### POLYSELENOMETHYLENE

During investigation on polymers of thioformaldehyde and selenoformaldehyde, the cyclic trimer of selenoformaldehyde, 1,3,5-triselenane (I) was polymerized to polyselenomethylene.



"Selenoformaldehyde" had been prepared long time ago (1) by reaction of hydrogen selenide with formaldehyde in aqueous solution, in the presence of concentrated hydrochloric acid, and its empirical formula had been obtained from elemental analysis (1,2). By molecular weight determination it has been ascertained that this compound is a trimer of selenoformaldehyde (3), however no ring structure was shown.

During this reaction we obtained a separation of a white solid, from which triselenane was extracted by treatment with ethanol in a Soxhlet extractor. By x-ray analysis, we have found that this compound is the cyclic trimer of selenoformaldehyde, 1,3,5-triselenane (I), with an orthorombic crystalline lattice isomorphous with 1,3,5-trithiane, but not with 1,3,5-trioxane (4).

However, after extraction, a large quantity of product remained unextracted. This material began to melt at  $133-139^{\circ}$ C. with partial decomposition and it was also insoluble in all usual organic solvents at temperatures above its melting point. X-ray analysis showed that this product was the linear polymer of selenoformaldehyde, polyselenomethylene. Its structure had been proved to be hexagonal (5), as polythiomethylene (6), and as one of the two structure of polyoxymethylene (7). Now linear polyselenomethylene had been obtained by bulk polymerization with cationic catalyst (e.g., BF<sub>3</sub>). This polymerization probably proceeds via a mechanism similar to that reported for the polymerization of trioxane (8) and of trithiane (9).



The complex (II) undergoes a reaction of ring opening with formation of a resonance-stabilized carbonium ion (III) and the initiation of the polymerization is completed.

## Preparation of 1,3,5-Triselenane and Polyselenomethylene in Water Solution

A large amount of hydrogen selenide was bubbled into a solution composed of 55 g. of aqueous formaldehyde 35 wt.-% and 145 g. of concentrated hydrochloric acid. After 15 min., the precipitation of a white solid starts. After 4 hr., the reaction was stopped and the crude product was separated (yield, calculated as  $CH_2Se$ , 57.7%), washed with water and ethanol, dried, and extracted with ethanol in a Soxhlet extractor. Triselenane goes into solution, while polyselenomethylene remained unextracted.

Triselenane was recovered from the solution (48 wt.-%) by evaporation of the solvent and crystallized twice by hot benzene. Analysis: found: C, 13.1; H, 2.3; Se, 84.3; calcd. for  $(CH_2Se)_3$ : C, 12.9; H, 2.15; Se, 85.0. The melting point of triselenane cannot be determined in air, owing to its tendency to sublime. However we have determined a sharp melting point at 226-228°C. in a sealed capillary with a microscope. Different values reported in literature (205-215°C) (1-3) may be due to the described phenomenum.

The unextracted polymer has been purified by further treatment in a Soxhlet extractor with benzene. Polyselenomethylene appears as a white powder that melts between  $133-139^{\circ}$ C., with partial decomposition. By annealing at  $125^{\circ}$ C. for 3 hr., this sample loses the 15% of its starting weight; after this treatment the sample is indefinitely stable at this temperature and shows a sharp melting point at  $174-178^{\circ}$ C.



Fig. 1. Powder patterns obtained by high angle spectrometer using CuKa radiation: (A) hexagonal polyselenomethylene; (B) hexagonal polythiomethylene; (C) hexagonal polyoxymethylene.

Analysis: found: C, 13.60; H, 2.35; Se, 84.2. Yield of extraction on the crude product, 51%.

# Polymerization of 1,3,5-Triselenane

In a pyrex polymerization tube, 10 g. of triselenane were heated at a temperature of  $235^{\circ}$ C. under a nitrogen atmosphere. When the triselenane

was completely melted, 0.01 g. of BF  $_3$ -etherate was added as a polymerization initiator.

The reaction goes very fast and, at the temperature of reaction, the resulting polymer appears as a brown viscous melt that becomes solid under 200°C.

The polyselenomethylene was then removed from the tube, extracted with hot benzene to remove unreacted triselenane, and vacuum dried at  $80^{\circ}$ C. Polymerization yield: 74.6%. Melting range:  $185-190^{\circ}$ C. Analysis: found: C, 12.8; H, 2.25; Se, 84.1%.

### Properties

Owing to the insolubility of polyselenomethylene in all common organic solvents, and in solvents for polyoxymethylene and polythiomethylene even at temperatures above its melting point, it was not possible to measure viscosity. Nevertheless, it is thought that the polymer obtained from the anhydrous reaction has a higher molecular weight than polymer obtained from an aqueous solution. This may be confirmed by the higher melting point of the polymer from bulk polymerization and by the kinds of reactions by which the polymers were obtained.

Both the products from bulk polymerization and from solution have been proved by x-ray analysis to be hexagonal polyselenomethylene which consists of an hexagonal unit cell with a = 5.22 A. and c = 46.25A., crossed by one helical chain parallel to the c axis;  $21 - CH_2Se$ units and 11 turns of the helix comprise the identity period of 46.25 A. (5).

A powder pattern obtained by a high angle spectrometer (using CuK $\alpha$  radiation) of polyselenomethylene is shown in Figure 1(A) together with the patterns of hexagonal polythiomethylene (B) and of hexagonal polyoxymethylene (C).

We have examined the thermal stability of polyselenomethylene obtained by cationic polymerization of 1,3,5-triselenane. This sample, heated at 220°C. for 1 hr. under vacuum, loses 8% of its starting weight.

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Received December 28, 1964 Revised March 30, 1965