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POLYSULFONES FOR CONSERVATION IN THE ETHYLENE POLYMER INDUSTRY

PROGRESS REPORT NO. 8
APRIL - JUNE 1980

MEYER STEINBERG, RICHARD JOHNSON, DAVID ELLING,
PHILIP BERNSTEIN, AND ALAN E. VARKER

August 1980

MASTER

DEPARTMENT OF ENERGY AND ENVIRONMENT

BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK 11973

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August 1980

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Summary

Ethylene SO_2 polysulfone copolymers were prepared by both cobalt-60 gamma irradiation and chemical catalysis as a means of incorporating a polluting waste material such as SO_2 into useful ethylene polymers and also for the purpose of conserving ethylene feedstock. In addition, ethylene- SO_2 copolymer was prepared with monomeric acrylates and vinyl acetate to produce a modified material. Discs of modified and unmodified ethylene- SO_2 copolymer were pressure molded.

I. Introduction

The objectives of this program are: (1) prepare polysulfone copolymers by the partial substitution of SO_2 for ethylene and (2) determine their usefulness in industry as a means of substituting a low-cost polluting energy-conserving material in the ethylene polymer and copolymer market.(1)-(9)

A joint program was established between Brookhaven National Laboratory (BNL) and the International Nickel Company (Inco) Research and Development Center, Inc. (IRDC) of the International Nickel Company, Inc. to prepare and evaluate ethylene- SO_2 (Et- SO_2) copolymers. These copolymers were prepared at BNL by cobalt-60 gamma radiation, as well as by electron-beam radiation and by thermocatalysis. The polymer were analyzed and characterized by Inco-IRDC.

The copolymerization of Et- SO_2 was studied in both liquid and gas phases at 10-13°C to determine the effect of pressure, SO_2 concentration, and radiation intensity on the polymerization rate and G-value yield. Maximum G-values of 1.3×10^5 molecules/100eV were obtained in the liquid phase saturated with ethylene above 35 atm. Gas phase copolymerization below 10 atm indicated peak instantaneous rates and G-values at SO_2 concentrations of approximately 2 and 50 mole %. Overall rates and G-values for gas mixtures in the 22.4 to 56.1 atm pressure range also indicated a peak in reactivity at approximately 2 mole % SO_2 . The peak instantaneous and overall G-values for gas-phase copolymerization were all in the range of 8×10^4 molecules/100eV.

Two-phase liquid-gas mixtures at initial pressures of 517 to 571 atm and final pressures of 204 to 245 atm copolymerized with G-values between 6×10^4 and 7×10^4 molecules/100eV at comparable radiation intensities (0.6-0.7 Mrad/hr). The effect of radiation over the 0.03 to 0.7 Mrad/hr range was very slight and showed a -0.12 power dependence of the G-value on the intensity, or a 0.88 power dependence of the overall polymerization rate on the intensity.

The feasibility of using electron-beam radiation to copolymerize Et-SO₂ mixtures was demonstrated with the BNL Dynamitron operated at 2 MeV and the SREL E-Linac at the University of Maryland operated at 7.5 MeV. G-values ranged between 1.3×10^3 to 4.0×10^3 molecules/100eV, which were comparable to the values obtained with cobalt-60 gamma runs made at comparable conditions and in similar vessels.

During this period, the work at BNL included preparation of additional batches of Et-SO₂ copolymer by Co-60 gamma irradiation and also by chemical CO₂. Work was continued on the preparation of modified copolymers by the inclusion of monomer additives in the ethylene-SO₂ system. Additional discs were pressure molded from Et-SO₂ copolymer and also from modified copolymers.

II. Preparation of Et-SO₂ Copolymer by Co-60 Gamma Irradiation

A number of batches of Et-SO₂ copolymer were prepared at BNL by Co-60 gamma irradiation to provide material for product characterization and evaluation for commercial applications by Inco. Liquid-phase SO₂ saturated with ethylene to an initial pressure of 900-1200 psig was irradiated by a procedure described in previous reports.(3),(4),(7)

A 77-cm³ one-inch I.D. high-pressure reaction vessel provided with a remote pressure gauge was used to carry out the copolymerizations at radiation intensities of 0.48-0.49 Mrad/hr and at an ambient gamma pool temperature of 18-20°C.

The operating conditions and yields are given in Table 1. Because of the long irradiation time periods, yields were high and the yield/initial SO₂ weight ratios ranged from 1.62 for an irradiation period of 18.35 hr in run 391 (total dose: 9.0 Mrad) to a ratio as low as 1.34 for an irradiation period of one hour in run 435 (total dose: 0.48 Mrad). These values can be compared to the theoretical yield/initial SO₂ weight ratio value of 1.44 for 100% conversion of SO₂ to a 1:1 molar ratio copolymer.

A pressure peak occurred in most runs after 10-15 min of irradiation with the pressure rising from 900-1200 psig to as much as 2100 psig, followed by a tailing off to around the initial pressure. This indicates ethylene solubility very close to the composition of the copolymer, i.e., ~ 50 mole %, for these operating conditions.

The product was a white, somewhat hard material that could be easily broken up into a powder. Unreacted SO₂ in the product was not evident in the longer runs but was readily detected by odor in the short runs of one hour or slightly longer.

III. Preparation of Et-SO₂ Copolymer by Chemical Catalysis

Et-SO₂ copolymerization by azo and peroxide catalysts was briefly investigated as an alternate to preparation by radiation means. The equipment and procedure were described in a previous report.⁽⁵⁾ A 110-cm³ high-pressure vessel was provided with a pressure gauge and a

rupture disc assembly. In each run one gram of catalyst was added to the vessel which was then sealed, chilled with ice, and evacuated prior to charging with SO_2 and ethylene. The charged vessel was shaken for several minutes and then placed in a water bath provided with electrical immersion heaters. The catalysts were thermally activated as the water bath temperature was rapidly increased to as much as 100°C . At the completion of each run, cooling water was rapidly added to the water bath, followed by venting, and disassembly of the vessel for recovery of product.

The operating conditions and yields are shown in Table 2. The highest yield/initial SO_2 weight ratios of 1.40 and 1.39 were attained in runs 421 and 440, respectively, made with 2,2' azobisisobutyronitrile and 2,2' azobis (2-methyl propionitrile). These values are close to the theoretical value of 1.44 for 100% conversion of SO_2 to a 1:1 molar ratio copolymer. The lowest yield/initial SO_2 ratios of 0.69 and 0.70 resulted in runs 439 and 442, respectively, made with di-t-butyl peroxide and benzoyl peroxide.

The runs were typified by a rapid increase in pressure to a maximum or peak value, which generally occurred 0.68 to 0.75 hr after start of heating and shortly after attainment of maximum water bath temperature, which was then followed by a rapid drop and a final tailing off at the completion of the run. In run 441 the peak pressure occurred only 0.38 hr after the start, possibly because of the increased quantity of SO_2 reactant and therefore greater exotherm. In run 442 the peak occurred after only 0.45 hr, which may have been the result of an increased initial catalytic effect.

In general, the product was discolored by catalyst byproducts, which were either yellow or brown from the azo catalysts or gray from the peroxides. The product from run 440 made with 2,2' azobis (2-methyl propionitrile), however, showed the least perceptible discoloration and had the least amount of outgassing.

IV. Preparation of Modified Et-SO₂ Copolymers

Modified Et-SO₂ copolymers were prepared at BNL for characterization and evaluation by Inco. In this procedure, which was described previously,⁽⁹⁾ small quantities of monomer additives were added to the reaction system together with ethylene and SO₂ and then irradiated with Co-60 gamma sources.

During this period, commercially prepared monomers of 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, methyl methacrylate, vinyl acetate, and trimethylolpropane trimethylacrylate were used without any purification to remove inhibitors. One, two, or four milliliters of modifier was introduced into a 77-cm³ one-inch I.D. high-pressure reaction vessel, which was then sealed, attached to a vacuum rack, chilled with ice or dry ice, and evacuated. SO₂ was next added by vapor transfer and condensation prior to the addition of ethylene at ~ 100 psia into the chilled vessel. The vessel was then valved off, detached from the vacuum rack, and attached to the support assembly with remote pressure gauge and rupture disc. The assembly was pressurized with ethylene to operating pressure with the vessel still chilled and then inserted into the gamma pool, but not into the Co-60 gamma source until after equilibration to the pool temperature (18-20°C). The reaction was monitored by observation of the system pressure (~ 1000 psig initially), which was essentially ethylene.

The results (see Table 3) show that high yields were obtained in runs 399 and 400 with 2-hydroxyethyl acrylate with perhaps nearly complete conversion of SO_2 to product. Although the product was a homogeneous white powder in run 399, the increased quantity of monomer used in run 400 (2 ml vs. 1 ml) resulted in the formation of some hard, yellow material in the bottom of the vessel in addition to white powder. The product from run 401 was similar to the previous run in appearance and also contained the hard, yellow material but less white powder, perhaps because of the decreased quantity of SO_2 used in that run (7.4 vs. 14.1 g).

Run 402 made with 2-hydroxyethyl methacrylate resulted in a poor yield of only 0.42 g of a white, gummy material. The increased irradiation time for run 403 (19.27 vs. 3.27 hr), however, increased the yield to 21.88 g, but resulted in a nonhomogeneous batch of white powder and hard, white material. The higher concentration of modifier in run 404 (2 vs. 1 ml) resulted in a comparable yield and similar product except for some hard, yellow material.

High product yields were obtained in runs 405 and 406 with 1 and 2 ml of methyl methacrylate, respectively, and a uniform white powder was produced. The increased modifier concentration in run 407, however, inhibited polymerization and only 1.80 g of a white, salt-like material was produced.

In runs 408-410 made with vinyl acetate and runs 411-413 made with trimethylpropane trimethylacrylate, a uniform white powder was produced with both modifiers at relatively good rates and with little apparent inhibition at the higher modifier concentrations.

V. Pressure Molding

Discs of Et-SO₂ copolymer were pressure molded in a Carver laboratory press and then visually examined. One-inch diameter discs were pressed at 20,000 pounds (25,000 psi) in the temperature range of 175-200°C and formed hard specimens up to 0.15 inches thick.

Discs pressed from copolymer produced in runs 391, 414, and 436 were compared and showed varying amounts of copolymer degradation. All specimens were opaque but run 391 produced a disc varying in color from buff to dark amber, while the disc from run 414 was lighter in color and run 436 produced a disc that was essentially white. These differences can probably be attributed to the different irradiation times for the three runs, which varied from 18.35 hr for run 391 to 2.45 hr for run 414 and 1.00 hr for run 436. The longer irradiation times cause a greater amount of degradation by scission, to which olefin polysulfones are particularly sensitive.⁽¹⁰⁾.

One-inch discs were pressed at 20,000 pounds (25,000 psi) and at 20, 150, and 200°C with product from run 400 made with 2-hydroxyethyl acrylate as a modifier. The disc pressed at 20°C was hard, white, and quite opaque. At 150°C the disc was also white but less opaque, while at 200°C the disc showed evidence of copolymer degradation and was buff in color. All three specimens showed good uniformity.

Discs that were pressed with product from run 409 made with vinyl acetate modifier at 125 and 150°C showed severe degradation as indicated by extensive dark zones in the specimens. A pressing at 20°C with product from run 410 also made with vinyl acetate produced a hard, well-bonded specimen that was slightly translucent and mostly white with some darkened areas.

VI. Conclusions

- A. Approximately 1200 g of Et-SO₂ copolymer was prepared by liquid-phase irradiation of ethylene-SO₂ mixtures for characterization and evaluation by Inco.
- B. The copolymerization of ethylene and SO₂ by azo and peroxide catalysts was investigated briefly.
- C. The Et-SO₂ copolymer was modified by the incorporation of various monomeric acrylates and also vinyl acetate.
- D. Discs of Et-SO₂ copolymer both modified and unmodified were pressure molded at BNL.

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Table 1

Co-60 GAMMA COPOLYMERIZATION OF ETHYLENE AND SO₂

Run No.	SO ₂ g	Irradiation Time, hr	Polymer Yield g	Yield/Initial SO ₂ Wt Ratio
391	33.8	18.35	54.80	1.62
392	33.9	1.70	52.80	1.56
414	33.9	2.45	53.17	1.57
415	33.7	2.37	51.28	1.52
416	33.9	1.40	54.01	1.59
417	33.9	5.38	51.46	1.52
418	33.9	2.58	53.67	1.58
419	33.7	6.48	51.19	1.52
420	33.8	4.65	50.31	1.49
423	33.8	1.37	49.20	1.46
424	33.9	4.67	50.10	1.48
425	34.5	3.08	49.27	1.43
426	33.9	3.73	50.07	1.48
427	33.7	5.33	51.29	1.52
428	33.9	5.58	50.29	1.48
429	34.0	2.32	51.28	1.51
430	33.9	4.60	51.32	1.51
431	33.9	4.38	53.12	1.57
432	33.9	3.68	51.13	1.51
433	33.6	4.70	51.45	1.53
434	34.0	1.25	49.85	1.47
435	34.0	1.00	45.59	1.34
436	33.9	1.00	49.56	1.46
437	33.9	1.00	48.50	1.43

Table 2

COPOLYMERIZATION OF ETHYLENE AND SO₂ BY CHEMICAL CATALYSIS

Run No.	SO ₂ g	Catalyst	Time, hr (e)	Max Temp. °C(f)	Pressure, psig		Yield g	Yield/Initial SO ₂ Wt Ratio
					Initial	Peak		
421	6.5	(a)	1.55	100	2400	7200	9.12	1.40
422	12.8	(a)	1.23	100	2000	7500	10.10	0.79
439	12.4	(b)	1.13	100	1100	7800	8.60	0.69
440	11.7	(c)	1.42	90(g)	1000	5300	16.32	1.39
441	22.5	(c)	0.87	76(h)	1000	7100	23.34	1.04
442	12.1	(d)	0.95	100	1000	5800	8.48	0.70

(a) 2,2' Azobisisobutyronitrile

(b) Di-t-butyl peroxide

(c) 2,2' Azobis (2-methyl propionitrile)

(d) Benzoyl peroxide

(e) Total time period from start of heating at 0°C to start of cooling water addition.

(f) Water bath temperature. Maximum temperature of 100°C was reached in 0.60-0.70 hr.

(g) Maximum temperature was not reached until completion of run due to reduced heat rate of 50%.

(h) Heat turned off after 0.48 hr.

Table 3

Co-60 GAMMA COPOLYMERIZATION OF ET-SO₂ MIXTURES WITH MODIFIERS

Run No.	Modifier	SO ₂ g	Reaction time, hr	Product wt, g	Product Description
399	1 ml HEA	13.7	2.67	21.6	White pwdr
400	2 ml HEA	14.1	3.12	22.7	White pwdr + hard, yellow mtl
401	2 ml HEA	7.4	1.43	7.85	" " " "
402	1 ml HEMA	13.7	3.27	0.42	White, gummy mtl
403	1 ml HEMA	12.4	19.27	21.88	White pwdr + hard, white mtl
404	2 ml HEMA	14.5	19.20	24.85	White pwdr + hard, yellow mtl
405	1 ml MMA	13.3	2.07	21.92	White pwdr
406	2 ml MMA	13.3	22.97	25.48	" "
407	4 ml MMA	13.5	22.85	1.80	White, salt-like mtl
408	1 ml VA	13.2	1.00	9.46	White pwdr
409	2 ml VA	13.6	1.13	15.12	" "
410	4 ml VA	13.5	2.45	16.02	" "
411	1 ml TMPTMA	16.5	6.07	16.49	" "
412	2 ml TMPTMA	23.7	10.00	23.72	" "
413	4 ml TMPTMA	19.3	10.20	19.26	" "

Radiation intensity: 0.52 Mrad/hr

Initial pressure: ~ 1000 psig

HEA: 2-hydroxyethyl acrylate

HEMA: 2-hydroxyethyl methacrylate

MMA: methyl methacrylate

VA: vinyl acetate

TMPTMA: trimethylpropane trimethylacrylate