Degree of Crystallinity

• $P_i$ is some intensive property of the polymer.

Intensive – a property that's independent of the total amount of material present;
Density; Refractive Index;
Mass, Volume or Specific Heat per mole.

• $P_a$ and $P_c$ are the partial properties of the amorphous and crystalline components of the polymer

– IN THE SAME STATE OF ORDER
AS EXISTS IN THE POLYMER SAMPLE.
Then if $\theta$ is the fractional degree of crystallinity:

$$P_i = \theta \cdot P_{ci} + (1 - \theta) \cdot P_{ai}$$

OR

$$\theta = (P_i - P_{ai}) / (P_{ci} - P_{ai})$$

The above is a rigorous definition of crystallinity and gives the same value of $\theta$ regardless of the method used to measure "crystallinity"; X-Ray, DSC, etc.

One problem – can’t yet measure $P_{ai}$ and $P_{ci}$. 
• To simplify we assume that our sample is composed of:
   a) only TWO phases
   b) these are IDEAL or STANDARD phases

   An ideal perfectly ordered crystalline phase.
   An ideally disordered liquid-like amorphous phase.

• Partial properties are now \( (P\text{a}^\text{i})^0 \) and \( (P\text{c}^\text{i})^0 \) and

\[
P\text{i} = \bar{\theta}_i (P\text{a}^\text{i})^0 + (1 - \bar{\theta}_i)(P\text{c}^\text{i})^0
\]

Note
   \( \bar{\theta}_i \) is now an APPARENT degree of crystallinity and varies with property measured.
Remember a real sample may have many subphases; for example what we normally call 'the crystalline phase' can consist of:

a) perfect 3D ordered material
b) crystals containing chains 'off position' by 1%
c) similarly 'off' by 2%, 3%, etc.

In a real sample we may have trouble deciding what polymer chains, or parts of chains, to count as 'crystalline' and what are 'amorphous'.

At least the previous definition removes that problem.
Compare two techniques measuring percentage crystallinity

A polymer sample, with material separated from 'crystalline' and 'amorphous' regions.

Chains in 'crystal' are aligned but not separated uniformly.

Method ‘a’ counts only straight chains as 'crystalline'. Method ‘b’ requires chains be in a perfect 2D lattice.

Method 'a' will measure a high degree of crystallinity and 'b' will report a low value.