Polysulfone from cis, cis-1,5-Cyclooctadiene and Sulfur Dioxide

Poly(9,9-Dioxo-9-Thiabicyclo[3.3.1]-Nonane-2,6-Diylsulfonyl)

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1. Procedure

Into a 1 L round-bottomed flask equipped with a thermometer, a magnetic stirrer (Note 1), and a dry ice cooled reflux condenser are placed 10.8 g (0.1 mol) of 1,5-cyclooctadiene (Note 2) and 150 mL of redistilled tetramethylene sulfone (Notes 3 and 4). The flask is cooled to -70° in a bath of acetone and solid carbon dioxide, and 16.0 g (0.25 mol) of condensed sulfur dioxide (Notes 5 and 6) is added. To the mixture at -70° are added 5 drops of ascaridole (Note 7) and 5 drops of concentrated hydrochloric acid (Note 8).

The cooling mixture is removed and the reaction is permitted to proceed with stirring for a period of 16 h at room temperature of 25°. The solution is poured into 150-200 mL of stirred solvent grade methanol in a blender under a hood. The precipitated polymer is filtered in a Büchner funnel and returned twice to the blender for washing with similar amounts of methanol. The polymer is dried overnight at 90° in a vacuum oven that has been purged with nitrogen, to yield 21 g (89%) of a white powder.

2. Characterization

The product contains 26.85% sulfur. A ratio of 2 moles of sulfur dioxide to 1 mol of 1,5-cyclooctadiene would have a theoretical value of 27.1% sulfur. The postulated intramolecular cyclization during propagation to form a [3.3.1] bicyclosulfone ring is further supported by IR spectroscopy. There is an absence of IR absorption in the region of unsaturation (1600-1670 cm⁻¹) and absorptions at 1120 and 1300 cm⁻¹ similar to those shown by pentamethylene sulfone are present.

The inherent viscosity of the product in dimethyl sulfoxide is 1.95 dL/g, even when of high molecular weight, further supports the linear structure postulated.

The polymer does not melt but decomposes with evolution of gases at temperatures over 250°.
3. Notes

1. The checkers found that an air driven stirrer is preferable to a magnetic stirrer in handling the thick mass present toward the end of the polymerization.
2. Purification of 1,5-cyclooctadiene is accomplished by distillation under reduced pressure. The portion boiling within the range 67-69° at pressures of 46-49 mm shows a purity of 99% by vapor phase analysis. The checkers used material from Ace Scientific Supply Company, 1420 East Lindon Avenue, Linden, NJ 07036, without further purification.
3. The tetramethylene sulfone was sulfolane supplied by Shell Chemical Company, One Shell Plaza, Houston, Texas 77001, purified by heating for 16 h at 180° while sparging with nitrogen. The still pot was then cooled to 150° and vacuum slowly applied to a pressure of 10 mm. A forerun of ca 2% was removed while the pot was being heated to 165° and a vapor temperature of 139°. The checkers used as received, 99% tetramethylene sulfone from Aldrich Chemical Company, 940 W. Saint Paul Avenue, Milwaukee, Wisconsin 53233.
4. The 1,5-cyclooctadiene and the tetramethylene sulfone should be well mixed at room temperature before cooling to -70°. If not, a mass of solid that is insoluble in the reaction medium can precipitate.
5. Anhydrous sulfur dioxide was withdrawn as a gas from the cylinder and condensed directly into the cooled reaction vessel. Both the authors and checkers used sulfur dioxide from Matheson Gas Products, 1275 Valley Brook Avenue, Lyndhurst, NJ 07071.
6. Concentrations of total monomer greater than 25 wt.% lead to insoluble, presumably cross-linked polymer.
7. Ascaridole is a natural-product based peroxide and was obtained from K & K Laboratories, 121 Express Street, Plainview, NY 11803, and kept frozen prior to use. Azo compounds and hydroperoxides do not initiate; other peroxides are dependent on exposure to atmospheric oxygen.
8. Hydrochloric acid decomposes the peroxide.¹
9. An \( \eta_{inh} \) of 0.93 dL/g corresponds to a \( M_w \) of 113,000. When 5 drops of methyl ethyl ketone peroxide are used as catalyst under the same conditions, 23.1 g (89%) of polymer is obtained with \( \eta_{inh} \) of 2.2, analyzing for 26.76% sulfur.

4. Methods of Preparation

Preparation of olefin-sulfur dioxide copolymers is described in many publications⁴,⁵,⁶,⁷,⁸,⁹,¹⁰,¹¹, both journal articles and patents. These and others are covered in review articles.¹²,¹³,¹⁴,¹⁵,¹⁶

5. References

2. Exxon Research and Engineering Company, P. O. Box 45, Linden, NJ 07036.