Recent topics on the crystallization and liquid-liquid phase separation in polyolefin blend

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Introduction

Polyolefin polymers are widely used material in the plastics industry. To get optimum properties suited to the various final products, Blending is often used.

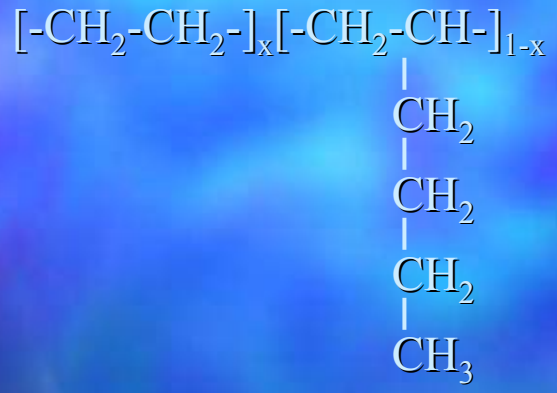
In the production process, olefin blend undergoes both liquid-liquid phase separation and crystallization. These phenomena complicate the physical properties of the olefin blend.

To control the properties, it is important to understand the phase diagram and morphology of the polyolefin blend.

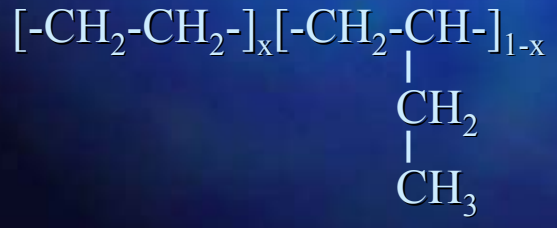
In order to attain it, I selected nearly isorefractive statistical copolymers of poly(ethylene/hexene) and poly(ethylene/butene) as a research target.
I did experiments of the differential scanning calorimetry (DSC) to decide the melting temperature and of the optical microscopy to know the morphological development in this blend.

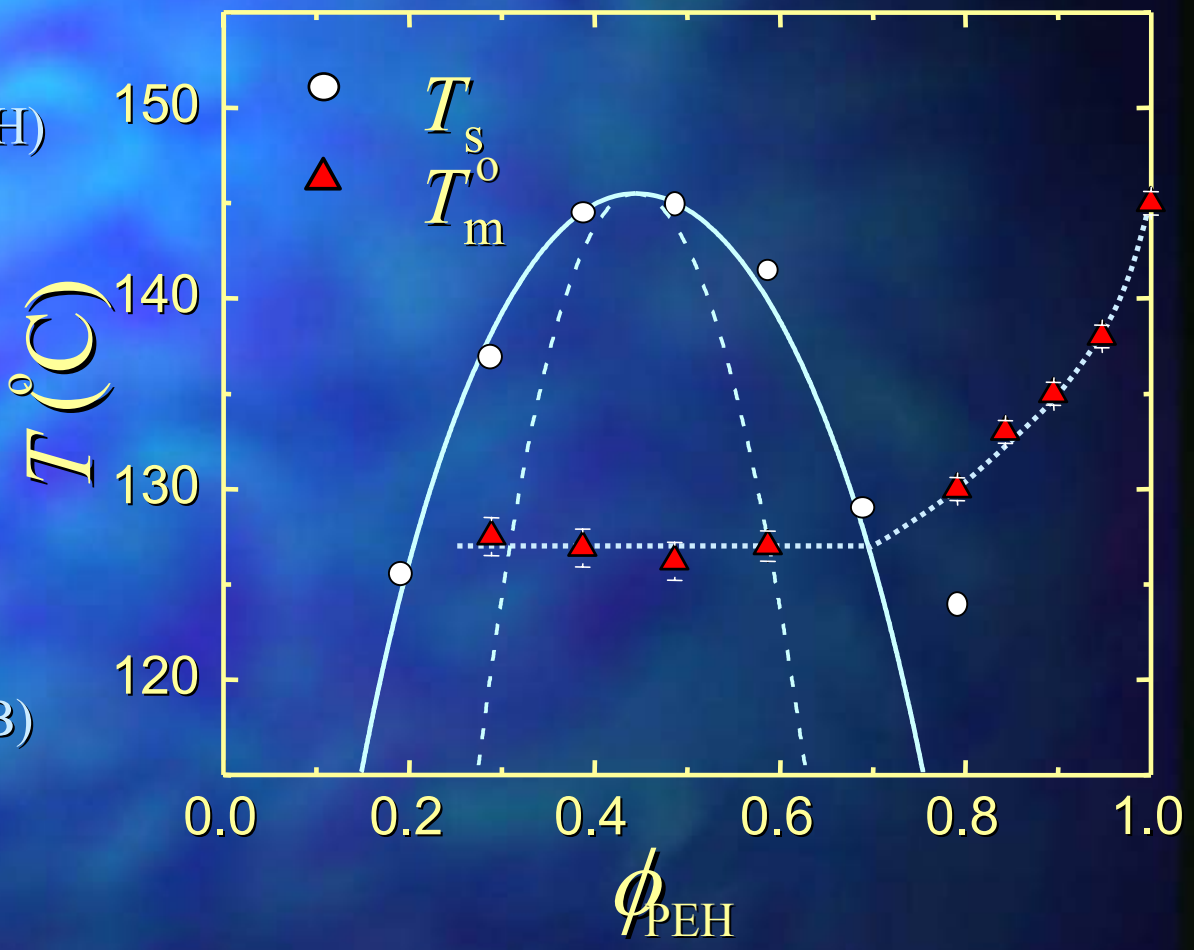
Introduction

Poly(ethylene-co-hexene) (PEH)



Poly(ethylene-co-butene) (PEB)





Phase diagram of the PEH/PEB blend

DSC measurement

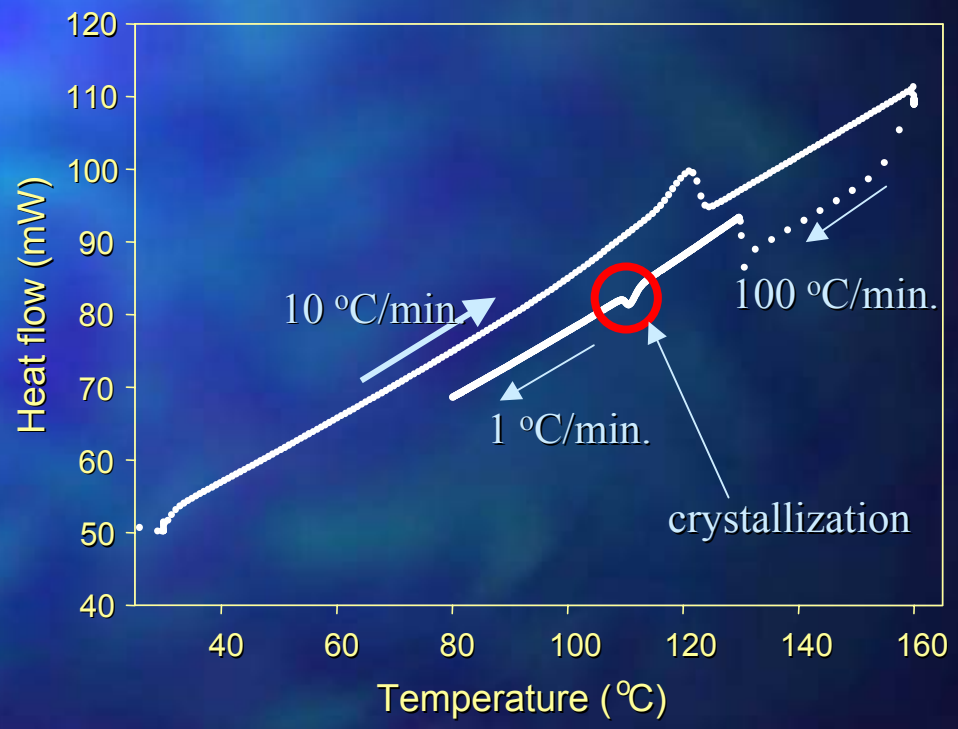
The melting temperature of the polymer depends on the crystallization temperature.

1st step To check the crystallization temperature region

2nd step To decide the melting temperature

1st step

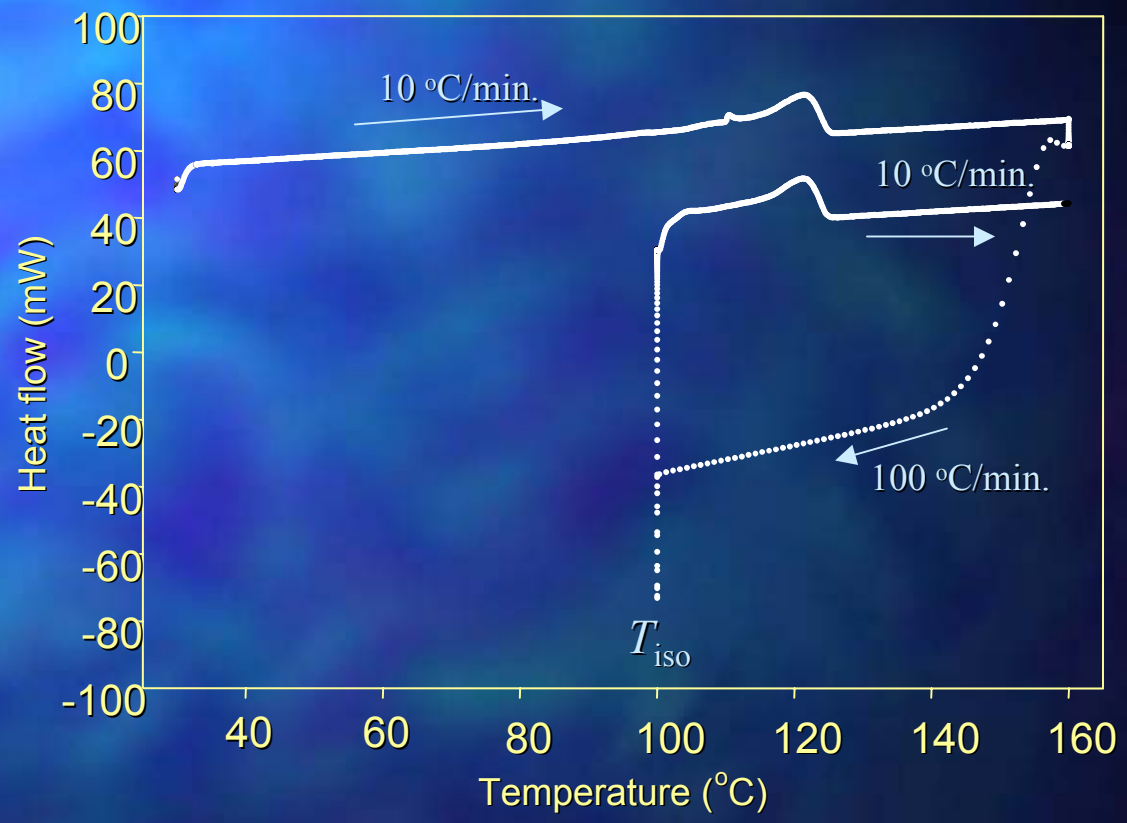
- heat up from R.T. to 160°C
- wait for 5min for annealing.
- quickly cool down to 130°C
- continuously cool down to 80°C



DSC scans on PEH, 1st step

DSC measurement

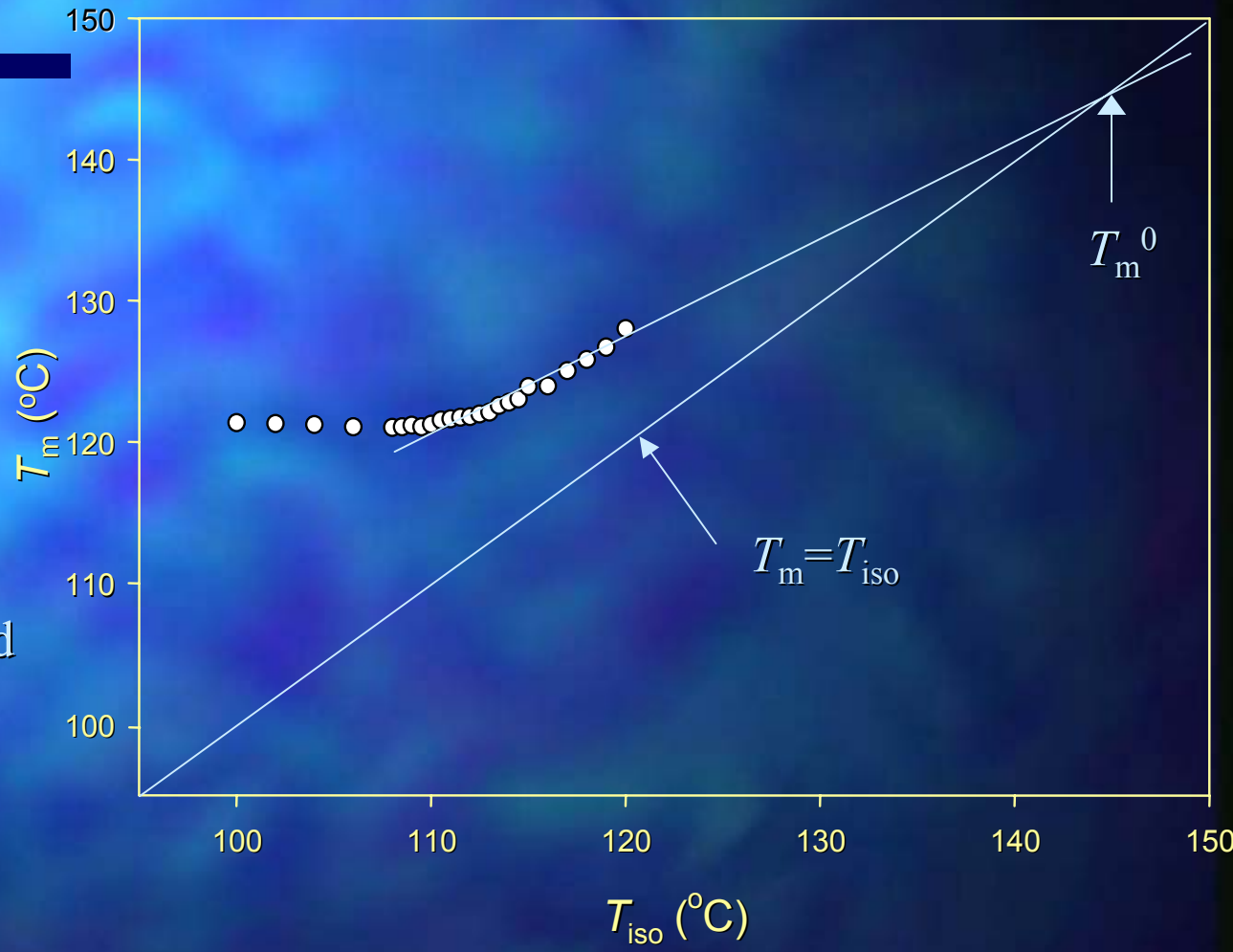
2nd step
- heat up from R.T. to 160°C and wait for 5 min.
- cool down to T_{iso}
- wait for a time (isothermal crystallization)
- heat up from T_{iso} to 160°C
- measure the peak position (melting temperature)



DSC scans on PEH, T_{iso}=100°C

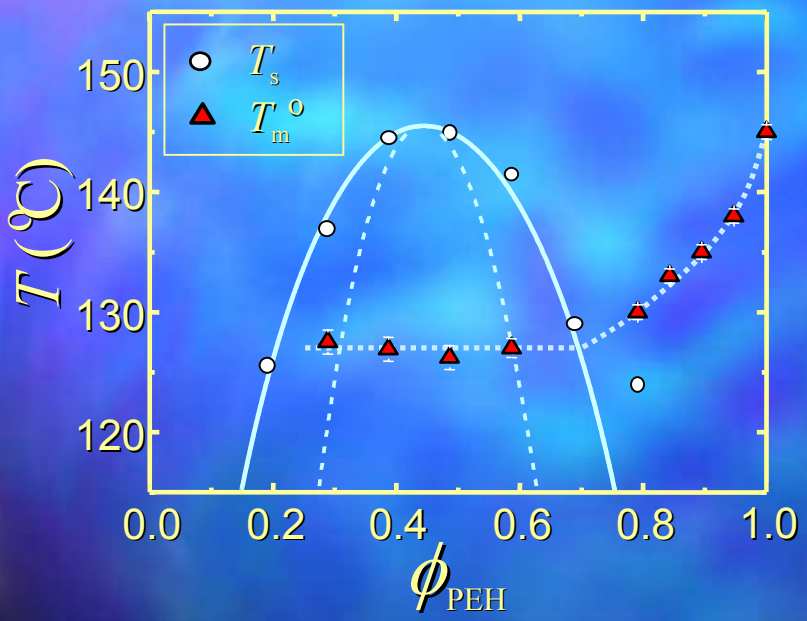
DSC measurement

- At low isothermal temperature region
  ---> T_m is almost constant.
- At high isothermal temperature region
  ---> T_m is linearly increased with T_{iso}.



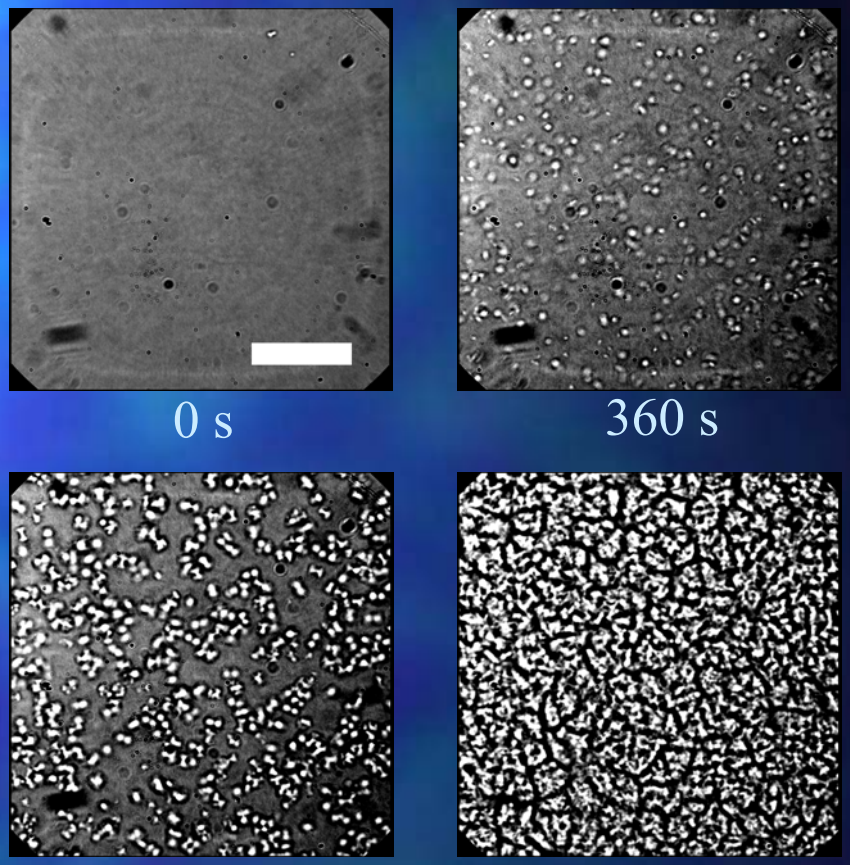
Isothermal temperature dependence of the melting temperature (PEH)

Optical microscopy



Sample: PEH, PEH/PEB 90/10, PEH/PEB 50/50

Temperature control
- heat up from R.T. to 160°C
- wait for 5min. for annealing
- cool down to different T_{iso}

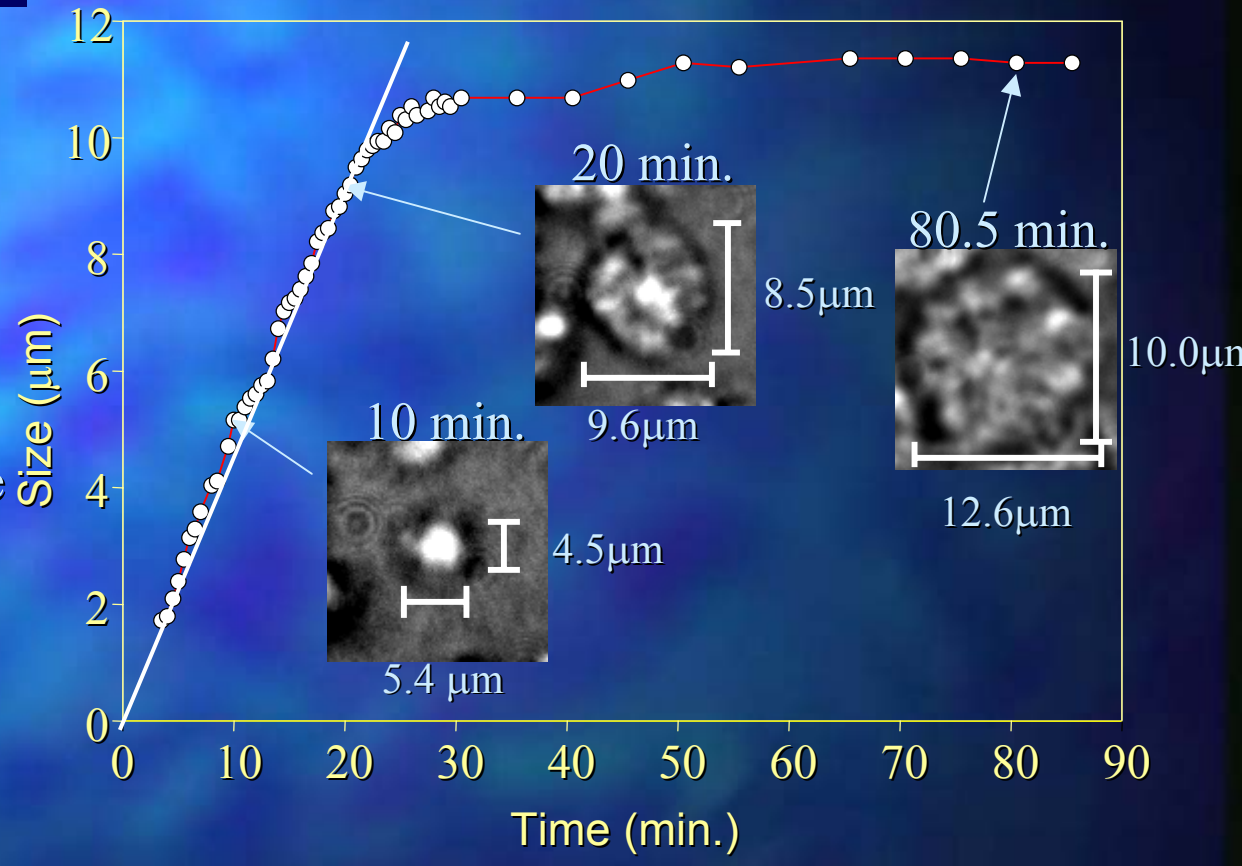


Optical micrographs of PEH isothermally crystallized at 116°C. White scale bar represents 40μm

Optical microscopy

Measurement
- draw the box using the software (Scion Image)
- (width+height)/2= average size of the spherulite

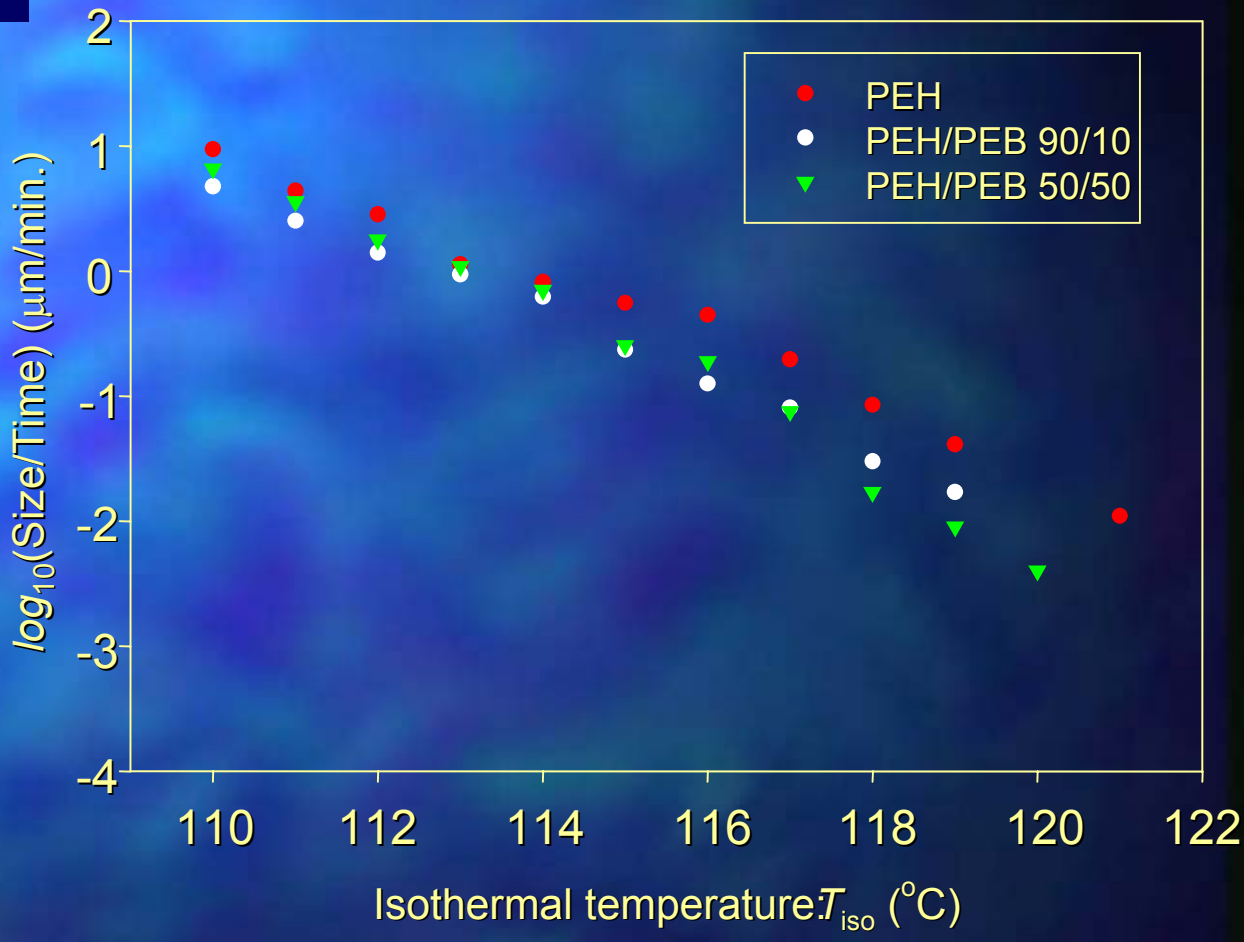
Growth rate
- select the initial part of the average value
- the value of the slope =growth rate



Time dependence of the size of the spherulite
Sample: PEH, T_{iso}=116°C

Optical microscopy

- At low temperature region growth rate between the three different samples is small.
- At high temperature region growth rate between the three different samples is larger than that in the low temperature region.



Spherulitic growth rate in PEH, PEB blend

Optical microscopy

In the previous optical microscopy, I could see the spherulitic growth, but I could not see the morphological change due to the phase separation.

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In order to see the phase separation, I did experiment of the optical microscopy using the double quench technique.

↓

Interconnected bicontinuous structure

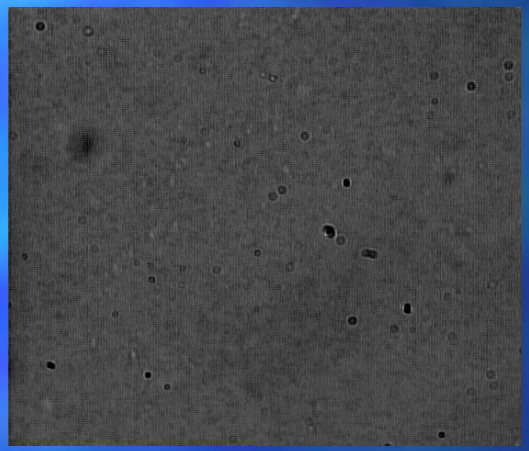
Optical microscopy

- After waited for 1 day,
  Interconnected bicontinuous structure was observed.

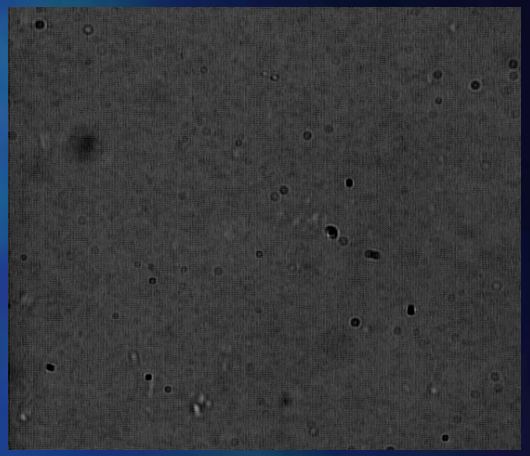
- By quenching the temperature from 130°C to R.T.,
  Interconnected bicontinuous structure was destroyed.
  Spherulite was appeared.

↓

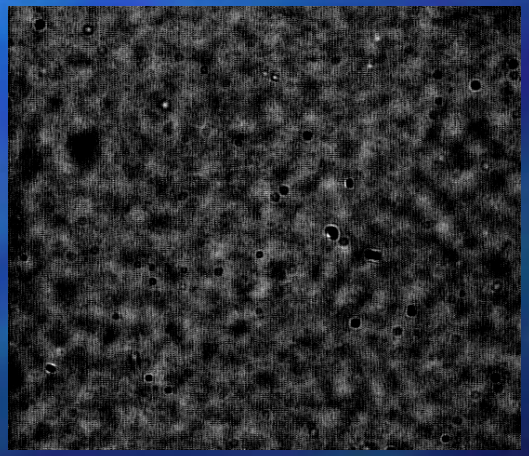
Crystal growth is dominant.



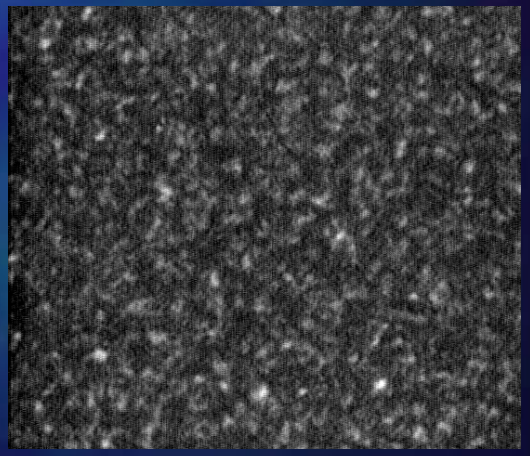
T=160°C



T=130°C
before waited for 1 day

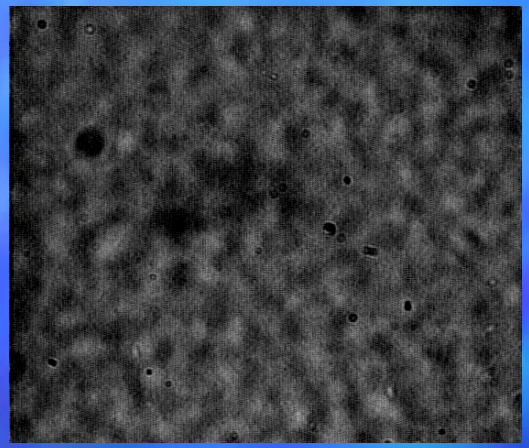


T=130°C
after waited for 1 day

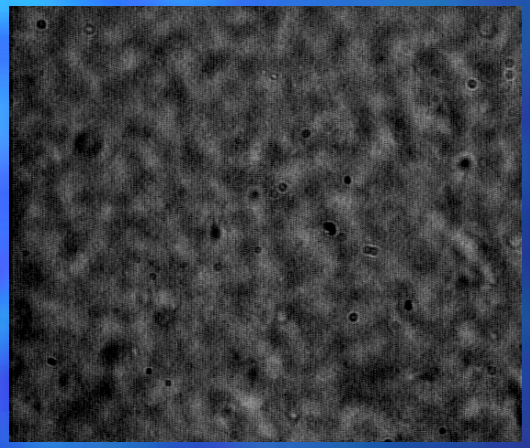


T=R.T.

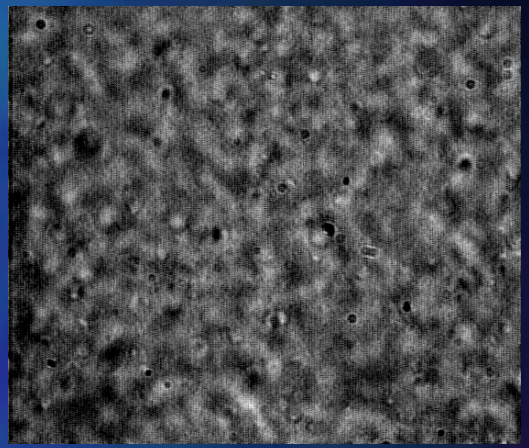
Optical microscopy



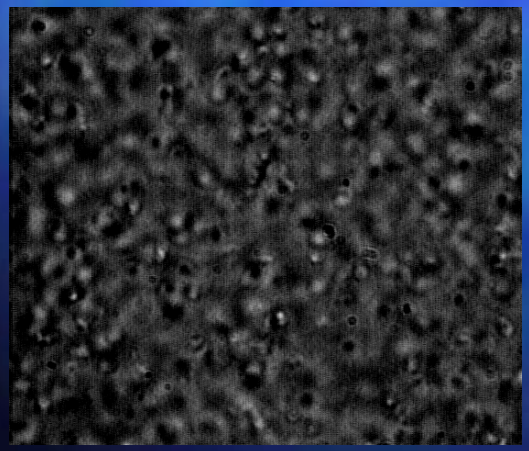
T=130°C



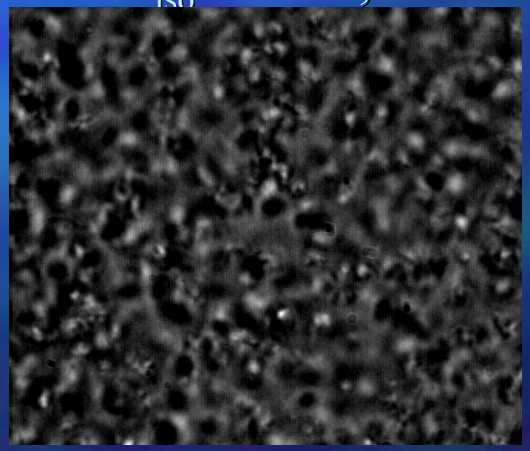
T_{iso}=115°C, 0s



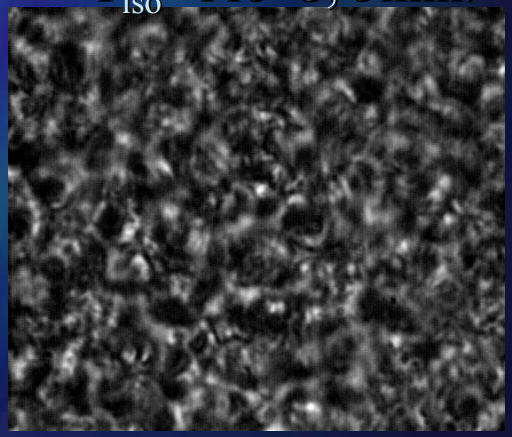
T_{iso}=115°C, 3min.



T_{iso}=115°C, 5min.

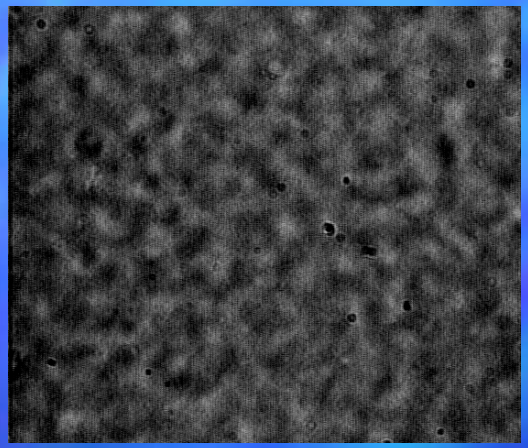


T_{iso}=115°C, 10min.

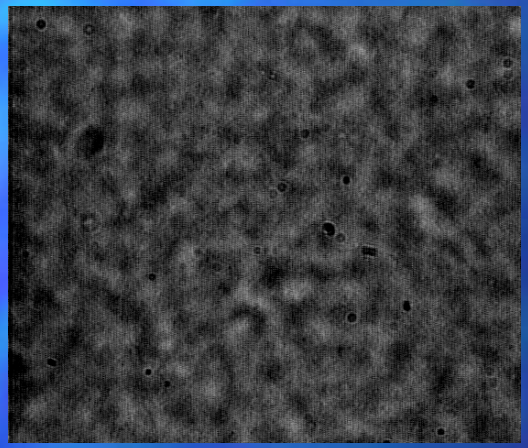


T_{iso}=115°C, 19min.

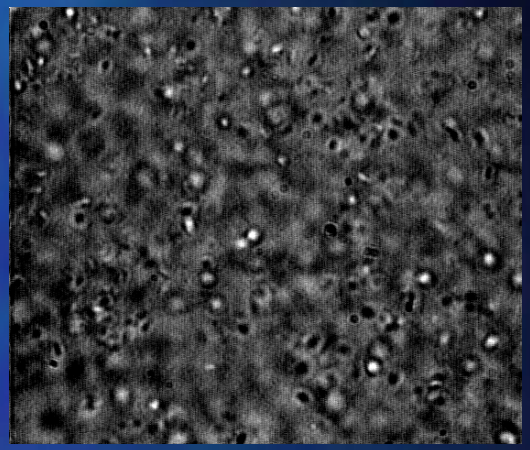
Optical microscopy



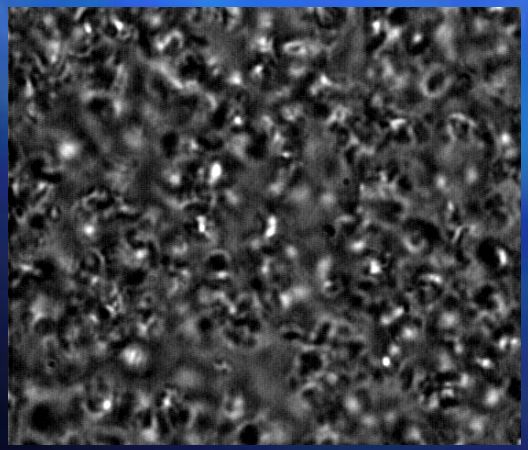
T=130°C



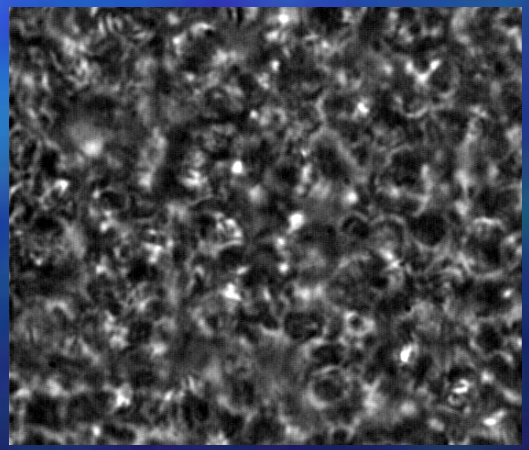
T_{iso}=119°C, 0s



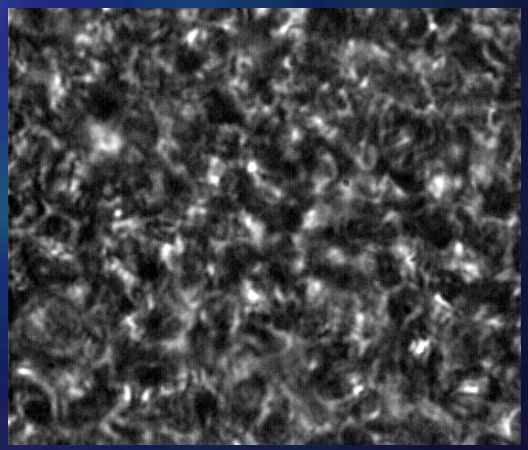
T_{iso}=119°C, 83min.



T_{iso}=119°C, 173min.



T_{iso}=119°C, 323min.



T_{iso}=119°C, 623min.

Optical microscopy

The size of the interconnected bicontinuous structure

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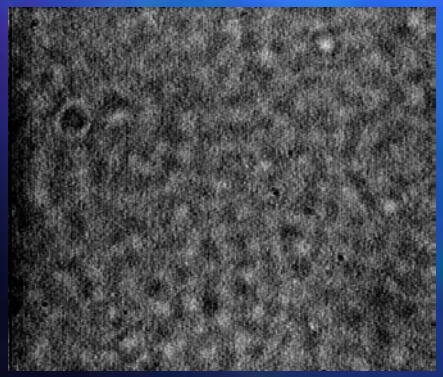
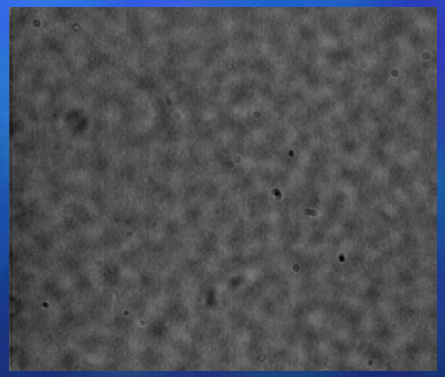
It depends on the time.

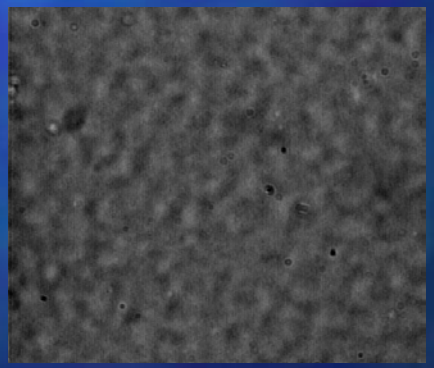
experimental time frame →



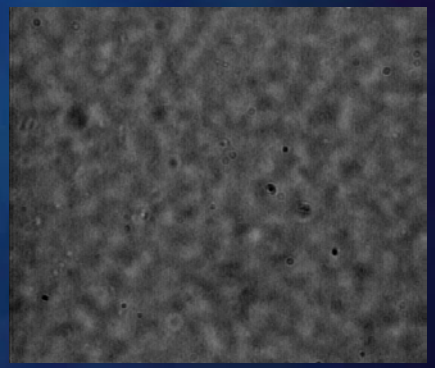
After annealing at 160°C then quenched to 130°C



Heat up from 110°C to 130°C

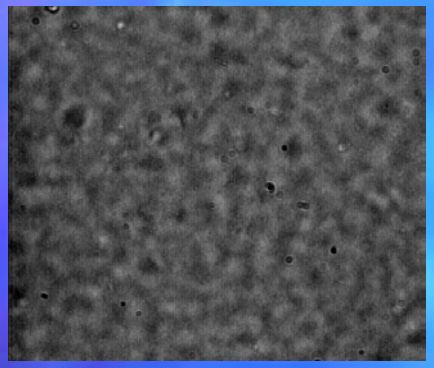


Heat up from 111°C to 130°C

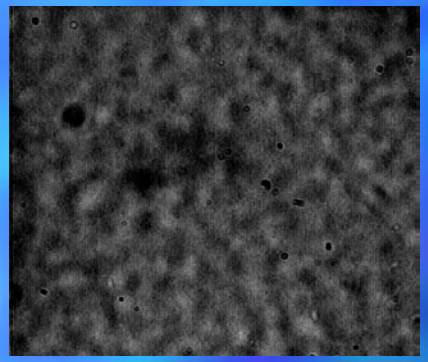


Heat up from 112°C to 130°C

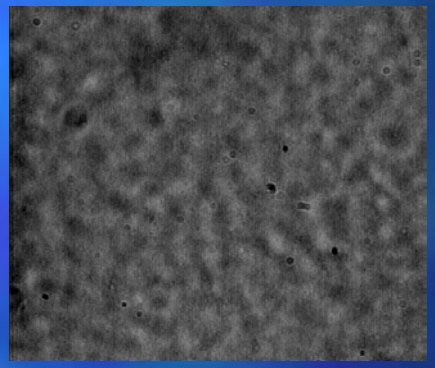
Optical microscopy



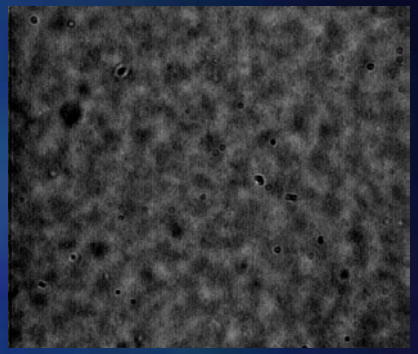
After heat up from 113°C to 130°C



After heat up from 114°C to 130°C

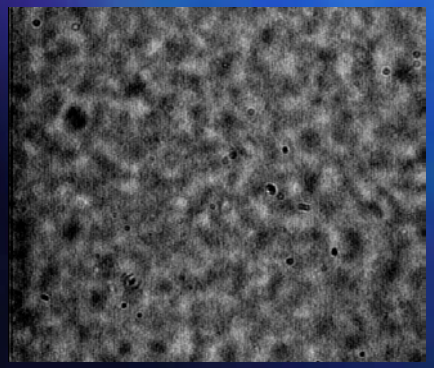


After heat up from 115°C to 130°C

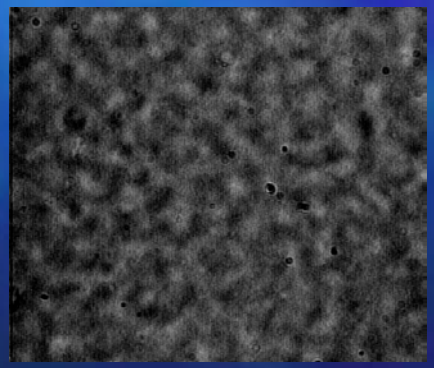


After heat up from 116°C to 130°C

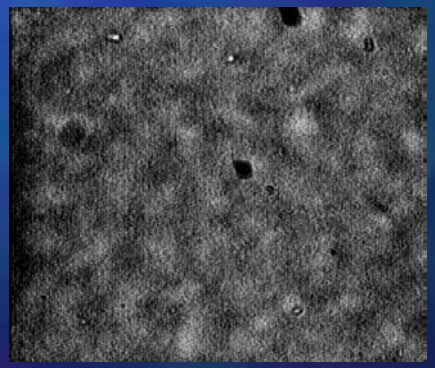
experimental time frame



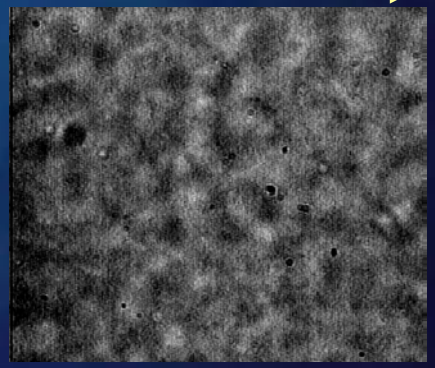
After heat up from 117°C to 130°C



After heat up from 118°C to 130°C



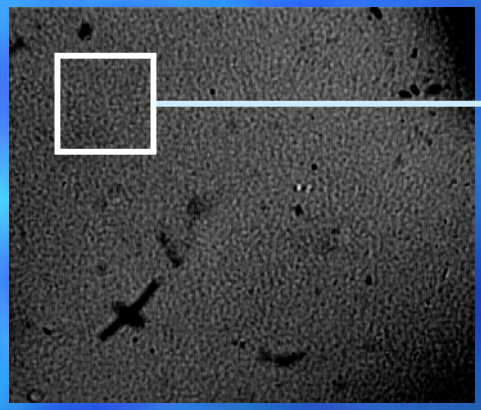
After heat up from 119°C to 130°C

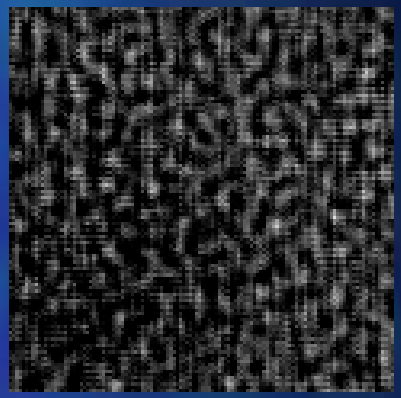


After heat up from 115°C to 130°C

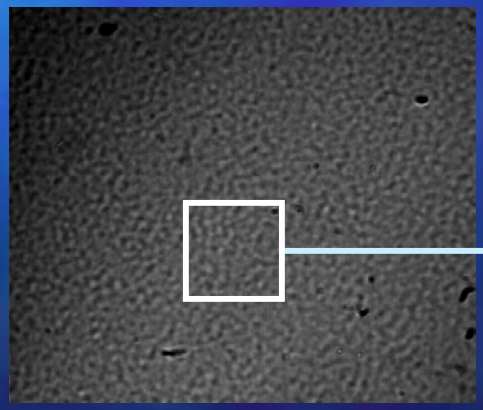
Optical microscopy

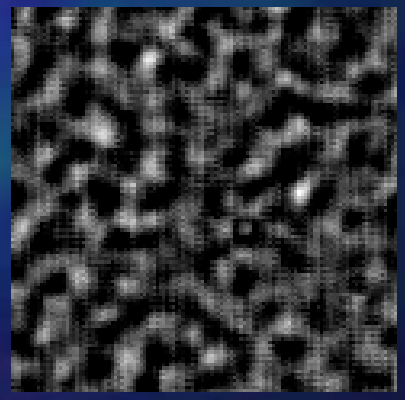
After waited for 19min.
at T_{iso}=113°C
Heated up to T=130°C.
Objective is x20.





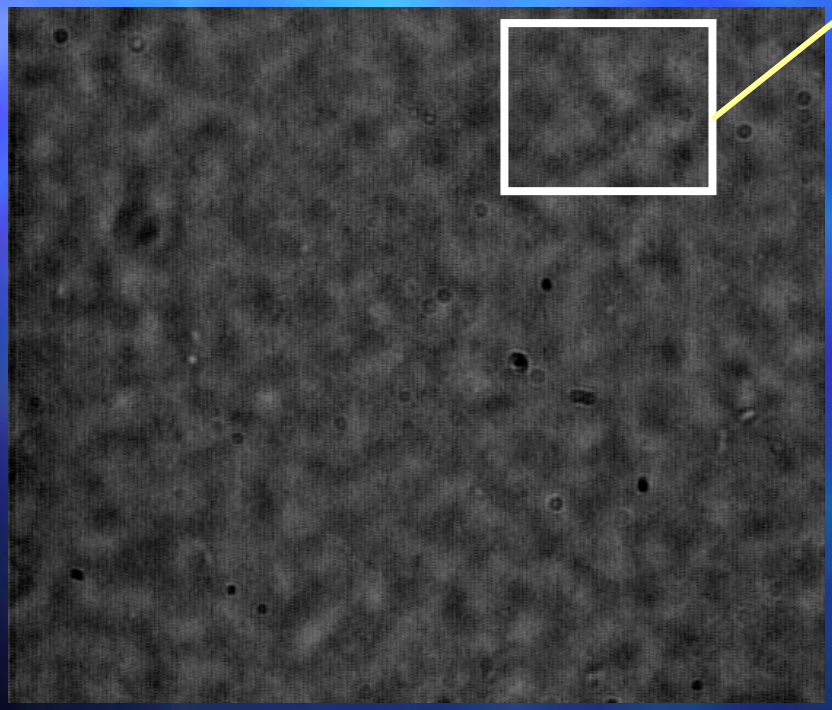
After waited for 48min.
at T_{iso}=115°C
Heated up to T=130°C.
Objective is x20.





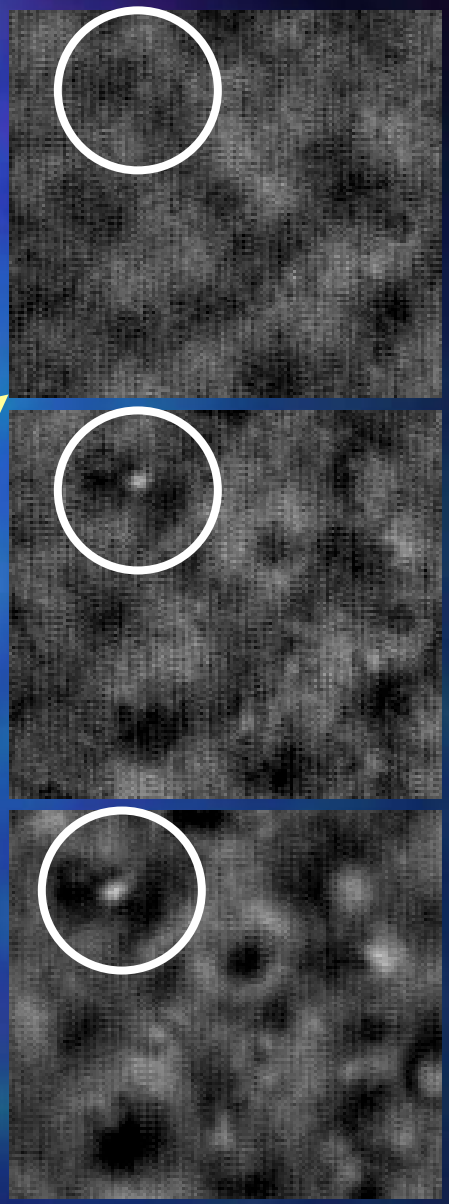
Optical microscopy

Which part is PEH rich phase?



Annealing at T=130°C then quenched to T=113°C, 0s

magnify



T=113°C 0min.

T=113°C 1min.

T=113°C 2min.

time

The spherulite comes from the black part.

Conclusion

In order to understand the phase diagram of PEH/PEB blend, I did experiment of differential scanning calorimetry (DSC) to decide the melting temperature.

- I could decide the equilibrium melting temperature.

In order to see the morphological development of PEH/PEB blend, I did experiment of optical microscopy using the PEH, PEH/PEB 90/10, PEH/PEB 50/50 and PEH/PEB 40/60 blends.

- By the single quench technique, I could see the spherulitic growth and I decided the growth rate.
- By the double quench technique, I could see the interconnected bicontinuous structure.