

## Effect of Fluid Motion on Radiation-Induced Polymerization of Ethylene in a Tubular Reactor

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### Synopsis

The influence of the turbulence of reactant on the radiation-induced polymerization of ethylene in 40 mole-% Freon-114 ( $C_2Cl_2F_4$ ) was studied using a tubular reactor at 400 kg/cm<sup>2</sup> and 25°C with a dose rate of  $1.3 \times 10^5$  rad/hr. At constant linear velocity and tube diameter, the polymer concentration was shown to increase linearly with the reactor tube length. This indicates that the polymerization is in a stationary state. By changing the linear velocity from 3.5 to 42.7 cm/sec and the tube diameter from 5 to 14 mm, the space time yield and the molecular weight of polymer were found to vary between 0.21 and 0.46 mole ethylene/l.-hr and from  $5.0 \times 10^3$  to  $10.5 \times 10^3$ , respectively. The space time yield and molecular weight decreased sharply to about one half those in the static polymerization with increasing fluid turbulence and then slowly increased in the highly turbulent state. Similar effects were observed in a tank reactor when the stirring speed was changed.

### INTRODUCTION

The first communication<sup>1</sup> pointed out the novel effects of agitation during radiation-induced bulk polymerization of ethylene in a stirred tank reactor. It was found that the sharp decrease in polymerization rate and polymer molecular weight was brought about by the agitation.

It is interesting to investigate the effects of fluid turbulence in a tubular reactor in connection with the agitation effects in the tank reactor. However, the continuous operation of bulk polymerization in a tubular reactor has been found difficult because the polymer sticks to the reactor wall.<sup>2</sup> To solve this problem, several solvents have been investigated,<sup>3-5</sup> and Hagiwara and co-workers<sup>6</sup> found that 1,2-dichlorotetrafluoroethane (Freon-114) was an excellent solvent because of its acceleration effect in the polymerization and its simple separation from polyethylene. In addition, no polymer deposit was found on the reactor wall. These observations indicate the possibility of continuous polymerization of ethylene in the tubular reactor by using Freon-114.

It is the purpose of the present communication to report the effects of fluid motion on the radiation polymerization of ethylene in a tubular reactor in the presence of Freon-114.

### EXPERIMENTAL

Figure 1 shows a schematic diagram of the experimental apparatus. Feeding and recycling pumps of the reactant were of the plunger type, and flow rate could be varied from 40 to 600 ml/min. The tubular reactor was composed of several vertical tubes. Diameters of the tubes were 5, 10, and 14 mm. The reactor volume was varied from 90 to 700 ml by changing tube length and diameter. The polymer separator was equipped with a sintered metal filter of 5-micron pores. All the apparatus and pipelines were made of stainless steel (SUS-27). Several experiments were carried out in a stainless steel cylindrical tank reactor equipped with a magnetically driven agitator.

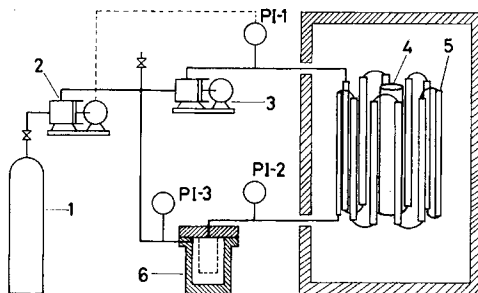


Fig. 1. Schematic diagram of experimental apparatus: (1) cylinder for ethylene-Freon mixture; (2) feeding pump; (3) recycling pump; (4)  $^{60}\text{Co}$  source; (5) tubular reactor; (6) polymer separator; (PI) pressure indicator.

The radiation source was 100,000 Ci of cobalt-60. Sixty cobalt pencils were arranged as a cylindrical bird cage.

The entire system was first swept out four times with 20 kg/cm<sup>2</sup> of ethylene. The solution of ethylene in Freon-114 was charged to the reactor and compressed to the reaction pressure by the feeding pump. Circulation of the solution was then started by the recycling pump. After a stationary flow was attained, polymerization reaction was started by bringing the source into the center of the reactor tubes. The reaction pressure was maintained constant by continuous addition of the solution. The concentration of ethylene in the reactor was slightly changed during the operation with the consumption of ethylene; the change was less than 3%. Polyethylene was formed as a suspension in the Freon-ethylene mixture and was transferred to the separator, where the polymer was separated from the solution. The polymer was removed from the separator and was dried and weighed.

The ethylene was polymerization grade and contained 5 ppm oxygen and 10 ppm acetylene but was free from carbon monoxide and hydrogen sulfide. The Freon-114 was commercial grade, and its oxygen content was less than 10 ppm; other impurities were not analyzed.

Approximately 30 kg of the mixture of Freon and ethylene was prepared in a high-pressure cylinder, and its composition was determined by gas chromatography. Concentration of ethylene was 58%–62%. Less than 1.5 kg of the mixture was used for one experiment. When about one third of the mixture in the cylinder was consumed, it was made up by the addition of ethylene and Freon, and the composition was again analyzed. Since the density of the mixture or solution is approximately the same as the polymer density (0.94 g/ml), the polymer suspension was stable, and the polymer was carried rather smoothly.

The molecular weight of polymer was determined from osmotic pressure measurements of tetralin solution at 110°C by using a Mechrolab high-speed membrane osmometer, Model 502.

## RESULTS AND DISCUSSION

### Effects of Flow Rate in Tubular Reactor

The results are summarized in Tables I and II. The space time yield of the polymer was found to vary from 0.21 to 0.46 mole ethylene/l.-hr., if the linear velocity was changed from 3.5 to 42.7 cm/sec and the tube diameter from 5 to 14 mm.

If the operation time is much longer than the residence time of the solution in the reactor, polymer yield and space time polymer yield are given by eqs. (1) and (2), respectively:

$$W = F \cdot M_p \cdot t \quad (1)$$

$$X = W/V \cdot t \quad (2)$$

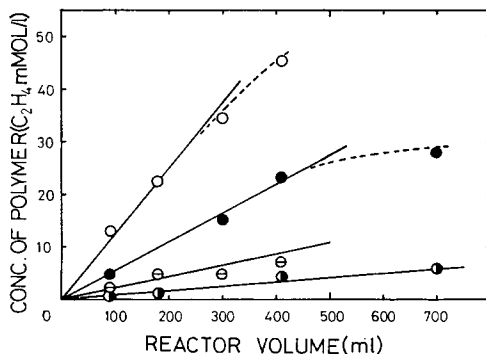


Fig. 2. Concentration of polymer at exit as a function of reactor volume at various flow rates. Tube diameter, 5 mm; linear velocity: (O) 3.5 cm/sec; (●) 6.2 cm/sec; (⊖) 14.1 cm/sec; (⊙) 42.4 cm/sec.

TABLE I  
Radiation-Induced Polymerization of Ethylene in the Presence  
of Freon-114 in a Tubular Reactor<sup>a</sup>

Tube diam., mm	Reactor volume, ml	Flow rate, ml/min	Linear velocity, cm/sec	Residence time, min	Polymer yield, g	Polymer concentration, mole ethylene/l.	Mol wt of polymer $\bar{M}_n \times 10^{-3}$
5	300	0	0	60	3.86	46.0	10.5
5	90	41.0	3.5	2.2	1.79	13.0	6.1
	180			4.4	3.10	22.5	—
	300			7.3	4.75	34.5	—
	460			11.2	6.23	45.2	5.8
5	90	72.7	6.2	1.2	1.20	4.9	—
	300			7.3	3.70	1.5	5.4
	460			6.3	5.72	2.3	5.4
	700			9.6	6.84	2.8	—
5	90	165	14.1	0.6	1.25	2.3	5.1
	180			1.2	2.63	4.7	—
	300			2.0	2.70	4.9	5.0
	460			3.0	4.00	7.2	4.9
	90	503	42.4	0.2	0.98	5.8	—
5	180			0.4	2.00	1.3	—
	460			0.9	7.45	4.4	5.8
	700			1.4	8.60	5.1	—
10	102	164	3.5	0.6	1.52	2.8	—
	306			1.9	3.82	6.9	—
10	102	291	6.2	0.4	1.59	1.6	—
	205			0.7	2.54	2.6	—
	306			1.1	3.24	3.3	—
14	163	323	3.5	0.5	2.11	1.9	—
	325			1.0	3.88	3.6	—
	489			1.5	5.10	4.7	—
14	163	554	6.0	0.3	2.30	1.3	—
	325			0.6	4.79	2.6	—

<sup>a</sup> Reaction pressure, 400 kg/cm<sup>2</sup>; temperature, 25°C; dose rate,  $1.3 \times 10^4$  rad/hr; operation time; 2 hr; and Freon-114, 40 mole-%.

where  $W$  = polymer yield, in moles ethylene;  $M_p$  = concentration of polymer at the outlet of the reactor, moles ethylene/l. of solution;  $F$  = flow rate of the solution in the reactor at operation pressure and temperature, in l./hr;  $t$  = operation time, in hr;  $X$  = space time yield, in moles ethylene/l. of reactor-hr; and  $V$  = reactor volume, in liters. From eqs. (1) and (2), the following equation is derived:

$$M_p = (X/F) \cdot V \quad (3)$$

According to eq. (3), the polymer concentration was plotted in Figure 2 against the reactor volume at different flow rates in the reactor having a 5-mm diameter. The same plots were made in Figures 3 and 4 for the results of the reactors with diameters of 10 and 14 mm, respectively. The

TABLE II  
Effects of Flow Rate on Space Time Yield and Molecular Weight  
of Polymer in a Tubular Reactor with Various Diameters<sup>a</sup>

Tube diam. $D$ , cm	Linear velocity $u$ , cm/sec	$uD$ , cm <sup>2</sup> /sec	Space time yield $X$ , mole ethylene/l.-hr	Mol wt of polymer $\bar{M}_n \times 10^{-3}$	$\epsilon_X$	$\epsilon \bar{M}_n$
0.5	0	0	0.46	10.5	1.0	1.0
0.5	3.5	1.75	0.31	6.0	0.67	0.58
	6.2	3.10	0.24	5.4	0.51	0.52
	14.1	7.05	0.21	5.0	0.47	0.48
	42.4	21.20	0.26	5.8	0.56	0.56
1.0	3.5	3.50	0.27	—	0.58	—
	6.2	6.20	0.22	—	0.47	—
1.4	3.5	4.95	0.22	—	0.48	—
	6.0	8.40	0.26	—	0.56	—

<sup>a</sup> These values were calculated from data in Table I.

fact that the plots give straight lines indicates that the polymerization rate is independent of the residence time. In addition, as indicated in Table I, the polymer molecular weight does not vary with the change in reactor volume. The polymerization is, therefore, considered to be in a stationary state. This is consistent with the results of the static polymerization in a tank reactor reported by Suganuma et al.<sup>7</sup> They pointed out that the polymerization was in a nonstationary state when the concentration of Freon-114 was low, and that it changed to stationary polymerization as the Freon concentration increased to 40%.

In case of very low linear velocity, the plots deviate from the line in the range of extended operation time. This may be caused by the change in conveying condition induced by partial segregation of polymer particles.

The space time yields calculated by multiplying the slope of the lines in Figures 2, 3, and 4 are listed in Table II at different flow rates and tube di-

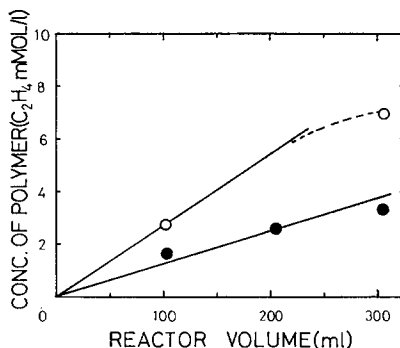


Fig. 3. Concentration of polymer at exit as a function of reactor volume. Tube diameter, 10 mm; linear velocity: (○) 3.5 cm/sec; (●) 6.2 cm/sec.

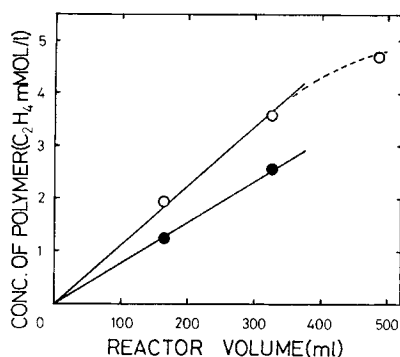


Fig. 4. Concentration of polymer at exit as a function of reactor volume. Tube diameter, 14 mm; linear velocity: (O) 3.5 cm/sec; (●) 6.0 cm/sec.

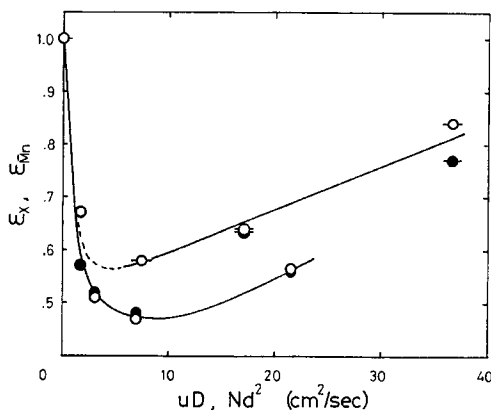


Fig. 5. Effects of fluid turbulence on polymer yield and molecular weight. Tubular reactor: (O)  $\epsilon_x$ ; (●)  $\epsilon_{\bar{M}_n}$ ; tank reactor: (-O-)  $\epsilon_x$ ; (-●-)  $\epsilon_{\bar{M}_n}$ .

ameters. In order to indicate the effects of flow rate, we use the ratios  $\epsilon_x$  and  $\epsilon_{\bar{M}_n}$ , defined as follows:

$$\epsilon_x = \frac{\text{polymer yield in flow or agitated system}}{\text{polymer yield in static system}}$$

$$\epsilon_{\bar{M}_n} = \frac{\text{mol wt of polymer formed in flow or agitated system}}{\text{mol wt of polymer formed in static system}}$$

The manner of flow in a tube can be expressed as a function of the Reynolds number,  $Re = \rho uD/\mu$ , where  $\rho$  is fluid density,  $\mu$  is fluid viscosity,  $D$  is tube diameter, and  $u$  is linear velocity. Since  $\rho$  and  $\mu$  are constant for these experiments,  $uD$  can be used as a parameter of the flow manner. Accordingly,  $\epsilon_x$  and  $\epsilon_{\bar{M}_n}$  are plotted against  $uD$  in Figure 5. A sharp decrease in the space time yield and polymer molecular weight with increasing  $uD$  can be seen; in the higher range of  $uD$ , they were found to slightly increase from the minimum with increasing  $uD$ . These effects of fluid turbu-

lence are similar to those of agitation in the tank reactor on bulk polymerization.<sup>1</sup>

### Effects of Agitation in Tank Reactor

In order to compare the effects of fluid turbulence in a tubular reactor with the agitation effects in the tank reactor, several experiments were carried out in a 100-ml cylindrical reactor equipped with a magnetically driven agitator. The results, summarized in Table III, indicate that remarkable decreases in polymer yield and molecular weight are brought about by slow agitation and at rapid agitation the yield and molecular weight increase with the agitation speed.

TABLE III  
Effects of Agitation on Polymer Yield and Molecular Weight in Tank Reactor<sup>a</sup>

Stirring speed $N$ , rpm	$Nd^2$ , cm <sup>2</sup> /sec	Polymer yield $W$ , g	Poly- merization rate $X$ , mole C <sub>2</sub> H <sub>4</sub> / l.-hr	Mol wt of polymer $\bar{M}_n \times 10^{-3}$	$\epsilon_X$	$\epsilon_{\bar{M}_n}$
0	0	0.764	0.272	13.4	1.0	1.0
72	7.50	0.439	0.172	—	0.58	—
165	17.19	0.489	0.174	8.6	0.64	0.64
352	36.67	0.640	0.228	10.3	0.84	0.77

<sup>a</sup> Reaction pressure, 400 kg/cm<sup>2</sup>; temperature, 25°C; dose rate,  $0.8 \times 10^5$  rad/hr; reaction time; 1.0 hr; and Freon-114, 40 mole-%; inner diameter of reaction vessel, 3.0 cm, impeller diameter, 2.5 cm.

Since the Reynolds number in a stirred tank is expressed as  $\rho Nd^2/\mu$ , where  $N$  is the stirring speed and  $d$  is the diameter of the impeller,  $Nd^2$  can be a parameter indicating the behavior of flow. In Figure 5,  $\epsilon_X$  and  $\epsilon_{\bar{M}_n}$  are accordingly plotted against  $Nd^2$ . The plots were found to exhibit curves similar to those of the tubular experiments.

### CONCLUSIONS

It is concluded that the polymerization rate and the polymer molecular weight decrease to about one half those during static polymerization when the reaction system is slightly agitated, and increase with the intensity of the turbulence at a higher turbulent state. These characteristic effects were observed in both the tubular reactor and the tank reactor. The fluid motion, or turbulence, caused by the flow in the tubular reactor is considered to have the same effects on the polymerization as the agitation in the tank reactor.

Since the polymer molecular weight is affected by the turbulence to the same degree as is the polymer yield, the number of polymer chains (calculated by dividing polymer yield by number-average molecular weight) is independent of the turbulence. This seems to indicate that the turbulence

influences primarily chain propagation and termination. It is hard to explain the mechanism of the novel effect of agitation or turbulence, since it contrasts with the more common effects of increasing reaction rate by increased diffusion of the reactants.

In the Freon-ethylene mixture, the polymer precipitates as a solid when it grows to a certain chain length. After the solidification of the polymer, propagation takes place in the heterogeneous phase. In bulk polymerization,<sup>8</sup> the morphology of polymer as polymerized in a static system is quite different from that of polymer formed in the agitated system. The polymer has also been found to have a very large specific surface area,<sup>9,10</sup> and is affected by the agitation speed.<sup>11</sup> Under these circumstances, complex effects of agitation might be expected on monomer diffusion and the mobility of polymer chains, which may influence overall polymerization.

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