



KEIRYO PACKAGING SA

Maximizing materials efficiency for a better environment

The Scientific Narrative

February 2019

About this document

This document has been created by Keiryō Packaging SA for the purpose of providing the reader with further detailed perspectives on the selected topic.

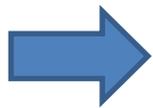
Although carefully established, the document does not seek to be complete or exhaustive on the selected topic.

The representatives of Keiryō Packaging are always available to provide further context and to enter into continued dialogue should this be desired. Please refer to the 'About Us' page on the website to find the appropriate contact details.

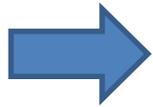
Meanwhile, enjoy the read and we are looking forward to be hearing from you.

Flow Enhanced Nucleation & Induced Crystallization

The ability of any **semi-crystallizable polymer** to alter its **crystallization kinetics** and resulting **material morphology** when being subjected to **deformational flows**

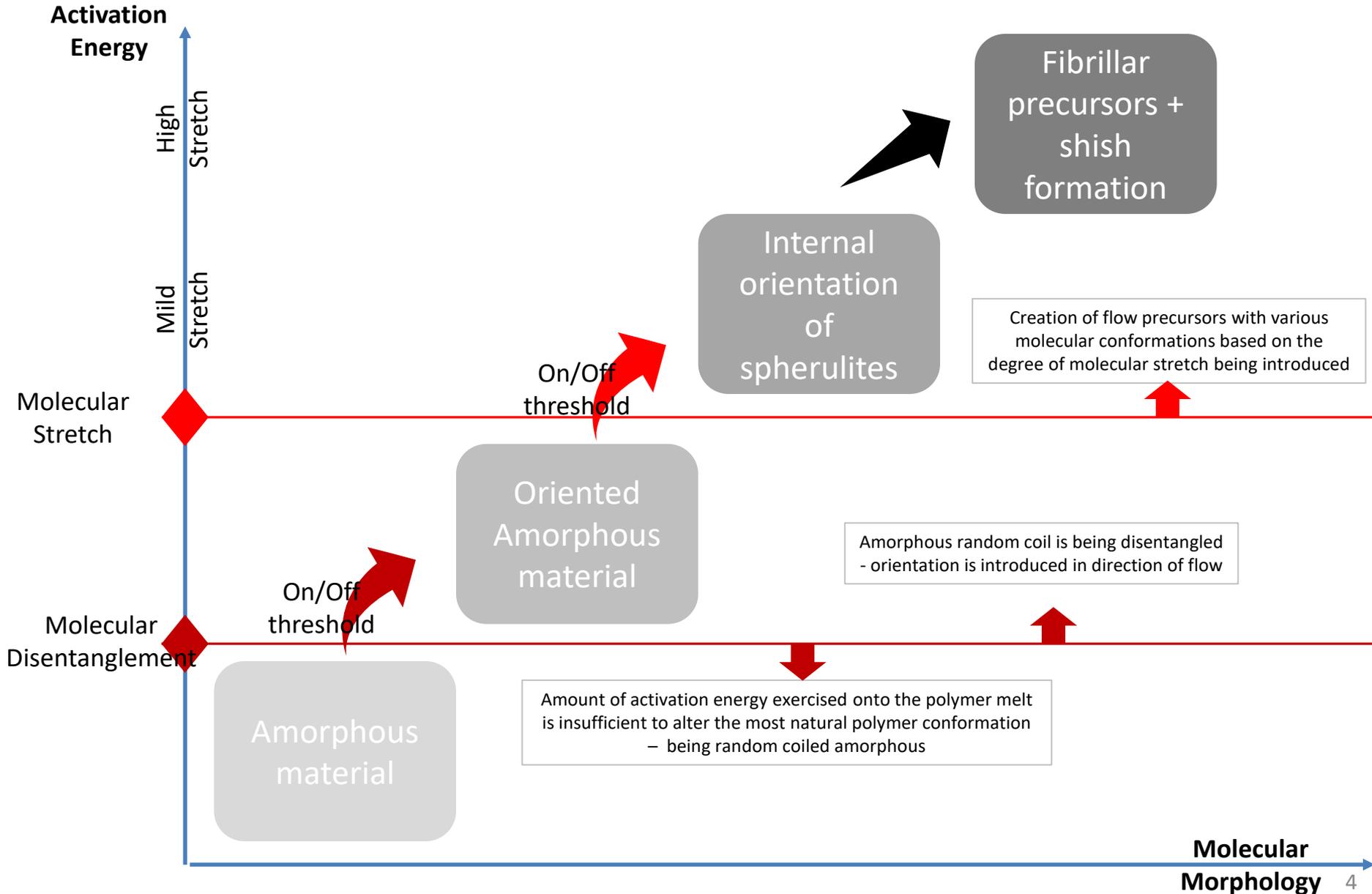


Pathway for modifying polymer (macro-) molecular conformation, increasing degree of 'organization' in the polymer mass (**molecular ordering**)



Driving force = **deformational flows** : exceeding polymer relaxation, herewith introducing alignment, orientation and/or stretching of the polymer backbone

The deformational flows provide the activation energy required to introduce changes to the molecular morphology of the polymer melt



Flow fields can be leveraged as a kinetic pathway to crystallization

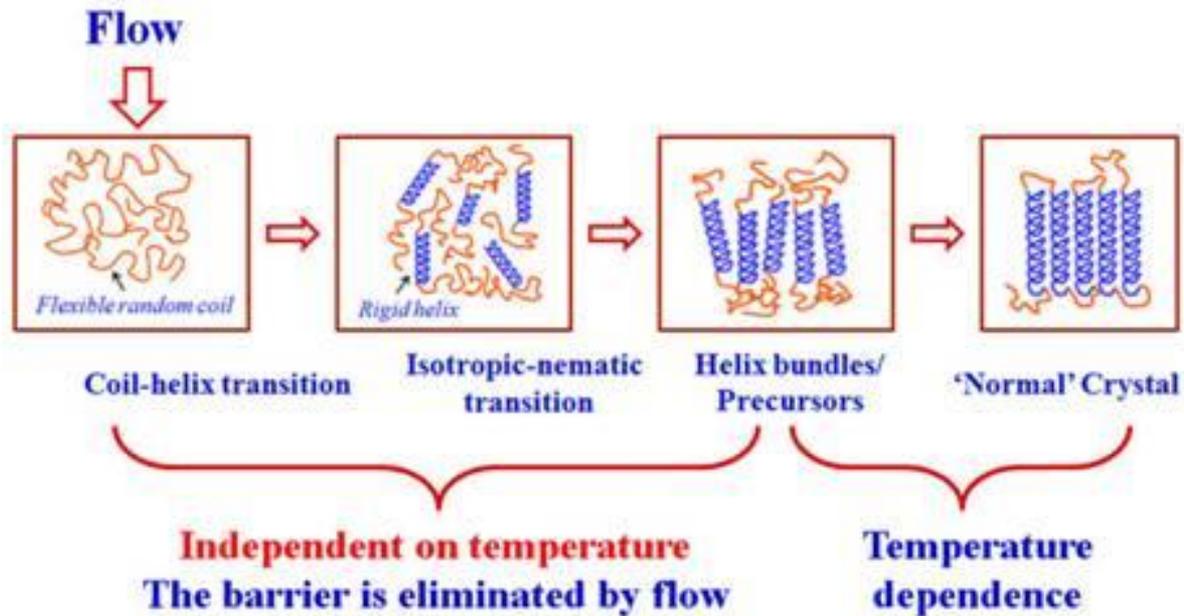


Illustration taken from Cui, K et al, "Non-equilibrium Nature of Flow-Induced Nucleation in Isotactic Polypropylene", Macromolecules, 2015, 48, 694–699

- Recent high-speed X-ray light scattering studies in conjunction with FIC measurements in extension have revealed stretch-induced hierarchical structural transitions in the kinetic pathway to nucleation
 - Exposure to a strong flow field induces a coil-stretch transition which leads to the formation of rigid helix structures
 - The bundling of rigid helix structures can subsequently lead to the formation of nuclei and then crystals depending on the temperature conditions

Flow-Induced Precursor Formation

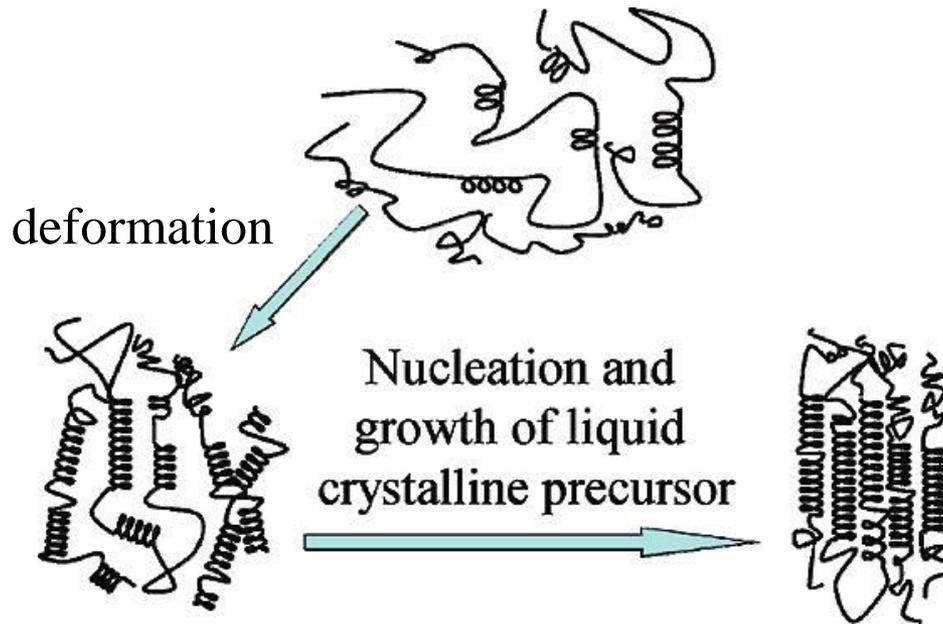


Illustration taken from Geng, Y et al, "Shear-Induced Nucleation and Growth of Long Helices in Supercooled Isotactic Polypropylene", Macromolecules 42(13), 2009

- As the flow field facilitates the bundling of stretch-induced rigid helix segments, transitional structures referred to as precursors exist in a liquid crystalline state which precede the formation of spontaneously growing nuclei and enhance the polymer crystallization rate
- Hence, the imposed flow field provides a flow-induced conformational ordering (low entropy state) of the polymer chain thereby promoting the formation of precursors, which have a "partial ordered" structure and provide a kinetic pathway to FIC

Flow-Induced Precursor Stability

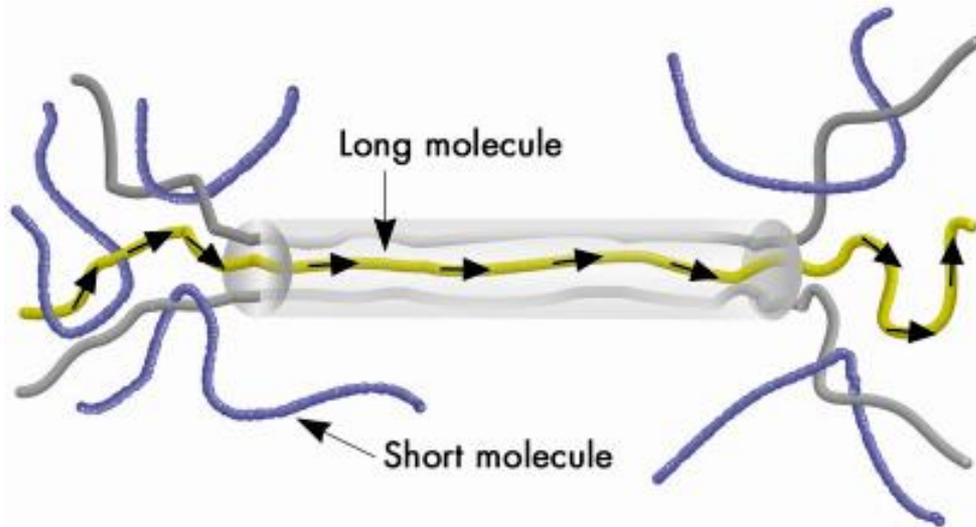


Illustration taken from Balzano, L et al, "Crystallisation and dissolution of flow-induced precursors", ESRF online publication, 2008

Hypothetical structure of a flow-induced precursors (FIP). This is a bundle made of the longest molecules of the melt that are stretched with the application of the deformational flows

- Above a threshold stress level, fibrillar flow-induced precursors that are partially crystalline remain stable after the flow has ceased even at conditions above the equilibrium melt temperature

Balzano, L et al, "Dynamics of fibrillar precursors of shishes as a function of stress", IOP Conference Series Materials Science and Engineering, December 2010

Azzurri, F. and Alfonso, G.C., "Insights into formation and relaxation of shear induced nucleation precursors in isotactic polystyrene", *Macromolecules* 2008, 41, 1377–1383.

Cavallo, D., Azzurri, F., Balzano, L., Funari, S.S., Alfonso, G.C., "Flow memory and stability of shear-induced nucleation precursors in isotactic polypropylene", *Macromolecules* 2010, 43, 9394–9400

Role of Molecular Weight on Flow-Induced Precursors

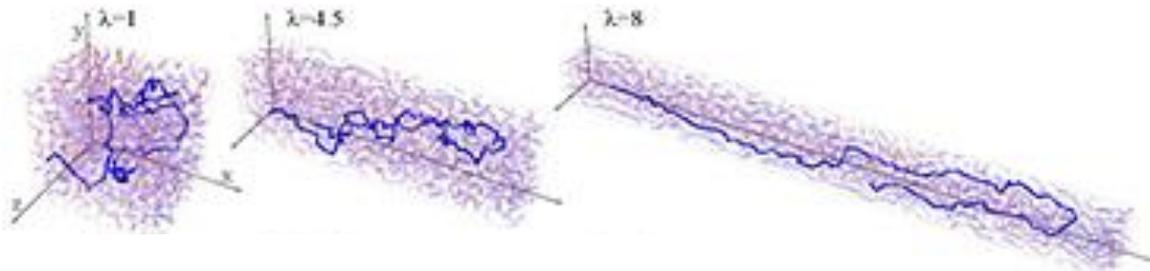


Illustration of the primitive path of a long polymer chain undergoing increasing stretch

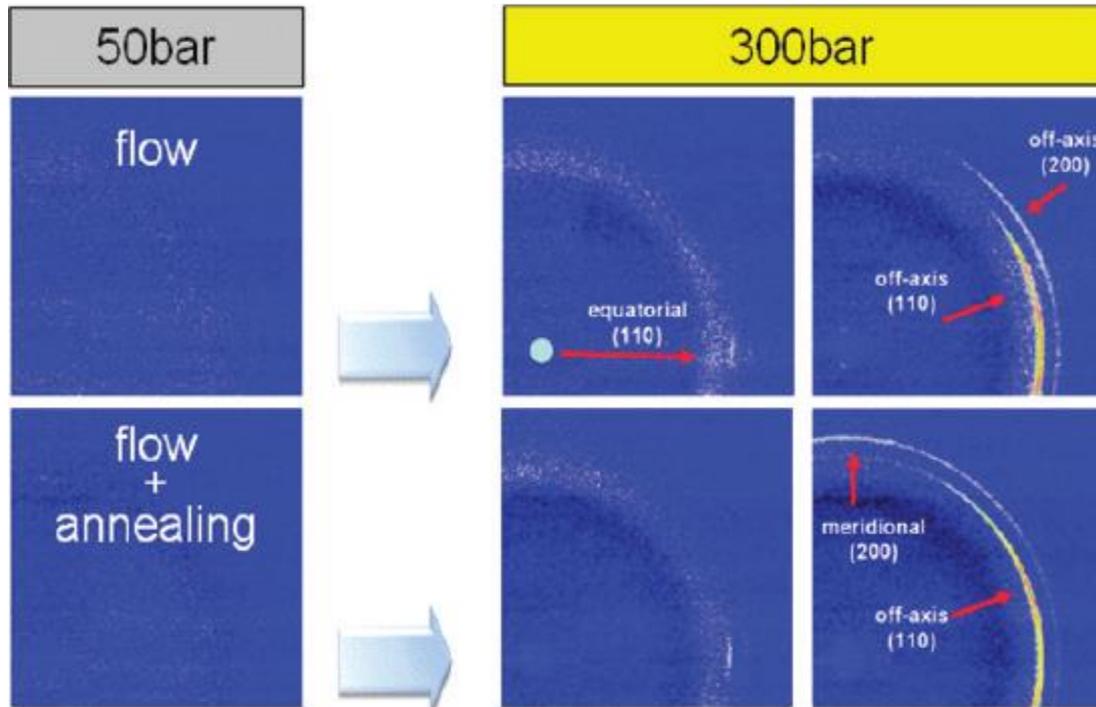
- The creation of flow-induced precursors is driven by the average stretch, not by the average orientation, of the primitive paths of chains in the HMW tail of the molecular weight distribution

Steenbakkens, R and G. W. M. Peters, A stretch-based model for flow-enhanced nucleation of polymer melts, *Journal of Rheology* 2011, 55, 401

- Upon the cessation of flow, flow induced precursors in the HMW fraction of the polymer can survive for several hours at temperatures above the equilibrium melt temperature

Azzurri, F. and Alfonso, G.C., Lifetime of Shear-Induced Crystal Nucleation Precursors, *Macromolecules* 2005, 38, 1723-1728

Effect of Pressure on Flow-Induced Precursors



Images taken from Ma, Z et al, "Pressure Quench of FIC Precursors", *Macromolecules* 45, 4216–4224, 2012

- Flow-Induced precursors are difficult to observe experimentally, even with high-resolution synchrotron X-ray scattering
- Pressure enhances the effects of the applied flow field enabling flow-induced precursors to be easily observed via X-ray scattering

Pathways to effecting precursor formation and the onset of polymer crystallinity

- Chemical
 - Structure, Molecular Weight, Molecular Weight Distribution, Nucleating Agents, Mobility Inhibitors, etc.
 - Controlling these chemical parameters can be complex and expensive

KP TECHNOLOGY APPROACH

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- Physical
 - Polymer Processing conditions, specifically: Temperature, Pressure and Molecular Ordering
 - Controlling these physical parameters is less expensive but to do so effectively requires non-conventional polymer processing approaches

The KP Technology : key processing parameters

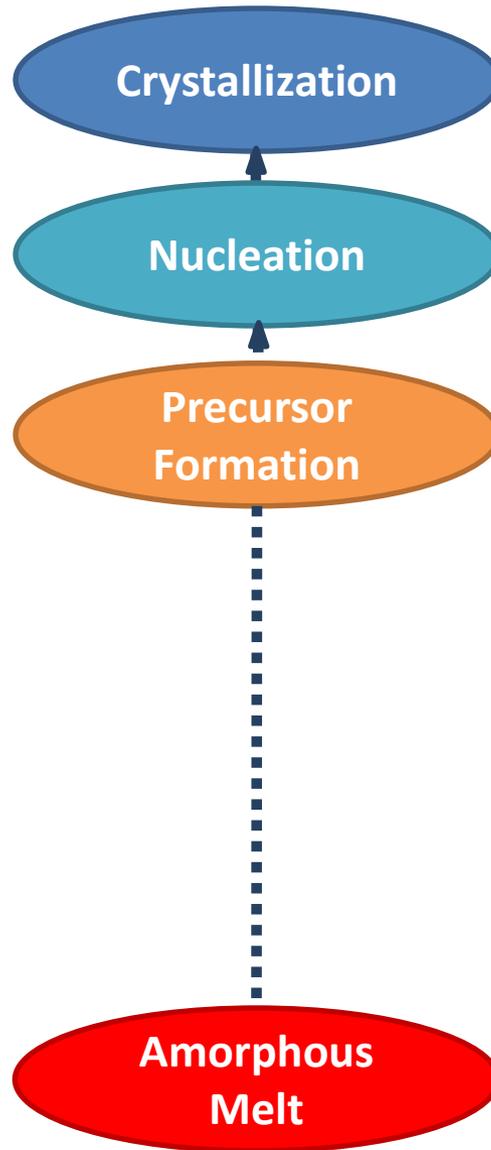
What specific features distinguish The KP Technology from conventional polymer processing technology?

The KP Technology enables a simultaneous control over three core parameters which govern the overall crystallization dynamics of any polymer, namely :

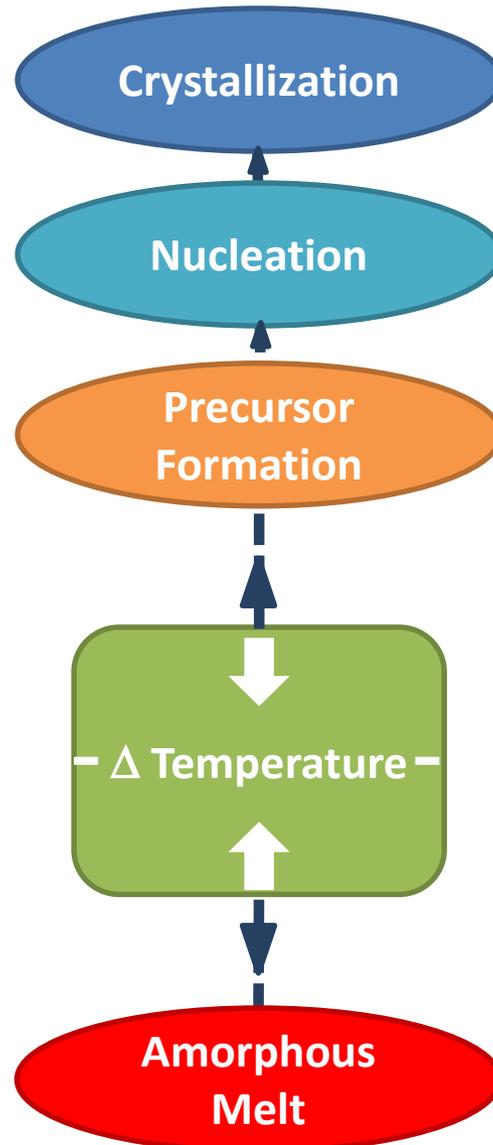
- (i) the pressure-dependent local polymer crystallization temperature
- (ii) the local pressure exerted on the polymer melt
- (iii) the degree of molecular ordering introduced into the polymer melt

It is the careful combination of these processing parameters that makes The KP Technology so unique

The KP Technology process seeks to template the amorphous melt for subsequent nucleation & crystallization

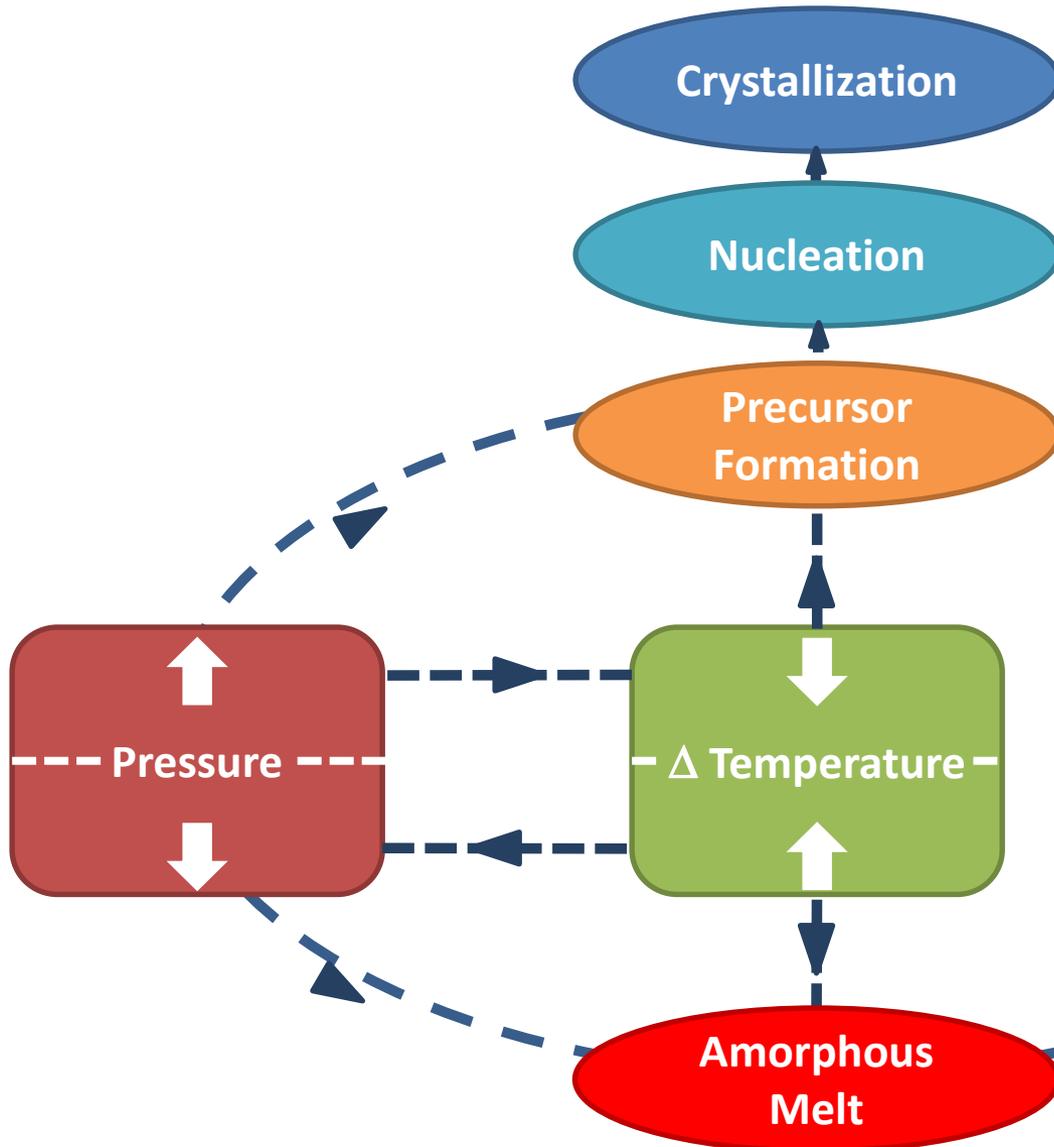


KP Technology process parameter : LOCAL CRYSTALLIZATION TEMPERATURE



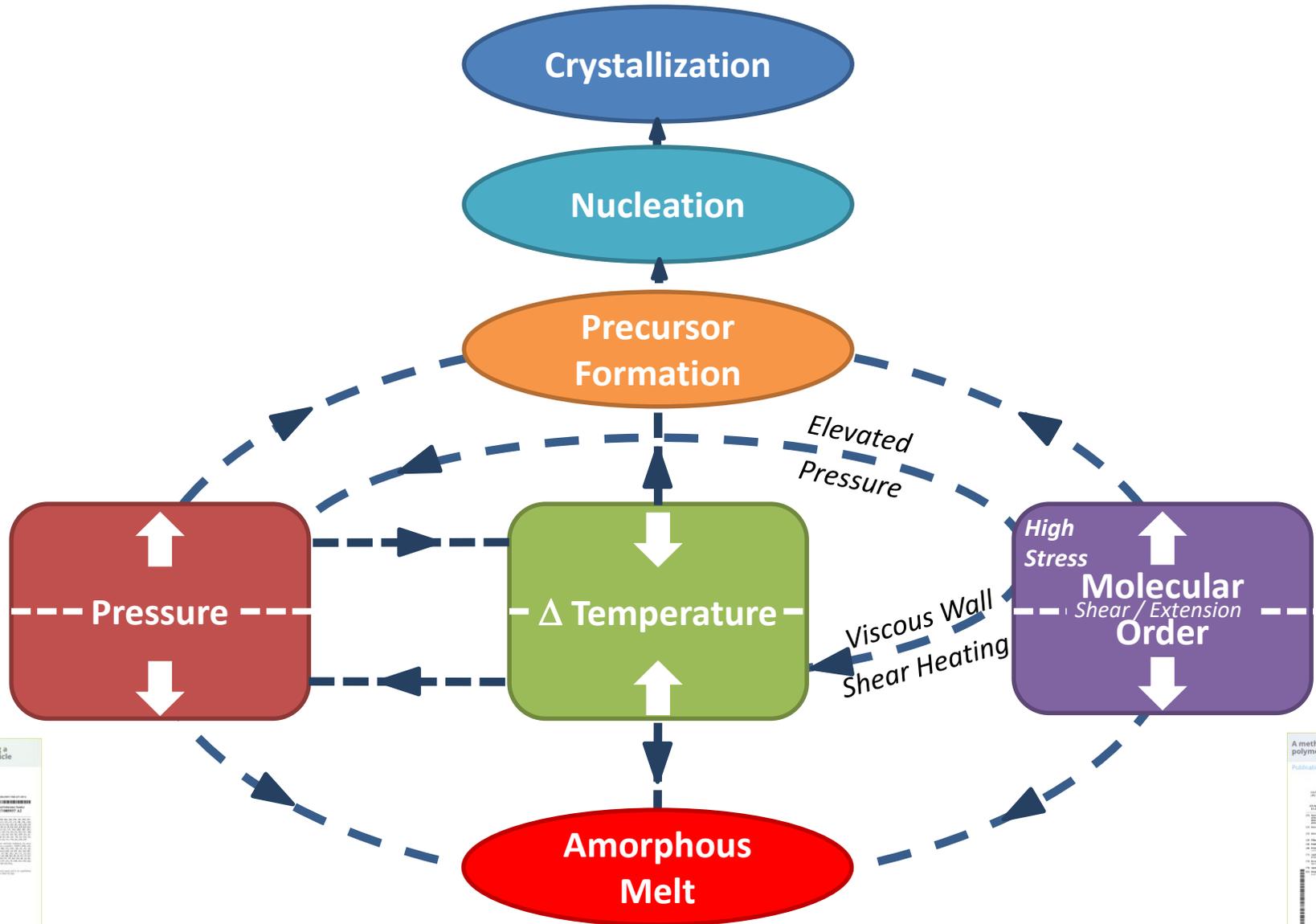
$$\Delta \text{ Temperature} = [\text{Processing Temperature}] - [\text{Crystallization Temperature}]$$

KP Technology process parameter : LOCAL PRESSURE



$$\Delta \text{ Temperature} = [\text{Processing Temperature}] - [\text{Crystallization Temperature}]$$

KP Technology process parameter : LOCAL MOLECULAR ORDERING



$$\Delta \text{ Temperature} = [\text{Processing Temperature}] - [\text{Crystallization Temperature}]$$

The KP Technology leverages the macromolecular dynamics of the semi-crystalline polymer material

CONVENTIONAL PARADIGM



Considering the material bulk dynamics only :
accepting associated limitations



Belief :

Exposure to deformational flow is inherently bad for the material



Molecular dynamics are not leveraged beyond the limitations imposed by the bulk polymer material



Conventional processing technologies have fully exploited material capabilities

KEIRYO PACKAGING PARADIGM



Leveraging the material macromolecular dynamics :
creating opportunities



Fact :

Controlled deformational flow does not harm the material



Activate flow enhanced nucleation & induced crystallization to leverage the molecular dynamics



KP Technology can further exploit material capabilities



KEIRYO

P A C K A G I N G

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