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POLYKETONES AND POLYSULFONES FOR CONSERVATION IN THE ETHYLENE POLYMER INDUSTRY

PROGRESS REPORT NO. 4
JANUARY-MARCH 1979

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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 are to: (1) prepare polyketones and polysulfones by the partial substitution of CO or SO_2 for ethylene; and (2) determine their market value as low-cost energy-conserving polymers.

Additional quantities of Et-CO copolymers were prepared at 680 atm, as well as at 340 atm, by Co-60 gamma radiation induced polymerization for product evaluation by Tenneco Chemicals, Inc. (TCI). The preparative phase of the joint program with TCI is thus concluded. The final results and summary of the product evaluation study by TCI will be forthcoming shortly.

Work was continued on polymerization rates for gas-phase Et-SO_2 mixtures at low pressure (< 10 atm) by Co-60 gamma radiation induced polymerization. Maximum rates were obtained in recharged vessels at SO_2 concentrations of < 5 mole % and at approximately 50 mole %. The peak rates appear to be directly proportional to the pressure. The peak G-values appear to be independent of pressure and are about the same for the two gas compositions, averaging approximately 8×10^4 molecules/100 eV.

POLYKETONES AND POLYSULFONES FOR CONSERVATION IN THE ETHYLENE POLYMER INDUSTRY

Progress Report No. 4
January-March 1979

I. Introduction

The objectives of this program are to: (1) prepare polyketones and polysulfones by the partial substitution of CO or SO_2 for ethylene; and (2) determine their usefulness in industry as a means of substituting low-cost energy-conserving materials in the ethylene polymer and copolymer market.[1,2,3]

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[4] reporting period, Et-CO copolymers were prepared in pound quantities by Co-60 gamma-induced radiation for advanced characterization studies by TCI. Additional quantities of copolymer were prepared during this period and the results in terms of yield, rate and G values are given below. The results of their studies will be forthcoming in the next report period.

In the previous reporting period, Et-SO_2 copolymer was prepared at low pressure (< 5 atm) in the gas phase by means of Co-60 gamma radiation, and polymerization rates and G-values were determined. Additional rate and G-value data were obtained during this period.

II. Preparation of Et-CO Copolymer by Gamma Radiation for Characterization Studies

A total of 843 g of Et-CO copolymer was prepared during this period for further characterization studies by TCI. The equipment was described previously[4] and consisted of 2-in. O.D. x 1-in. I.D. high pressure vessel assemblies with shortened interconnecting tubing and without a pressure gauge. The vessels were charged to either 10,000 psi (680 atm) or 5,000 psi (340 atm) at ∿ 20°C and irradiated in the BNL Co-60 gamma facility by immersion in the water-filled pool maintained at 10-13°C.

The yields, integral polymerization rates and integral G-values for the runs made with vessels filled to 10,000 psi pressure are given in Table 1. Polymerization rates ranged between 49.1 and 73.1 g/l-hr and G-values ranged between 2175 and 3480 molecules/100 eV for the 49.0% CO gas mixture. However, higher values were obtained for the 49.6% CO mixture, with rates between 83.7 and 107.4 g/l-hr and G-values between 3930 and 5154 molecules/100 eV. These higher values are most likely due to differences in gas impurities rather than gas composition.

The results for the runs made at 5,000 psi are given in Table 2. The integral rates and G-values were lower in comparison to the previous values at 10,000 psi and ranged between 21.9 and 36.1 g/l-hr and 1130 to 2104 molecules/100 eV for a radiation intensity of 2.0 Mrad/hr with gas containing 49.0% CO. [Previous experimental data indicated a 0.81 power dependence of G value on pressure for gas of this composition.] Differences in rate and G-value were observed for the two different gas mixtures and as in the previous runs are probably due to differences in gas impurity content.

III. Low Pressure Gas-Phase Copolymerization of Et-SO_2 by Gamma Radiation

Experimental work was continued[4] on Co-60 gamma-induced copolymerization of Et-SO_2 mixtures in the gas phase at low pressure (< 10 atm). The mixtures were irradiated at 0.58 Mrad/hr in 2-in. O.D. x 1-in. I.D. high pressure vessels either 77 or 110 cm^3 in volume. As in the previous runs, the vessels were in direct contact with the water in the gamma pool maintained at 10-13°C. Gas mixtures were prepared from C.P. grade ethylene and anhydrous SO_2, both supplied by Matheson Gas Products.

The first series of four runs were made with gas mixtures containing either 10 or 20 mole% SO_2 initially (see Table 3). Pressure gauge measurements were taken and from the plot of pressure vs. time for each run, slope measurements were used to determine polymerization rates and G values. In each run the rate of pressure drop increased with time to a peak value when the pressure was within 1-2 psi of the final pressure (see Fig. 1 for run 182, which is typical for the four runs). This corresponds to an SO_2 concentration of < 5 mole % at the peak rate based on 1:1 molar ratio Et-SO_2 product formation, as indicated by chemical analysis. The tailing-off portion of the pressure plot was due to reaction of residual SO_2 at a slower rate, which was to some extent controlled by the rate of diffusion of SO_2 from the lines and pressure gauge into the reaction vessel. Analysis of the gas from the reaction vessel at the completion of run 175 showed 0.04 vol % SO_2 indicating a high conversion of SO_2 to copolymer. The peak polymerization rate varied from 1.35 g/l-hr at a G-value of 2.38×10^4 molecules/100 eV in run 178 at 50.9 to 41.0 psia pressure range to a maximum peak of 39.5 g/l-hr at a G-value of 1.20×10^5 molecules/100 eV in run 182 at 169.6 to 147.5 psia pressure range.

Additional gas-phase rate measurements were made in the same manner as above, except that in this next series the vessels were recharged with Et-SO_2 gas after each previous charge was partly or entirely reacted and the copolymer product was left in the vessel. Generally, higher peak rates were obtained, apparently as a result of a reduced vessel wall inhibition effect due to product buildup on the vessel surfaces. Also, the introduction of moisture, oxygen and other contaminants, other than that present in the feed gas, was thus avoided. The results are given in Table 4.

In run 192, the Et-SO_2 mixture was introduced intermittently from a three-liter feed tank after each previous charge was partly reacted. The system pressure increased after each successive reaction because of buildup of excess unreacted ethylene. After 12 charges a maximum peak rate of 16.8 g/l-hr and a G-value of 6.73×10^4 molecules/100 eV were obtained at 111 psia. Runs 195 and 214 were made in a similar manner, but the system was occasionally vented of excess ethylene before recharging so as to obtain a peak rate at a lower pressure. In runs 195 and 214, maximum peak rates of 9.2 and 15.4 g/l-hr and G-values of

6.87×10^4 and 7.35×10^4 molecules/100 eV runs were observed at 59 and 93 psia, respectively. The SO_2 concentration for these mixtures at the peak values could not be determined accurately but were estimated to be < 10%.

For the subsequent runs a pressure transducer and recorder were installed in the system so as to improve the rate determinations. Runs 241, 244, 245, 247, and 248 were made with one charge each but product from each of these runs was left in the vessel after the initial run 241 was made. The system was reevacuated but not disassembled between runs. In the initial run 241 a low G-value of 5.10×10^4 molecules/100 eV at 1.95 g/l-hr was obtained, probably because of the increased inhibition effect. The subsequent runs (244, 245, 247 and 248) resulted in peak G-values ranging from 7.78×10^4 to 9.03×10^4 molecules/100 eV at peak rates of 2.10 to 5.70 g/l-hr and at 12 to 28 psia. The SO_2 concentrations for these mixtures at the peak values was estimated to be < 5%.

The initial rates in runs 241, 244, 245, 247, and 248 showed a general increase with each successive run. A rate of 1.66 g/l-hr was attained in run 248 during the initial pressure drop from 30 to 20 psia. This corresponds to a G-value of 1.97×10^4 electrons/100 eV for a gas mixture containing close to 40% SO_2. Analysis of the product from all of the runs in Table 4 showed approximately a 1:1 molar Et-SO_2 copolymer composition.

The peak rates in Table 4 indicate direct proportionality of rate to pressure. Also, the G-values appear to be constant over the pressure range investigated, with values ranging between $6.73\text{x}10\text{x}^4$ and $9.03\text{x}10^4$ molecules/100 eV (excluding run 241).

In run 219 the reaction vessel was recharged nine times and also reevacuated between charges without disassembly and removal of product. A gas mixture almost equimolar in composition (46.8%) SO_2) was used, and since the polymer product was approximately of 1:1 Et-SO_2 molar ratio as indicated by chemical analysis, the gas mixture therefore remained essentially constant during each reaction period.

Peak rates were observed during the initial reaction period for each charge rather than near the final period as in the previous runs. A maximum peak rate of 10.87 g/l-hr occurred with the seventh charge (see Table 5) as the pressure fell from 45 to 30 psia. The rates for the entire reaction period for this charge also show some degree of direct proprotionality to pressure, but are somewhat higher than those in Table 4. However, because of the compensating effect of the gas mixture (46.8% SO_2 for run 219 vs. 3.5% SO_2 for those in Table 4) as expressed on a weight basis in the G-value* computation, the average G values for run 219 are comparable to those in Table 4 ($8.10\text{x}10^4$ vs. $7.82\text{x}10^4$ molecules/100 eV) respectively.

$$* \; G = \frac{9.65\text{x}10^{11}P}{M.W.\text{x}D\text{x}R} \; ,$$

Where P is the weight of product in grams, M.W. is the molecular weight of average unit polymer (46 for 1:1 Et-SO_2), D is the total dose in rads, and R is the weight of reactants in grams.

The results of the low-pressure gas-phase Et-SO_2 polymerization work indicate that, in general, rates were higher in recharged vessels containing product from previous runs, probably because of a reduced vessel wall inhibition effect. No attempt was made to determine the effect of impurities in the gases on the rate. Runs made in recharged vessels indicated maximum peak rates at SO_2 concentrations of $<$ 5 mole % and at approximately 50 mole %. The peak rates appear to be directly proportional to the pressure over the range investigated ($<$ 10 atm). The peak G-values appear to be independent of pressure and are about the same for the two gas composition, averaging approximately 8×10^4 molecules/100 eV. In all cases a product of approximately 1:1 molar ratio Et-SO_2 composition was formed.

Previously obtained[2,3] integral or overall G-values for gas-liquid mixtures at 200-570 atm ranged from 5.6×10^4 to 9.5×10^4 molecules/100 eV and were thus in the same range as the present peak values at low pressure. These results indicate a zero power dependence of the G-value on pressure rather than the 2.1 power dependence previously obtained.[3] The previous data included runs made at $<$ 100 atm in smaller size 1/2 in. O.D. vessels which probably had a greater surface inhibition effect, and those G-values were therefore at least an order-of-magnitude smaller in value.

Conclusions

1. A total of 843 g of Et-CO copolymer was prepared during this period at 680 and 340 atm for evaluation by TCI.
2. Maximum peak polymerization rates for Et-SO_2 mixtures by Co-60 gamma-induced radiation were obtained in recharged vessels at SO_2 concentrations of < 5 mole % and at approximately 50 mole %. The peak rates appear to be directly proportional to the pressure over the range investigated (< 10 atm). The peak G-values appear to be independent of pressure and are about the same for the two gas compositions, averaging approximately $8x10^4$ molecules/100 eV.

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2. M. Steinberg, R. Johnson, W. Cordes, and D. Goodman, Polyketones and Polysulfones for Conservation in the Ethylene Polymer Industry, Progress Report No. 1, October-December 1977, BNL 50884.

3. M. Steinberg, R. Johnson, W. Cordes and D. Goodman, Polyketones and Polysulfones for Conservation in the Ethylene Polymer Industry, Progress Report No. 2, April-September 1978, BNL 50955.

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Table 1

Co-^{60} GAMMA RADIATION COPOLYMERIZATION OF ETHYLENE AND CO AT 10,000 PSI FILLING PRESSURE 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, 0500 g/cm^3
System Volume: 110 cm^3 in radiation field
115 cm^3 total
Radiation Intensity: 1.87 Mrad/hr

Run No.	% CO	Time, hr	Dose Mrad	Product weight, g	Overall rate, g/l-hr	Overall G-value, molecules/100 eV
184	49.0[a]	3.21	6.00	25.8	73.1	3480
185	49.0[a]	3.00	5.61	22.8	69.0	3182
187	49.0[a]	3.00	5.61	16.9	51.1	2210
188	49.0[a]	3.00	5.61	20.8	63.2	2845
189	49.0[a]	3.00	5.61	17.6	53.2	2320
191	49.0[a]	3.00	5.61	20.2	61.2	2745
193	49.0[a]	3.00	5.61	21.3	64.6	2920
194	49.0[a]	3.24	6.06	18.0	50.4	2205
196	49.0[a]	3.00	5.61	20.6	62.5	2815
197	49.0[a]	3.00	5.61	19.2	58.2	2578
198	49.0[a]	3.00	5.61	16.2	49.1	2175
199	49.0[a]	3.00	5.61	20.4	61.9	2778
200	49.0[a]	3.00	5.61	19.2	58.1	2570
201	49.0[a]	3.00	5.61	22.7	68.8	3168
202	49.0[a]	3.00	5.61	22.1	67.0	3060
204	49.0[a]	3.00	5.61	20.3	61.6	2762
205	49.0[a]	3.00	5.61	22.0	65.6	3038
207	49.0[a]	3.00	5.61	23.6	71.5	3315
208	49.6[b]	3.50	6.55	32.2	83.7	4280
209	49.6[b]	2.75	5.14	26.7	88.3	4242
210	49.6[b]	2.50	4.68	23.4	85.0	3930
211	49.6[b]	2.50	4.68	24.9	90.6	4220
212	49.6[b]	2.25	4.21	22.4	90.4	4144
213	49.6[b]	2.25	4.21	26.6	107.4	5154

[a] Cyl. No. 48251
[b] Cyl. No. 1444P

Table 2

Co^{60} GAMMA RADIATION COPOLYMERIZATION OF ETHYLENE AND CO AT 5,000 PSI FILLING PRESSURE FOR CHARACTERIZATION STUDIES

Filling Pressure: 5,000 psi (680 atm) at approx. 20°C
Irradiation Temp.: 10-13°C
Initial Total Gas Weight and Density: 45.1 g, 0.392 g/cm^3
System Volume: 110 cm^3 in radiation field
115 cm^3 total
Radiation Intensity: 2.0 Mrad/hr

Run No.	% CO	Time, hr	Dose, Mrad	Product weight, g	Overall rate, g/l-hr	Overall G-value, molecules/100 eV
119	49.0[a]	6.50	13.00	22.4	31.3	1840
121	49.0[a]	6.50	13.00	20.4	28.6	1630
122	49.0[a]	6.50	13.00	24.6	34.4	2088
123	49.0[a]	7.50	15.00	25.8	31.3	1940
124	49.0[a]	5.50	11.00	16.6	27.4	1484
126	49.0[a]	5.50	11.00	21.8	36.1	2104
127	49.0[a]	5.50	11.00	19.1	31.5	1768
147	49.9[b]	16.33	9.80[d]	14.9	13.8	1455
169	49.0[c]	5.50	11.00	20.1	33.1	1880
171	49.0[c]	5.50	11.00	21.1	34.9	2010
172	49.0[c]	5.50	11.00	13.2	21.9	1130
173	49.0[c]	5.50	11.00	19.7	32.5	1834
174	49.0[c]	5.50	11.00	19.9	32.9	1864
176	49.0[c]	5.50	11.00	20.0	33.0	1870
179	49.0[c]	5.50	11.00	17.3	28.6	1562
181	49.0[c]	5.50	11.00	18.8	31.1	1736

[a] Cyl. No. 45295
[b] Cyl. No. FF20298 with 0.22% air impurity.
[c] Cyl. No. 48251
[d] Radiation intensity: 0.6 Mrad/hr.

Table 3

LOW-PRESSURE GAS-PHASE Co-^{60} GAMMA COPOLYMERIZATION OF ETHYLENE AND SO_2 AT LOW SO_2 CONCENTRATIONS

Irradiation Temp.: 10-13°C
Radiation Intensity: 0.58 Mrad/hr

Run No.	Initial Mole% SO_2	Pressure, psia Initial	Final	Total Time, hr	Yield, g	Peak rate g/l hr	Peak G-Value molecules/100 eV
175	20	68.6	46.1	3.89	——	7.61	7.03×10^4
177	10	103.1	86.0	2.38	0.245	8.73	4.40×10^4
178	10	50.9	41.0	1.72	0.152	1.35	2.38×10^4
182	10	169.6	147.5	0.50	0.754	39.5	1.20×10^5

Table 4

LOW-PRESSURE GAS-PHASE Co-^{60} GAMMA COPOLYMERIZATION OF ETHYLENE AND SO_2 IN RECHARGED SYSTEMS

Irradiation Temp.: 10-13°C
Radiation Intensity: 0.58 Mrad/hr

Run No.	Initial mole% SO_2	Pressure at peak rate, psia	Peak rate g/l-hr	Peak G-value molecules/100 eV
192	< 50	111	16.8	6.73×10^4
195	< 50	59	9.2	6.87×10^4
214	< 50	93	15.4	7.35×10^4
241[a]	40	17	1.95	5.10×10^4
244	40	28	5.40	8.57×10^4
245	40	28	5.70	9.03×10^4
247	40	12.5	2.36	8.40×10^4
248	40	12	2.10	7.78×10^4

7.82×10^4 avg.
(excluding No. 241)

[a] System not previously charged.

Table 5

LOW-PRESSURE GAS-PHASE Co-^{60} GAMMA COPOLYMERIZATION OF ETHYLENE AND SO_2 - RUN 219 (SEVENTH CHARGE)

Irradiation Temp.: 10-13°C
Radiation Intensity: 0.58 Mrad/hr
Initial gas composition: 46.8 mole% SO_2 - 53.2 mole% Et

Reaction Time, min.	Pressure, psia	Rate, g/l-hr	G-value, molecules/100 eV
0 - 25	45 - 30	10.87	7.88×10^4
35	25	8.21	8.94×10^4
47	20	7.65	10.40×10^4
63	15	4.64	8.40×10^4
96	10	1.81	4.90×10^4
			8.10×10^4 avg.

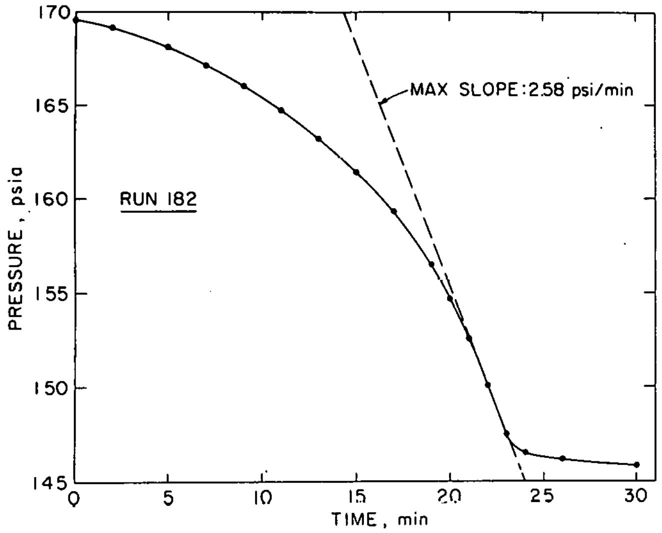

Figure 1. Polysulfone formation - Co^{60} gamma radiation induced pressure vs. time.

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