Morphology Control through Crystallization and Phase-separation in Polyolefin Blends

Howard Wang

and

George Z. G. Wang, Katsumi Shimizu, Charles C. Han

National Institute of Standards and Technology, Polymers Division, Gaithersburg, MD 20899

May 2, 2001

Outline

- ***Motivation and objectives***
- ***Phase-diagram determination***
  (photography, differential scanning calorimetry)
- ***Micron-scale morphology***
  (optical microscopy, light scattering)
- ***Nano-scale morphology***
  (SAXS and WAXS, atomic force microscopy)
- ***Summary***

Motivation and Objective

Motivation:

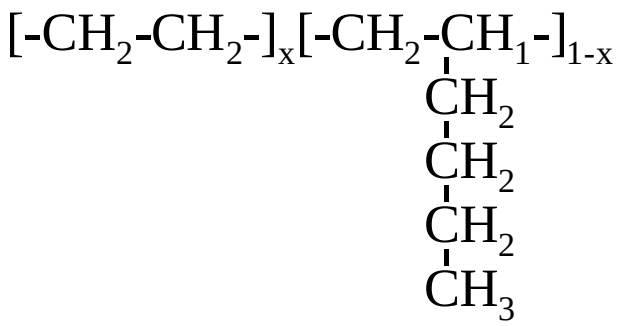
Processing, morphology and property relationship.

Objective:

Investigate the morpholgoy development during the interplay between the crystallization and phase separation in a polyolefin blend.

The Polyolefin Statistical Copolymers

PEH: ethylene/hexene

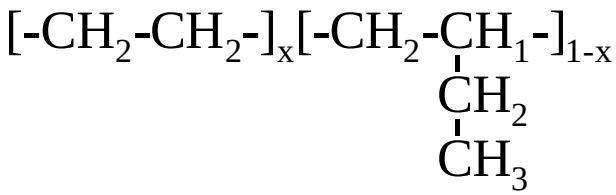


M_w=113 k g/mol

x = 0.98

ρ_{branch}: 9/1000 backbone C

PEB: ethylene/butene



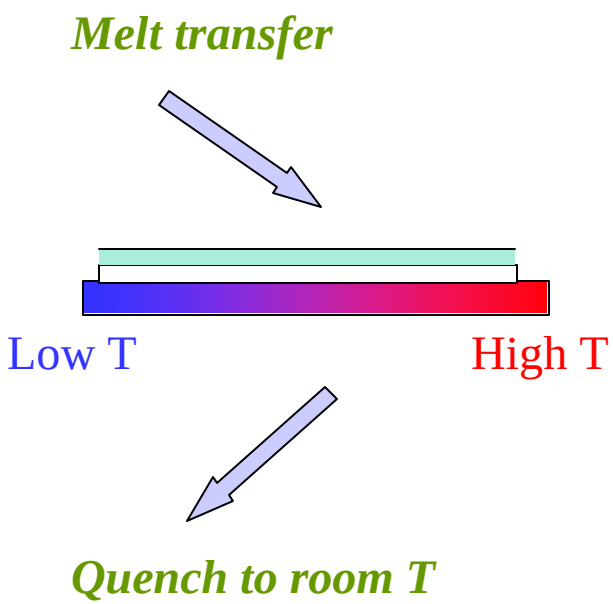
M_w=70 k g/mol

x = 0.86

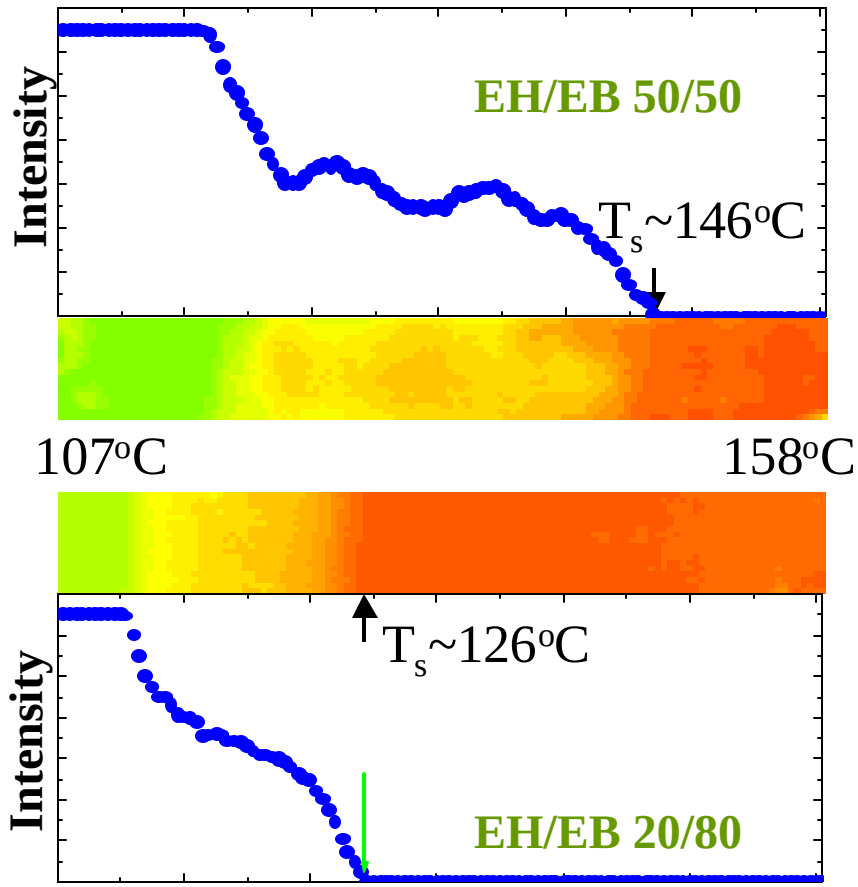
ρ_{branch} : 77/1000 backbone C

Method for determining the liquid-liquid phase separation boundary:

Anneal a film of blend on a temperature gradient hot stage and quench to room temperature.

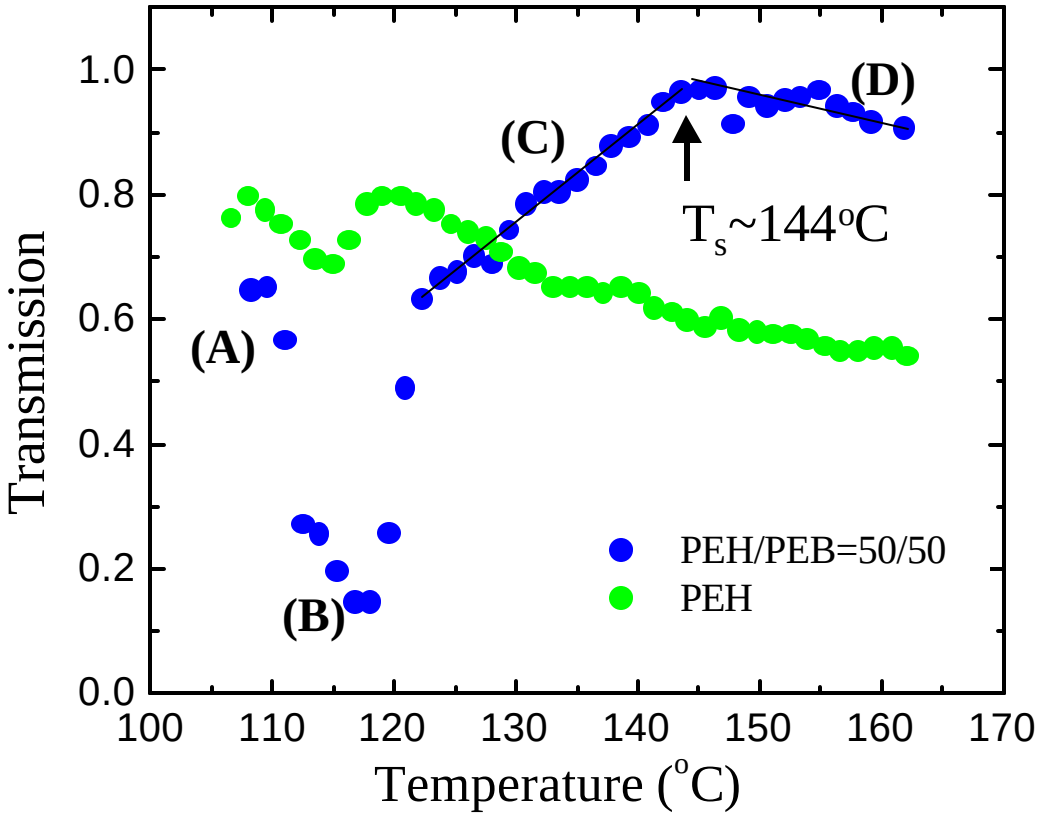


Characterization I: photography

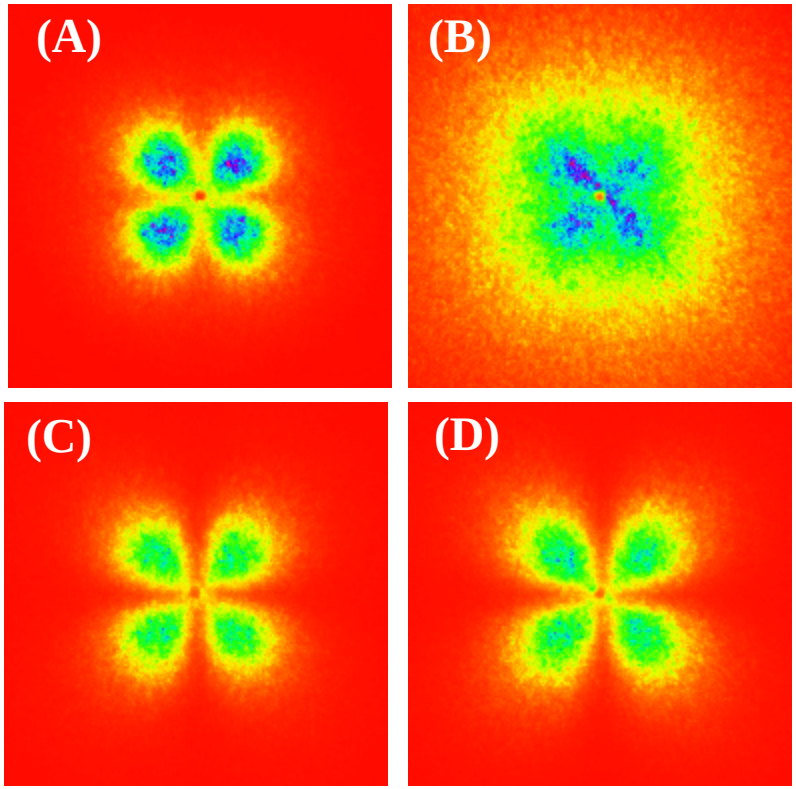


Determining phase boundary:

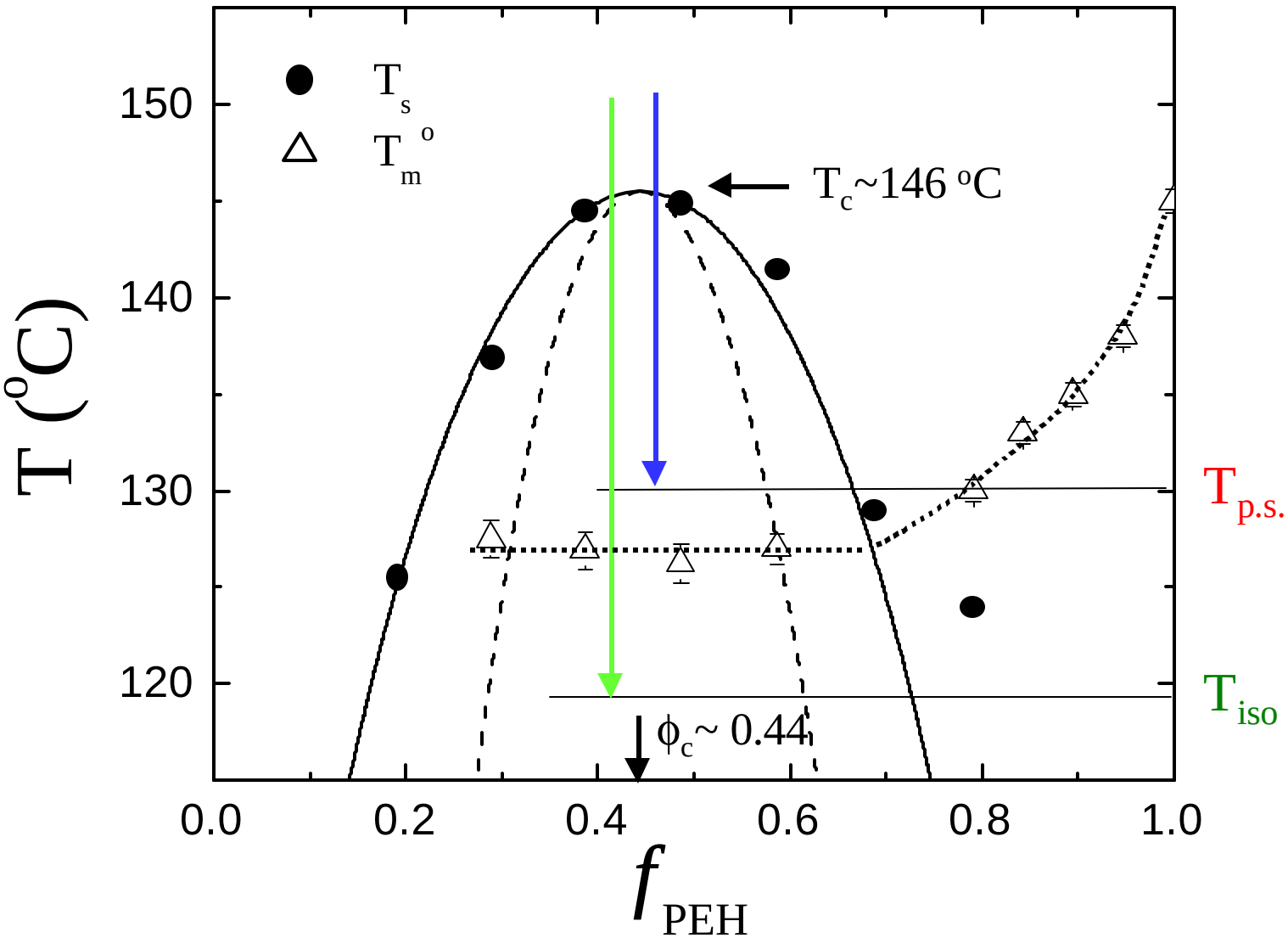
Characterization II: light transmission



Characterization III: SALS

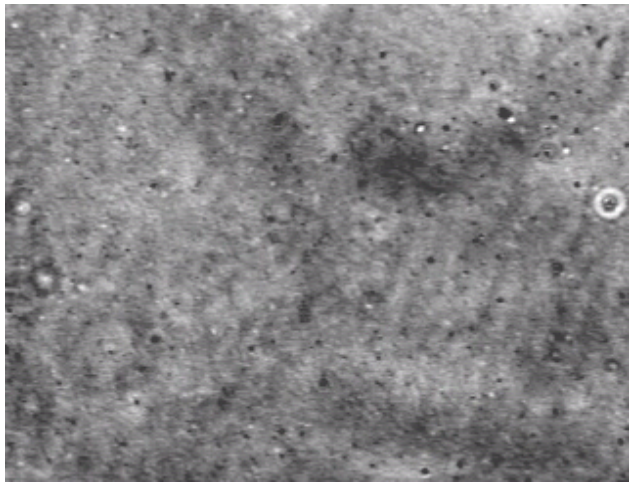


Phase Diagram of PEH/PEB Blend
($c = -1.1\times10^{-3} + 1.0/T$)

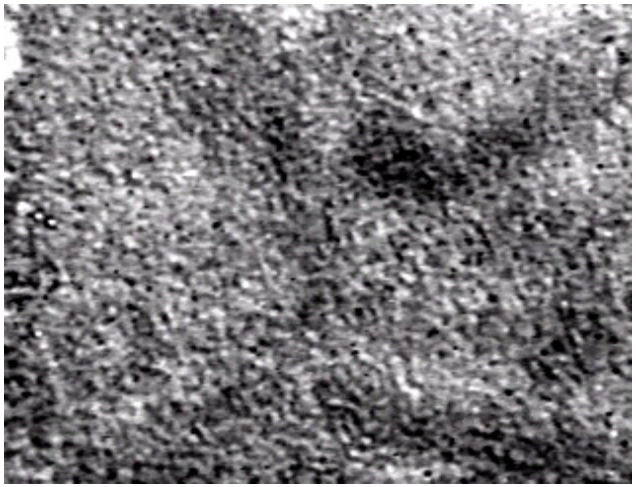


50/50 blend (H50), phase-separation at 130°C

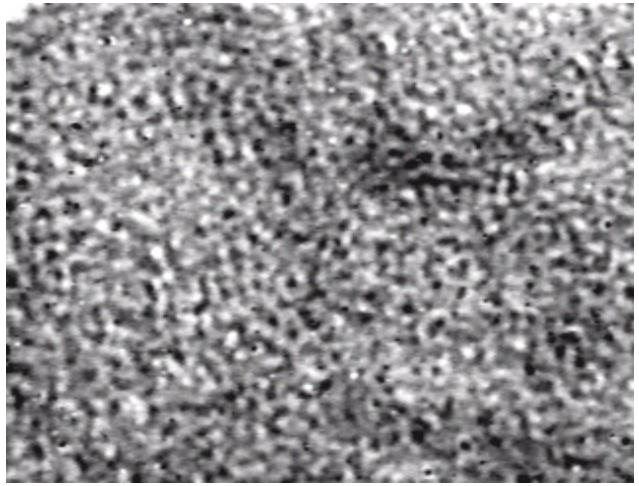
135 min



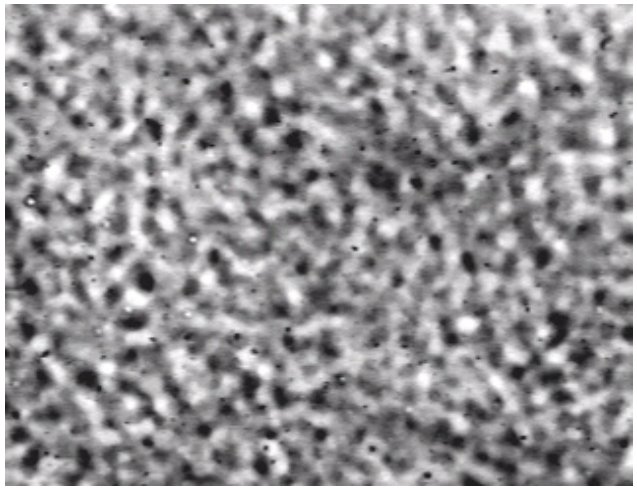
255 min



495 min

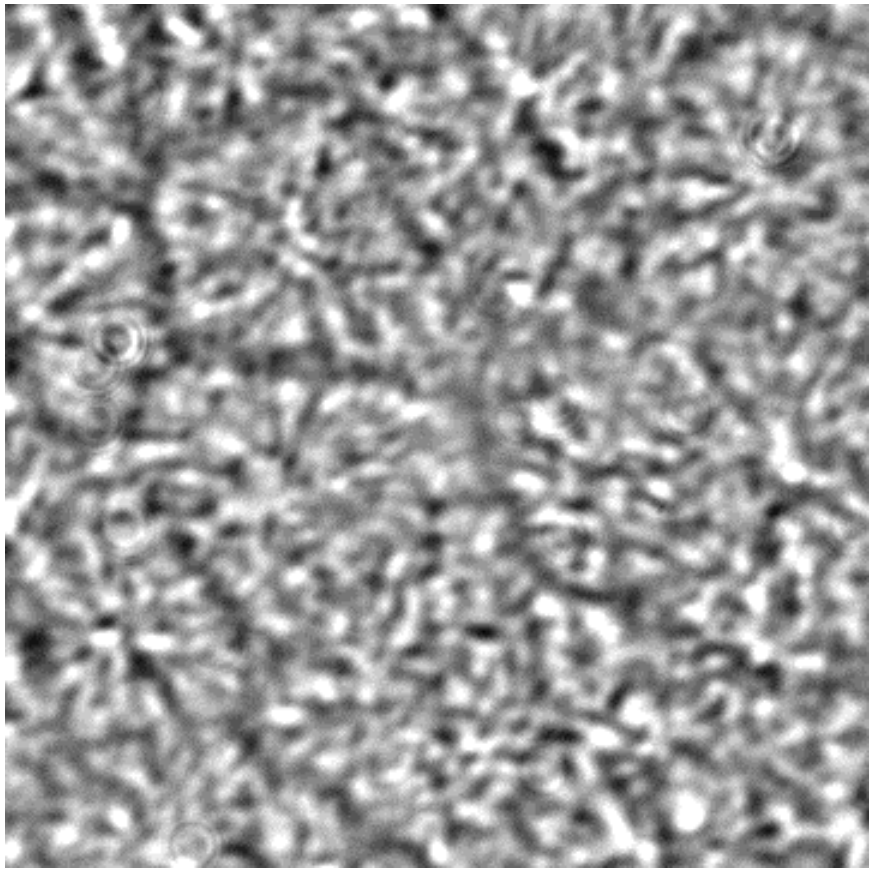


1035 min



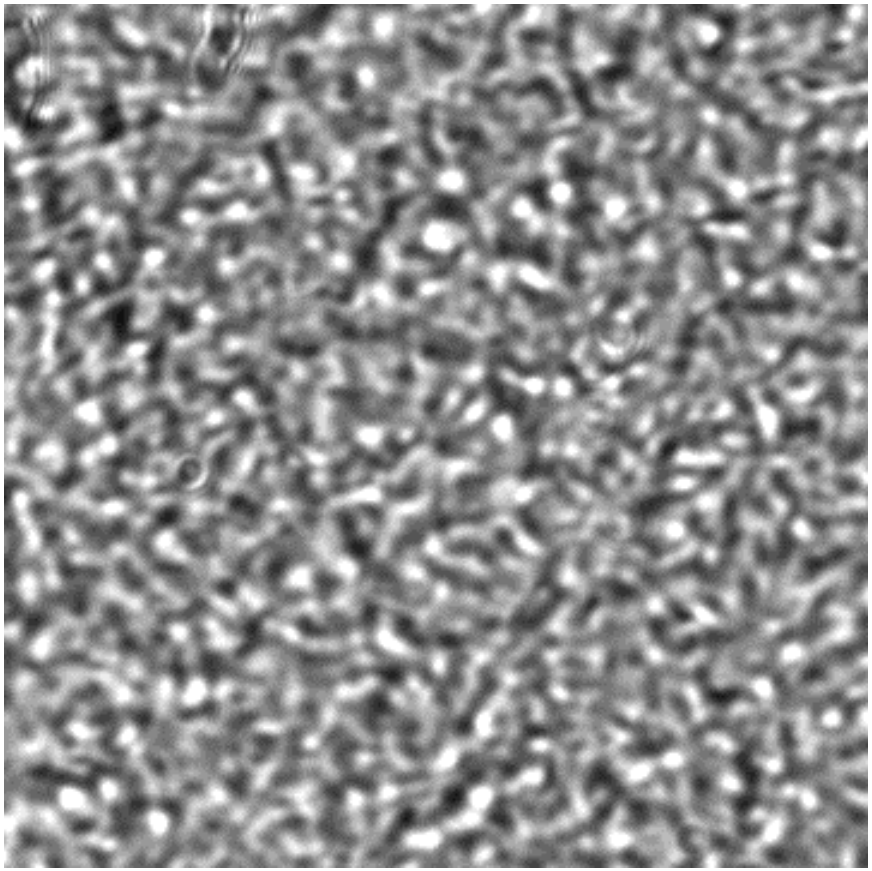
100 μm

H50, 160°C (5 min), T_{iso}=112°C



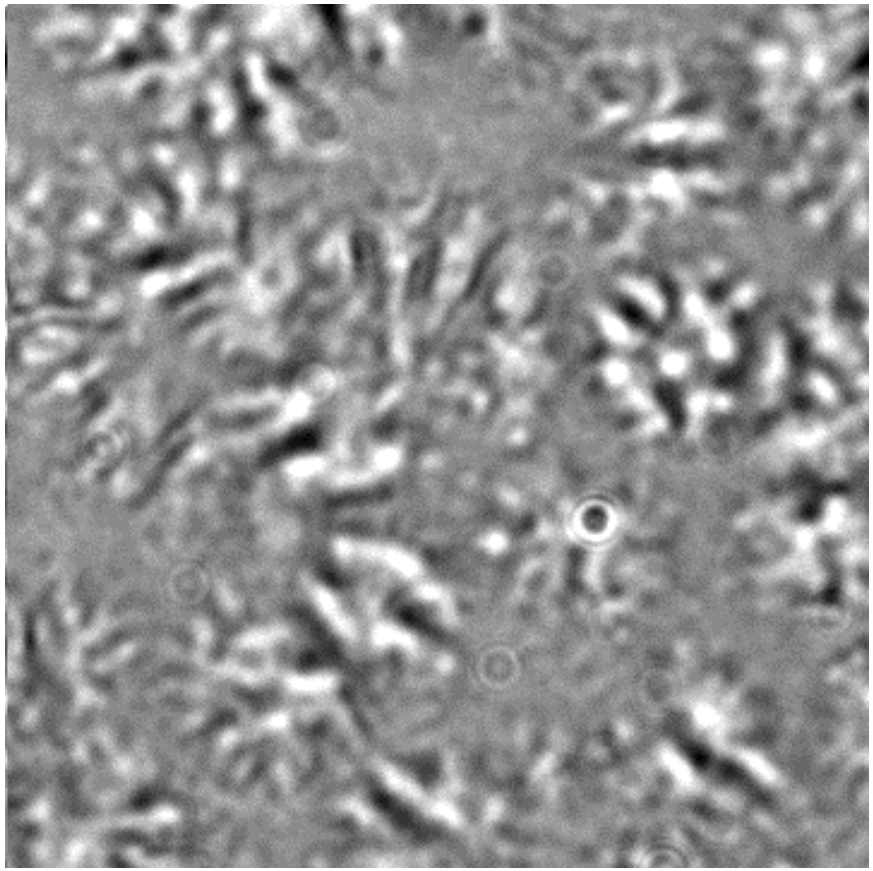
10 mm

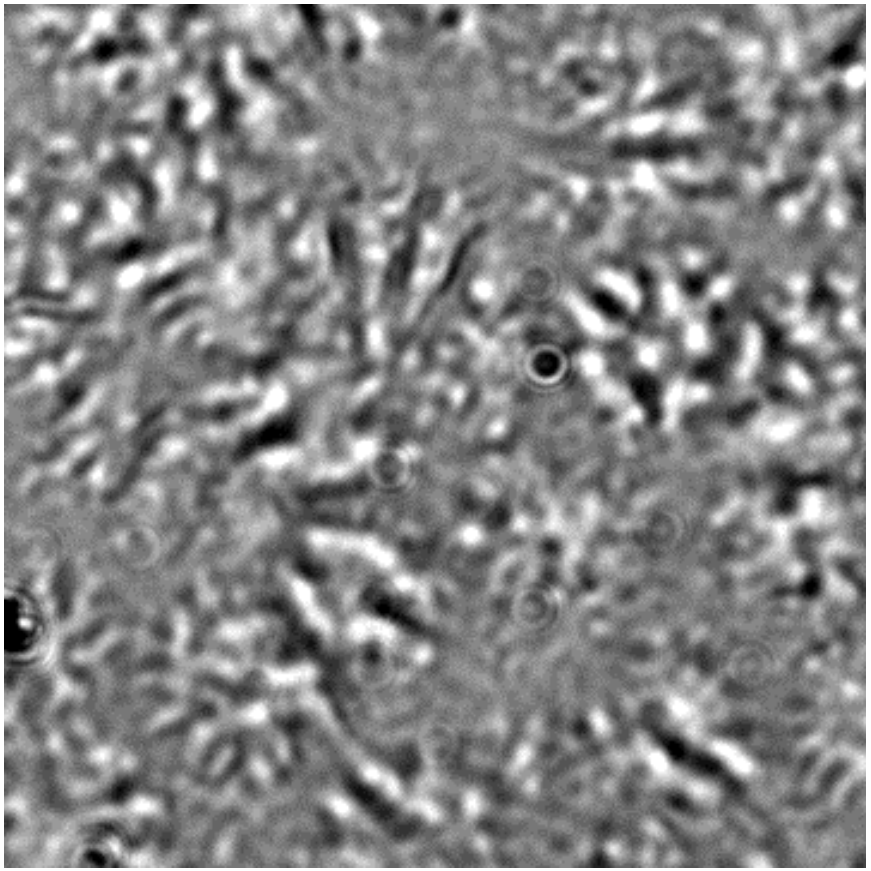
10 min



to room T

H50, 160°C (5 min), T_{iso}=115°C



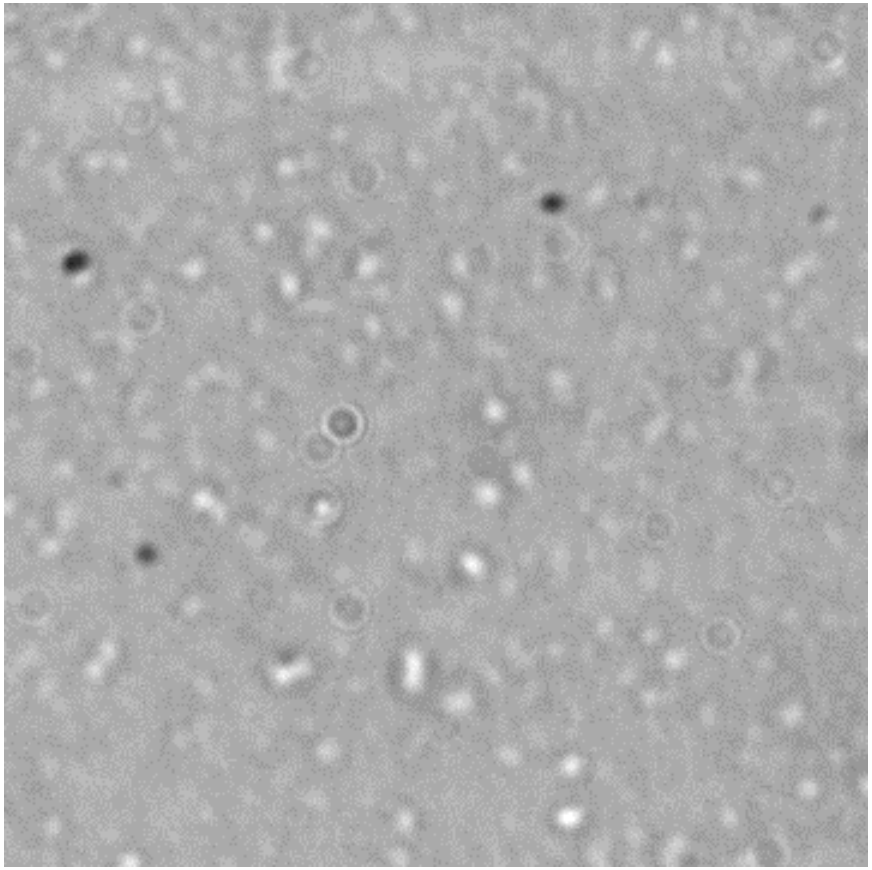


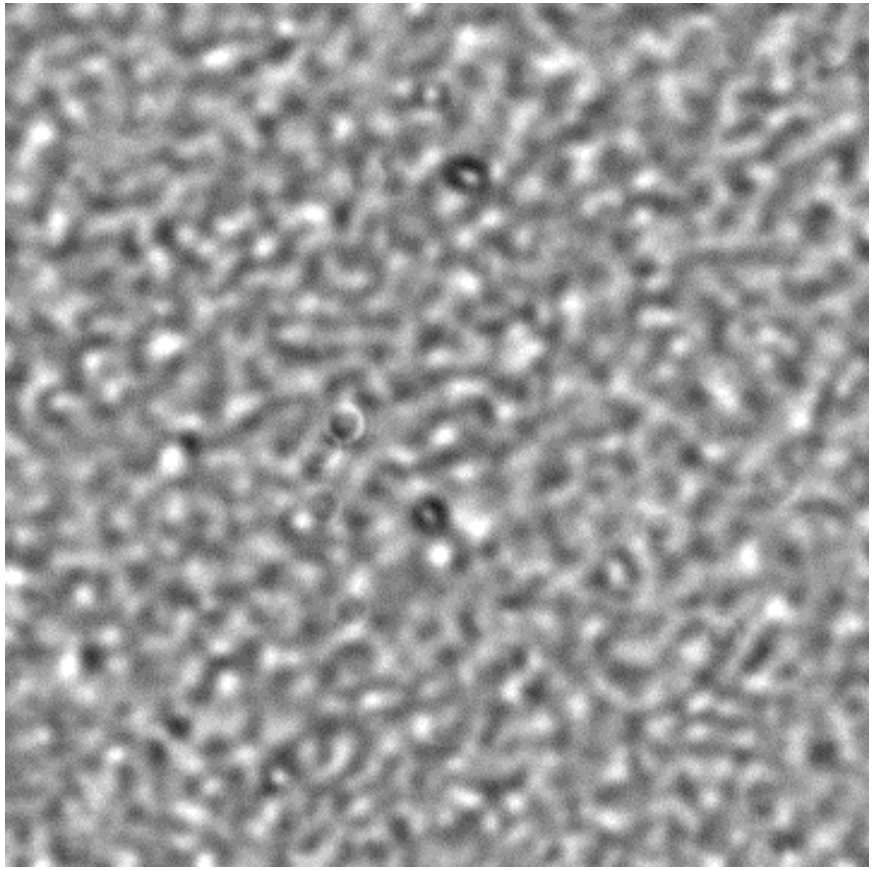
10 mm

8 h

to room T

H50, 160°C (5 min), T_{iso}=121°C



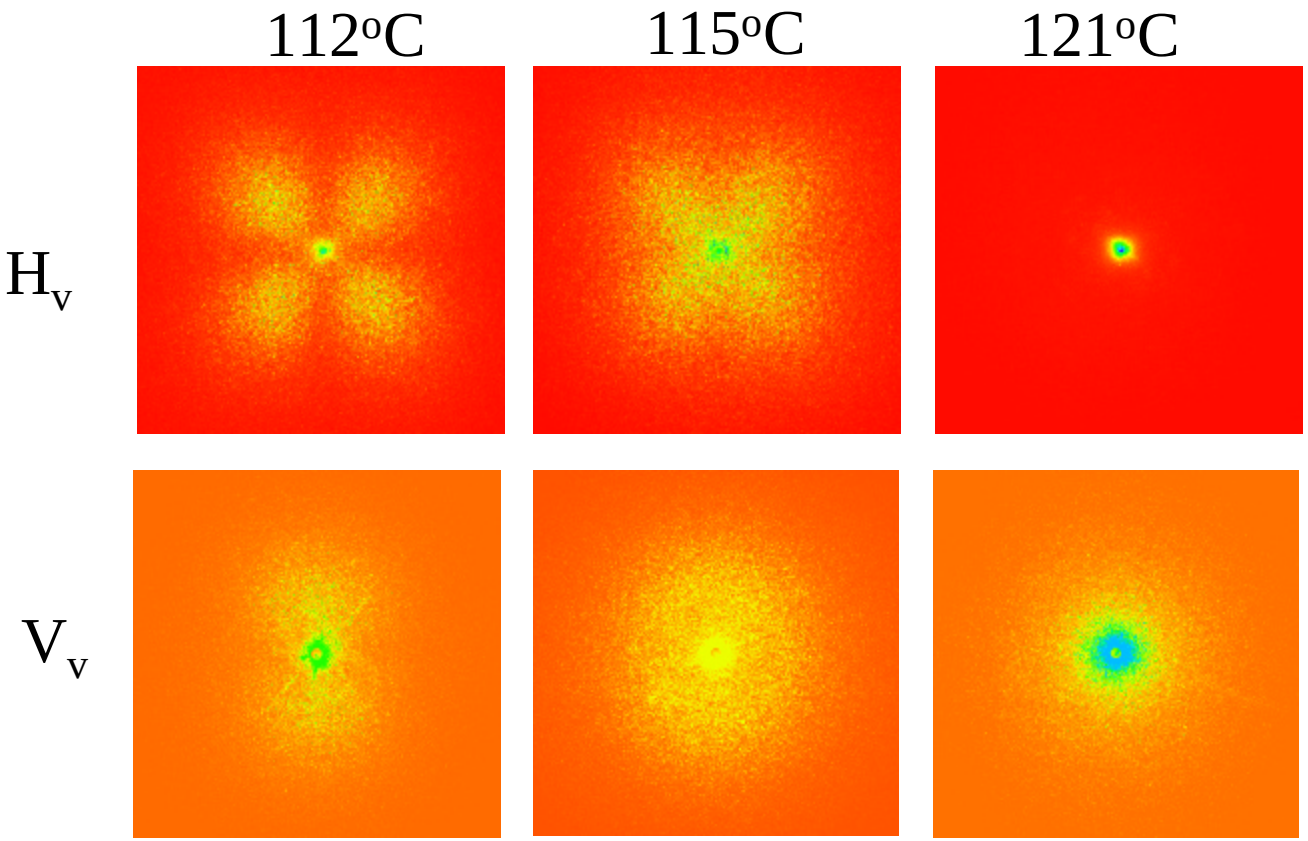


10 mm

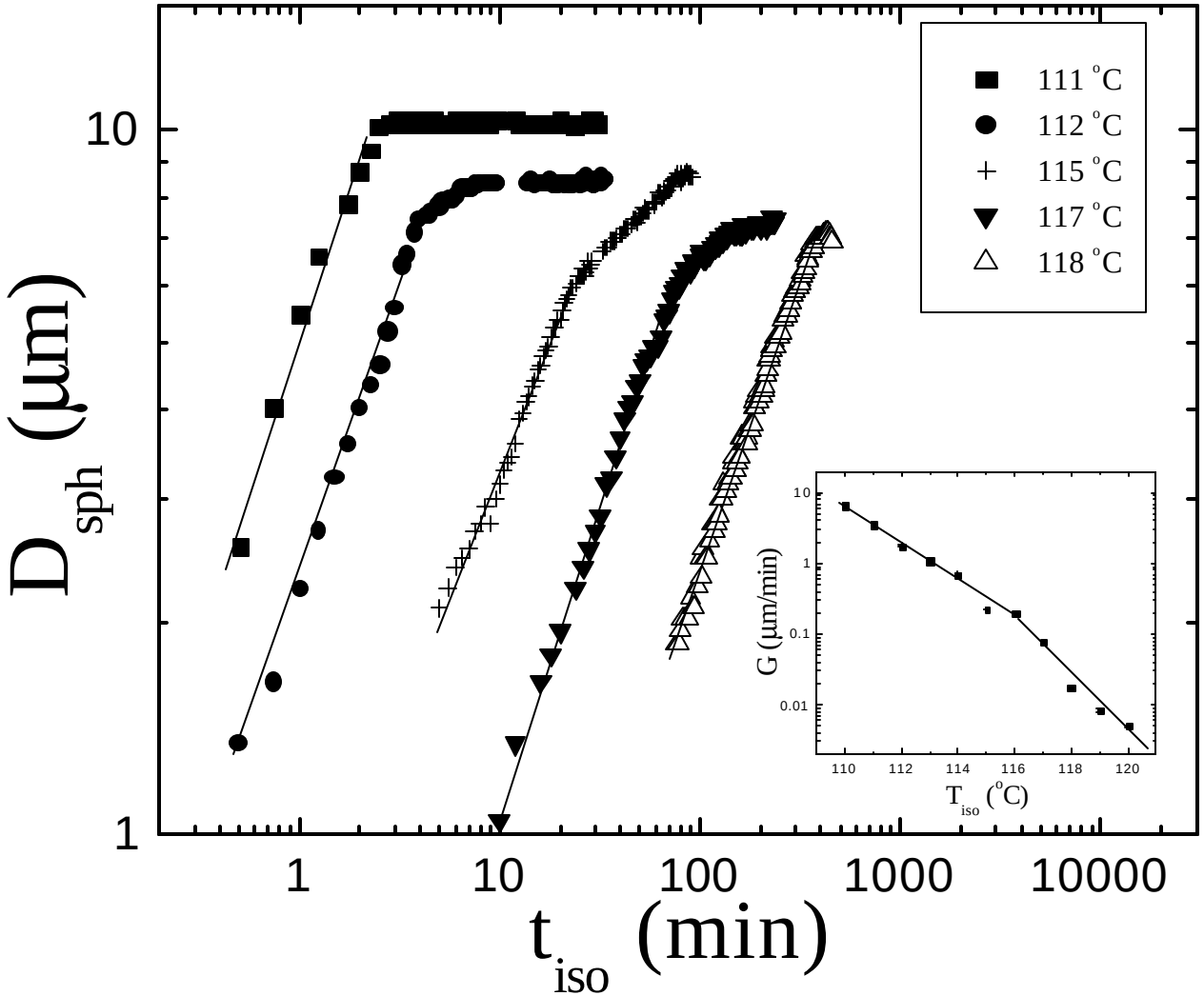
21 h

to room T

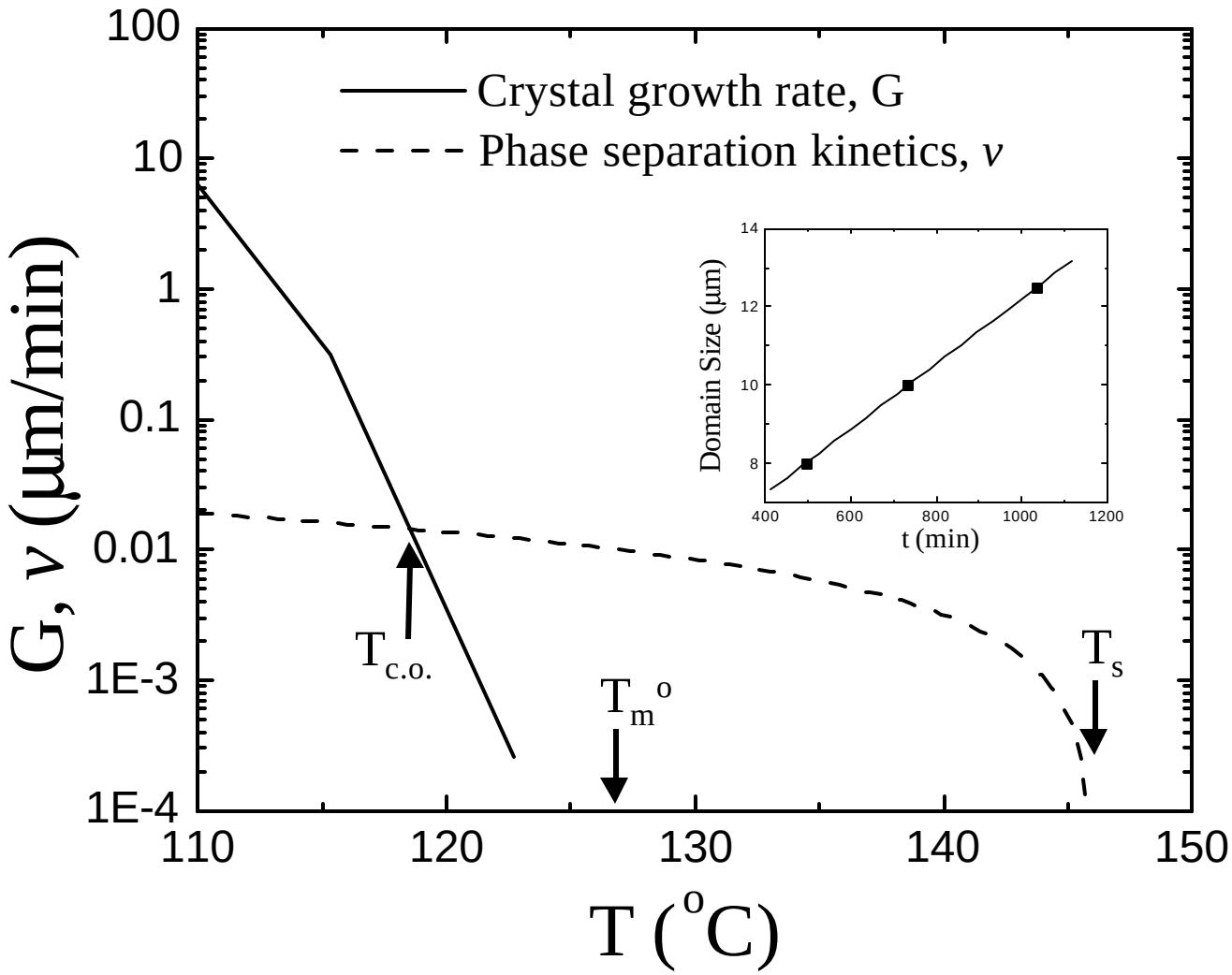
SALS on H50 crystallized at various temperatures and cooled to room T



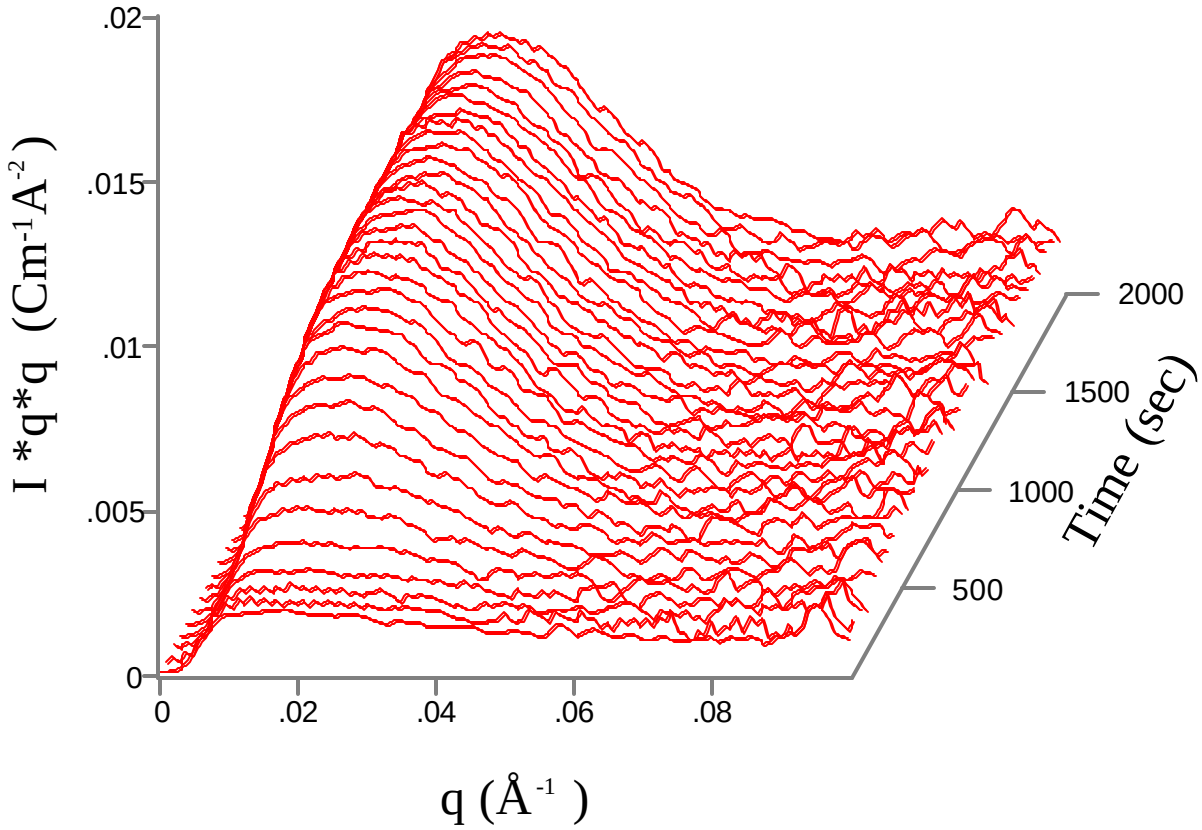
Growth rate of spherulites in H50



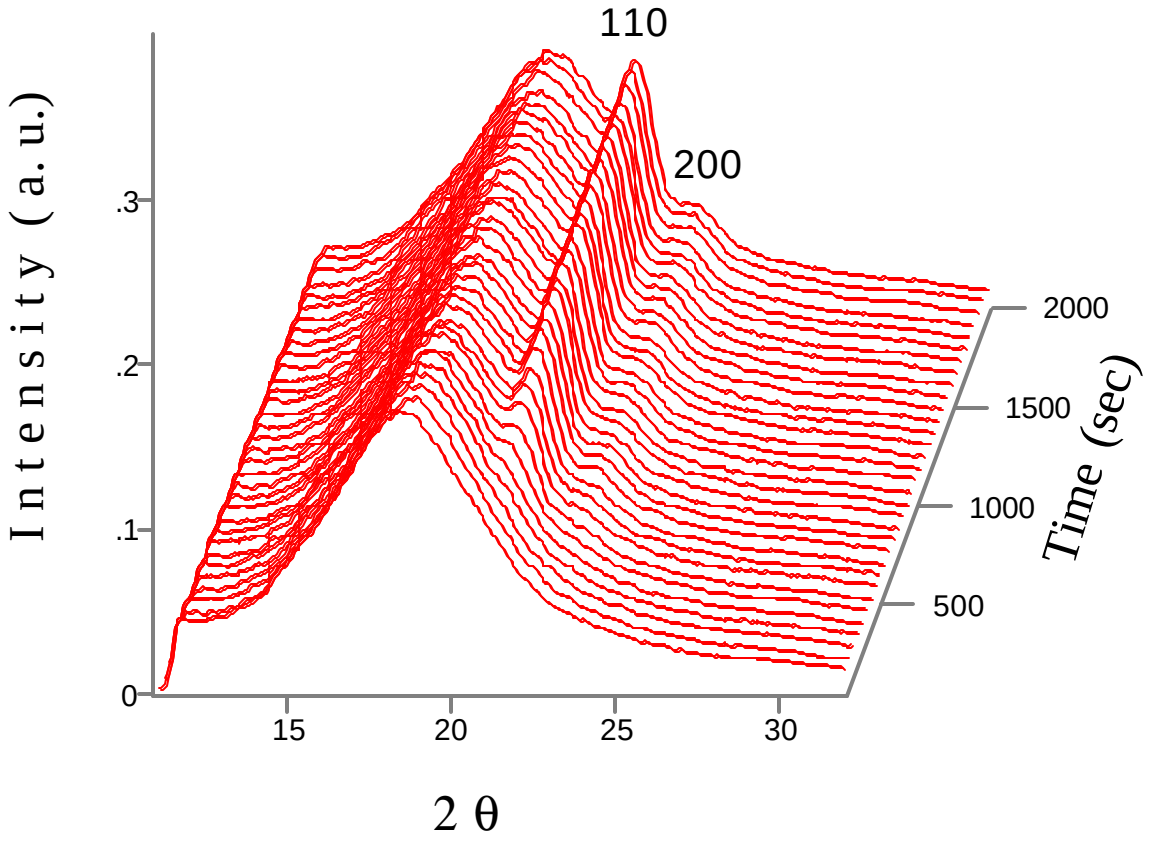
Kinetics cross-over in competing phase separation and crystallization



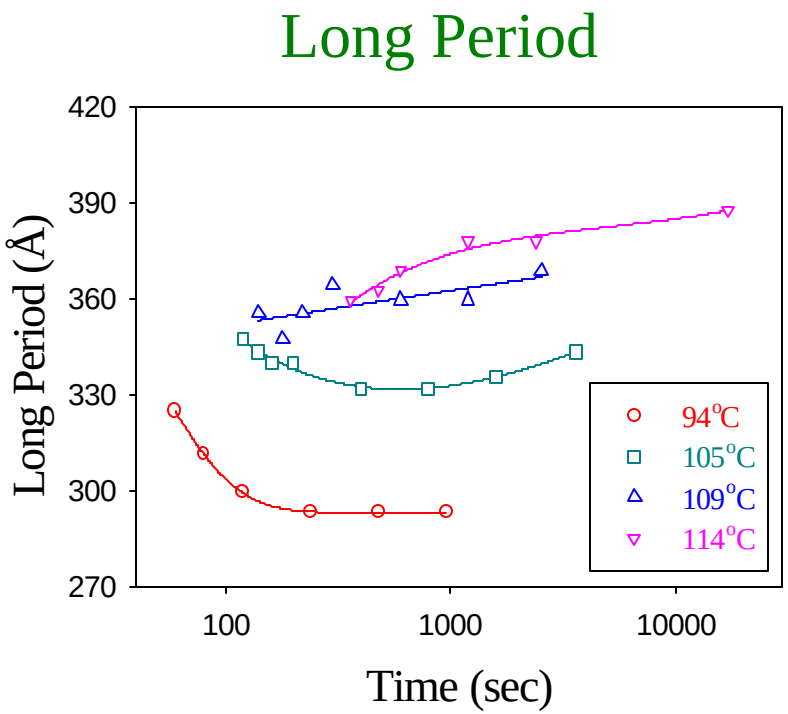
SAXS profiles of H50 during isothermal crystallization at 114 °C

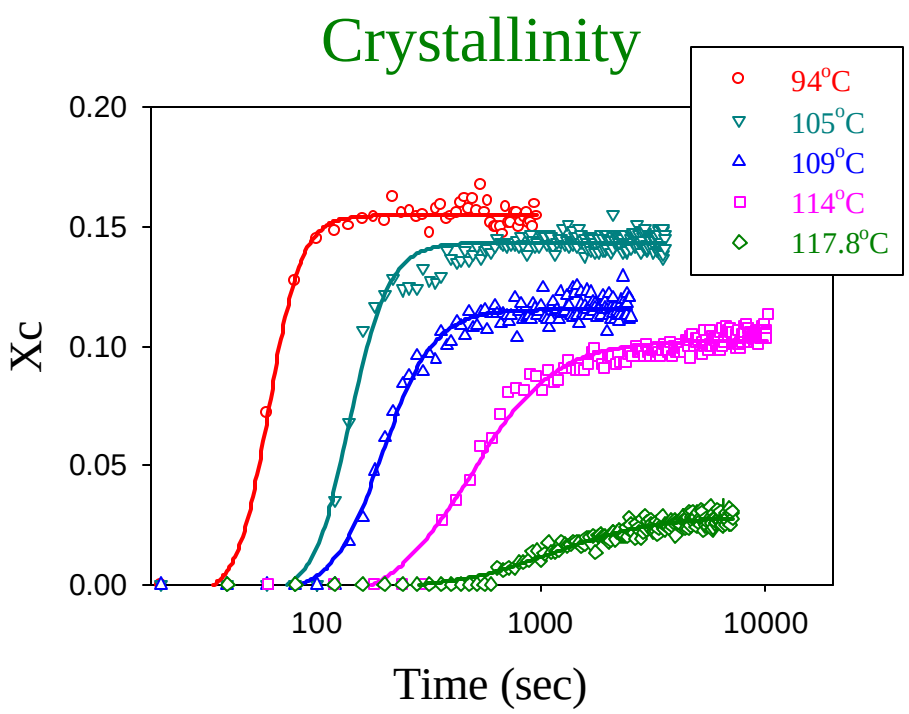


WAXS profiles of H50 during isothermal crystallization at 114 ºC



Evolution of *L* and *X*c of H50 during isothermal crystallization

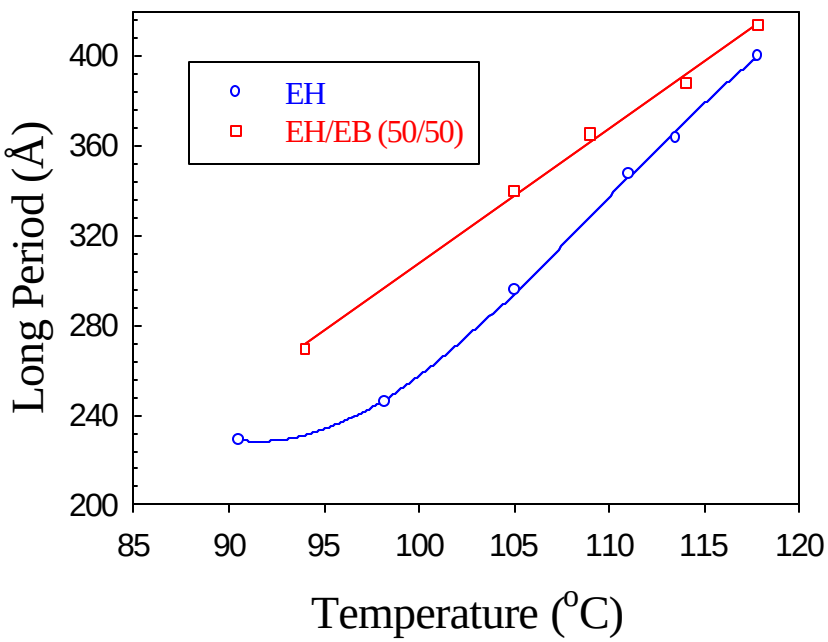




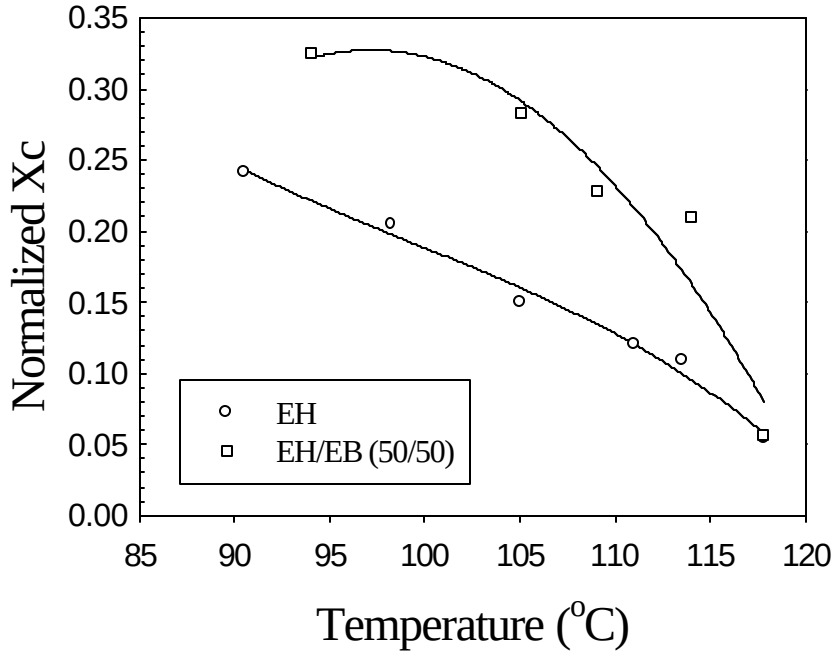
- ***L* decreases with time at low T_{iso} and increases at high T_{iso} due to varying crystal growth environment.**
- ***Crystallinity can be controlled by both T_{iso} and time.***

Final *L* and *X*c of H50 and PEH at diff. T_{iso}

Final Long Period

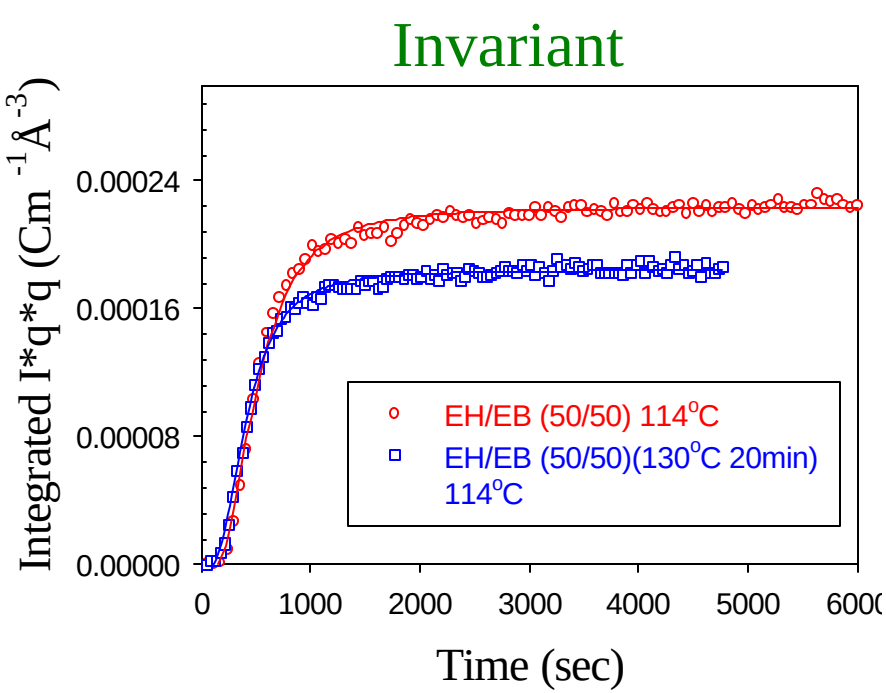


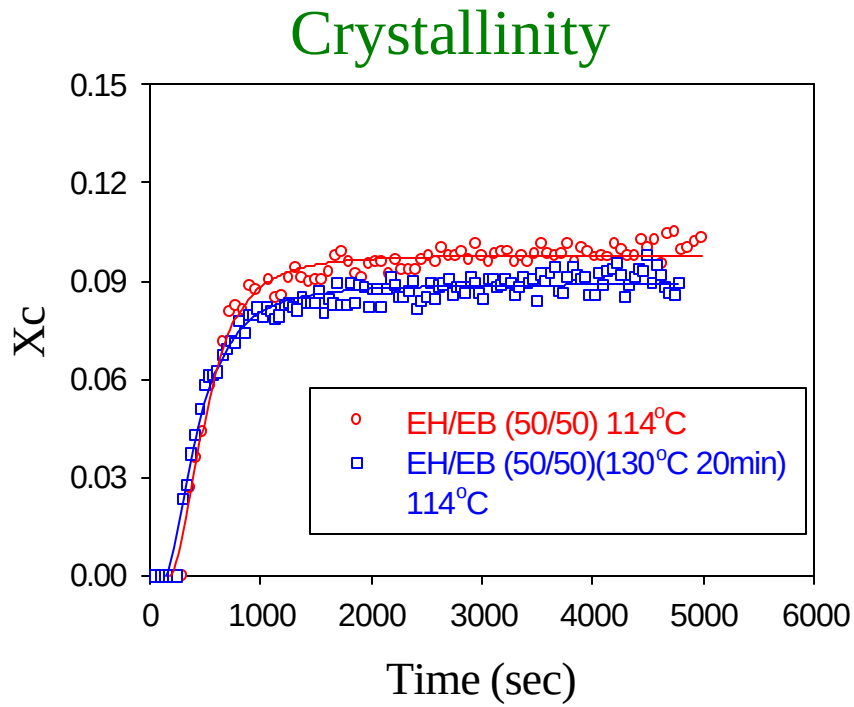
Normalized Crystallinity



- ***$L_{PEH} < 2L_{H50}$ indicates segregation of the PEH copolymer away the lamellar stacking.***
- ***Crystallinity is larger in H50, suggesting the cocrystallization of the long ethylene segment of PEB.***

H50 at 114°C, one-quench *vs*. two-quench



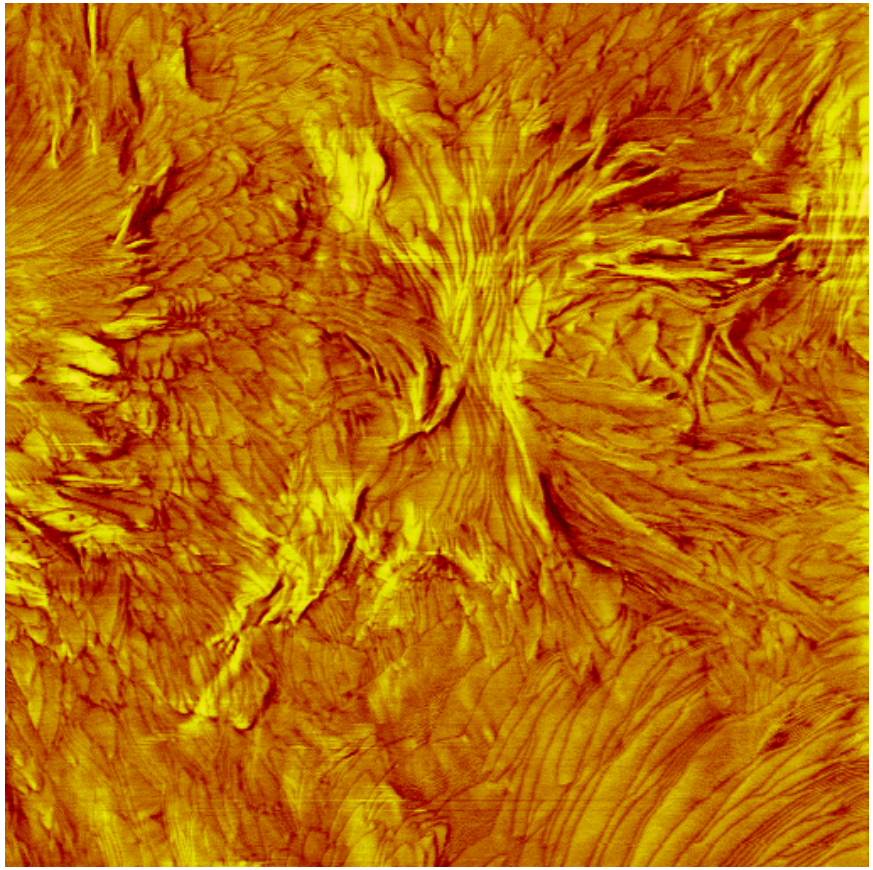


- ***Higher invariant and crystallinity in one-quench blend indicates co-crystallization of the long ethylene segments of PEB; pre-phase-separation reduces the cocrystallization effect.***

AFM study on Crystal and Phase Morphology

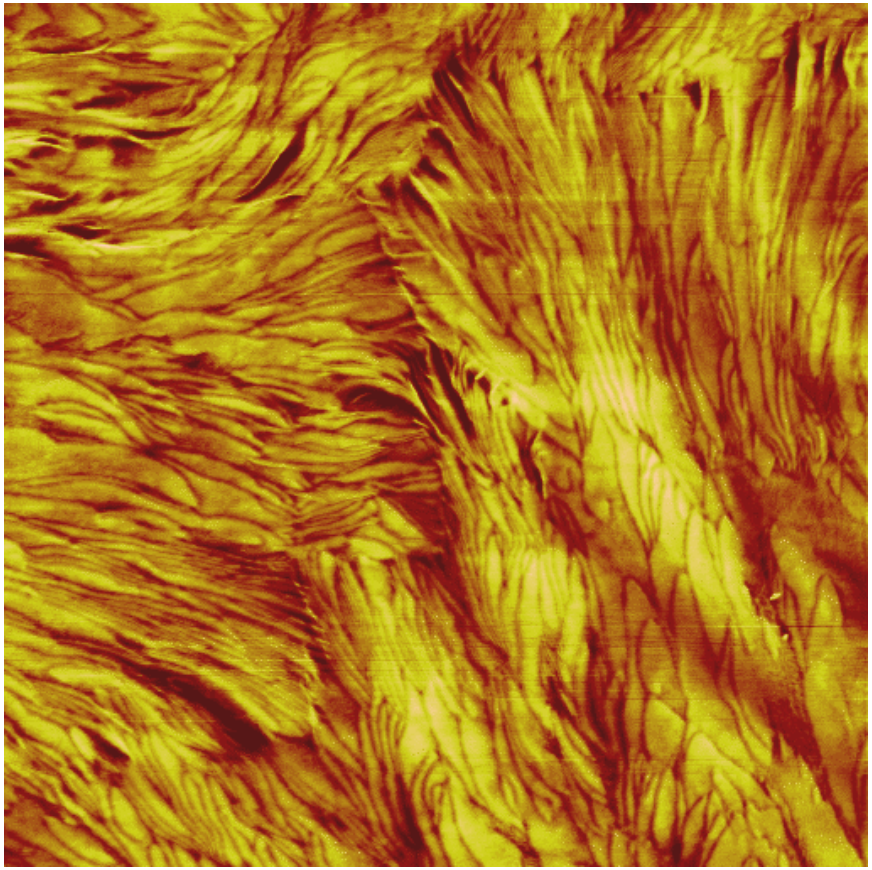
H50, T_{iso}= 115°C, cooled to 110 °C.

A lamella bundle



15 mm ´ 15 mm

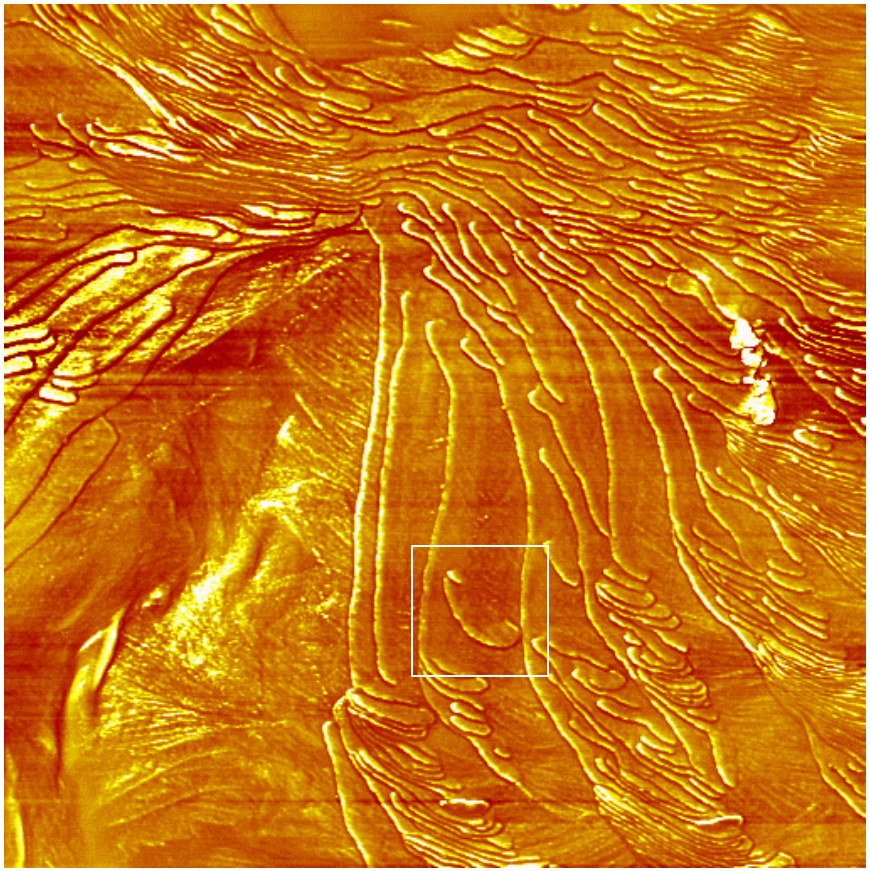
Boundary of spherulites



10 mm ´ 10 mm

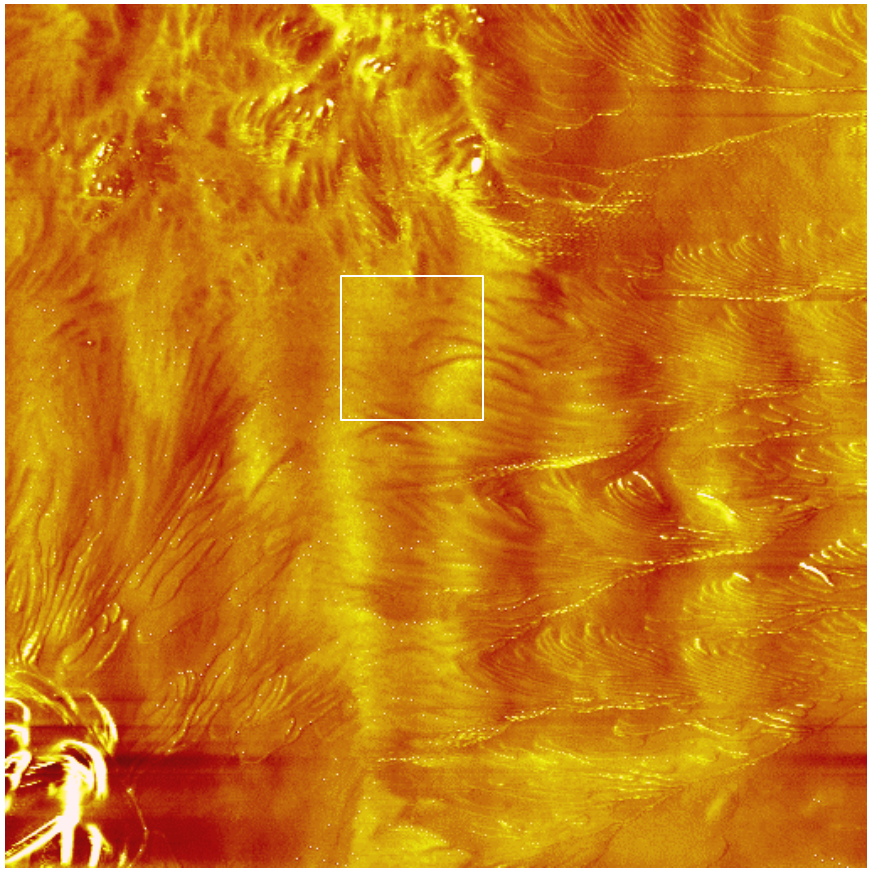
H50, T_{iso}= 118°C, cooled to 110 °C.

Center of a spherulite



10 mm ´ 10 mm

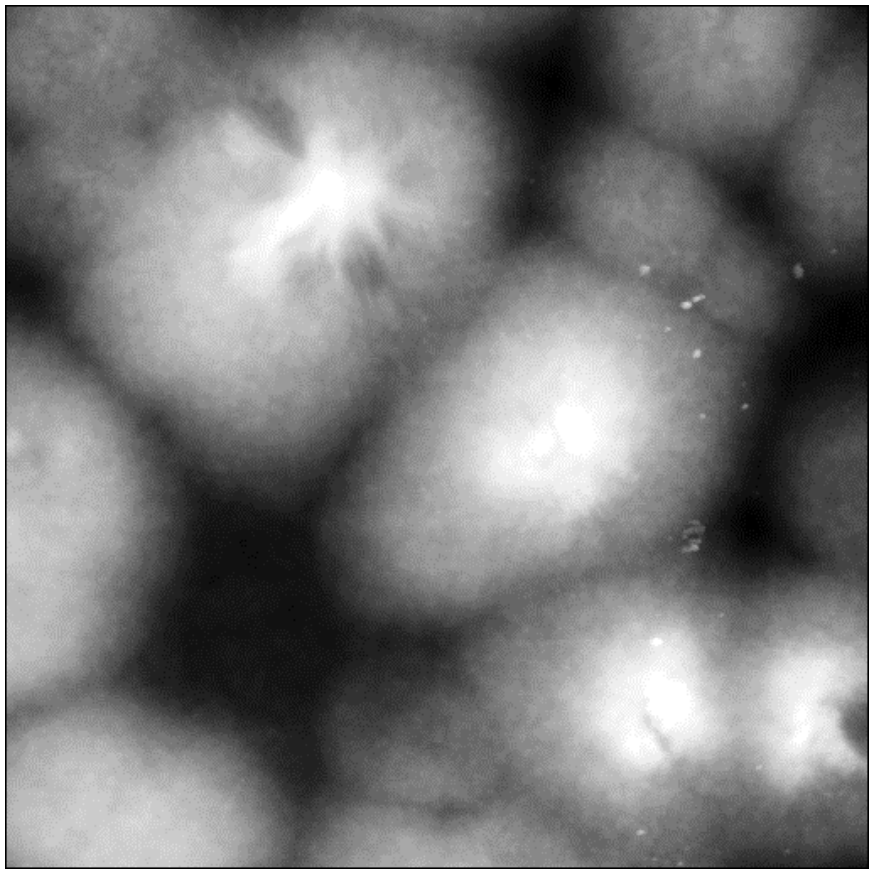
Inter-spherulitic region



10 mm ´ 10 mm

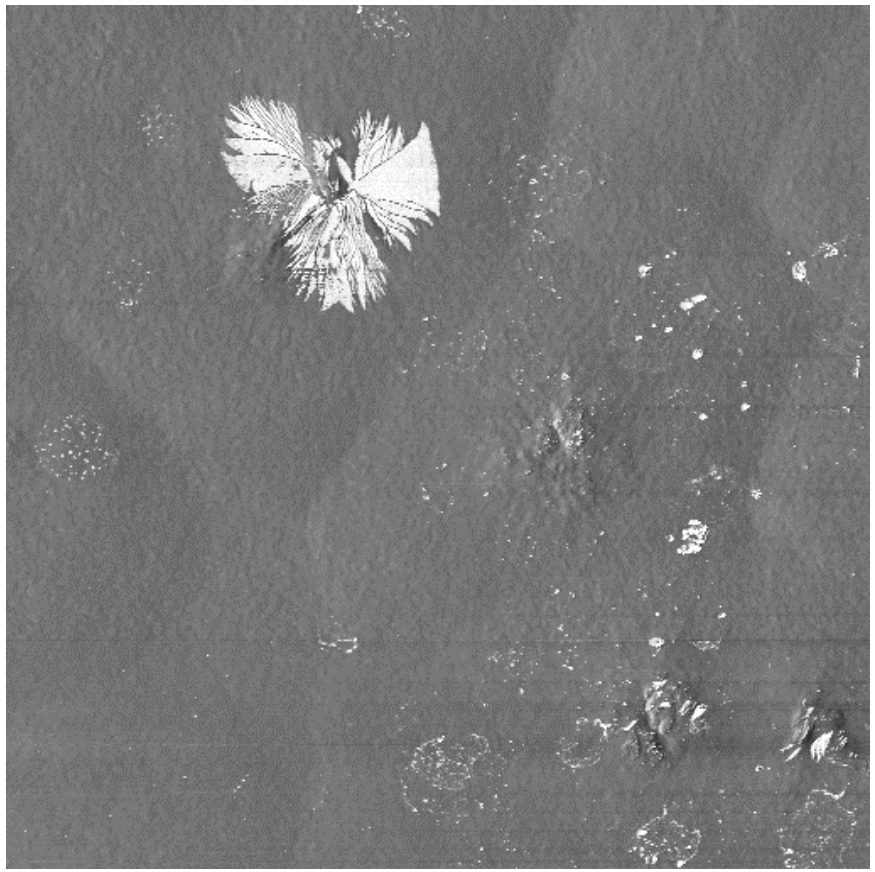
H50, T_{iso}=115°C for 10 min, quench to ice water

Height contrast



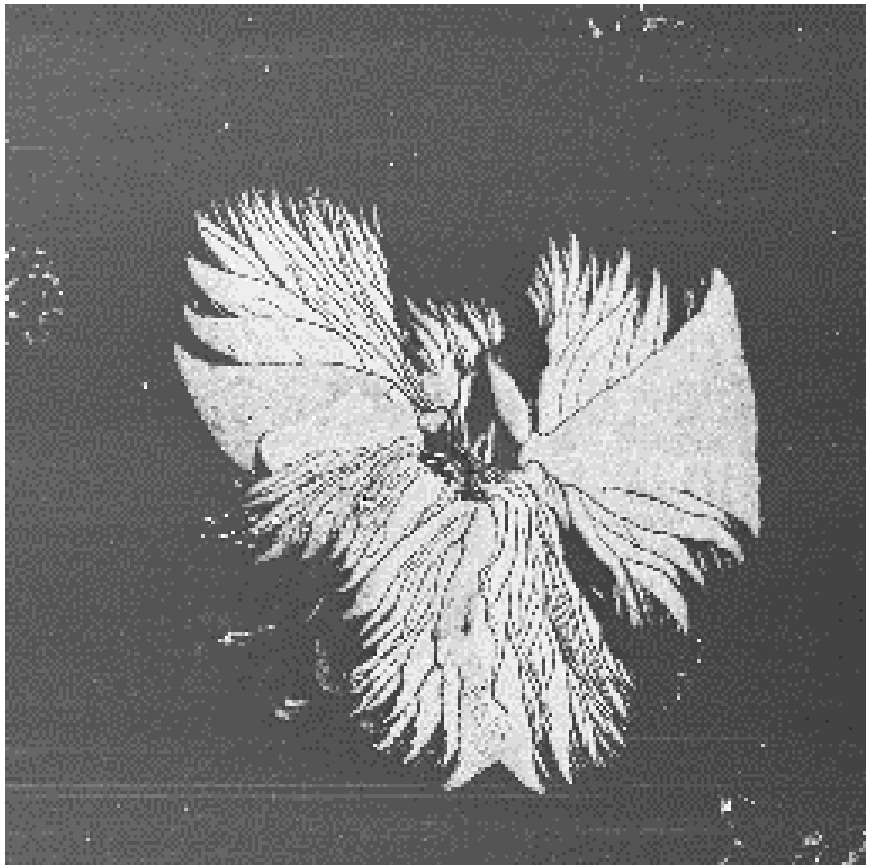
40 mm ´ 40 mm

Phase contrast

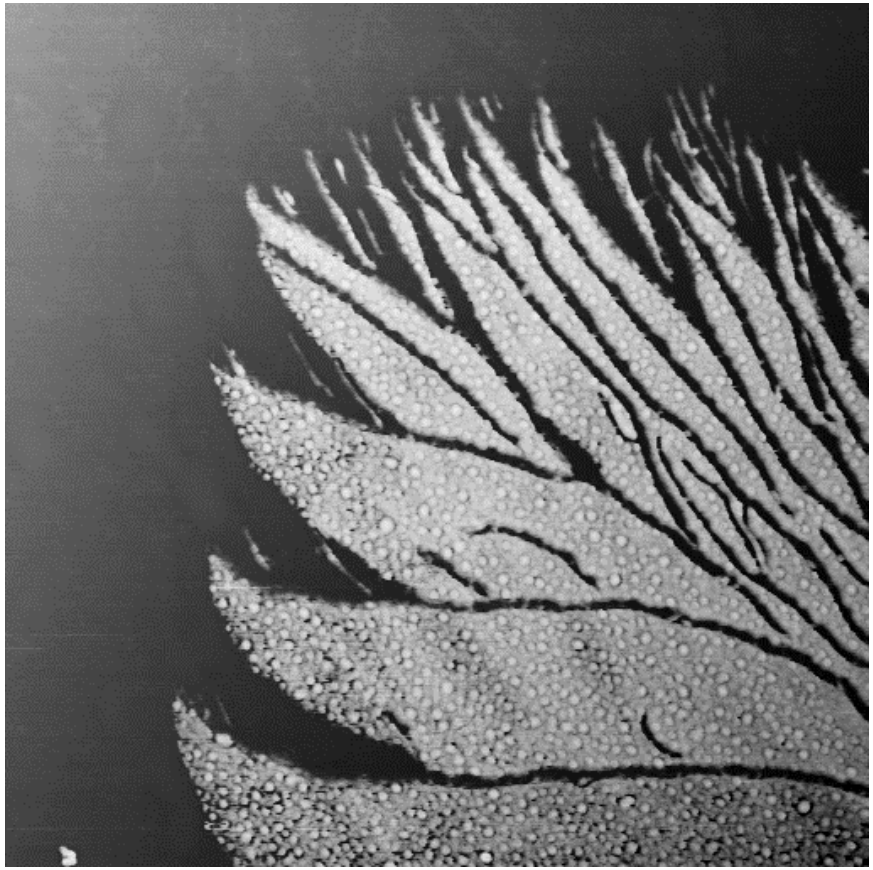


40 mm ´ 40 mm

H50, T_{iso}=115°C for 10 min, quench to ice water (continued)

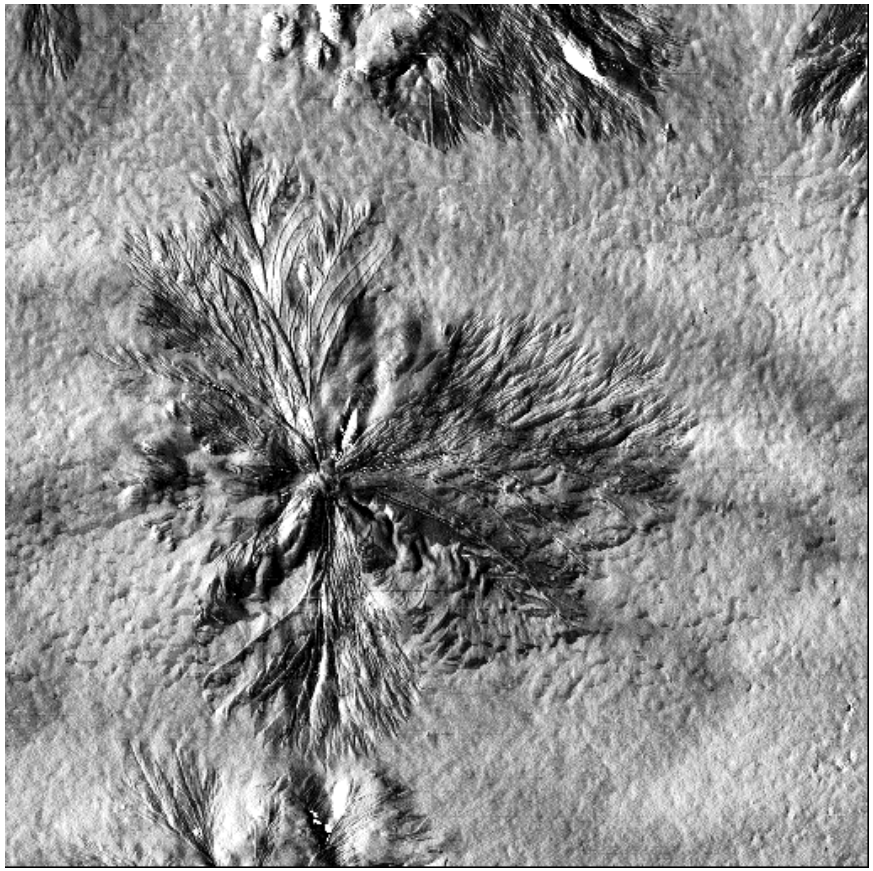


15 mm ´ 15 mm

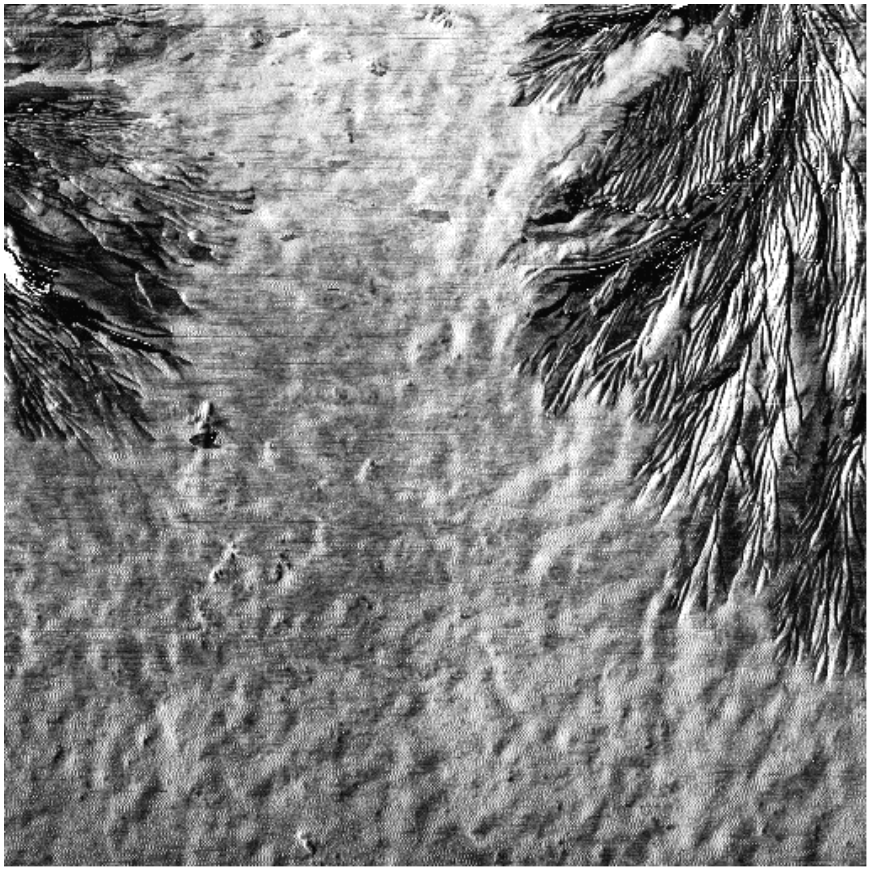


4 mm ´ 4 mm

H50, T_{iso}=113°C for 10 min, quench to ice water



35 mm ´ 35 mm



15 mm ´ 15 mm

Summary

- Phase diagram of PEH/PEB blend has been determined.
- A variety of techniques, including optical microscopy, photography, light scattering and transmission, atomic force microscopy, differential scanning calorimetry and SAXS/WAXS, has been used to understand the morphology during the crystallization and phase separation.
- This understanding has led to the morphological control in both the predominant features and fine crystal structures.
- Studies on further complications such as morphological development under shear force is underway.

Acknowledgment

National Institute of Standards and Technology

Dr. David J. Lohse ***(Exxon-Mobile)***
Dr. Freddy A. Khoury ***(NIST)***
Dr. Benjamin Hsiao ***(SUNY)***
Dr. Vincent Ferreiro ***(CNRS, France)***
Dr. J. Carson Meredith ***(Georgia Tech)***
Dr. Robert A. Weiss ***(UCONN)***