Crystallization during polymerization of selenium from the vapour phase

H. -C. Shu* **and B. Wunderlich**
Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181, USA

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The kinetics of crystal growth of trigonal selenium from the vapour phase has been studied between 440.5 and 473.0K at vapour pressures ranging from 34.4 to 293 Pa. The crystal growth was found to be dependent upon the supercooling to the 2.5 power, in contrast to melt crystallization which has an exponential supercooling dependence. From the vapour pressure–growth rate correlation there is evidence that the active species in crystallization is Se_2. Crystallization of Se from the gas phase is an example of crystallization during polymerization.

INTRODUCTION

Selenium has been the subject of many investigations because of its interesting properties and important technological applications[1,2]. In the gaseous state, selenium contains a mixture of various rings (Se_n, $n = 4$ to 10) and short chain molecules (Se_n, $n = 1$ to 3)[3–8]. In the solid state, selenium occurs in four allotropic forms. The stable crystal form is trigonal, containing helically arranged flexible macromolecules[9]. Two metastable crystal forms[10] are monoclinic; they contain Se_8 rings[11]. Glassy, amorphous selenium, finally, is composed of a mixture of Se_8 rings and macromolecules[12]. In the liquid state, selenium is composed of a similar mixture of rings and chains. The latter decrease in molecular weight with increasing temperature, while the concentration of rings decreases with increasing temperature[13,14].

Selenium is particularly amenable to crystallization during polymerization[15] from the molten[16,17] and the gaseous phases[18–21] to yield large crystals of extended-chain macroconformation. The transitions among the various solid phases[21,22] and crystallization and melting[17,21,23] have been discussed elsewhere. In this paper, the first quantitative kinetic study of selenium single crystal growth from the vapour phase is presented.

EXPERIMENTAL

Material

The selenium used for all experiments was of 99.999% purity (supplied by the Materials Research Corporation, Orangeburg, New York). It was utilized without further purification.

X-ray diffraction

Diffraction patterns for identification were taken with a General Electric XRD-3 Diffraction unit with nickel-filtered Kα radiation.

Thermal analysis

Differential scanning calorimetry (d.s.c.) was carried out with a Perkin–Elmer DSC-2 or a DuPont 990 thermal analyser (DuPont 910 DSC cell). Dry nitrogen was continuously flowing through the d.s.c. cell. The temperature calibrations were carried out by melting standard compounds[24].

Microscopy

Selenium crystals were, when needed, analysed by standard optical microscopy (Leitz, polarizing microscope) or electron microscopy (JEOL-JEM-30, carbon–chromium replica with 6–10 nm resolution).

Isothermal crystal growth

A constant temperature crystal growing system was set up as shown schematically in *Figure 1*[25]. A ceramic boat served as the Se source. The crystallization chamber was

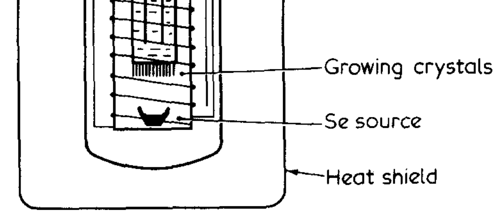

Figure 1 Schematic representation of the isothermal crystal growing apparatus

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[*] Present address: General Electric Company, Product Technology Group, Selkirk, New York 12158, USA

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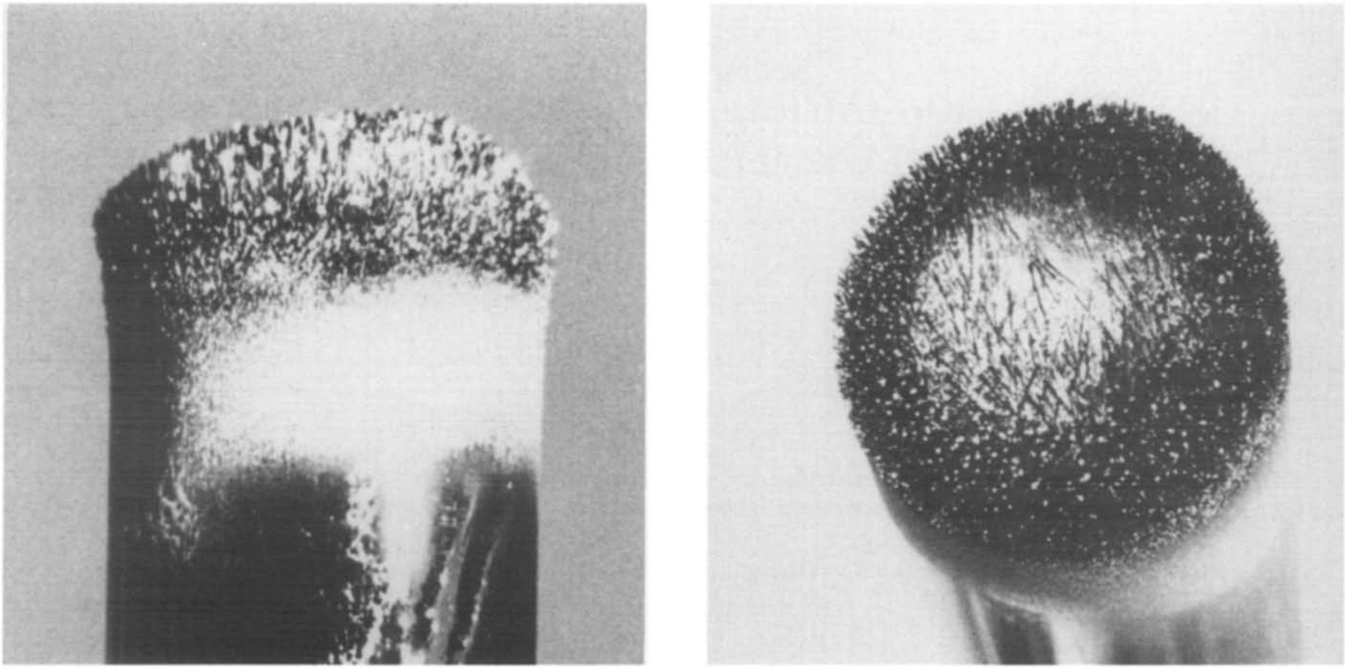

Figure 2 Typical photograpns of Se crystals grown in the crystal growing apparatus (Diameter of the cold finger about 1.6 cm)

initially evacuated to pressures less than 3×10^{-2} Pa. The selenium pressure was then set by heating the source to temperatures between 543 and 653K, controlled to ±0.5K. The crystals grow at the tip of a cold finger which was kept at a given temperature below the melting temperature, controlled by circulating silicone fluids to ±0.5K. The advance of the tips of the growing selenium needles was measured with a cathetometer to ±0.1 mm. After a period of growth (usually days), the system was allowed to cool to room temperature for analysis of the crystals. Isothermal conditions during growth were maintained within a few tenths of 1°C because of the large thermal conductivity difference between gaseous and crystalline selenium at the temperature in question (ratio about 300).

RESULTS

A total of 11 successful growth experiments were carried out at various crystallization temperatures and Se source temperatures (vapour pressures). *Figure 2* shows two views of a typical group of selenium crystals on the cold finger of the crystal-growing apparatus (*Figure 1*). The data are listed in *Table 1*.

The melting temperature of the grown crystals was determined to be 494.2 ± 0.1K. Their heat of fusion was 6.20 kJ (mol Se)$^{-1}$, in good accord with literature data[1]. X-ray diffraction showed the crystals to be trigonal and that the growth direction (needle-axis) was, as expected, the molecular helix axis. Each needle represented a single crystal.

Also listed in *Table 1* are values of the overall vapour pressure of liquid selenium at the source temperature, calculated from[26]:

$$\ln P = 23.568 - 1.1538 \times 10^4/T \qquad (1)$$

and values of the crystal vapour pressure calculated from[27]:

$$\ln P = 36.157 - 1.760 \times 10^4/T \qquad (2)$$

Table 1 Vapour phase crystal growth rates

Run No.	T_s(K)[a]	T_c(K)[b]	J(nm s^{-1})[c]	P_s(Pa)[d]	P_0(Pa)[e]
9	576	440.5	8.2	34.4	0.022
7	587	440.5	17.4	50.0	0.022
12	609	440.5	50.0	101.7	0.022
8	618	440.5	84.8	134.1	0.022
10	645	440.5	267.0	293.0	0.022
16	624	473.0	5.3	160.5	0.347
20	624	466.0	11.8	160.5	0.199
15	621	464.0	14.1	146.8	0.169
19	630	460.0	12.9	191.4	0.127
14	626.5	455.5	19.0	172.8	0.084
17	621.3	450.5	26.7	148.1	0.054

[a] Temperature at the selenium vapour source (see *Figure 1*)
[b] Temperature of the growing crystal at the cold finger (see *Figure 2*)
[c] Linear crystal growth rate in direction [001] (helix-axis direction)
[d] Vapour pressure in the crystal growing chamber, set by the source temperature (equation 1)
[e] Vapour pressure of the growingcrystal, calculated from equation (2)

The pressures, P, in equations (1) and (2) are in Pa, the temperatures, T, in K.

DISCUSSION

Runs 8, 14 to 17, 19 and 20 were carried out at largely constant vapour pressure so that the changes in crystal growth rate are a measure of the supercooling dependence. Assuming a functional relationship:

$$J = A \Delta T^x \qquad (3)$$

leads to an exponent of about 2.5 (standard deviation of J, ± 12%). Assuming a functional relationship:

$$J = A \exp[-1/T\Delta T] \qquad (4)$$

gives a somewhat poorer fit (standard deviation of J, ± 20%).

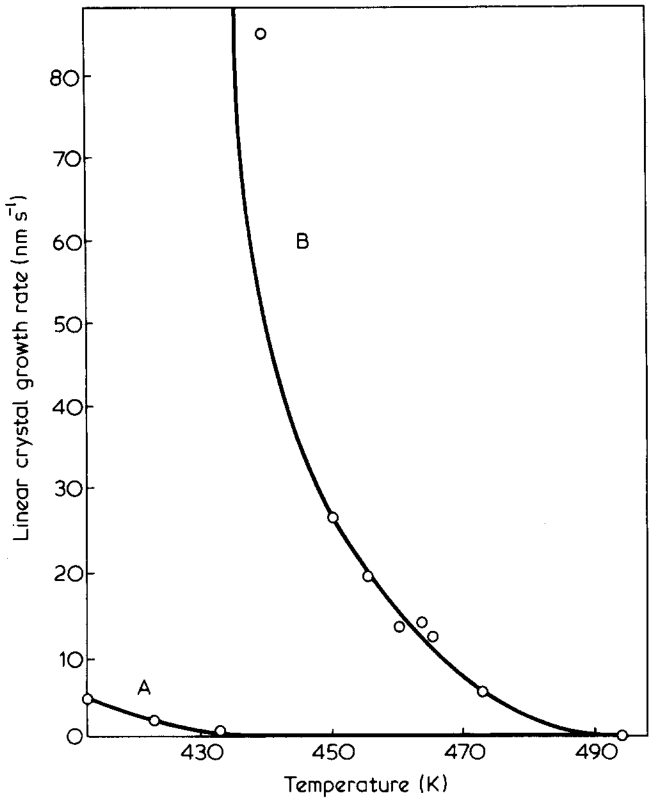

Figure 3 Linear crystal growth rates of selenium. A, Data on melt crystallization by Crystal[16]; B, Data on vapour phase growth from Runs 8, 14 to 17, 19, and 20. Average vapour pressure 160 Pa

A comparison with linear growth rate data from the melt is shown in *Figure 3*. Considering the low overall vapour pressure in the gas phase (~160 Pa), melt growth is considerably retarded relative to crystal growth from the vapour phase. Also, the melt growth follows clearly an exponential supercooling dependence (equation 4) as is typical for all analysed flexible linear macromolecules crystallizing from polymeric melt or solution[28]. It was shown earlier that on crystallization from the melt, which consists of a mixture of rings and chains, the chains are depleted first[17]. The main reason for an exponential supercooling dependence is the need of molecular nucleation before addition of a new molecule to the crystal[28]. For crystallization from the vapour phase there seems to be no need for molecular nucleation. The process is thus most likely a simultaneous crystallization and polymerization. Equation (3) with an exponent 2 would suggest a normal growth spiral crystallization mechanism[28] as found frequently in the crystallization of small molecules from the vapour phase.

The constant crystallization temperature data of *Table 1* (Runs 7 to 10 and 12) have been taken in an attempt to establish the active species in the crystallization. Vapour pressure curves of the various species were derived from their mole fractions in the vapour phase[3] using the general equation:

$$\ln P_v = B - \Delta H_v/(RT) \qquad (5)$$

For the species Se_2, Se_3, Se_5, Se_6, and Se_7 the equations are listed below in sequence; ΔH_v gives an estimate of the molar heat of evaporation (J):

$$\ln P_2 = 24.64 - 1.124 \times 10^5/(RT) \qquad (6)$$

$$\ln P_3 = 22.10 - 1.172 \times 10^5/(RT) \qquad (7)$$

$$\ln P_5 = 23.69 - 1.005 \times 10^5/(RT) \qquad (8)$$

$$\ln P_6 = 17.58 - 0.742 \times 10^5/(RT) \qquad (9)$$

$$\ln P_7 = 17.50 - 0.784 \times 10^5/(RT) \qquad (10)$$

Fitting the separate vapour pressures to a linear least squares expression to the growth rates gives the best fit for the species Se_2 (the standard deviation ± 6 nm s^{-1}, Se_2 vapour pressure 2–40 Pa):

$$J(\text{in nm s}^{-1}) = -11.651 \pm 7.3576\, P_2\, (\text{in Pa}) \qquad (11)$$

All other species, and also the overall vapour pressure (equation 1), give standard deviations ranging from 14 to 24 mol s^{-1} when fitted to a least squares straight line equation. Comparing our crystallization studies with evaporation studies[29] reveals that the primary species involved in evaporation is also Se_2. Before equilibrium is reached in the gas phase, Se_2 is present in excess.

The efficiency of collisions of Se_2 molecules with the growth surface was estimated from the above vapour pressure and crystal growth rate data. At 576K (Run 9), one out of every 172 molecules hitting the crystal surface would have to crystallize. The fraction increases with temperature and reaches at 645K vapour temperature (Run 10) one out of every 65 molecules. Using an Arrhenius-type expression, an activation energy of 43 kJ (mol Se_2)$^{-1}$ in the adsorption process can be calculated from these data.

A study of the condensation of liquid selenium from the vapour seems to indicate that polymerization is also in this case the rate determining step[21]. In addition, there seems to be little evidence for any ring species other than Se_8 in the liquid state. The Se_8 is thought to be formed by 'backbiting' depolymerization of the macromolecule. It may be thus suggested that for all evaporation and condensation, Se_2 is the major species, while crystallization and melting involves mainly the macromolecule.

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