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**POLYKETONES AND POLYSULFONES FOR CONSERVATION
IN THE ETHYLENE POLYMER MARKET**

by

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MASTER

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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 SO₂, utilizing high energy radiation, offers one such possibility. The process has the additional advantage in that CO and SO₂ 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, or decompose at temperatures of 250°C or higher. The higher temperature

($> 100^{\circ}\text{C}$) 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. consumption in the PE 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 lower 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 supported 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 ($< 50^\circ\text{C}$), 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 ($> 100^{\circ}\text{C}$) 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 ($< 50^{\circ}\text{C}$) 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 however, be molded into film. Generally the molding conditions were difficult and the films formed tended to be brittle. In the case of the Et-SO₂ 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 exceedingly 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 oil embargo, the cost of chemical feedstock has skyrocketed 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 SO₂ to the extent of 50% into a commodity polymer such as polyethylene, thus reducing ethylene requirements, the cost savings would be about 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/year market, savings of 2 billion pounds of ethylene could conserve annually as much as 6.7 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 SO₂ to the tune of 2 million tons annually, an amount readily available from environmentally controlled coal burning power plants. The annual dollar savings in ethylene would be \$280 million per year, let alone the reduction in the cost of waste disposal. Table 1 summarizes the impact on the polyethylene market. The incentives under present conditions for pursuing the

ethylene copolymerization with CO and SO₂ 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 Co⁶⁰ 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 2 lists an estimate of the Co^{60} source requirements and the power for electron on x-ray radiation machines needed to generate 4×10^9 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 spent 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 to radioactive waste disposal instead of dispersing by utilization in various and sundry production processes. Assuming a production rate in a single plant of say 100×10^6 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 3 or 4 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. Indeed the important effect of high dose rate which is a characteristic of electron machine radiation on the G-value and the product quality is yet to be determined.

From a capital investment point of view, Co^{60} used to cost \$0.60 per curie on the commercial market, so that for 331×10^6 curies, an investment of about \$200 million would be required, while for machine radiation, at a mass production rate of \$10,000/kw, the total investment would be \$100 million, which is a factor of 2 lower than for Co^{60} . Fission product wastes might be less expensive, however, they are not even readily available now and could be dangerous to handle. There thus appears to be a significant advantage in favor of machine radiation. In terms of unit cost of investment in machine radiation, at an annual 25% depreciation on investment, the incremental cost of the polyketone or the polysulfone amounts to only 0.62¢/lb, a very small cost.

For an order of magnitude estimate of the design of an electron machine irradiator for polymerizing ethylene with either CO or SO₂, let us assume a tubular system upon which the electron beam is playing externally. A schematic is shown in Figure 1. The gas at high pressure 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 SO₂) 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,

ρ_e = density ethylene, lbs/ft³

ρ_m = density of metal, lbs/ft³

P = internal tube pressure, psi

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

Wt of contained Et-Co (or SO₂) = $\frac{0.785 d^2}{144} \rho_e$

Wt of metal = $\frac{3.14}{4} d \times t \times \rho_m$

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

$$\text{Energy Dep. Eff } e \approx R \frac{\text{Mass Et-CO (or SO}_2\text{)}}{\text{Mass Metal}} = 0.5 \frac{S}{P} \frac{\rho_e}{\rho_m}$$

Values of the ratio R are given in Table 3 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:

$$d = \frac{2St}{P} = \frac{2 \times 50,000 \times 0.25}{5,000} = 5"$$

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

For Co⁶⁰ 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 titanium is approximately 0.333" so that at least 25% of 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. One type of conceptual electron beam process irradiation configuration is shown in Fig. 1.

A preliminary capital and production cost estimate for a 100 million lb/yr polyketone plant is given in Table 4 which would operate with 4-60 KW 3 mev electron beam accelerators.

Assuming a 25% irradiation efficiency and a 50% electrical to beam power efficiency, the energy requirements to produce a pound of polyketone by machine radiation is only 0.036 kwh/lb Et-CO. Thus the cost, even at 40 mills/kwh, amounts to only 0.14¢/lb. Adding the cost of CO and a 25% annual depreciation of the plant gives a direct incremental cost of 1.43¢/lb polyketone which is added to the remaining conventional part of the plant costs. There is thus a net savings of 6.57¢/lb which is 26% of the conventional PE cost and results in an annual savings of \$6.6 million.

Conclusion

It appears presently appropriate, from a conservation point-of-view, to make a study of the Et-CO and Et-SO₂ copolymer systems.

The possible savings in gas and oil reserves substituting an essentially low cost waste product such as CO or SO₂, coupled with a high commodity U. S. and world market for polyethylene, presents a strong incentive for pursuing the required development effort. A listing of the R & D effort required is listed in Table 5. 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.

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Table 1

RADIATION INDUCED POLYKETONE AND POLYSULFONE PRODUCTION

Impact on Polyethylene Market and Conservation

U. S. - 1974/5

Market

Polyethylene Market = 8.0×10^9 lbs/year

Cost of ethylene = 14¢/lb

Production cost = 25¢/lb

Total value = \$ 2×10^9 /yr

Assume replacement of 50% of PE market with 50% substitutions of CO or SO₂ in polymer

Ethylene conservation = 2×10^9 lbs/yr

Dollar Savings = \$0.28 x 10^9 /yr

Fraction of PE Market = 14%

Conservation of Natural Gas and Oil

Ethylene = 2×10^9 lbs/yr

Natural gas = 54×10^9 cu.ft/yr

BTU value = 0.05 Q/yr

Oil Savings = 6.7×10^6 Bbl/yr

SO₂ availability from Coal operations (Et/SO₂ = 1)

3% S Coal equivalent = 38×10^6 tons/yr

Coal Production = 600×10^6 tons/yr

CO from Coal and Blast Furnace operations (Et/CO = 1)

Coal Equivalent of CO = 0.5×10^6 tons/yr

CO available from Blast Furnace = 100×10^6 tons/yr

Table 2

ESTIMATE OF RADIATION POWER REQUIREMENTS
FOR PRODUCING POLYKETONE OR POLYSULFONE

1. Production rate = 4×10^9 lb/yr = $\frac{4 \times 10^9}{300 \times 24}$ = 5.56×10^5 lb/hr
(50% of market)
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 and Costs
 - a) Co⁶⁰ gamma = 331 megacuries at \$0.60/Ci = \$200 x 10⁶
for 50% energy deposition eff. (assuming internal source)
 - b) Beta or x-ray = 9800 KW at \$10,000/kw = \$100 x 10⁶ for
25% energy deposition eff. (assuming beam external to
reactor)

Table 3

**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	0.1111	0.5555
Titanium	10,000	50,000	0.5	4.5	5	0.111	0.278

For titanium tube operating at 5000 psi and W.T. = 0.25"

$$d = \frac{2St}{P} = \frac{2 \times 50,000 \times 0.25}{5000} = 5" \text{ I.D.}$$

Table 4

PRELIMINARY COST ESTIMATE

Polyketone production
by Radiation Induced Copolymerization

Capital Investment

Production Capacity of Et-CO copolymer = 100×10^6 lb/yr
Machine radiation = 250 KW (4-60 KW machines)
Investment = 250 x 10,000 KW = \$ 2,500,000
Estimated Cost of Conventional PE plant = \$32,000,000

Production Cost

	<u>c/lb</u>
Electricity at 40mills/kwh, 50% Mach.Eff and 25% Rad. Eff	= 0.14
Cost of CO at \$1.50/MMBTU	= 0.66
<u>Amortization at 25%/yr</u>	<u>= 0.63</u>
Direct Et-CO cost	= 1.43
Amortization on Remainder of plant	= 8.00
Et. material cost/lb Et-CO	= 7.00
<u>Maintenance and labor</u>	<u>= 2.00</u>
Total Conventional Cost	= <u>17.00</u>
Total Production Cost	= 18.43
<u>Present Est. PE Cost</u>	<u>= 25.00</u>
Net Savings	= 6.57

Annual Savings = $\$6.6 \times 10^6$ billions

Table 5

ET-CO AND ET-SO₂ RADIATION COPOLYMERIZATION

Research and Development Required

To Determine

1. Uniqueness of Radiation Process

- a. Determine thermocatalytic Kinetics and DP with low temperature and azo catalysts
- b. Confirm yields with electron machine radiation especially effect of radiation intensity.

2. Processability of Copolymers

- a. Extrude with plasticizers
- b. Rotational molding

3. Marketability

- a. produce 100 lb quantities for distribution
- b. Determine applications and stability

4. Process Economics

- a. Design of machine radiation process reactor
- b. Capital and production cost estimate
- c. Value of waste CO and SO₂ and environmental benefits

ELECTRON BEAM RADIATION INDUCED POLYMERIZATION
OF Et-CO AND Et-SO₂

Fig. 1