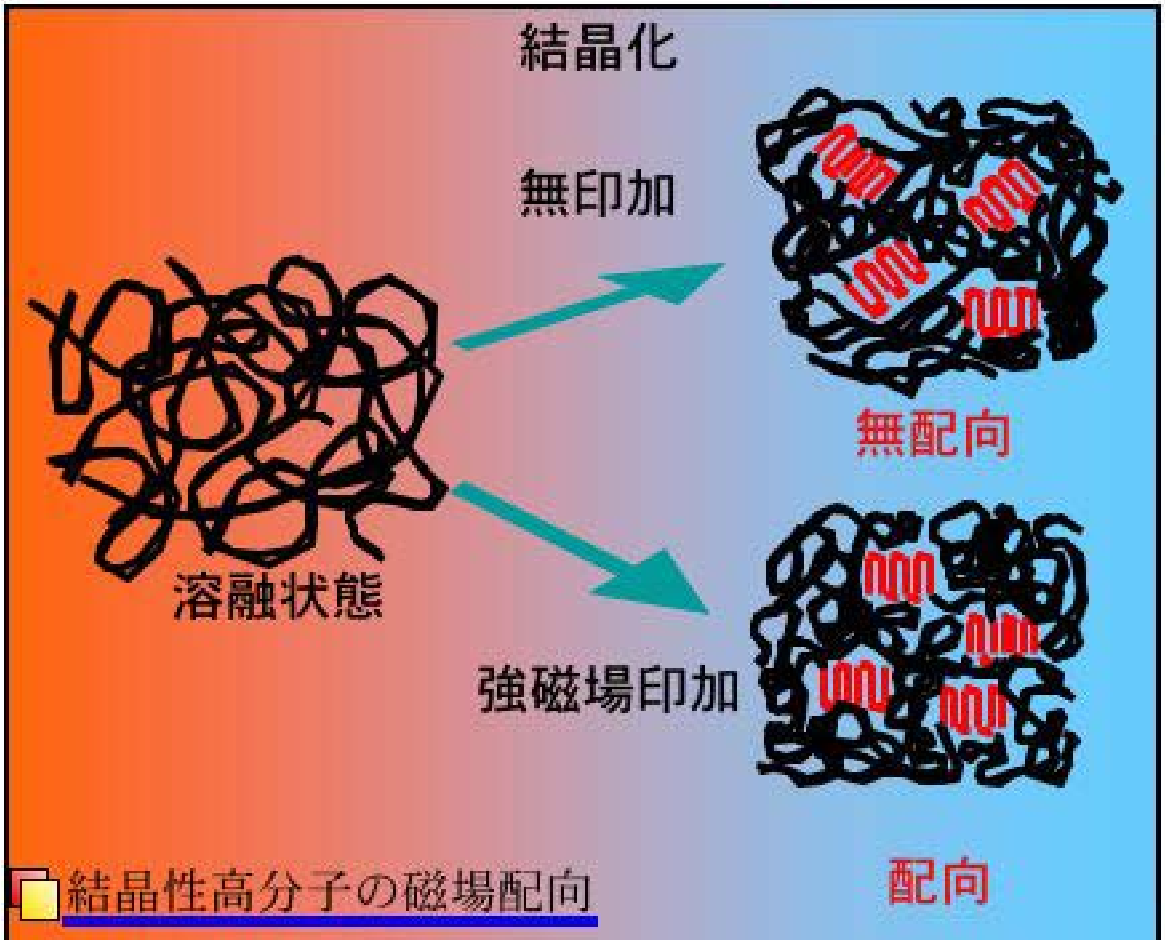
研究の背景

結晶性高分子の磁場配向



磁場配向の条件

1.反磁性磁化率の異方性があること

2.配向の秩序を持った サブミクロンオーダー のドメインの存在

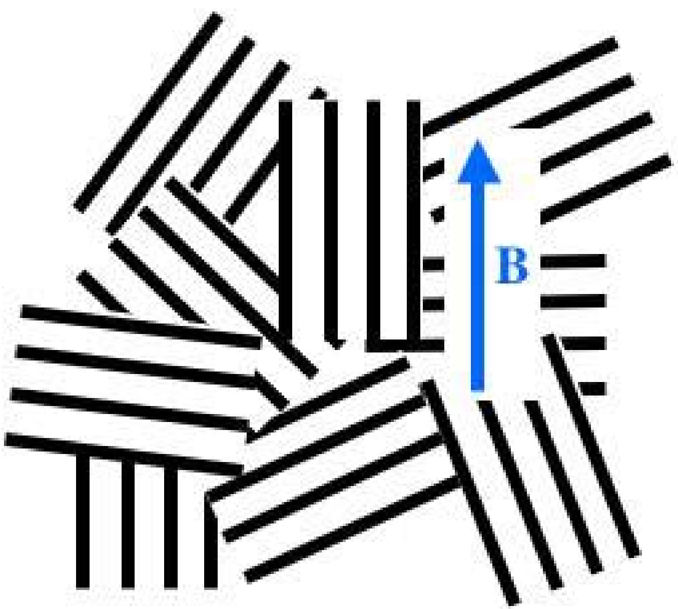
3.低粘度の環境

T. Kimura ,T .Kawai ,Y. Sakamoto. *Polymer* 2000;41:809.
T. Kimura ,T. Kawai. *Polymer* 2000;41:155.

However, our previous studies have revealed that …

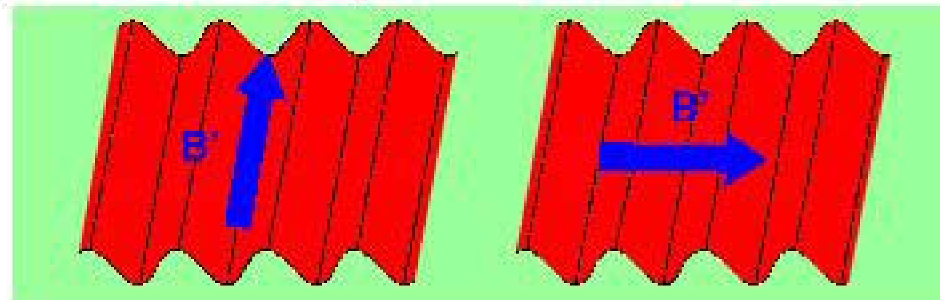
Magnetic orientation was not very feasible for amorphous block copolymer microdomains.

Magnetic torque is not promising!



Convert the plan

Magnetic torque ⇨ **Local controls of interfacial shapes**



The magnetic field causes…

Symmetry Breaking & Mode Selection for Undulation of Interfaces

Formed cylinders are necessarily oriented parallel to the applied magnetic filed.

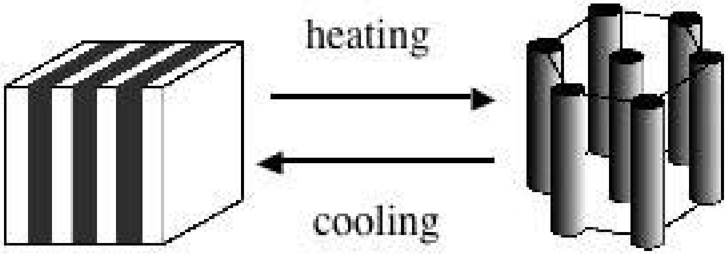
Spontaneous undulation of the interface

→ **Can be induced by a morphological transition (OOT)**

① Thermally reversible OOT

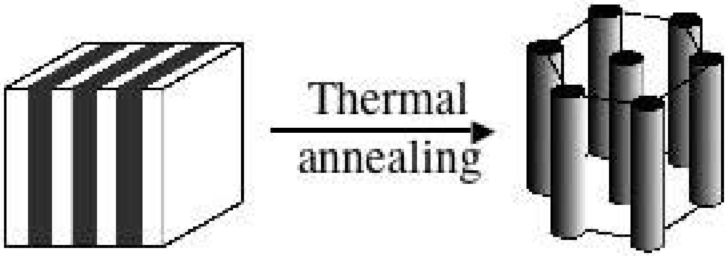
This takes place only in a narrow window of composition.

→ Not universally applicable.



② Irreversible OOT

This can be induced by thermal annealing of non-equilibrium morphology that is kinetically frozen in, due to glass transition, etc.



The non-equilibrium morphology should be prepared in advance. → Can be performed by solution casting with a selective solvent

→ **A single method, *solution casting with a selective solvent* will meet both of the requirements!!!**

sample

polystyrene-*block*-poly(ethylenebutylene)
-*block*-polystyrene (SEBS) triblock copolymer

$Mn = 6.6\times10^4$, $Mw / Mn = 1.03$

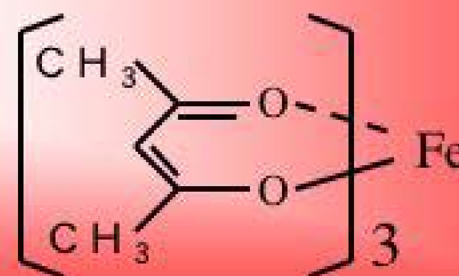
Volume fraction of PS $\varphi_{PS} = 0.16$

Metal Chelate

Tris(2,4-pentanedionato)iron(Ⅲ)　(Fe(Ⅲ)-AA)

Paramagnetic Powder at RT (dark red)

Melting temperature 178~186℃



Step 1 Casting in a high magnetic field

Dissolve SEBS sample in dichloromethane at the polymer concentration 5wt%.

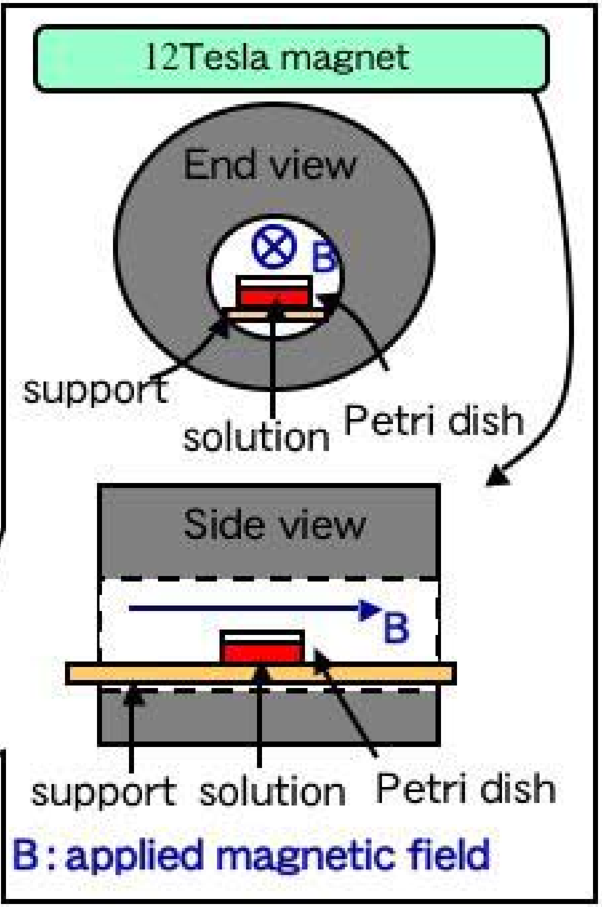
↓

Add the metal chelate 5wt% with respect to polymers.

↓

Place the Petri dish containing the casting solution in 12Tesla super conducting magnet.

Solvent evaporation in the magnet at room temperature for ca. 12 hours for complete evaporation.



Step 2 Thermal annealing in a high magnetic field

190℃、3 hours

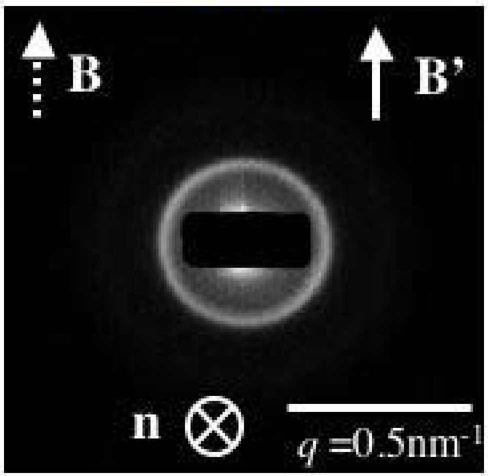
Structural Analyses by Small-angle X-ray Scattering

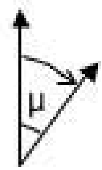
At Photon Factory (KEK), Tsukuba Japan (BL-9C , 15A)

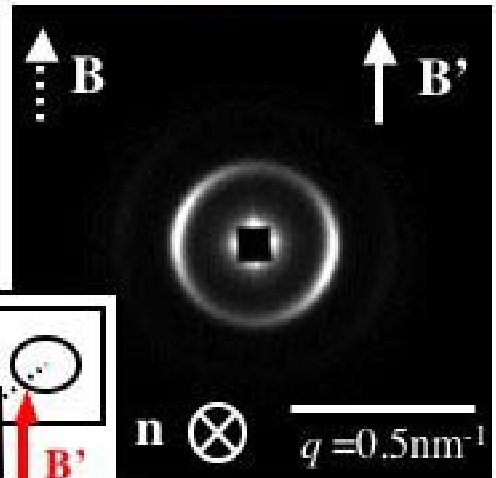
Roles of OOT and Interfacial Undulation

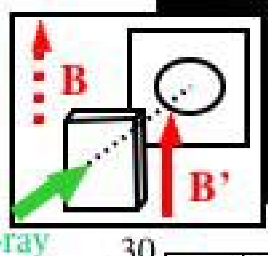
Cast & Thermal Annealing at 12T

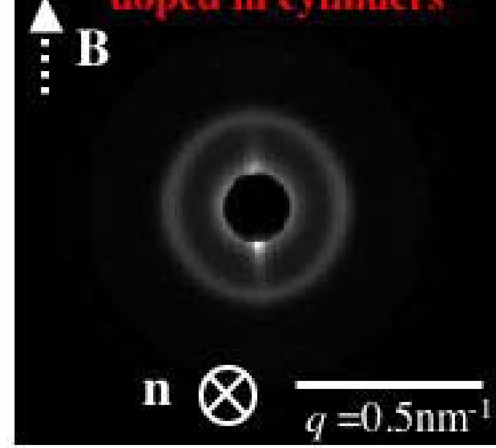
Direct Cylinders SEBS16 cast from Toluene	via OOT SEBS16 cast from Dichloromethane	Direct Cylinders with chelate SEBS8 cast from Dichloromethane
Cylinders (as-cast) Cylinders (annealed)	Lamellae (as-cast) Cylinders (annealed)	Cylinders (as-cast) No annealing
No chelate	No chelate	Chelate 5wt% selectively doped in cylinders

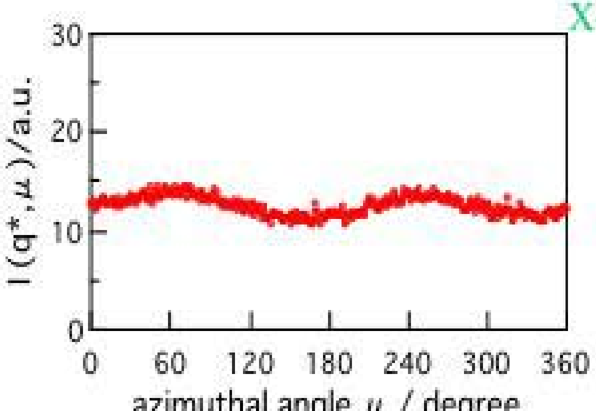


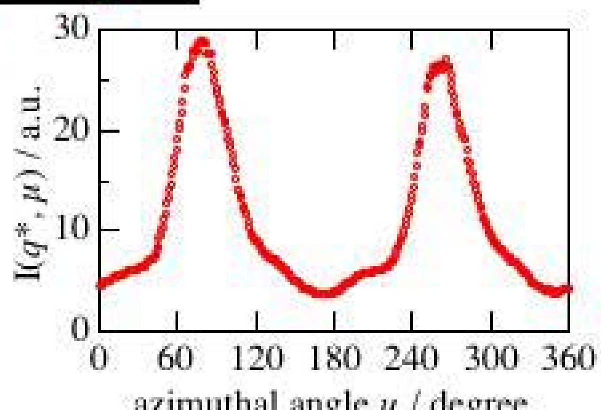


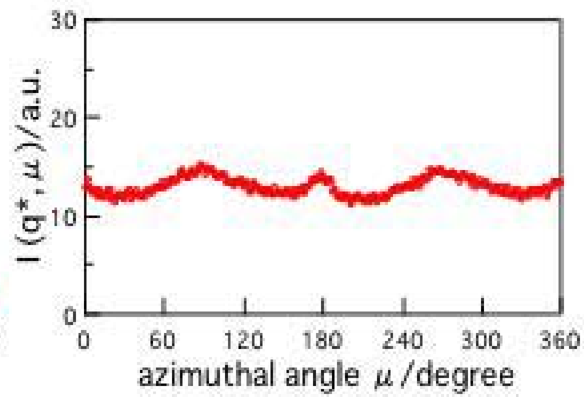






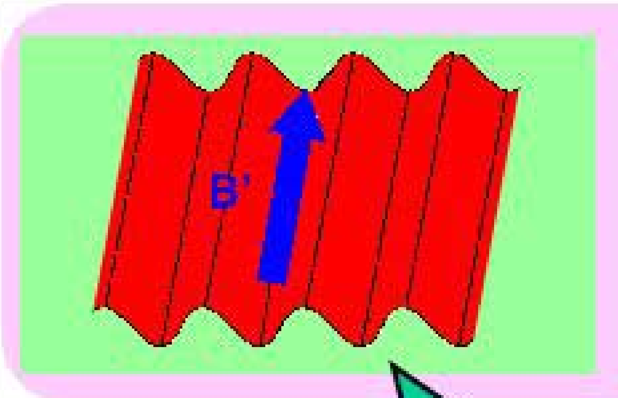




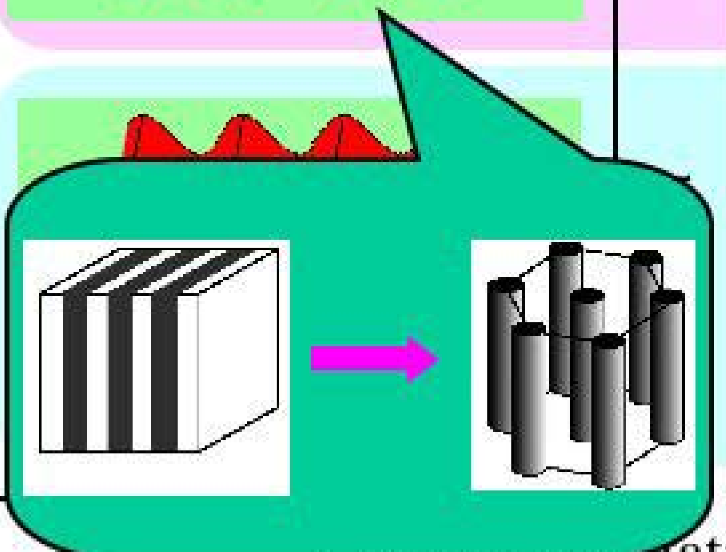


Orientation of Cylinders (// B')

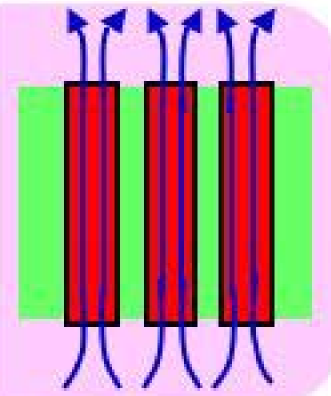
Undulation of the lamellar interface

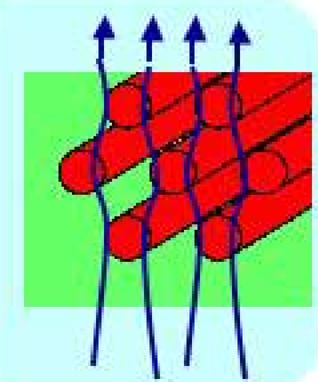


stable



Stability of cylinders under a magnetic field (Chelate selectively doped in cylinders)





The lines of the magnetic force should

- Go through the region having relatively large susceptibility
- Be free from distortion

$$\chi_c > \chi_m$$

χ_c : average susceptibility in cylinders

χ_m : average susceptibility in the matrix

Parallel orientation of cylinders can be ascribed to *symmetry breaking and mode selection*

Effect of Chelate Doping on Annealed Films

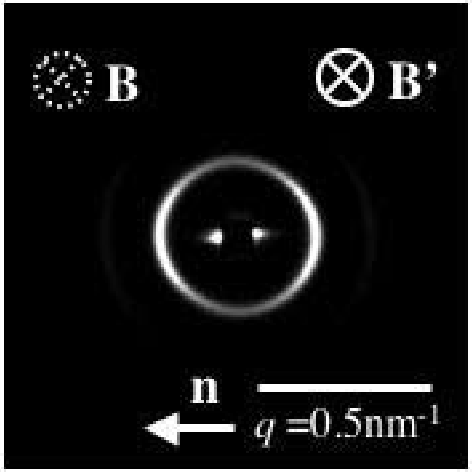
(Non-equilibrium lamellae were well ordered parallel to the substrate.)

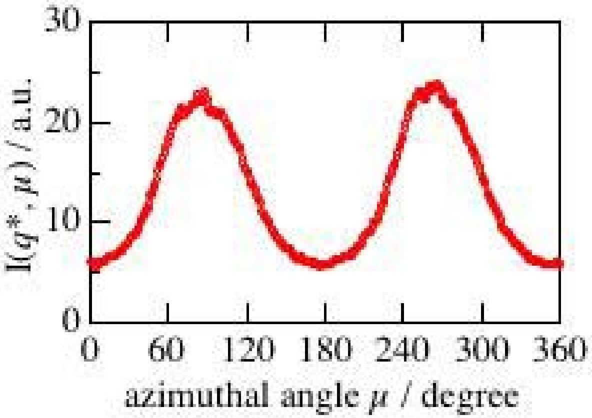
Cast & Thermal Annealing at 12Tesla, 190℃, 3h

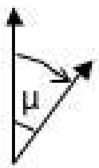
B: magnetic field during casting **B':** magnetic field during annealing

n: film normal

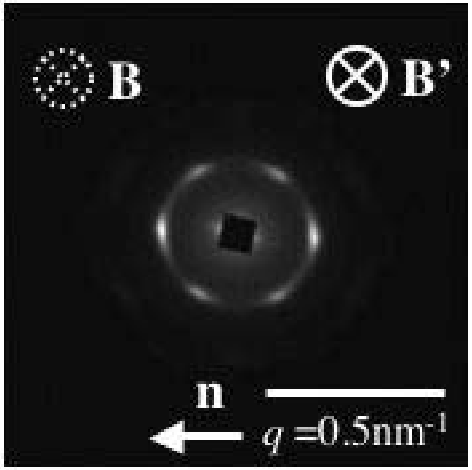
No chelate

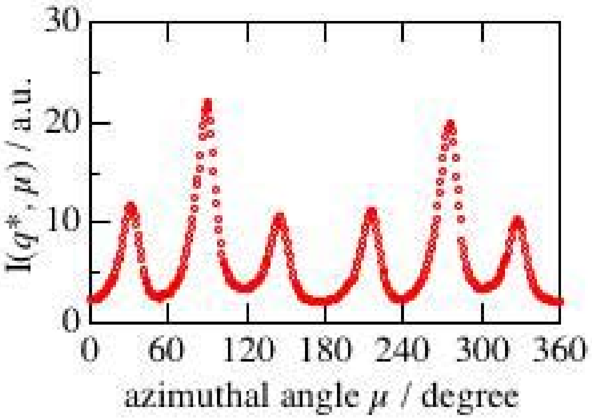


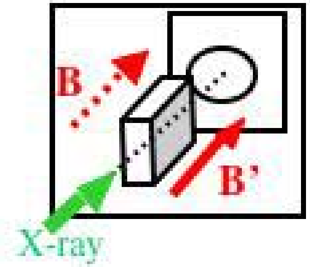




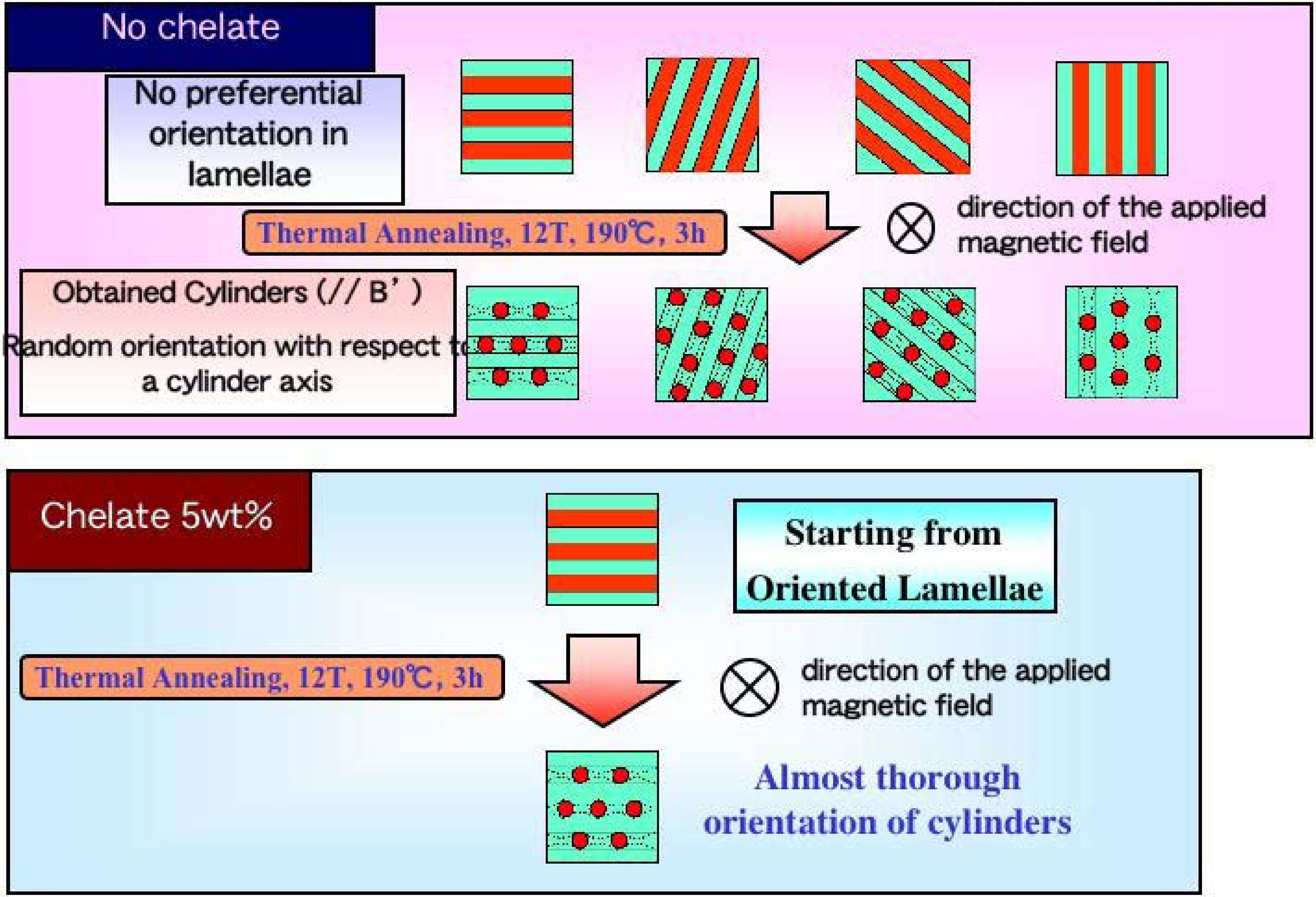
Chelate 5wt%







Effects of Orientation of the Original Lamellae



薄膜試料に与える強磁場の効果

用いた試料は、SEBSトリブロック共重合体
ポリスチレン (PS) の体積分率　$\phi_{PS} = 0.16$
数平均分子量　$M_n = 6.6 \times 10^4$
多分散指数　$M_w / M_n = 1.03$

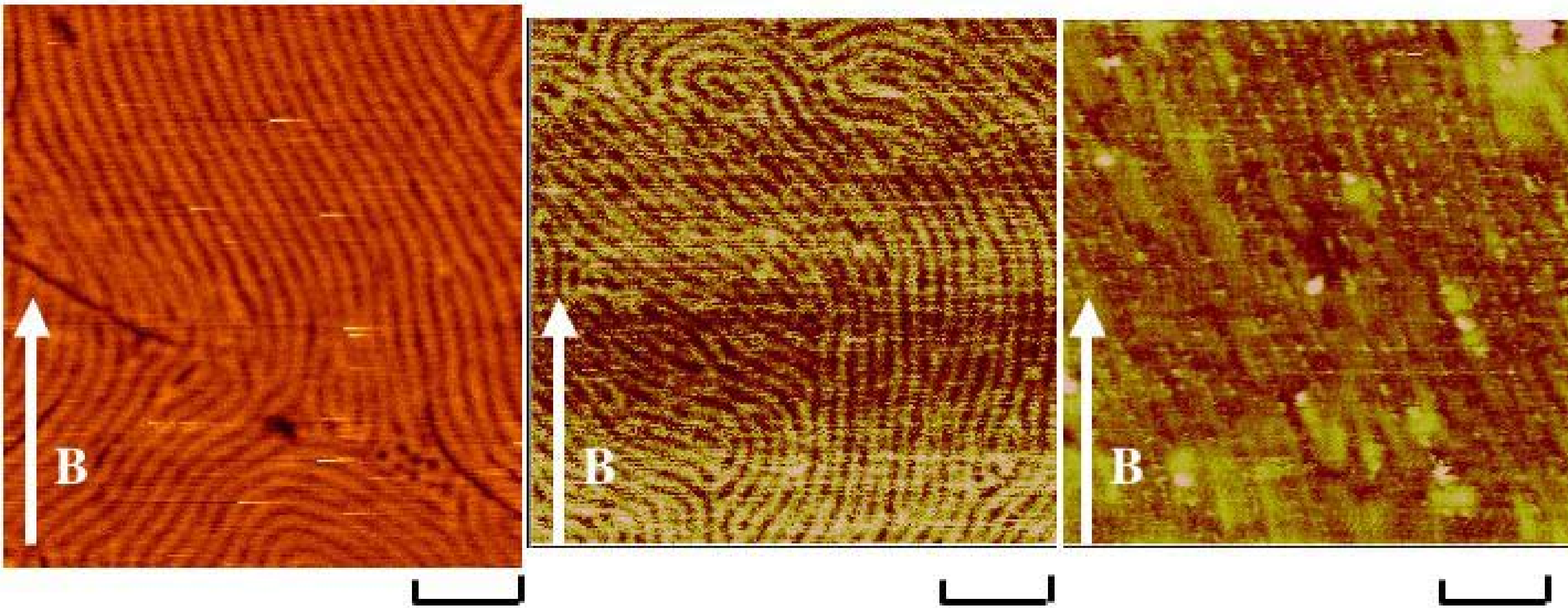
↓

PS成分がシリンダー状構造 (直径 約13 nm)を形成する
秩序-無秩序転移温度　$T_{ODT} = 247$ ℃　（粘弾性測定）

溶媒としてトルエンを用いて、1.0 wt%の溶液を作製
この溶液をシリコンウェハー上に滴下
スピンコート法を用いて薄膜を作製
膜厚　約２０nm

超薄膜中におけるシリンダー構造の強磁場配向（基板と平行の場合）

About 20nm thick | About 60nm thick | About 260nm thick



200 nm | 200 nm | 200 nm

Thermal Annealing (180 ℃, 3 hours) | Thermal Annealing (180 ℃, 5 hours) | Thermal Annealing (180 ℃, 5 hours)

超薄膜中におけるシリンダー構造の強磁場配向（基板と垂直の場合）