Shear-Enhanced Crystallization of Polymers: The Role of Melt Dynamics

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Examples of Semicrystalline Polymers

- Sterile, disposable
- Electrical applications
- Strong lightweight

Examples of polymers with various applications.
Processing Semicrystalline Polymers

Processing operations subject polymer melts to complex flow and thermal histories.

Examples: Film Blowing
Molding
Fiber Spinning

Typically:
• High stresses (0.1 MPa)
• Brief intervals of intense deformation just prior to / during cooling

Effect of Processing Flows on Polymer Crystallization

Flow affects
• crystallization kinetics
• semicrystalline morphology
• material properties (thermal, mechanical, & transport)

Oriented skin layers
• high modulus
• tends to delaminate
Polymer Crystallization

- Kinetic Frustration

- Chain-folded lamellae

- Lamellae form superstructures
  - “spherulites”
  - “shish-kebabs”

General Physical Picture of Shear-Induced Oriented Growth

In the “shish-kebab” morphology, thread-like precursors template oriented growth.

Schematic view of precursors developing during flow (Janeschitz-Kriegl, Keller)

Point-like nuclei form due to shear flow

Point-like nuclei grow into threads and more point nuclei form

Thread-like precursors grow, increasing the density of threads per volume…

What is the molecular basis of the observe phenomena?
Flow-Enhanced Crystallization: The Role of Melt Dynamics

**Literature: Effects of Shear on Crystallization of Semicrystalline Polymers**

<table>
<thead>
<tr>
<th>Reference</th>
<th>Effect Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Haas and Maxwell (1969)</td>
<td>Impose shear, continuous shear deforms melt as well as crystallites</td>
</tr>
<tr>
<td>Fritzche and Price (1974)</td>
<td>High shear rates, brief shear intervals, 22 kg required per experiment!</td>
</tr>
<tr>
<td>Andersen and Carr (1978)</td>
<td></td>
</tr>
<tr>
<td>Kobayashi and Nagasawa (1970)</td>
<td></td>
</tr>
<tr>
<td>Fritzche, Price and Ulrich (1976)</td>
<td></td>
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<tr>
<td>Lagasse and Maxwell (1976)</td>
<td></td>
</tr>
<tr>
<td>Wernet and Gogos (1971)</td>
<td></td>
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<tr>
<td>Wolkowicz (1978)</td>
<td></td>
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<td>Stein (1976)</td>
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</tbody>
</table>

**Schematic of Apparatus**

- **Real time:** turbidity, $\Delta n$, WAXD, SAXS, IR dichroism
- **Ex-situ:** TEM, optical microscopy

Dr. Julie Kornfield, Caltech (ITP Complex Fluids Program 4/16/02)
Experimental Protocol

Samples

- Quantum commercial iPP: PP-300/6
  - Mw 300,000 g/mol, PDI ~ 6-8
  - MFR 12 (230°C, 2.16 kg)

- Dow developmental iPP resin: PP-186/2.1
  - Mw 185,500 g/mol, PDI 2.14
  - MFR 22 (230°C, 2.16 kg)

- Dow developmental iPP resin: PP-825/2.3
  - Mw 825,000 g/mol, PDI 2.3
  - MFR fractional (230°C, 2.16 kg)

Polydisperse
industrial grade
iPP

Narrow
distribution
model materials
and binary blends
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**PP-300/6 : Crystallization Kinetics**

![Graph showing crystallization kinetics](image)

- **PP-300/6**: Crystallization Kinetics
- **141°C**: Temperature
- **σ_w = 0.06 MPa**: Applied stress

**Graph Details**
- **Time, t_{cryst} (s)**: X-axis
- **Transmitted intensity (a.u.)**: Y-axis
- **Various time points**:
  - 0.25 s
  - 0.375 s
  - 0.5 s
  - 0.75 s
  - 1 s
  - 1.5 s
  - 2 s
  - 3 s
  - 4 s
  - 6 s
  - 8 s
  - 12 s

**Images Below Graph**
- **t_s = 1s, 2s, 4s, 8s**

**Images**
- Scale bars: 50 µm, 10 µm

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**PP-300/6: Anisotropic Structure Development**

- **Short Shearing time**
  - Depolarization
  - $I_{\perp}/I_{\text{tot}}$ vs. time ($t_{\text{cryst}}$) for PP-300/6

- **Long Shearing time**
  - Depolarization
  - $I_{\parallel}/I_{\text{tot}}$ vs. time ($t_{\text{cryst}}$) for PP-300/6

**PP-300/6: Effect of Shear on Morphology**

- $\sigma_w = 0.06$ MPa
  - $t_s = 2$ s
  - $141^\circ$C

- $\sigma_w = 0.06$ MPa
  - $t_s = 12$ s
  - $141^\circ$C
PP-300/6: Response of Melt During Shear

PP-300/6: WAXD During Shear

T = 141°C
\( \sigma_w = 0.06 \text{ MPa} \)
\( t_s \sim 6 \text{ s} \)

- WAXD peaks correspond to monoclinic \( \alpha \)-phase
- SAXS and WAXD are both evident in the first acquired frame

All Synchrotron scattering experiments done collaboratively with Prof. Ben Hsiao (SUNY-Stony Brook) and Dr. Fengji Yeh (BNL, NSLS)
PP-300/6: Structure Evolution

$t = 141^\circ C$, $\sigma_w = 0.06 \text{ MPa}$, $t_s = 12 \text{ s}$

1 minute 10 minutes 20 minutes

PP-300/6: Development of orientation: $t_{\text{cryst}} \sim O(t_s)$

Azimuthal scan 110 peak

Azimuthal angle, $\phi$
Thread spacing ~750 nm near boundary with fine grained layer

\[ v = \sim 7 \text{nm/s quiescent growth velocity at 141°C} \]

\[ \rightarrow \text{impingement at } \sim 100 \text{s!} \]

Thread spacing ~250 nm near the wall

\[ t_s = 8 \text{s} \]

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**Take-Home Lessons**

- Threadlike precursors can be detected using birefringence (high time resolution); according to WAXD they correlate with formation of highly oriented \( \alpha \)-iPP
- Threads template oriented growth
- Thread spacing dictates impingement time
- It is essential to model thread formation to predict morphology and kinetics
  - Yet they are conspicuously absent from all models (Ziabicki, McHugh,…), except the recent work of H. Meijer
- So, what governs the rate of formation of the threads?
**Flow-Enhanced Crystallization: The Role of Melt Dynamics**

**PP-300/6 : Crystallization Kinetics (150°C)**

- **Kinetic Pathway to Oriented Precursors**
  - Quiescent ~ exponential slowing with decreasing subcooling
  - Attributed to activation barrier for nucleus formation.
  - Threads formation time ~ melt relaxation time!
**Take-Home Lessons**

- The classic idea of Flory, that reduced entropy of the melt effectively shifts the subcooling to deeper quench does not describe shish formation.
- All literature models, which effectively shift the quiescent kinetics to faster rate, effectively preserving the T-dependence of quiescent crystallization, are missing something.
- Melt dynamics play a profound role: the rate of molecular motion is the rate-limiting factor in formation of the "shish".
- So, is the timescale that required to reach
  - a given average level of segmental orientation?
  - a given strain?
  - a given orientation of the longest chains?

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**Low Polydispersity Materials**

For *both* low and high $M_w$

1. No "Melt Feature"
2. No "Skin" layers
3. Accelerated kinetics

So reaching a given average orientation is *not* the rate limiting factor in shish formation.
What Role Do Long Chains Play?

Long Standing hypothesis that long chains are significant in flow-induced crystallization
Keller et al., 1973; Andersen & Carr, 1978; Jerschow & Janeschitz-Kriegl, 1997; Vleeshouwers and Meijer, 1996; Duplay et al., 2000

However, ill-defined materials could not answer:
How long is “long”?  
How many chains are involved?  
• Single-chain effect? or cooperative?  
Must the long chains also be the most stereo-regular?

We prepare blends with known amounts of long chains of known length and known stereo-regularity.

Bimodal Blends

<table>
<thead>
<tr>
<th>Stereo-matched Blends with [mmmm]_L = [mmmm]_Bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Long iPP”</td>
</tr>
<tr>
<td>[mmmm] = 96 mol%</td>
</tr>
<tr>
<td>M_w = 825 kg/mol</td>
</tr>
<tr>
<td>M_w/M_n = 2.83</td>
</tr>
<tr>
<td>(Kumaraswamy, et al., Macromol 2002)</td>
</tr>
<tr>
<td>Sample</td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td>BL2.5</td>
</tr>
<tr>
<td>BL6</td>
</tr>
<tr>
<td>BL12</td>
</tr>
</tbody>
</table>

| “Base iPP” |
| [mmmm] = 96 mol% |
| M_w = 186 kg/mol |
| M_w/M_n = 2.3 |

<table>
<thead>
<tr>
<th>Blends with [mmmm]_L &gt; [mmmm]_Bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Long iPP”</td>
</tr>
<tr>
<td>[mmmm] = 98 mol%</td>
</tr>
<tr>
<td>M_w = 923 kg/mol</td>
</tr>
<tr>
<td>M_w/M_n = 1.31</td>
</tr>
<tr>
<td>Sample</td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td>BL0.25</td>
</tr>
<tr>
<td>BL0.5</td>
</tr>
<tr>
<td>BL1</td>
</tr>
<tr>
<td>BL2</td>
</tr>
</tbody>
</table>
**Effect of Stereo-Matched Long Chains**

Blends with \([\text{mmmm}]_L = [\text{mmmm}]_{\text{Bulk}}\)

- Base iPP (186 k)
- \(\sigma_w = 0.1\ \text{MPa}\)
- \(T_{\text{cryst}} = 142^\circ\C\)
- Long iPP (825 k)

**Conclusions:**
- \(M_L = 4.5M_{\text{base}}\) is long enough
- \(c \geq c_c^*\) is concentrated enough
- Long chains do \textbf{not} need to be more stereo-regular

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**Significance of Polydispersity**

- **Long (Narrow Distribution)**
  - \(\sigma_w\)
  - \(\rightarrow\)

- **Short (Narrow Distribution)**
  - \(\sigma_w\)
  - \(\rightarrow\)

- **Bimodal Distribution**
  - \(\sigma_w\)
  - \(\rightarrow\)

  Long chains become particularly highly oriented
Concentration of Long Chains near c*

Blends with \([\text{mmm}]_c > [\text{mmm}]_{\text{bulk}}\)

Base IPP (c/c* = 0)
BL025 (c/c* = 0.25)
BL05 (c/c* = 0.5)

Optical micrographs

Rheo-optical data

\[ \sigma_w = 0.14 \text{ MPa} \]
\[ T_c = 137 ^\circ \text{C} \]

Effect Saturates near c*

\[ \sigma_w = 0.14 \text{ MPa} \]
\[ T_c = 137 ^\circ \text{C} \]
**Broad Physical Picture of Shear-Induced Oriented Growth**

In the “shish-kebab” morphology, thread-like precursors template oriented growth.

Schematic view of precursors developing during flow (Janeschitz-Kriegl, Keller)

- Point-like nuclei form due to shear flow
- Point-like nuclei grow into threads and more point nuclei form
- Thread-like precursors grow, increasing the density of threads per volume…

...until saturation, perhaps due to impingement

At what point(s) are long chains involved? In the generation of the point-like nuclei? In the elaboration into threads? What is the role of long-chain long-chain overlap?

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**Weak Influence of Long Chains on Formation of Point-like Nuclei**

• For $\sigma_w < \sigma_w^*$, weak influence on turbidity ($t_{1/2}$)

![Diagram showing weak influence of long chains on formation of point-like nuclei](image)

- For $\sigma_w < \sigma_w^*$, weak influence on turbidity ($t_{1/2}$)
**Final Morphology**

<table>
<thead>
<tr>
<th>TEM</th>
<th>Base iPP $(c/c^* = 0)$</th>
<th>BL025 $(c/c^* = 0.25)$</th>
<th>BL05 $(c/c^* = 0.5)$</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="TEM Image" /></td>
<td><img src="image2.png" alt="TEM Image" /></td>
<td><img src="image3.png" alt="TEM Image" /></td>
<td></td>
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</table>

$T_c = 137 \, ^\circ C$

$\sigma_w = 0.14 \, MPa$

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**Final Morphology**

<table>
<thead>
<tr>
<th>TEM</th>
<th>BL05 $(c/c^* = 0.5)$</th>
<th>BL1 $(c/c^* = 1)$</th>
<th>BL2 $(c/c^* = 2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image4.png" alt="TEM Image" /></td>
<td><img src="image5.png" alt="TEM Image" /></td>
<td><img src="image6.png" alt="TEM Image" /></td>
<td></td>
</tr>
</tbody>
</table>

$T_c = 137 \, ^\circ C$

$\sigma_w = 0.14 \, MPa$
Conclusions & Remaining Questions

• How long is long? $M_L > 4.5M_{\text{base}}$ is long enough; $M_L > 2.7M_{\text{base}}$ is not.
  → How does the effect of long chains vary with length?

• Do the long chains need to be more stereo-regular than the rest? No.
  → How does the effect of long chains vary with their [mmmm]?

• Is the effect of long chains cooperative? Yes.
  → What is the physics behind the nonlinear dependence on $c_L$?

• At what point(s) in the process are long chains involved? L-chains are involved in formation of thread-like precursors but not point-like precursors

Funding/Acknowledgements

• NSF (DMR-9901403)
• Mitsubishi Chemical Corporation
• Guruswamy Kumaraswamy
• Dr. Robert Sammler (Dow)
Threads appear in 2s, then saturate

$\tau_s = 1\text{s}$  $2\text{s}$  $4\text{s}$  $8\text{s}$