Project 3: Effect of Branching on Flow-Induced Crystallization and Crystalline Orientation of Polyolefins

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Team: Jan Ilavsky[4], Jimmy Mays[5], Nikos Hadjichristidis[6]

1 Univ. Michigan; 2 Univ. Cincinnati; 3 Eclipse Film Technologies; 4 Argonne National Lab; 5 Univ. Tennessee/ORNL; 6 Univ. Athens/KAUST

Proposed Budget: $150,000/year; In Kind Support Eclipse Film Technologies $75,000/year, Argonne National Lab $25,000/year, ORNL $25,000/year

Project Duration: 4 years

Outcomes/Deliverables

- Correlation of polyolefin branching structure on crystallization kinetics, crystallization morphology (e.g. spherulite size and density) and orientation.
- Quantification of effect of linear and long- and short-chain branched fraction on polyolefin crystallization kinetics and morphology
- Measurements of interaction of branching structure and shear deformation on crystallization kinetics, orientation and morphology
- Development of scattering and rheological tools to probe effect of branching on crystallization

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Impact

- Improved ability to link long chain branching structure to crystallization kinetics, crystallization morphology and orientation of polyolefins
- Potential to manipulate crystallite morphology (e.g. size, density and orientation) by means of polyolefin branching structure
- Processing/structure interaction in long and short chain-branched polyolefins.

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Prior work and project scope

- A comb-shaped long-chain branched molecule added at approximately the overlap concentration significantly increased the crystallization kinetics of a hydrogenated polybutadiene blend[1]
- Isotactic polypropylenes of varying branching index showed enhanced crystallization kinetics and oriented crystallites due to long chain branching[2]

To extend the state-of-the-art, we should apply an integrated set of scattering, rheology and modeling studies to a series of polyolefin materials in which long-chain branch structure is homologously varied.

[1]E.L. Heeley et al., "Shear-induced crystallization in blends of model linear and long-chain branched hydrogenated polybutadienes," Macromolecules, 39, 5058 (2006).)

[2]P.K. Agarwal et al, "Shear-induced crystallization in novel long chain branched polypropylenes by in situ rheo-SAXS and -WAXD," Macromolecules, 36, 5226 (2003).

Prior work and project scope

- Beaucage in collaborative work with LyondellBasell over a number of years has published in this area , J. of Polym. Sci. B **39**, 2923-36 (2001); **45**, 1834-44 (2007); **46**, 607-18 (2008); Polymer **42**, 3103-13 (2001); **44**, 1103-15 (2003); Curr. Opin. In Sol. St. Mat. Sci. **8** 436-48 (2004).
- These papers detail the use of SAXS and WAXS to understand the relationship between the properties of polyolefin films and the nano- and crystallographic structure and orientation.
- Orientation in processed films is linked to long chain branching.

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Shear Induced Orientation and Associated Property Enhancement in Polymer/Clay Nanocomposites

University of Cincinnati

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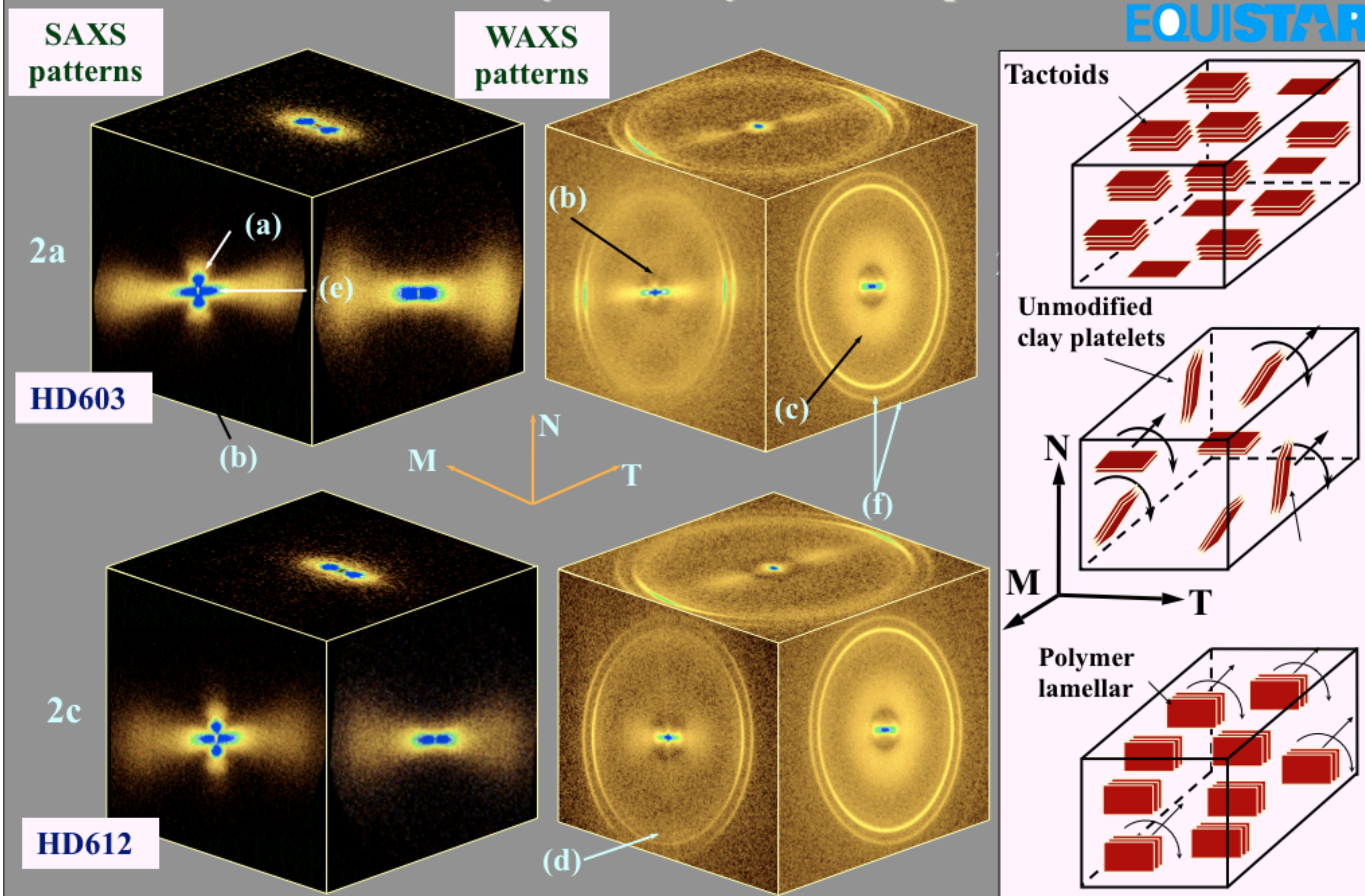

Bafna/Beaucage et al. Polymer 44, 1103-15 (2003)

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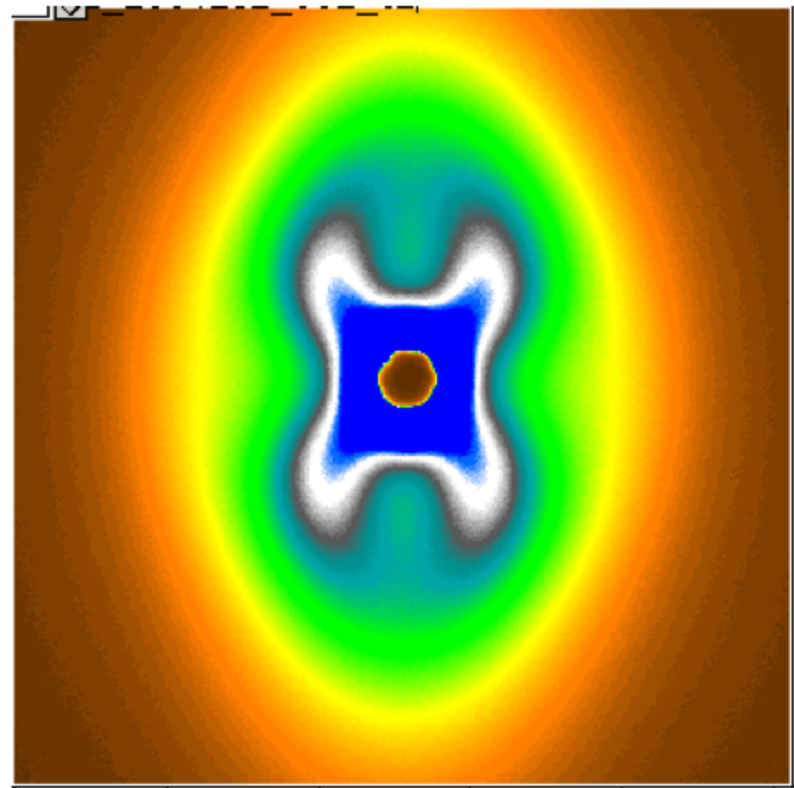
Ryan Breese:

In Situ Studies of MDO
Polyolefin Films
At SSRL and CHESS
Teach Tech Line



Mono-Axial Stretching Units MDO-AT and MDO-BT

By mono-axial stretching the physical properties of polymers can be drastically changed, widening the range of applications. Not only are mechanical properties like tear strength improved, but also optical behaviour or barrier effect against vapor or gases.

A modular system has been developed for the mono axial stretching of film, strap or monofilament consisting of cooling systems for the primary product, holding back godet MDO-AT, different types of heating zones, and take-off godets with winder, Type MDO-BT.

The units can be delivered for:
a) short gap stretching of film of PE or PP
b) long gap stretching of film of PET
c) long gap stretching with heated wedge for strap or monofilament.

Breese/Beaucage et al. J. of Polym. Sci. B 46, 607-18 (2008)

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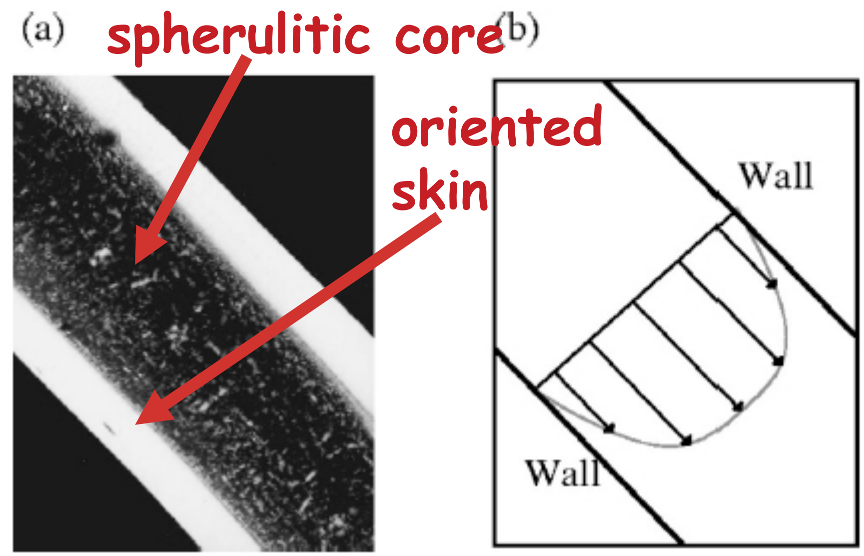
Shear-induced crystallization of polypropylene

- crystallization kinetics and morphology affected by shear

- controlled experiments with short shear times best model processing conditions *(Liedauer et al., 1993)*

- crystallization time depends on M_w, g and t_s



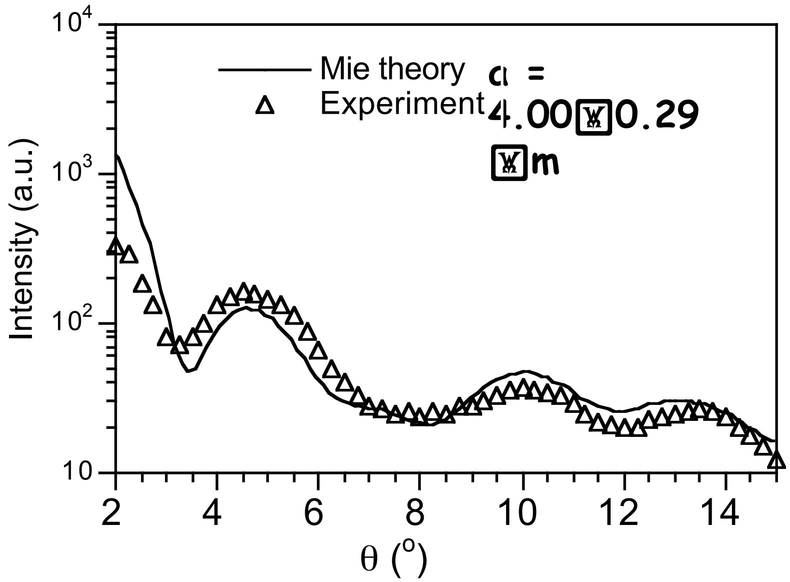
Polarized light micrograph

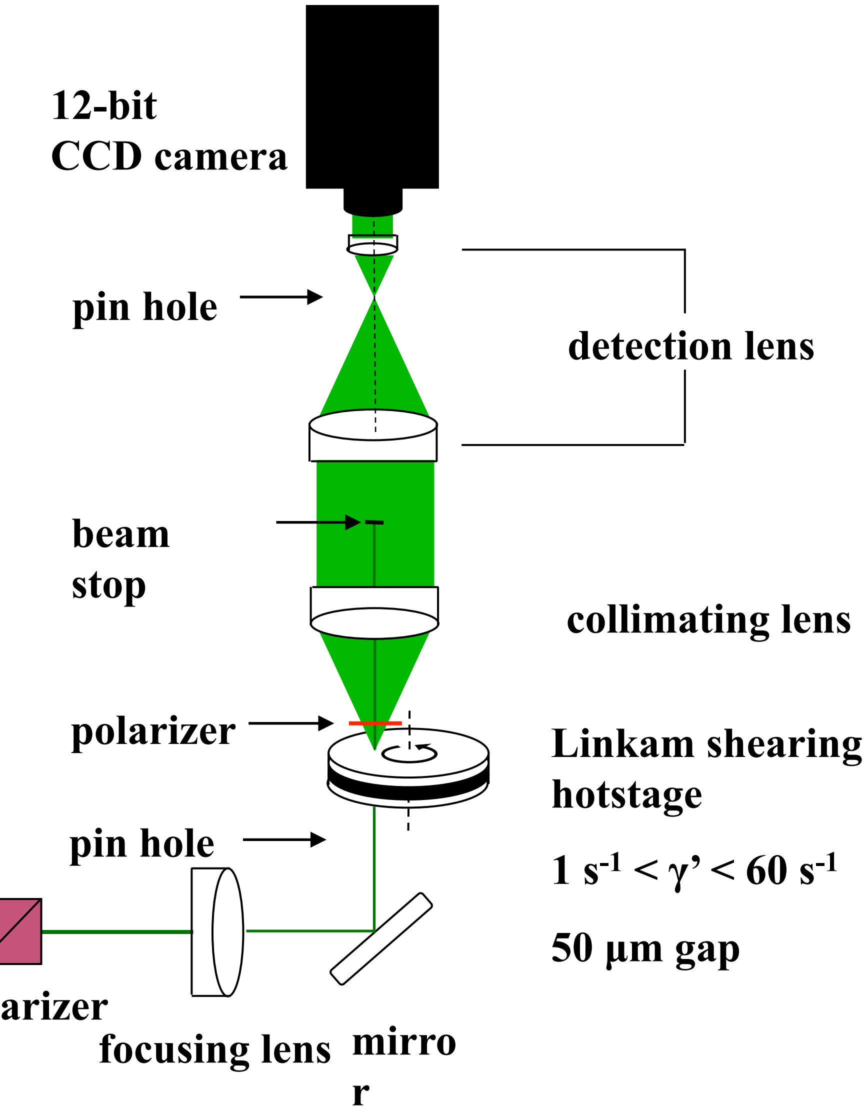
cross slot flow profile

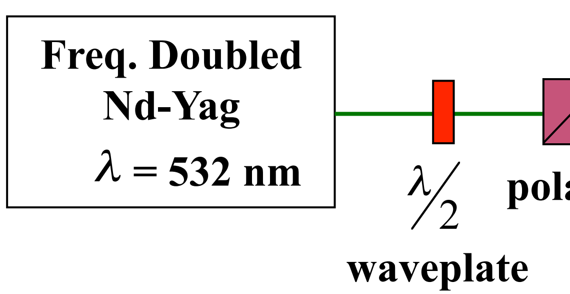
Spatially dependent PP crystallization in cross slot flow (gap = 0.5 mm, t_w =0.05 MPa, ts = 4 s)

(Kumaraswamy et al., 1999)

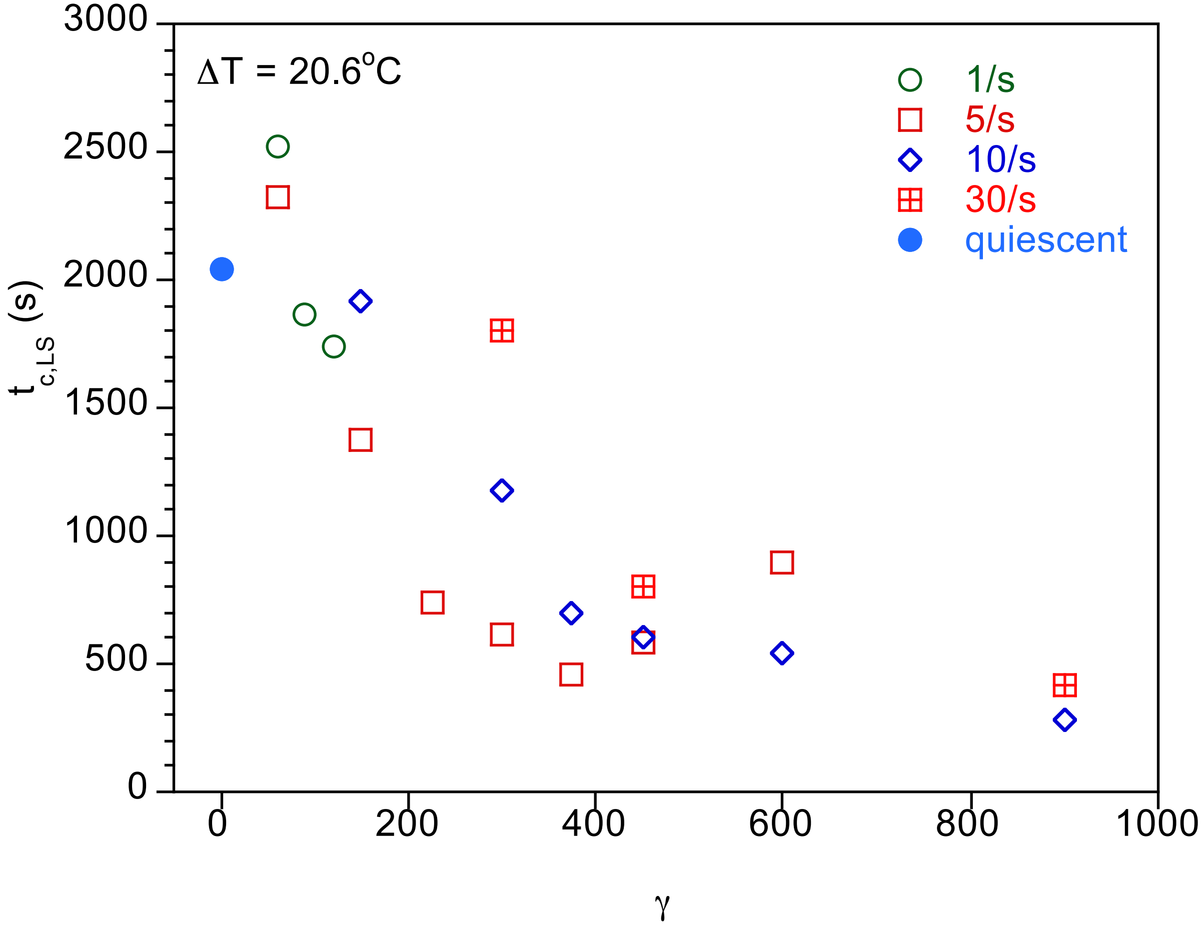
Methods: light scattering







Master curve behavior: effect of shear strain



For PP nanocomposites, effect appears to scale with strain over range probed

Project will present a comprehensive understanding of topological control over crystallinity in processing

-Growth rate and structural effects under controlled shear

-In situ and ex situ orientation studies of crystallographic and nano-structures

-Study of cold drawing through MDO processing of films produced from branched polyolefins

-Use of model polymers and commercial grade polymers