On the Growth Rate of Selenium Spherulite

Shuichi Hamada

Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo

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The radial growth rates of the selenium spherulites were measured by the microscopic method at temperatures ranging from 128.4°C to 192.3°C. The radial growth rate increased with an increase in the crystallization temperature up to about 180°C, reached a maximum value of 87.0 μ/min, and then decreased abruptly, judging from the observation of organic polymers at crystallization temperatures near their melting points. The process of the spherulite growth of selnium near the melting point could not be interpreted by only two elementary processes, that of the segmental jump and that of the formation of a two-dimensional nucleus of a critical size. The variation in the radial growth rates of selenium with the temperature was explained by considering the bond-breaking process as an elementary process. The estimated surface free energy at the liquid-crystal interface was 25.1 erg/cm^2; this value was a reasonable one.

When amorphous selenium is crystallized under atmospheric pressure, it grows in a spherulite form,[1] just like such organic polymers as polyethylene adipate, polyethylene succinate, and nylon 6. In general, the rate-determining step of the spherulite growth well below the melting point is considered to be the process of the segmental jump at the liquid-crystal interface, whereas the process of the spherulite growth near the melting point is governed mainly by the effort needed to overcome the surface free energy of the two-dimensional nucleus formed on the liquid-crystal interface.[2,3]

Because the temperature coefficient of the growth rate of the selenium spherulite is much larger than that expected from the process of the segmental jump well below the melting point, the process of the Se-Se bond breaking was suggested as one of the elementary processes associated with the spherulite growth.[4] In the present work, this concept will be discussed on the basis of the behavior of the selenium spherulite growth near the melting point.

Experimental

Materials. The selenium was obtained from the Yokozawa Chemical Company; its purity was guaranteed to be better than 99.999%. The selenium was melted at 230°C for 1 hr in an electric furnace and was then quenched on a microscopic cover-glass in order to prepare the sample. The samples were stored in a cooled desiccator.

Procedure. An Olympus reflecting microscope, Model STS, was used to measure the radial growth rates of selenium spherulites. The sample was at first melted at 230°C for 1 hr in a heating block mounted on the microscope, was cooled rapidly to 130°C in order to develop the nuclei, and was then heated again quickly to the specified temperatures. The selenium spherulites were grown isothermally at temperatures ranging from 128.4°C to 192.3°C. The radii of the spherulites formed on the surfaces of the selenium samples were estimated by measuring microscopic photographs. The temperatures of the heating block were calibrated by using materials of known melting points.

An X-ray diffractometer, Model JDX-5P, from the Japan Electron Optics Laboratory was used to obtain the X-ray powder diffraction patterns of the selenium crystallized in the temperature range from 99.5°C to 174.4°C.

Results

The radii of the spherulites varied linearly with the heating times, and the slopes of all the radius-time curves were nearly equal at a specified temperature, regardless of the developing periods of the nuclei, as was observed in a previous work.[4] Figure 1 shows the linear variations of the radius-time curve of the selenium spherulites at temperatures ranging from 128.4°C to 192.3°C. The slopes of the linear relationships increased as the crystallization temperatures increased up to about 180°C, whereas they decreased above 180°C. The radial growth rate, G, of the selenium spherulite was estimated from the slope of the radius-time relationship,

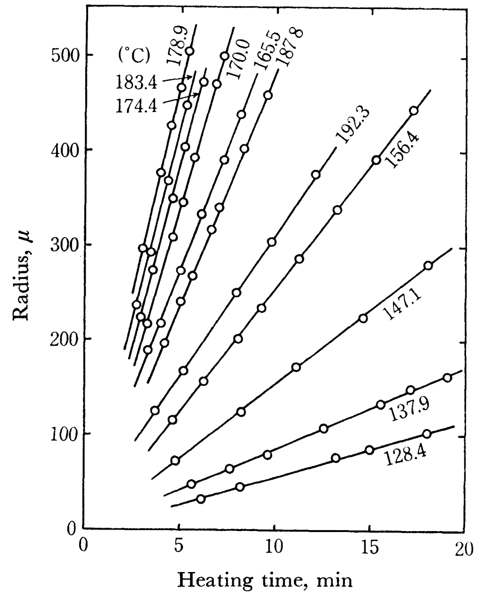

Fig. 1. Radial variation of selenium spherulite with heating time.
(The figure is illustrated by voluntary shifts of the heating times.)

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[1] P. T. Kozyrev, *Soviet Physics-Technical Physics*, **28**, 470 (1958).

[2] M. Takayanagi, M. Nakao, and S. Machida, *Kogyo Kagaku Zasshi*, **59**, 549 (1956).

[3] B. B. Burnet and W. F. McDevit, *J. Appl. Phys.*, **28**, 1101 (1957).

[4] S. Hamada, T. Sato, and T. Shirai, This Bulletin, **40**, 864 (1967).

Table 1. Radial growth rates of selenium spherulites

Temp., °C	G, μ/min	Temp., °C	G, μ/min
128.4	6.0	174.4	77.9
137.9	8.7	178.9	87.0
147.1	15.8	183.4	81.0
156.4	26.2	187.8	50.3
165.5	52.0	192.3	29.7
170.0	72.6		

shown in Fig. 1. The values of G at the specified temperatures are given in Table 1.

The dependence of G on the crystallization temperature is shown in Fig. 2. The radial growth rate increased with an increase in the crystallization temperature up to about 180°C, reached a maximum value, and then decreased abruptly. Figure 3 shows the dependence of $\log G$ on $1/T$. The relationship of $\log G$ to $1/T$ at temperatures ranging from 128.4°C to 165.5°C is regarded as linear, and the slope in the temperature range is nearly equal to that at temperatures ranging from 70°C to 120°C.[4] The linear relationship varied discontinuously at about 125°C, though the slopes in the temperature ranges both above and below 125°C did not change. The results on the spherulite growth rate below 120°C presented in the previous work[4] were obtained from a crystallization without preheating, as has been described in the "Procedure" section of this paper. The discontinuity in the growth rate at approximately 125°C was also observed from the crystallization without preheating in the temperature range above 125°C, but slightly lower values were obtained than those with preheating. Such discontinuous changes in the radial growth rates, G, have often been observed in the growth of organic chain-polymer spherulites.[2]

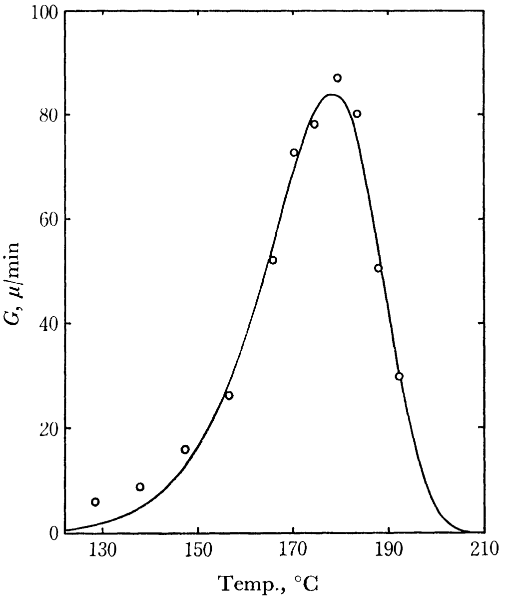

Fig. 2. Plot of radial growth rate of selenium spherulite against crystallization temperature.
○: observed —: calculated

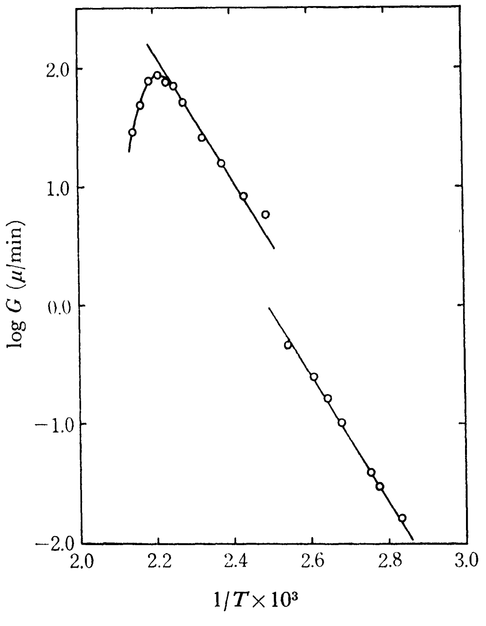

Fig. 3. Arrhenius plot of log G.
(The results below 120°C are reproduced from Ref. 4.)

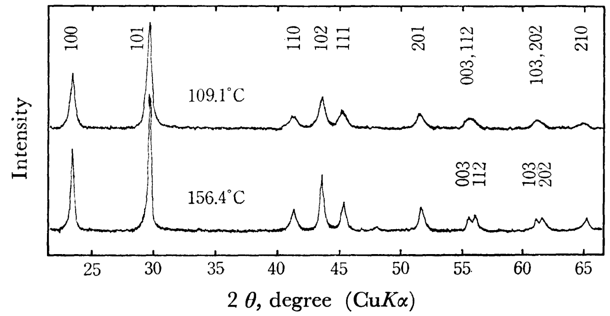

Fig. 4. X-Ray powder diffractograms of selenium crystallized at 109.1°C and 156.4°C.

Figure 4 shows X-ray powder diffraction intensity diagrams of the selenium crystallized at 109.1°C and 156.4°C, as examples for the samples obtained below and above 125°C respectively. A slight shift in the diffraction peaks was observed at crystallization temperatures between 118.9°C and 128.4°C. The values of the unit cell axes, a and c, were estimated by using the diffraction peaks of (003), (112), (103), and (202). The ratios of the axes, c/a, at the specified temperatures are given in Table 2.

The ratios of the axes, c/a, of the crystallized selenium changed discontinuously from 1.118 to 1.131 at temperatures between 118.9°C and 128.4°C, but the details of the change are obscure.

Discussion

Hoffman and Weeks[5] expressed the radial growth rate of spherulite, G, as follows:

$$G = G_0 \exp(-\Delta G^*/kT) \exp(-\Delta G_c/kT) \qquad (1)$$

where G_0 is the specific rate; ΔG^*, the free energy of activation for the segmental jump process at the supercooled liquid-crystal interface, and ΔG_c, the free energy

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[5] J. D. Hoffman and J. J. Weeks, *J. Chem. Phys.*, **37**, 1723 (1962).

Table 2. Ratios of axes in hexagonal selenium

Cryst. temp., °C	99.5	109.1	118.9	128.4	137.9	147.1	156.4	165.5	174.5
c/a	1.118	1.118	1.118	1.131	1.133	1.134	1.134	1.133	1.134

of the formation of a two-dimensional nucleus of a critical size. The ΔG_c is expressed by the following equation:

$$\Delta G_c = 4\sigma_s\sigma_e h T_m/\Delta h_f \Delta T \tag{2}$$

where σ_s and σ_e are the lateral and end surface free energies of the two-dimensional, bundlelike nucleus respectively; h, the thickness of the nucleus; T_m, the melting point of the crystallized polymer; Δh_f, the heat of fusion at T_m, and ΔT, the difference in the melting point and the crystallization temperature, $T_m - T$. Therefore, the radial growth rate of spherulite may be expressed as follows:

$$\ln G = \ln G_0 - \Delta G^*/kT - CT_m/(\Delta T)T \tag{3}$$

where $C = 4\sigma_s\sigma_e h/k\Delta h_f$

Hoffman and Weeks[5] expressed the free energy of activation for the segmental jump process, ΔG^*, as follows, in conjunction with the WLF equation:

$$\Delta G^* = 2.303C_1{}^gC_2{}^g RT/(C_2{}^g + T - T_g) \tag{4}$$

In the crystallization of an organic-chain polymer, the radial growth rate of the spherulite near the melting point was considered to be governed by the third term on the right side of Eq. (3), and the variation in $(\ln G + \Delta G^*/kT)$ with $T_m/(\Delta T)T$ fit well into Eq. (3).

The application of Eq. (3) to selenium spherulite growth was examined. Harrison[6] reported the viscosities of the liquid selenium to be as follows:

Table 3. Viscosities[6] and densities[7] of liquid selenium

Temp. °K	η, poise	ρ, g/cm^3	Temp. °K	η, poise	ρ, g/cm^3
533	5.63	3.923	603	1.08	3.810
556	3.03	3.885	615	0.838	3.791
573	2.01	3.858	623	0.723	3.718
591	1.35	3.830			

The values in Table 3 were extremely adaptable to the WLF equation, though the temperatures in Table 3 were much higher than the glass transition temperature of amorphous selenium (305°K). The parameters, $C_1{}^g$ and $C_2{}^g$, in the WLF equation were estimated to be 12.88 and 131.2 respectively from the shift factors calculated by means of the values in Table 3. These values for selenium were different from those for the usual polymers (17.44 and 51.6 respectively); it is probable that this difference arises from the fact that the temperatures used in the experiment were much higher than the T_g of amorphous selenium.

The apparent activation energy for the viscous flow of the liquid selenium was estimated to be 17.8 kcal/mol from the Arrhenius plot of the viscosities of the liquid selenium at temperatures ranging from 220°C to 240°C.[8] On the other hand, the calculated value of the activation energy for the viscous flow of liquid selenium at 230°C was found to be 17.3 kcal/mol by using the estimated parameters, $C_1{}^g$ and $C_2{}^g$, and the following equation derived from the WLF equation:[5]

$$E_a = 2.303C_1{}^gC_2{}^g RT^2/(C_2{}^g + T - T_g)^2 - RT + \alpha RT^2 \tag{5}$$

where α is the expansion coefficient of liquid selenium, 4.8×10^{-4} °C^{-1}. Since the two values of the activation energy for the viscous flow nearly agreed with each other, the estimated values of the parameters, $C_1{}^g$ and $C_2{}^g$, were considered to be reasonable.

The free energies of activation, ΔG^*, for the segmental jump process of amorphous selenium were estimated to be 17.10 and 13.35 kcal/mol at 401.6 and 465.5°K respectively, for example, by using Eq. (4). If the selenium spherulite growth obeys Eq. (3), the plots of $(\ln G + \Delta G^*/kT)$ should be linear with $T_m/(\Delta T)T$. Figure 5 shows the relationship between $(\ln G + \Delta G^*/RT)$ and $T_m/(\Delta T)T$. No linear relationship can be observed, as is shown in Fig. 5. It becomes clear that the process of the selenium spherulite growth can not be interpreted by only two terms, the segmental jump at the liquid-crystal interface and the free energy of the formation of a two-dimensional nucleus of a critical size.

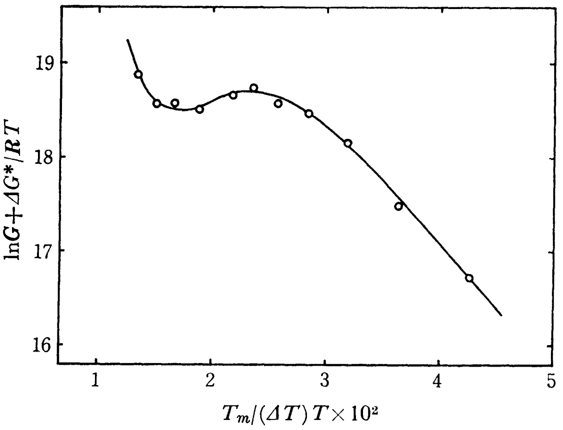

Fig. 5. Plot of $\ln G + \Delta G^*/RT$ against $T_m/(\Delta T)T$.

Turnbull and Cohen[9] pointed out that the crystallization of selenium was performed by the reconstruction of the irregularly-distributed chain molecules created by the breaking of the Se–Se bonds. The concept of the reconstruction in the selenium crystallization is due to a large barrier to internal rotation about Se–Se bonds,[10] which barrier is caused by the repulsion

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6) D. E. Harrison, *J. Chem. Phys.*, **41**, 844 (1964).

7) "Gmelin's Handbuch der anorganischen Chemie," 8th ed., Selen, Teil A, Verlag Chemie, G. m. b. h., Weinheim (1953).

8) T. Shirai, S. Hamada, and K. Kobayashi, *Nippon Kagaku Zasshi*, **84**, 968 (1963).

9) D. Turnbull and M. H. Cohen, *J. Chem. Phys.*, **29**, 1049 (1958).

10) J. A. Semlyen, *Trans. Faraday Soc.*, **63**, 743 (1967).

between lone-pair electrons around selenium chains. Mamedov[11] reached the same conclusion on the basis of X-ray diffraction studies of the bulk crystallization in the selenium. Also, Hillig[12] doubted whether the treatment of Turnbull and Fisher[13] for the homogeneous nucleation on selenium, work based on the molecules across the phase boundary and work which needed to overcome the surface energy of a nucleus of a critical size, was applicable without modification.

Considering the breaking process of Se–Se bonds, that is, $\mathrm{Se}_n \rightleftarrows \mathrm{Se}_{n-i} + \mathrm{Se}_i$, the elementary processes of selenium crystallization at the liquid-crystal interface may be expressed as follows:

$$\begin{array}{ccccccc} & \text{seg. jump} & & \text{bond breaking} & & \text{build up} & \\ \text{State A} & \xrightarrow[k_1]{} & \text{State B} & \underset{k_3}{\overset{k_2}{\rightleftarrows}} & \text{State C} & \rightleftarrows & \text{State D} \\ \text{(amorph. Se)} & & & & & & \text{(cryst. Se)} \end{array}$$

where k_1, k_2, and k_3 are the rate constants. Since the activity of amorphous selenium, a_0, at the crystal-liquid interface is regarded as constant, the rate from the A state to the C state can be expressed as $k_1Ka_0/(1+K)$, where K is k_2/k_3, from the treatment of the reaction kinetics. If the bond-breaking process of an amorphous selenium chain is nearly equal to the opening process of the ring selenium molecule, the values[14] of K can be calculated to be of orders from 10^{-9} to 10^{-7} at the temperatures ranging from 128.4°C to 192.3°C; therefore, the rate from the state A to the state C can be expressed as k_1Ka_0.

Accordingly, the overall radial growth rate of selenium spherulite can be expressed as follows:

$$\ln G = \ln G_0 - \Delta G^*/kT - \Delta G_s^*/kT - CT_m/(\Delta T)T \quad (6)$$

where ΔG^* and C are the same as in Eq. (3), and ΔG_s^*, the free energy for the bond-breaking process of chain molecules. The ΔG_s^* is considered to be nearly equal to the ΔG for the process of opening ring molecules, Se_8. Eisenberg and Tobolsky[14] estimated the values of ΔH and ΔS for the ring-opening process to be 25 kcal/mol and 23.0 e. u. respectively. Assessing the ΔH_s^* and ΔS_s^* to be 25 kcal/mol and 23.0 e. u. respectively, the plots of the terms of $(\ln G+\Delta G^*/\boldsymbol{R}T+\Delta G_s^*/\boldsymbol{R}T)$ against $T_m/(\Delta T)T$ given in Fig. 6 are obtained. From the linear relationship in Fig. 6, it is clear that the selenium spherulite growth is governed by the breaking process of Se–Se bonds as well as by the processes of the segmental jump and the formation of a two-dimensional nucleus of a critical size.

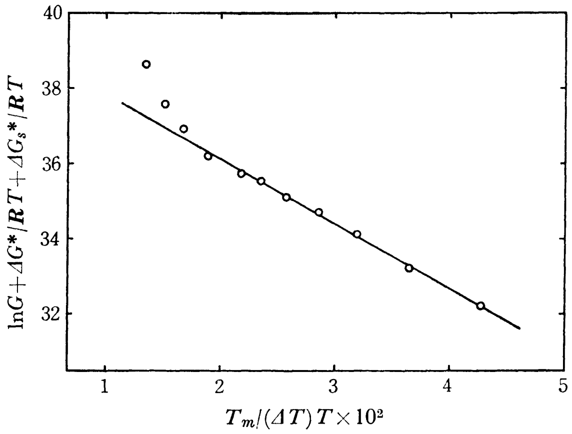

Fig. 6. Plot of $\ln G+\Delta G^*/\boldsymbol{R}T+\Delta G_s^*/\boldsymbol{R}T$ against $T_m/(\Delta T)T$.

The constant, C, was estimated to be 173.3 from the slope in Fig. 6. The radial growth rate of the selenium spherulite at temperatures ranging from 128.4°C to 192.3°C can be expressed by the following empirical formula:

$$\ln G = 39.60 - \Delta G^*/\boldsymbol{R}T - (2500-23.0T)/\boldsymbol{R}T - 173.3T_m/(\Delta T)T \quad (7)$$

The calculated values of G are plotted by the solid line in Fig. 2. The thickness of the two-dimensional nucleus at the liquid-crystal interface was calculated to be 3.78 Å on the basis of the crystal dimensions of hexagonal selenium, assuming the two-dimensional nucleus to be a monolayer of the selenium chain. The geometric average of $\sigma_s\sigma_e$, σ^*, was estimated to be 25.1 erg/cm² from the estimated value of the term of $4\sigma_s\sigma_e h/k\Delta h_f$ and from the values of h and Δh_f.[15]

Zadumkin[16] calculated the free energies of the melt-crystal interface for selenium and 36 metals to be 8—15% of the surface tension, σ, of their liquids at the melting points, except for Ge, Si, and Sb. The interfacial free energy of selenium at the liquid-crystal interface was calculated to be 15.9 erg/cm², assuming its value to be 15% of the surface tension of liquid selenium at the melting point, 217°C, 106 erg/cm².[17] Though the empirical value of the geometric average, σ^*, is slightly larger than the calculated value, it is considered to be reasonable.

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[11] K. P. Mamedov, *Akad. Nauk Azerb. SSR, Inst. Fiz.*, **1965**, 30.

[12] W. B. Hillig, *J. Phys. Chem.*, **60**, 56 (1956).

[13] D. Turnbull and J. C. Fisher, *J. Chem. Phys.*, **17**, 71 (1949).

[14] A. Eisenberg and A. V. Tobolsky, *J. Polym. Sci.*, **46**, 19 (1960).

[15] 3.98×10^9 erg/cm³; "Handbook of Chemistry," ed. by N. A. Lange, McGraw-Hill, New York (1961), p. 107.

[16] S. N. Zadumkin, *Akad. Nauk Ukr., SSR*, **1**, 21 (1961).

[17] K. V. Astakhov, N. A. Penin, and E. Dobkina, *Zh. Fiz. Khim.*, **20**, 403 (1946).