

071126 Quiz 8 Morphology of Complex Materials

The rate of crystallization is governed by the slower of two processes. Crystallization relies on transport of crystallizable species to the growth front. Crystallization also relies on supersaturation.

- 1)
 - a) Supersaturation represents the degree to which thermodynamic conditions exceed those present at the equilibrium condition between crystalline and amorphous states. How can supersaturation be achieved in polymer crystallization from the melt?
 - b) What happens to the rate of transport under high supersaturation for a polymer melt?
 - c) Sketch a plot of the overall rate of crystallization versus supersaturation.
 - d) In the most general sense all rate equations depend on a rate constant which follows an Arrhenius behavior such as an Eyring rate law. Give the Arrhenius equation.
 - e) Explain what plot is suggested by the Arrhenius equation.

- 2)

A rate limiting process involves two or more steps needed to perform a process.

 - a) Sketch a cartoon of the crystallization process denoting A as the crystallizable species in the melt; B as A near the crystal surface and C as the material in the crystal. Show the two steps needed to perform crystallization.
 - b) Write an equation that equates the overall rate, the rate of crystallization and the rate of transport.
 - c) If the final amount of crystal, C_f , is given by the sum of the initial amounts of A_i and B_i , write an expression for the final amount of crystal, C_f , in terms of A_i only using the expression of part b.
 - d) Use part c to obtain an expression for A_i and use this expression to describe the initial rate of crystallization, R_i .
 - e) The equation for part d is valid only during the initial states of crystallization. Under what conditions would this expression be valid throughout crystallization?

- 3)

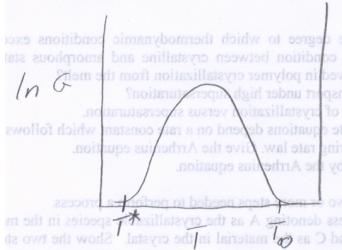
Hoffman described three regimes for polymer crystallization.

 - a) Describe these three regimes of crystallization in terms of the nucleation rate, i , and the substrate completion rate, g .
 - b) What type of chain folding would you expect in these three regimes?
 - c) Hoffman proposed a plot of $\ln G - Q^*/\{R(T-T^*)\}$ versus $1/(T(T_\infty-T))$ where T^* is the Vogel temperature (glass transition), Q^* is the energy barrier for transport, G is the crystallization growth rate and T_∞ is the equilibrium melting point. This plot differs from the plot you proposed in question 1e. Explain the x-axis by first writing an expression for the Hoffman lamellar thickness, l^* , at temperature T and an expression for the free energy difference, ΔG , between a melt and crystal for a lamellar crystal of thickness l .
 - d) Use the Hoffman thickness, l^* , in the ΔG expression to obtain the barrier energy for crystallization, ΔG^* .
 - e) Use this barrier energy, ΔG^* , in the Arrhenius function to explain the x-axis in the Hoffman plot.

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1) a) Supersaturation is achieved in the melt by a thermal quench below the equilibrium melting point. In solution it can be achieved by a rapid increase in concentration or partial pressure in the vapor phase.

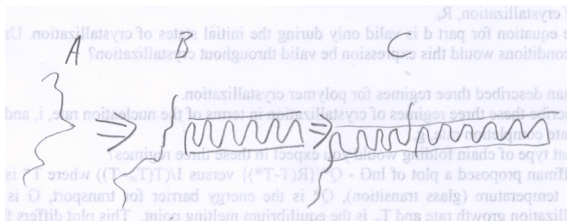
b) High supersaturation occurs at low temperatures. Transport slows at low temperatures due to Arrhenius behavior, Rate of Transport $\sim \exp(-Q^*/(T - T^*))$ where Q^* is the activation energy for transport and T^* is the Vogel temperature.



c)

d) Rate = $k A$, A is the concentration of the species involved in the process and the rate constant, k , is given by $k = k_0 \exp(-\Delta E^*/kT)$, where ΔE^* is the energy barrier for the process.

e) The Arrhenius function suggest $\ln(\text{Rate})$ versus $1/T$ as a linear plot to obtain k_0 and ΔE^* .



2) a)

b) Rate = $Ak_D = Bk_G$

c) $C_f = A_i + B_i = A_i (1 + k_D/k_G)$

d) $A_i = k_G C_f / (k_G + k_D)$

Rate = $A_i k_D = k_D k_G C_f / (k_G + k_D)$

e) This rate can be generalized if there is an infinite source of melt, A , that is not depleted during crystallization.

3) a) Regime I, $i \ll g$; Regime II, $i \sim g$; Regime III, $i \gg g$.

b) Regime I, regular adjacent reentry; Regime II, Synoptic, dangling chains, well stacked lamellae due to interconnection of lamellae; Regime III, Defective crystals with few adjacent folds. Generally disorganized crystals are expected in Regime III.

c) $l^* = 2 \sigma_e T_\infty / (\Delta H(T_\infty - T)) = 2 \sigma_e / \Delta F$

$\Delta G = 2va^2\sigma_e + 2a\sigma - va^2l\Delta F$

where $\Delta F = (\Delta H(T_\infty - T))/T_\infty$, v is the number of stems, σ_e is the fold surface energy, σ is the side surface energy, a is the stem size and l is the stem length.

d) $\Delta G^* = 2va^2\sigma_e + 2a\sigma (2 \sigma_e / \Delta F) - va^2\Delta F (2 \sigma_e / \Delta F) = 4a\sigma\sigma_e / \Delta F = 4a\sigma\sigma_e T_\infty / (\Delta H(T_\infty - T))$

e) $k_G = k_0 \exp(-\Delta G^*/kT) = k_0 \exp(-4a\sigma\sigma_e T_\infty / (k\Delta H(T_\infty - T)))$

so $\ln k_G = \ln k_0 - 4a\sigma\sigma_e T_\infty / (k\Delta H(T_\infty - T))$

so the plot is linear using an x-axis of $1/(T(T_\infty - T))$