Spherulitic Growth in Amorphous Selenium under Pressure

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Abstract

The temperature (T) dependence of the spherulitic growth rates (g) during the crystallization of amorphous selenium under pressure (p) has been obtained by microscopic observations on partially crystallized bulk specimens. The spherulitic growth was observed to proceed at a uniform rate under isobaric-isothermal conditions over a p - T range 0.3-0.7 GPa and 385-410 K. At each p, g increased by about an order of magnitude for an increase in crystallization temperature (T_C) of 10-15 K. At a given T_C, g decreased by about two orders of magnitude for an increase in p from 0.3 to 0.7 GPa. These data have been analyzed using the concepts developed for the crystallization of supercooled polymeric melts. The g - T_C data at 0.28, 0.69 GPa, and the earlier data at atmospheric pressure are shown to lie on a master curve similar to that observed for a number of crystallizable organic polymers. The implications of the master curve on the crystal growth rate during the solidification of the Se-melt under pressure is discussed.

1 Introduction

Glass forming tendency of selenium is so strong that the solidification of the melt at atmospheric pressure normally results in an amorphous solid. Amorphous Se (a-Se) transforms{sup 1-7} completely into the polymeric trigonal form under prolonged isothermal annealing at temperatures over the range 343-473 K. In these studies{sup 1-7}, the crystallization temperatures were reached either by supercooling the melt or by heating a-Se from room temperature, and then the samples were annealed. The crystalline regions were observed to develop in the form of spherulites in a similar way as they do in a majority of crystallizable polymers. The details of the spherulitic morphology and the crystallization kinetics have been interpreted in these studies{sup 1-7}.
using the theories of the crystallization of organic polymers. The basis for such an approach been the suggestion\textsuperscript{8,9} that the Se-melt is polymeric in nature.

The glass forming tendency of Se is seen to vanish\textsuperscript{10-14} when the melt is cooled at moderately high pressures (a few tenths of GPa). The solidification of the Se-melt at 0.4 GPa resulted in the growth of single crystals at a rate \( \sim 5 \times 10^{-4} \) cm s\(^{-1}\) compared to \( \sim 10^{-7} \) cm s\(^{-1}\) obtained in the solidification of the Se-melt at atmospheric pressure. The increased rates of crystallization at high pressures involve\textsuperscript{12} the effect of higher freezing temperatures, \( T_m(p) \), [ \( dT_m(p)/dp \) for Se\textsuperscript{15} is \( \sim 200 \) K GPa\(^{-1}\)] in the pressure range 0 - 0.7 GPa on the liquid-solid interface kinetics.

Recently, we have investigated\textsuperscript{16} the pressure and temperature dependence of the kinetics of the crystallization of bulk a-Se to the trigonal phase under isobaric-isothermal conditions. For this, we obtained the temperature dependence of the incubation period, the time for 50 % crystallized fraction, and the spherulitic growth velocities \((g)\) at different pressures. It was found that the rate of crystallization increased with increase in \( T_C \) at a constant \( p \), and decreased with increase in \( p \) at a constant \( T_C \). The decrease in the isothermal crystallization rate at higher \( p \) was attributed to the increase in the activation energy for viscous flow which was found to govern the crystallization process in the temperature range 382-409 K.

It is to be noted that while single crystals of Se can be grown \( \sim 10^3 \) times faster from the melt at 0.4 GPa, the isothermal-isobaric annealing of a-Se indicates that the crystallization rate decreases with increase in \( p \). However, it must be pointed out that in these two sets of experiments, the crystallization temperatures lie in different ranges; the temperatures are closer to \( T_m(p) \) in the growth of single crystals from the melt, and are very much below \( T_m(p) \) in the annealing experiments.

In this paper, we present a detailed analysis of the \( T \) dependence of \( g \) at different \( p \) obtained by microscopic observations on Se specimens recovered after partial crystallization under isobaric-isothermal conditions. The \( T \) dependence of \( g \) obtained at 0.3 and 0.7 GPa (present study) and at atmospheric pressure (earlier studies\textsuperscript{2,5}) are shown to lie on a master curve with a reduced temperature as a variable. This indicates that the pressure behaviour of the \( g - T_C \) data correlates with the increase with \( p \) of the glass transition temperature \((T_G)\), and \( T_m \). The master curve has been used to explain the increased crystal growth rates from the melt at high pressures.

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2 Experimental Technique

2.1 Preparation of Materials

The bulk pure Se, in the form of ingots, was purified by the technique of zone refining and recrystallization. The material was ground in a mortar and pestle under dry nitrogen atmosphere to get a porous powder. The bulk powder was then reacted with Se to give a homogenous sample which was then annealed at 125 °C for 24 hours in a Schlenk bottle kept in a dry box. The sample powder was then placed in a Pyrex bottle and sealed with a rubber septum which was then connected to a gas burette and 

2.2 Characterization

The structural characterization of the material was done using powder X-ray diffractometry (PXRD). The samples were characterized by wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS). The spin calorimetry (SC) was used to study the magnetic properties of the sample. The thermal properties of the sample were studied using differential scanning calorimetry (DSC).

The sample was characterized using optical microscopy. The samples were characterized by using a combination of infrared spectroscopy and Raman spectroscopy. The samples were characterized using Raman spectroscopy at 532 nm excitation. The samples were characterized using X-ray photoelectron spectroscopy (XPS) and electron paramagnetic resonance (EPR) spectroscopy. The samples were characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

The sample was characterized using neutron diffraction. The samples were characterized using neutron diffraction at the Materials Research Laboratory (MRL) of the University of California at Berkeley. The samples were characterized using neutron diffraction at the High Flux Beam Reactor (HFR) of the University of California at Berkeley. The samples were characterized using neutron diffraction at the Advanced Photon Source (APS) of the Argonne National Laboratory.
2 Experimental growth in a-Se

2.1 Preparation of bulk a-Se specimens

The bulk Se specimens were prepared by melting selenium granules in vacuum, and quenching the melt in air. A quartz tube containing ~ 20 g batches of 99.999 % pure Se granules (Kochlight Chemicals, UK) was evacuated to $10^{-3} \cdot 10^{-4}$ torr. The sample was heated at a rate 15 K min$^{-1}$ to 630 ± 2 K using a tubular furnace. The melt was continuously degassed under vacuum for ~ 4 h, and allowed to cool in air after this period. The quartz-melt interface was free from bubbles. After the sample cooled to room temperature, the vacuum pump was turned off and the tube disconnected. The solidified mass (12 mm in diameter and 30 mm in length) could be easily pushed out of the quartz tube by cooling it in ice-water, and was found to be free from air bubbles or cavities.

2.2 Characterization of the specimen

The starting material was inferred to be amorphous by X-ray, infrared and density measurements. The diffractogram of the Se sample (Fig 1) shows only broad peaks centered on $2\theta = 27^\circ$ and $52^\circ$, which are characteristic of a-Se$^{17}$. The diffractograms of all freshly prepared Se glass specimens were similar to that shown in Fig 1. The specimens stored at room temperature exhibited some sharp diffraction peaks indicating the presence of a crystalline phase. These peaks disappeared when the surface layer was removed by polishing, and the X-ray diffractograms similar to that shown in Fig 1 were obtained. The experiments were performed only on specimens with freshly polished surfaces.

The specimens having optically flat surfaces for infrared studies were prepared by polishing the flat ends of Se cylinders, typically 5 mm thick and 12 mm in diameter. The infrared transmission spectrum (2.5 - 50 μm; Perkin-Elmer infrared spectrophotometer) of a typical specimen (Fig 2) consists of two absorption bands at 13.7 and 20.3 μm characteristic of pure a-Se$^{18}$. The spectrum does not contain any additional absorption bands arising from impurities, especially oxygen. It has been earlier reported$^{18}$ that Se specimens doped with 500 ppm O$_2$ exhibit characteristic bands in the region 10-20 μm, and these have been shown to arise only if O$_2$ is chemically bound to Se, like in SeO$_2$. Otherwise, no influence on the infrared spectrum was observed even when O$_2$ was bubbled through liquid Se. Further, traces of SeO$_2$, if any, are known$^{19}$ to be removed from molten Se during vacuum degassing. It is
clear from these considerations that the a-Se specimens used in the present work were not contaminated with any impurities. It must be pointed out that for trigonal Se specimens (0.25 mm thick), the transmitted intensity dropped to 20 % compared to 70 % for a-Se, and the infrared spectrum was featureless.

Figure 1: X-ray diffractogram of the starting a-Se specimens.

Figure 2: Infrared transmission spectrum of a-Se showing the characteristic absorption bands at 13.7 and 20.3 μm.

The density of the specimens determined by weighing them in air and in deionized water gave an average value of 4.278 ± 0.005 g cm⁻³ which is in excellent agreement with the reported value of 4.278 ± 0.002 g cm⁻³ for porc-free Se glass specimens, indicating that the present specimens were free from pores.

The molecular structure and the physical properties of a-Se are known to vary with the changes in the thermal history of the specimens. The structure of molten Se existing at the equilibrating temperatures (before quenching) is frozen when the melt solidifies into glass. In order to obtain specimens with the same thermal history,
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it is essential to equilibrate the melt at the same temperature. In the present study, the melt was equilibrated at 630 ± 2 K prior to quenching in air. The choice of this temperature was based\textsuperscript{16} on the crystallization behaviour, at atmospheric pressure, of a-Se specimens obtained with different thermal histories.

2.3 Microscopic observations of the partially crystallized specimens

The procedure adopted was to interrupt the progress of crystallization, occurring in a specimen under a desired \( p \) and \( T_C \), after known time intervals \( (t) \), and then to examine the recovered specimen for spherulitic growth under an optical microscope.

Pieces (4x3x3 mm\(^{-3}\)) of a-Se, immersed under silicone oil in a teflon cup, were subjected to desired \( p - T \) conditions in a piston-cylinder device in the manner described elsewhere\textsuperscript{16}. These experiments were performed at 0.28 and 0.69 GPa at different \( T_C \) over the range 385-409 K. At a given \( p \) and \( T_C \), the specimens were annealed for atleast five different time intervals, and then quenched to ambient conditions. Typically at 0.28 GPa and 399 K, the annealing times were in the range 7.5 - 26 min, whereas at 0.69 GPa and 391.5 K, these were in the range 10-45 h. The annealing times were chosen such that the crystallization was still in the early stages where the impingement of spherulites was not serious. The \( p \) and \( T \) were maintained constant at the desired values to within 0.01 GPa and ±0.5 K during annealing.

One of the surfaces of the partially crystallized specimen (mounted on a polishing jig) was hand ground, under a stream of water on a 600 grit emery paper till the thickness of the specimen reduced to half its original value. This process removed the surface layers and exposed a flat surface (4 × 3 mm\(^2\)) around the central region of the specimen. This surface was further polished using the standard metallographic techniques. The specimen was recovered from the jig, cleaned and then dried in a stream of air. The polished surface of the specimen (examined under polarized light in a Neophot-2 optical microscope) contained a planar distribution of circular sections arising from a randomly cut spatial distribution of the spherulites. The photograph (Fig 3) shows a distribution of spherulites typical of that obtained over the entire area of a specimen (crystallized at 0.28 GPa and 391 K for 32 minutes). The spherulites are well resolved and uniformly distributed.

2.4 Spherulitic growth rate

Typical photomicrographs of the spherulitic growth in specimens annealed for
different $t$ at 0.28 GPa and 384.5 K are shown in Fig 4. The growth rate was obtained on the assumption, that the diameter, $d_L$, of the largest circular section was equal to the diameter of largest spherulite. For this, the distribution of the diameters of the circular sections was obtained by measuring the diameters of at least 300 sections selected randomly over the entire area of the specimen. Out of these, at least 10% of the sections had diameters ranging between $d_L$ and $(d_L-1)$ μm.

![Image](image.png)

Figure 3: Uniform distribution of spherulites in a partially crystallized specimen. The pressure, temperature and time are respectively 0.28 GPa, 391 K and 32 min.

Typically, the $d_L$ versus $t$ data showed a linear relationship (Fig 5). This is in accordance with the general observation that spherulites grow such that the radius, $R$, is proportional to $t$. This shows that the spherulitic growth is an interface-controlled process, and the radial diffusion processes ($R \propto t^{1/2}$) are not the rate controlling step. The rate controlling step in the growth of spherulites is the nucleation process occurring at the growing tips of a radial lamelle. The spherulitic growth rate, $g = dR/dt$, was calculated from the slope of the $d_L$ versus $t$ data.
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Figure 4: Photomicrographs of spherulitic growth in a typical specimen annealed for different $t$ at 0.28 GPa and 384.5 K; (a) 30 (b) 60 (c) 130 and (d) 163 minutes.
3 Theoretical aspects

Many polymers crystallize from the melt in the form of spherulites\textsuperscript{22,23}. The overall rate of crystallization of a supercooled polymeric liquid is determined by the nucleation and the growth rates of spherulites. The spherulitic growth is also a nucleation controlled process\textsuperscript{24}. Homogeneous or primary nucleation takes place through the formation of three dimensional nuclei, and the growth takes place through secondary (two dimensional) or tertiary (one-dimensional) nucleation. The secondary and the tertiary nucleation processes occur on the existing crystallite surfaces, and therefore the surface area newly created is smaller. Accordingly, the work of formation of the nuclei through these processes is low.

The rate of homogeneous nucleation, $I$, has been derived\textsuperscript{25} using the absolute reaction rate theory\textsuperscript{26} as

$$I = I_0 \exp \left[ - \frac{\Delta G_p^* + \Delta G_f^*}{RT_C} \right]$$  \hspace{1cm} (1)

where $I_0$ is a constant, $\Delta G_p^*$ the activation energy governing the short distance diffusion of the crystallizing element across the interphase, $\Delta G_f^*$ the work of formation of a critically sized primary nucleus, and $T_C$ the crystallization temperature. $\Delta G_p^*$ has been shown\textsuperscript{27} to be of the form

$$\Delta G_p^* = \frac{32 \gamma_s^2 \gamma_b}{\Delta G^2}$$  \hspace{1cm} (2)

where $\gamma_s$ is the interfacial free energy per unit area parallel to the chain, $\gamma_b$ the interfacial free energy per unit area perpendicular to the chain and $\Delta G$ the molar free energy difference between the crystal and the melt.

The basic equation\textsuperscript{28} describing the $T$ dependence of $g$ is

$$g = g_0 \exp \left[ - \frac{\Delta G_s^* + \Delta G_f^*}{RT_C} \right]$$  \hspace{1cm} (3)

where $g_0$ is a constant and $\Delta G_s^*$ the work of formation of critically sized nucleus. The expression for $\Delta G_s^*$ depends on the type of nucleation controlling the growth, and for secondary nucleation\textsuperscript{29} is of the form

$$\Delta G_s^* = \frac{4 \frac{b_0 \gamma_s \gamma_b}{\Delta G}}{\Delta G}$$  \hspace{1cm} (4)

where $b_0$, $T_C$, and $\Delta G$ are the temperature, heat of fusion and crystal energy.
where \( b \), is the thickness of the chain molecule. \( \Delta G \) can be expressed as

\[
\Delta G = \frac{\Delta H_m}{T_m} \Delta T
\]

(5)

where \( \Delta H_m \) is the heat of melting per unit volume, \( T_m \) the equilibrium melting temperature, and \( (T_m - T_C) = \Delta T \) the supercooling. It is seen that \( \Delta G = 0 \) at \( T_m \), and increases with increasing \( \Delta T \).

The general crystallization behaviour of polymeric melts with increase in \( \Delta T \) is explained using the Eqs (1) to (5). For small values of \( \Delta T \), the melt exists in a metastable zone in which the nuclei do not form at a detectable rate. However, if the crystals are nucleated by heterogeneous nucleation, the growth continues through secondary nucleation. As the melt cools further, both \( I \) and \( g \) increase due to rapid increase of \( \Delta G \) until a high viscosity zone is reached. With further lowering in temperature, the formation of the nuclei is inhibited, and the growth does not take place at a detectable rate. Both \( I \) and \( g \) show maxima because at higher temperatures \( \Delta G \) decreases, and at lower temperatures the rate of mass transfer decreases drastically due to high viscosity. Thus, the rate of crystallization increases as \( T_C \) decreases below \( T_m \), reaches a maximum at \( T_K \) and decreases again as \( T_C \) is lowered towards \( T_G \), the glass transition temperature.

At very large supercooling, i.e. the temperature region \( T_C < T_C < T_K \), \( \Delta G \) is large, and consequently \( \Delta G^*_p \) and \( \Delta G^*_s \) are negligibly small. Eqs (1) and (3) reduce to

\[
I = I_0 \exp \left( -\frac{\Delta G^*_d}{RT_C} \right)
\]

(6)

\[
g = g_0 \exp \left( -\frac{\Delta G^*_d}{RT_C} \right)
\]

(7)

In this region of temperature, both \( I \) and \( g \), and hence the overall crystallization rate are governed by \( \Delta G^*_d \), and the rate of crystallization increases with increase in temperature.


4 Results and discussion

4.1 Temperature dependence of spherulitic growth rate at different pressures

The $g - T_C$ data at 0.28 and 0.69 GPa, obtained in the present studies, are shown in Fig 6. Also shown are the data at atmospheric pressure obtained on thin films of a-Se by Hamada et al\textsuperscript{2} and Crystal\textsuperscript{5}. The data of Hamada et al cover a temperature range 353-393 K whereas those of Crystal cover a wider temperature range 353-433 K. It is seen that $g$ increases with increase in $T_C$ at constant $p$, typically the increase is by an order of magnitude for a temperature increase of 25 K at atmospheric pressure and $\sim 10$ K at 0.69 GPa. This is consistent with the observation\textsuperscript{16} that the overall crystallization rate increases with increase in $T_C$.

The data of Crystal exhibit the bell-shaped curve (section 3) resulting from the interaction of enhancement of crystallization with supercooling and a decrease of crystallization with increased viscosity; the maximum in $g$ occurs at 403 K. Coughlin and Wunderlich\textsuperscript{6} also reported largest rates of crystallization at 399 K for the crystallization of Se from the melt at atmospheric pressure. These studies\textsuperscript{5,6} indicate that the value of $T_K$ for Se at atmospheric pressure is $\sim 400$ K. Further, since $T_K$ lies between $T_G$ and $T_m$ (for a-Se, $T_G = 305$ K\textsuperscript{31} and $T_m = 490$ K at atmospheric pressure), and $T_G$ and $T_m$ increase with increasing $p(dT_G/dp \simeq 130$ K GPa$^{-1}$ and $dT_m/dp \simeq 200$ K GPa$^{-1}$ for Se\textsuperscript{32,15}), it is reasonable to expect that $T_K$ should increase with increasing $p$. The temperature range (Fig 6), over which $g$ increases, thus lies between $T_G$ and $T_K$ at each $p$. In such a case, the temperature dependence of $g$ can be described by Eq (7).

A linear fit to the $\ln g$ versus $1000/T_C$ data at atmospheric pressure, 0.28 GPa and 0.69 GPa by the method of least squares gave respectively the equations

$$\ln g = (25.7 \pm 0.5) - (11.99 \pm 0.2) \frac{1000}{T_C}$$

$$\ln g = (49.6 \pm 4.1) - (21.45 \pm 1.6) \frac{1000}{T_C}$$

$$\ln g = (56.4 \pm 11.4) - (25.6 \pm 3.5) \frac{1000}{T_C}$$

Figure 5: Variation of $T_G$, $T_m$ and $T_K$ with pressure for a-Se at atmospheric pressure and 0.69 GPa.

The pressure dependencies of $T_G$ and $T_m$ should show a small increase with increasing $p$. The pressure dependence of $T_K$ should be determined by the $p$ dependence of $T_C$. The $p$ dependence of $T_C$ can be determined from the $T_C$ versus $p$ data obtained in the present studies.
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The data of Hamada et al.\(^2\) have been used in obtaining Eq. (8), and agree quite well with the data of Crystal\(^5\) over the range 353-383 K. The values of \(\Delta G_d^*\) calculated from the slopes of these lines are 23.7 \(\pm\) 0.4, 42.5 \(\pm\) 3 and 50.7 \(\pm\) 7 kcal mol\(^{-1}\) respectively at atmospheric pressure, 0.28 GPa and 0.69 GPa. The values of \(g_0\) obtained from the intercepts of these lines increase from \(\sim 1.5 \times 10^{11}\) \(\mu\)m s\(^{-1}\) at atmospheric pressure to \(3.1 \times 10^{24}\) \(\mu\)m s\(^{-1}\) at 0.69 GPa. The large uncertainties in \(g_0\) and \(\Delta G_d^*\) at 0.28 and 0.69 GPa are due to the limited temperature range over which the measurements could be made. However, \(\Delta G_d^*\) is seen to increase with increase in \(p\).

Figure 5: A typical plot of the largest diameter, \(d_L\), versus annealing time.

Figure 6: Temperature dependence of the spherulitic growth rate in a-Se at different pressures. (a) data of Hamada et al (ref.2) and (b) data of Crystal (ref.5) at atmospheric pressure, (c) present studies - 0.28 GPa and (d) present studies - 0.69 GPa.

The spherulitic growth velocity is seen (Fig. 6) to decrease with increase in \(p\) at constant \(T_G\). Typically, at 392 K, \(g\) decreases by two orders of magnitude for an increase in \(p\) from atmospheric value to 0.69 GPa; the extrapolations of the data
at 0.28 and 0.69 GPa to lower \( T_C \) (350-375 K) indicate a larger decrease in \( g \) with increase in \( p \). However, such extrapolations are limited to \( T_G(p) \). The effect of \( p \) in decreasing the isothermal growth velocity may be due to the increase of \( \Delta G^*_d \) with increase in \( p \).

The \( g \) versus \( 1000/T_C \) lines at atmospheric pressure and 0.28 GPa cross each other at \( \sim 396 \) K. Beyond this temperature, \( g(0.28 \text{ GPa}) > g(\text{atmospheric pressure}) \). This is due to a higher value of the prefactor \( g_0 \) at 0.28 GPa. Similarly, the lines at 0.28 and 0.69 GPa intersect at \( \sim 610 \) K. Such extrapolations are limited to \( T_K(p) \), and further \( g \) decreases in the region \( T_K < T_C < T_m \).

The values of \( g_0 \) of different amorphous covalent materials are expected to be of the order of \( \sim 3 \) to \( 5 \times 10^9 \mu \text{m s}^{-1} \) (speed of sound in these materials). Kim and Turnbull\(^7\) obtained \( g_0 \) for the growth of cindrlites in a-Se films as \( 6 \times 10^{10} \mu \text{m s}^{-1} \), 10\(^{10}\) times the normally expected value. It has been suggested\(^3\) that such values of \( g_0 \) might be accounted for by supposing that interfacial rearrangements during crystallization is a highly co-operative process involving a considerable number of normal modes of vibration. It is interesting to note that \( g_0 \) is still larger at higher \( p \); the values are \( \sim 3.4 \times 10^{21} \mu \text{m s}^{-1} \) at 0.28 GPa and \( 3.1 \times 10^{24} \mu \text{m s}^{-1} \) at 0.69 GPa.

### 4.2 Master curve for \( g \)

The changes in the crystallization rate with \( T_C \), for \( T_C < T_C < T_m \) of a polymer were discussed in Section 3. It was seen that a maximum in the crystallization rate would occur at \( T_K \). Correspondingly \( g \) would exhibit a maximum \( g_{max} \) at \( T_K \). On the basis of the maximum linear growth rate, Gandica and Magill\(^34\) showed that it is possible to find a reduced temperature \( T_r = (T_C - T_{ch})/(T_m - T_{ch}) \) in terms of which the ratios of \( g \) at \( T_C \) relative to \( g_{max} \) at \( T_K \) can be reproduced, for all the polymers investigated, by a single master curve. \( T_{ch} \) is a characteristic temperature, equal to \( (T_G - 50 \text{ K}) \), at which polymer chain segmental transport tends to zero. It must be noted that \( T_G, T_K \) and \( T_m \) are characteristic of a polymer, and have different values for different polymers. The master curve represented by a dimensionless functional relationship

\[
\ln \frac{g(T_C)}{g_{max}(T_K)} = f(T_r)
\]

exhibited a maximum at \( T_r = 0.63 \) and tends to \(-\infty\) at \( T_{ch} \) and \( T_m \) respectively.

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Consider the relationship

\[
\frac{T_K}{T_m} = \frac{1}{1 + \frac{g_0}{g_0(T_m)}},
\]

and this

\[
T_K = 403 \text{ K}.
\]

Eq (13) with \( T_K = 403 \text{ K} \). It is interesting to note that a maximum in \( g \) at 403 K can be obtained.

It is interesting to note that the maximum in \( g \) is maximum at a higher \( T \) as shown in the \( \ln g \) versus \( T \) plot. It is also interesting to note that the experimental data for the \( g-T \) curve are shown in Fig. 7. The master curve for the spherulite is obtained by using the spherulite:

\[
T_m = 403 \text{ K}.
\]

It is seen that the maximum in \( g \) is at \( \sim 0.7 \) for a polymer with moderate crystallinity with high spherulite growth at the following:

The master curve is characteristic because \( T_{max} \) is a function of \( g \) and the growth at this temperature is represented by the following:

\[
g = 0 \quad \text{at} \quad T_{max}.
\]
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Considering that \( T_C = T_K \) at \( \tau = 0.63 \) one can write

\[
\frac{T_K + 50 - T_G}{T_m + 50 - T_G} = 0.63
\]

(12)

and this leads to

\[
T_K = 0.37 \ T_G + 0.63 \ T_m - 18.5
\]

(13)

Eq (13) with \( T_G = 305 \) K and \( T_m = 490 \) K, gives \( T_K \) for Se at atmospheric pressure as 403 K. It is interesting to see from Fig 6 that the data of Crystal exhibit a maximum in \( g \) at 403 K.

It is instructive to examine whether the \( g - T_C \) data at different \( p \) (Fig 6) can be represented by a similar master curve because there exists a distinct \( T_G \) and \( T_m \) at each \( p \). For this, the temperature \( T_K(p) \), at each \( p \), at which the growth rate of Se is maximum, was estimated using Eq (13) and \( T_G(p) \) and the \( T_m(p) \) values, and are shown in Table 1. The value of \( g_p(T_K) \) at each \( p \) was calculated by extrapolating the \( \ln g \) versus \( 1000/T_C \) lines (Eq 8-10) to \( T_K(p) \), and is also shown in Table 1 along with the experimentally observed values at atmospheric pressure. Using these values, and the \( g-T \) data (Fig 6), the \( \ln [g_p(T_C)/g_p(T_K)] \) versus \( \tau \) data were obtained, and are shown in Fig 7. It is interesting to see that the data points lie on a master curve. The master curve indicates that the effect of pressure on the temperature dependence of the spherulitic growth rate in Se correlates with the pressure variations of \( T_G \) and \( T_m \).

It is seen from Table 1 that \( T_K(p) \) increase at a rate \( \sim 170 \) K GPa\(^{-1}\), and \( g_p(T_K) \) at \( \sim 0.7 \) GPa is \( \sim 10^5 \) times that at atmospheric pressure. Thus the application of moderate pressure (a few tenths of a GPa) allows crystallization to be carried out, with higher \( g \), at temperatures substantially higher than can be achieved during the crystallization at 1 atmosphere.

The master curve should extrapolate to \(-\infty\) at \( \tau = 1 \), i.e at \( T = T_m \). This is because \( \Delta G = 0 \) (Eq 5) at \( T_m \), and consequently \( \Delta G^* \) (Eq 4) tends to infinity and \( g = 0 \) (Eq 3). However, if the crystallization of a-Se were to occur by spherulitic growth at \( T_C \) close to \( T_m(p) \), for instance at \( \tau = 0.9 \), the master curve would lead to the following interpretation. \( \tau = 0.9 \) leads to

\[
1000 = \frac{T_K + 50 - T_G}{T_m + 50 - T_G}
\]

(11)

respectively.
Figure 7: Master curve for the pressure and temperature dependence of the spherulitic growth rate in a-Se. (a) - (d) are same as in Fig 6.

\[ T_C(p) = 0.9T_m(p) + 0.1[T_C(p) - 50] \]  

(14)

and the corresponding crystallization temperatures are \( \sim 467 \) K at atmospheric pressure, and \( \sim 596 \) K at \( p = 0.7 \) GPa. At \( T_r = 0.9 \), the quantity \( \left\{ g_p[T_C(p)]/g_p[T_K(p)] \right\} \) is a constant independent of \( p \). This suggests that

\[ \frac{g_{atm}[T_C(\text{atm})]}{g_{atm}[T_K(\text{atm})]} = \frac{g_p[T_C(p)]}{g_p[T_K(p)]} \]

(15)

which leads, in a typical case, to

\[ \frac{g_{st}}{g_{st}} \]

Thus, crystallite size decreases with increasing \( T \), leading to the \( T \) dependence.

It must be noted that the atmosphere gas pressure in the two experiments was that of the molten Se. It may be seen from our earlier discussion of the crystallite size in the melt that the crystallite size decreases with increasing atmospheric pressure, leading to a decrease in crystallite size.

\[ \frac{g_{atm}}{g_{atm}} \]
Table 1: The values of $T_K(p)$ calculated using Eq (13)

<table>
<thead>
<tr>
<th>$p$ (GPa)</th>
<th>$T_G(p)$†</th>
<th>$T_m(p)$‡</th>
<th>$T_K(p)$ (K)</th>
<th>$g_p(T_K)$ (μm s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 atm.</td>
<td>305</td>
<td>490</td>
<td>403</td>
<td>$1.8 \times 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$E5.83 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.28</td>
<td>341</td>
<td>559</td>
<td>460</td>
<td>19.1</td>
</tr>
<tr>
<td>0.69</td>
<td>395</td>
<td>624</td>
<td>521</td>
<td>1336</td>
</tr>
</tbody>
</table>

† $T_G(p)$ was calculated using $T_G = 305$ K (ref.31) at atmospheric pressure and $dT_G/dp = 130$ K GPa⁻¹ (ref.32).
‡ $T_m(p)$ was obtained from the data of Klement et al (ref.15).
E Experimental value.

\[
\frac{g_{\text{atm}}(467K)}{g_{\text{atm}}(403K)} = \frac{g_{0.7}(596K)}{g_{0.7}(521K)}
\]  

(16)

where 403 K and 521 K are respectively the values of $T_K$ at atmospheric pressure and 0.7 GPa. It is seen from Eq (16) that

\[
\frac{g_{0.7}(596K)}{g_{\text{atm}}(467K)} \simeq 10^5
\]  

(17)

Thus, crystal growth rate from the melt at 0.7 GPa can be $10^5$ times the growth rate at atmospheric pressure. Thus the master curve provides a complete description of the $T$ dependence of $g$ at various $p$ over the temperature range $T_G(p) < T_C < T_m(p)$.

It must be pointed out here that trigonal Se can be grown from the melt at atmospheric pressure either as spherulites\textsuperscript{13} or as single crystals\textsuperscript{13}, the growth habits in the two cases being widely different. Under high pressure, the crystallization from molten Se will lead to some novel morphological features because of higher $T_m$. In our earlier studies\textsuperscript{38} on the solidification of Se melt up to 6.5 GPa, the morphology of the crystal growth was seen to depend on the cooling rate as well. The slow cooling of the melt (2 K s⁻¹) at high pressure yielded a polycrystalline mass wherein the crystallites had well-grown facets. At higher cooling rates (500 K s⁻¹), the crystallite size decreased, and the morphology of the crystal growth changed to plate-like.
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