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POLYKETONES AND POLYSULFONES FOR CONSERVATION IN THE ETHYLENE POLYMER INDUSTRY

PROGRESS REPORT NO. 3
OCTOBER-DECEMBER 1978

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PROCESS SCIENCES DIVISION
DEPARTMENT OF ENERGY AND ENVIRONMENT

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WORK PERFORMED FOR THE
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Summary

The objectives of this program is to substitute relatively large quantities of CO into ethylene copolymers forming polyketones and determine their market value as a low cost and energy conservative polymer. Preliminary studies have also been performed with Et-SO_2 mixtures forming polysulfone copolymers. The work accomplished during this period is summarized below.

Pound quantities of Et-CO copolymers have been produced at pressures of 680 atm with G-values range from 1000 to 3600. Oxygen acts as an inhibitor to polymerization. Tenneco Chemicals, Inc. is in the process of evaluating the properties of the copolymer.

Et-CO gas copolymerized at low pressures in the order of 5 atm indicated low yields and produced a low molecular weight waxy material.

Et-SO_2 copolymer can be produced at low pressure (< 5 atm) in the gas phase by means of Co-60 gamma radiation with chemical and physical properties that appear to be comparable to that of the copolymer made at higher pressure (> 50 atm). The yield in terms of G-values are high ranging to 10,000. Oxygen which initially acts as an inhibitor on subsequent radiation may act as a catalyst enhancing the rate of polymerization.

Et-SO_2 can be produced by thermocatalytic means, however, the most stable 1:1 Et-SO_2 copolymer was not produced. The properties of the copolymer have yet to be measured to determine the relative value of the thermal versus the radiation treatment.

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I. Introduction

The principal objective of this investigation is to prepare ethylene polyketones and ethylene polysulfones for determination of their usefulness in industry as a means of substituting low-cost and energy conservative materials in the ethylene polymer and copolymer market.[1,2] In the case of the Et-CO polyketones, a joint program was set up between BNL and Tenneco Chemicals, Inc. (TCI) in which BNL would prepare the copolymers by radiation induced means and Tenneco would assist in characterization of the copolymers and also compare the results with thermochemical means of copolymerization.

In the case of the Et-SO_2 polysulfones, a similar joint program with another industrial firm (The International Nickel Company, Inc.) is being proposed.

In the previous reporting period[3], Et-CO copolymers, as well as Et-SO_2 copolymers and Et-SO_2-CO terpolymers, were prepared by means of electron beam machine radiation and compared with Co-60 gamma radiation produced polymers. The yields and G-values for Et-CO copolymers appear to be lower when polymerization is induced by electrons in comparison with bremsstrahlung or gamma radiation ($G=10^2$ to 10^3 for electrons vs $G=10^3$ to 10^4 for Co-60). The yields and G-values for Et-SO_2 copolymers appear to be about the same for electron and gamma-induced radiation.

During the present reporting period, larger quantities of Et-CO copolymers were prepared for more advanced characterization studies. Repetitive falling-pressure runs were made in existing small-size, high pressure vessels using Co-60 gamma radiation.

II. Preparation of Et-CO Copolymer for Characterization Studies

A total of 877g of Et-CO copolymer was prepared during this period for further characterization studies by TCI. Existing 2-in. O.D. x 1-in. I.D Inconel and stainless steel high pressure vessels (110 cm^3 volume) were used in the BNL Co-60 gamma facility. The pressure vessel assembly with a pressure gauge and rupture disc attachment used in previous runs was modified by removing the pressure gauge and shortening the interconnecting 1/4-in. O.D. tubing to facilitate the handling and filling of the vessels. Figure 1 shows a modified vessel assembly with shut-off valve and rupture disc assembly. After filling to 10,000 psi (680 atm) at room temperature with the Et-CO gas mixture containing 49.0 to 49.9% CO (c.p. grade supplied premixed by Matheson Gas Products), the charged vessel assembly was either attached to a long pole and irradiated by being inserted into the gamma pool directly into a Co-60 source holder cage or lowered by means of a chain into an air tube containing water located in a Co-60 source holder cage. In either case, this vessel was in direct contact with water maintained at 10 to 13°C, which served as a constant temperature bath.

The yields, integral polymerization rates and integral G-values for the 48 runs made during this period are given in Table 1. The total dose ranged between 2.40 and 16.23 Mrad and dose rates were 0.6 and 2.0 Mrad/hr. Average polymer mass formed was approximately 18g per run;

a maximum yield of 33.7g was attained in run 85 at the maximum dose of 16.23 Mrad. A maximum integral rate of 80.8 g/l-hr and a maximum integral G-value of 3625 molecules/100 eV were achieved in run 99. Consistent differences in the overall rates and G-values were apparent for the four different batches of gas mixtures that cannot be attributed merely to their slight difference in CO content. Analysis of the gas mixture used in runs 138, 140, 142-144, which gave low G-values of 1048-1305 molecules/100 eV indicated 0.22% air impurity in the monomer gas. Oxygen is known to be an inhibitor in free-radical polymerization and this effect was demonstrated in a run made with the deliberate addition of oxygen. A 49.0% CO mixture (cyl. No. 45295) containing 0.3% oxygen was given a dose of 11.0 Mrad at 2 Mrad/hr and produced only 0.51g of discolored polymer product.

Since the vessels were not provided with a pressure gauge, estimates of the pressure at the gamma pool temperature of 10-13°C were made on the assumption that the compressibility of the mixture is equal to the sum of the product of concentration and compressibility of each gas. On this basis the initial pressure was estimated to be 9400 psi (639 atm). In previous runs initial pressures of 8750 (595 atm) or less were observed for these conditions, thus indicating that an appreciable error exists in the above assumption. Final pressures at 10 to 13°C for various yields were estimated to be as follows.

	Final Pressure	
Yield, g	psi	atm
10	6800	465
20	4750	325
30	3050	205

The product was removed as a solid white plug (See Figure 2) by pushing it out of the opened vessel with a rod. No attempt was made to remove the small amount of material remaining on the walls between runs.

III. Et-CO Copolymerization at Low Pressure

The Co-60 gamma-induced copolymerization of Et-CO at low pressure (approximately 5 atm) was briefly investigated. A mixture containing 48.8% CO was irradiated at 0.6 Mrad/hr in a 77 cm^3 high pressure vessel provided with a pressure gauge (104 cm^3 total volume). The apparatus was similar to that used previously in runs 1-16.

A drop in pressure from 74.0 to 71.7 psia during the initial 25 hr period was followed by a less rapid but linear drop to 67.1 psia after a total of 139.2 hr of irradiation (83.5 Mrad total). On the basis of the pressure vs time relationship established during the later period, a G-value of 40 molecules/100 eV and a polymerization rate of 4.12 mg/l-hr were determined. Comparison with previous runs 7, 9, 10, 15, 16, and 23 made in the 148 to 575 atm range[3] indicates a 0.97 power dependence of the G-value on the pressure. More data, of course, are needed in the 5 to 148 atm range to establish this relationship. The product was clear, wax-like material that coated the interior of the vessel and was probably of low molecular weight.

IV. Et-SO_2 Copolymerization at Low Pressure by Co-60 Gamma Radiation

The Co-60 gamma-induced copolymerization of Et-SO_2 at low pressure (< 5 atm) was investigated in the same system described in the previous section. Gas mixtures of Et-SO_2 containing up to 50 vol % SO_2 and also oxygen, in some cases, up to 3.4 vol % were irradiated at 0.6 Mrad/hr to

determine reaction kinetics and to prepare samples for analysis. The polymerization rates and G-values were determined from the rate of pressure drop in the system during irradiation. The results are shown in Table 2. It should be pointed out that at 10°C any partial pressure of SO_2 above 35 psia will produce a liquid phase of SO_2 in the vessel. These low pressure runs have been made with all the SO_2 in the gas phase.

In run 86 made with a 27 mole % mixture, a maximum polymerization rate of > 1.77 g/l-hr and a maximum G-value of > 9.80×10^3 molecules/100 eV occurred just prior to the depletion of the SO_2 constituent in the gas mixture, assuming 1:1 molar ratio of Et/SO_2 in the polymer. Runs 89 and 120 made with a 50 mole % mixture gave essentially a constant polymerization rate (0.38 and 0.32 g/l-hr, respectively) after a 2 to 4 hr induction period. Since the analysis of the product from both of these runs also indicated approximately a 1:1 Et/SO_2 ratio, the gas mixture remained constant at 50 mole % SO_2 during the run. The G-values were 3.04×10^3 and 2.53×10^3 molecules/100 eV for runs 89 and 120, respectively.

In run 114, a mixture containing 34% SO_2, 60% Et, and 5.8% air (1.2% O_2) resulted in a maximum polymerization rate of 1.51 g/l-hr and a maximum G-value of 1.23×10^4 molecules/100 eV, which are comparable to the values obtained in run 86 for a 27% SO_2 mixture without air. However, a long induction period (> 6 hr) was observed in run 114, indicating an initial inhibiting effect due to the presence of oxygen which was subsequently overcome. The highest polymerization rate (2.14 g/l-hr) and G-value (1.80×10^4 molecules/100 eV) occurred in run 125 with a 49% SO_2 mixture containing 1.7% O_2 (introduced as pure oxygen). These values are

approximately 6 to 7 times greater than obtained in runs 89 and 120 with a 50% SO_2 mixture without oxygen. A more pronounced induction period was also observed in run 114, which apparently was also due to the presence of oxygen. However, the subsequent effect of the oxygen was catalytic, possibly due to the formation of peroxides during irradiation which are known free radical catalysts.

A similar catalytic effect was observed in run 129A with a 48% SO_2 mixture containing 3.4% O_2. Here, however, the higher initial oxygen content resulted in a very prolonged induction period (> 20 hr). In run 129B, the addition of a 50% SO_2, 50% Et mixture to the residual mixture from run 129A produced an immediate rapid reaction with no noticeable induction period, thus indicating the presence of a catalytic agent.

The product in all cases was a white powdery material that formed spongy plugs in the vessel when produced in sufficient quantity. Thermogravimetric and differential scanning calorimetric analysis indicated properties similar to Et-SO_2 copolymers made previously at higher pressure.

V. Et-SO_2 Copolymerization by Chemical Catalyst

Several Et-SO_2 copolymerization runs were made by means of a chemical catalyst (azobis-2-methylpropionitrile). In each run, one gram of catalyst was placed in a 110 cm^3 high pressure vesses provided with a pressure gauge and rupture disc assembly. The charged vessel was rapidly heated from room temperature to 100°C and maintained at that temperature by means of a water bath. The results are given in Table 3.

Run 77 was made with no catalyst and produced only 8 mg of white powder. Runs 133 and 139 were made with a sufficient amount of SO_2 (10.6 and 20.0 g, respectively) so that liquid phase SO_2, as well as gas phase SO_2, was present for the duration of each run. A higher product yield was obtained in run 133 (19.07g vs 8.70g) despite the reduced SO_2 quantity but probably because of the higher initial quantity of ethylene in run 133 (47.3g vs 7.4g). Run 141 was made entirely in the gas phase and yielded only 0.87g copolymer because of the reduced initial quantity of SO_2 (0.81g).

In the three runs, chemical analysis of the product indicated a SO_2 molar content ranging from 27.4 to 41.9%. Apparently the 1:1 Et-SO_2 copolymer (50% SO_2) was not produced alone by thermocatalytic means. Thermogravimetric and differential scanning calorimetric analysis indicated a phase transition (melting point) in the product from runs 133 and 141 at 105 and 73°C, respectively. This may be due to the presence of low molecular weight polyethylene homopolymer. The characterization of the Et-SO_2 copolymer produced by thermocatalytic means must be made for comparison with that produced by radiation means in order to determine the relative value of each method.

VI. Conclusions

1. Pound quantities of Et-CO copolymers have been produced at pressures of 680 atm. G-values range from 1000 to 3600. Oxygen acts as an inhibitor to polymerization. Tenneco Chemicals, Inc. is in the process of evaluating the properties of the copolymer.

2. Et-CO gas copolymerized at low pressures in the order of 5 atm indicated low yields and produced a low molecular weight, waxy material.

3. Et-SO_2 copolymer can be made at low pressure (< 5 atm) in the gas phase by means of Co-60 gamma radiation with chemical and physical properties that appear to be comparable to that of the copolymer made at higher pressure (> 50 atm). The yield in terms of G-values are high ranging to 10,000. Oxygen which initially acts as an inhibitor on subsequent radiation may act as a catalyst enhancing the rate of polymerization.

4. Et-SO_2 can be produced by thermocatalytic means, however, the most stable 1:1 Et-SO_2 copolymer was not produced. The properties of the copolymer have yet to be measured to determine the relative value of the thermal versus the radiation treatment.

5. Low pressure polymerization rates for Et-SO_2 copolymer of approximately 1 g/l-hr and higher and G-values of approximately 10^4 indicate potential commercial application with regard to reaction kinetics.

References

1. M. Steinberg et al., Polyketones and Polysulfones for Conservation in the Ethylene Polymer Industry, Progress Report No. 1, October-December 1977, BNL 50884.

2. M. Steinberg, Polyketones and Polysulfones for Conservation of Ethylene Polymers, Chem. Engr. Prog. 72 (9), 75-79 (1976).

3. M. Steinberg et al., Polyketones and Polysulfones for Conservation in the Ethylene Polymer Industry, Progress Report No. 2, April-September 1978, BNL 50955.

Table 1

Co^{-60} GAMMA RADIATION COPOLYMERIZATION OF ETHYLENE AND CO FOR CHARACTERIZATION STUDIES

Filling Pressure: 10,000 psi (680 atm) at approx. 20°C
Irradiation Temp.: 10-13°C
Initial Total Gas Weight and Density: 57.5 g, 0.500 g/cm^3
System Volume: 110 cm^3 in radiation field
115 cm^3 total

Run No.	% CO	Intensity, Mrad/hr	Time, hr	Dose, Mrad	Product weight, g	Overall rate, g/l-hr	Overall G value, molecules/100eV
85	49.7(a)	2.0	8.12	16.23	33.7	37.7	1844
87	49.7(a)	0.6	16.60	9.95	18.0	9.9	1345
88	49.7(a)	2.0	4.58	9.17	14.5	28.8	1134
90	49.7(a)	2.0	6.00	12.00	18.0	27.3	1115
91	49.7(a)	0.6	15.42	9.25	16.9	10.0	1345
92	49.7(a)	0.6	16.25	9.75	17.5	9.8	1320
93	49.7(a)	2.0	6.25	12.50	23.9	34.8	1507
94	49.0(b)	0.6	4.00	2.40	2.8	6.3	744
95	49.0(b)	0.6	4.00	2.40	3.1	7.0	822
96	49.0(b)	0.6	6.00	3.60	7.5	11.4	1404
97	49.0(b)	2.0	3.50	7.00	27.4	71.1	3207
98	49.0(b)	0.6	8.00	4.80	11.6	13.1	1680
99	49.0(b)	2.0	3.00	6.00	26.7	80.8	3625
100	49.0(b)	2.0	3.00	6.00	21.4	64.8	2742
101	49.0(b)	2.0	3.00	6.00	16.2	49.1	2202
103	49.0(b)	2.0	3.00	6.00	23.5	71.3	3084

Table 1 (Cont.)

Run No.	% CO	Intensity, Mrad/hr	Time, hr	Dose, Mrad	Product weight, g	Overall rate, g/l-hr	Overall G value, molecules/100eV
104	49.0(b)	2.0	3.00	6.00	11.5	34.9	1338
106	49.0(b)	2.0	3.00	6.00	10.6	32.2	1222
107	49.0(b)	2.0	3.00	6.00	22.7	68.7	2947
108	49.0(b)	2.0	3.00	6.00	22.8	69.0	2966
110	49.0(b)	2.0	3.00	6.00	18.0	54.6	2230
111	49.0(b)	2.0	2.50	5.00	10.4	37.7	1430
112	49.0(b)	2.0	2.75	5.50	13.4	44.4	1734
113	49.0(b)	2.0	2.75	5.50	13.3	43.9	1716
115	49.0(b)	2.0	2.75	5.50	21.9	72.3	3074
130	49.0(b)	2.0	3.00	6.00	2.6	7.9	276
131	49.0(b)	2.0	3.00	6.00	22.3	67.7	2888
132	49.0(b)	2.0	3.00	6.00	16.6	50.4	2030
134	49.0(b)	2.0	3.00	6.00	20.8	63.2	2660
135	49.0(b)	2.0	3.00	6.00	17.2	50.2	2112
136	49.0(b)	2.0	3.00	6.00	20.8	63.0	2654
138	49.9(c)	2.0	4.00	8.00	12.0	27.2	1048
140	49.9(c)	2.0	4.50	9.00	13.3	26.9	1050
142	49.9(c)	2.0	5.00	10.00	16.5	30.0	1212
143	49.9(c)	2.0	5.00	10.00	17.7	32.1	1305
144	49.9(c)	0.6	16.75	10.05	20.9	11.3	1590
150	49.0(d)	0.6	17.00	10.20	30.3	16.2	2530
151	49.0(d)	2.0	4.00	8.00	30.6	69.6	3284

Table 1 (Cont.)

Run No.	% CO	Intensity, Mrad/hr	Time, hr	Dose, Mrad	Product weight, g	Overall rate, g/l-hr	Overall G value, molecules/100eV
152	49.0(d)	2.0	3.00	6.00	21.7	65.8	2792
154	49.0(d)	2.0	3.00	6.00	22.7	68.7	2946
156	49.0(d)	2.0	3.00	6.00	21.3	64.5	2720
158	49.0(d)	2.0	3.00	6.00	21.6	65.4	2772
160	49.0(d)	2.0	3.00	6.00	20.9	63.4	2672
162	49.0(d)	2.0	3.00	6.00	21.7	65.8	2788
163	49.0(d)	2.00	3.00	6.00	16.4	49.7	2003
165	49.0(d)	2.00	3.00	6.00	18.5	55.9	2295
166	49.0(d)	2.00	3.00	6.00	20.7	62.6	2635
167	49.0(d)	2.00	3.00	6.00	23.0	69.8	2992

(a) Cyl. No. 82601.

(b) Cyl. No. 45295.

(c) Cyl. No. FF 20298. 0.22% air impurity.

(d) Cyl. No. 48251.

Table 2

LOW PRESSURE Co-60 GAMMA COPOLYMERIZATION OF ETHYLENE AND SO_2 IN GAS PHASE

Irradiation Temp: 10-13°C
Radiation Intensity: 0.6×10^6 rads/hr
Total System Volume: 104 cm^3
Radiation Volume: 77 cm^3

Run No.	Initial Vol% SO_2	Initial Vol% O_2	Pressure, psia Initial	Pressure, psia Final	Total time, hr	Yield, g	Max. Rate, g/l-hr	Max. G Value molecules/100eV	SO_2 in Product, Vol%
86	27	0.0	62.7	35.9	5.33	0.427	> 1.77	> 9.80×10^3	50.2
89	50	0.0	55.2	9.8	21.7	0.767	0.38	3.04×10^3	50.3
114	34	1.2[a]	61.7	25.7	19.78	0.561	1.51	1.23×10^4	48.8
120	50	0.0	51.9	9.3	24.14	0.640	0.32	2.53×10^3	47.4
125	49	1.7	71.7	12.7	18.56	0.940	2.14	1.80×10^4	48.8
129A	48	3.4	71.9	18.2	33.73	———	0.90	5.90×10^3	———
129B	50[b]	(b)	71.2	19.2	5.72	1.51(c)	1.42	9.33×10^3	49.2

[a] 5.8% air.

[b] Approximate 1:1 Et-SO_2 feed mixture added to residual mixture from run 129A.

[c] Total combined weight from runs 129A and 129B.

Table 3

COPOLYMERIZATION OF ETHYLENE AND SO_2 BY CHEMICAL CATALYST

Temp.: 20-100°C
Catalyst: 1g of azobis-2-methylpropionitrile in each run except No. 77

Run No.	Initial Weight, g Et	Initial Weight, g SO_2	Press Range, psig	Time, hr	Product Weight, g	SO_2 in Product, M%
77	46.4	10.0*	2200-7100	2.82	0.008	———
133	47.3	10.6*	2500-5400	1.03	19.07	27.4
139	7.4	20.0*	600-700	0.95	8.70	41.9
141	26.4	0.81	850-1230	1.62	0.87	32.1

* Under these conditions SO_2 is also present in the liquid state.

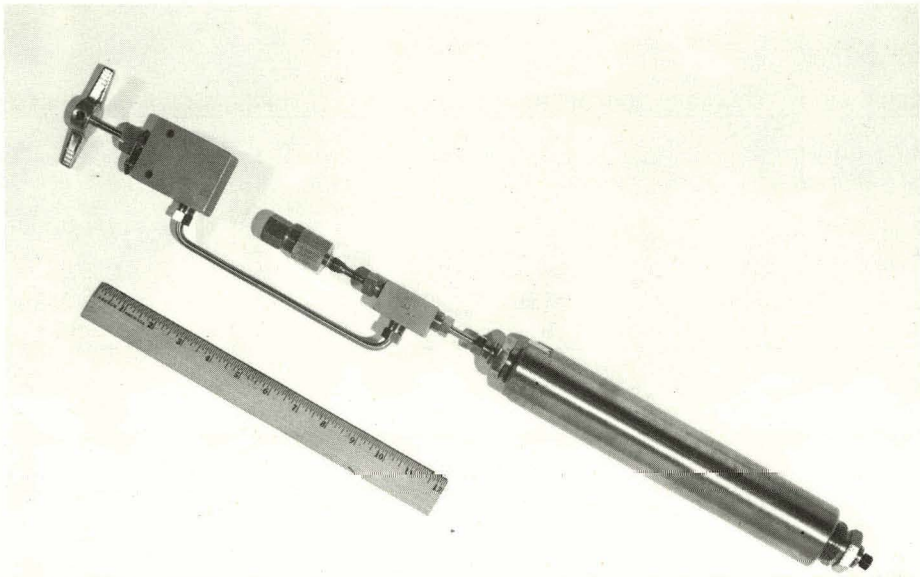

Figure 1. High pressure vessel assembly with shutoff valve and rupture disc.

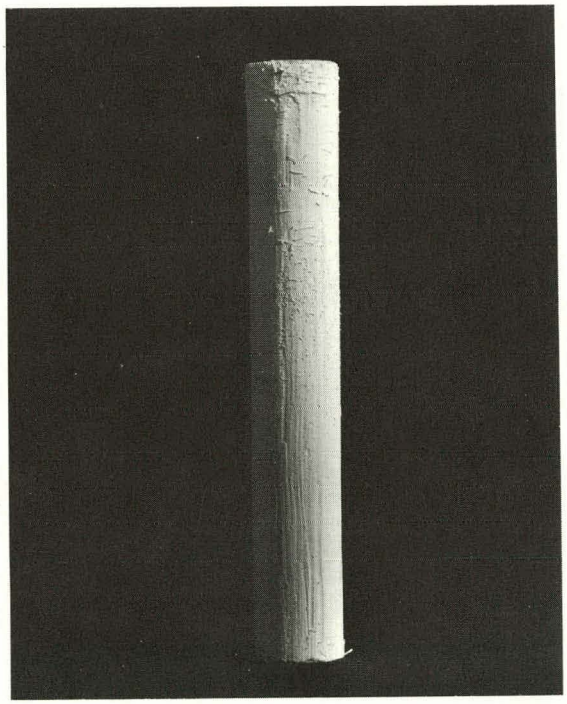

Figure 2. Typical Et-CO copolymer product after removal from vessel.

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