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PROGRESS REPORT ON THE ETHYLENE POLYMERIZATION FLOW EXPERIMENT
AT BROOKHAVEN NATIONAL LABORATORY*

MASTER

by

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In March 1965, an industry-wide meeting was held at Brookhaven National Laboratory on the Radiation-Induced Polymerization and Copolymerization of Ethylene. At this meeting, all of the work on the Co^{60} gamma-radiation-induced polymerization of ethylene which had been performed at Brookhaven in capsule experiments was reviewed. Evaluation of this information indicated that at temperatures above the polyethylene melting point and above 680 atm, the polymerization rates and product characteristics could lead to a commercially competitive process. The concensus of the meeting was that a small-scale flow experiment which was then in the planning stage at Brookhaven should be performed for the purpose of confirming the kinetic data obtained in the capsule experiments and to produce sufficient quantities of polymer (up to approximately 1 lb/batch) for distribution to the industry. An informal

committee was established during the meeting for the purpose of evaluating the characteristics of the polyethylene produced in the flow system. Since this meeting, an irradiation facility has been constructed, the small-scale experiment has been installed, and the operation has started. The purpose of this report is to describe the system, the problems that have been encountered, the results obtained to date, and the current status of the program.

Description of Experiment

The flow experiment, a schematic of which is shown in Figure 1, consists of an ethylene supply, diaphragm-type compressor, flowmeter, preheater, reaction vessel, control valve, and product separator. Interconnecting lines are 9/16 x 3/16 in. and 1/4 x 0.083 in. diameter high pressure tubing. Heating of the components is accomplished electrically. The system is designed to contain pressures up to 2000 atm at 200°C, but experience has shown that the inability to remove the heat of polymerization, limited the maximum operating pressure to approximately 900 atm. The reaction vessel assembly is placed in a pool-type gamma facility similar to that used for the capsule experiments. Radiation intensities up to 5×10^5 rads/hr

can be obtained using a Co^{60} source containing $\sim 10^4$ curies.

Descriptions of the main components are listed below.

1. Ethylene Supply

Cylinders containing 30 lb >99% ethylene are used as a gas supply. A typical analysis of the gas is as follows:

Ethylene, mol %	99.8
Other hydrocarbons, mol %	0.2
Acetylene, ppm, wt.	8
Sulfur, ppm, wt.	3
Carbon monoxide, ppm, wt.	4
Carbon dioxide, ppm, wt.	20
Oxygen, ppm, wt.	20
Water, ppm, wt.	20

All previous capsule experiments were performed using high purity ethylene containing <5 ppm of oxygen. Due to the cost of high purity ethylene, \$1,200/cylinder, it was necessary to use the less pure gas. The earlier capsule experiments had indicated a negligible inhibitory effect of oxygen when present in concentrations <60 ppm. Tests were also made with the above gas to confirm the static rate data.

2. Compressor

A Corblin B4C-2000 diaphragm-type compressor with a 20/1 compression ratio is used. The unit is designed to deliver 200 lbs/hr of ethylene at 2000 atm when the suction pressure is at 680 atm.

3. Reaction Vessel

The reaction vessel used for the initial runs was a Type 316 stainless steel 100 cc volume cylinder, 1 in. i.d. x 3 in. o.d. x 10 in. long. A tapered insert was installed in the cylinder to provide a smooth transition from the vessel to the 3/16 in. i.d. discharge line, thereby reducing the reaction volume to 89 cc. Two thermocouple wells were provided through the wall of the vessel at locations 2 in. from the top and bottom of the vessel.

4. Control Valve

A Worthington Control Company, "Wee Willie" type valve is used to control the reaction vessel pressure. A strain-gauge type pressure transducer, located on the inlet gas line to the reactor, is used as a sensing device. The control valve is located approximately 15 ft away and at an elevation 9 ft above the reaction vessel. This location is necessitated by

the requirement of operating the reaction vessel under 7 ft of water. The product discharge line and control valve are maintained at temperatures varying between 150° and 200°C. The volume of the line is approximately 90 cc.

Results

The system has been operated for six months under a variety of conditions. Approximately 26 runs were made. The range of conditions covered was as follows:

Pressure	565 to 910 atm
Radiation intensity	0.35 to 4.6×10^5 rads/hr
Temperature	120 to 200°C
Conversion	1 to 7%

In order to simplify initial operation, the unreacted monomer was vented to the atmosphere rather than recycled as indicated in Figure 1. Several decompositions have occurred during operation of the experiments. One decomposition resulted in complete plugging of the reaction vessel and discharge line with carbon, and necessitated the replacement of these components. All other decompositions resulted in the formation of a blackish material which could be flushed from the system by continued operation. On September 22, a decomposition occurred

while attempting to clean out the system after an earlier decomposition. The conditions at the time were 1400 atm pressure, 200°C, with no radiation field present. It is possible that the presence of particulate carbon from the previous decomposition sensitized the reaction. The decomposition resulted in the failure of a rupture disc which necessitated the disassembly of the system.

It became apparent that with the geometry imposed by the gamma pool and the small size of the reaction vessel that it is very difficult to reach a steady state condition. This is illustrated by the data from an experiment as shown in Figure 2. A possible explanation of this erratic behavior is the hold-up of polymer in the long discharge line resulting in fluctuations of pressure, gas flow, and polymer liquid level in the vessel. A momentary decrease in gas flow could then cause a rapid increase in local vessel temperature which leads to a decomposition.

The effects of pressure and radiation intensity on the polymerization rate are shown in Figures 3 and 4. Due to the non-steady state type of operation, the polymerization rates plotted are average values based on the entire operating time

for the experiment, ~ 7 hr, and a reaction volume of 89 cc. At a radiation intensity of 2.59×10^5 rads/hr, the dependence of pressure on rate was found to be $p^{2.4 \pm 0.6}$ over the pressure range of 565 to 890 atm. Earlier capsule experiments indicated a dependence of $p^{2.7 \pm 1.0}$. Since no mechanical stirring devices are used, and monomer injection is only at the head end of the vessel, the fluid temperature increases markedly along the vessel length. An average of the two thermocouple readings was assumed for the reaction temperature in correlating the polymerization rates. For this average temperature, the rate predicted by an equation derived from capsule data has been plotted on Figure 3. It should be pointed out that the rates in the flow experiment are calculated on the basis of the entire vessel volume (89 cc) not taking into account polymer buildup. This gives a lower rate value than that predicted by the capsule rate equation which is based on the volume of unconverted gas in the reaction vessel.

The effect of radiation intensity on rate is shown in Figure 4. At a pressure of 900 atm, and the intensity range of 3.5×10^4 to 4.6×10^5 rads/hr, a dependence of $I^{0.46}$ was observed. A similar effect was found at a pressure of 835 atm. The capsule experiments indicated a dependence of $I^{0.48}$.

Product Characteristics

The polymers produced over the entire range of experimental conditions differed in characteristics from that which would have been predicted from the earlier capsule experiments. Whereas the capsule experiments produced polymers that were completely soluble in Decalin at 135°C, the polymers produced in the flow system under many of the conditions mentioned above had a zero melt index as measured on the Micromelt Indexer. The polymers produced also had an insoluble portion ranging up to 70%. In some experiments, the melt index of material formed towards the beginning of a run had a high value. As the run proceeded, the melt index decreased to zero. A similar effect was noted with the solubility. The data for experiment 21 are shown in Figure 2. In one experiment the entire yield of polymer was found to be soluble while the melt index started at 100 and decreased to 1.2. The conditions for this experiment were pressure 816 atm, radiation intensity 4.6×10^5 rads/hr, percent conversion 7%, and average reaction temperature 170°C.

There are three apparent differences between the capsule and flow experiments. These are as follows: (1) Ethylene gas purity, (2) Holdup in the discharge line and vessel which

could cause recirculation of product in the vessel and excessive radiation doses to part of the polymer resulting in crosslinking and (3) The product discharge line acting as a tubular reactor to produce a material with a broad molecular weight distribution with a very high molecular weight fraction.

In an attempt to determine the reason for the insoluble material, a series of experiments were carried out statically both in capsule-type vessels and in the flow equipment. The capsule experiments were conducted using ethylene of the same purity as that used in the flow system. Conditions for the experiments were 680 atm, 1.78×10^5 rads/hr, and 200°C . The results indicated that up to a total radiation dose of 7.5×10^5 rads, all polymers were completely soluble and had a melt index >100 . Polymer produced at the same pressure, temperature, and radiation intensity and at a total dose of 5×10^5 rads, which was held at 200°C for 4 hr under an ethylene pressure of 680 atm to simulate a post irradiation effect equivalent to the long line, was also completely soluble and had a melt index >100 .

In the series of experiments performed with the flow system under static conditions, the experimental procedure was to

pressurize the system with the control valve closed, irradiate the gas for a known period of time, remove the Co^{60} source, and then discharge the polymer through the control valve. Samples were taken of the material discharged initially and of the final material. Experiments were carried out at conditions similar to those for the capsule and flow experiments. For a total dose of 4.6×10^5 rads, the material discharged initially exhibited a melt index of >100 and was completely soluble. Material discharged at the end had a melt index of 0 and was 89% soluble. A radiation dose of 9.2×10^5 rads indicated a melt index of 27 with complete solubility for initial material, and 0 melt index with 58% solubility for final material. Experiments at the same conditions in the flow system produced soluble, high melt index, $>30 <100$, material for the initial period of 3 hours after which the solubility decreased to 86% after 4 hr and to 74% after 6 hr. These data are shown in Figure 2.

The results from these experiments would seem to indicate that the difference in gas purity is not contributing to the insolubility of the product. Radiation-induced crosslinking would seem to be a possible cause although flow experiments in which the radiation dose for the entire experiment was

$<5 \times 10^5$ rads resulted in polymer with 30% solubility. It is still questionable whether the product discharge line is acting as a tubular reactor and partially producing a material which is of very high molecular weight and thus insoluble. The experimental evidence that material formed in capsules is completely soluble while material formed in the flow equipment under similar conditions of P, T, and I, and without a gas flow was partially insoluble tends to support this view. However, there is conflicting evidence in that post irradiation heating of material formed in a capsule for a period greater than the holdup time in the discharge line did not affect the solubility. It also seems unlikely that material with a molecular weight $>2 \times 10^6$ could be formed at temperatures of 150° to 200°C . Furthermore, earlier work has also indicated the complete solubility of material up to this molecular weight.

Batches of polymer weighing between 100 and 400 g have been made in each of these flow experiments. This material is not being distributed to the informal industrial committee for evaluation because of the high variability of the characteristics and the production conditions. It is anticipated that with the redesign of the system, polymer will be obtained

under steady state conditions. The material obtained under these improved conditions will be available for distribution.

Improvements and Modifications to Flow System

The experiment has been shut down as a result of a decomposition which resulted in the failure of a rupture disc. The probable cause of the decompositions is the interruption of gas coolant flow due to blocking of the long product discharge line with polymer.

It is planned to replace the 100 cc volume reaction vessel with a 420 cc vessel similar to that used for the "fall-through" type capsule experiments. The lower portion of the reaction vessel will be shielded in order to prevent any post-irradiation of the polymer which may be held up in the lower portion of the vessel due to the long discharge line. Cooling of the reaction vessel will be accomplished by circulating gas upward and countercurrent to the downward flow of polymer. The lower part of the vessel would then separate molten polymer from gaseous monomer thereby providing a clear path for the coolant which cannot be blocked by polymer as is the case with the present setup. A small amount of gas will be maintained in the product discharge line due to the solubility of ethylene in the polymer at these conditions. The upper

part of the vessel is acting as the polymerizer while the bottom part of the vessel is acting as a polymer-gaseous monomer separator. A schematic of the reaction vessel assembly is given in Figure 5. The modifications to the system are presently being made with completion scheduled for November. In the event that these modifications do not solve the problems, the experiment will be transferred to a dry-type gamma cell which is presently under construction. Operation in the cell will permit the elimination of the long discharge line and the installation of the control valve directly coupled to and beneath the reaction vessel. Adequate room to permit consideration of the use of heat transfer fluids to control vessel and line temperatures in place of electrical heating will also be available.

It should be noted that the only other reported flow-type experiment being conducted on the radiation-induced polymerization of ethylene is at Takasaki Radiation Chemistry Research Establishment near Tokai-Nura in Japan. Reaction vessel sizes up to 10 liters are being used. However, the process conditions for synthesis of polymer are temperatures below the melting point, $<120^{\circ}\text{C}$, and at pressures up to 400 atm. Under these conditions, solid polymer precipitates directly from the

gas phase at a relatively low rate compared to that obtained at the high temperatures and pressures used in this study. Furthermore, from the capsule studies the polymer formed at the lower temperatures was found to have an intermediate density and low melt index compared to the commercially desirable low density, and high melt index material formed at the higher temperature conditions.

RADIATION POLYMERIZATION OF ETHYLENE

FIGURE 1

RADIATION INDUCED POLYMERIZATION OF ETHYLENE FLOW EXPERIMENT

FIG. 2

RADIATION INDUCED POLYMERIZATION OF ETHYLENE
FLOW EXPERIMENT
POLYMERIZATION RATE vs PRESSURE

FIG. 3

RADIATION INDUCED POLYMERIZATION OF ETHYLENE
FLOW EXPERIMENT
POLYMERIZATION RATE vs INTENSITY

FIG. 4

SCHEMATIC OF REVISIONS TO ETHYLENE FLOW EXPERIMENT

FIG. 5