Viscoelasticity of Copolymers and Polymer Blends with Bicontinuous and Other Structures

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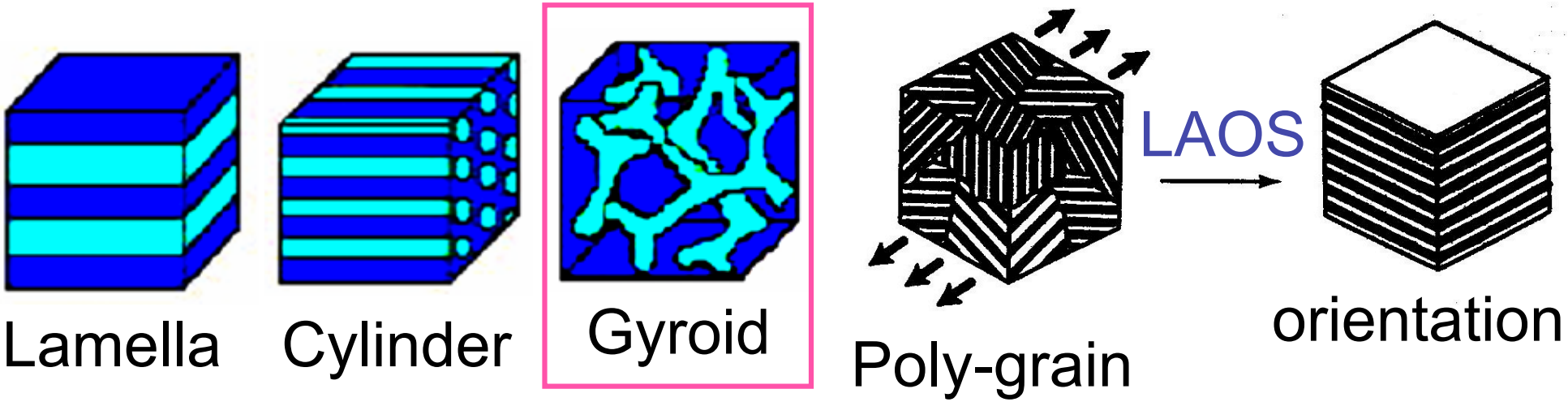
Part I

Structure and Rheology of Block and Starblock Copolymers

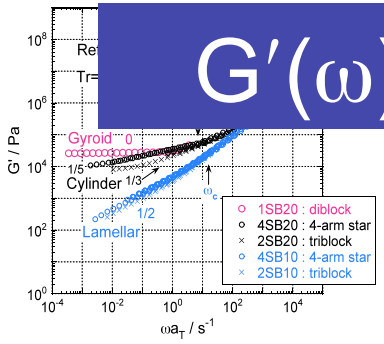
Objectives

For SB block and starblock copolymers, to clarify

1. Structure-rheology relationships for lamellar-, cylinder- and gyroid-forming samples
2. Flow-induced orientations by large amplitude oscillatory shear (LAOS) and steady flow (SF)



G′(ω) of SB Block Copolymers



chain motion

defects and grain boundary

motion of lamellar, cylinder, and gyroid domains

Gyroid-Forming
SB Diblock Copolymer

SB Diblock Copolymer

Code	M_n(S)	M_n(B)	f(B)	M_w/M_n
1SB20	20.1K	10.8K	0.36	1.09

Anti-oxidant (2 wt%)

Kneader : 160°C
15min , 20rpm

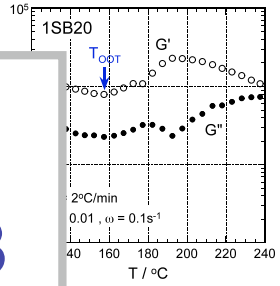
Hot press : 160°C
15min , 2MPa

Disk

Temperature Sweep of G’ and G”

20K 10K

S B



Gyroid

Cylinder

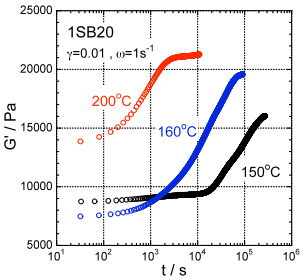
Time Sweep of G' for 1SB20

20K 10K

S B

$T_{OOT} \simeq 160^oC$

G' becomes stable
after 74 hr at 150°C
after 25 hr at 160°C
after 40 min at 200°C



C

Gyroid

B

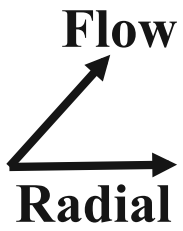
Cylinder

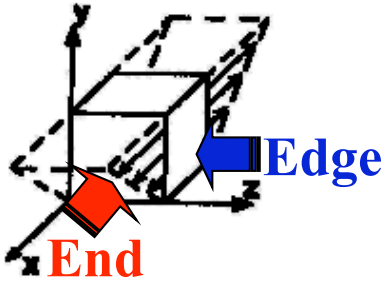
A

TEM Micrographs of 1SB20

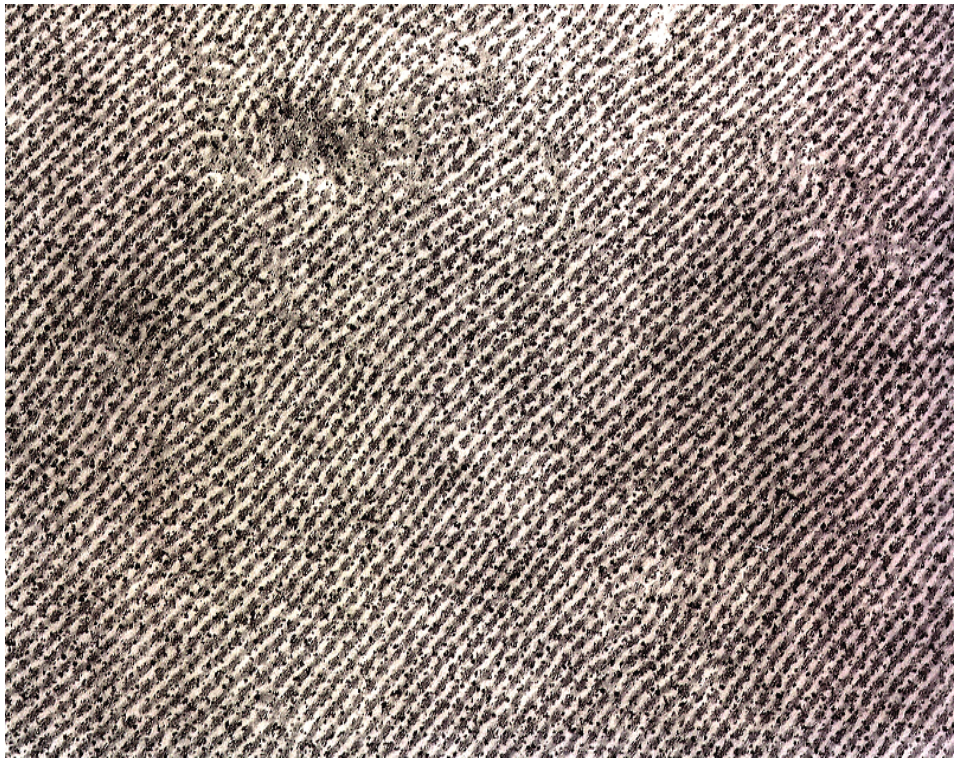
Cylinder

Ⓐ Initial State





End ◔ **Flow** ↙ **Radial**



100nm

Edge ◔ **Radial** ↓ **Flow**

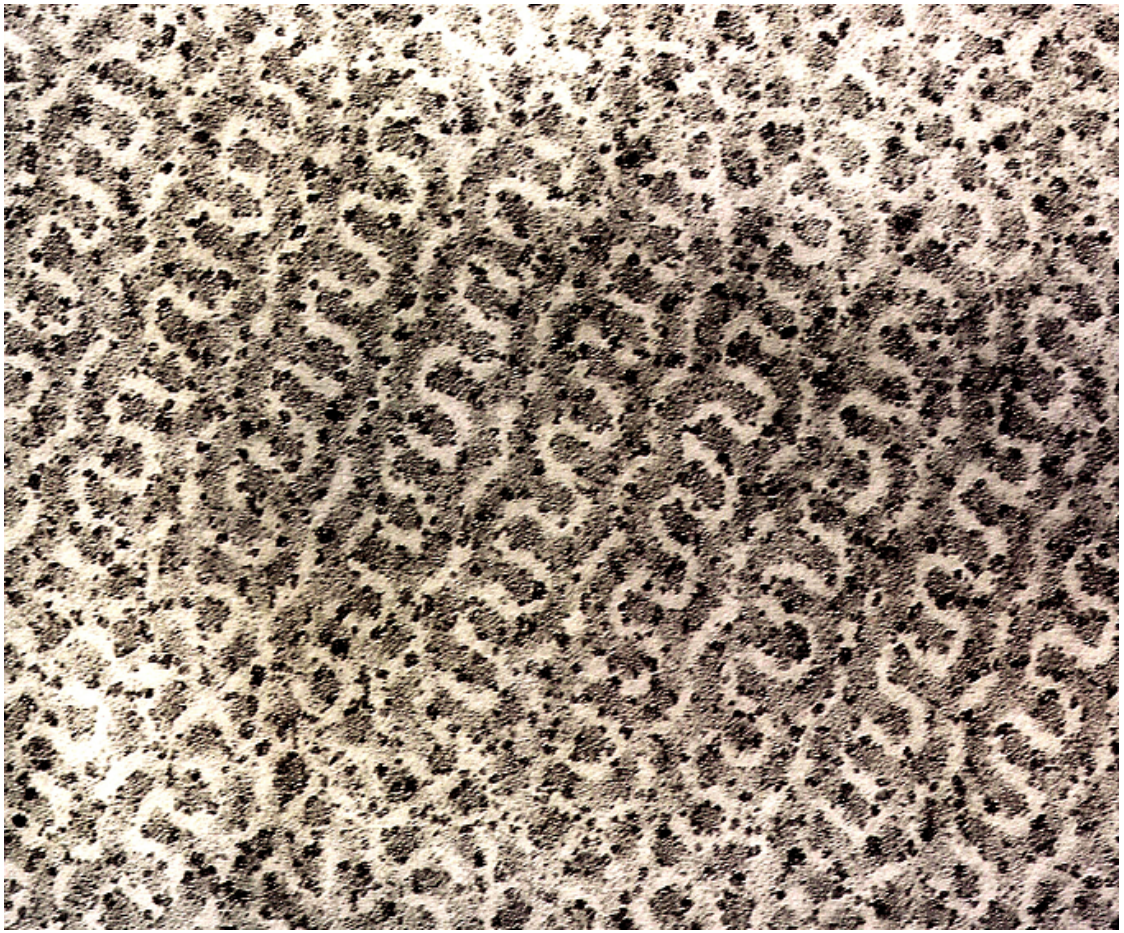
50nm

Quenched from T=160°C after Stabilization

Ⓑ

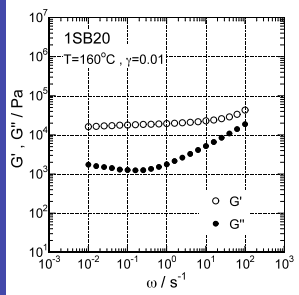
Gyroid

Edge ◉ **Radial → Flow**



50nm

G’ and G” at T=160°C after Stabilization

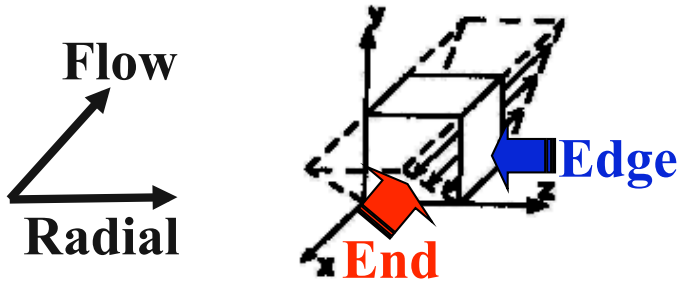


Ⓑ

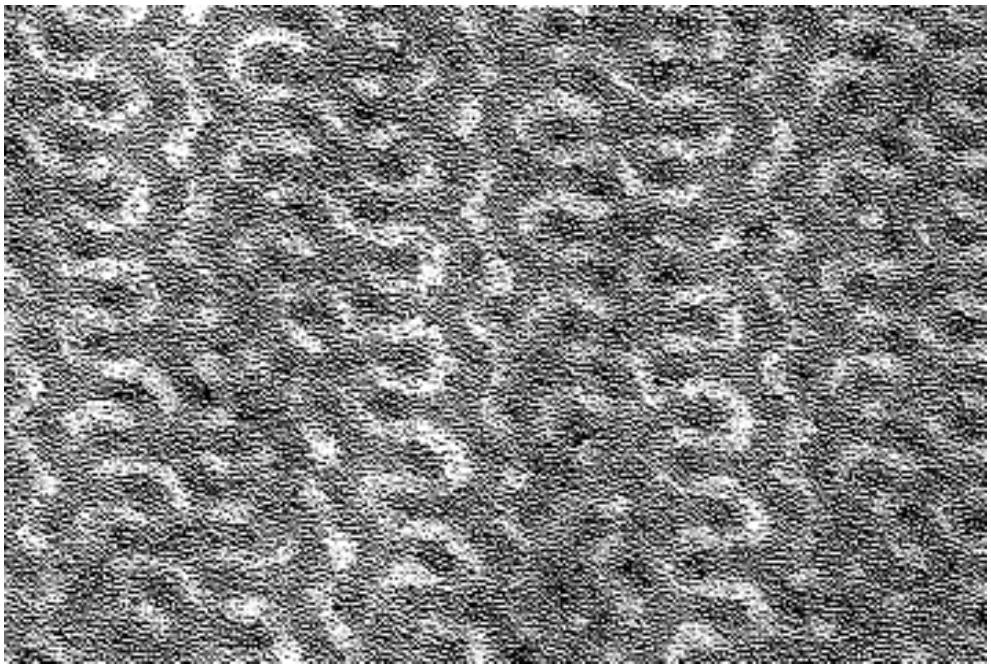
$G_{cubic} = 1.85 \times 10^4$ Pa

Quenched from T=200°C after Stabilization

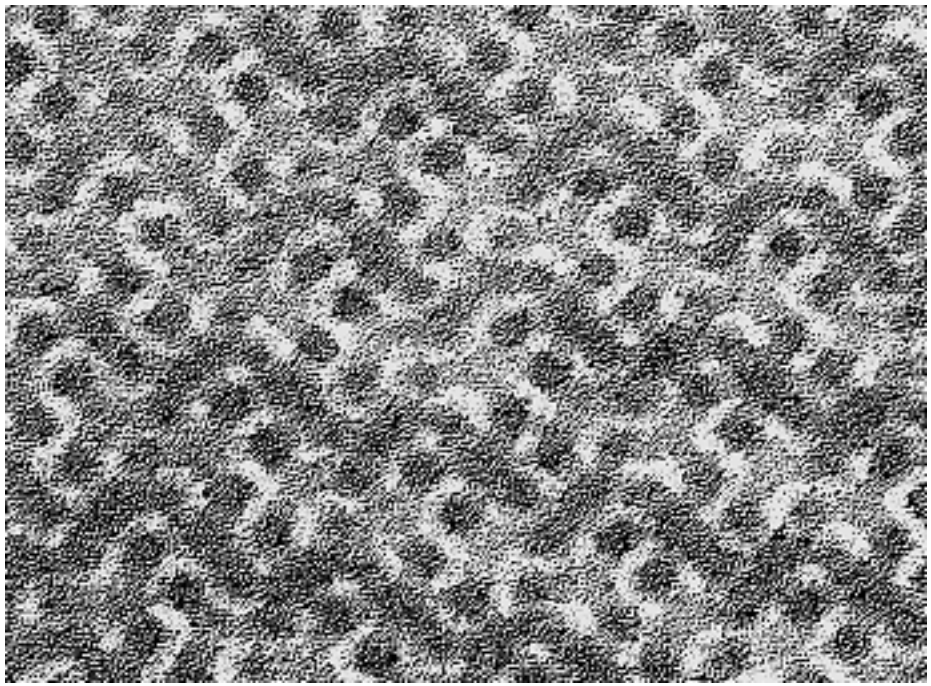
Gyroid ©



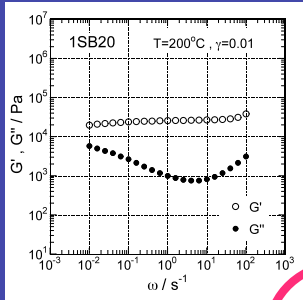
End ◔ **Flow**



Edge ◔ **Radial**



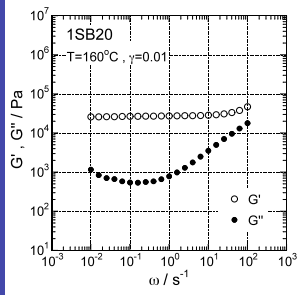
G’ and G” at T=200°C after stabilization



C

$G_{cubic} = 2.61 \times 10^4$ Pa

G’ and G” at T=160°C after stabilized at T=200°C

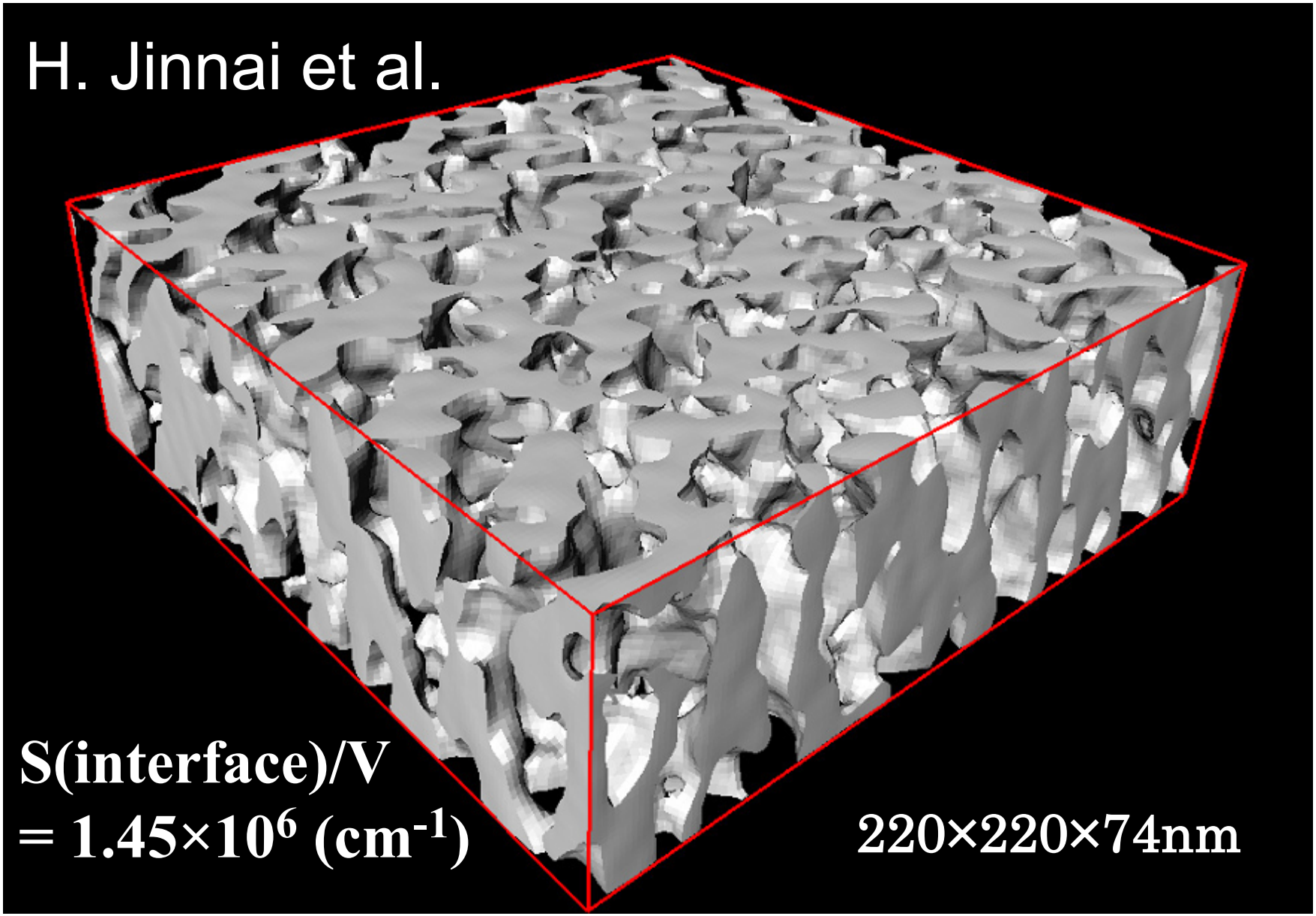


200°C→160°C

G_{cubic}= 2.71×10^4 Pa

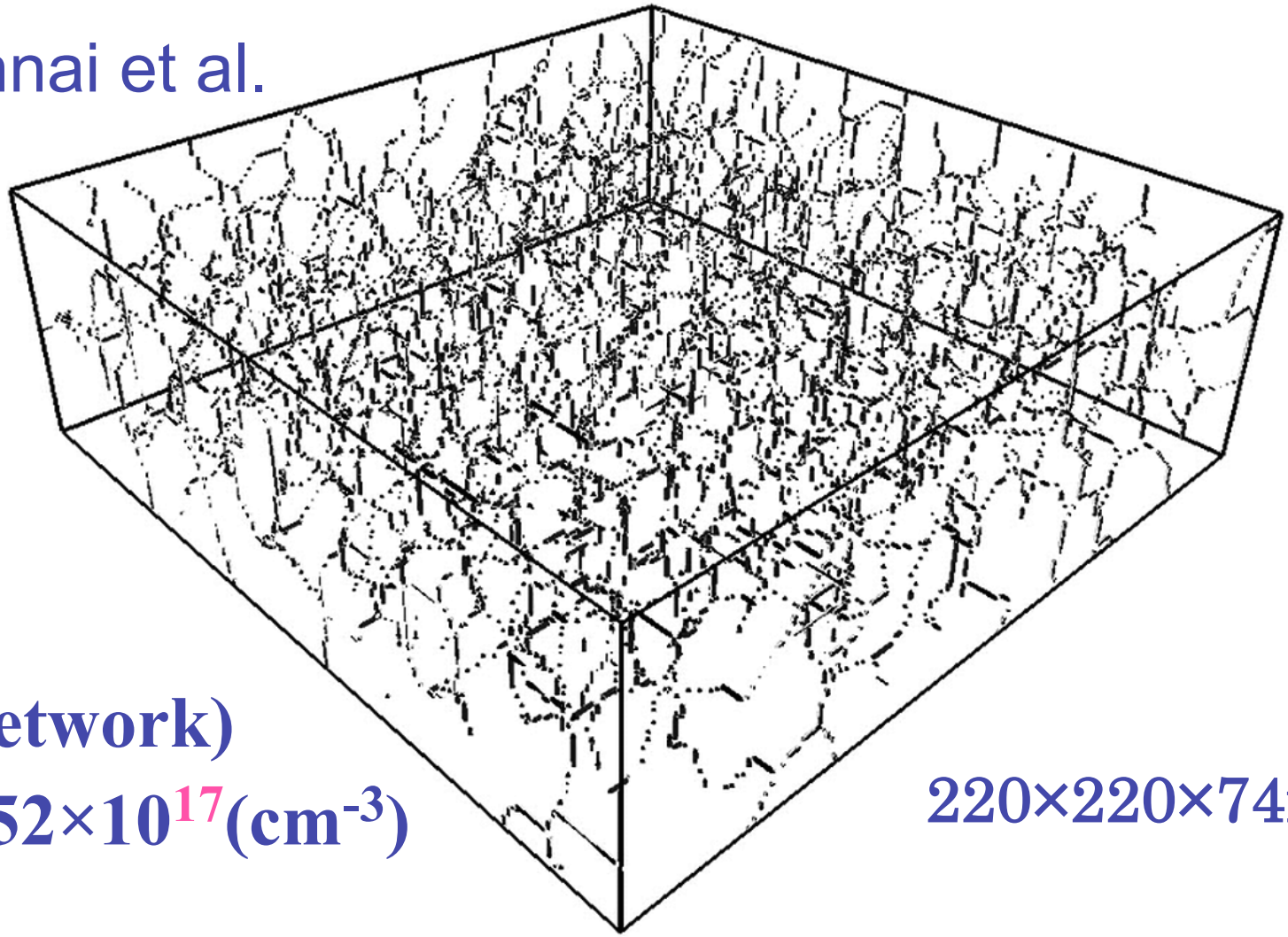
3D TEM Image of 1SB20

(quenched from 160°C after stabilization at 200°C)



Result of 3D Thinnig for 1SB20
(quenched from 160°C after stabilization at 200°C)

H. Jinnai et al.



ν(network)
=3.52×10^{17}(cm^{-3})

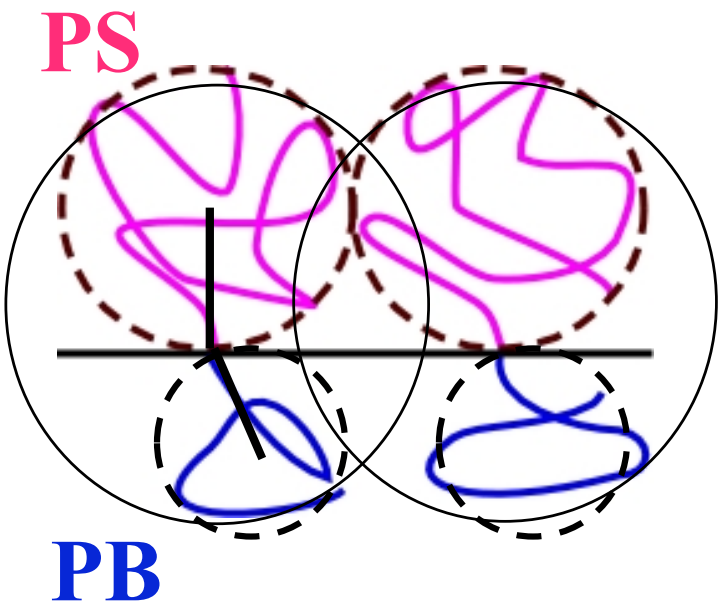
220×220×74nm

3-branch: 75% average length: 15.3nm

$G_{cubic} = \nu\, kT$

ν : # of molecules per unit volume

$\nu(G_{cubic}) = 4.58\times10^{18}\ (cm^{-3})$
$\nu(network) = 3.52\times10^{17}\ (cm^{-3})$
$\nu(interface) = \dfrac{S(interface)\ /\ V}{S(per\ chain)} = 3.63\times10^{18}\ (cm^{-3})$



$S(interface)\ /\ V = 1.45\times10^{6}\ (cm^{-1})$

$S(per\ chain) = \pi \langle S^2 \rangle$

$$\langle S^2 \rangle = \frac{1}{6}\left[(C_\infty N l^2)_{PS} + (C_\infty N l^2)_{PB} \right]$$

$G_{cubic} = \nu\, kT$

ν : # of molecules per unit volume

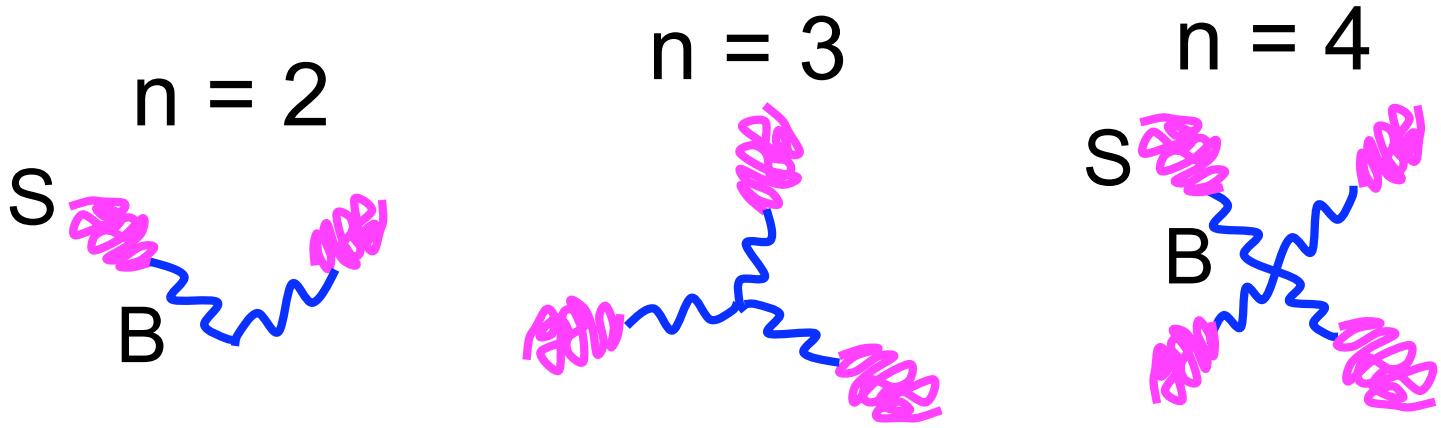
	160°C after stabilized at 200°C	stabilized at 200°C (C)	stabilized at 160°C (B)
$\nu(G_{cubic})$ (cm^{-3})	4.58×10^{18}	4.00×10^{18}	3.10×10^{18}
ν(network) (cm^{-3})	3.52×10^{17}	3.28×10^{17}	2.20×10^{17}
ν(interface) (cm^{-3})	3.63×10^{18}	2.78×10^{18}	3.36×10^{18}

Lamellar-Forming

SB Starblock Copolymer

(SB)n Star Block Copolymers

		Arm			
n	Code	M_n(PS)	M_n(PB)	f_{PB}	
2	2SB10	9.31K	11.6K	0.56	L
3	3SB10	9.53K	11.4K	0.55	L
4	4SB10	9.51K	11.4K	0.55	L

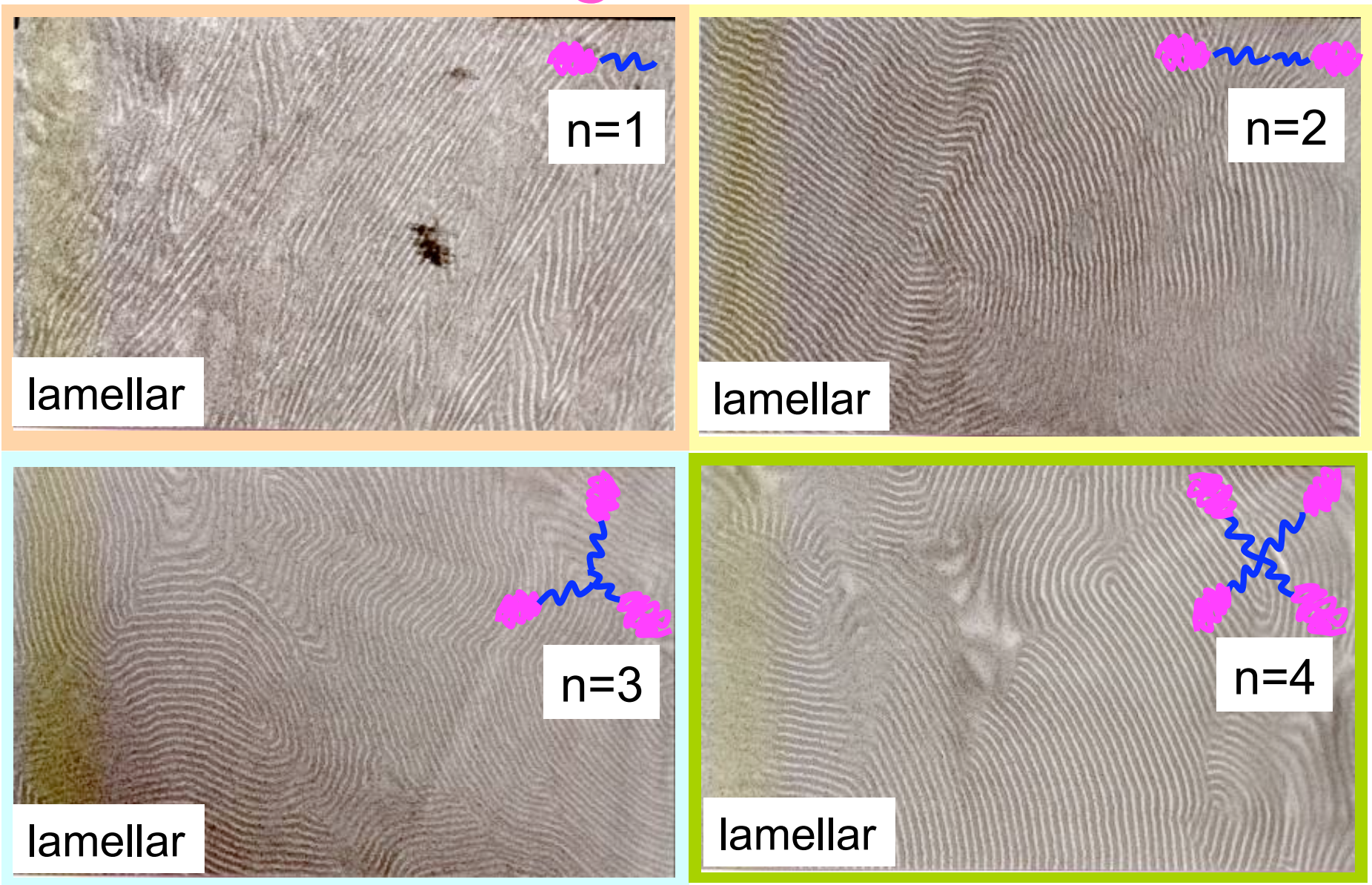


2-3 wt% anti-oxidant was melt blended at $T>T_{ODT}$
Melt pressed at $T<T_{ODT}$ at 3MPa for 15 min.

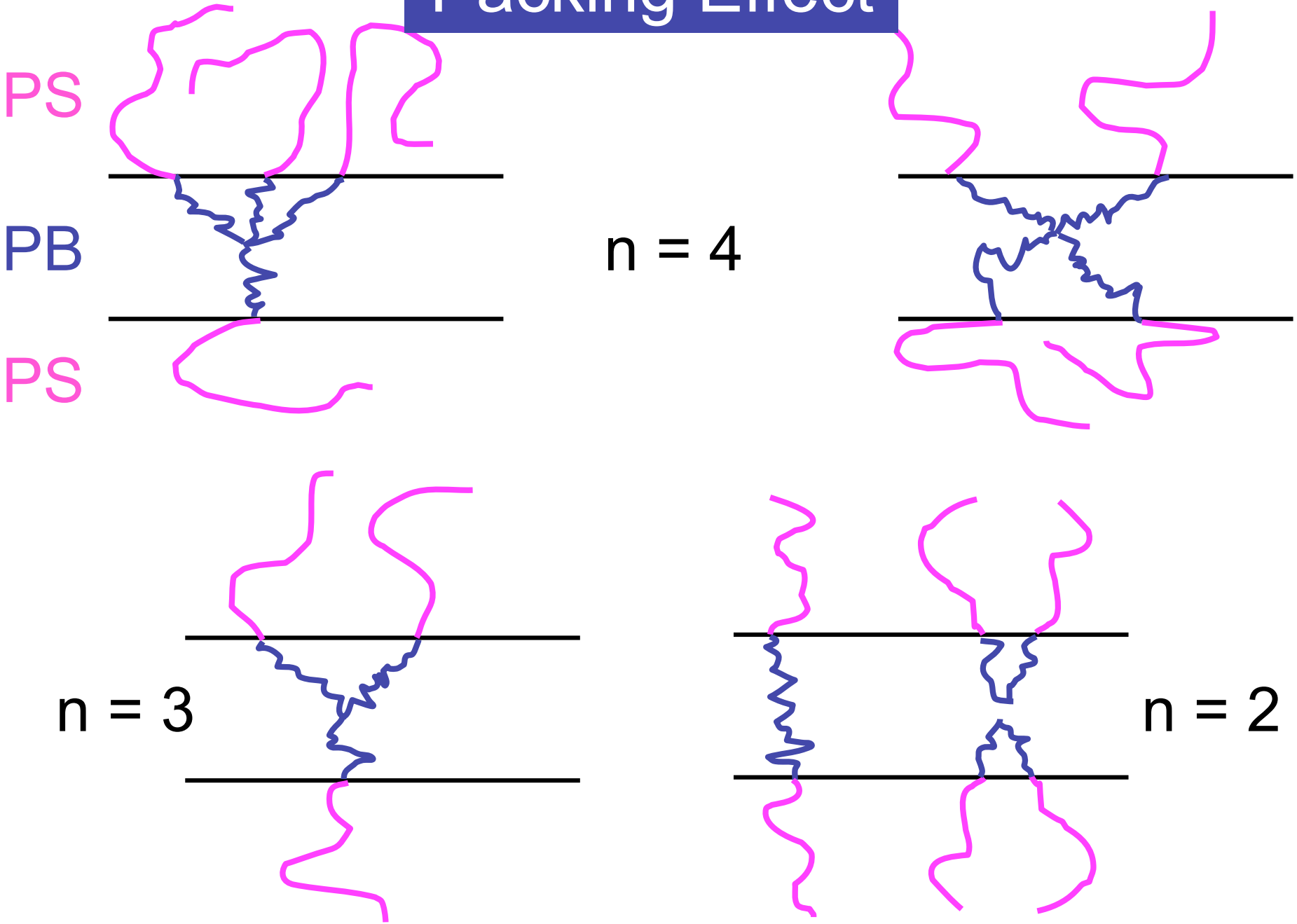
TEM Micrographs of Toluene Cast Films

Arm 10K S 10K B

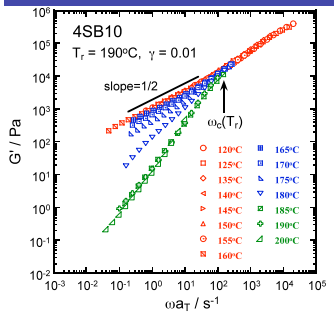
100nm



Packing Effect



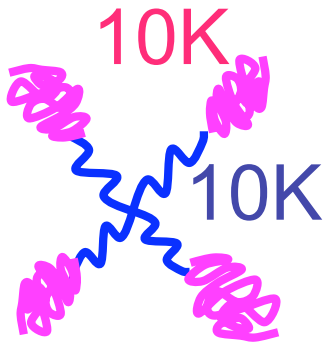
Freq. Despersion of G' for Lamellar-forming 4SB10



motion of lamellar domain

slope=1/2

chain motion



Superposition is possible in ordered and disordered states

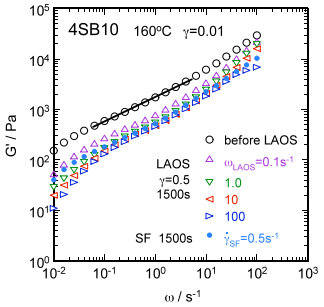
concentration fluctuation

disordered , one phase

Poly-grain states

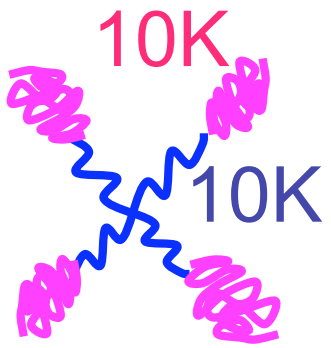
$$G' \sim \omega^{1/2} \quad \text{at } \omega < \omega_C$$

Decrease in G' after LAOS for 4SB10



$0.1\omega_C$

slope=1/2



After LAOS

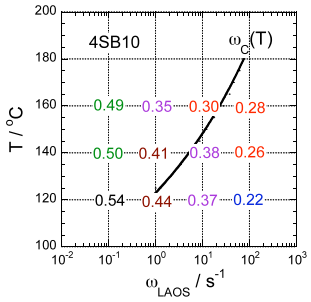
ω_{LAOS} ↗ G' ↘

Evaluate

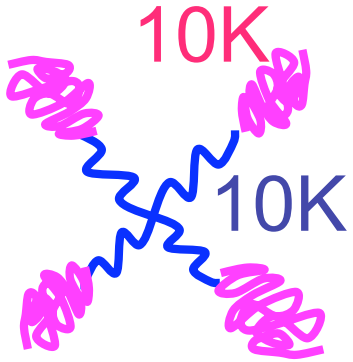
G'_{after}/G'_{before}

at $\omega = 0.1\ \omega_c$

Decrease in G’ after LAOS for 4SB10



Ⓐ Ⓑ Ⓒ



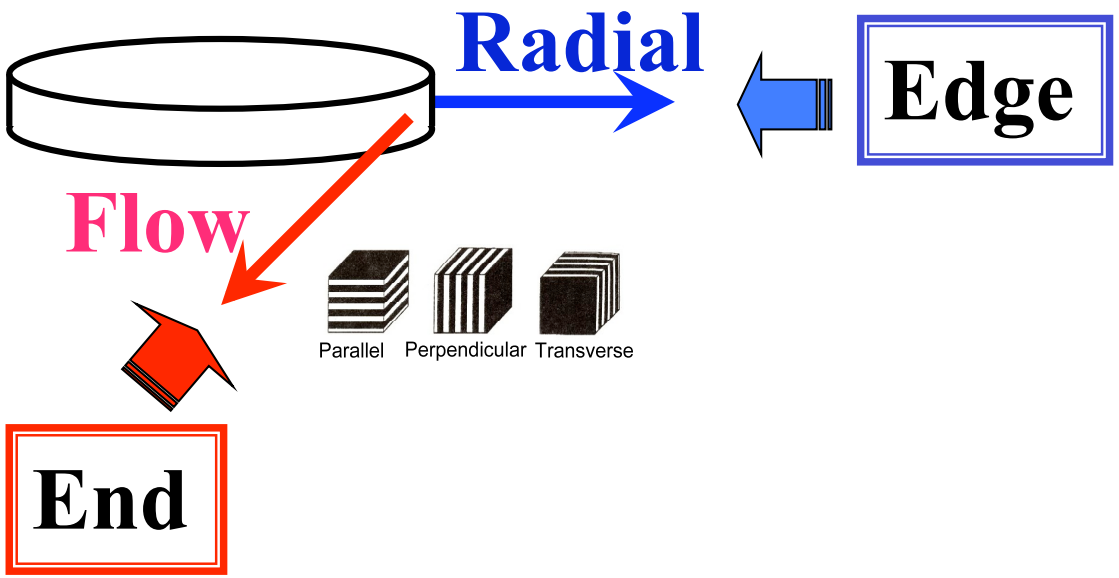
Ⓓ

At each T

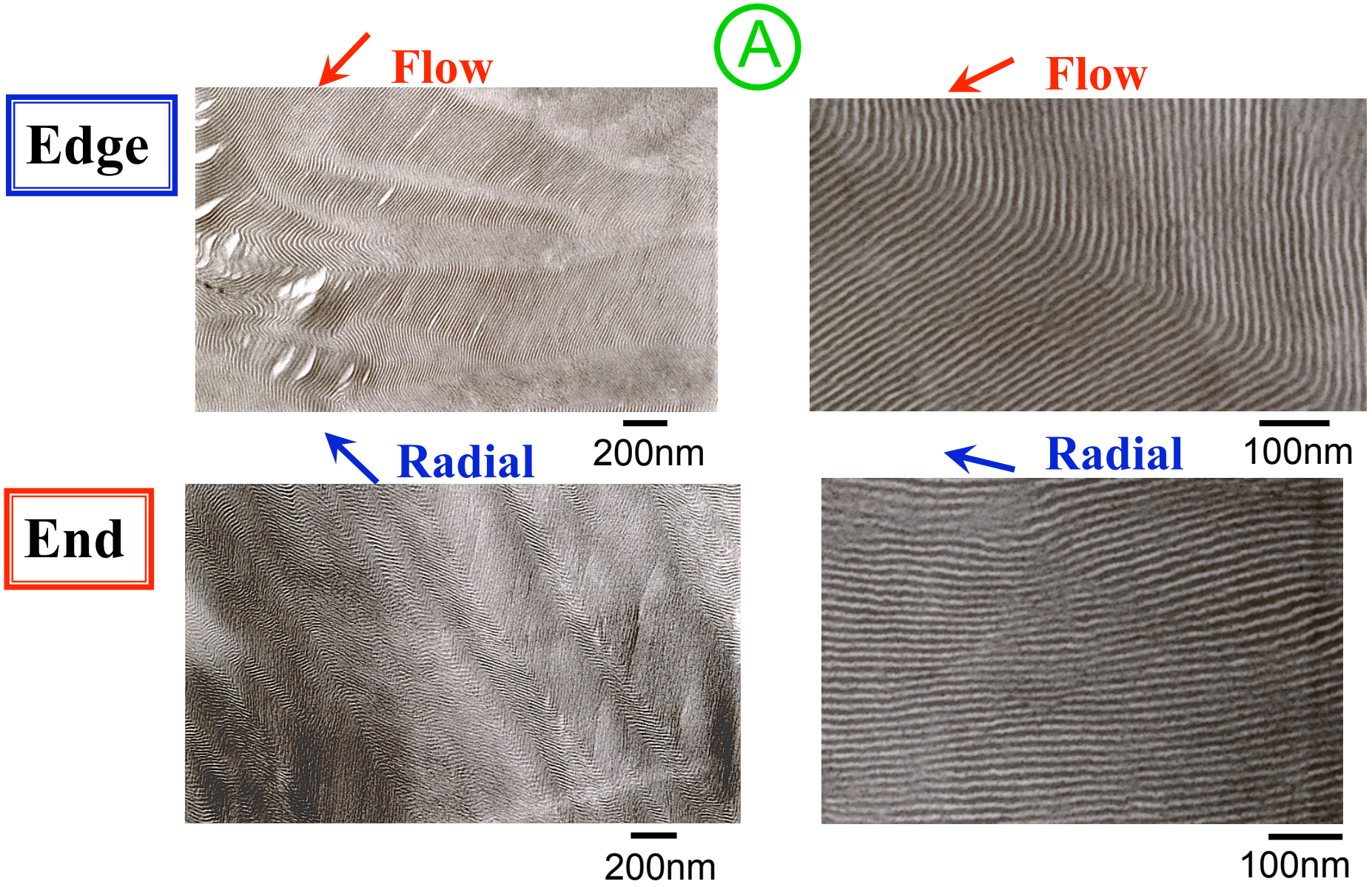
G'_{after}/G'_{before} ↘

ω_{LAOS} ↗

Observation of Lamellar Orientation

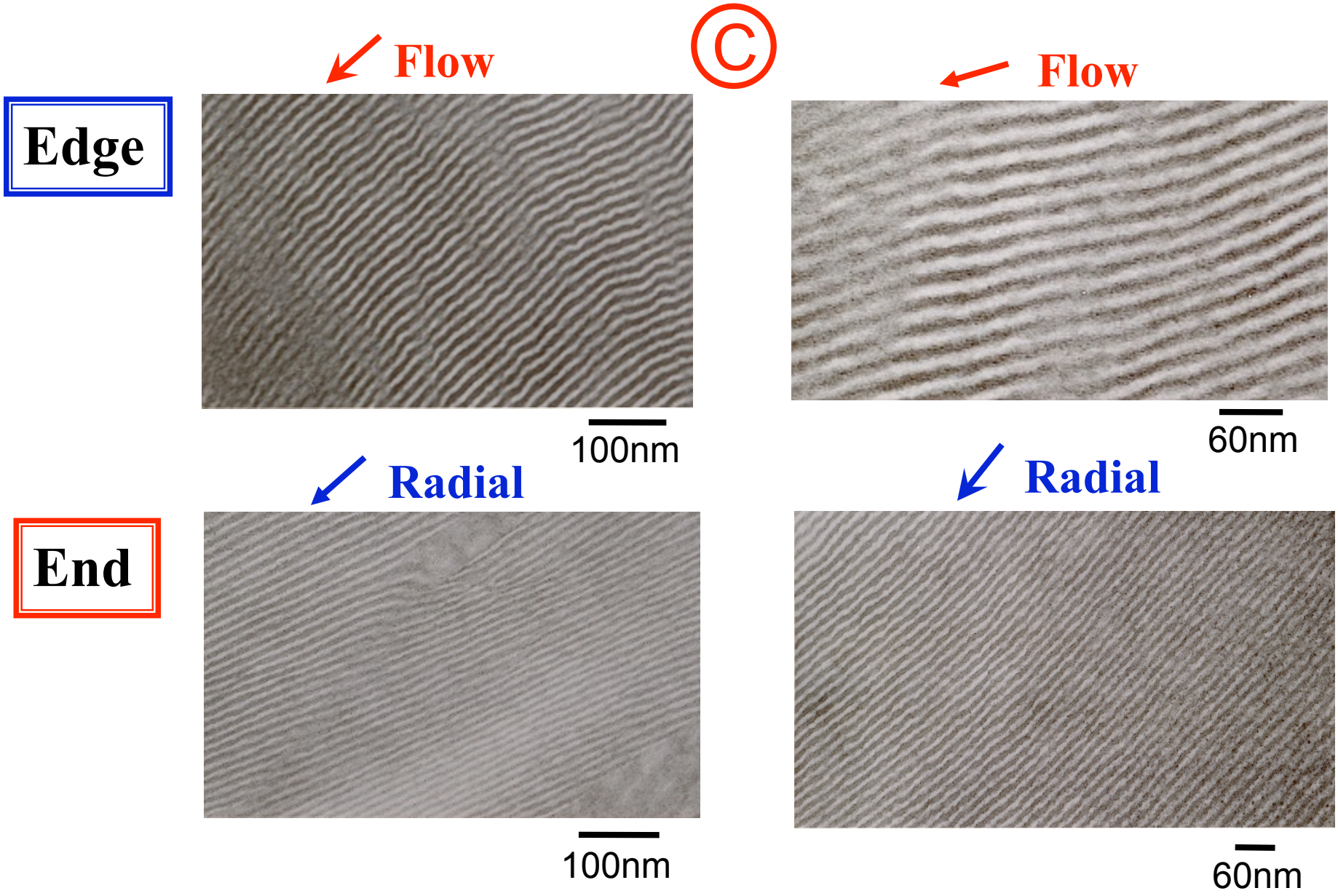


TEM Micrographs of 4SB10 after LAOS (ω_{LAOS}=0.1s^{-1}, 160°C)



Parallel > Perpendicular ≫ Transverse

TEM micrographs of 4SB10 after LAOS (ω_{LAOS}=10s^{-1}, 160°C)

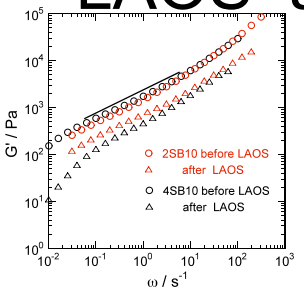


Parallel orientation is prevailing

Effect of n (=2,4) on G' Reduction

LAOS at $\gamma = 0.5$

$\omega_{LAOS}/\omega_C \cong 0.80$ $T/T_{ODT} \cong 0.90$



slope=1/2

Data of 2SB10 are superposed onto those of 4SB10 at $\omega \geq \omega_C$

n=2

n=4

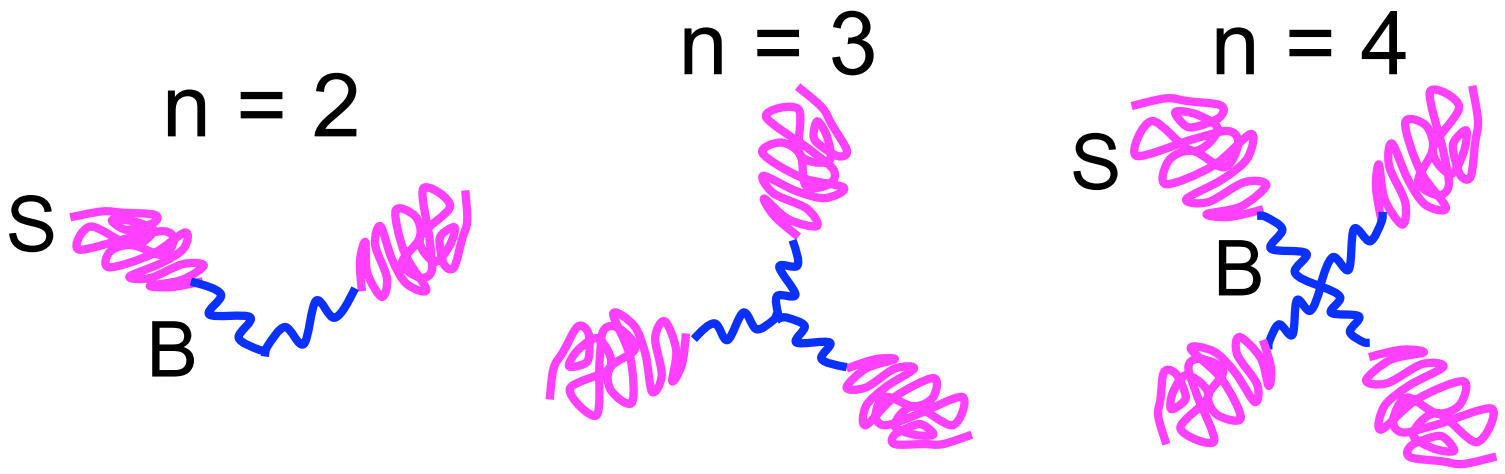
When n↗, G'↘ due to stronger orientation of lamellae

Cylinder-Forming

SB Starblock Copolymers

(SB)n Star Block Copolymers

		Arm			
n	Code	M_n(PS)	M_n(PB)	f_{PB}	
2	2SB20	20.0K	10.5K	0.34	C
3	3SB20	19.9K	10.8K	0.35	C
4	4SB20	19.9K	10.2K	0.34	C

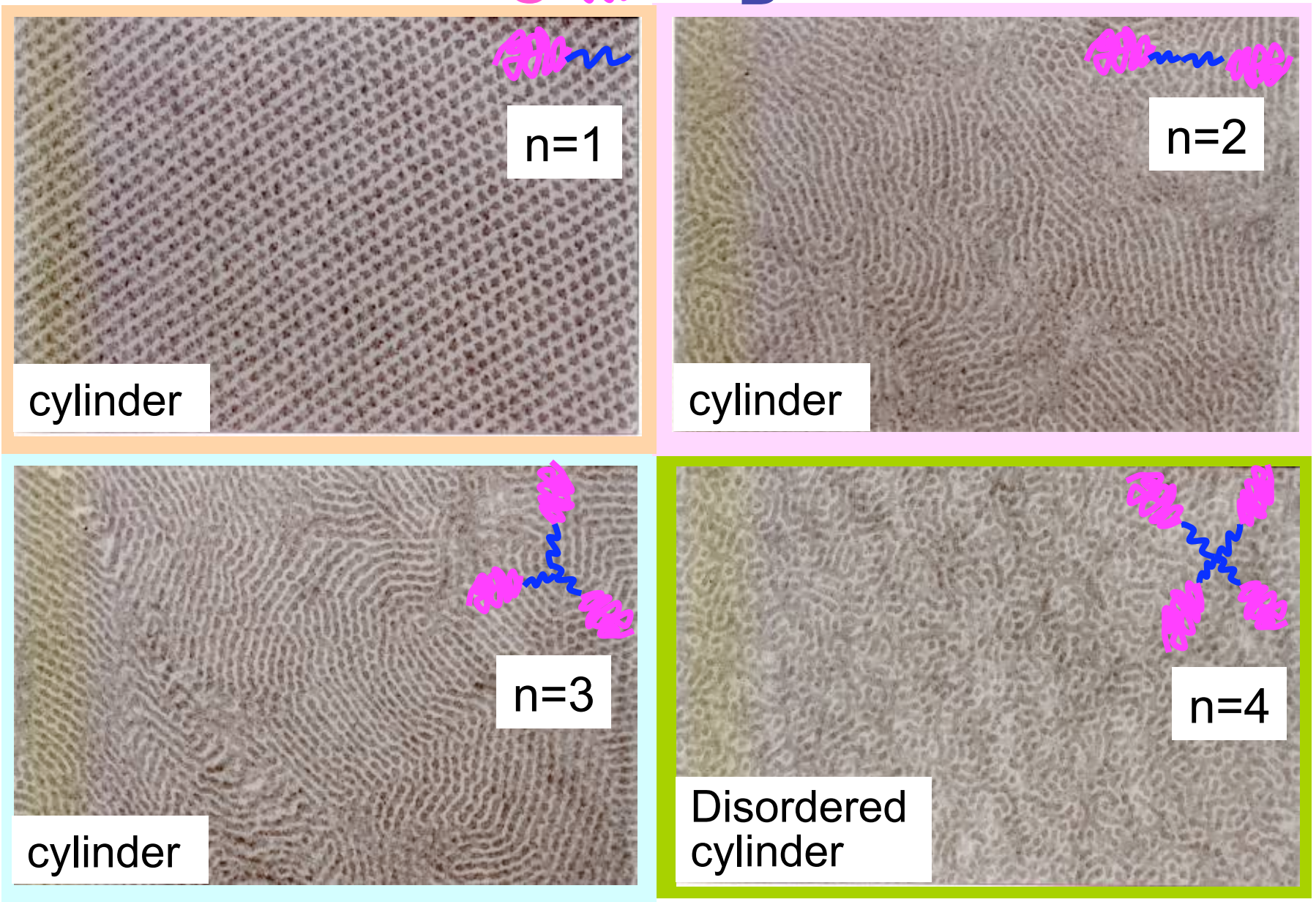


2-3 wt% anti-oxidant was melt blended at $T>T_{ODT}$
Melt pressed at $T<T_{ODT}$ at 3MPa for 15 min.

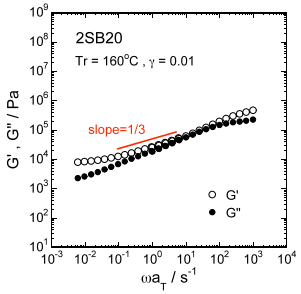
TEM Micrographs of Toluene Cast Films

Arm 20K S 10K B

100nm



Freq. Despersion of G',G" for Cylinder-forming 2SB20



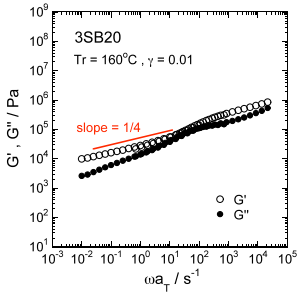
20K 10K

ω_C

In poly-grain state

$$G' \sim \omega^{1/3} \quad \text{at } \omega < \omega_C$$

Freq. Despersion of G',G" for Cylinder-forming 3SB20

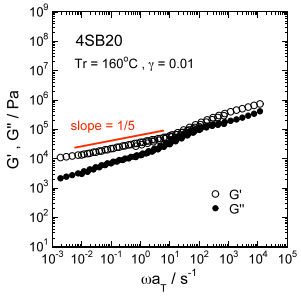


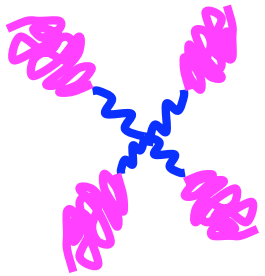
ω_C

In poly-grain state

$$G' \sim \omega^{1/4} \quad \text{at } \omega < \omega_C$$

Freq. Despersion of G',G" for Cylinder-forming 4SB20





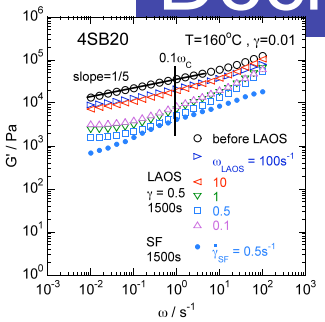
ω_C

↓

In poly-grain state

$$G' \sim \omega^{1/5} \quad \text{at } \omega < \omega_C$$

Decrease in G' after LAOS and SF for 4SB20

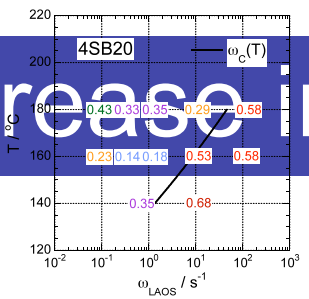


After LAOS G' shows minimum at $\omega_{LAOS} = 0.5s^{-1}$

$$\omega_{LAOS} = \dot{\gamma}_{SF} = 0.5s^{-1}$$

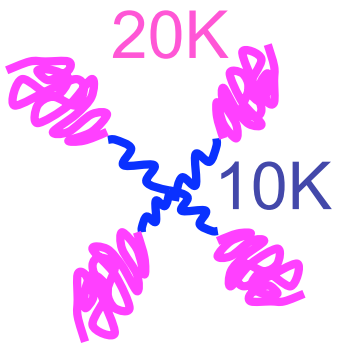
SF is more effective for cylinder orientation

Decrease in G due to LAOS



y = (m1*log(M0)+m2)/(m3-log(...

m1	226.77	1.79e+308
m2	2155.3	1.79e+308
m3	15.727	1.79e+308
R	1.6156e-27	NA
R	1	NA



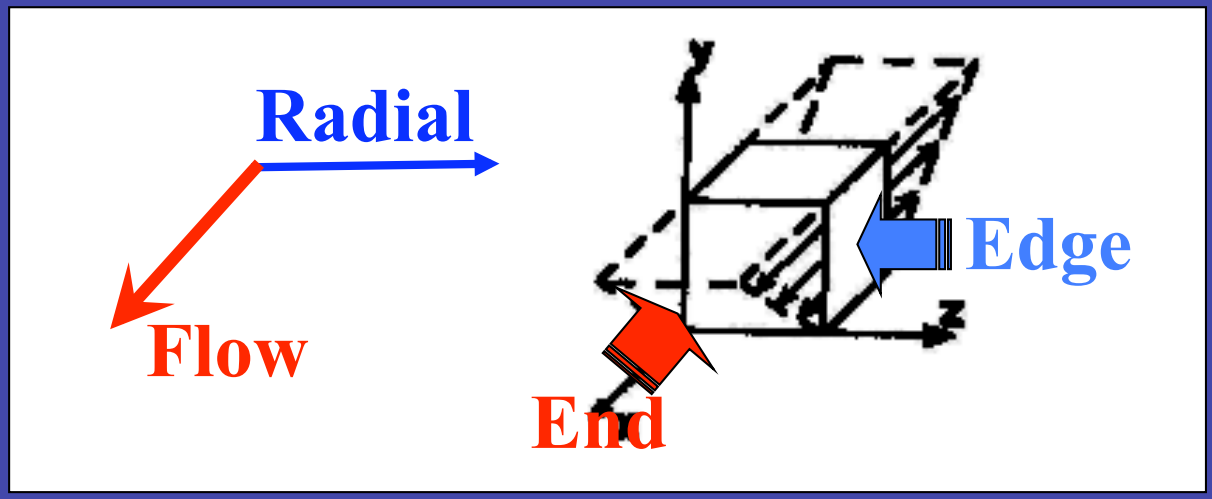
At 160°C, 180°C

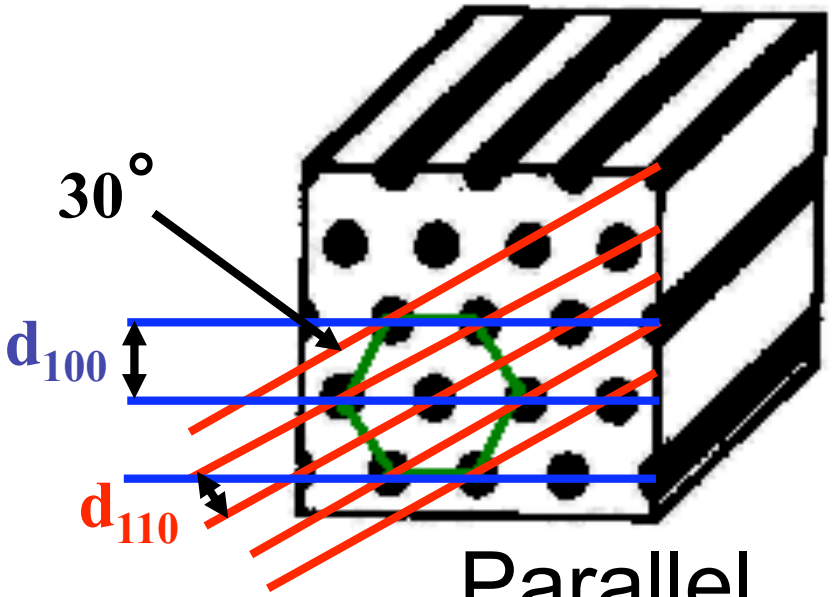
ω_{LAOS}↗ ⇨ G' ↘↗

For SF

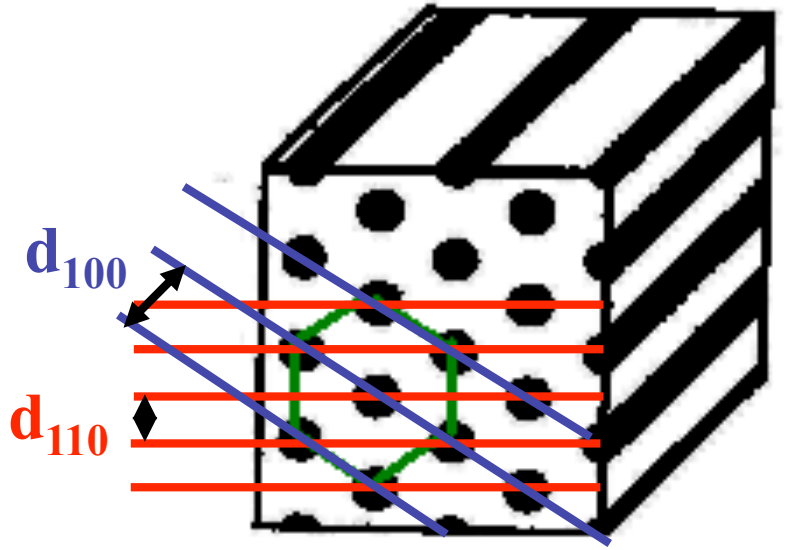
G'_{after} / G'_{before}=0.10

Orientation of Hexagonal Cylinders





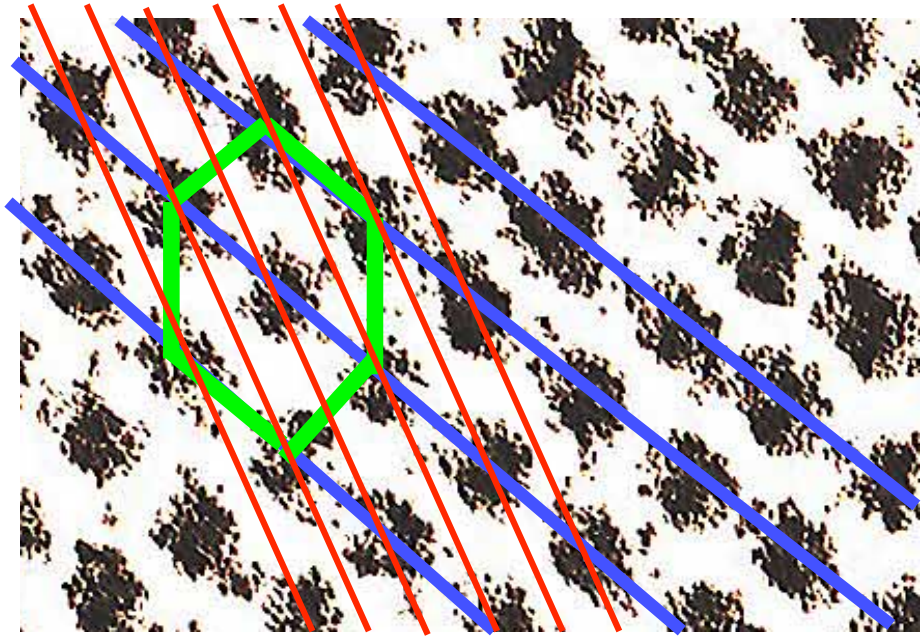
Parallel



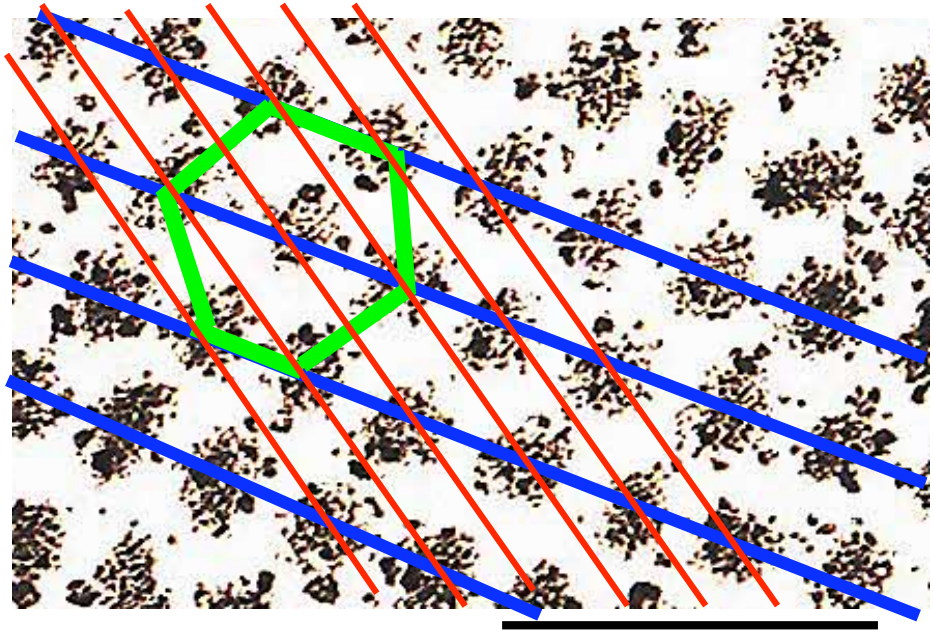
Perpendicular

4SB20 at $\omega_{LAOS} = \dot{\gamma}_{SF} = 0.5s^{-1}$ (160°C)

After LAOS



After SF

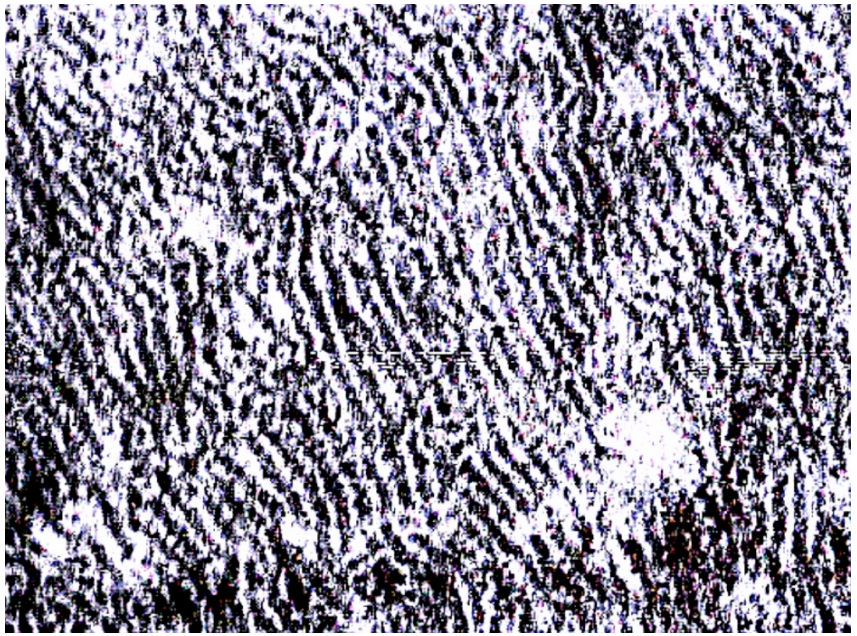


SF is more effective for Parallel Orientation

4SB20 after LAOS (ω_{LAOS} = 100s^{-1}, 160°C)

End

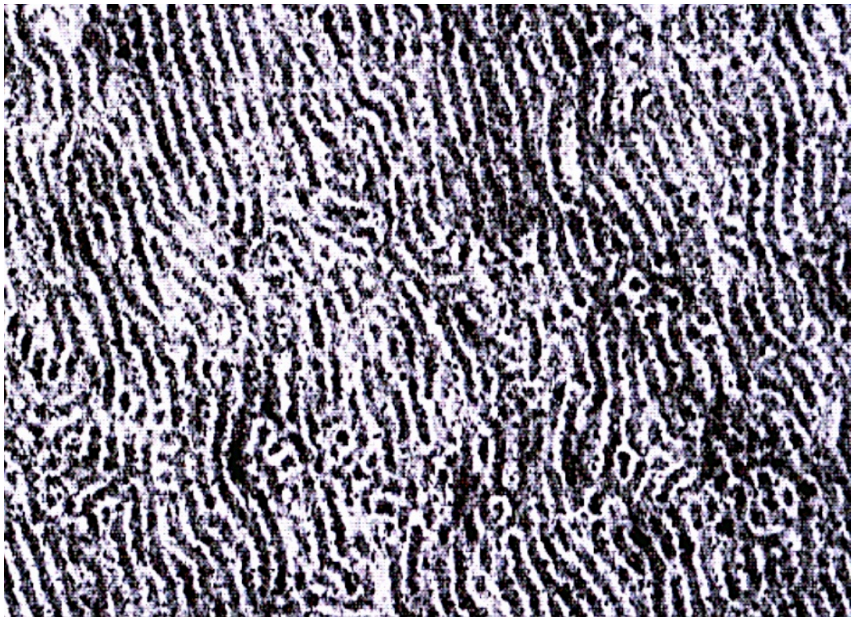
Flow ↙ Radial



100nm

Edge

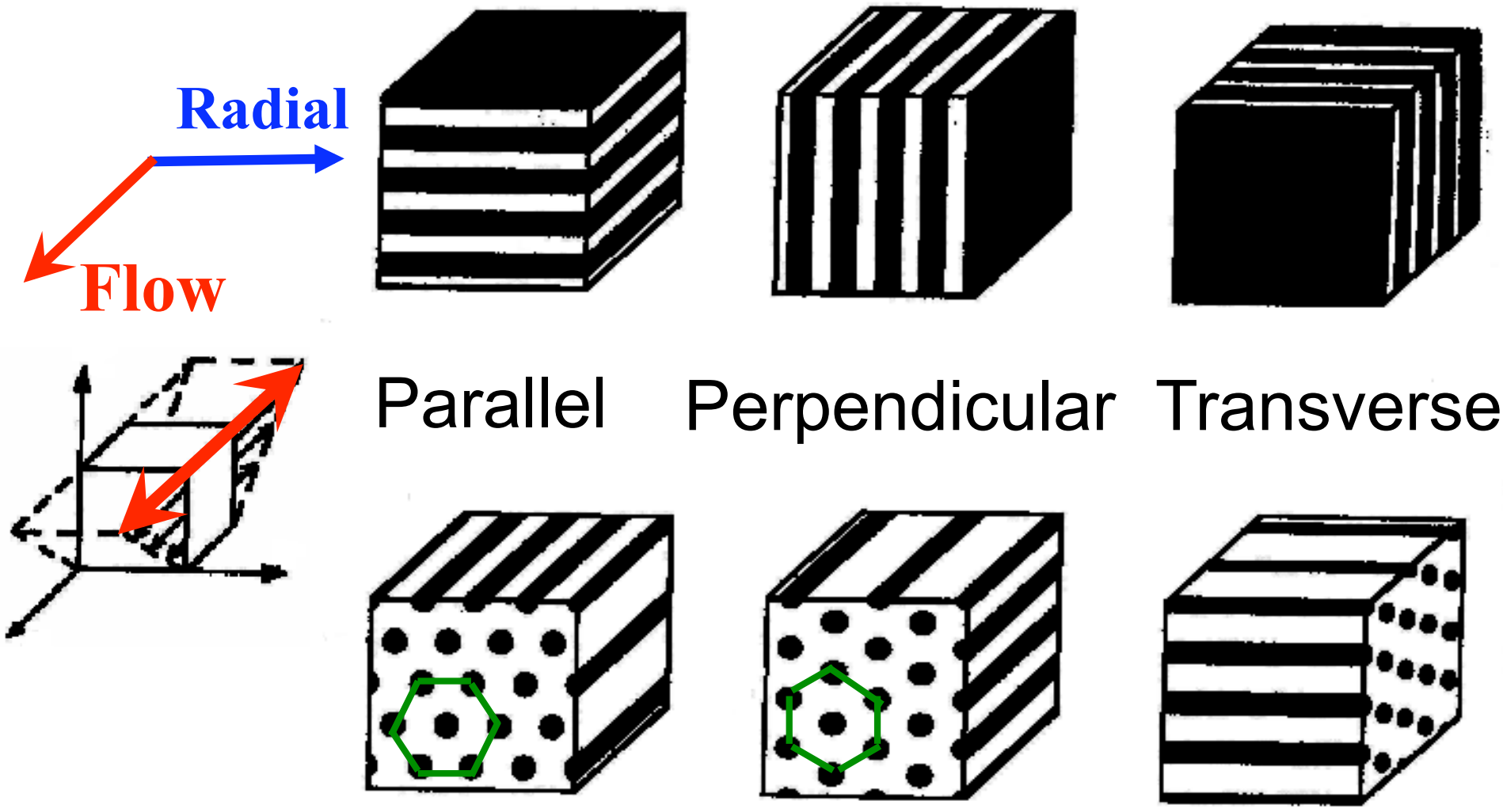
Radial ↙ Flow



100nm

Cylinders are perpendicular to the disc surface!!

Orientations of Lamellae and Cylinders



Conclusions

For lamellar-forming samples

1) In ordered state, G' ~ $\omega^{1/2}$.
2) After LAOS, G' decreases with increasing ω_{LAOS} due to parallel orientation.
3) Perpendicular orientation is also observed for low ω_{LAOS}.

For cylinder-forming samples

1) In ordered state, G' ~ $\omega^{1/(n+1)}$.
2) After LAOS, G' decreases with decreasing ω_{LAOS} (showing minimum) due to parallel orientation.
3) SF is more effective for parallel orientation.
4) For $\omega_{LAOS} > \omega_C$, cylinders orient perpendicular to disc.

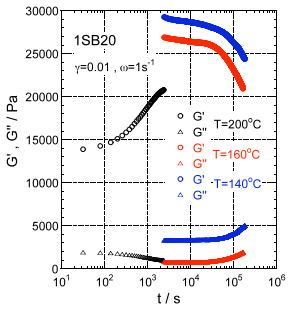
Time sweep of G’, G” for 1SB20

20K 10K

S B

C → G is fast

G → C is slow



G

G’

G

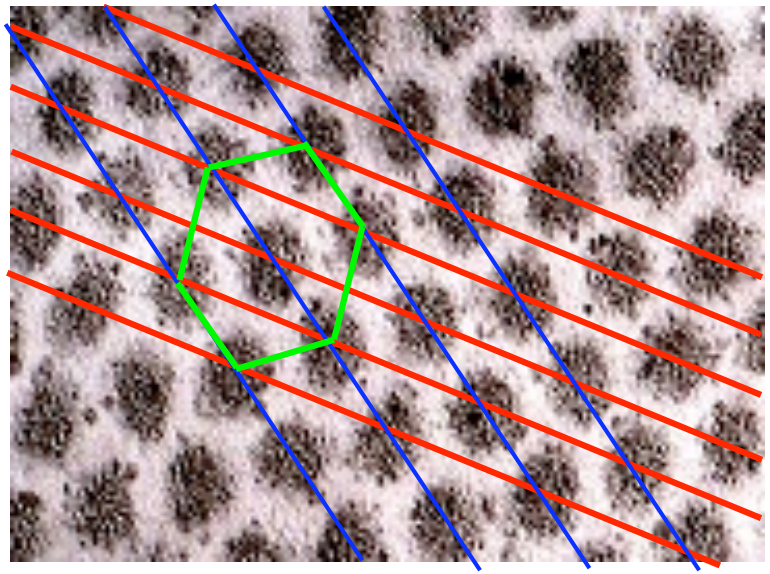
C

C

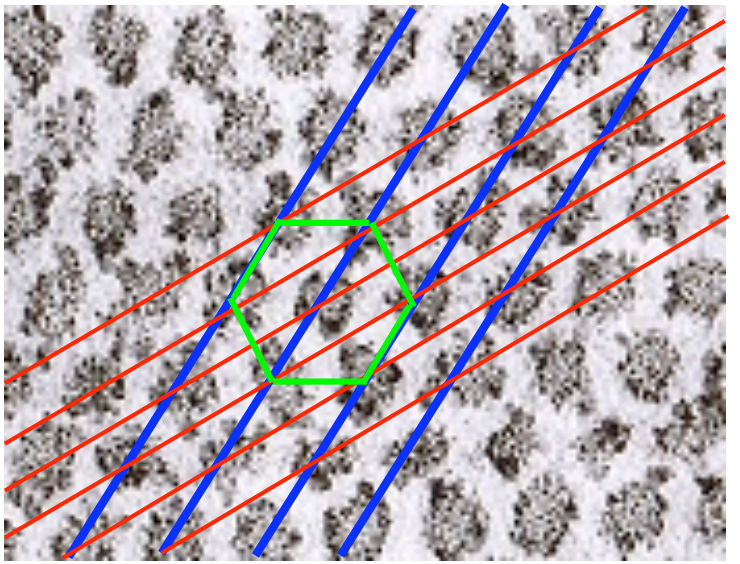
G”

2SB20 at $\omega_{LAOS} = \dot{\gamma}_{SF} = 0.5s^{-1}$ (160°C)

After LAOS



After SF



Perpendicular orientation

Parallel orientation

Theories for Slow Relaxation behavior

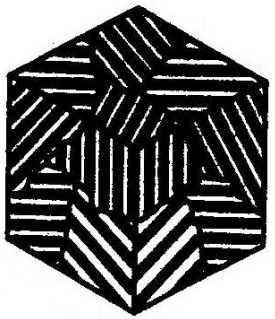
Lamellar-forming, Poly-grains (randomly oriented)

Kawasaki-Onuki (1990)

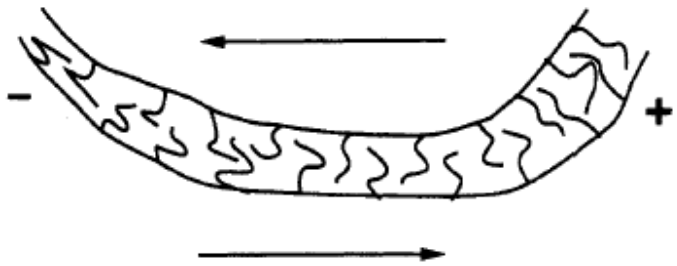
Hydrodynamic mode of lamellar motion
Overdamped second-sound mode

$$G'(\omega) \cong G''(\omega) \cong \frac{\pi}{24\sqrt{2}} (B\eta_0)^{1/2}\omega^{1/2}$$

B : bending modulus of lamella
η_0 : viscosity in the disordered phase



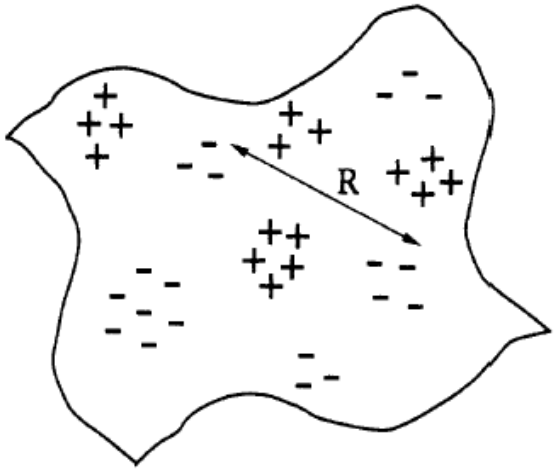
randomly oriented



Rubinstein-Obukhov (1993)

Collective diffusion of copolymer chains along the interface controlled by defects

$$G'(\omega) \cong G''(\omega) \sim \omega^{1/2}$$



Mechanisms of lamellar orientation

1. Selective rotation of grains
2. Selective melting and reformation of lamellae
3. Defect migration
4. Reduction of mechanical resistance
5. Tube orientation (for entangled chains)
6. Coupling of the lamella motion and the shear field (shear-induced lamella formation)

H.Watanabe in “Structure and Properties of Multiphase Polymeric Materials”, pp. 317-360, Marcel Dekker, New York (1998)