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# CONSERVATION OF ETHYLENE FEEDSTOCK FOR THE COMMODITY POLYMER MARKET THROUGH THE RADIATION INDUCED PRODUCTION OF POLYKETONES AND POLYSULFONES

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## ABSTRACT

Because of the increase in cost of foreign oil, ethylene costs have increased markedly within the last several years. There is presently a sizable incentive to reduce raw material cost for basic polymer manufacture. The polyketones, synthesized from ethylene and CO, and the polysulfones, synthesized from ethylene and $SO_2$, utilizing high energy radiation, offers one such possibility. The process has the additional advantage in that CO and $SO_2$ usually considered as wastes and pollutants from fossil fuel burning power plants are converted to useful materials.

The polyketones and polysulfones formed from the gas phase below 100°C have been found to be high molecular weight polymers which, depending on composition either melt with difficulty,

temperature (> 100°C) catalyst induced reaction produces low molecular weight waxes. Design calculations indicate that for a G value of 10,000 and 50% energy deposition efficiency, it would take 331 megacuries of $Co^{60}$ to conserve 2 billion pounds of ethylene or 25% of the overall U.S. market by substituting CO and $SO_2$. This savings amounts to as much as $280 million at today's market price. Electron machine radiation with a 25% energy deposition efficiency requires a total beam power of 9800 KW. The use of machine radiation is preferred because of safety, availability, and initial investment. The challenge presented by the development of the described substituted polymer systems, depends on (1) the determination of the uniqueness of the radiation process, and confirming the yields with electron machine radiation, (2) the processability and market acceptability of the substituted polymers, and (3) the ability to design an efficient radiation process reactor.

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In the late 1950's and early 1960's a strong effort was made at BNL to apply radiation induced polymerization to the large scale synthesis of such basic polymers as polyethylene.(1) The advantages of the radiation process included (1) elimination of catalyst impurity fractions and the cost of the catalyst, (2) a versatile and inherently safer process operating at lower pressures and temperatures, (3) production of an intermediate density polymer having a high molecular weight and high surface area, (4) capability of production of a variety of polymer grades in one reactor, (5) process control using $Co^{60}$ gamma radiation was much better than for the conventional process (ICI or DuPont Process) and (6) the production cost could be lower. Based upon the work at BNL, several large U.S. chemical manufacturers were reported to have setup pilot plant facilities utilizing $Co^{60}$ gamma radiation sources. The large Japanese laboratory at Takasaki undertook extensive work on piloting various polyethylene processes, mainly utilizing $Co^{60}$ gamma radiation.(2) However, none of these efforts reached commercial-scale operations, probably because either the operating and economic advantages over conventional processes (ICI, DuPont or Ziegler) were not great enough, or the safety problems in handling $Co^{60}$ were too severe. Furthermore, by the late 1960's the U.S. AEC, Division of Isotope Development which supported the basic and applied radiation chemistry work for over 20 years and which led to the development of the process was, eliminated from the government's budget and thus went out of existence. Without the government's interest, even though $Co^{60}$ sources could be obtained commercially, the U.S. industry for the most part also lost interest in its utilization. Towards the end of the program on the development of the basic radiation chemistry, kinetics, and process technology for the radiation polymerization of polyethylene, BNL undertook some basic studies on the copolymerization of ethylene with a variety of monomers.(3) It was shown that indeed radiation induced copolymerization can form copolymers which could not be readily formed by conventional thermal and catalytically induced processes. Two copolymers were especially selected for study in considerable depth. These were the copolymers of ethylene with CO and with $SO_2$. It was shown that at a lower ambient temperature ($< 50^{o}C$) ethylene could be copolymerized with CO(4) to form polyketones over a wide range of compositions (from 0 to 100% CO) and that ethylene could be made to react with $SO_2$(5) forming polysulfones over a wide range of $SO_2$ compositions. Both copolymers formed by radiation induced reactions were white solid polymers which exhibited high molecular weights and which had partially crystalline structures. Up to that time, there was no evidence in the literature that thermal and catalytically induced reactions could produce high molecular weight solid polymers.(6,7) The Et-CO copolymer reportedly formed using benzoyl peroxide catalysts were low molecular weight waxes. This is principally attributed to the fact that the kinetics of copolymerization are such that at elevated temperatures (> 100°C) the rate of the termination reaction is high, thus causing low molecular weight compounds. The radiation induced copolymerization reaction can take place at lower temperatures (< 50°C) and higher pressures (up to 10,000 psi). As a result, high DP (degree of polymerization) material is formed. The copolymer of Et-CO containing 40% CO, formed by $Co^{60}$ radiation, was stable up to about 250°C and tended to be refractory, in that the melt indexes were high and the material tended not to soften until thermal decomposition was induced above 250°C. The decomposition products contained carbon and methane. Depending on the CO content, Et-CO copolymers could be molded into film. However, generally the molding conditions were difficult and the films formed tended to be brittle. In the case of the Et-$SO_2$ copolymers, the material was stable to a somewhat higher temperature of up to 350°C. Above this temperature, the copolymer unzipped itself reforming $SO_2$ and ethylene. In both cases the chemistry and kinetics of the copolymerization reactions were exceedingsly interesting. It was also found that in the 1930's and 1940's one of the large chemical manufacturers had spent a considerable effort in attempting to copolymerize ethylene and other olefins with $SO_2$ and found that they could not form high DP material with Et and $SO_2$ using thermocatalytic techniques. High copolymers could be formed from the higher olefinic homologues, such as propylene, butylene and others. The project was dropped never to be undertaken by the same management again because of the large financial research burden incurred.

One of the reasons for selecting CO and $SO_2$ by BNL for an in-depth investigation was the potential in further reduction of low-cost polymers. For example, in the 1950's and 1960's the cost of ethylene for the manufacture of polyethylene was as low as 2¢/lb and polyethylene production cost was known to be in the range of 8¢ to 10¢/lb. If up to 50% CO or $SO_2$ could have been introduced into the large polymer market at that time, a reduction of 50% in raw material cost amounting to a savings of about 1¢/lb of polymer could have been realized. The cost of CO and $SO_2$ is practically zero because usually it is a waste or byproduct.

from coal burning plants and other chemical operations. This may not appear like a large reduction but even at that time, a 10% savings in cost was indeed significant. However, no further development work was undertaken by industry. It is possible that the manufacturers may have feared that the radiation process was complex, especially when considering the handling of radiation sources and that this would have more than offset the 1¢/lb or 10% savings. Today, however, the story is quite different. Since the advent of the energy crisis, the cost of chemical feedstock has skyrocketted and ethylene now costs as much as 14¢/lb (7 times, tied to the almost same proportionate increase in the cost of a barrel of oil) and polyethylene manufacturing cost is about 25¢/lb today. Now if one introduces·low cost CO or $SO_2$ to the extent of 50% into a commodity polymer such as polyethylene, thus reducing ethylene requirements, the cost savings would be at least 7¢/lb or 30% of the manufacturing cost, a savings highly worthwhile pursuing. Not only is the cost savings argument potent, but with polyethylene reaching the 8 billion pound market savings of 4 billion pounds of ethylene could conserve annually as much as 13 million barrels of oil or 54 billion cu. ft. of natural gas and would, furthermore, put to use waste products such as CO and especially $SO_2$ to the tune of 2 millions tons annually, an amount readily available from environmentally controlled coal burning power plants. The annual dollar savings would be $280 million per year, let alone the reduction in the cost of waste disposal. The incentives under present conditions for pursuing the ethylene copolymerization with CO and $SO_2$ appears to be rather strong indeed.

Certain items will have to be proven out first before a large effort can be undertaken for development of these materials. First, although a number of physical and chemical properties of the copolymers were measured, it was never shown satisfactorily that the materials could be molded into usable forms. As mentioned, both copolymers exhibited refractory properties and did not soften easily before decomposition, which is more characteristic of thermosetting polymers. It is believed that with modern plastic molding techniques, either rotational molding, or using high pressure and temperature molding machinery and incorporating plasticizers, the molding or forming problem can be solved. However, enough material must be made available to demonstrate the workability, processability, and marketability of the polymers. Pilot plant operations producing about 100 lb/day of the material for product acceptance is needed. Secondly, it has not been shown, unequivocally, that a nonradiation process could be used to form high DP products especially with the availability of low temperature free radical (Azo type) catalysts. Thirdly, assuming that the radiation polymerization is indeed unique in this respect, what is the availability and, most important, restrictive controls imposed by government agencies in handling radiation sources such as $Co^{60}$ with a half life or 5.3 years? Could machine radiation sources be applied to these high pressure systems, especially with their inherent operational safety advantages over isotopic sources in that machines are capable of being turned off when not in use?

As a first approximation, Table 1 lists an estimate of the $Co^{60}$ source requirements and the power for electron or x-ray radiation machines needed to generate $4 \times 10^9$ pounds of polyethylene equivalent to polyketones or polysulfones representing about 50% of the total production of all polyethylene polymer produced in the U.S. in 1974.

On first sight, it appears that $Co^{60}$ gamma source or other isotopic source requirement may be too high (331 megacuries) for the entire country's production. It is understood that there are limited quantities of about 10 megacuries stored in the Savannah River Laboratory (SRL). Cs-137 or burned fuel elements might be used, but there is always an inventory charge for the U and Pu contained in these elements and there is also difficulty inserting them into chemical reactors of the desired geometrical configuration. At present, the policy of ERDA is to attempt to find a permanent long-term solution for radioactive waste disposal instead of dispersing

## Table 1

## ESTIMATE OF RADIATION POWER REQUIREMENTS FOR PRODUCING POLYKETONE OR POLYSULFONE

1. Production rate = $4 \times 10^9$ lb/yr

$$= \frac{4 \times 10^9}{300 \times 24} = 5.56 \times 10^5 \text{ lb/hr}$$

2. Radiation condition: -

Pressure = 2000 to 10,000 psi

Temp. = 25-50°C

3. Radiation yield:-

G value = 10,000 molecules/100 eV

Dose requirement = 6.85 megarads

4. Power levels:-

a) $Co^{60}$ gamma = 331 megacuries

for 50% energy deposition eff. (assuming internal source)

b) Beta or x-ray = 9800 KW

for 25% energy deposition eff. (assuming beam external to reactor) by utilization in various and sundry production processes. Assuming a production rate in a single plant of say 100 x $10^6$ lbs/yr, the plant would require 8.3 megacuries; still high but manageable. On the other hand, machine radiation located in say 40 plants around the country, would require perhaps 2 or 3 machines of 60 KW capacity each in any one location, a size presently available from electron machine manufacturers. Machine radiation seems to be the way to go. The main disadvantages are the lower efficiency of penetration of beam energy into high pressure equipment and the difficulty of obtaining the desired low radiation intensity.

From a capital investment point of view, $Co^{60}$ used to cost $0.60 per curie on the commercial market, so that for 331 x $10^6$ curies, an investment of about $200 million would be required, while for machine radiation at a mass production rate of $5,000/kw the total investment would be $50 million, which is almost a factor of 4 lower than $Co^{60}$. Fission product wastes might be less expensive, however, they are not even readily available now and could be dangerous to handle. Even if the per kw cost is 2 times higher than assumed here ($10,000/kw) there appears to be a significant margin in favor of machine radiation. In terms of unit cost of investment in machine radiation, at an annual 25% depreciation on investment, the cost of the polyketone or the polysulfone amounts to only 0.31¢/lb, a very small cost.

For an order of magnitude estimate of the design of a electron machine irradiator for polymerizing ethylene with either CO or $SO_2$, let us assume a tubular system upon which the electron beam is playing externally. The gas at high pressures is internal to the tubes and a screw conveyor and scraper transports the condensed polymer out of the reaction zone continuously. The screw also serves to scrape the inner wall surfaces of the reactor clean. The basic design criteria is to maximize the mass of ethylene and CO (or $SO_2$) relative to the containing mass of metal vessel in order to maximize the energy deposition efficiency. Taking a cylindrical cross-section of the metal vessel, the energy deposition efficiency can be calculated as follows:

d = inside diam of metal tube, in.

D = outside diam of metal tube, in.

t = wall thickness of metal tube, in.

a 1 ft unit length of reactor is assumed,

$\rho_e$ = density ethylene, $lbs/ft^3$

$\rho_m$ = density of metal, $lbs/ft^3$

P = internal tube pressure, psi

S = allowable design tensile strength of metal in reactor, psi

Wt of contained Et-CO (or $SO_2$) $= \frac{0.785}{144} d^2 \rho_e$

Wt of metal $= \frac{3.14}{144}\, d \times t \times \rho_m$

Thickness of metal $t = \frac{Pd}{2S}$

e = Energy deposition efficiency, %

R = Ratio of mass of process gas to mass of metal in the containing reactor

$$\text{Energy Dep. Eff } e \cong R \; \frac{\text{Mass Et-CO (or } SO_2)}{\text{Mass Metal}} = 0.5\,\frac{S}{P}\,\frac{\rho_e}{\rho_m}$$

Values of the ratio R are given in Table 2 for several metal reactors including stainless steel, high strength stainless steel, and titanium for a range of reactor operating pressures.

Thus with high strength stainless steel tubes, efficiencies of energy deposition of up to 17% can be obtained and with titanium tubes up to 25% at 10,000 psi and up to 55% at 5,000 psi operating pressure can be obtained. As a first approximation, titanium could be used at 5,000 psi. The lower efficiency is assumed because of beam absorption as discussed below. A typical diameter of reaction pressure vessel assuming 0.25" wall thickness can therefore be calculated as follows:

$$d = \frac{2St}{Pd} = \frac{2 \times 50{,}000 \times 0.25}{5{,}000} = 5''$$

A 5" diam tubular vessel seems to be a reasonable size reaction vessel. These design calculations will be further refined in more detailed future studies.

For $Co^{60}$ the above calculation is fairly good. However, for electron beam radiation, the slowing down and absorption of the beam in the tube wall must be taken into account. For a 3 MeV beam, the range in

## Table 2

## ELECTRON MACHINE RADIATION COPOLYMER REACTOR MASS RATIO AND ENERGY DEPOSITION EFFICIENCY

$$e = R = 0.5 \frac{S}{P} \frac{\rho_e}{\rho_m}$$

| Material | P, psi | S, psi | $\rho_e/62.4$ | $\rho_m/62.4$ | S/P | $\frac{\rho_e}{\rho_m}$ | e = R |
|---|---|---|---|---|---|---|---|
| St. St. | 2,000 | 10,000 | 0.5 | 7.5 | 5 | 0.0666 | 0.167 |
| Hi. St. St.St. | 5,000 | 25,000 | 0.5 | 7.5 | 5 | 0.0666 | 0.167 |
| Hi. St. St.St. | 10,000 | 50,000 | 0.5 | 7.5 | 5 | 0.0666 | 0.167 |
| Titanium | 5,000 | 50,000 | 0.5 | 4.5 | 10 | 0.111 | 0.555 |
| Titanium | 10,000 | 50,000 | 0.5 | 4.5 | 5 | 0.111 | 0.278 |

titanium is approximately 0.333" so that at least 25% of the beam can get through a 0.25" wall. Thus the efficiency of the energy deposition is assumed 25%. High Z materials such as gold foil can be placed around the tube to convert beam energy to more penetrating x-rays. High strength aluminum oxide fiber reinforced aluminum (a recent DuPont material development) can also be used to reduce the vessel density and obtain less absorption of beam energy. However, for this preliminary estimate, suffice it to say that the system can be designed.

Assuming a 25% efficiency, the energy requirements to produce a pound of polyketone by machine radiation is only 0.018 kwh/lb Et-CO. Thus the cost, even at 20 mills/kwh, amounts to less than 0.04¢/lb which is negligible and indicates a truly conservation-oriented process.

## Conclusion

It appears presently appropriate, from a conservation point-of-view, to make a study of the Et-CO and Et-$SO_2$ copolymer systems.

The possible savings in gas and oil reserves, substituting an essentially low cost waste products such as CO or $SO_2$, coupled with a high commodity U.S. and world market for polyethylene, presents a strong incentive for pursuing the required development effort. The development effort must determine the uniqueness of the radiation process which at present is to be directed towards electron machine radiation. Thorough investigation of the possibility of a low-temperature catalytic process must be made. Design of the radiation chemical reactor is an important problem requiring detailed design analysis. Of major importance, enough polysulfones and polyketones must be produced in bench or pilot scale equipment for the purpose of determining its processability and its market acceptance. Since those copolymers are more refractory than the homopolymer, polyethylene which it is to replace, modern techniques must be devised and applied for making these materials useful in the market place.

## References

1. M. Steinberg, P. Colombo, L. E. Kukacka, R. N. Chapman and G. Adler, "$Co^{60}$ Gamma Radiation Induced Polymerization of Ethylene" in Proc. Intern. Symp. Radiation Induced Polymerization and Copolymerization, Battelle Mem. Inst., Columbus, Ohio, Nov. 1962, pp. 70-106, TID 7643 (Nov. 1962).

2. S. Machi, M. Hagiwara, M. Gotoda, and T. Kagiya, Bulletin of the Chem. Soc. Japan 39, N.Y. pp. 675-80 (1966).

3. M. Steinberg and P. Colombo, in Industrial Uses of Large Radiation Sources (Pres. IAEA Conf., Salzburg, Austria, May 1963) Vol. 1, pp. 121-50 IAEA, Vienna (1963).

4. P. Colombo, L. E. Kukacka, J. Fontana, R. N. Chapman, and M. Steinberg, "$Co^{60}$ Gamma Radiation Induced Copolymerization of Ethylene and Carbon Monoxide", BNL 8554R, Brookhaven National Laboratory, Upton, N.Y. (October 1964).

5. P. Colombo, J. Fontana, and M. Steinberg, "Radiation Induced Copolymerization of Ethylene and Sulfur Dioxide in the Liquid and Gas Phases, BNL 11347-R and J. Polymer Sci., Part A-1, 6, 3201-15 (1968).

6. M. M. Brubaker and D. D. Coffman and H. H. Hardin, J. AM. Chem. Soc. 74, 1509-15 (1952) and D. D. Coffman, P. S. Pinkney, F. T. Wall, W. H. Wood, and H. S. Yang, J. Am. Chem. Soc. 75, 3391-3 (1952).