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THE PRODUCTION OF POLYETHYLENE AND RELATED COMPOUNDS
BY RADIATION AT THE BROOKHAVEN NATIONAL LABORATORY*

MASTER

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INTRODUCTION

I would like to state at the outset, that I am not an "expert" in the topic of this talk, but that I am acting in the capacity of an "agent" for those people at Brookhaven on whose work I shall report. My ability, therefore, to answer very detailed questions may prove to be quite limited.

My approach to the subject will be along the following lines. Firstly, I would like to outline for you the underlying philosophy of this investigation, covering such questions as "What interest does a National Laboratory have in a process such as this?", "Why choose polyethylene production?", "Where does this investigation stand, and what are the future plans?" Secondly, I would like to present the data--in a much condensed form--that has been obtained as a result of this study. Thirdly, I will indicate some of the interesting copolymers with ethylene that have been formed. Finally, I would like to very briefly outline the current thinking at Brookhaven regarding the economics of a plant constructed to produce polyethylene and using ⁶⁰Co as the source of energy for initiating the reaction.

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PHILOSOPHY

According to the provisions of the United States Atomic Energy Act of 1954, the National Laboratories are, among many other things, given the responsibility of performing research and development aimed towards promoting the use of nuclear energy for practical purposes. Among many practical end purposes which one could envision is the synthesis and production of useful chemicals.

For many years, now, radiation has been known to be an initiator for vinyl polymerizations. Various people have pointed out the advantages of using radiation in this fashion. In the first place, conventional vinyl polymerizations generally employ a chemical initiator, fragments of which are either chemically united to or occluded by the polymer which is formed. Initiation by radiation does not introduce any "foreign" material into the polymer. This may be an advantage in certain applications.

Secondly, the temperature coefficients for many chemically initiated vinyl polymerizations are such that the rate of the overall process is slow at room temperature, and to achieve higher rates, the temperature must be raised. This is generally accompanied by a corresponding decrease in the average molecular weight of the polymer. With radiation, initiation can be conveniently accomplished even at room temperature. However, what is more appealing is that, if the temperature is raised, not only does the rate increase, but

also the average molecular weight.

Thirdly, it is sometimes difficult to establish a truly homogeneous distribution of the chemical initiator through the reaction medium. The achievement of a homogeneous rate of initiation by radiation can be much more readily accomplished.

For these, and several other reasons, it has long been pointed out that radiation initiated polymerization might have certain advantages to offer over more conventional means of initiation. There have been, however, several stumbling blocks to overcome, not the least of which has been the important question of economics.

Two viewpoints have been proposed. It has been held that radiation initiated processes, in general, would stand a chance of being competitive if the end product were a low total volume but intrinsically expensive item, so that any additional cost incurred by employing radiation would be representative of a very small fractional increase in production cost. Alternatively, it has been argued that another successful approach would be to find an inexpensive but high total volume product which could be produced by radiation. It is this latter approach that played an important role in selecting polyethylene as the product for the investigation presently under discussion.

At the present, the total production of polyethylene, in the United States, is of the order of one and one-half million tons a year, and is increasing at the rate of about 8% per year.

The raw material is inexpensive and in plentiful supply, and present estimates indicate that both these situations should continue.

Preliminary capsule type experiments indicated that fairly high rates of reaction could be attained at nominal temperatures and pressures using ^{60}Co gamma rays. More intensive and extensive investigation has revealed that the properties of the polymers are of commercial interest and it appears that the cost of producing polyethylene by such a process on an industrial scale should be quite competitive with that encountered in conventional high pressure plants.

THE BROOKHAVEN PROGRAM

Static Experiments

Data obtained from capsule (batch) experiments have established the following relationships between the rate of polymerization, Q , in grams per liter per hour, and temperature, T , pressure, P , and dose rate, I , over the two indicated temperature ranges:

$$\underline{20^{\circ}\text{C} < T < 100^{\circ}\text{C}}$$

$$Q = 1.39 \times 10^{-8} e^{-200/RT} P^{2.7} I^{0.5} \quad (\pm 27\%)$$

$$\underline{120^{\circ}\text{C} < T < 200^{\circ}\text{C}}$$

$$Q = 0.32 e^{-14,500/RT} P^{2.7} I^{0.5} \quad (\pm 42\%)$$

The range of pressures and dose rates investigated were

$$170 \text{ atm} < P < 1360 \text{ atm}$$

$$5.8 \times 10^4 \text{ rad/hr} < I < 8.5 \times 10^5 \text{ rad/hr}$$

These data were obtained in a 100 ml volume capsule using high purity ethylene gas (99.9 v/o ethylene, 1000 ppm saturated C_1-C_4 hydrocarbons and <5 ppm oxygen).

It will be noted that below $100^{\circ}C$ (which is also below the crystalline melting point of the polymer) the temperature coefficient for the process is very small. Above $120^{\circ}C$, the system exhibits a much higher temperature coefficient. This is felt to be partially due to the greater solubility of the monomer in the molten polymer.

Table I is a very brief recapitulation of some of the properties of the polymers which are formed by this process. Two types of capsule experiments were performed. In the first type, the entire volume of the capsule was in the radiation field, hence any polymer which is formed is, after formation, exposed to the radiation field. These are referred to in Table I as "Static Capsule". The second set of experiments utilized a capsule so constructed that much, if not all, of the polymer fell into a shielded well at the bottom, and was thus removed from the radiation field. These experiments are called "Fall-through Capsule" data in Table I.

It is apparent from these data that polymers having a fairly wide range of properties, all within the commercially interesting range, can be made in this process. For a much more detailed description of the variation of these properties with temperature, pressure and dose rate, I refer you to the first reference in the

Some Properties of Radiation Produced Polyethylene

Property	Static Capsule		Fall-through Capsule	
	Pressure (at ~26°C)	Temperature 26° - 120°C (Initial pressure 8 x 10 ³ psi)	Pressure (at 200°C)	Temperature (20° - 200°C) (at 10 ⁴ psi)
Density (density gradient column @23°C)	0.940 (2 - 26 x 10 ³ psi)	0.940 - 0.907	0.906 - 0.915 (5 - 14 x 10 ³ psi)	0.940 - 0.913
Crystalline Melting Point (DSC @ 10°C/min)	126° - 134° (2 - 26 x 10 ³ psi)	126° - 96°	105° - 109° (5 - 14 x 10 ³ psi)	128° - 108°
Methyl Groups/100 C		0.7 - 6.1		0.7 - 3.2
Melt Index (ASTM D 1238 - 62 T, E)	<0.01 - <0.001 (2.5 - 10 x 10 ³ psi)		100 - 0.20 (7.5 - 15 x 10 ³ psi)	~0 (20 - 130°C) 2 - 31 (150° - 200°C)
$\bar{M}_w / \bar{M}_n$		6 - 2.5	2.8 - 3.6 (10 - 14 x 10 ³ psi)	16.9 (26°C) 3.0 - 2.8 (150° - 200°C)
$\bar{M}_w$ (GPC chlorobenzene @130°C)	4 - 42 x 10 ⁴ (2.5 - 10 x 10 ³ psi)	21 - 17 x 10 ⁴	4.5 - 12 x 10 ⁴ (10 - 14 x 10 ³ psi)	44.5 x 10 ⁴ (26°C) 7.5 - 4.5 x 10 ⁴ (150° - 200°C)

Table I

general bibliography.

Flow Experiments

From the previous data on rates and polymer properties, it is apparent that additional data, preferably on a larger scale and in a flow-type system, is needed for a fuller evaluation of the whole process and its products. A flow experiment has been designed and is shown schematically in Figure 1.

This system is designed to produce polymer at the rate of 150 grams per hour at 200°C and a pressure of 680 atm. The operating temperature was chosen above the melting point of polyethylene for several reasons, among which are high rates and ease of handling the product in the molten state as opposed to a powdery product. Several preliminary runs have been made with this system, and the rate data appear to agree quite well with that obtained in the capsule experiments.

Copolymers with Ethylene

In addition to studying the radiation induced homopolymerization of ethylene, the copolymerization of ethylene and other "monomers" has also been cursorily looked at. These experiments have been done initially at 20°C and an initial pressure of 680 atmospheres. Since ethylene is a gas under these conditions, while most of the monomers investigated are liquids, the reacting system is heterogeneous, and the product formed is not homogeneous. However, in most cases studied a copolymer has been formed.

Radiation Induced Polymerization of Ethylene Flow Experiment

MAXIMUM OPERATING CONDITIONS

$P = 2000 \text{ atm}$

$T = 230^\circ \text{C}$

$I = \sim 2 \times 10^6 \text{ Rads/hr.}$

REACTOR

$V = 0.1 \text{ Liter}$

at $P = 680 \text{ atm}$

$I = 3 \times 10^5 \text{ Rads/hr}$

$T = 200^\circ \text{C}$

$Q = 150 \text{ g/hr}$

Figure 1

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Table II is a list of monomers which have been successfully copolymerized with ethylene under the conditions given above.

TABLE II

Monomers Copolymerized with Ethylene by Radiation

Styrene	Carbon monoxide
Methy methacrylate	Vinyl pyrrolidone
Vinyl acetate	Methyl vinyl ketone
Acrylonitrile	Propylene
Chlorotrifluroethylene	2-Butene (cis and trans)
Methyl acrylate	1-Butene
Vinyl Chloride	Isoprene

The copolymer between ethylene and carbon monoxide is a very interesting one, and is being extensively studied. A description of the process and some of the properties of the product can be found in references 2, 3 and 4.

Also, the ethylene-chlorotrifluroethylene mixture exhibits some strange characteristics as a reaction medium. Certain ratios of co-monomer feed and radiation intensities lead to explosive decompositions. This has been reported in reference 5.

Present Status and Future Plans

From the brief description given here it appears reasonable to state that a feasible chemical process for the conversion of ethylene to polyethylene by radiation has been demonstrated, at least as far as the capsule experiments have gone. The rates of

formation are interestingly high and the properties that have been measured indicate materials of commercial grade.

At this point, then, it becomes of interest to make some estimate of the economics of a large-scale industrial plant based on an irradiation process. Such estimates, of course, are always subject to criticism. In the final analysis, the only way to answer critics is to build the plant and operate it. However, based on a fairly critical evaluation of the process parameters, as far as they are presently known, and using the standard engineering techniques of making cost estimates, the current feeling of the Brookhaven people is that an irradiation based plant with an operating capacity of 25,000 tons a year would convert ethylene to polyethylene at 200°C and 2000 atmosphere pressure at a cost of between 1.2 and 1.5 cents a pound, compared with an estimated 1.6 to 1.9 cents a pound for a "conventional" plant operating at the same conditions. The complete analysis that leads to this estimate is contained in reference 6. Lower pressure operation at lower cost may also be possible.

Further experimental data from the newly constructed flow-experiment may cause a re-evaluation of these estimates. Preliminary runs, however, appear to agree with the capsule data on which this estimate is based.

In addition to providing additional kinetic data, the flow experiment is also designed to produce sufficient quantities of material so that pound lots of a given polymer will be available

for fabrication into test samples for evaluating, on a fairly large scale basis with statistical significance, the physical properties of the material from the process. These will include mechanical, electrical and other properties of interest.

This type of evaluation will not be done only at Brookhaven; the proper persons to do it are producers and consumers of polyethylene. There has been formed, from among these people, an informally constituted group of companies which has agreed to evaluate the radiation produced polymer and compare it with that made by more conventional means. Thus, the flow experiments at Brookhaven hopefully will fill the gap between the laboratory stage capsule experiments and a more meaningful pilot plant level investigation of the process.

There are at least two ways that the pilot plant type of investigation can be accomplished. It can be undertaken wholly by an industrial concern, where its complete financial support would be the burden of the company or, perhaps, a co-sponsored industry-government undertaking may be called for, as an intermediate phase.

At the moment there appears to be no patent position established with regard to the radiation polymerization of ethylene in the United States. Present thinking is that as American industry becomes interested and more actively involved in the process, government support and experimental work at Brookhaven will be slowly phased out.

The entire program, then, as supported by the USAEC at Brookhaven has, as its prime objective, the demonstration to American industry of the feasibility of a radiation process for polyethylene production. If and when American industry either definitively rejects the process or adopts it, on the basis of its merits, it shall have been adjudged that the Commission has fulfilled a job which it envisioned, and its support is no longer deemed necessary or desirable in the national interest.

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Since my only connection with the work reported here has been that of a part-time consultant and full-time onlooker, I would like to point out that the work in this area has been done under the leadership of and by the following people: B. Manowitz, M. Steinberg, L. Kukacka, P. Colombo, J. Fontana and supporting staff. A much more complete description of the experimental details, results, etc. can be found in the following list of references.

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