

The Synthesis of Selenium Condensation Polymers Using Bis(2-hydroxyethyl) Selenide and Bis(2-aminoethyl) Selenide

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Synopsis

Procedures were developed for the large-scale synthesis of bis(2-hydroxyethyl) selenide and bis(2-aminoethyl) selenide. These bifunctional selenides were converted into a series of polyesters, polyureas, and polyurethanes. Methods of syntheses and properties of these condensation polymers are described.

INTRODUCTION

Organic selenium polymers have received little attention, possibly because of their complex chemistry. The carbon-selenium bond is labile and is readily cleaved both thermally and under mild conditions by a variety of reagents. Organic selenides are oxidized by peroxidic reagents and may act as inhibitors to free radical-initiated polymerizations.

Originally two approaches were followed in an investigation of preparative methods for macromolecules containing selenium as a hetero atom: (1) The synthesis of vinyl derivatives of selenium and the evaluation of their polymerizing tendencies. (2) The synthesis of polyhydroxy and polyamino derivatives of aliphatic selenium compounds and their incorporation into condensation polymers, i.e., polyesters, polyureas and polyurethanes.

There appear to be no references in the literature to the polymerization of vinyl selenium compounds. However, Price and Morita¹ studied the copolymerization of vinyl phenyl sulfide and sulfone as part of an investigation on the nature of the carbon-sulfur bond and concluded that the monomers did not have strong polymerization tendencies. In the present work, studies were carried out on vinyl phenyl selenide using the sealed tube technique of Price and Zomlefer.² Neither benzoyl peroxide nor azobis(isobutyronitrile) were effective as catalysts in inducing polymerization in bulk or in benzene solution. Emulsion polymerization using a redox

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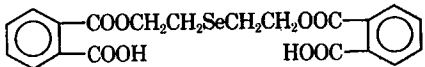
formulation based on ammonium persulfate was also unsuccessful. Thus it would appear from this exploratory investigation that the intermediate vinyl selenide radical required for chain propagation was too unstable, if it existed at all.

The failure of vinyl phenyl selenide to polymerize using standard procedures and the chemical instability of vinyl selenium derivatives supported the conclusion that this route to organic selenium polymers would not be particularly rewarding. Accordingly, investigations were carried out using bis(2-hydroxyethyl) selenide (I) and bis(2-aminoethyl) selenide (II) as starting intermediates in the preparation of condensation polymers.

Results

The condensation of bis(2-hydroxyethyl) selenide and bis(2-aminoethyl) selenide with a variety of polyfunctional isocyanates, epoxides, carboxylic acids, carboxylic acid chloride, carboxylic esters, and carboxylic anhydrides was explored. These reactions yielded polymeric materials which varied from oils to brittle solids. As a rule, the polymerizing reactions had to take place at temperatures below 150°C. At higher temperatures, decomposi-

TABLE I
Selenium Condensation Polymers Prepared from
Bis(2-hydroxyethyl) Selenide (I) and Bis(2-aminoethyl) Selenide (II)

Selenium compound	Second reactant	Results
II	Adipic acid	Bis(2-aminoethyl) selenide adipic acid salt
II	Dimethyl sebacate	Soft wax
I	Dimethyl terephthalate	Heated up to 220°C; decomposition
II	Bitolylene diisocyanate	Yellow solid; dec. 300°C, insoluble to organic solvents
II	Poly(methylene phenylisocyanate)	Tan solid; dec. 280–285°C
I	Bitolylene diisocyanate	Yellow solid; dec. 260–270°C; forms brittle films
I	Poly(methylene phenylisocyanate)	Rubber-like solid; insoluble in organic solvents
I	3,3'-Dimethyl diphenylmethane diisocyanate	Tan, brittle solid; thermoplastic, forms film
I	3,3'-Dimethoxy biphenyl 4,4'-diisocyanate	Tan, brittle solid; thermoplastic
I	Poly(methylene phenylisocyanate)	Prepolymer formed followed by cure with I; brown brittle solid
I	3,3'-Dimethoxy biphenyl 4,4'-diisocyanate	Prepolymer formed; appears to have heat-bonding properties
I	Phenylene diisocyanate	Viscous oil; Can be cured to form clear film; has adhesive properties
I	Terephthaloyl chloride	Polyol prepolymer
I	Tolylene diisocyanate	Prepolymer; sets on standing to yellow solid
I	Phthalic anhydride	 (intermediate for polyurethane)
I	Terephthaloyl chloride	Tan paste solid
II	EPON 834	Clear light yellow solid; very hard
II	Adiprene L 100	White solid; cured with II

tion resulted characterized by the appearance of elemental selenium in the product.

Table I lists the condensation reactions studied.

EXPERIMENTAL

Synthesis of Reaction Intermediates

Hydrogen Selenide. An intimate mixture of very finely divided aluminum powder (30 g, 1.11 mole) and very finely divided selenium (50 g, 0.63 mole) was converted to aluminum selenide in the following manner, using a well-ventilated area: Five grams of the mixture was charged to a 200-ml heavy-walled clay crucible fitted with a cover. A small piece of magnesium ribbon was ignited and carefully placed into the crucible, and the cover was replaced immediately. After a few seconds, 3.0 g of the aluminum-selenium mixture was added to the glowing mass in the crucible, and again the cover was replaced immediately. The remainder of the aluminum-selenium mixture was reacted in similarly small portions. After the mass in the crucible had cooled, the crusty material was removed and pulverized with a mortar and pestle. The resulting aluminum selenide is extremely reactive with water and must be used promptly or stored under anhydrous conditions.

Hydrogen selenide was generated from a four-necked flask equipped with an addition funnel, stirrer, nitrogen intake, and gas outlet. The aluminum selenide powder (80.0 g, 0.28 mole) was slurried in the generator with 100 ml of dry dimethoxymethane, and the resulting mixture was swept with nitrogen for 10 min. Water (100 g, 5.56 moles) was added dropwise over 90 min. This addition was followed by the dropwise addition of 6*N* hydrochloric acid (100 ml, 0.60 mole), then 12*N* hydrochloric acid (100 ml, 1.20 mole).

The hydrogen selenide was passed through a calcium chloride trap and then through a phosphorus pentoxide trap before being delivered to the reaction flask.

Bis(2-hydroxyethyl) Selenide. Hydrogen selenide, generated from 30 g of aluminum powder and 50 g of selenium metal as detailed above, was dissolved in 750 g of dimethyl formamide. The flask containing the hydrogen selenide solution was connected with a closed ethoxylation apparatus and cooled to 0°C. Ethylene oxide (65 g, 1.266 mole) was introduced into the DMF solution over 1 hr. The temperature was allowed to rise to 25°C. The DMF was removed by distillation in vacuo under nitrogen. The residue was distilled through a packed column. The major fraction was collected at 135–140°C at 2.6 mm Hg.

ANAL. Calcd for $C_4H_{10}O_2Se$: C, 28.4%, H, 5.96%. Found: C, 28.8%, H, 6.36%.

Bis(2-aminoethyl) Selenide. Ethylenimine (64.5 g, 1.50 mole) was charged to a four-necked flask equipped with a gas inlet extending beneath the liquid surface, a stirrer, a thermometer extending into the liquid, and a

gas outlet through a water-cooled condenser. The exit gas was passed through a calcium chloride tube and an aqueous solution of lead nitrate.

The hydrogen selenide, prepared according to the above procedure, was passed through the ethylenimine with stirring and cooling to maintain a reaction temperature below 55°C. When the hydrogen selenide generation was complete (all hydrochloric acid had been added), the system was flushed with nitrogen for 1 hr with stirring. Excess ethylenimine was removed from the reaction mixture by distillation at atmospheric pressure (bp 55°–56°C) into a receiver containing sodium hydroxide pellets. The yield of recovered ethylenimine was 20.6 g (32%). The weight of crude product remaining was 80.1 g.

The product was fractionally distilled at 0.5 mm pressure, using a 30-cm Vigreux column, collecting all distillate up through 95°C. The yield of water-white liquid was 73.3 g (66%).

ANAL. Calcd for $C_2H_{12}N_2Se$: neutralization equivalent, 83.5. Found: neutralization equivalent, 83.5.

Synthesis of Selenium Condensation Polymers

Bis(2-hydroxyethyl) Selenide. Bitolyene Diisocyanate. To 3.40 g bis(2-hydroxyethyl) selenide and 10 ml dimethyl sulfoxide was added a solution of 5.29 g bitolyene diisocyanate and 10 ml 4-methylpentanone. The mixture was heated to 115°C and maintained at this point for 1.5 hr. The reaction mixture was poured into 200 ml water to yield a tan solid. The product decomposed at 260°–270°C. It was insoluble in the usual organic solvents. The polymer could be shaped into a thin brittle film.

Bis(2-hydroxyethyl) Selenide. Poly(methylene Phenylisocyanate). Bis(2-hydroxyethyl) selenide, 4.25 g, was dissolved in 13 ml dimethylsulfoxide. To this was added a solution of 6.72 g poly(methylene phenylisocyanate) in 13.0 ml 4-methylpentanone. On warming, an exothermic process resulted in a rubbery mass. The product was dried in vacuo to yield a rubbery brown-orange solid, insoluble in organic solvents.

Bis(2-hydroxyethyl) Selenide. 3,3'-Dimethyl Diphenylmethane 4,4'-Diisocyanate. Bis(2-hydroxyethyl) selenide, 3.3 g, was dissolved in 10 ml dimethyl sulfoxide. To this was added 5.56 g 3,3'-dimethyl diphenylmethane 4,4'-diisocyanate in 10 ml 4-methylpentanone. After heating for 1.5 hr, the reaction mixture was poured into water to yield a gelatinous precipitate. The gel was dried in vacuo to a tan solid. The polymer was soluble in DMF, and this solution was used to cast a thin brittle film.

Bis(2-hydroxyethyl) Selenide. 3,3'-Dimethoxybiphenyl 4,4'-Diisocyanate. Polymer was prepared from 3.4 g bis(2-hydroxyethyl) selenide and 6.2 g 3,3'-dimethoxybiphenyl 4,4'-diisocyanate using the same procedure as above. The product was a tan, brittle solid with thermoplastic properties.

Bis(2-Hydroxyethyl) Selenide. Poly(methylene Phenylisocyanate). Bis(2-hydroxyethyl) selenide, 4.2 g, and 6.7 g poly(methylene phenyliso-

cyanate) were mixed with 3.0 ml dimethyl sulfoxide. The mixture was stirred till uniform. On standing, a dark-brown solid formed.

Bis(2-hydroxyethyl) Selenide. 3,3'-Dimethylbiphenyl 4,4'-Diisocyanate. Bis(2-hydroxyethyl) selenide, 3.38 g, and 5.2 g 3,3'-dimethylbiphenyl 4,4'-diisocyanate were mixed. To this solution was added 3.0 ml dimethyl sulfoxide, and the solution was stirred vigorously. The reaction took place immediately with the formation of a foam. After the initial reaction had subsided, the mixture was heated at 100°C for 1 hr. The product was a rigid foam.

Bis(2-hydroxyethyl) Selenide. Toluene Diisocyanate. Bis(2-hydroxyethyl) selenide, 3.38 g, was mixed with 3.34 g toluene diisocyanate (Mondor FD-80). Three milliliters of dimethyl sulfoxide was added and the solution was agitated. An exothermic reaction developed, and, when it subsided, the mixture was heated to 60°C for 6 hr. The product was a clear, viscous oil. The product exhibited adhesive properties when pressed between aluminum foil under pressure.

Bis(2-hydroxyethyl) Selenide. Terephthaloyl Chloride. The purpose of this synthesis was to prepare a prepolymer ester composed of 2 moles bis(2-hydroxyethyl) selenide and 1 mole terephthalic acid. Terephthaloyl chloride, 5.8 g, 0.029 mole, and bis(2-hydroxyethyl) selenide, 10.0 g, 0.059 mole, were mixed and reacted under a nitrogen atmosphere. The evolution of hydrogen chloride gas began immediately, and after 1/2 hr, the temperature was raised to 60°C for 1 hr. The hydrogen chloride was removed under reduced pressure. The final product was a low-melting yellow paste.

Bis(2-hydroxyethyl) Selenide. Prepolymer from Toluene Diisocyanate. The purpose of this preparation was to prepare a prepolymer from 2 moles toluene diisocyanate and 1 mole bis(2-hydroxyethyl) selenide. Toluene diisocyanate, 22.0 g, 0.118 mole, and bis(2-hydroxyethyl) selenide, 10 g, 0.059 mole, were mixed. After slight warming, the reaction was initiated and the temperature was maintained at 60°C with external cooling. The reaction was complete in several hours. The product was a very viscous, light-yellow oil.

Bis(2-hydroxyethyl) Selenide. Prepolymer from Phthalic Anhydride. **Bis(O,O'-2-carboxybenzoyl 2-oxyethyl) Selenide.** Phthalic anhydride, 14.9 g, 0.10 mole, and bis(2-hydroxyethyl) selenide, 8.44 g, 0.05 mole, were mixed and heated at 80°C for 8 hr. The final product was a viscous oil, acid number 258.5, neutralization equivalent 217.

Bis(2-aminoethyl) Selenide. Bitoluene Diisocyanate. Bis(2-aminoethyl) selenide, 3.34 g, 0.02 mole, was dissolved in 50 ml dimethyl formamide. To this solution was added bitoluene diisocyanate, 5.28 g, 0.02 mole, and the mixture stirred at ambient temperature for 1 hr. The product was poured into 500 ml vigorously agitated water. A yellow solid was isolated. The solid decomposed at 300°C and was insoluble in dimethyl formamide, dimethyl sulfoxide, methylene chloride, 80% ethanol, and acetone. The polymer was soluble in 20% sulfuric acid.

Bis(2-aminoethyl) Selenide. Polyphenyl Isocyanate. The reaction was carried out as described above using bis(2-aminoethyl) selenide, 4.2 g, DMF, 95 ml, and poly(phenyl isocyanate). Reaction was exothermic and viscosity of solution increased to a gel state. After 1 hr, the product was poured into 500 ml water. A tan solid with a decomposition point at 280°–285°C was obtained. The product was insoluble in organic solvents.

Bis(2-aminoethyl) Selenide. Adeprene L-100 (du Pont). Adeprene L-100, 100 g, was charged to a resin flask and heated to 100°C under vacuum. Nitrogen gas was introduced into the flask and 6.8 g bis(2-aminoethyl) selenide was introduced and the mixture agitated for 3 min. The viscous liquid was converted into a gel in the flask which on warming solidified to an almost white solid.

Bis(2-Aminoethyl) Selenide. Epoxy Resins. In a 100-ml beaker, 20.0 g Epon 828 was mixed with 4.0 g bis(2-aminoethyl) selenide. The solutions were mixed and poured into an aluminum foil mold and placed in an oven at 80°C for 2 hr and a final bake at 200°C for 3 hr. The product was a hard, amber-colored solid. A similar reaction was carried out with Epon 834 to yield a very tough, light-yellow solid.

Polymers Prepared from Prepolymers

Preparation EEB-50-59. The prepolymer prepared from 2 moles bis(2-hydroxyethyl) selenide and 1 mole terephthaloyl chloride, 3.01 g, was reacted with 3.81 g tolylene diisocyanate. The reaction was heated at 80°C for 5 hr in a flask protected from atmospheric moisture. The product was a yellow-green paste.

Preparation EEB-50-60. In a 50-ml resin flask, and protected from atmospheric moisture in a nitrogen atmosphere, were placed 12.14 g of the prepolymer prepared from 2 moles of tolylene diisocyanate and 1 mole bis(2-hydroxyethyl) selenide, and 2.83 g of diethylene glycol. The temperature of the flask contents was raised to 70°C, and an exothermic process resulted. A hard, yellow solid formed within a few minutes.

Preparation EEB-50-61. The preparation EEB-50-59 was reacted at 50°C with 0.8 g diethylene glycol. The paste was converted to a brittle, tan-colored solid.

Preparation EEB-50-62. Five grams of the prepolymer prepared from 2 moles bis(2-hydroxyethyl) selenide and 1 mole terephthaloyl chloride, and 2.9 g tolylene diisocyanate were mixed in a resin flask protected from atmospheric nitrogen. The mixture was heated to 60°C for 5 hr. The product was converted to a viscous liquid which contained a small amount of reactive isocyanate.

Polyurethanes from Castor Oil. To a 50-ml resin flask was added 10.2 g of the prepolymer made from tolylene diisocyanate and bis(2-aminoethyl) selenide. Chloroform, 15 ml, was added, and the mixture was agitated until complete solution was attained. The temperature was not permitted to exceed 60°C. Castor oil, 6.2 g, was added, and the solution

was heated at 60°C for 2 hr. At this point, the contents of the flask were converted to a rubbery solid.

CONCLUSION

The polymerization processes investigated in the present work indicate that, although vinyl selenium polymers cannot be synthesized by standard procedures, numerous selenium condensation polymers can be prepared using bis(2-hydroxyethyl) selenide and bis(2-aminoethyl) selenide as reaction intermediates.

Thus, polyisocyanates react readily with bis(2-hydroxyethyl) selenide and bis(2-aminoethyl) selenide. Toluene diisocyanate yielded light-colored prepolymers which were readily cured. The resulting polyurethanes had a versatile range of physical properties (oil, or rubbery or hard solids).

Dibasic acid chlorides and bis(2-hydroxyethyl) selenide form low molecular weight polyesters. However, dibasic acids and esters cannot be used for preparing selenium polymers because the high temperatures required to effect the reactions decomposed the selenide intermediate.

Prepolymerized epoxy resins react readily with bis(2-hydroxyethyl) selenide and bis(2-aminoethyl) selenide to yield clear, hard polymers.

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