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POLYSULFONES FOR CONSERVATION IN THE ETHYLENE POLYMER INDUSTRY

PROGRESS REPORT NO. 7
OCTOBER 1979 - MARCH 1980

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

June 1980

DEPARTMENT OF ENERGY AND ENVIRONMENT

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BNL 51234
UC-95f
(Energy Conservation-Industry -
TID-4500)

POLYSULFONES FOR CONSERVATION IN THE ETHYLENE POLYMER INDUSTRY

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June 1980

Work Performed for the
Division of Industrial Energy Conservation
United States Department of Energy
Washington, D.C. 20545

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DEPARTMENT OF ENERGY AND ENVIRONMENT
BROOKHAVEN NATIONAL LABORATORY
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UNDER CONTRACT NO. DE-AC02-76CH00016 WITH THE
UNITED STATES DEPARTMENT OF ENERGY

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Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
Price: Printed Copy \$4.00; Microfiche \$3.00

Table of Contents

	<u>page</u>
Summary	iv
I. Introduction	1
II. Pressure Molding	2
III. Thermal Stability	4
IV. Preparation of Modified Copolymers	6
V. Summary of Characterization Studies by the INCO Research and Development Center	7
VI. Conclusions	10
References	12

Summary

Ethylene-SO₂ polysulfone copolymers were prepared by cobalt-60 gamma radiation, as well as by electron-beam radiation and by thermocatalysis, as a means of incorporating a polluting waste product material such as SO₂ into ethylene polymers for the purpose of conserving ethylene feedstock. Ethylene-SO₂ copolymer was pressure molded into discs which had a high degree of hardness as well as partial transparency, but were also very brittle. Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA) indicated peak decomposition at 350°C. Long term heat aging tests showed stability to 175°C and initiation of decomposition at 200°C in air after 900 hr. Decomposition became severe as the temperature was increased to 300°C. The activation energies for decomposition were 57.3 and 56.8 kcal/mole for liquid-phase and gas-phase formed copolymers, respectively. The ethylene-SO₂ copolymer was modified by the incorporation of monomeric styrene, 2-vinyl pyridine, 4-vinyl pyridine, and N-vinyl pyrrolidine. A summary of characterization studies by INCO which includes solubility, infra-red and x-ray analysis of the ethylene-SO₂ copolymer and with additives are presented.

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)-(8)

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, for analysis and characterization 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. 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 approximately 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 and 4.0×10^3 molecules/100eV, which were comparable to the values obtained in cobalt-60 gamma runs made at comparable conditions and in similar vessels.

During this period, the work at BNL included pressure molding and longer-term heat stability measurements of the copolymer. In addition, the Et-SO₂ copolymer was modified by the addition of other monomers to modify and possibly form terpolymers. These polymers are presently being evaluated by INCO and a summary of the preliminary results are included in this report.

II. Pressure Molding

Discs of Et-SO₂ copolymer were pressure molded in a Carver laboratory press over a range of conditions and then visually examined. Copolymer material for pressure molding was prepared in 12 to 18 g batches by polymerization of two-phase liquid-gas mixture of Et-SO₂ by means of Co-60 gamma radiation at 0.52 Mrad/hr for 15 mins. over a pressure range of 530-660 atm.

A one-half inch diameter disc was successfully pressed at room temperature from 200 mg of copolymer at 24,000 pounds (122,000 psi) and formed a hard, white specimen approximately 0.040 in. thick that was unevenly translucent. A number of discs of one-half and one-inch diameter were pressed in the temperature range of 120-200°C for 1 to 20 min at 10,000 to 24,000 pounds and up to 0.040 in. thick. Generally, these discs were clear over 50% or more of their total area but some yellow zones and black spots were also present throughout. This discoloration was more evident in the specimens pressed at higher temperatures and was no doubt due to thermal degradation of the copolymer. A disc pressed at 290°C for one minute had very pronounced discoloration.

The lack of uniformity in transparency and the presence of discoloration indicates nonhomogeneity in the physical and chemical properties of the copolymer, perhaps due to some crosslinking in the polymer structure. Although the results were not conclusive, there was some indication that the coarser fraction, which was produced in the SO₂ liquid phase in the bottom of the reaction vessel, generally formed discs with more transparency and also little or no discoloration when pressed at 175-200°C.

A density of 1.57 g/cm³ was determined from a one-inch-diameter disc pressed at 175°C and 20,000 pounds for 10 min with a final weight of 1.822 g and an average thickness of 0.090 inches. All of the discs were very hard but were also very brittle, and except for the thicker ones could easily be broken into sharp-edged fragments.

The partial success achieved in pressing transparent discs in the 175 to 120°C temperature range is perhaps due to a sintering effect rather than true melting. A melting or transition temperature as determined by differential scanning calorimetry (DSC) had been reported at 155°C in a previous report.⁽⁴⁾ A peak at that temperature has been confirmed in recent DSC measurements, but reheated copolymer specimens do not show this transition. This nonreversible exothermic effect is possibly due to formation of a stable more-dense lower energy level polymeric structure.

III. Thermal Stability

Previous thermal stability measurements for copolymers containing 50 mole % SO₂ heated for one hour in air indicated onset of decomposition at 225°C and also indicated very rapid decomposition at >275°C.⁽⁴⁾ The present study was conducted over longer time periods at 200, 225, and 250-300°C.

Equimolar Et-SO₂ copolymer previously prepared by liquid-phase SO₂ reaction with ethylene in run 246 was used in this study and compared with copolymer from the gas phase portion taken from run 373, which was performed this period. In run 373, 19.8g of SO₂ was reacted with ethylene at 537-425 atm with a 0.49 Mrad/hr Co-60 gamma source for 0.25 hr to produce a total of 18.0g of product. Approximately three grams of the top layer of this product was removed and used in this study. It is presumed that this top layer is mainly product of gas-phase reaction. The major portion of the SO₂ is present as a liquid in the bottom of the reaction vessel and produces a product that is less powdery than the material at the top of the vessel.

As in the previous study, very rapid weight losses occurred with both samples in the 250 - 300°C range (see Fig. 1). After eight hours the liquid-phase (run 246) and gas-phase (run 373) copolymers lost 56 and 85% of their respective initial weights. The liquid-phase sample retained some of its original cylindrical shape and hardness but was blackened on the initially exposed surfaces, and the subsequent exposed surfaces which formed as a result of cracking and degradation were distinctly lighter in color. The vapor-phase copolymer, which was less dense and more powdery, turned more uniformly dark gray or black in color even into the interior. At 225°C the weight losses were 26 and 54% after 94 hr., and at 200°C (see Fig. 2) the weight losses were 16 and 36% after 900 hr. for the liquid-phase and vapor-phase copolymers, respectively. Darkening and degradation in these subsequent samples was not as severe. At 175°C there were no significant weight losses in either sample after 900 hrs of exposure to air other than the initial ~2% loss which also occurred with the other samples.

In the three sets of runs at 200°C and above, the liquid-phase produced copolymer had weight losses approximately half that of the gas-phase produced copolymer. Although there were no significant differences in composition (approximately 1:1 molar ratio Et/SO₂) or in the infrared spectra of the two copolymers prior to heating, increased crosslinking could have occurred in the liquid-phase copolymer. This then could have improved its stability as a result of a reduced tendency for the ethylene and SO₂ molecules to "unzip" as had previously been suggested.⁽⁷⁾ Also, the effect of oxygen on the liquid-phase copolymer could have been reduced because of its harder and more impervious physical structure.

The linearity of the plots suggest a zero-order mechanism for decomposition. From the linear portions of the 225 and 200°C plots, activation energies

for decomposition of 57.3 and 56.8 K cal/mole were determined for the liquid-phase and gas-phase copolymers, respectively.

Et-SO₂ copolymer was prepared in run 374 under conditions almost identical to those in run 373, and samples of the mixed product were heated in air for one hour at 70, 210, and 280°C. The infrared spectra of these samples after heating are shown in Fig. 3. A significant reduction in absorbancy is apparent in the double peaks in the 3500 to 3700 cm⁻¹ wavenumber range after exposure of the copolymer to higher temperature. These peaks are due to hydroperoxide formation in the presence of oxygen and are less stable at higher temperatures. A similar change can be observed in the 1600 cm⁻¹ wavenumber region due to carbon double bonds. No other significant changes in the spectra are otherwise apparent.

IV. Preparation of Modified Copolymers

Modified Et-SO₂ copolymers were prepared for characterization by INCO by the introduction of small quantities of monomer additives to the reaction system which was initiated by Co-60 gamma radiation. Styrene, 2-vinylpyridine, 4-vinylpyridine, and N-vinyl pyrrolidone monomers purified by INCO to remove inhibitors was measured either gravimetrically or volumetrically and introduced into a 77 cm³ one-in. I.D. high-pressure reaction vessel described in previous reports.⁽³⁾⁻⁽⁸⁾ The vessel was then sealed, attached to a vacuum rack, chilled with 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 Cobalt-60 source until after equilibration to pool temperature. The reaction was monitored by observation of the pressure gauge, which at the higher pressure was

essentially ethylene pressure. After venting, the vessel was disassembled and the product, if any, removed carefully to note differences relative to position in the vessel.

The results (see Table 1) indicate that little or no polymer was formed in runs 353 - 355 and 357 with styrene. Runs 358 and 359, made at longer time periods of 70.00 and 66.55 hr, respectively, produced good yields, but the product lacked homogeneity since it contained both powder and fragments of solid material, all of which were white. Run 359 made with a larger quantity of styrene (2 ml vs. 1 ml) indicated decreased reactivity, since only 11.32 g of product was formed compared to 35.35 g in run 358. Some darker powder was also present in the product from run 359.

Additional runs made with 2-vinyl pyridine (360 and 361) and with 4-vinyl pyridine (366 and 367) also indicated sharply reduced reactivity of the three-component mixtures in comparison to pure Et-SO₂, especially in the runs that had the higher modifying monomer content (2 ml vs. 1 ml). The reduced reactivity effect was minimized in runs 364 and 365, which were made with N-vinyl pyrrolidone. The product from runs 360 - 367 also showed variation in both texture and color that was more pronounced where the additive content was higher.

V. Summary of Characterization Studies by INCO Research and Development Center

Previous work at BNL shows the relative ease and efficiency of SO₂-olefin polymerization initiated by gamma radiation. However, practical uses for the polymers have not been found. A practical, widespread application for such polymers would not only conserve our natural gas supplies, from which ethylene is made, but also consume SO₂, an inexpensive polluting waste product.

INCO has a history of successfully taking laboratory results and building them into commercially successful products. This base of experience will be used to find and develop commercially useful ethylene-SO₂ copolymers by

evaluating these polymers and recommending methods of modifying both the products and polymerization process at BNL.

During this period, the evaluation consisted of determining infra-red spectral characteristics, solubility properties and thermal formability. Samples were to be made for physical property evaluation by dynamic mechanical analysis. Transition temperatures were also to be determined by differential scanning calorimetry (DSC).

Monomeric styrene, 2-vinyl pyridine, 4-vinyl pyridine and N-vinyl pyrrolidone were purified by standard techniques (i.e., washing with aqueous alkali or acid, followed by multiple vacuum distillation over drying agents), stored under an argon atmosphere and hand delivered to BNL.

Small quantities, 1 or 2 ml. of these modifying monomers were introduced into the polymerization vessel by BNL personnel. Ethylene and SO₂ were admitted at various partial pressures and polymerization initiated by gamma radiation. Samples of the reaction products were sent to IRDC for evaluation. In addition, several samples of unmodified ethylene-SO₂ copolymers were submitted for evaluation.

To measure the physical properties of the SO₂-ethylene copolymers by the Dynamic Mechanical Analyzer (DMA) technique, we attempted to compression mold thick films (~20-30 mils). No reasonable size, handleable specimens could be prepared in the temperature range studied, 200-350°C. Small, very brittle, semi-transparent discs of ~1/4 inch diameter were obtained, but they readily shattered when handled. The use of polymeric binders at low concentrations will be examined to prepare coherent specimens.

Attempts to prepare composites of the copolymers with either polyethylene homopolymer or a polyether sulfone were unsuccessful. The copolymers were incompatible with both polymers.

The solubility of the copolymers was evaluated in the following solvents: acetone, ethanol, acetic acid, formic acid, toluene, decalin, dimethylformamide, dimethylsulfoxide, N-methyl pyrrolidone, alpha-chloronaphthalene, m-cresol, fluorobenzene, methylene chloride, distilled water, concentrated sulfuric acid and 45% w/w potassium hydroxide. The copolymers were found to be soluble only in sulfuric acid and potassium hydroxide.

Attempts at recovering the polymers from these solutions were unsuccessful. No polymer precipitated out when the solutions were poured into cold distilled water. It is quite probable that the polymer decomposed to the starting materials, SO_2 /ethylene gas, both of which might have volatilized out of the solvents, or formed soluble products.

Solubility studies on the modified terpolymers have just begun. There is some indication that these modified polymers have some solubility in several of the test solvents. These tests are ongoing.

All ethylene- SO_2 copolymers submitted for DSC analysis exhibit one well-defined transition at 350°C , a melting point accompanied by decomposition and gas evolution. No glass transitions were detected in the temperature range studied, viz. 23° - 400°C (see Figure 4).

DSC scans have just begun on the terpolymers. There is some evidence that glass transitions may exist below the decomposition temperature.

Infrared spectra, from 400 to 250 cm^{-1} , of the copolymers show only sulfone and hydrocarbon absorption along with some oxygenated species, e.g., water, hydroperoxide or hydroxyl. This is illustrated in Figure 5(a). Copolymers formed in the liquid phase and gas phase have essentially the same IR spectra.

The spectrum of sample 359A, from the lower section of the product formed in the presence of 2 ml styrene, Figure 5(b), shows the characteristic 1601 and 1450 cm^{-1} . The series of weak bands in the $2000 - 1800\text{ cm}^{-1}$ region also indicate

aromaticity. The final broad double peak at 700 cm^{-1} is also characteristic of polystyrene. This suggests that styrene may have been incorporated into the polymer as a coreactant, but further work in solvent properties will have to be done to exclude the possibility of forming the styrene-SO₂ copolymer in the presence of ethylene-SO₂ copolymer.

Both the 4-vinyl and 2-vinyl pyridine modified polymers, Figure 6(a) and (b), show characteristic absorption in the $1600 - 1400\text{ cm}^{-1}$ region. Again, whether this represents a terpolymer or a mixture of two different copolymers will be determined after further solvent studies are completed.

Low-angle x-ray diffraction patterns on the ethylene-SO₂ copolymer indicate the presence of some degree of crystallinity. The patterns resemble perturbed polyethylene peaks, as are observed in ethylene-vinyl acetate copolymers. This crystallinity, along with the presumed high molecular weight could account for the insolubility and intractability of the copolymers.

Further work will involve additional preparation of modifying monomers, characterizing the terpolymers by IR and solubility, and applying high-pressure forging or sintering techniques to obtain specimens for physical property measurements.

VI. Conclusions

A. Discs of Et-SO₂ copolymer one-half and one inch in diameter were pressure molded at BNL. They were very hard, as well as transparent to some extent, but were also very brittle.

B. Heat aging tests of Et-SO₂ copolymer indicated stability to 175°C with onset of decomposition at 200°C after 900 hr. in air. Decomposition became severe as the temperature was increased to 300°C . The activation energies for decomposition were 57.3 and 56.8 K cal/mole for liquid-phase and gas-phase formed copolymers, respectively.

C. The Et-SO₂ copolymer was modified by the incorporation of monomeric styrene, 2-vinyl pyridine, 4-vinyl pyridine, and N-vinyl pyrrolidone. Characterization work is underway at INCO.

References

1. P. Colombo, J. Fontana, and M. Steinberg, Radiation-Induced Copolymerization of Ethylene and Sulfur Dioxide in the Liquid and Gas Phases, Brookhaven National Laboratory, Report No. BNL 11347R; J. of Polymer Sci., Part A-1, 6, 3201-3215 (1968).
2. M. Steinberg, Polyketones and Polysulfones for Conservation of Ethylene Polymers, Chem. Engr. Prog. 72 (9), 75-79 (1976).
3. 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.
4. 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.
5. M. Steinberg, R. Johnson, W. Cordes, and D. Goodman, Polyketones and Polysulfones for Conservation in the Ethylene Polymer Industry, Progress Report No. 3, October-December 1978, BNL 50984.
6. M. Steinberg, R. Johnson, W. Cordes, and D. Goodman, Polyketones and Polysulfones for Conservation in the Ethylene Polymer Industry, Progress Report No. 4, January-March 1979, BNL 51034.
7. M. Steinberg, R. Johnson, W. Cordes, and D. Goodman, Polyketones and Polysulfones for Conservation in the Ethylene Polymer Industry, Progress Report No. 5, April-June 1979, BNL 51080.
8. M. Steinberg, R. Johnson, D. Elling, W. Cordes, and D. Goodman, Polyketones and Polysulfones for Conservation in the Ethylene Polymer Industry, Progress Report No. 6, July-September 1979, BNL 51155.

Table 1

Co-60 Gamma Copolymerization of Ethylene - SO₂ Mixtures with Modifiers

Run No.	Modifier	SO ₂ , g	System pressure, psig	Reaction time, hr	Product wt, g	Product Description
353	1.78 g styrene	23.1	76-83	0.33	--	No reaction
354	1.30 g styrene	10.4	975-990	2.00	--	Gummy mtl with benzaldehyde odor
355	2.67 g styrene	0.0	1520-1540	2.33	--	No reaction
357	1 ml styrene	20.0	7700-6700	0.43	--	Small amount of solids
358	1 ml styrene	19.5	7350-3630	70.00	35.35	White pwdr + solids
359	2 ml styrene	20.1	7700-6100	66.55	11.32	White + off-white pwdr
360	1 ml 2-VP	20.8	900 7420-5350	3.27 66.70	38.80	Tan powder
361	2 ml 2-VP	20.3	8080-7350	48.67	4.55	Light + dark brown pwdr
364	1 ml N-VP	20.2	1300 7000-6200	2.58 2.97	5.00	White pwdr & yellow solids
365	2 ml N-VP	19.3	8600-6650	7.00	7.24	White pwdr & yellow solids
366	1 ml 4-VP	19.5	9200-6300	13.40	13.85	White powder + solids + dark powder in bottom
367	2 ml 4-VP	19.7	7780-7005	32.08	4.62	Black powder + dark green oil-like mtl

Radiation intensity : 0.52 Mrad/hr

Pool Temp : 25 - 26°C

2-VP : 2-vinyl pyridine

4-VP : 4-vinyl pyridine

N-VP : N-vinyl pyrrolidone

Figure 1. Heat Aging of Et-SO₂ Copolymer at 225°C and 250-300°C in Air. Run 246: liquid phase; Run 373: gas phase

Figure 2. Heat Aging of Et-SO₂ Copolymer at 200°C in Air. Run 246: liquid phase; Run 373: gas phase

Figure 3. Infrared Spectra of Et-SO₂ Copolymer after Heating for one hour at 70, 210, and 280°C in air

Figure 4. Differential Scanning Calorimetry for Ethylene- SO_2 Copolymer

Figure 5. Infrared Spectra of: (a) unmodified Ethylene- SO_2 Copolymer; and (b) Copolymer modified with 2 ml of Styrene

Figure 6. Infrared Spectra of Ethylene-SO₂ Copolymer modified with:
(a) 1 ml of 2-vinyl pyridine; and with (b) 2 ml of 2-vinyl pyridine