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

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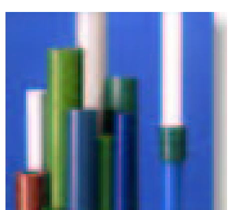
Examples of Semicrystalline Polymers

Sterile, disposable

Electrical applications

Strong lightweight

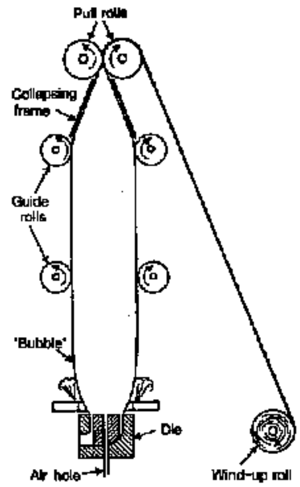


Processing Semicrystalline Polymers

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

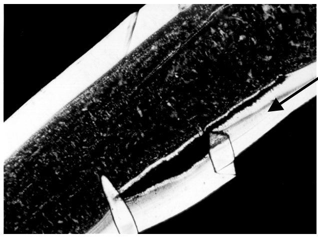
Examples: Film Blowing
Molding
Fiber Spinning

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



Effect of Processing Flows on Polymer Crystallization

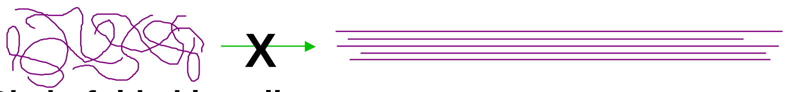
Flow affects
- **crystallization kinetics**
- **semicrystalline morphology**
- **material properties (thermal, mechanical, & transport)**



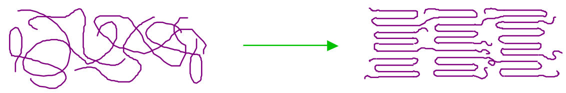
Oriented skin layers
- high modulus
- tends to delaminate

Polymer Crystallization

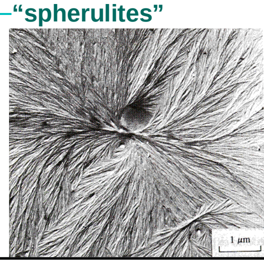
- Kinetic Frustration

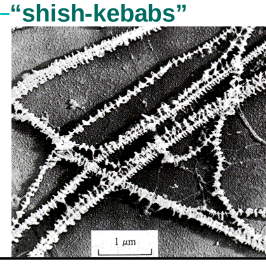


- Chain-folded lamellae



- Lamellae form superstructures
  - "spherulites"
  - "shish-kebabs"

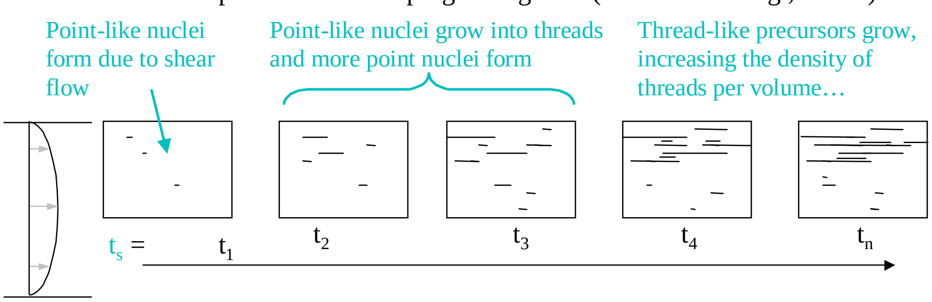




General Physical Picture of Shear-Induced Oriented Growth

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

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



What is the molecular basis of the observe phenomena?

Literature: Effects of Shear on Crystallization of Semicrystalline Polymers

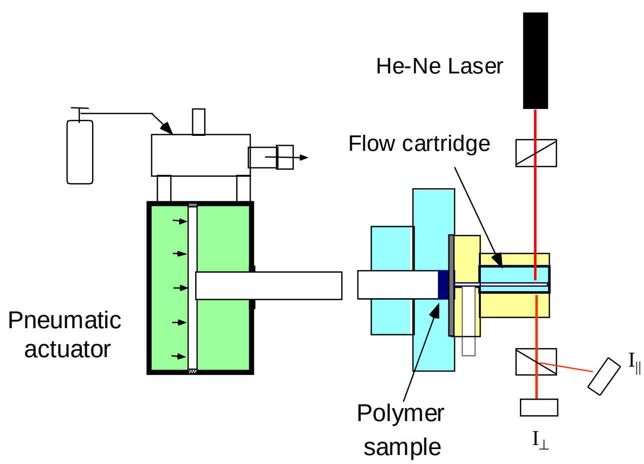
Haas and Maxwell (1969)	Kobayashi and Nagasawa (1970)	Wereta and Gogos (1971)
Fritzsche and Price (1974)	Fritzsche, Price and Ulrich (1976)	Wolkowicz (1978)
Andersen and Carr (1978)	Lagasse and Maxwell (1976)	Stein (1976)

T_m → T_C → Impose shear → Continuous shear deforms melt as well as crystallites

Janeschitz-Kriegl et al.	High shear rates Brief shear intervals 22 kg required per experiment!

T_m → T_C → Short shear pulse $t_s << t_{cryst}$ → Crystallization monitored after shear cessation

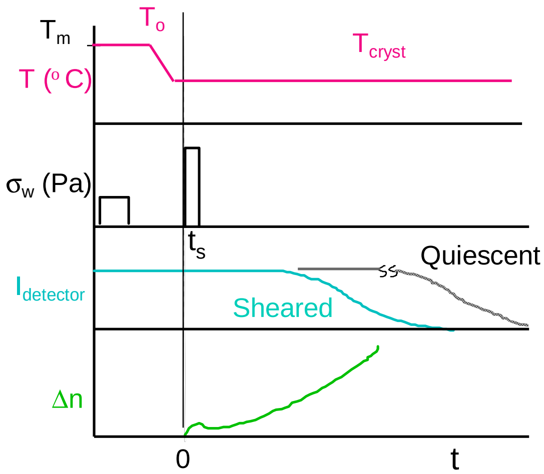
Schematic of Apparatus



Real time: turbidity, Δn, WAXD, SAXS, IR dichroism

Ex-situ: TEM, optical microscopy

Experimental Protocol



Samples

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

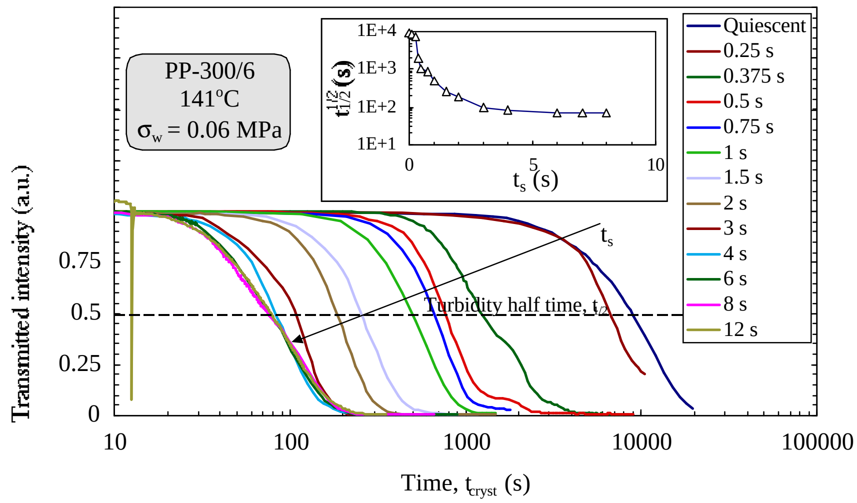
- Dow developmental iPP resin: PP-186/2.1
  Mw 185,500 g/mol, PDI 2.14
  MFR 22 (230°C, 2.16 kg)

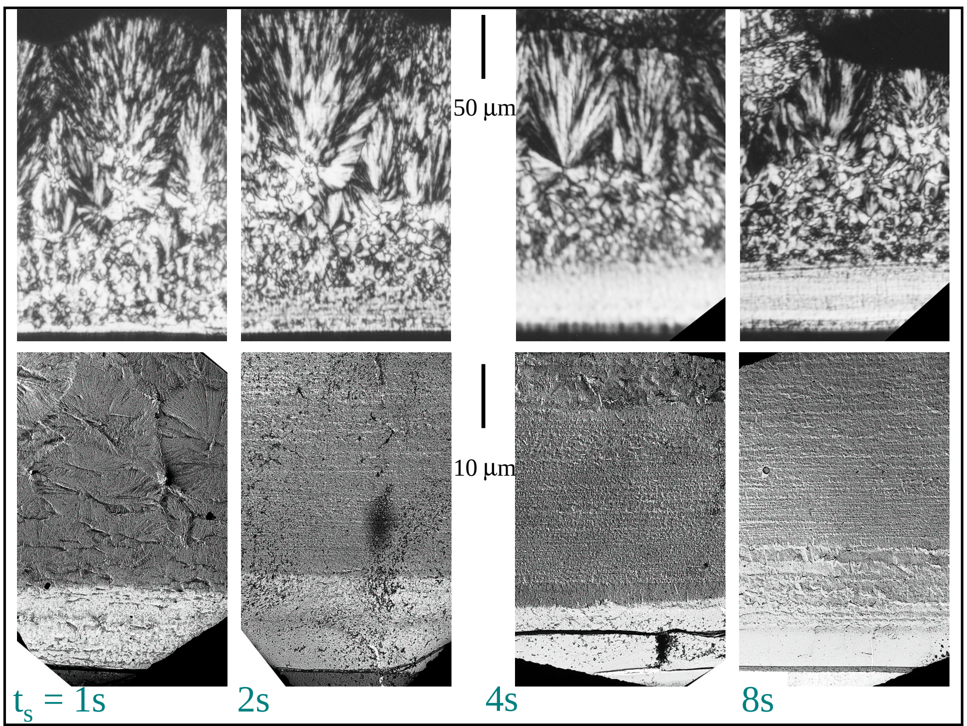
- Dow developmental iPP resin: PP-825/2.3
  Mw 825,000 g/mol, PDI 2.3
  MFR fractional (230°C, 2.16 kg)

Polydisperse industrial grade iPP

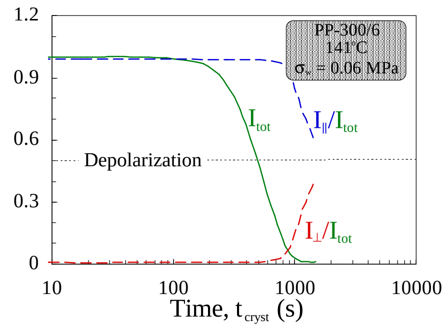
Narrow distribution model materials and binary blends

PP-300/6 : Crystallization Kinetics



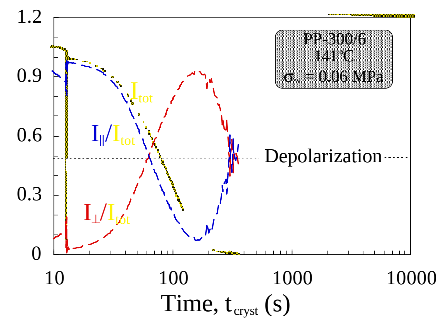


PP-300/6 : Anisotropic Structure Development



Short Shearing time

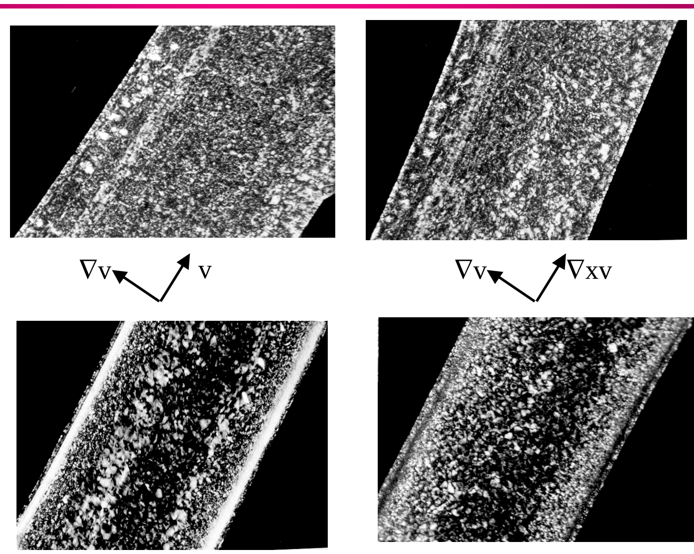
Long Shearing time



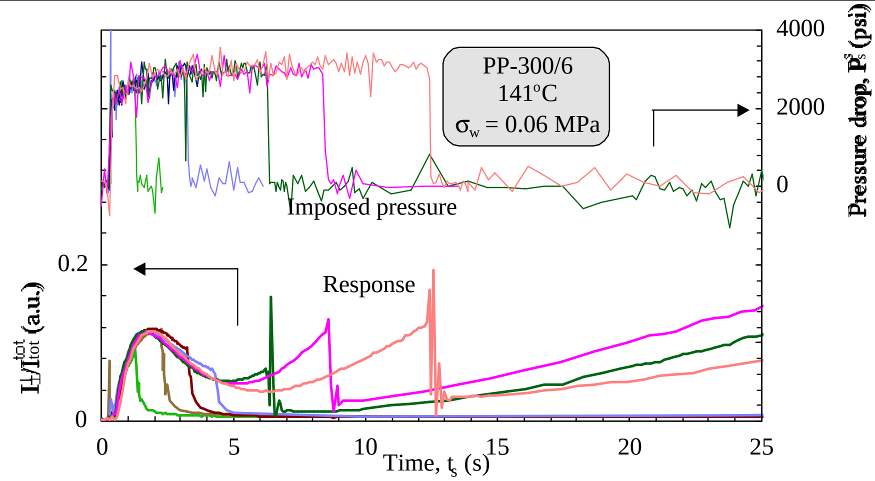
PP-300/6 : Effect of Shear on Morphology

σ_w = 0.06 MPa
t_s = 2 s
141°C

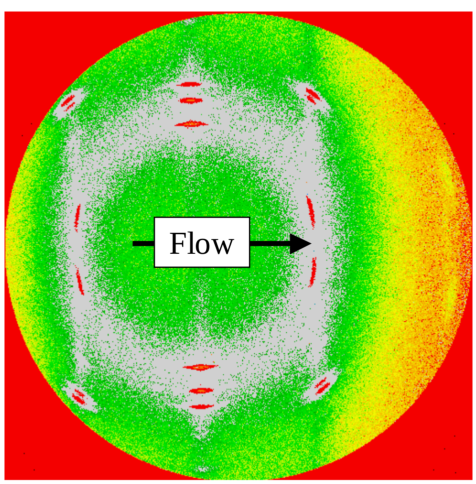
σ_w = 0.06 MPa
t_s = 12 s
141°C



PP-300/6 : Response of Melt During Shear



PP-300/6: WAXD *During* Shear

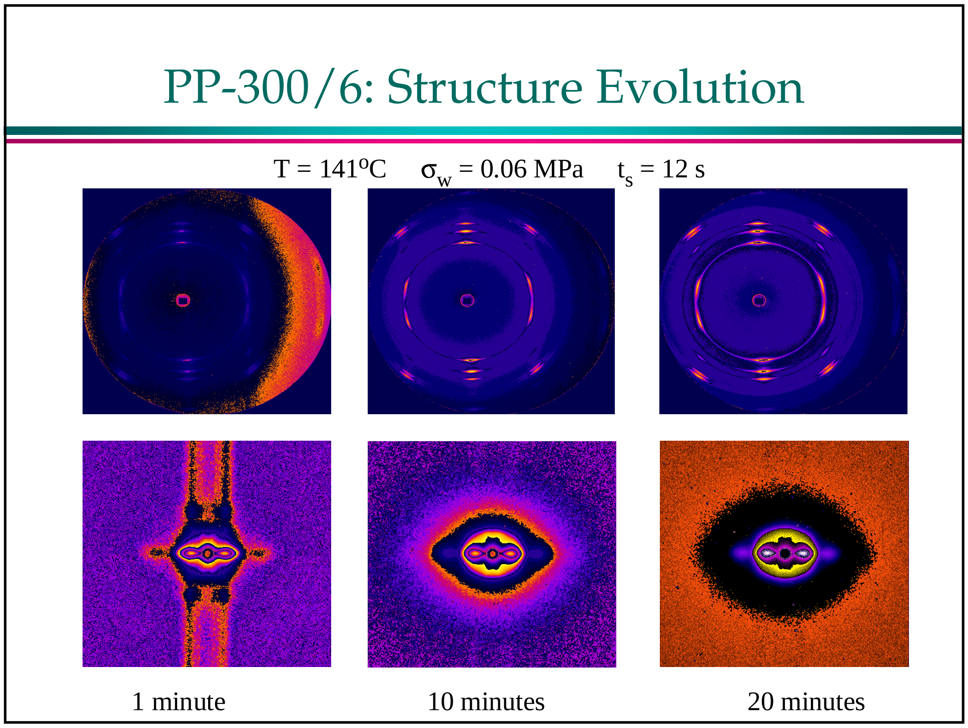


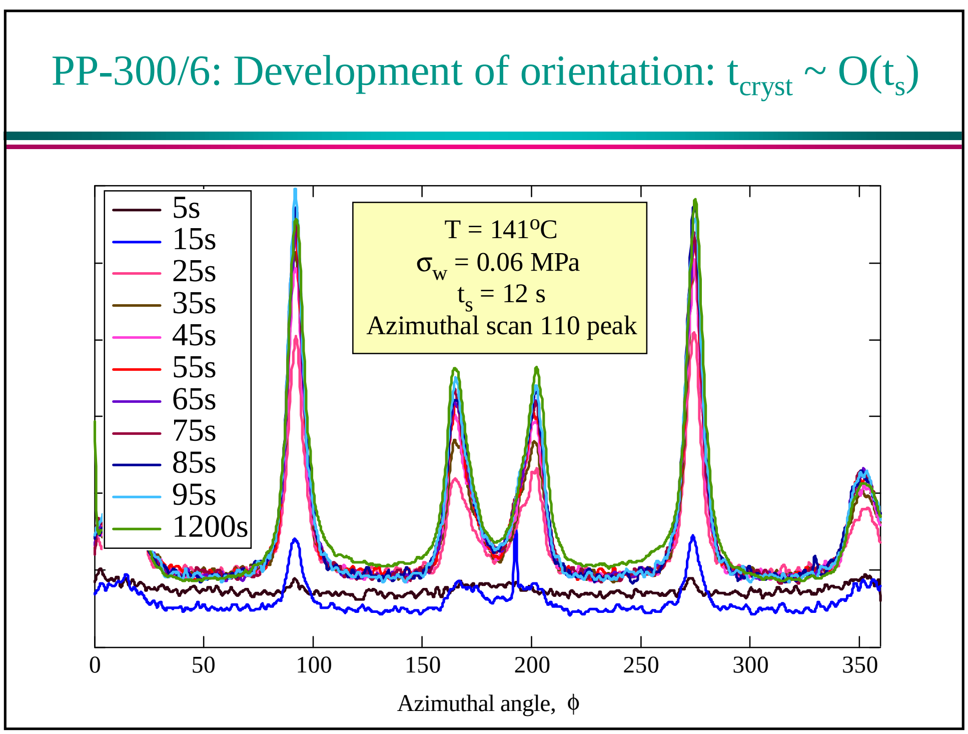
$T = 141^oC$
$\sigma_w = 0.06$ MPa
$t_s \sim 6$ s

WAXD peaks correspond to monoclinic α-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°C σw = 0.06 MPa ts = 12 s
1 minute
10 minutes
20 minutes


PP-300/6: Development of orientation: tcryst ~ O(ts)
5s
15s
25s
35s
45s
55s
65s
75s
85s
95s
1200s
T = 141°C
σw = 0.06 MPa
ts = 12 s
Azimuthal scan 110 peak
0
50
100
150
200
250
300
350
Azimuthal angle, ϕ

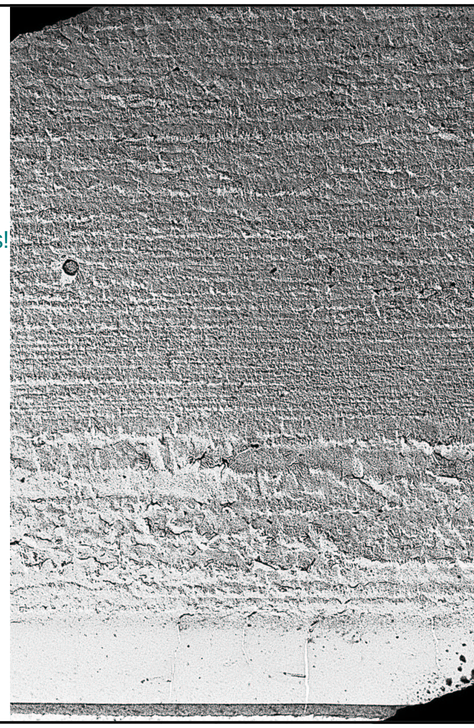
Thread spacing ~750 nm near boundary with fine grained layer

v = ~7nm/s quiescent growth velocity at 141° C

--> impingement at ~100s!

Thread spacing ~250 nm near the wall

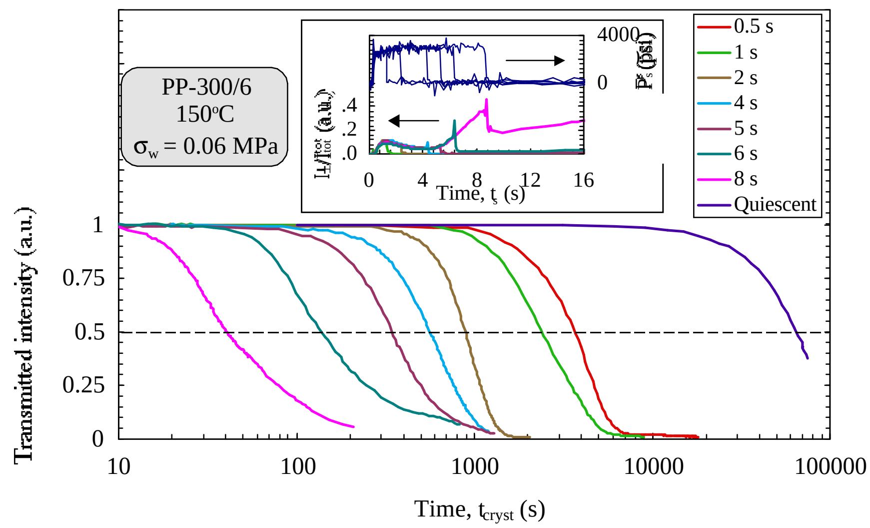
$t_s = 8s$

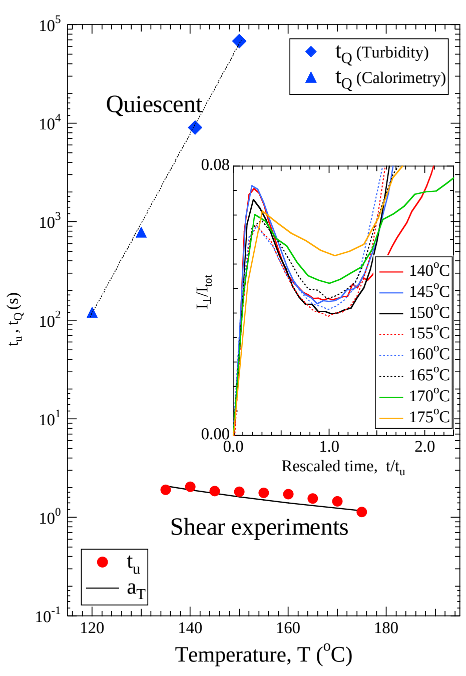


Take-Home Lessons

- **Threadlike precursors can be detected using birefringence (high time resolution); according to WAXD they correlate with formation of highly oriented α-iPP**
- **Threads template oriented growth**
- **Thread spacing dictates impingment 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?**

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





Kinetic Pathway to Oriented Precursors

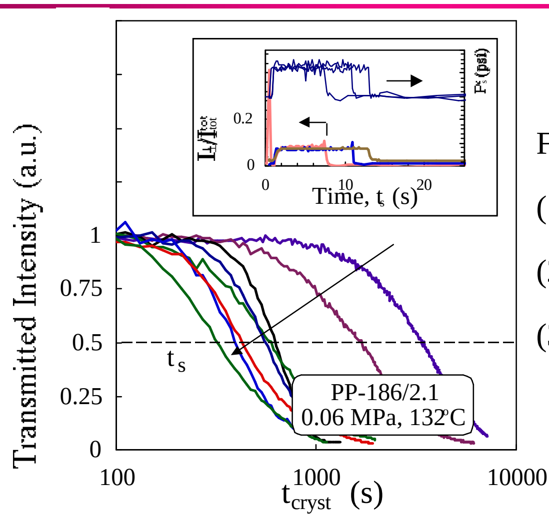
Quiescent ~ exponential slowing with decreasing subcooling
Attributed to activation barrier for nucleus formation.

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?**

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

Stereo-matched Blends with $[mmmm]_L = [mmmm]_{Bulk}$

"Long iPP"
[mmmm] = 96 mol%
M_w = 825 kg/mol
M_w/M_n = 2.83

(Kumaraswamy, *et al.*, Macromol 2002)

Sample	c/c_L^*	Weight %
BL2.5	2.46	2.0
BL6	6.14	5.0
BL12	12.3	10.0

"Base iPP"
[mmmm] = 96 mol%
M_w = 186 kg/mol
M_w/M_n = 2.3

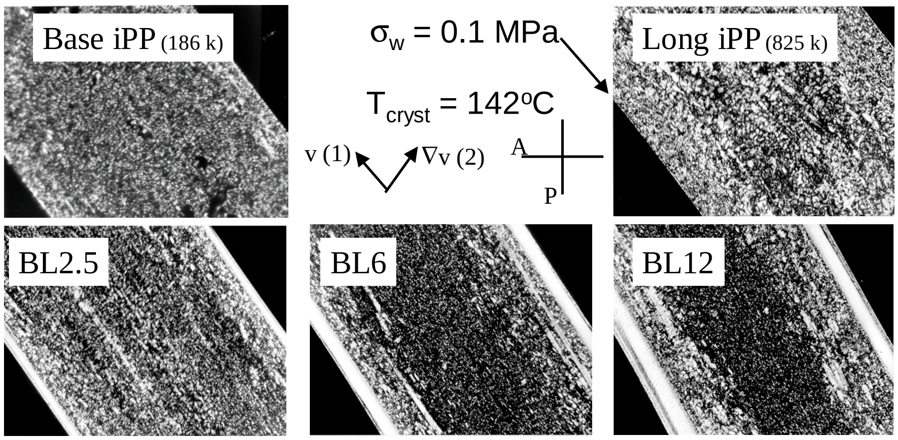
Blends with $[mmmm]_L > [mmmm]_{Bulk}$

"Long iPP"
[mmmm] = 98 mol%
M_w = 923 kg/mol
M_w/M_n = 1.31

Sample	c/c_L^*	Weight %
BL0.25	0.25	0.194
BL0.5	0.5	0.386
BL1	1.0	0.768
BL2	2.0	1.53

Effect of Stereo-Matched Long Chains

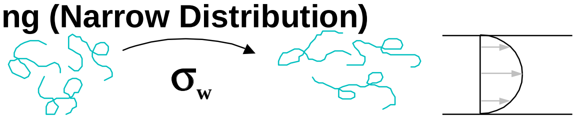
Blends with $[mmmm]_L = [mmmm]_{Bulk}$



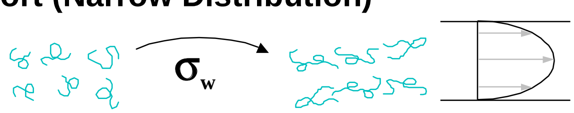
Conclusions:
- $M_L \approx 4.5 M_{base}$ is long enough
- $c \geq c_L^*$ is concentrated enough
- Long chains do <u>not</u> need to be more stereo-regular

Significance of Polydispersity

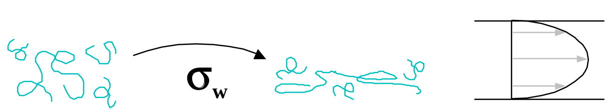
- **Long (Narrow Distribution)**



- **Short (Narrow Distribution)**



- **Bimodal Distribution**



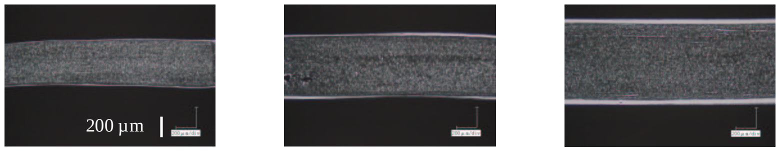
long chains become particularly highly oriented

Concentration of Long Chains near c*

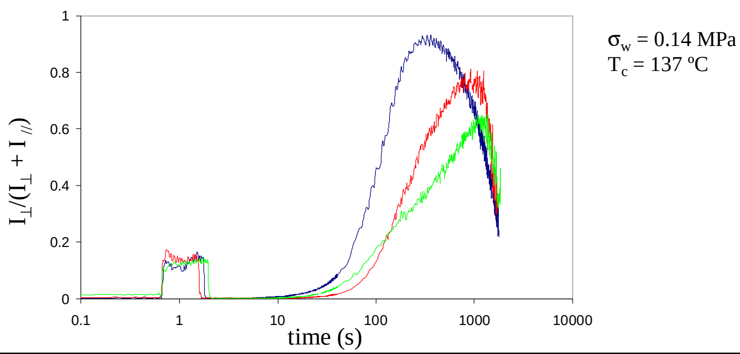
Blends with $[mmmm]_L > [mmmm]_{Bulk}$

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

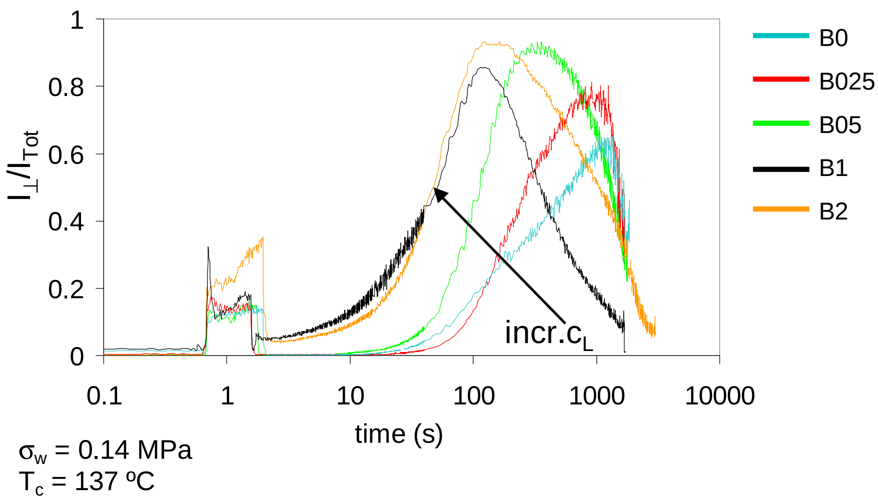
Optical micrographs



Rheo-optical data



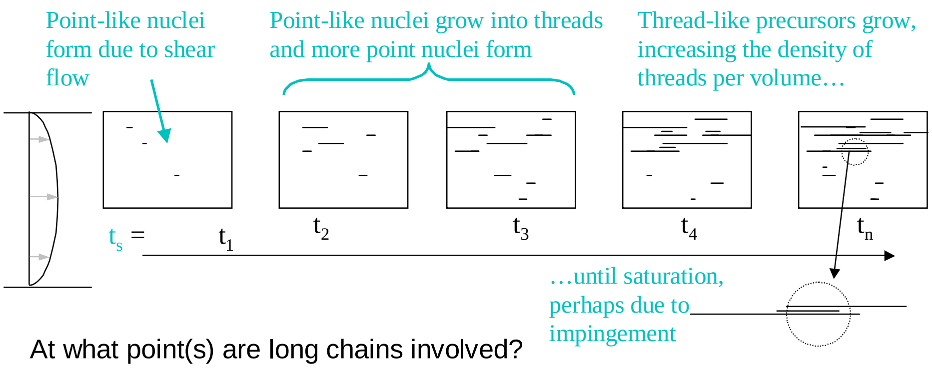
Effect Saturates near c*



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)



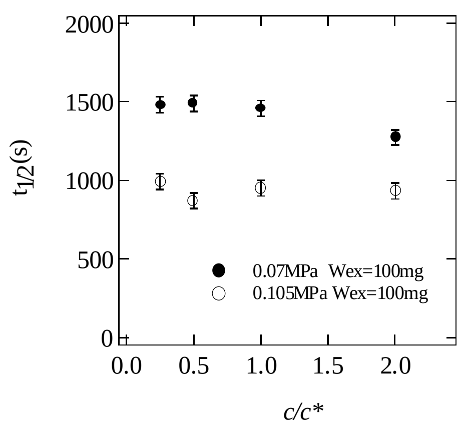
At what point(s) are long chains involved?

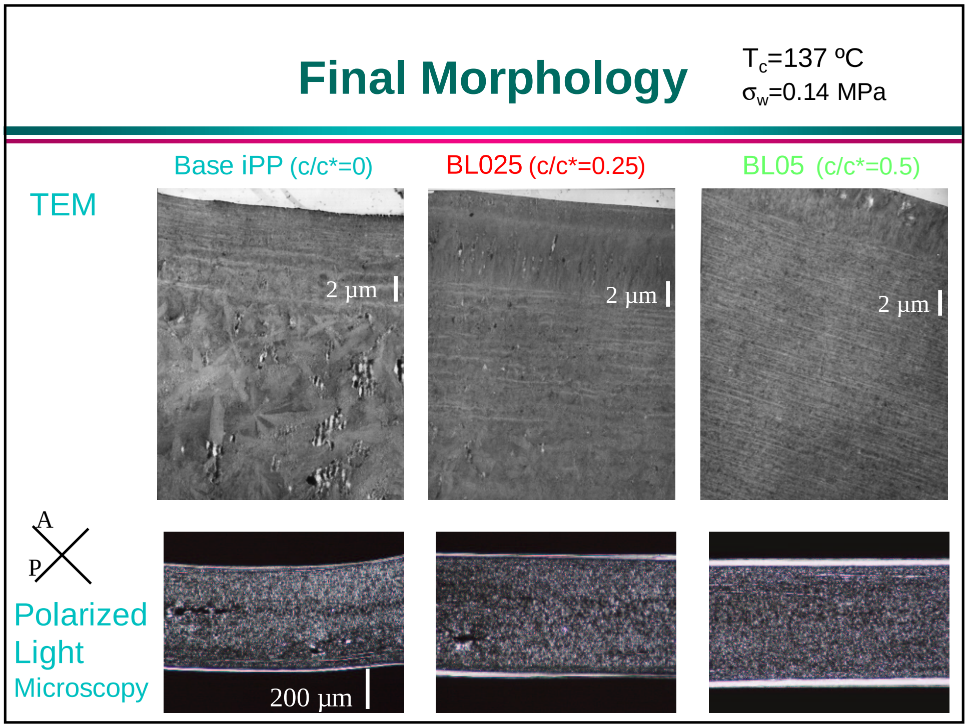
In the generation of the point-like nuclei? In the elaboration into threads?

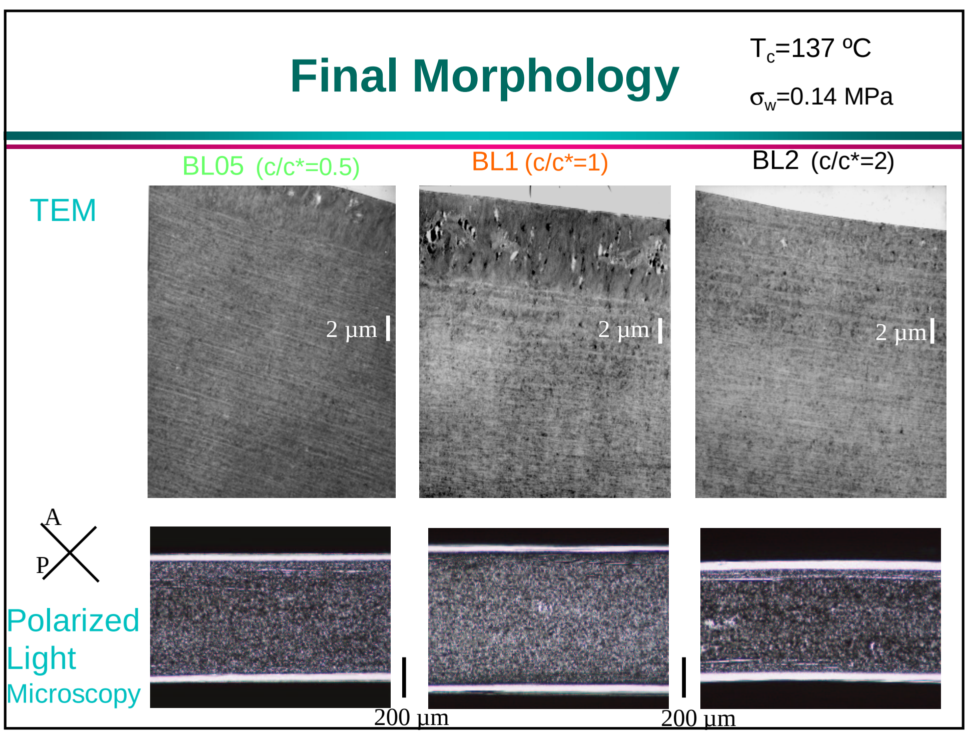
What is the role of long-chain long-chain overlap?

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

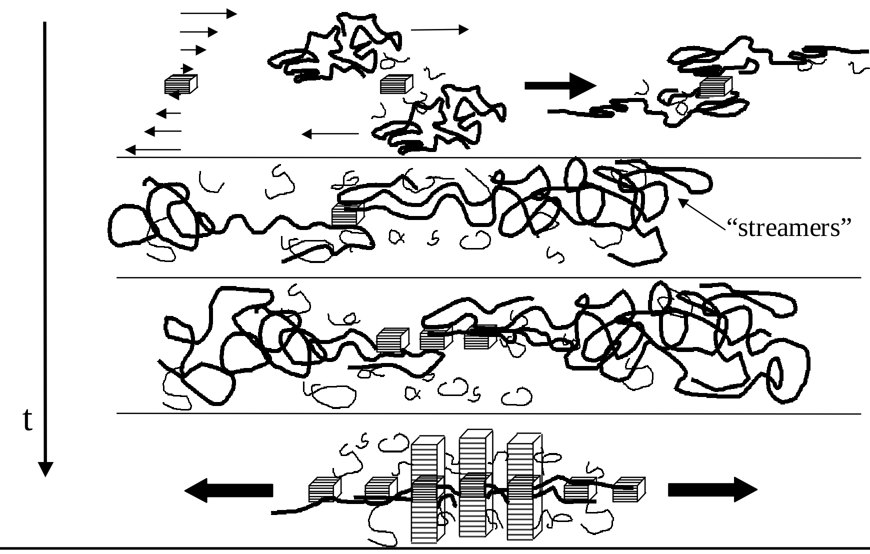
- For $\sigma_w < \sigma_w^*$, weak influence on turbidity ($t_{1/2}$)




Final Morphology
Tc=137 ºC
σw=0.14 MPa
Base iPP (c/c*=0)
BL025 (c/c*=0.25)
BL05 (c/c*=0.5)
TEM
2 µm
2 µm
2 µm
A
P
Polarized Light Microscopy
200 µm


Final Morphology
Tc=137 ºC
σw=0.14 MPa
BL05 (c/c*=0.5)
BL1 (c/c*=1)
BL2 (c/c*=2)
TEM
2 µm
2 µm
2 µm
A
P
Polarized Light Microscopy
200 µm
200 µm

Schematic View of the Role of Long Chains



Conclusions & Remaining Questions

- How long is long? $M_L > 4.5M_{base}$ is long enough; $M_L > 2.7M_{base}$ 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

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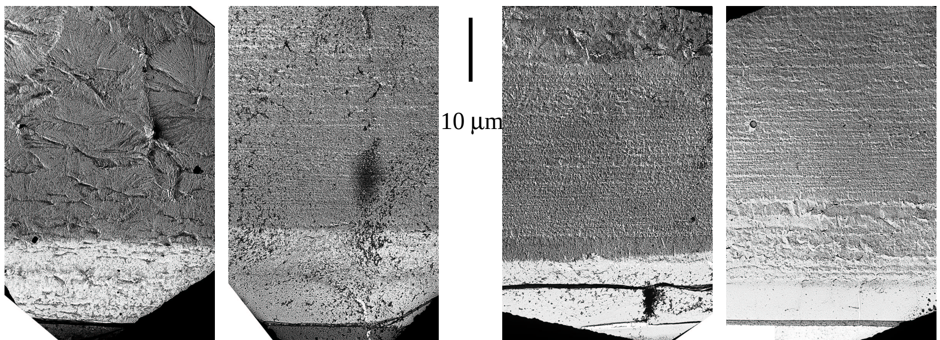
- Mitsubishi Chemical Corporation
- Guruswamy Kumaraswamy
- Dr. Robert Sammler (Dow)

Threads appear in 2s, then saturate



t_s = 1s 2s 4s 8s