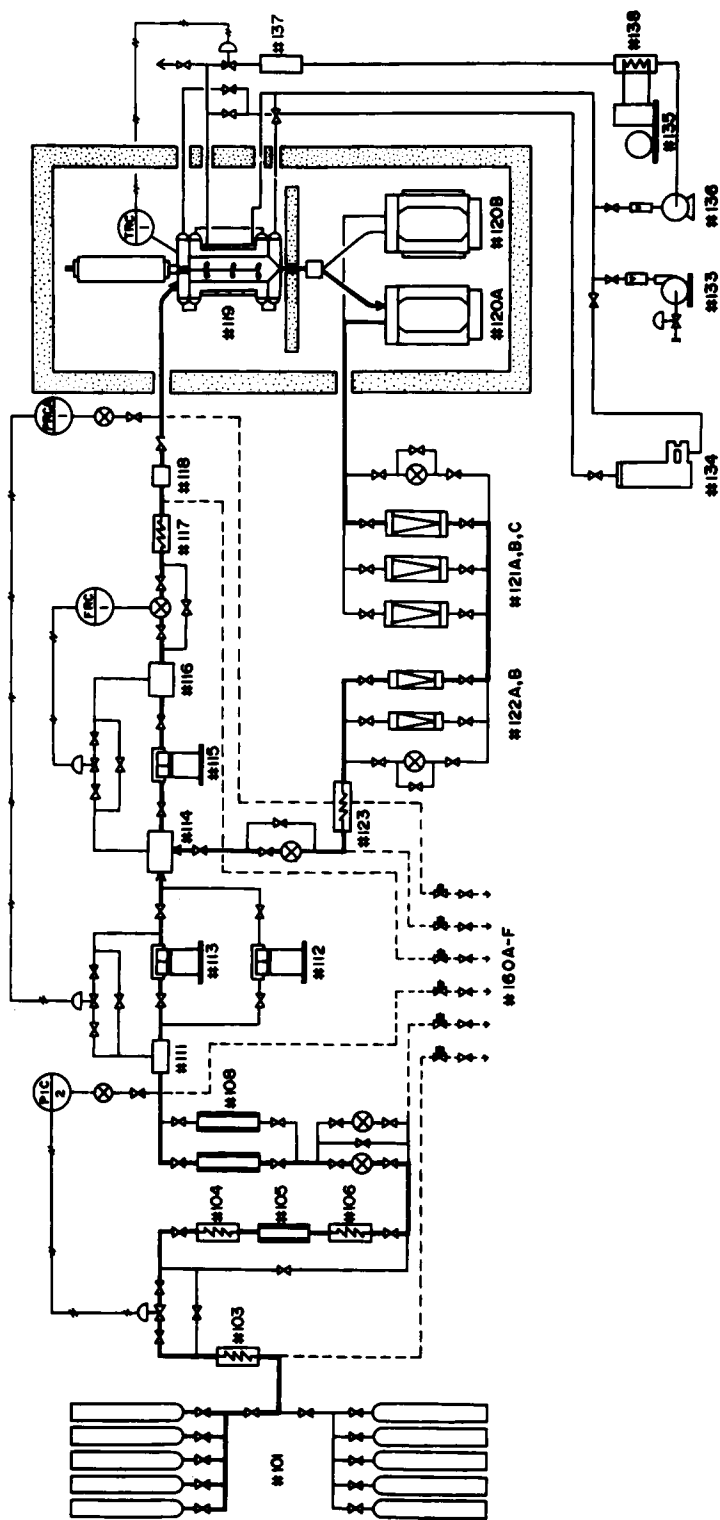
Fig. 1. Flow sheet of the pilot plant for bulk process: No. 101, ethylene cylinders; Nos. 103, 104, 117, ethylene heater; No. 105, oxygen remover; Nos. 106, 123, ethylene cooler; No. 108, humidity remover; Nos. 111, 114, 116, ethylene buffer tank: No. 112, start-up ethylene compressor; No. 113, make-up ethylene compressor; No. 115, ethylene recycle pump; No. 118, flame arrester; No. 119, pilot reactor; Nos. 120A and 120B, polymer receiver; Nos. 121, 122, filter; Nos. 160A–160F, sampling port for oxygen analysis; No. 133, air blower; No. 134, steam boiler; No. 135, refrigerator; No. 136, water pump; No. 137, head tank; No. 138, water chiller.
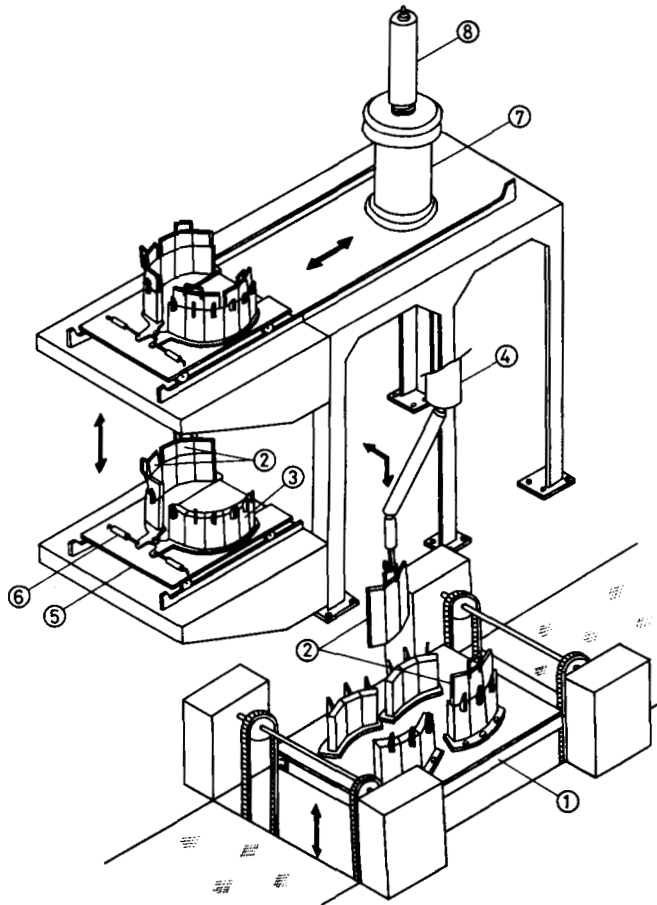
Fig. 2. Schematic sketch of radiation source holder together with the reactor; (1) elevator for source transfer from bottom of the pool to the hot cave, (2) Co-60 radiation source, (3) source holder, (4) power manipulator, (5) source carrier remotely operated with winch, (6) pneumatic power cylinder, (7) reactor, (8) magnetically driven agitator.

nipulators. The source was transferred from the elevator to a source holder of the pilot plant, lifted to reactor level, and horizontally transferred beside the reactor with remotely operated winches. The source was then closed to the outside wall of the reactor by power cylinders.

Dose rate in the reactor measured by Fricke's dosimeter was 3.8×10^5 rad/hr, which was in fairly good agreement with a calculated value using the built-up factor by Goldstein and Wilkins.[12] An efficiency of radiation energy absorption in ethylene was 0.28%.[13]

KINETIC ANALYSIS OF PILOT PLANT OPERATION

Table I summarizes the results of the pilot plant operation. The analysis of the results were carried out based on the kinetics derived from bench plant experiment.[14]

TABLE I
Operational Results of Bulk Process[a]

Run No.	Pressure, kg/cm²	Temperature, °C	Reaction time, hr	Mean residence time, hr		Type of agitation blade[c]	Agitation speed, rpm	Polymer yield (g)		Space-time yield, g/liter hr	Molecular weight (× 10⁴)
				gas (t)	polymer (t_p)			Powder	Deposit		
1	400	32	5	0.55	0.50	A	135	359	313	7.2	6.2
2	400	95	5	0.28	0.35	A	300	298	206	6.0	2.1
3	400	30	20	0.32	0.37	P	300	1071	59	5.4	4.3
4	400	30	13	0.85	0.64	P	300	1709	575	13.1	14.0
6	400	30	13	0.53	0.49	A&P	300	1621	743	12.5	14.0
7	400	30	6	0.31	0.39	P	300	377	8	6.3	4.2
8	400	60	20.5	0.31	0.39	A&P	300	1295	1201	6.3	2.8
9	400	75	24	0.31	0.39	A&P	300	2564	283	10.7	2.5
10	400	30	34	0.16	0.30	P	300	2636	1485	7.8	7.1
11	325	30	47	0.33	0.38	P	300	2856	891	6.1	5.8
12	400	70	28.6	0.32	0.37	P	300	2401	3277	8.4	3.5
13	400	30	13.6	0.35	0.40	P	300	1276	326	9.4	8.9
14	400	30	19.3	0.53	0.49	P	300	2370	1663	12.3	13.5
15	225	30	58.3	0.34	0.39	P	300	2085	283	3.5	2.4
16	400	45	23.2	0.37	0.43	P	300	2033	1633	8.8	8.8
18	225	30	66	0.38	0.44	P	300	2571	562	3.9	2.8
19[h]	400	20	24	0.50	0.58	P	300	889	22	3.7	2.5
21[b]	400	20	48	0.45	0.52	P	300	849	48	1.8	1.6
22[b]	400	20	24	0.38	0.44	P	300	1286	111	5.4	4.4
23	400	30	24	0.50	0.48	P	300	2157	1275	9.0	9.2
24	400	30	36	0.50	0.48	P	300	2979	3217	8.3	8.2
25	400	30	36	0.16	0.31	P	300	2599	2552	7.2	7.5
26	400	30	36	0.16	0.31	P	300	2771	2696	7.7	7.5
27	400	30	32	0.50	0.48	P	200	1188	2109	3.7	11.6
29	400	30	27.5	0.50	0.48	P	500	2440	2410	8.9	8.4
31	400	30	20	0.16	0.31	P	500	1790	1660	9.0	12.0

[a] Reaction condition; dose rate is 3.8×10^5 rad/hr.
[b] Ethylene–carbon dioxide system. Molar fractions of carbon dioxide are 0.24 in run 19, 0.495 in run 20, and 0.057 in run 21, respectively.
[c] A, anchor; P, propeller; A&P, anchor and propeller.

Effect of Ethylene Flow Rate on Polymer Yield at 30°C

Figure 3 shows relation between space-time yield of polyethylene and mean residence time of ethylene in the reactor. Space-time yield was calculated from the powder polymer yield; in other words, deposited polymer yield, and decrease in effective reactor volume by the deposition were neglected in the calculation.

The space-time yield at steady state is calculated from eq. (1) which is derived by assuming that polymer and monomer are thoroughly mixed in flow system:

$$Y = K_p K_i t / (1 + t K_t) \tag{1}$$

where Y (mole/liter hr), K_p (hr^{-1}), K_t (hr^{-1}), K_i (mole/liter hr), and t (hr) are space-time yield, apparent rate constants of propagation, termination and initiation, and mean residence time of ethylene, respectively. Analysis of the bench plant experiments[14] gave $K_i = 1.56 \times 10^{-4}$, $K_p = 9.0 \times 10^3$, and $K_t = 1.4$ at 30°C, 400 kg/cm^2, and 3.8×10^5 rad/hr. The calculated space-time yield from eq. (1) is also shown in Figure 3 as a function of t. A deviation of space-time yield from eq. (1) was also observed in the bench plant runs. This deviation is due to a difference in mean residence time between the solid polymer and gaseous monomer.

The broken line in Figure 3 represents the space-time yield calculated with appropriate correction for the polymer residence time (t_p) assuming a particular flow pattern in the bench plant experiment.[14] It should be noted that result of the pilot plant experiment coincides well with the broken line. This coincidence indicates that the flow pattern in the reactor of the pilot plant is similar to that of the bench reactor, i.e., scale effect on the flow pattern is small.
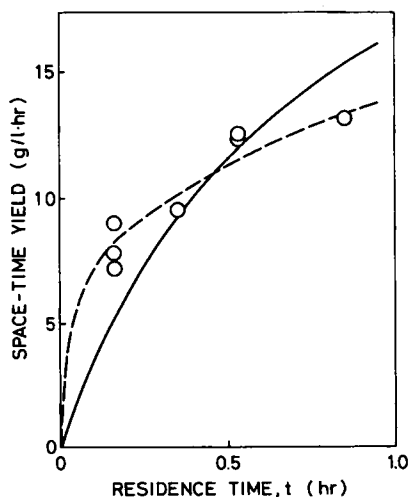

Fig. 3. Space-time yield of polyethylene vs. mean residence time of monomer at 400 kg/cm^2, 30°C, and 3.8×10^5 rad/hr: solid line, calculated from eq. (1); broken line, calculated with appropriate correction for the polymer residence time according to ref. 14.

Molecular Weight of Polymer at 30°C

Molecular weight of the polymer is calculated from eq. (2), if polymer is in backmix flow in the reactor:

$$\overline{M}_n = t_p K_p/(1 + t_p K_t) \tag{2}$$

Figure 4 shows plots of molecular weight of polymer against t_p. The molecular weight of polymer produced in the pilot plant is higher than that calculated from the equation. This fact is mainly due to effect of acetylene which is formed from radiolysis of ethylene and acts as a crosslinking agent for polyethylene under irradiation.[15]

Effect of Pressure on Space-time Yield at 30°C

Space-time yield and molecular weight of the polymer were proportional to 2.4 and 2.0 powers of ethylene pressure, respectively, in the batch experiment.[16] Accordingly, the space-time yield is plotted against 2.4 powers of pressure in Figure 5, which gives a straight line through the origin. The results are also in accord with the bench plant experiments.

Polymerization at High Temperature (45–95°C)

Long period operation of the pilot plant was unsuccessful at high temperatures because the deposited polymer on the reactor wall rapidly grew to a block and stopped agitation. As shown in Figure 6, both the space-time yield and molecular weight decrease with temperature. The decrease in the molecular weight is more remarkable than that in space-time yield. These results are in accord with those of the small scale batch experiments.[16]
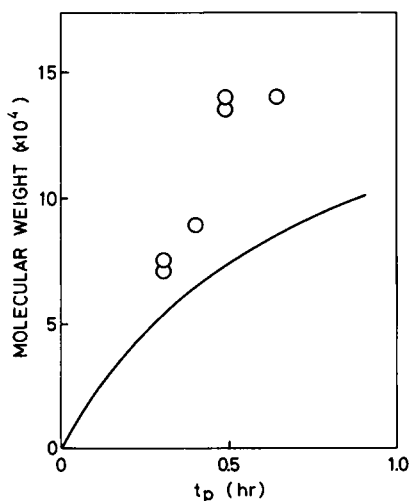

Fig. 4. Molecular weight of polymer vs. mean residence time of polymer (t_p) at 400 kg/cm², 30°C, and 3.8×10^5 rad/hr; solid line, calculated from eq. (2).
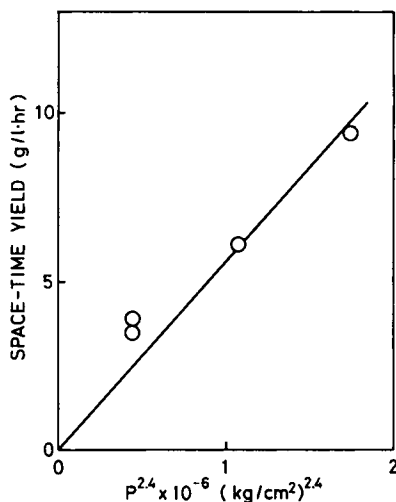
Fig. 5. Space-time yield vs. 2.4 powers of reaction pressure at 30°C, 13 to 14.2 kg C_2H_4/hr, and 3.8 × 10^5 rad/hr.
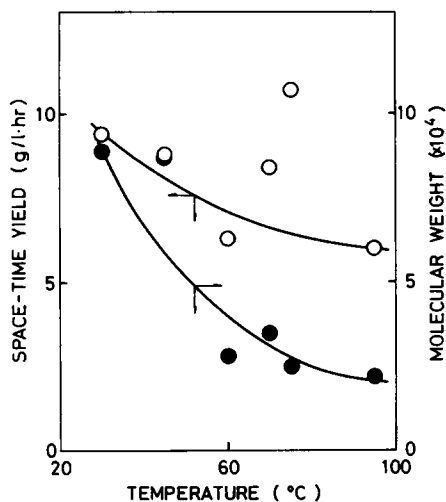

Fig. 6. Space-time yield and molecular weight vs. reaction temperature at 400 kg/cm^2, 12 to 15 kg C_2H_4/hr, and 3.8 × 10^5 rad/hr.

Polymerization in the Presence of CO_2 as a Solvent

Small scale batch experiments[17] showed that the deposited polymer in the ethylene-carbon dioxide system was negligible.   Figure 7 shows space-time yield of polymer at 400 kg/cm^2, 20°C, and 3.8 × 10^5 rad/hr in the presence of various amounts of carbon dioxide.   The space-time yield and molecular weight of polymer decrease rapidly with molar fraction of carbon dioxide.   This tendency is consistent with the batch experiment.[17]

The amount of deposited polymer was not markedly reduced in the long period operation even in the ethylene-carbon dioxide system.
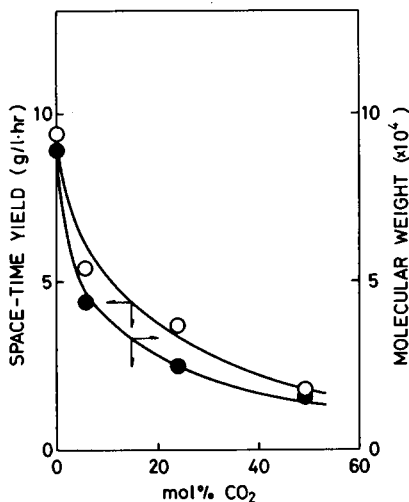
Fig. 7. Space-time yield and molecular weight vs. carbon dioxide concentration at 400 kg/cm^2, 20°C, 12.5 to 14 kg C$_2$H$_4$/hr, and 3.8 × 10^5 rad/hr.

POLYMER DEPOSIT TO REACTOR WALL

Polymer deposit to reactor wall decreases the reactor volume, heat transfer through reactor wall, and interferes with agitation. These phenomena prohibit continuous operation. The deposited polymer which was crosslinked by irradiation sometimes mixes in ordinary powder polyethylene. The mixed polyethylene cannot be practically used because of its heterogeneity. Therefore, prevention of polymer deposit is important for process development.

Appearance of Deposited Polymer

Three stages were visually observed for polymer deposit with reaction time. At the initial stage, the reactor surface was covered with polyethylene powder which could be easily wiped off with a cloth. The polymer was dissolved in hot tetralin.

At the second stage, the reactor surface was completely covered with a layer of white polyethylene. The polyethylene was soft and sticky, and could be scraped off with a bamboo applicator or metal spatula.

At the third stage, the deposited polymer changed to a hard solid. A chisel and hammer were necessary to dislodge the polymer from the reactor wall. The porcelainlike deposited polymer was harder than a commercial injection-molded polyethylene and was insoluble in hot tetralin.

Distribution of deposited polymer on the reactor surface was affected with the turbulence of ethylene. When a marine propeller was used as agitator, the deposit on the reactor surface near the propeller was less than that on other part of the surface. Marine propeller and turbine type agitators resulted in smaller amounts of deposit than with the helical ribbon-type agitator scraping the wall. This difference is mainly due to large amounts of deposit on the helical ribbon-type agitator shaft, where ethylene was not turbulent.

Effect of Reaction Conditions on Amount of Deposited Polymer

The amount of deposited polymer was nearly proportional to the square of reaction time as shown in Figure 8, and is expressed as follows:

$$D = K_d T^2 \tag{3}$$

where D (g), K_d (g/hr^2), and T (hr) are the amounts of deposited polymer, proportionality constant of polymer deposit, and reaction time, respectively.

When agitation was not applied, most of the polymer remained in the reactor due to polymer coagulation and clogging at the outlet nozzle. The deposit rate reduced markedly with mild agitation. At higher agitation speed above 200 rpm, rate of polymer deposit was decreased slowly with agitation speed.

As shown in Figure 9, K_d is proportional to polymer concentration in the reactor and to the cube of the reaction pressure. The pressure exponent is much higher than that of the polymerization rate. A similar pressure exponent, 3.4, was observed in grafting reaction of ethylene on preirradiated polyethylene powder. This similarity suggests that the grafting plays an important role for the polymer deposit.

Physical Properties of Deposited Polymer

The deposited polymer had a lower density and higher methyl branching than powder polyethylene in the same run. The deposited polymer was highly crosslinked by irradiation of only 1 to 10 Mrad during polymerization. The crosslinking of polyethylene seemed to be enhanced in the presence of ethylene due to the grafting.
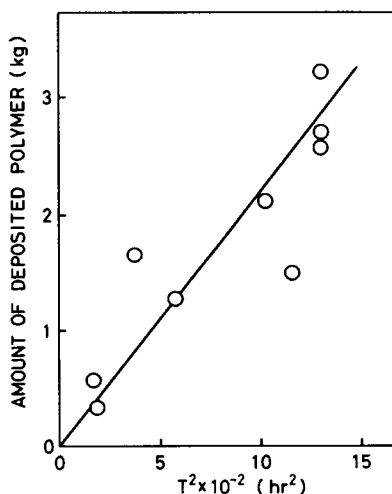

Fig. 8. Amount of deposited polymer vs. square of reaction time at 400 kg/cm^2, 30°C, 5 to 28 kg C$_2$H$_4$/hr, and 3.8 × 10^5 rad/hr.
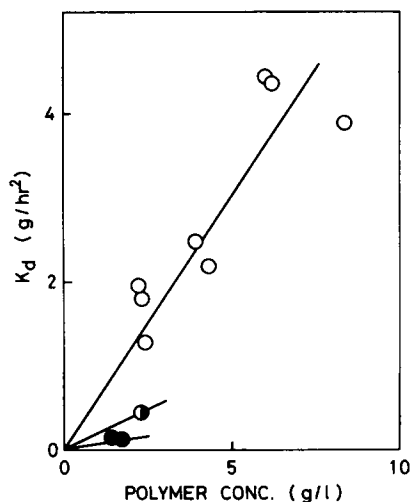
Fig. 9. Rate of polymer deposit (K_d) and polymer concentration at various pressures of 400 kg/cm^2 (O), 325 kg/cm^2 (◑), and 225 kg/cm^2 (●), and at 30°C.

Mechanism of Polymer Deposit

Stickiness of polymer is the primary cause of polymer deposit. Volatile hydrocarbons collected from the powder polyethylene were C_4 and C_{10} oligomers. The stickiness of polymer was decreased when the polymer was evacuated at 50°C or heated at 100°C in a flow of high-pressure ethylene. These facts suggest that the stickiness is due to low-molecular-weight oligomers.

The sticky fine polyethylene powder adheres to the reactor surface. The adhered polymer is subjected to irradiation and continues its propagation in high-pressure ethylene. The propagating polymer chains fill the room between the wall and the adhered polymer, and causes the strong adhesion which was not observed without irradiation.

We concluded that the polymer deposit cannot be solved in the bulk process by changing reaction conditions, because most of reaction conditions decreasing the polymer deposit also reduce the polymer yield.

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