Crystallization Kinetics via Spherulitic Growth

**Heterogeneous nucleation and growth prior to impingement.** When stereoregular polymers crystallize below the melting temperature and a spherulitic superstructure develops, it is possible to measure time-dependent growth of these three-dimensional birefringent aggregates via polarized optical microscopy. Heterogeneous nucleation represents a crystallization mechanism where all "seeds" are "planted" at time \( t_0 \) and lamellae grow radially outward from these nucleation centers. Hence, all spherulites should be of similar size if this mechanism dominates the crystallization process. One requirement of polarized optical microscopy is that the focal plane of the microscope must be coincident with the equatorial plane of an isolated spherulite to measure accurate growth rates. This condition will be satisfied if the spherulite of interest in the field of view is identified during its early stages of growth when it appears as a "point" at 50x to 200x magnification. The temperature-dependent growth rate \( \dot{G}(T) \) is defined by the time rate of change of the radius \( r \) of a single spherulite;

\[
\dot{G}(T) = \frac{dr}{dt}
\]

When the growth rate \( \dot{G}(T) \) is essentially constant during the early stages of isothermal crystallization, one calculates the spherulite radius as follows;

\[
r(t) = \int_0^r \dot{r} = \int_{t_0}^t \dot{G}(T) dt' = \dot{G}(T) \{ t - t_0 \}
\]

The volume of one space-filling three-dimensional spherulite is;

\[
V_{\text{spherulite}} = \frac{4}{3} \pi \{ r(t) \}^3 = \frac{4}{3} \pi [\dot{G}(T)]^3 \{ t - t_0 \}^3
\]

Since all of the nucleation centers were planted at \( t = t_0 \), the number density of nucleation centers \( N_s \) is the same as the number of spherulites per unit volume of polymer. Hence, the volume fraction of spherulites, which represents the total volume of spherulites per volume of polymer, is synonymous with the volume fraction of crystallinity, \( X_v(t) \). The simple model described above yields;

\[
X_v(t;T) = (4/3) \pi N_s \ G^3(T) \ ( t - t_0 )^3
\]
which is an accurate representation of the crystalline volume fraction during the early stages of spherulitic growth before impingement occurs. The scaling law for this process at early times (i.e., $t \approx t_0$) is;

$$X_v(t) \approx (t - t_0)^n$$

where $n$ is the dimensionality of crystal growth. In this example, $n=3$. Time-dependent patterned crystal growth in circular or rectangular fashion on a catalytic surface or inert substrate exhibits a scaling exponent of $n=2$. These simple models break down when the growth of a single spherulite is affected by neighboring spherulites, which causes growth rates to decrease.

**Avrami equation for heterogeneous nucleation which accounts for impingement of spherulites.** The primary objective of this section is to predict the time dependence of the volume fraction of crystallinity when spherulitic growth rates are reduced by the presence of neighboring spherulites, as illustrated below via polarized optical micrographs for poly(ethylene oxide) with a quarter-waveplate in the field of view;

Let's consider the time rate of change of the volume of a single isolated spherulite prior to impingement, as discussed in the previous section. Differentiation of $V_{1\text{-Spherulite}}$ yields;

$$\left(\frac{dV}{dt}\right)_{1\text{-Spherulite}} = 4\pi \{r(t)\}^2 \frac{dr}{dt} = (\text{External Surface Area})(\text{Growth Rate})$$

The following strategy is adopted after impingement occurs;
(1) Multiply the previous expression by the number density of spherulites $N_S$ which have been nucleated heterogeneously at time $t_0$. This provides one with a rate equation for the volume fraction of crystallinity, because:

$$X_V(t;T) = N_S V_{1-Spherulite}(t;T)$$

$$\frac{dX_V}{dt} = N_S \left( \frac{dV}{dt} \right)_{1-Spherulite}$$

(2) Calculate the external surface area of a single spherulite by assuming constant growth rate during isothermal crystallization:

$$\text{External Surface Area} = 4 \pi \{ r(t) \}^2 = 4 \pi G^2(T) (t - t_0)^2$$

(3) Introduce a truncation factor $f$, which represents the probability that impingement does not occur, to account for the fact that (i) spherulitic growth rates decrease after impingement, and (ii) the external surface area of a single spherulite is not $4\pi \{ r(t) \}^2$. The truncation factor is proportional to the volume fraction of amorphous material. Justification for this claim is based on geometrical considerations of intersecting spheres and circles. Hence:

$$f(t) = 1 - X_V(t)$$

This is reasonable because the probability of impingement increases at higher crystalline volume fractions.

These considerations yield the following expression for the time rate of change of the volume of a single spherulite after impingement occurs:

$$\left( \frac{dV}{dt} \right)_{1-Spherulite} = 4\pi \{ r(t) \}^2 \frac{dr}{dt} = 4\pi \left[ G(T) \right]^2 (t - t_0)^2 G(T)f(t) = 4\pi \left[ G(T) \right]^3 (t - t_0)^2 \{ 1 - X_V(t) \}$$

One calculates the time dependence of the volume fraction of crystallinity from:

$$\frac{dX_V}{dt} = N_S \left( \frac{dV}{dt} \right)_{1-Spherulite} = 4\pi N_S \left[ G(T) \right]^3 (t - t_0)^2 \{ 1 - X_V(t) \}$$
Separation of variables yields the Avrami equation for heterogeneous nucleation, or the time dependence of the spherulite volume fraction during isothermal crystallization, \( X_V(t;T) \). The initial condition is \( X_V = 0 \) at \( t = t_0 \);

\[
\int_{X_V(t_0)}^{X_V(t)} \frac{dX_V}{1 - X_V} = 4\pi N_S \left[ G(T) \right]^3 \int_{t=t_0}^{t} (t' - t_0)^2 \, dt'
\]

\[
-\ln\{1 - X_V(t;T)\} = \frac{4}{3} \pi N_S [G(T)]^3 (t - t_0)^3
\]

\[
X_V(t;T) = 1 - \exp\left\{ -\frac{4}{3} \pi N_S [G(T)]^3 (t - t_0)^3 \right\}
\]

This result is consistent with predictions of \( X_V(t;T) \) prior to impingement, as discussed in the previous section. If one expands the exponential function in the Avrami equation when \( t \approx t_0 \) during the early stages of spherulitic growth and truncates terms that scale as \((t-t_0)^6\) or higher, then;

\[
X_V(t;T) \approx \left( \frac{4}{3} \pi N_S G^3(T) \right) (t - t_0)^3 + \ldots
\]

If the crystallization mechanism proceeds via heterogeneous nucleation and spherulites are observed in the optical microscope fitted with cross polars, then one predicts that impingement occurs when there is a significant difference between \( X_V(t;T) \) calculated from the previous two equations, as illustrated in the figure below;

<table>
<thead>
<tr>
<th>Volume Fraction of Crystallinity; Avrami Equation</th>
</tr>
</thead>
</table>

![Graph showing the volume fraction of crystallinity over crystallization time, with a red line indicating prior to impingement and a blue line indicating after impingement. The rate constant is given as \(10^{-4}\) [Minutes]^{-3}.]
If temperature-dependent crystallization rate constants, with dimensions of \{\text{time}\}^{-3}, are defined by;

\[ K_{\text{Crystallization}}(T) = \frac{4}{3} \pi N_s G^3(T) \]

then impingement occurs earlier when \( K_{\text{Crystallization}} \) is larger. For example, the time required for impingement to occur for two different crystallization rate constants is summarized below;

<table>
<thead>
<tr>
<th>( K_{\text{Crystallization}} ) {\text{minute}}^{-3}</th>
<th>( t_{\text{Impingement}} ) {minutes}</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10^{-3} )</td>
<td>6</td>
</tr>
<tr>
<td>( 10^{-4} )</td>
<td>11</td>
</tr>
</tbody>
</table>

Since macromolecules do not exhibit 100% crystallinity due to (i) the presence of stereo-irregular units along the chain when centers of chirality exist, (ii) head-to-head vs. head-to-tail addition of monomer units during free-radical polymerization, (iii) irregularities in the vicinity of chain ends and the fold regions, etc., it is necessary to modify the Avrami equation such that \( X_V < 1 \) as \( t \rightarrow \infty \). Hence;

\[
\frac{X_V(t;T)}{X_V(t \rightarrow \infty)} = 1 - \exp\left\{ -\frac{4}{3} \pi N_s [G(T)]^3 (t-t_0)^3 \right\}
\]

**Crystallization kinetics and the Avrami equation for homogeneous nucleation of spherulites.** This mechanism proceeds via continuous nucleation and growth of spherulites throughout the entire crystallization process. Nucleation occurs in the amorphous molten material below the melting temperature. During the time interval from \( \lambda \) to \( \lambda + d\lambda \), the number of spherulites nucleated in the amorphous phase per volume of polymer is given by \( dN_S \). The temperature-dependent nucleation rate is proportional to the volume fraction of amorphous material, and this rate process is assumed to proceed via 1\textsuperscript{st}-order kinetics, as illustrated below, where the appropriate concentration variable is the amorphous volume fraction;

\[
dN_S/d\lambda = K_{\text{Homogeneous}}(T) \{ 1 - X_V \}
\]

\( K_{\text{Homogeneous}}(T) \) is a temperature-dependent rate constant for homogeneous nucleation, with dimensions of \{volume-time\}^{-1}, that decreases at higher temperature. If spherulites are nucleated at time \( \lambda \) and exhibit constant growth rate \( G(T) \) during isothermal crystallization, then their radius at time \( t \) is;
The volume of this single isolated spherulite at time \( t \), which was nucleated homogeneously at time \( \lambda \), is;

\[
V_{1, \text{Spherulite}}(t; \lambda) = \frac{4}{3} \pi \{ r(t; \lambda) \}^3 = \frac{4}{3} \pi G^3(T) (t - \lambda)^3
\]

The incremental volume fraction of crystallinity at time \( t \), \( dX_V \), due to spherulites that were nucleated between time \( \lambda \) and \( \lambda + d\lambda \), is given by the product of the incremental number density of spherulites which occurred between \( \lambda \) and \( \lambda + d\lambda \) and the volume of these spherulites at time \( t \). Hence;

\[
dX_V = V_{1, \text{Spherulite}}(t; \lambda) dN_S = \frac{4}{3} \pi G^3(T) K_{\text{Homogeneous}}(T) \{ 1 - X_V \} (t - \lambda)^3 d\lambda
\]

Now, consider all possible nucleation times from \( \lambda = t_0 \) to \( \lambda = t \). This allows one to determine the total volume fraction of spherulites during isothermal crystallization at time \( t \), \( X_V(t; T) \), via separation of variables with an initial condition of \( X_V = 0 \) at \( t = t_0 \);

\[
X_V(t; T) = \exp \left\{ -\frac{1}{3} \pi \left[ G(T) \right]^3 K_{\text{Homogeneous}}(T)(t-t_0)^4 \right\}
\]

Once again, this form of the Avrami equation must be modified to account for the fact that macromolecules do not exhibit 100% crystallinity. This is accomplished as follows;

\[
\frac{X_V(t; T)}{X_V(t \to \infty)} = 1 - \exp \left\{ -\frac{1}{3} \pi \left[ G(T) \right]^3 K_{\text{Homogeneous}}(T)(t-t_0)^4 \right\}
\]

**Linear least squares analysis of the kinetics of crystallization via the generalized Avrami equation.** Results from the previous two sections are
summarized below for the time dependence of the volume fraction of spherulites during isothermal crystallization;

\[
\frac{X_V(t;T)}{X_V(t \to \infty)} = 1 - \exp\{-k_n(T)t^n\}
\]

where \(t_0 = 0\) without loss of generality, \(n\) is the generalized Avrami exponent and \(k_n(T)\) is the temperature-dependent crystallization rate constant with dimensions of \{time\}^n. The analyses above suggest that the following values and expressions are appropriate for two different crystallization mechanisms;

<table>
<thead>
<tr>
<th>Crystallization mechanism</th>
<th>Avrami exponent</th>
<th>Rate constant {time}^n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heterogeneous nucleation</td>
<td>(n = 3)</td>
<td>(k_n(T) = (4/3) \pi N_s G^3(T))</td>
</tr>
<tr>
<td>Homogeneous nucleation</td>
<td>(n = 4)</td>
<td>(k_n(T) = (1/3) \pi G^3(T) K_{Homogeneous}(T))</td>
</tr>
</tbody>
</table>

When the Avrami exponent \(n\) is greater than unity, the time dependence of the volume fraction of crystallinity follows a sigmoidal increase from zero at the inception of the process to the upper limit given by \(X_V(t \to \infty)\). Larger values of the Avrami exponent and smaller rate constants correspond to a longer induction period, or time delay, before crystallization occurs isothermally at temperatures below the melting point. Nucleating agents operate via the heterogeneous mechanism and provide a foreign solid surface in the molten amorphous polymer upon which spherulites grow. Relative to homogeneously nucleated crystals, the presence of nucleating agents is consistent with smaller Avrami exponents, larger crystallization rate constants, and higher temperatures between \(T_g\) and \(T_m\) where the maximum rate of crystallization occurs. Natural aerosols in the air originate from sea spray, dust storms, wildfires and volcanoes. Pollution-based aerosols, primarily due to diesel exhaust and coal-burning power plants, are concentrated above industrialized cities and, together with natural aerosols, they provide nucleation sites within storm clouds where water vapour condenses into liquid droplets, subsequently forming ice crystals during winter. Hence, snowflakes that form in polluted storm clouds are generated at a relatively faster rate via this heterogeneous nucleation process, and the rate of crystallization scales linearly with the number density of aerosol particles. However, these heterogeneously nucleated snowflakes that form around pollution-based aerosols are smaller in size, undergo less frequent collisions with other water droplets in the same
storm clouds and, ultimately, contain less moisture, supporting the theory that air pollution contributes to reduced snowpack in the mountains and lower spring runoff [see RD Borys, DH Lowenthal, & DL Mitchell, *Atmospheric Environment*, 34, 2593-2602 (2000)]. At the same temperature below the melting point of a given polymer, nucleating agents accelerate the rate of crystallization relative to the formation of homogeneously nucleated crystals. Hence, a larger volume fraction of crystallinity is expected after the process occurs for a given time t in the presence of a nucleating agent relative to $X_V$ when the nucleating agent is absent, but the upper limit of crystallinity is not affected much. Polarized optical micrographs, illustrated below, reveal the effect of the nucleating agent, lithium perchlorate (i.e., LiClO$_4$), on the spherulitic morphology and increased rate of crystallization in poly(ethylene oxide). Crystallization time and temperature (i.e., ambient) are invariant in both micrographs;

![Pure PEO](image1.png) ![95% PEO, 5% LiClO$_4$](image2.png)

Experimentally, one measures the rate at which thermal energy is liberated during isothermal crystallization via DSC when the calorimeter operates in constant-temperature mode. Hence, quantitative information about $X_V(t;T)$ is available from differential scanning calorimetry, regardless of whether semicrystalline polymers form spherulites or disordered lamellae. When the calorimeter operates in an isothermal mode, it provides information about the rate at which thermal energy must be added to or removed from the sample to maintain constant temperature. Since the formation of crystallites from the amorphous molten material is an exothermic process, the calorimeter removes thermal energy from the sample at the same rate at which it is generated by the crystallization process. The sample behaves similar to a constant volume batch reactor. Detailed reactor analysis in the next chapter reveals that the time rate of change of $X_V$ is proportional to the rate at which thermal energy must be removed during isothermal operation. Knowledge of the heat of fusion for the semicrystalline polymer under investigation, and integration of the DSC output curve vs. time yield $X_V(t;T)$. Experimental determination of the Avrami exponent n and
the crystallization rate constant $k_n(T)$ is achieved via linear least squares analysis of the generalized Avrami equation after performing the following algebraic rearrangement;

$$1 - \frac{X_v(t;T)}{X_v(t \rightarrow \infty)} = \exp\left\{-k_n(T)t^n\right\}$$

$$\ln\left\{1 - \frac{X_v(t;T)}{X_v(t \rightarrow \infty)}\right\} = -k_n(T)t^n$$

$$\ln\left[-\ln\left\{1 - \frac{X_v(t;T)}{X_v(t \rightarrow \infty)}\right\}\right] = \ln\{k_n(T)\} + n \ln t$$

The experimental DSC data from isothermal crystallization at temperature $T$ are processed as follows, excluding the initial data point at $X_v(t=0;T) = 0$;

1. Integrate the isothermal DSC output curve at several different crystallization times $t$ and divide the integrated results by the tabulated heat of fusion to determine $X_v(t;T)$. It is necessary to account for the fact that calorimetry provides a measure of the mass fraction of crystallinity, whereas the Avrami equation was developed in terms of the volume fraction of spherulites. Hence, crystalline and amorphous densities are also necessary to obtain accurate values of $X_v(t;T)$ from the isothermal DSC output curve.

2. Perform linear least squares analysis of $X_v(t;T)$ using a 1st-order polynomial. In other words, the model is; $y(x) = a_0 + a_1x$

3. The independent variable is $x = \ln t$, where crystallization time $t$ appears on the horizontal axis of the DSC output curve.

4. The dependent variable is;

$$y = \ln\left[-\ln\left\{1 - \frac{X_v(t;T)}{X_v(t \rightarrow \infty)}\right\}\right]$$

5. The 1st-order coefficient $a_1$ (i.e., slope) in the model is the generalized Avrami exponent $n$. 

9  Kinetics of crystallization  
Annealing and spherulitic growth
(6) The zeroth-order coefficient $a_0$ (i.e., intercept) in the model is related to the crystallization rate constant $k_n(T)$ as follows;

$$a_0 = \ln \{k_n(T)\}$$

**Half-time analysis of crystallization isotherms.** Once the generalized Avrami exponent is known from linear least squares analysis of $X_V(t; T)$, as described above, one should calculate the crystallization rate constant from half-time analysis and compare the result with step#6 in the previous section. The half-time, $t_{1/2}$, is defined as the time required to achieve 50% of the maximum crystallinity during an isothermal experiment. Hence;

$$X_V(t = t_{1/2}) = (1/2) X_V(t \Rightarrow \infty)$$

Rearrangement of the generalized Avrami equation allows one to calculate $k_n(T)$ if the exponent $n$ is known;

$$\frac{X_V(t = t_{1/2})}{X_V(t \Rightarrow \infty)} = \frac{1}{2} = 1 - \exp\left\{-k_n(T)t_{1/2}^n\right\}$$

$$k_n(T) = \frac{\ln 2}{t_{1/2}^n}$$

The Avrami exponent $n$ can be verified by calculating the slope of a normalized crystallization isotherm at $t_{1/2}$. The development proceeds as follows;

$$\frac{X_V(t; T)}{X_V(t \Rightarrow \infty)} = 1 - \exp\left\{-k_n(T)t^n\right\}$$

$$\left[\frac{d}{dt} \left\{ \frac{X_V(t; T)}{X_V(t \Rightarrow \infty)} \right\}\right]_{t=t_{1/2}} = nk_n(T)t_{1/2}^{n-1} \exp\left\{-k_n(T)t_{1/2}^n\right\}$$

The previous expression for the rate of crystallization is simplified via the definition of $t_{1/2}$;
\[
\left[ \frac{d}{dt} \frac{X_V(t; T)}{X_V(t \to \infty)} \right]_{t=t_{1/2}} = \frac{n \ln 2}{2 t_{1/2}^{1/2}}
\]

Hence;

\[
n = \frac{2 t_{1/2}^{1/2}}{\ln 2} \left[ \frac{d}{dt} \frac{X_V(t; T)}{X_V(t \to \infty)} \right]_{t=t_{1/2}}
\]

Half-time analysis and linear least squares analysis should yield consistent results and allow one to quantify isothermal rates of crystallization via the generalized Avrami equation.

**Maximum rate of isothermal crystallization.** Based on the generalized Avrami equation for the time dependence of the volume fraction of crystallinity, one calculates the isothermal rate of crystallization as follows;

\[
\frac{d}{dt} \left[ \frac{X_V(t; T)}{X_V(t \to \infty)} \right] = n k_n(T) t^{-1} \exp\{ -k_n(T) t^n \}
\]

For a crystallization mechanism in which the exponent \( n > 1 \), the crystallization rate approaches zero at the beginning of the process (i.e., \( t \to 0 \)) and when the process nears completion (i.e., \( t \to \infty \)). The maximum rate of isothermal crystallization occurs at time \( t_{\text{max}} \), which corresponds to the inflection point of the sigmoidal-shaped curve of \( X_V \) vs. time where the 2\text{nd} derivative of \( X_V(t; T) \) vanishes. Hence, \( t_{\text{max}} \) is calculated from the following equation;

\[
\frac{d^2}{dt^2} \left[ \frac{X_V(t; T)}{X_V(t \to \infty)} \right] = n k_n(T) t^{-2} \left[ n - 1 - n k_n(T) t^n \right] \exp\{ -k_n(T) t^n \} = 0
\]

The rate of isothermal crystallization proceeds quickest when;

\[
t_{\text{max}} = \left\{ \frac{n - 1}{n k_n(T)} \right\}^{1/n}
\]
The half-time $t_{1/2}$ is coincident with the inflection point of $X_V$ vs. time when the Avrami exponent $n = 3.26$, which implies that $t_{1/2} = t_{\text{max}}$. The half-time is greater than $t_{\text{max}}$ when $n < 3.26$, and $t_{1/2}$ occurs prior to the inflection point of $X_V$ vs. time when $n > 3.26$, but differences between $t_{1/2}$ and $t_{\text{max}}$ could be difficult to resolve for reasonable values of $n$ between 3 and 4. These trends are summarized below. The maximum rate of crystallization is evaluated when $t = t_{\text{max}}$:

$$
\left[ \frac{d}{dt} \left\{ \frac{X_V(t;T)}{X_V(t = \infty)} \right\} \right]_{t = t_{\text{max}}} = nk_n(T) t_{\text{max}}^{n-1} \exp\left\{ -k_n(T) t_{\text{max}}^n \right\}
$$

$$
= \varphi(n) \left\{ k_n(T) \right\}^{1/n}
$$

where;

$$
\varphi(n) = (n-1)^{(n-1)/n} n^{1/n} \exp\left\{ -\frac{n-1}{n} \right\}
$$

and $\varphi=1$ when $n=1$. One identifies $\{k_n(T)\}^{1/n}$ as the crystallization rate constant with dimensions of (time)$^{-1}$. Temperature dependence of this rate constant allows one to predict the optimum crystallization temperature (i.e., $T_c$) where the kinetics of crystallization proceed most rapidly. The following sections address the temperature dependence of $k_n(T)$. Since half-time measurements provide a route to calculate $k_n(T)$, the important results of this section are summarized in terms of $t_{1/2}$;

$$
t_{\text{max}} = \left\{ \frac{n-1}{n \ln 2} \right\}^{1/n} t_{1/2}
$$

and the maximum rate of crystallization is;

$$
\left[ \frac{d}{dt} \left\{ \frac{X_V(t;T)}{X_V(t \to \infty)} \right\} \right]_{t = t_{\text{max}}} = \varphi(n) \left\{ k_n(T) \right\}^{1/n} = \frac{\varphi(n) \{ \ln 2 \}^{1/n}}{t_{1/2}}
$$

Sigmoidal-shaped crystallization isotherms are illustrated below for two values of the Avrami exponent (i.e., $n=2$ and $n=4$), together with a comparison between the half-time and the time at which the rate of crystallization proceeds the fastest when the crystallization rate constant is $10^{-3}$ (minute)$^n$. 

12  Kinetics of crystallization
Annealing and spherulitic growth
**Effect of the Avrami exponent on the half-time and $t_{\text{max}}$**

$k_n = 10^{-3} \text{ (minute)}^{-n}$

<table>
<thead>
<tr>
<th>Avrami exponent</th>
<th>Half-time (minutes)</th>
<th>$t_{\text{max}} / t_{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>26</td>
<td>0.85</td>
</tr>
<tr>
<td>3</td>
<td>8.8</td>
<td>0.99</td>
</tr>
<tr>
<td>3.26</td>
<td>7.4</td>
<td>1.00</td>
</tr>
<tr>
<td>4</td>
<td>5.1</td>
<td>1.02</td>
</tr>
<tr>
<td>5</td>
<td>3.7</td>
<td>1.03</td>
</tr>
</tbody>
</table>

Larger relative differences between $t_{1/2}$ and $t_{\text{max}}$ exist, for $n = 2$, when the crystallization isotherm exhibits significant asymmetry about the inflection point where $t = t_{\text{max}}$.

**Avrami Crystallinity and Rate of Crystallization; $n=2$**

![Avrami Crystallinity and Rate of Crystallization; n=2](image-url)
**Avrami Crystallinity and Rate of Crystallization; n=4**

![Graph of Volume Fraction of Crystallinity and Rate of Crystallization vs. Crystallization Time]

*Thermodynamics and kinetics of homogeneous nucleation.* Consider nucleation and spontaneous growth of a spherulite of radius \( r \) that accompany the following "reaction";

\[
\text{Molten Amorphous Polymer} \leftrightarrow \text{Spherulite}
\]

There are at least two processes which contribute to the extensive total free energy change, \( \Delta G_{\text{Spherulite}} \), for the formation of a spherulite.

1. A favourable volumetric process given by;

\[
\frac{4}{3} \pi r^3 \Delta g
\]

where;

\[
\Delta g = g_{\text{Spherulite}} - g_{\text{Amorphous}}
\]

In the previous equation, \( g \) represents a free energy density (i.e. energy/volume) for each specific phase in the above-mentioned "reaction".
Since the favoured phase corresponds to the one with lower free energy, the following qualitative temperature dependence of $\Delta g$ is appropriate:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$\Delta g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T = T_{\text{melt}}$</td>
<td>0</td>
</tr>
<tr>
<td>$T &lt; T_{\text{melt}}$</td>
<td>$&lt; 0$</td>
</tr>
<tr>
<td>$T &gt; T_{\text{melt}}$</td>
<td>$&gt; 0$</td>
</tr>
</tbody>
</table>

For typical crystallization temperatures below the melting point, $\Delta g$ is negative and this volumetric process represents a favourable contribution to $\Delta G_{\text{spherulite}}$.

(2) An unfavourable surface-related process given by;

$$4 \pi r^2 \sigma$$

where $\sigma$ is the surface free energy change (i.e., energy/area) that accompanies the formation of "foreign" spherulitic surfaces in the molten amorphous phase. This process is unfavourable because $\sigma > 0$.

Now, it is possible to predict the total free energy change for the formation of a spherulite of radius $r$. However, it should be emphasized that this model for the Gibbs free energy change that accompanies spherulite formation, and the next model that considers the addition of an N-stem crystal layer to a growing lamella, do not capture effects of (i) chain microstructure (i.e., configurational isomers), (ii) packing of left- and right-handed helices in the unit cell, or (iii) chain branching;

$$\Delta G_{\text{spherulite}} = (4/3) \pi r^3 \Delta g + 4 \pi r^2 \sigma = 4\pi r^2 \left\{ \frac{1}{3} r \Delta g + \sigma \right\}$$

For crystallinity to develop in the molten amorphous phase below $T_{\text{melt}}$, nucleation and subsequent growth of spherulites should occur spontaneously. The corresponding mathematical statement from thermodynamics is;

$$\left\{ \frac{\partial}{\partial r} \Delta G_{\text{spherulite}} \right\}_T < 0$$

such that radial growth occurs in a regime where the total free energy decreases continuously. There is a thermodynamic driving force to minimize the total free energy change that accompanies spherulite formation, and this driving force is
assisted by the fact that spheres exhibit maximum volume-to-surface ratio, relative to flat plates or long cylinders. When crystallization occurs below $T_{\text{melt}}$ where $\Delta g < 0$, $\Delta G_{\text{Spherulite}}$ vs. $r$ exhibits a double root at $r = 0$, and another root at:

$$r_{\text{root}} = \frac{3\sigma}{-\Delta g}$$

During isothermal crystallization, the slope of $\Delta G$ vs. $r$ is given by:

$$\left(\frac{\partial}{\partial r} \Delta G_{\text{Spherulite}}\right)_T = 4\pi r (r\Delta g + 2\sigma)$$

and the second derivative of $\Delta G$ vs. $r$ is:

$$\left(\frac{\partial^2}{\partial r^2} \Delta G_{\text{Spherulite}}\right)_T = 8\pi (r\Delta g + \sigma)$$

Hence, zero slopes occur at $r = 0$, and:

$$r_{\text{critical}} = \frac{2\sigma}{-\Delta g}$$

The zero slope at $r = 0$ represents a local minimum in $\Delta G_{\text{Spherulite}}$. The extremely important zero slope at $r_{\text{critical}}$ corresponds to a maximum in $\Delta G_{\text{Spherulite}}$, denoted by $\Delta G_{\text{critical}}$. Hence, random thermal fluctuations in the amorphous phase below $T_{\text{melt}}$ must provide sufficient thermal energy to overcome the barrier represented by $\Delta G_{\text{critical}}$ such that spontaneous spherulitic growth can occur. The magnitude of this energy barrier is:

$$\Delta G_{\text{critical}} = \Delta G_{\text{Spherulite}}(r = r_{\text{critical}}) = \frac{4}{3} \pi r_{\text{critical}}^3 \Delta g + 4 \pi r_{\text{critical}}^2 \sigma = \frac{16 \pi \sigma^3}{3(-\Delta g)^2}$$

Hence, random thermal fluctuations due to Brownian motion in the molten amorphous phase below $T_{\text{melt}}$ must overcome $\Delta G_{\text{critical}}$ for chain segments to (i) rearrange conformationally, (ii) adopt the appropriate sequence of rotational isomeric states within the unit cell, (iii) undergo chain folding in a lamellar structure, and (iv) exhibit spontaneous spherulitic growth via homogeneous nucleation. The temperature
dependence of this energy barrier is obtained by considering the free energy density difference between a spherulite and the amorphous molten polymer below the melting point;

$$\Delta g = g_{\text{spherulite}} - g_{\text{amorphous}} = \Delta h - T \Delta s$$

where the enthalpy change (i.e., $\Delta h$) and the entropy change (i.e., $\Delta s$) are negative because the isothermal crystallization process is exothermic and chains are more ordered in the crystallites relative to the disordered amorphous phase. Since $\Delta g$ vanishes at the melting temperature, the ratio of $(-\Delta h)$ to $(-\Delta s)$ is given by;

$$\frac{-\Delta h}{-\Delta s} = T_{\text{melt}}$$

This ratio is assumed to remain the same at other temperatures where $\Delta g$ does not vanish. Hence, the temperature dependence of $\Delta g$ is approximated as follows;

$$\Delta g = \Delta h \left(1 - T \left(\frac{\Delta s}{-\Delta h}\right)\right) = \Delta h \left(1 - \left(\frac{T}{T_{\text{melt}}}\right)\right) = \Delta h \left(\frac{T_{\text{melt}} - T}{T_{\text{melt}}}\right)$$

This temperature dependence of $\Delta g$ allows one to predict the energy barrier that must be surpassed and the critical spherulite size above which spontaneous growth occurs;

$$\Delta G_{\text{critical}} = \frac{16\pi \sigma^3 T_{\text{melt}}^2}{3(-\Delta h)^2 \left(T_{\text{melt}} - T\right)^2}$$

$$r_{\text{critical}} = \frac{2\sigma T_{\text{melt}}}{(-\Delta h)(T_{\text{melt}} - T)}$$

The "degree of supercooling" is defined as $T_{\text{melt}} - T$, when crystallization occurs at temperature $T$. Now, it should be obvious that homogeneous nucleation of spherulites at the melting temperature is highly unfavourable because the energy barrier is infinitely high and the critical spherulite size is infinitely large. This is synonymous with the fact that the rate of homogeneous nucleation is vanishingly small. Nucleation rates increase at lower crystallization temperatures because the barrier height decreases and the critical spherulite size is smaller. However, the final spherulite size
is smaller when crystallization proceeds at lower temperatures, due to increased surface free energy, and the melting temperature of these smaller "imperfect" spherulites is lower than that of spherulites which form at higher temperature. The crystallite imperfection content is greater and $T_{\text{melt}}$ is lower when crystallization occurs more rapidly at lower temperature.

**Temperature dependence of the crystallization rate constant.** The rate of crystallization is proportional to the crystallization rate constant with dimensions of inverse time, \( \{k_n(T)\}^{1/n} \), as described previously in this chapter. Two different models are proposed to simulate the effect of temperature on rates of crystallization, in agreement with the following qualitative trends;

1. The rate constant for homogeneous nucleation $K_{\text{Homogeneous}}$ increases at lower temperature. Hence;
   \[
   \frac{d}{dT} K_{\text{Homogeneous}} < 0
   \]

2. The energy barrier which must be surpassed to allow spontaneous growth of homogeneously nucleated spherulites increases at higher temperature, as one approaches $T_m$. Hence;
   \[
   \frac{d}{dT} \Delta G_{\text{critical}} > 0
   \]

3. Spherulitic growth rates, defined by $G = dr/dt$, increase at higher temperature. This growth process requires sufficient mobility for disordered chain segments in the amorphous phase to reorganize conformationally and adopt the appropriate rotational isomeric states in the crystal. An increase in fractional free volume at higher temperature allows faster growth rates above the glass transition. Hence;
   \[
   \frac{dG}{dT} > 0
   \]

Rates of crystallization are growth-rate controlled at low temperatures and nucleation-rate controlled at higher temperatures. A window of plausible temperatures to induce crystallization exists between $T_g$ and $T_{\text{melt}}$, and one expects vanishingly small rates at both of these phase transition temperatures. The first model combines all of the above-mentioned effects into one temperature-dependent exponential function. For
temperatures between $T_g$ and $T_{\text{melt}}$ where a maximum in the rate of crystallization exists;

$$\left\{ k_n(T) \right\}^{1/n} \approx \exp \left\{ \frac{-\Delta G_{\text{critical}}(T)}{\zeta(T - T_g)^a} \right\}$$

The exponent "a" is positive and the constant $\zeta$ has dimensions of energy/K$^a$. This functional form for the crystallization rate constant yields a slower rate of crystallization when the energy barrier for spontaneous nucleation increases as one approaches the melting temperature, and when mobility decreases at lower temperature. It is not true that conformational rearrangements are “frozen” and chain mobility ceases completely at the glass transition temperature, but the concept of inducing crystallization in macromolecules below $T_g$ is somewhat contradictory because glasses exhibit exceedingly large motional time constants. The second model accounts for temperature-dependent nucleation and growth rates separately. The rate of homogeneous nucleation is modeled as an activated process with a temperature-dependent energy barrier given by $\Delta G_{\text{critical}}(T)$. Hence;

$$\left\{ K_{\text{Homogeneous}}(T) \right\}^{1/n} = \exp \left\{ \frac{-\Delta G_{\text{critical}}(T)}{RT} \right\}$$

where R is the gas constant. Temperature-dependent growth rates are modeled analogous to rate processes like diffusion and molecular motion in the vicinity of the glass transition, resulting from a redistribution of useful free volume (i.e., not interstitial free volume) that is easy to manipulate without an activation barrier;

$$\left\{ G^3(T) \right\}^{1/n} = \left( \frac{dr}{dt} \right)^3_n \approx \exp \left\{ \frac{-f^*}{f(T) - f(T_g)} \right\}$$

where f(T) represents fractional free volume and f* is the critical fractional free volume required for conformational reorganization via rotation about single bonds in the backbone as chains in the amorphous phase diffuse, reptate, fold, and adopt the correct conformation for crystallization within lamellae. A reasonable value for f* is 0.025, which corresponds to 2.5% relative empty space between chains at the glass transition. Hence;
\[
\{k_n(T)\}^{1/n} = \{G^3(T)K_{Homogeneous}(T)\}^{1/n}
\]

\[
\approx \exp\left\{\frac{-\Delta G_{critical}(T)}{RT}\right\} \exp\left\{\frac{-f^*}{f(T) - f(T_g)}\right\}
\]

**Optimum crystallization temperatures---comparison between theory and experiment.** Based on two different models for temperature-dependent crystallization rate constants in the previous section and the maximum rate of isothermal crystallization at \(t = t_{max}\) via the generalized Avrami equation, it is possible to predict the optimum annealing temperature \(T_C\) where crystallization proceeds fastest. This occurs between \(T_g\) and \(T_{melt}\). One calculates \(T_C\) from the following extremum condition;

\[
\lim_{t \to \infty} \frac{d}{dt} \left\{ \frac{x(t;T)}{x(T)} \right\} = \phi(n) \frac{d}{dT} \left[ \{k(T)\}^{1/n} \right] = 0
\]

The 1\textsuperscript{st} model yields;

\[
\phi(n)\{k_n(T_C)\}^{1/n} \gamma T_{melt}^2 \left[ \frac{a \zeta(T_C - T_g)^{a-1} (T_{melt} - T_C)^2 - 2 \zeta(T_C - T_g)^a (T_{melt} - T_C)}{\zeta(T_C - T_g)^a (T_{melt} - T_C)^2} \right] = 0
\]

\[
\gamma = \frac{16 \pi \sigma^3}{3(-\Delta h)^2}
\]

The parameter \(\gamma\) has dimensions of energy. For \(a > 1\), the previous equation is satisfied when \(T_C\) is either \(T_g\) or \(T_{melt}\), which corresponds to the absolute minimum rate of crystallization. The maximum rate of crystallization occurs at annealing temperature \(T_C\) when the following nonlinear algebraic equation is satisfied;

\[
a \zeta(T_C - T_g)^{a-1} (T_{melt} - T_C)^2 - 2 \zeta(T_C - T_g)^a (T_{melt} - T_C) = 0
\]
This yields an optimum crystallization temperature given by:

\[ T_C = T_g + \frac{a}{2 + a} (T_{melt} - T_g) \]

which agrees with empirical observations when \( a = 4 \). Hence, the optimum annealing temperature is:

\[ T_C = T_g + \frac{2}{3} (T_{melt} - T_g) \]

The 2\(^{nd}\) model yields:

\[
\varphi(n) \left\{ k_n(T_C) \right\}^{1/n} \frac{d}{dT} \left\{ \frac{-f^*}{\Delta \alpha (T - T_g)} - \frac{\gamma T_{melt}^2}{RT (T_{melt} - T)^2} \right\} = 0
\]

One calculates the optimum annealing temperature \( T_C \) from:

\[
\frac{f^*}{\Delta \alpha (T_C - T_g)} + \gamma T_{melt}^2 \left\{ \frac{R(T_{melt} - T_C)^2 - 2RT_C(T_{melt} - T_C)}{RT_C(T_{melt} - T_C)^2} \right\} = 0
\]

which simplifies to the following nonlinear algebraic equation for \( T_C \):

\[
\frac{f^*}{\Delta \alpha} T_C^2 (T_{melt} - T_C)^3 = \frac{\gamma}{R} T_{melt}^2 (3T_C - T_{melt})(T_C - T_g)^2
\]

where the discontinuous increment in the coefficient of thermal expansion at the glass transition is \( \Delta \alpha \approx 4.8 \times 10^{-4} \text{ K}^{-1} \). To illustrate the correspondence between \( T_g \) and the free energy parameter \( \gamma \) for optimum crystallization kinetics, if \( T_{melt} = 523 \text{ K} \), \( T_g \) varies from 173 K to 423 K, and \( T_C \) assumes its optimum value based on the 1\(^{st}\) model with \( a = 4 \), then the previous equation which represents the extremum condition for the 2\(^{nd}\) model reveals that \( \gamma/R \) decreases linearly as \( T_g \) increases.
Relation between the free energy parameter $\gamma$ for spherulite formation and the glass transition temperature of a semicrystalline polymer with $T_{\text{melt}} = 523$ K and optimum crystallization temperature given by:

$$T_C = T_g + \left(\frac{2}{3}\right) [T_{\text{melt}} - T_g]$$

<table>
<thead>
<tr>
<th>$\gamma/R$ (K)</th>
<th>$T_g$ (K)</th>
<th>$T_C$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.32</td>
<td>173</td>
<td>406</td>
</tr>
<tr>
<td>1.21</td>
<td>203</td>
<td>416</td>
</tr>
<tr>
<td>1.11</td>
<td>233</td>
<td>426</td>
</tr>
<tr>
<td>1.00</td>
<td>263</td>
<td>436</td>
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<tr>
<td>0.89</td>
<td>293</td>
<td>446</td>
</tr>
<tr>
<td>0.78</td>
<td>323</td>
<td>456</td>
</tr>
<tr>
<td>0.67</td>
<td>353</td>
<td>466</td>
</tr>
<tr>
<td>0.56</td>
<td>383</td>
<td>476</td>
</tr>
<tr>
<td>0.40</td>
<td>423</td>
<td>490</td>
</tr>
</tbody>
</table>

To illustrate the relation between $T_{\text{melt}}$ and $\gamma$ for optimum crystallization kinetics, if $T_g = 223$ K, $T_{\text{melt}}$ varies from 273 K to 523 K, and $T_C$ assumes its optimum value based on the 1st model with $a=4$, then the previous equation reveals that $\gamma/R$ increases as $T_{\text{melt}}$ increases, but with slightly negative curvature.

Relation between the free energy parameter $\gamma$ for spherulite formation and the melting temperature of a semicrystalline polymer with $T_g = 223$ K and optimum crystallization temperature given by:

$$T_C = T_g + \left(\frac{2}{3}\right) [T_{\text{melt}} - T_g]$$

<table>
<thead>
<tr>
<th>$\gamma/R$ (K)</th>
<th>$T_{\text{melt}}$ (K)</th>
<th>$T_C$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.39</td>
<td>273</td>
<td>256</td>
</tr>
<tr>
<td>0.55</td>
<td>303</td>
<td>276</td>
</tr>
<tr>
<td>0.68</td>
<td>333</td>
<td>296</td>
</tr>
<tr>
<td>0.79</td>
<td>363</td>
<td>316</td>
</tr>
<tr>
<td>0.88</td>
<td>393</td>
<td>336</td>
</tr>
<tr>
<td>0.95</td>
<td>423</td>
<td>356</td>
</tr>
<tr>
<td>1.02</td>
<td>453</td>
<td>376</td>
</tr>
<tr>
<td>1.08</td>
<td>483</td>
<td>396</td>
</tr>
<tr>
<td>1.14</td>
<td>523</td>
<td>423</td>
</tr>
</tbody>
</table>
Perhaps the best application of the previous equation uses experimental values for $T_g$, $T_{melt}$, and $\gamma$ for semicrystalline polymers to identify the optimum crystallization temperature. For example, consider a semicrystalline polymer in which $T_g \approx 373$ K and $T_{melt} \approx 523$ K. The optimum annealing temperature, where the kinetics of crystallization proceed most rapidly, is 473 K based on the 1$^{st}$ model with $a=4$. The 2$^{nd}$ model reveals that this optimum crystallization temperature decreases nonlinearly (i.e., with positive curvature) as the energy parameter $\gamma$ increases. This effect is illustrated below.

Notice that the 2$^{nd}$ model predicts a range of crystallization temperatures, above and below $T_{C,optimum} = 473$ K based on the 1$^{st}$ model, for reasonable values of the energy parameter $\gamma$. If there is no surface free energy change (i.e., penalty) that accompanies the formation of spherulites in the amorphous phase (i.e., both $\sigma$ and $\gamma$ vanish), then the previous simulations reveal that the optimum crystallization temperature coincides with $T_{melt}$. Obviously, this is an ideal situation that most likely doesn’t occur in practice.

**Suggested literature on crystallization kinetics.** The classic papers on crystallization growth rates which describe the Lauritzen-Hoffman theory are;


A more recent reference is;


**The Energetics of Chain Folding in Semicrystalline Polymer-Polymer Blends that Exhibit Multiple Melting Endotherms**

**Overview**

The melting and crystallization behaviour of semicrystalline homopolymers has received much attention both in academic and industrial research because the morphological aspects of polymer crystals and spherulites influence mechanical, optical, and other macroscopic properties. Changes in crystallization or melting may cause dramatic variations in the properties of engineering materials from an application and processing viewpoint. An interesting feature of melting behaviour, the presence of multiple endotherms, has been observed in some semicrystalline homopolymers such as polyethylene, poly(ethylene oxide), poly(butylene terephthalate), and poly(ether ether ketone). It has been suggested that multiple melting endotherms are caused by;

1. recrystallization and subsequent melting of as-formed unstable crystals that melt initially at relatively low temperatures,

2. melting of crystals that have different lamellar thicknesses and/or different spherulitic superstructures,
(3) melting of quasi-stable crystals that have been produced from different crystallization conditions and thermal histories, with subsequent recrystallization to a more stable form, and

(4) melting of crystals that have an inequivalent distribution of internal defects and/or surface defects.

Different tie-molecule segment lengths between lamellae could affect the mobility of the intercrystalline component and contribute to the conformational entropic stabilization or destabilization of the crystallites. Localized surface free energy differences also produce multiple melting, and stereo-irregular defects produce different melting temperatures. $T_m$ associated with the segments that contain a few stereo-irregular units can be increased by thermal treatment. This is a concept that has been verified experimentally for segmented polyurethane block copolymers. Suggestions (1) and (2) mentioned above represent the most probable origins of multiple melting behaviour. Kinetic models have also been proposed to explain multiple melting.

A systematic study of multiple melting in partially compatible polymer-polymer blends has not been documented sufficiently, despite the fact that semicrystalline blends of two macromolecules represent an important research area from the viewpoint of chemically designing multicomponent systems. The thermodynamic driving force for compatibility in many blends results from the exothermic energetics of specific interactions, such as hydrogen bonding, interpolymer complexation, and transition metal coordination because the entropic contribution to chemical stability is extremely small when the component molecular weights are large. Strong interactions between dissimilar functional groups in the amorphous phase of a crystalline/amorphous polymer-polymer blend could produce changes in crystalline morphology and surface free energy on the periphery of the lamellae. Consequently, the melting transitions of the semicrystalline polymer could be distorted due to the presence of the energetically attractive amorphous component in the mixtures.
Dependence of Multiple Melting Behaviour on the Chemical Structure of the Crystallizable Component in Polymer-Polymer Blends

Multiple melting behaviour has been observed recently for a variety of strongly interacting polymer blends in which the crystallizable component is either poly(ethylene oxide), poly(vinylidene fluoride), or main-chain polyesters. It was postulated that hydrogen-bond strength and specificity might have a strong influence on crystallization and melting, leading to complex heating traces in the differential scanning calorimeter. Polyesters with different [COO]/[CH₂] molar ratios were blended with the hydrogen-bond donor poly(vinylphenol), PVPh, to investigate multiple melting and the effects attributed to hydrogen bonding. The crystalline morphology of main-chain polyesters is sensitive to hydrogen-bond strength and concentration. This sensitivity, coupled with the fact that, in all of the main-chain polyesters chosen, the carbonyl group is equally accessible to the hydroxyl functional group of PVPh, allows for a systematic study of the effect of hydrogen-bond concentration on multiple melting phenomena. Blends of PVPh with a variety of main-chain polyesters reveal unique melting behaviour in each case.

Figure
Right figure: DSC thermograms illustrating multiple melting behaviour in solid state binary mixtures of poly(vinylphenol), MW = 30 kda., with (i) 60 wt% poly(ethylene succinate), PES, MW = 11 kda., (ii) 90 wt% poly(1,4-butylene adipate), PBA, (iii) 70 wt% poly(hexamethylene sebacate), PHMS, MW = 62 kda., (iv) 70 wt% polycaprolactone, PCL, MW = 32 kda., and (v) 80 wt% poly(ethylene adipate), PEA,
MW = 11 kda. Right figure; Multiple melting behaviour in binary solid state mixtures of poly(vinylphenol) and poly(ethylene succinate), at various blend compositions indicated at the left of each endotherm.

High-resolution solid state carbon-13 NMR and FTIR spectroscopic data have identified strong interactions between the hydroxyl functional group of PVPh and carbonyl oxygens in the polyester repeat unit. Association between PVPh hydroxyl groups and the polyester carbonyl moiety is rather strong, although weaker than the self-association of hydroxyl groups in undiluted PVPh. This attraction between functional groups in dissimilar chain segments can be detected \textit{indirectly} via high-resolution NMR spectroscopy of the carbon-13 site that is only one bond removed from the lone pairs of electrons on oxygen. The figure below reveals NMR chemical shift lineshapes for the carbonyl carbon (i.e., between 170-180 ppm) in high-resolution solid state spectra of semicrystalline/amorphous polymer-polymer blends of poly(vinylphenol) with (i) poly(ethylene adipate), PEA; (ii) poly(1,4-butylene adipate), PBA; and (iii) polycaprolactone, PCL;

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{Dipolar decoupled carbon-13 NMR spectra of poly(ethylene adipate), MW = 11 kda. (left), poly(1,4-butylene adipate), (center), and polycaprolactone, MW = 32 kda. (right), in the carbonyl carbon chemical shift region via cross-polarization and magic-angle spinning, in blends with poly(vinylphenol), MW = 30 kda. High-resolution spectra with red triangles correspond to isotropic carbonyl $^{13}$C NMR line shapes that reflect polyester chain mobility at experimental temperatures that are above the glass-transition temperature, rather than the presence or absence of a polyester-rich crystalline phase.}
\end{figure}

The carbonyl $^{13}$C NMR signal in the crystalline domains exhibits a full-width-at-half-
height of 1-2 ppm when the glass transition temperature of the blends is below the temperature of the NMR experiment (i.e., indicated by red triangles in the spectra above). In all cases, a single concentration-dependent glass transition temperature is measured by DSC, which increases monotonically from below ambient for polyester-rich blends to well above ambient for blends that are rich in poly(vinylphenol). When the concentration of the amorphous proton donor, PVPh, is sufficient to thwart crystallization of the polyester and increase the glass transition temperature of the blends above the temperature of the NMR experiment (i.e., $\approx 15^\circ$C), the linewidth of the carbonyl resonance increases three- to four-fold (i.e., 5-6 ppm). When the blends are completely amorphous and the glass transition temperature is above $\approx 15^\circ$C, the polyester carbonyl $^{13}$C lineshape reveals at least two morphologically inequivalent microenvironments. A partially resolved carbonyl signal in rigid amorphous blends is (i) identified at higher chemical shift relative to the crystalline component, and (ii) attributed to hydrogen bonding in the amorphous phase. This interaction-sensitive hydrogen-bonded carbonyl signal, which is rather broad, accounts for an increasing fraction of the overall NMR absorption envelope of the carbonyl carbon site when the polyester is saturated with PVPh. It has been suggested that surface energetics due to hydrogen bonds between semicrystalline and amorphous blend components in the vicinity of the fold surface, alter the crystallization, melting, and recrystallization processes of the polyester. The existence of hydrogen bonds on the lamellar surface favourably decreases the surface free energy of the crystallites. This interaction at the interface between crystalline and amorphous domains stabilizes the formation of rather thin lamellae with more chain folds. Consequently, thinner lamellae are consistent with (i) more surface area per unit volume between dissimilar segments of the crystalline and amorphous components, and (ii) higher probability that the interacting functional groups will form hydrogen bonds and provide energetic stabilization for partial mixing of two high-molecular-weight polymers.

**Theoretical Considerations that Account for Strong Interactions**

With the aid of Hoffman's theory that explains homopolymer crystallization, a simple modification is proposed to illustrate how multiple melting endotherms might be generated for the semicrystalline component in strongly interacting blends. The formalism begins by postulating the functional dependence of the Gibbs free energy of formation for an N-stem crystal layer, $\Delta G_{N\text{-stem}}$, upon cooling below $T_m$ from the molten state. An N-stem crystal layer is defined as a polymer chain that folds (N-1) times as it adds to the lateral surface of a growing lamella. As lamellae grow, chain folding of crystal stems on the lamellar surface is consistent with a reduction of the overall free
energy for crystal growth. Another factor that contributes to chain folding is a reduction in packing density of the chain in the vicinity of the fold surface. This reduction in density allows for easy rotation about carbon-carbon backbone bonds, which is required for chain folding. If it can be demonstrated that this free energy function exhibits local kinetic minima and/or a global thermodynamic minimum corresponding to a preferred lamellar thickness, then the concept of multiple melting will be justified by calculating the preferred crystal stem height (i.e., the lamellar thickness) from the extremum condition. Thermodynamically or kinetically favoured lamellar thicknesses should decrease when stronger intermolecular interactions exist. These rather thin lamellae, that are stabilized by surface free energy effects on the periphery of the crystallites, melt below the primary transition temperature. As mentioned above, multiple endotherms result when these chains recrystallize to a more stable form during the heating trace in the calorimeter and subsequently melt again at higher temperature. The appropriate extensive free energy function for the addition of an N-stem crystal layer to a growing lamella is represented by the following equation;

$$\Delta G_{N\text{-stem}} = N a b \left\{ \sigma_{\text{ends/folds}} + \sigma_{\text{HydrogenBonds}} \right\} + (N a + 2 b) L \sigma_{\text{Lateral}} + \left( \Delta G_{\text{HydrogenBonds}} \right)_{\text{FoldSurface}} - \left( \Delta G_{\text{HydrogenBonds}} \right)_{\text{AmorphousPhase}} - N a b L (\Delta h_{\text{Melting}})$$

**Geometric considerations;**

“a” is the width of one crystal stem.

“b” is the depth of one stem.

L is the height of each stem or, more appropriately, the lamellar thickness.

N represents the number of stems that add to a growing lamella.

Hence, \( N a b \) represents either the upper or lower surface area of the N-stem layer. Half of the folds reside on the upper surface and the other half protrude from the lower surface. The lateral surface area of the aggregation of N stems that are exposed to the amorphous material can be represented by \((N a + 2 b)L \approx N a L\). The total volume of this newly formed N-stem crystal layer is given by \( N a b L \).

**Energetic considerations for chain folds, chain ends, and the presence of lateral surfaces;**

\( \sigma_{\text{end}} \) is the surface free energy density for one chain end on the lamellar surface.

\( \sigma_{\text{fold}} \) is the surface free energy density for one chain fold on the lamellar surface.

\( \sigma_{\text{Lateral}} \) represents the surface free energy density on the lateral periphery of a lamella.
These surface free energy densities, with dimensions of energy per area, allow one to construct contributions to the extensive Gibbs free energy for the formation of an N-stem segment of one lamella. The unfavourable non-specific surface free energy density due to two chain ends and \( N - 1 \) chain folds on the upper and lower lamellar surfaces is:

\[
\sigma_{\text{ends/folds}} = 2\sigma_{\text{end}} + (N - 1)\sigma_{\text{fold}}
\]

Non-specific energetics due to the presence of a foreign lamellar surface in the amorphous molten phase, as described by \( \sigma_{\text{Lateral}} \), occur across NaL where the N-stem layer contacts amorphous material only on one side (i.e., the other side of the stem contacts the growing lamella) and across \( 2bL \) which accounts for stem segments at both ends of the chain.

**Melting:**
\( \Delta h_{\text{Melting}} \) is the endothermic (i.e., \( >0 \)) enthalpy of melting per volume of the crystalline phase, which contributes favourably to the extensive free energy of formation of an N-stem crystal.

**Hydrogen bonding in the amorphous phase and on the periphery of the lamellae:**
\( \varphi_{\text{Amorphous}} \) is the volume fraction of the amorphous phase.
\( \varepsilon_{\text{HydrogenBond}} \) represents the volumetric energy density for hydrogen-bond formation between dissimilar blend components in the amorphous phase.

When hydrogen bonds form between dissimilar blend components on the fold surface of the crystallites, there is a favourable contribution to the extensive Gibbs free energy. The exothermic surface free energy density (i.e., per unit area) due to these interactions is expressed as follows;

\[
\sigma_{\text{HydrogenBonds}} = - \frac{\varphi_{\text{Amorphous}}}{1 - \varphi_{\text{Amorphous}}} \varepsilon_{\text{HydrogenBond}} \left\{ \frac{NabL}{Nab} \right\} = - \frac{\varphi_{\text{Amorphous}}}{1 - \varphi_{\text{Amorphous}}} L\varepsilon_{\text{HydrogenBond}}
\]

The ratio of amorphous to crystalline volume fractions corresponds to the ratio of total amorphous volume to total crystalline volume, \( NabL \) represents the volume of the newly formed N-stem segment of one lamella, and Nab is the total surface area for contact between functional groups on the fold surface and those in the amorphous phase that interact via hydrogen bonds. An unknown multiplication factor is required.
to relate \(NabL\) to the total volume of the crystalline phase, but this same factor relates \(Nab\) to the total surface area for contact between hydrogen bonding partners, where one functional group is part of the chemical structure of the completely amorphous component and the complementary functional group belongs to the semicrystalline component on the fold surface of the lamellae. The extensive Gibbs free energy change that accounts for dissociation of hydrogen bonds in the amorphous phase represents an unfavourable contribution to the formation of an N-stem crystal layer. Energy is required to disrupt these interactions and provide motional freedom to those chain segments of the semicrystalline polymer that participate in hydrogen bonding in the amorphous phase;

\[
\{-\Delta G_{\text{HydrogenBonds}}\}_\text{AmorphousPhase} = \frac{\varphi_{\text{Amorphous}}}{1 - \varphi_{\text{Amorphous}}} \varepsilon_{\text{HydrogenBond}} (NabL)
\]

where \(NabL\) represents the volume of chain segments that previously interacted with the completely amorphous component via hydrogen bonds in the amorphous phase. Now, these segments diffuse, reptate, and fold into an N-stem layer within one lamella. Hence, these segments of the semicrystalline polymer in the amorphous phase undergo the appropriate conformational rearrangements that are necessary for crystallization, participate in the formation of the N-stem crystal layer, and interact via hydrogen bonds on the fold surface. The chemical structure of the semicrystalline polymer does not contain complementary functional groups that interact strongly via hydrogen bonds or any other energetic attractions between similar molecules. Hence, hydrogen bonding is an exothermic process that does not occur within a lamella, but only on its fold surface where contacts are possible with the completely amorphous component. The following favourable contribution to the overall free energy change is given by;

\[
\{\Delta G_{\text{HydrogenBonds}}\}_\text{FoldSurface} = -\frac{\varphi_{\text{Amorphous}}}{1 - \varphi_{\text{Amorphous}}} \varepsilon_{\text{HydrogenBond}} ab(L_{\text{Contour}} - NL)
\]

where \(L_{\text{Contour}}\) is the contour length of the semicrystalline chain that traverses a lamella and \(NL\) represents the length of the same chain in the N-stem crystal. If the N-stem crystalline segment follows a square-tooth pattern and all segments of the polymer chain reside in one lamella or on its surface, then the following relation is valid:

\[
L_{\text{Contour}} = NL + (N - 1)a
\]
If the folds involve a few additional chain segments that protrude slightly into the amorphous phase and the remaining segments of the polymer chain reside in one lamella, then:

$$L_{\text{Contour}} = NL + (N - 1)\kappa a$$

$$\kappa \geq 1$$

When the contour length of a single chain is constant, this relation between the number of crystal stems $N$ in one lamella and the lamellar thickness $L$ provides a constraint in the optimization problem, as described below.

**Total free energy function for the formation of an N-stem crystal layer;**

The free energy change for hydrogen bond formation on the fold surface excludes any possibility that strong association between similar or dissimilar chain segments occurs within the bulk of the lamellae, due to the chemical structure of the semicrystalline polymer and the fact that the totally amorphous component cannot reside in the lamellar regions. The extensive Gibbs free energy change associated with the addition of an N-stem crystal layer to a growing lamella reduces to the following expression;

$$\Delta G_{N-\text{stem}} = Nab\left[2\sigma_{\text{end}} + (N - 1)\sigma_{\text{fold}} - \frac{\rho_{\text{Amorphous}}}{1 - \rho_{\text{Amorphous}}} L\varepsilon_{\text{HydrogenBond}}\right] + (Na + 2b)L\sigma_{\text{Lateral}}$$

$$+ \frac{\rho_{\text{Amorphous}}}{1 - \rho_{\text{Amorphous}}} \varepsilon_{\text{HydrogenBond}}\left[NabL - (N - 1)\kappa a^2 b\right] - NabL(\Delta h_{\text{Melting}})$$

$$L_{\text{Contour}} = NL + (N - 1)\kappa a = \text{constant}$$

$$\kappa \geq 1$$

Hoffman's crystallization theory has been modified for strongly interacting polymer blends by the terms in the previous equation that contain the volumetric energy density for hydrogen-bond formation between dissimilar blend components, $\varepsilon_{\text{HydrogenBond}}$. If all of the important phenomena that contribute to the formation of an N-stem crystal layer have been considered and modeled correctly, then thin unstable lamellae with a larger number of chain folds should form more rapidly and experience stable growth in blends that experience strong interactions on the lamellar surface. This description of the formation of thin lamellae, coupled with crystallization kinetics that could dictate a distribution of stem heights $L$, supports the concept and observation.
of multiple melting endotherms. As mentioned earlier in this chapter, this model does not capture effects of (i) chain microstructure (i.e., configurational isomers), (ii) packing of left- and right-handed helices in the unit cell, or (iii) chain branching, but the trends illustrated below represent reasonable conclusions when strong intermolecular interactions occur on the periphery of the crystallites. Lamellae with rather small stem heights will melt invariably at temperatures below the primary transition that is characteristic of larger crystals. Upon melting or high-temperature annealing, the crystallizable segments of these thin lamellae will undergo chain unfolding and form more stable crystals with larger stem heights $L$. Experimental conditions such as heating rate and annealing temperature, and physical properties such as the glass transition temperature and melt viscosity also govern the stability and melting temperature of the newly formed crystals.

**Optimum lamellar thickness.** Consider the following calculations and supporting graphs based on developments in the previous section that yield an optimum lamellar thickness at the free energy minimum for a specific set of conditions. This is the numerical analog of the “method of Lagrange multipliers”, where optimization is performed with one constraint (i.e., the contour length of the chain is constant). Lengths are given in nanometers (i.e., $a$, $b$, $L$, and $L_{\text{Contour}}$), and energies are provided in micro-Joules (i.e., $\Delta G_{\text{N-stem}}$), $\mu$J per nm$^2$ (i.e., $\sigma_{\text{end}}$, $\sigma_{\text{fold}}$, and $\sigma_{\text{Lateral}}$), or $\mu$J per nm$^3$ (i.e., $\varepsilon_{\text{HydrogenBond}}$ and $\Delta h_{\text{Melting}}$).

**Numerical calculations:**

\[
\begin{align*}
\varphi_{\text{Amorphous}} &= 0.80 \quad a = 1.5 \quad b = 1.3 \quad \kappa = 5 \quad L_{\text{Contour}} = 10000 \\
\varepsilon_{\text{HydrogenBond}} &= 100 \quad \sigma_{\text{end}} = 1 \quad \sigma_{\text{fold}} = 2 \quad \sigma_{\text{Lateral}} = 10 \quad \Delta h_{\text{Melting}} = 150
\end{align*}
\]
**Summary of multiple melting behaviour.** The consequences of strong interactions between dissimilar components of a polymer-polymer blend in which one component is semicrystalline are (i) a larger decrease in the Gibbs free energy change for crystal formation when the hydrogen bond strength increases, and (ii) several sequential melting events that occur below the primary transition temperature. In addition to the effect of stem height and number of folds on $\Delta G_{N\text{-stem}}$, the energetic balance between $\Delta h_{\text{Melting}}$ and $\varepsilon_{\text{HydrogenBond}}$ is an important factor that governs the optimum lamellar thickness (i.e., see the graphs below). Due to the exothermic nature of the crystallization process, $\Delta h_{\text{Melting}}$ contributes favourably to the free energy of formation.
formation of an N-stem crystal layer below $T_m$. The magnitude of this enthalpic crystallization term is proportional to lamellar volume (i.e., $N_{ab}L$) and the defect-free nature of the crystals that are formed. The volumetric energy density for hydrogen-bond formation, $\varepsilon_{\text{HydrogenBond}}$, participates in competing factors when crystallization occurs in hydrogen-bonded blends. For example, in addition to cooling below $T_m$, it is necessary to disrupt hydrogen bonds between chain segments of the semicrystalline polymer and the totally amorphous polymer in the amorphous phase so that the former can undergo diffusion or reptation into the lamellae. However, only a small fraction of these hydrogen bonds reform on the fold surface. Consequently, the free energy change for hydrogen bond disruption and formation exhibits competing effects on the overall process. Some of these effects favor thinner lamellae and others favor thicker lamellae. In the absence of kinetic factors, the crystallization process will search for a thermodynamic minimum in the free energy function that corresponds to an optimal value of $L$, or an optimal distribution of lamellar thicknesses, subject to the constraint that the contour length of a single chain which traverses one lamella $N$ times is constant. When hydrogen bonds are stronger and the value of $\varepsilon_{\text{Hbond}}$ is larger, the crystallization equilibrium shifts in favor of shorter stem heights or lamellar thicknesses. This trend is illustrated below.

Furthermore, the minimum value of the Gibbs free energy for the formation of an N-stem crystal layer from the amorphous phase, which corresponds to the optimum lamellar thickness, decreases when the hydrogen bond strength increases, as
illustrated below. These calculations were performed using the parametric values defined above, except for the fact that hydrogen bond strength was varied over a reasonable range, with an upper limit that matches the enthalpy of melting.

**Effect of Hydrogen Bond Energy on the Optimum Free Energy**

Melting point depression in polymer-polymer and polymer-diluent blends that contain a high-molecular-weight semicrystalline component. When a semicrystalline polymer above its melting point is diluted with a miscible low-molecular-weight component in the liquid state and cooled to a temperature range where crystallization occurs, the measured melting temperature upon heating is lower than \( T_m \) of the pure polymer. Depression of the melting temperature is not due to differences in cooling rate, crystallization temperature, or subsequent heating rate required to measure \( T_m \), but to the presence of an impurity (i.e., diluent) that interferes with the crystallization process, producing more imperfect crystals composed of thinner lamellae. Thermodynamic analysis of the effect of low-molecular-weight miscible impurities on the equilibrium melting temperature of a semicrystalline polymer begins by equating the polymer’s chemical potential in both phases. The liquid phase binary mixture contains a semicrystalline polymer above its melting point and a miscible diluent. Based on the Flory-Huggins lattice model, the extensive Gibbs free energy of mixing was derived in Chapter#3 as:

\[
\Delta G_{mixing} = RT \left\{ n_{Diluent} \ln \varphi_{Diluent} + n_{Polymer} \ln \varphi_{Polymer} + \chi n_{Diluent} \varphi_{Polymer} \right\}
\]
where \( n_i \) represents mole numbers, \( \phi_i \) corresponds to volume fraction, and \( \chi \) is the dimensionless polymer-diluent energetic interaction parameter. The liquid phase chemical potential of the polymer that is consistent with the Flory-Huggins mean-field model is;

\[
\mu_{\text{Polymer}}(T, p, \phi_{\text{Diluent}}) - \mu_{\text{PureLiquidPolymer}}(T, p) = \left\{ \frac{\partial \Delta G_{\text{mixing}}}{\partial n_{\text{Polymer}}} \right\}_{T, p, \phi_{\text{Diluent}}}
\]

\[
RT \left\{ \ln(1 - \phi_{\text{Diluent}}) + \frac{n_{\text{Diluent}}}{\phi_{\text{Diluent}} \frac{\partial \phi_{\text{Diluent}}}{\partial n_{\text{Polymer}}} \left\{ T, p, \phi_{\text{Diluent}} \right\}} + \frac{n_{\text{Polymer}}}{\phi_{\text{Polymer}} \frac{\partial \phi_{\text{Polymer}}}{\partial n_{\text{Polymer}}} \left\{ T, p, \phi_{\text{Polymer}} \right\}} + \frac{\chi n_{\text{Diluent}}}{\frac{\partial \phi_{\text{Polymer}}}{\partial n_{\text{Polymer}}} \left\{ T, p, \phi_{\text{Diluent}} \right\}} \right\}
\]

\[
= RT \left\{ \ln(1 - \phi_{\text{Diluent}}) - (x - 1)\phi_{\text{Diluent}} + x\chi\phi_{\text{Diluent}}^2 \right\}
\]

where \( x \) is the ratio of the molar volume of polymer to that of the diluent, or the polymer’s degree of polymerization, and the standard state \( \mu_{\text{PureLiquidPolymer}}^0 \) is defined as pure liquid polymer. One equates this expression for the chemical potential of the polymer in a single-phase binary liquid phase mixture to the chemical potential of pure crystalline polymer at the depressed melting temperature \( T_{m,\text{Depressed}} \) due to the presence of the diluent. Hence;

\[
\mu_{\text{Polymer}}(T_{m,\text{Depressed}}, p, \phi_{\text{Diluent}}) = \mu_{\text{PureCrystallinePolymer}}^0(T_{m,\text{Depressed}}, p)
\]

Subtract the standard state chemical potential of pure liquid polymer from both sides of the previous statement of chemical equilibrium and use the Flory-Huggins lattice results for the activity of the polymer in the liquid phase, which is valid for concentrated polymer solutions;

\[
\mu_{\text{Polymer}}(T_{m,\text{Depressed}}, p, \phi_{\text{Diluent}}) - \mu_{\text{PureLiquidPolymer}}^0(T_{m,\text{Depressed}}, p)
\]

\[
= RT_{m,\text{Depressed}} \left\{ \ln(1 - \phi_{\text{Diluent}}) - (x - 1)\phi_{\text{Diluent}} + x\chi\phi_{\text{Diluent}}^2 \right\}
\]

\[
= \mu_{\text{PureCrystallinePolymer}}^0(T_{m,\text{Depressed}}, p) - \mu_{\text{PureLiquidPolymer}}^0(T_{m,\text{Depressed}}, p)
\]

The difference between the chemical potentials of pure crystalline polymer and pure liquid polymer at temperature \( T_{m,\text{Depressed}} \) is equivalent to the molar Gibbs free energy of crystallization of the undiluted polymer which vanishes only at the melting
temperature of the undiluted polymer. In terms of the enthalpy and entropy of crystallization, one writes;

\[ \mu_{\text{PureCrystallinePolymer}}^0(T_{m,\text{Depressed}}, p) - \mu_{\text{PureLiquidPolymer}}^0(T_{m,\text{Depressed}}, p) = \Delta g_{\text{Crystallization}} = \Delta h_{\text{Crystallization}} - T_{m,\text{Depressed}} \Delta s_{\text{Crystallization}} \]

\[ = \Delta h_{\text{Crystallization}} \left[ 1 - T_{m,\text{Depressed}} \left( \frac{\Delta s_{\text{Crystallization}}}{\Delta h_{\text{Crystallization}}} \right) \right] \]

\[ = \Delta h_{\text{Crystallization}} \left[ 1 - \frac{T_{m,\text{Depressed}}}{T_{m,\text{Pure}}} \right] \]

where \( \Delta h_{\text{Crystallization}} \) is the molar enthalpy change upon solidification, based on the molar mass of the entire polymer chain. Since the molar Gibbs free energy of crystallization of the undiluted polymer vanishes at the pure-component melting temperature \( T_{m,\text{Pure}} \), the ratio of \( \Delta h_{\text{Crystallization}} \) to \( \Delta s_{\text{Crystallization}} \) is given by \( T_{m,\text{Pure}} \) and this ratio is assumed to be temperature-independent between the pure-component and depressed melting temperatures. The statement of chemical equilibrium for the semicrystalline polymer in the binary liquid mixture and the undiluted crystalline phase yields;

\[ RT_{m,\text{Depressed}} \ln \left( 1 - \varphi_{\text{Diluent}} \right) - \left( x - 1 \right) \varphi_{\text{Diluent}} + x \chi \varphi_{\text{Diluent}}^2 = \Delta h_{\text{Crystallization}} \left[ 1 - \frac{T_{m,\text{Depressed}}}{T_{m,\text{Pure}}} \right] \]

The first two terms on the left side of the previous equation represent entropic contributions to the polymer’s activity in binary liquid mixtures, whereas the term that contains the Flory-Huggins interaction parameter \( \chi \) represents an energetic contribution. The entropic terms can be neglected when melting point depression in semicrystalline-amorphous polymer-polymer blends is considered because the high-molecular-weight nature of both species minimizes the combinatorial aspects of mixing. Begin with the previous equation for polymer-diluent blends, replace the enthalpy change for crystallization, per mole of the entire chain, by \( -\Delta h_{\text{Fusion}} \), expand the logarithmic term because the diluent volume fraction is exceedingly small [i.e., \( \ln(1 - \varphi_{\text{Diluent}}) \approx -\varphi_{\text{Diluent}} - (1/2) \varphi_{\text{Diluent}}^2 - ... \)], and algebraically rearrange the prediction for diluent-induced melting point depression;
\[
\frac{1}{T_{m,\text{Depressed}}} - \frac{1}{T_{m,\text{Pure}}} = \frac{xR}{\Delta h_{\text{Fusion}}} \left\{ \varphi_{\text{Diluent}} + \left( \frac{1}{2x} - \chi \right) \varphi_{\text{Diluent}}^2 \right\}
\]

Linear least squares analysis of the melting point depression equation is performed when one has data pairs that correspond to \(T_{m,\text{Depressed}}\) vs. \(\varphi_{\text{Diluent}}\) at low diluent concentrations. The data point at \(\varphi_{\text{Diluent}} = 0\) yields \(T_{m,\text{Pure}}\), which is used to force the zeroth-order coefficient of the polynomial, as illustrated below. Choose a 2nd-order polynomial, \(y(z) = a_0 + a_1z + a_2z^2\), and make the following association between the polynomial and the physical models;

(i) independent variable; \[z = \varphi_{\text{Diluent}}\]

(ii) dependent variable; \[y = \{T_{m,\text{Depressed}}\}^{-1}\]

(iii) zeroth-order coefficient; \[a_0 = \{T_{m,\text{Pure}}\}^{-1}\] (forced, based on the data point at \(\varphi_{\text{Diluent}} = 0\))

(iv) first-order coefficient; \[a_1 = \frac{xR}{\Delta h_{\text{Fusion}}}\]

(v) second-order coefficient; \[a_2 \approx -\frac{x\chi R}{\Delta h_{\text{Fusion}}}, \text{ when } x>>1\]

Knowledge of the degree of polymerization \(x\) yields the enthalpy of fusion per mole of repeat units (i.e., \(\Delta h_{\text{Fusion}}/x\)) for a hypothetical 100% crystalline polymer from the 1st-order coefficient and the Flory-Huggins dimensionless polymer-diluent interaction parameter \(\chi\), on a repeat-unit basis, from the 2nd-order coefficient. If the molar volume of the polymeric repeat unit \(v_{\text{RepeatUnit}}\) is different from the molar volume of diluent \(v_{\text{Diluent}}\), then this ratio (i.e., \(v_{\text{RepeatUnit}}/v_{\text{Diluent}}\)) must be included as a factor in both the 1st-order and 2nd-order coefficients of the linear least squares analysis. The Flory-Huggins lattice model assumes that diluent molecules and polymer segments each occupy one site. Hence, the degree of polymerization \(x\) was identified as the ratio of molar volumes of the entire polymer chain to that of the diluent, excluding the possibility that \(v_{\text{RepeatUnit}}\) might be different from \(v_{\text{Diluent}}\). Another linear least squares procedure for the melting point depression equation of high-molecular-weight materials (i.e, \(x>>1\)), in the presence of low-molecular-weight miscible impurities, is based on the following algebraic rearrangement when the first data point at \(\varphi_{\text{Diluent}} = 0\) and \(T_{m,\text{Pure}}\) is used to identify the melting temperature of the pure polymer, but this data point is excluded from the analysis;
Now, a 1st-order polynomial is employed, \( y(z) = a_0 + a_1 z \), and the following association between the polynomial and physical models yields:

(i) independent variable; \( z = \varphi_{\text{Diluent}} \)

(ii) dependent variable;

\[
y = \frac{1}{\varphi_{\text{Diluent}}} \left[ \frac{1}{T_{m,\text{Depressed}}} - \frac{1}{T_{m,\text{Pure}}} \right]
\]

(iii) zeroth-order coefficient; \( a_0 = \frac{xR}{\Delta h_{\text{Fusion}}} \)

(iv) first-order coefficient; \( a_1 \approx -\frac{x\chi R}{\Delta h_{\text{Fusion}}} \), when \( x >> 1 \)

The intercept and slope yield numerical values for the enthalpy of fusion and the interaction parameter, per mole of polymeric repeat units (i.e., \( \Delta h_{\text{Fusion}}/x \) and \( \chi \), respectively). Once again, a factor of \( \nu_{\text{RepeatUnit}}/\nu_{\text{Diluent}} \) must appear in \( a_0 \) and \( a_1 \) if this molar volume ratio is not unity. Analysis of melting point depression in semicrystalline-amorphous polymer-polymer blends requires the neglect of the entropic contribution to the semicrystalline polymer’s activity in miscible binary liquid mixtures because high-molecular-weight chains have negligible combinatorial freedom when they are placed on a lattice. Upon replacing \( \varphi_{\text{Diluent}} \) by the volume fraction of the amorphous polymer in a miscible molten-state blend, and the degree of polymerization \( x \) by the ratio of molar volumes of the semicrystalline polymer to the amorphous polymer, the melting point depression equation reduces to:

\[
\frac{1}{T_{m,\text{Depressed}}} - \frac{1}{T_{m,\text{Pure}}} = -\frac{R}{\Delta h_{\text{Fusion}}} \left( \frac{\bar{V}_{\text{SemicrystallinePolymer}}}{\bar{V}_{\text{AmorphousPolymer}}} \right) \chi \varphi_{\text{AmorphousPolymer}}^2
\]

Now, linear least squares analysis of \( T_{m,\text{Depressed}} \) vs. \( \varphi_{\text{AmorphousPolymer}} \), with knowledge of the pure-component melting temperature of the semicrystalline polymer from the initial data point at \( \varphi_{\text{Amorphous}} = 0 \), requires a 1st-order polynomial; \( y(z) = a_0 + a_1 z \), such that:

(i) independent variable; \( z = \varphi_{\text{AmorphousPolymer}}^2 \)
(ii) dependent variable; \[ y = \frac{1}{\frac{1}{T_{m,Depressed}} - \frac{1}{T_{m,Pure}}} \]

(iii) zeroth-order coefficient; \[ a_0 = 0 \text{ (forced)} \]

(iv) first-order coefficient; \[ a_1 = -\frac{R}{\Delta h_{\text{Fusion}}} \left( \frac{\bar{V}_{\text{SemicrystallinePolymer}}}{\bar{V}_{\text{AmorphousPolymer}}} \right) \chi \]

Knowledge of the molar volumes of both polymers, as well as the enthalpy of fusion per repeat unit of the semicrystalline polymer allows one to calculate the dimensionless binary energetic interaction parameter \( \chi \) from the slope of the polynomial model. This procedure invariably yields a negative \( \chi \)-parameter when melting point depression occurs. Exothermic energetic interactions in the molten state are required for two high-molecular-weight polymers to exhibit miscibility. Melting point depression of the semicrystalline polymer is a consequence of this compatibilization in the molten state, due to specific interactions such as hydrogen bonding, ionic attractions of charged functional groups, or metal complexation. If energetic interactions in the molten state are endothermic and unfavourable, then the blend is immiscible because favourable entropic contributions to the Gibbs free energy of mixing are negligible for high-molar-mass species. Consequently, the \( \chi \)-parameter is greater than zero and the melting point depression equation incorrectly predicts an increase in the melting temperature of the semicrystalline polymer. The predictions are incorrect because the lattice model assumes a homogeneous liquid phase that is not applicable for immiscible binary mixtures of two high-molecular-weight polymers in the molten state. When polymer-polymer blends are immiscible in the molten state and one component is potentially crystallizable, negligible melting point depression is observed. This insensitivity of the semicrystalline polymer’s melting temperature to blend composition at low concentrations of the impurity (i.e., the amorphous component) is a reasonable diagnostic probe of the incompatible nature of these blends in the molten state.

**Hoffman-Weeks analysis.** As a final note about melting point depression, the equations developed in this section are based on the statement of chemical equilibrium via the polymer’s chemical potential in each phase. Hence, equilibrium melting temperatures (i) for pure polymer \( T_{m,Pure} \), and (ii) in the presence of an impurity \( T_{m,Depressed} \) are required in these equations. Linear least squares analysis of actual experimental data employs melting temperatures \( T_{\text{Experimental}} \) that are lower than
the equilibrium melting points, because when crystallization occurs at temperatures below $T_{m,Pure}$ or $T_{m,Depressed}$, relatively fast rates of crystallization produce imperfect crystals which contain lamellae that are not infinitely thick. As initially developed by Hoffman and Weeks, it is necessary to extrapolate experimentally measured melting temperatures $T_{\text{Experimental}}$ vs. crystallization temperatures $T_C$ until these two temperatures asymptotically approach each other. For example, $T_{\text{Experimental}}$ increases when crystallization occurs at higher temperatures $T_C$ below the melting point, with $T_{\text{Experimental}} > T_C$. Equilibrium melting temperatures $T_{m,Pure}$ or $T_{m,Depressed}$ are obtained by extrapolating $T_{\text{Experimental}}$ vs. $T_C$ until $T_{\text{Experimental}} = T_C$. This corresponds to vanishingly slow rates of crystallization at the melting point, which yields the equilibrium melting temperature that is almost impossible to achieve under realistic experimental conditions because the driving force for nucleation vanishes at the melting point.

### Problems

**Problem #1**

Qualitatively sketch the temperature dependence of the density of semicrystalline isotactic polystyrene from ambient temperature (i.e., 25°C) to 300°C, and be extremely quantitative on the horizontal temperature axis. The glass transition temperature $T_g$ is 105°C, and the actual melting temperature $T_{melt}$ is 220°C.

**Problem #2**

Isotactic polystyrene (i.e., 99% isotactic) is cooled rapidly (i.e., quenched) from 300°C (state #1) to room temperature (state #2). The sample is heated to 175°C and maintained at that temperature for a length of time given by $3\tau_{\text{Crystallization}}$ (state #3), where the time constant for crystallization is;

$$\tau_{\text{Crystallization}} = 1 / \{ k_n(T) \}^{1/n}$$

Then, it is cooled slowly to room temperature (state #4).

(a) Sketch the temperature dependence of specific enthalpy for this cool-heat-cool scheme, be quantitative on the temperature axis, and identify states #1 through #4 on the graph.

(b) Sketch the isothermal response of this sample in a differential scanning calorimeter while the temperature is held at 175°C for a length of time given by $3\tau_{\text{Crystallization}}$. Put time on the horizontal axis. On the vertical axis, endothermic
events are represented by upward deflections and exothermic events correspond to downward deflections.

(c) The sample in state #4 is heated at 20°C per minute via DSC from 25°C to 130°C. Sketch the DSC heating trace from ambient to 130°C.

**Problem #3**
A differential scanning calorimeter, operating in isothermal mode, provides quantitative information about the time dependence of the volume fraction of crystallinity, $X_V(t; T)$ vs. $t$, for a semicrystalline polymer that crystallizes at temperature $T$ between $T_g$ and $T_melt$.

(a) Obtain an expression for the Avrami exponent $n$ during isothermal crystallization at temperature $T$ in terms of the slope of $X_V(t; T)$ vs. time $t$ at the half-time $t_{1/2}$ when this semicrystalline polymer achieves 50% of its maximum volume fraction of crystallinity. Express your answer in terms of the slope $\frac{d}{dt}X_V(t; T)$ vs. $t$ at $t = t_{1/2}$,

$$\left[ \frac{d}{dt} \left( \frac{X_V(t; T)}{X_V(t \rightarrow \infty)} \right) \right]_{t = t_{1/2}}$$

and the half-time, only.

(b) Calculate a numerical value for the Avrami exponent $n$ if the half-time is 3 hours at temperature $T$ and the slope of the crystallization isotherm $\frac{d}{dt}X_V(t; T)$ at $t_{1/2}$ is 0.4 $\text{hr}^{-1}$. In other words,

$$\left[ \frac{d}{dt} \left( \frac{X_V(t; T)}{X_V(t \rightarrow \infty)} \right) \right]_{t = t_{1/2} = 3\text{hr}} = 0.4\text{hr}^{-1}$$

**Problem #4**
At the optimum annealing temperature $T_c$, your analysis of the crystallization isotherm, $X_V(t; T_c)$ vs. $t$, in problem #3 yields an Avrami exponent of $n = 4$ when the half-time $t_{1/2}$ is 2 hours. How long should you anneal this polymer at $T_c$ to induce a significant amount of crystallinity? A numerical answer is required, here.
**Problem #5**
Use your knowledge of the solid-state morphology and properties of polymeric materials and explain why the two products, illustrated below, behave differently when the temperature is 87°C, as revealed by the obsolete thermometer. The container on the left is transparent, while the container on the right is opaque.

**Problem #6**
Isotactic polypropylene with repeat unit \{CH\_2CH(CH\_3)\} exhibits a glass transition at -10°C and a melting transition at 185°C. Thermal degradation does not occur below 300°C. This polymer crystallizes in a 3/1 helical conformation where the backbone bond rotation angles alternate between trans and gauche.

a) What annealing temperature should be used to induce crystallization in the 3/1 helical conformation most rapidly under vacuum?

The major coherent Bragg reflection from wide-angle x-ray powder diffraction using Cu K-\(\alpha\) radiation with a wavelength of 1.541 Å occurs at scattering angle of 2\(\theta=13.6^\circ\) (i.e., degrees). The d-spacing via Bragg's law corresponds to the c-dimension of a monoclinic unit cell, where two of the unit cell angles are 90° and the 3rd unit cell angle is 99°. The other unit cell dimensions are:

\[a = 6.65 \, \text{Å} \quad \text{b} = 20.96 \, \text{Å}\]

where 1 Å = 10\(^{-8}\) cm and Avogadro's number is 6.02214 \times 10\(^{23}\). There are 4 chains in each unit cell, and 3 repeat units per chain are required for periodic behaviour of the 3/1 helix. Hence, there are 12 repeat units in each unit cell.

b) Calculate the density of isotactic polypropylene that is 100% crystalline.

Pychnometry measurements for an actual sample of isotactic polypropylene, with methanol as the non-solvent, are tabulated below at 20°C. The density of methanol at 20°C is 0.7914 g/cm\(^3\).

- mass of the pychnometer; 10.003 g
- mass of the pychnometer; filled to the meniscus with methanol; 13.926 g
- mass of the semicrystalline sample of isotactic polypropylene; 1.566 g
- mass of the pychnometer, polypropylene, and methanol; 14.116 g
c) Calculate the **weight** fraction of crystallinity in the actual sample at 20°C if the amorphous polymer density is 0.854 g/cm³.

d) Calculate the **volume** fraction of crystallinity in the actual sample at 20°C if the amorphous polymer density is 0.854 g/cm³.

e) Sketch the density of the actual sample of isotactic polypropylene from -30°C to 200°C, during the 1st heating scan at 20°C per minute. Be careful.

The handbook value for the heat of fusion of 100% crystalline isotactic polypropylene is:

\[(\Delta h_{\text{fusion}})_{100\%\text{ crystal}} = 2100 \text{ calories per mole of repeat units}\]

f) Predict the **experimental** heat of fusion in **calories** for isotactic polypropylene if the DSC experiment is performed on 20 milligrams of the actual polymer.

**Numerical calculations that accompany the solution to Problem#6:**

Calculations for isotactic polypropylene which crystallizes as a 3/1 helix;

- \(T_g = -10°C\), glass transition temperature
- \(T_m = 185°C\), melting temperature
- \(T_{c,\text{optimum}} = T_g + 0.67\{T_m - T_g\}\), optimum crystallization temperature

**WAXD parameters for a monoclinic unit cell where two of the angles are 90 degrees and the third unit cell angle is 99 degrees;**

\[a = 6.65Å\]
\[b = 20.96Å\]
\[\alpha = 90^0\]
\[\beta = 90^0\]
\[\gamma = 99^0\]
\[\lambda = 1.541Å\], wavelength of copper K-\(\alpha\) radiation

c-dimension of the unit cell from coherent Bragg scattering at 2\(\Theta\);
\[2\Theta = 13.6^0\]
\[n = 1, \text{ for 1st-order reflections}\]
\[n\lambda = 2c \sin\Theta\]

\[V_{\text{Unit Cell}} = abc \sin\alpha \sin\beta \sin\gamma \times 10^{-24}, \text{ cm}^3\]

\[\text{MW}_{\text{repeat}} = 42 \text{ daltons, mass of one mole of repeat units}\]
\[ N_{\text{Avogadro}} = 6.02214 \times 10^{23} \text{ molecules/mol} \]

Number of repeat units in one unit cell; there are 4 chains per unit cell, and 3 repeat units per chain are required for periodic behaviour of the 3/1 helix;

\[ N_{\text{UnitCell}} = 12 \]

Density of the 100% crystalline polymer, g/cm³

\[ \rho_{100\%\text{CrystallinePolymer}} = \frac{N_{\text{UnitCell}} \times MW_{\text{repeat}}}{V_{\text{UnitCell}} \times N_{\text{Avogadro}}} \]

Pychnometry measurements for the density of semicrystalline isotactic polypropylene;

Mass of the pychnometer and the non-solvent, methanol, filled to the meniscus;

\[ \rho_{\text{Methanol}} = 0.7914 \text{ g/cm}^3, \text{ density of methanol at } 20^\circ\text{C} \]

Mass of the pychnometer, the polymer, and MeOH filled to the meniscus;

\[ \rho_{\text{Polymer}} = 1.566 \text{ g/cm}^3, \text{ mass of semicrystalline isotactic polypropylene} \]

Density of semicrystalline isotactic polypropylene via pychnometry;

\[
\rho_{\text{SemiCrystallinePolymer}} = \frac{\rho_{\text{Methanol}} \times \text{mass}_{\text{Polymer}}}{\text{mass}_{\text{Pychnometer}\text{+Methanol}} + \text{mass}_{\text{Polymer}} - \text{mass}_{\text{Pychnometer, Polymer, Methanol}}}
\]

\[ \rho_{\text{AmorphousPolymer}} = 0.854 \text{ g/cm}^3, \text{ density of completely amorphous polypropylene} \]

Volume fraction of crystallinity;

\[
\varphi_{\text{Crystallinity}} = \frac{\rho_{\text{SemiCrystallinePolymer}} - \rho_{\text{AmorphousPolymer}}}{\rho_{100\%\text{CrystallinePolymer}} - \rho_{\text{AmorphousPolymer}}}
\]

Mass fraction of crystallinity;

\[
\omega_{\text{Crystallinity}} = \frac{\rho_{100\%\text{CrystallinePolymer}}}{\rho_{\text{SemiCrystallinePolymer}}} \varphi_{\text{Crystallinity}}
\]

Enthalpy of fusion for hypothetical 100% crystalline isotactic polypropylene;

\[ \{\Delta h_{\text{fusion}}\}_{100\%\text{Crystalline}} = 2100 \text{ calories per mole of repeat units} \]

Experimental enthalpy of fusion for the actual DSC heating trace, cal/g;
\[ \omega_{\text{Crystallinity}} = \frac{MW_{\text{repeat}} \{ \Delta h_{\text{fusion}} \}_\text{Experimental}}{\{ \Delta h_{\text{fusion}} \}_{100\% \text{Crystalline}}} \]

mass\text{\_PolymerDSC} = 20 \text{ mg}, \text{ mass of polypropylene tested via DSC}

Integration of \( C_p \) vs. \( T \) in the vicinity of \( T_m \) for the actual DSC sample of polypropylene;

\[ \text{Enthalpy}_{\text{DSC}} = \{ \Delta h_{\text{fusion}} \}_\text{Experimental} \left[ \frac{\text{mass}_{\text{PolymerDSC}}}{1000} \right] \]

The numerical solution to \textit{Problem\#6} is summarized below:

\[
\begin{array}{c|c|c}
\text{a} & 0.530 \text{ [Angstroms]} & \text{actualDSCmass} = 20.000 \text{ [milligrams]} \\
\text{b} & 90.000 \text{ [degrees]} & \text{AmorphousDensity} = 0.854 \text{ [g/cc]} \\
\text{Avogadro} & 6.022 \times 10^{23} \text{ [number/mol]} & \text{b} = 20.960 \text{ [Angstroms]} \\
\beta & 90.000 \text{ [degrees]} & \text{c} = 6.507 \text{ [Angstroms]} \\
\text{CrystalDensity} & 0.334 \text{ [g/cc]} & \Delta h_{\text{fusion}} = 2100 \text{ [cal/mol]} \\
\text{DeltaHfusionExp} & 30.183 \text{ [cal/gram]} & \text{DSCareaCp} = 0.604 \text{ [calories]} \\
\gamma & 95.000 \text{ [degrees]} & \lambda = 1.541 \text{ [Angstroms]} \\
\text{MassFraction} & 0.504 \text{ [%X\text{\%allinity}]} & \text{MassPoly} = 1.566 \text{ [grams]} \\
\text{MassTotal} & 14.116 \text{ [grams]} & \text{McHdensity} = 0.751 \text{ [g/cc]} \\
\text{MWrepeat} & 42.000 \text{ [g/mol]} & \text{NumberInUnitCell} = 12.000 \text{ [*repeat]} \\
\text{PolyDensity} & 0.901 \text{ [g/cc]} & \text{PychMass} = 10.903 \text{ [grams]} \\
\text{PychSolventMass} & 13.926 \text{ [grams]} & \text{TGcpl} = 120.000 \text{ [degrees C]} \\
\text{Tg} & -10.000 \text{ [degrees C]} & \theta = 6.600 \text{ [degreesAngle]} \\
\text{Tm} & 105.000 \text{ [degrees C]} & \text{VolumeFraction} = 0.502 \text{ [%X\text{\%allinity}]} \\
\text{VolUnitCell} & 8.95a-22 \text{ [cc]} & \\
\end{array}
\]

\textit{Problem\#7}

An isotactic vinyl polymer (i.e., 90% isotactic), like poly(propylene) \([\text{CH}_2\text{CH(CH}_3)\text{]}\), exhibits a glass transition at \(-10^\circ\text{C}\) and an actual melting transition at \(170^\circ\text{C}\). This polymer crystallizes in a 3/1 helical conformation where the backbone bond rotation angles alternate between trans & gauche. The semicrystalline polymer is heated under vacuum from ambient to \(225^\circ\text{C}\) at a rate of \(10^\circ\text{C/}\text{min}\). Then, it is removed from the vacuum oven and immersed in liquid nitrogen. The crystallization time constant for isotactic poly(propylene) at its optimum annealing temperature is 4 hours. It is reasonable to assume that the crystallization time constant is much longer than 4 hours at all other temperatures. The polymer's molecular weight is \(\approx 5 \times 10^5\) daltons.

(a) Calculate the optimum annealing temperature to induce a significant amount of crystallinity in isotactic poly(propylene), i-PP, in the 3/1 helical conformation.
(b) The sample of i-PP, described above, is recovered from the liquid nitrogen dewar and allowed to equilibrate at ambient temperature for 10 minutes. Now, the sample is placed in a pycnometer that contains a non-solvent, like methanol, and its density is measured. Estimate the density of this sample of isotactic poly(propylene) at 25°C. A numerical answer is required, here.

**Problem#8**

As a continuation of problem#7, 20 different dog-bone-shaped samples of i-PP, quenched from the molten state in liquid nitrogen, are removed from the liquid nitrogen dewar and annealed under vacuum at the optimum crystallization temperature. One sample is removed from the vacuum oven every 15 minutes for ambient-temperature stress-strain testing at a strain rate of 1 inch per minute. Remember that $T_g$ is below ambient, but $T_m$ is above ambient. The modulus of elasticity is calculated from the initial slope of the stress-strain curve.

(a) Sketch the ambient-temperature stress-strain curve for the sample of i-PP that was removed from the vacuum oven after 15 minutes of annealing at the optimum crystallization temperature. Put stress on the vertical axis and strain on the horizontal axis.

(b) Sketch the ambient-temperature stress-strain curve for the sample of i-PP that was removed from the vacuum oven after 5 hours of annealing at the optimum crystallization temperature. Put stress on the vertical axis and strain on the horizontal axis. Be semi-quantitative with respect to your sketch in part (a).

(c) Sketch ambient-temperature elastic modulus vs. annealing time in the vacuum oven at the optimum crystallization temperature for all 20 samples of i-PP. Put modulus on the vertical axis and annealing time on the horizontal axis.

(d) Estimate the ambient-temperature density of the 20th (i.e., last) sample of isotactic poly(propylene) that was removed from the vacuum oven after 5 hours of annealing at the optimum crystallization temperature.

**Problem#9**

An isotactic vinyl polymer with repeat unit $(\text{CH}_2\text{CHR})$ exhibits a glass transition at $80^\circ\text{C}$ and a melting transition at $200^\circ\text{C}$. Thermal degradation does not occur below $350^\circ\text{C}$. When this polymer is cooled from the molten state to temperatures between $T_m$ and $T_g$, the time required for recrystallization is about 8 hours. There is not enough chain mobility for the polymer to crystallize below $T_g$. This polymer is heated above the
melting temperature at a rate of 25°C per minute. Then, it is cooled from 250°C to 140°C at a rate of 25°C per minute, and a spherulitic superstructure develops during isothermal crystallization at 140°C.

a) Sketch the total free energy change $\Delta G_{\text{Spherulite}}$ for spherulite formation as a function of the radius of the spherulite. $\Delta G_{\text{Spherulite}}$ accounts for volumetric and surface-related thermodynamic phenomena as spherulites nucleate and grow. Include two curves on one set of axes; one for isothermal crystallization at 140°C, and another curve that corresponds to isothermal crystallization at 175°C.

b) During isothermal crystallization at 140°C, a spherulitic superstructure develops via heterogeneous nucleation at time $t=0$. The spherulite number density $N_s$ and growth rate $G$ produce the following crystallization rate constant for spherulitic growth:

$$(4/3) \pi N_s G^3 = 10^{-4} \text{ hr}^{-3}$$

Do the spherulites impinge upon each other after 8 hours of growth at 140°C?