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# Polyselenoacetals

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## Summary

The results of some investigations into the synthesis and characterization of a new class of oligomers and polymers, the polyselenoacetals, are described.

The investigation of acetalic and thioacetalic cyclic oligomers and polymers has been largely developed for industrial or for theoretical purposes. Particularly interesting in the theoretical investigations have been the discovery of a new crystalline modification of polyoxymethylene (orthorhombic) (*1*,*2*) and the resolution of the crystal structure of polythiomethylene (*4*).

Orthorhombic polyoxymethylene, together with the well-known hexagonal form, is an interesting case of a polymeric monotropic dimorphic system (*3*), and polythiomethylene structure has been shown to be hexagonal as one of the two crystalline modifications of isologous polyoxymethylene (*4*).

Of the *sym*-cyclic isologous oligomers the substances trioxane, trithiane, and tetraoxocane have long been well known. In recent years 1,3,5,7-tetrathiocane (*5*) and 1,3,5,7,9-pentathiacyclodecane (*6*) have been discovered and characterized, while 1,3,5,7,9-pentaoxacyclodecane is still unknown in the literature.

On the other hand, no corresponding selenium series had been reported, except some not well-defined compounds described as "selenoformaldehyde," "selenoacetaldehyde," and "selenobenzaldehyde" (*7*).

This paper deals with the results of our recent investigations of the preparation, characterization, and structures of *sym*-cyclic selenoacetalic oligomers, co-oligomers, polymers, and copolymers.

## POLYSELENOFORMALDEHYDES (CYCLIC OLIGOMERS AND POLYMERS)

Our investigations have shown that it is possible to classify the polymerizations of selenoformaldehyde (unkown in the free state) according to the following three methods: (a) polycondensation to cyclic oligomers and polymers of solvated selenoformaldehyde, obtained either from hydrogen selenide and aqueous formaldehyde or from sodium selenide and dichloromethane; (b) cationic polyaddition of *sym*-cyclic selenoformals to linear polymers, and (c), solid-state radiation polymerization of a cyclic oligomer.

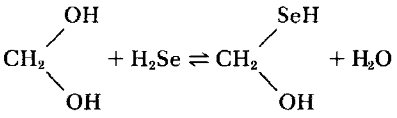
### Polycondensation

The reaction between hydrogen selenide and aqueous formaldehyde in the presence of concentrated hydrochloric acid was carried out long ago; in fact, Vanino and Schinner in 1915 (*7*) obtained by this reaction a product which, after several crystallizations, gives a crystalline solid (melting point 215°C) corresponding to the empirical (by elemental analysis) formula $CH_2Se$. It was called "selenoformaldehyde."

In 1950 Bridger and Pittman (*8*) repeated Vanino's experience: they ascertained by molecular-weight determinations that the compound described as "selenoformaldehyde" is the trimer of selenoformaldehyde and proposed a cyclic structure.

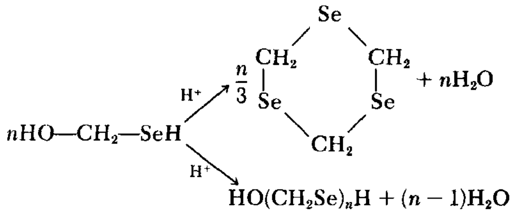
Only recently (1965) we and others proved (*9,10*) that the reaction between hydrogen selenide and aqueous formaldehyde in the presence of hydrochloric acid gives the cyclic trimer of selenoformaldehyde, namely 1,3,5-triselenane, together with the linear polymer of selenoformaldehyde, polyselenomethylene.

It is well known that formaldehyde in its dilute aqueous solutions is almost completely hydrated in the form of *gem*-diol (methylene glycol); therefore, it is reasonable to suppose that, when hydrogen selenide is bubbled in this system, a reaction between hydrogen selenide and formaldehyde will take place with the formation of methylene selenoglycol in equilibrium with methylene glycol through an interchange of hydrogen selenide and water:



$$CH_2\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix} + H_2Se \rightleftharpoons CH_2\begin{matrix}\diagup SeH\\ \diagdown OH\end{matrix} + H_2O$$

In a second step, catalyzed by hydrochloric acid, there is elimination of water among methylene selenoglycol molecules, giving the trimer and the polymer:



The cyclic trimer (separated from the solid by a Soxhlet apparatus with benzene or ethanol) is a crystalline solid (needles) with a melting point (determined in a sealed narrow capillary, to avoid sublimation or decomposition) of 226 to 228°C. At 20° its solubility is 0.53% in dioxane, 0.39% in benzene, 0.47% in tetrahydrofuran, and 0.76% in dimethyl formamide. Its cyclic structure has been proved by x-ray analysis, owing to its isomorphism with the isologous 1,3,5-trithiane; therefore, the triselenane is orthorhombic with the chair configuration.

The polyselenomethylene obtained from $CH_2O—H_2O—H_2Se$ system appears as a white powder, highly crystalline to x-rays and highly insoluble, which begins to melt at 133 to139°C with partial decomposition.

The high-polymer crystallinity is a consequence of the selenoformaldehyde solvation (as methylene selenoglycol) in the aqueous system, in which the driving force of addition to the selenocarbonyl group is not present; therefore, the driving force of crystallization is now of sufficient importance to cause the polymer to be highly crystalline.

By annealing the polymer at 125°C it is made to undergo at first a limited weight loss (of a few per cent), after which it remains quite stable at this temperature; the melting range of the annealed product rises to 174 to 178°C. The annealing causes either a loss of oxymethylenic units at the extremity of the chains or a condensation between the selenomethylenic residues; the last hypothesis is justified by the increase of the melting range.

The crystalline structure of this polyselenomethylene, recently solved (*11*), has been proved to consist of a hexagonal unit cell with twenty-one —$CH_2Se$— units and eleven turns of the helix in the identity period of 46.25 A.

It is interesting that the isologous polythiomethylene (*4*) and polyoxymethylene (*12*) have a hexagonal unit cell, the latter in one of the two crystalline modifications of its dimorphic system. Hexagonal polyselenomethylene and triselenane have also been prepared by us and others, together with a new *sym*-cyclic oligomer (tetramer) of selenoformaldehyde, namely 1,3,5,7-tetraselenocane (*13*), by polycondensation between sodium selenide and dichloromethane in aqueous methanol medium. The polymer obtained in this way shows the same characteristics of polyselenomethylene obtained by the $CH_2O$—$H_2O$—$H_2Se$ system: the crystalline structure is hexagonal, and the melting range is low (120 to 130°C) but increases to 150 to 165°C by melting under vacuum. The initial low melting range (and, therefore, the low molecular weight) is a consequence of the relatively slow rate of condensation in connection with the high insolubility of the polymer.

1,3,5,7-Tetraselenocane is a crystalline solid with a melting point of 80 to 81°C. It is soluble in organic solvents, such as benzene, dichloromethane, and chloroform, and insoluble in water (like all *sym*-cyclic thio- and selenoformals). The crystalline system of tetraselenocane is orthorhombic.

## Polyaddition

Until now this has been the only polymerization method of obtaining high-molecular-weight polyselenomethylene. We have ascertained that both 1,3,5-triselenane (*10*) and 1,3,5,7-tetraselenocane (*13*) polymerize in bulk, with cationic initiators (probably via a mechanism similar to the one reported for the cationic polyaddition of isologous *sym*-cyclic formals and thioformals), to polyselenomethylenes, which melt at 185 to 190°C and 187 to 195°C, respectively.

Owing to the insolubility of polyselenomethylene in all the common organic solvents and in solvents for polyoxymethylene and polythiomethylene, even at temperatures above its melting point, it was not possible to measure its viscosity. However, the higher melting ranges of the polymers obtained by polyaddition show that they have higher molecular weights than the polymers obtained by polycondensation. Moreover, we have ascertained that, whereas bulk polymerization of triselenane gives polyselenomethylene with a hexagonal unit cell, similar to that obtained in the polycondensation process, the bulk polymerization of tetraselenocane gives a polyselenomethylene with a new crystalline structure. A polyselenomethylene with the same structure has been obtained also by Carazzolo and Mammi by solid-state radiation polymerization of triselenane (*14*). This new crystalline modification of polyselenomethylene has been solved and consists of an orthorhombic unit cell with two —$CH_2Se$— units and one turn of the helix in the identity period of $C = 4.27$ A (*14*). The two crystalline modifications of polyselenomethylene give rise to a monotropic system with an orthorhombic-to-hexagonal transition temperature near the melting range of hexagonal polyselenomethylene (185 to 190°C).

It is very interesting that the same monotropic dimorphism, orthorhombic-hexagonal, discovered in the polyselenomethylene appears also in the isologous polyoxymethylene.

### Solid-State Radiation Polymerization of Triselenane

Carazzolo and Mammi (*14*) obtained orthorhombic polyselenomethylene by exposition of crystals of triselenane to a gamma radiation dose of 64 Mrad at room temperature; radiated crystals have been subsequently annealed at various temperatures in the range 60 to 120°C. The sample annealed at 100°C and below proved to be unchanged triselenane, but the sample annealed at 120°C proved to be partially polymerized (about 20%) to orthorhombic polyselenomethylene.

## COPOLYMERS WITH FORMALDEHYDE AND SELENOFORMALDEHYDE UNITS

By the reaction of $\alpha,\alpha'$-dichlorodimethyl ether with sodium selenide in anhydrous methanol or in water–methanol medium we obtained (*15*) a linear copolymer $-\!(-CH_2O-CH_2Se-)_{\overline{n}}-$, together with a cyclic cooligomer formaldehyde–selenoformaldehyde, 1,3,5-oxadiselenane.

The low melting range (80 to 95°C) and the solubility in hot benzene of the copolymer proves that it has a low molecular weight.

Oxadiselenane is a crystalline solid (scales) melting at 74 to 76°C. It is soluble in organic solvents such as dichloromethane, benzene, and acetone and is insoluble in water. We ascertained that oxadiselenane polymerizes in bulk with cationic initiators, giving a linear high-molecular-weight copolymer $-[-CH_2O-(-CH_2Se)_2-]_n-$ melting at 193 to 198°C.

The copolymeric nature of the two polymers with different $CH_2O/CH_2Se$ ratios has been proved by x-ray analysis: x-ray powder spectra of both polymers show that the more intense reflection corresponds to an interplanar spacing intermediate between that of hexagonal polyoxymethylene (*1*) and that of hexagonal polyselenomethylene (*10*).

## OLIGOMERS AND COOLIGOMERS OF SELENOACETALDEHYDE

Selenoacetaldehyde, as its lower homologue, is unknown in the free state.

In 1915 Vanino and Schinner (*7*), through the reaction of hydrogen selenide with ethanolic acetaldehyde in the presence of hydrochloric acid, obtained some crystalline products corresponding to the empirical formula $CH_3CHSe$ (by elemental analysis), described as different modifications of "selenoacetaldehyde."

Our work, carried out on the anhydrous system acetaldehyde + hydrogen selenide + ethanol in the presence of hydrochloric acid, have shown that at room temperature the formation of the cyclic trimer of selenoacetaldehyde, namely, 2,4,6-trimethyl-1,3,5-triselenane (triselenoacetaldehyde), takes place.

Triselenoacetaldehyde is a crystalline solid melting at 144°C: its crystalline system is orthorhombic. In the reaction of hydrogen selenide with acetaldehyde in aqueous solution in the presence of hydrochloric acid, the temperature maintained in the range 0 to 5°C, the formation of 2,4,6-trimethyl-1,3,5-dioxaselenane (monoselenoparaldehyde) takes place.

Monoselenoparaldehyde is a crystalline solid with a melting point of 55°C, soluble in acetone and insoluble in water: its crystalline system is tetragonal.

Both monoselenoparaldehyde and triselenoacetaldehyde have a characteristic biting odor. Their cyclic structure has been proved by x-ray analysis (*16,17*).

## "TELLUROFORMALDEHYDE"

Hoping to obtain cyclic oligomers and polymers of telluroformaldehyde we attempted the reaction of sodium telluride and dichloromethane in methanol and in aqueous methanol medium (by refluxing for 4 hr). The experiments were unsuccessful.

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## Zusammenfassung

Dieser Artikel beschreibt die Ergebnisse einiger von uns ausgeführten Forschungen über die Synthese und das Kennzeichnen einer neuen Reihe von Oligomeren und Polymeren, den Polyselenacetalen.

## Résumé

On décrit les résultats de quelques recherches sur la synthèse et la caractérisation d'une nouvelle catègorie d'oligomères et de polymères, les polysélénoacétals.

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