Cheiron Summer School (2008. 9. 29 – 10. 8)

Small-Angle X-Ray Scattering (2): Grazing Incidence X-Ray Scattering & Solution X-Ray Scattering

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PAL 포항가속기연구소 POHANG ACCELERATOR LABORATORY

Outline

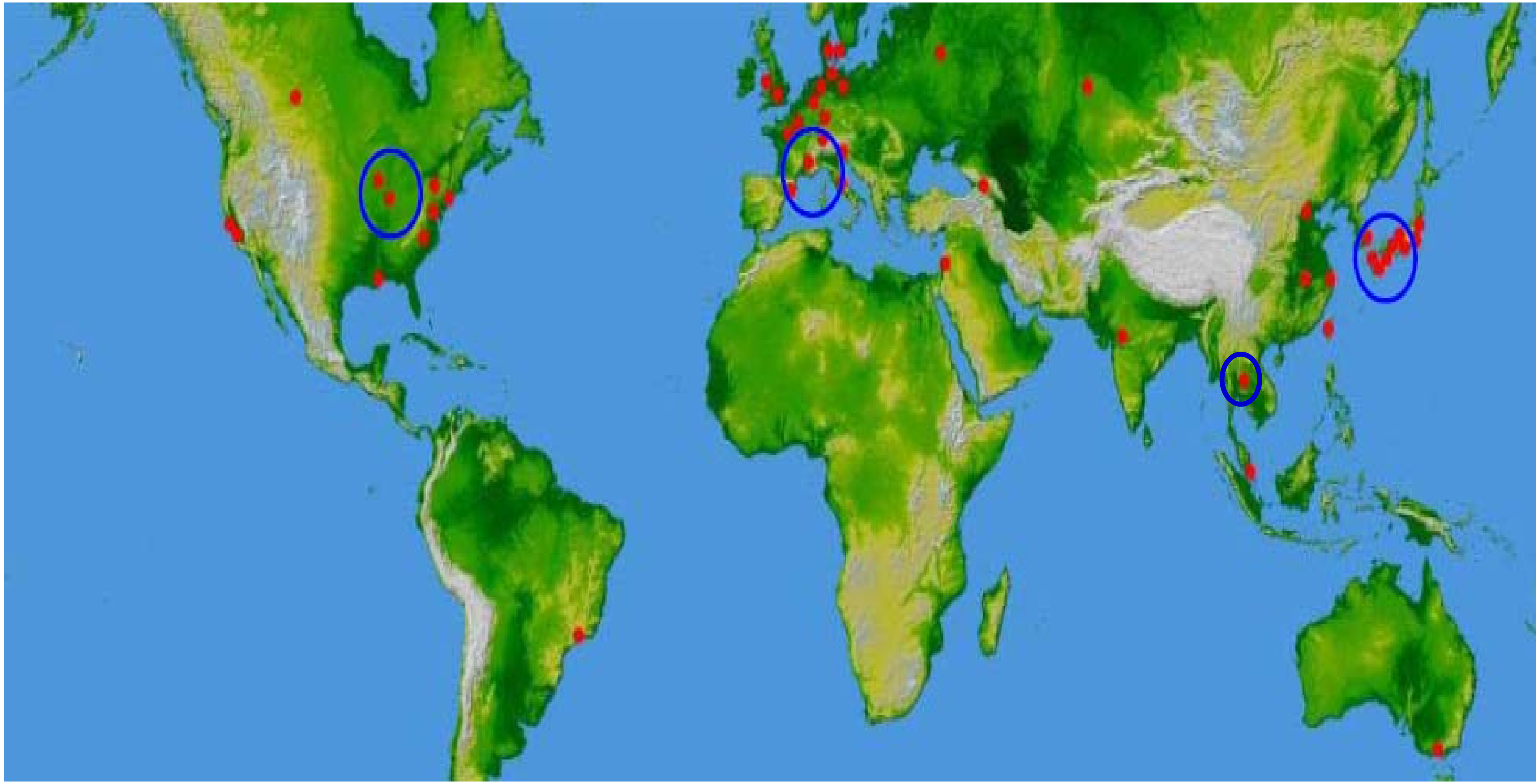
A. Introduction – Pohang Light Source & Postech
B. Optics, Beamlines and Equipments of SAXS
C. Fundamentals of SAXS

D. Fundamentals of Grazing Incidence X-Ray Scattering (GIXS)
E. Applications of GIXS in Nano-Science and Technology
   12 Examples of Recent Research Results

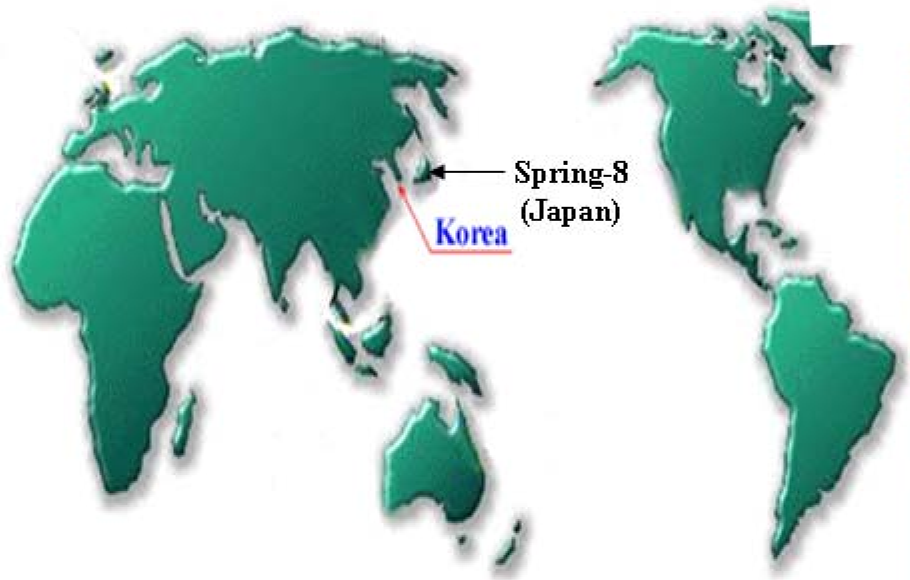
F. Solution X-Ray Scattering

G. Conclusions – I, II
H. References
I. Coworkers
J. M. Ree's Group at Postech

Synchrotron Radiation Facilities

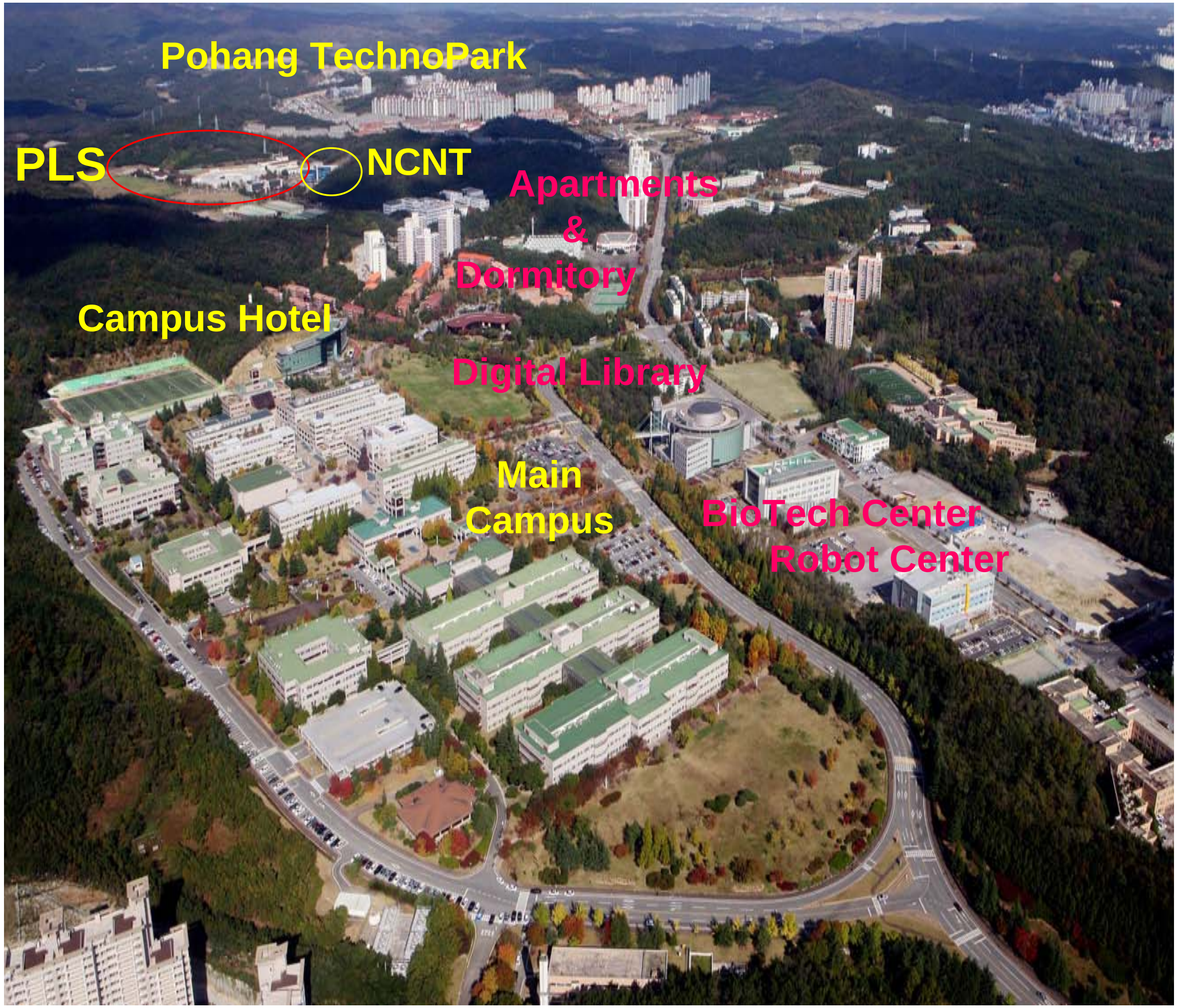


PAL

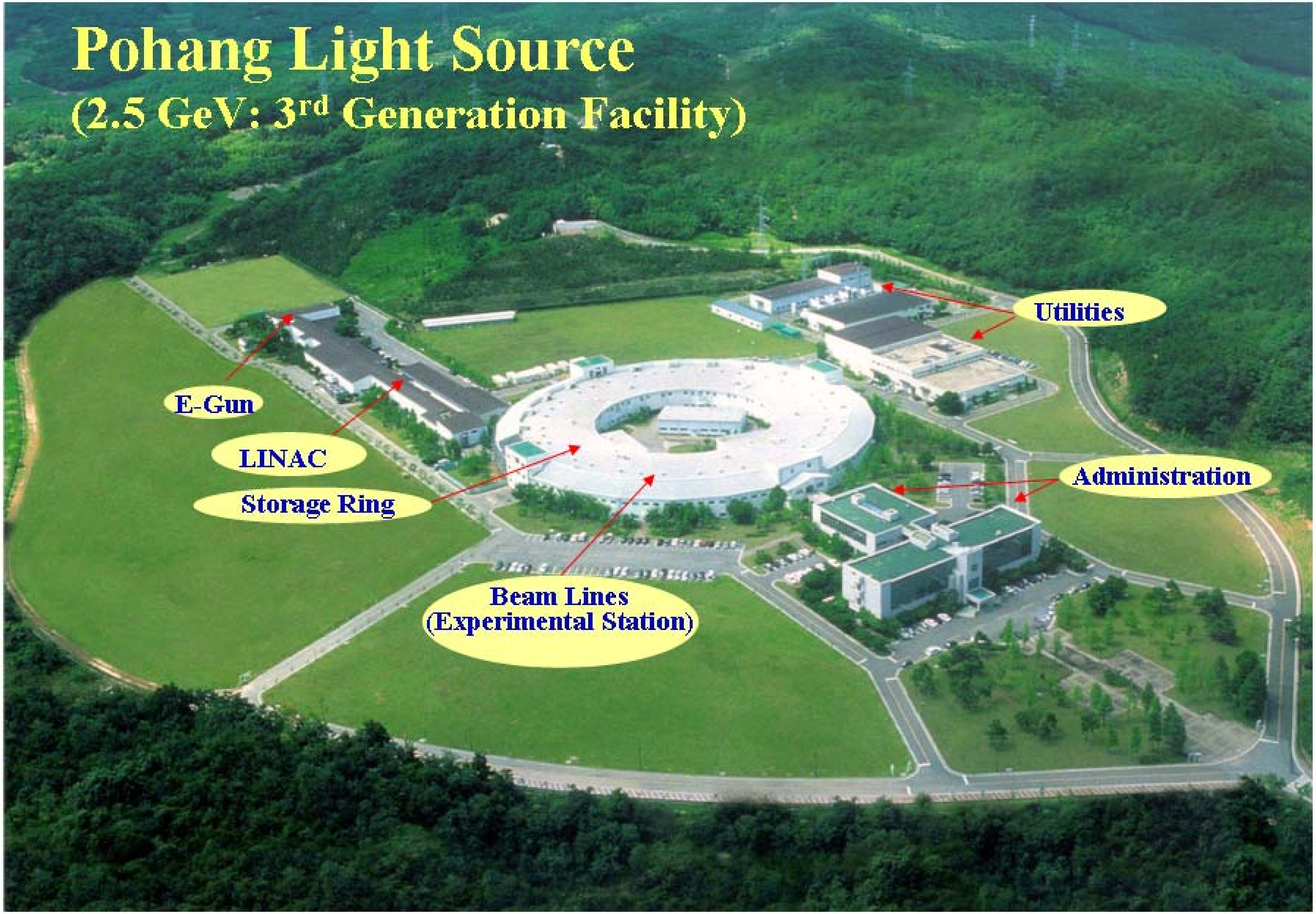

Spring-8
(Japan)
Korea


Kimpo International Airport
Seoul
Seoul Station
Express bus Station
Pohang
Pusan
Kimhae International Airport
Cheju Island


Korea
Seoul
Daejeon
Pohang
Gwangju
Busan

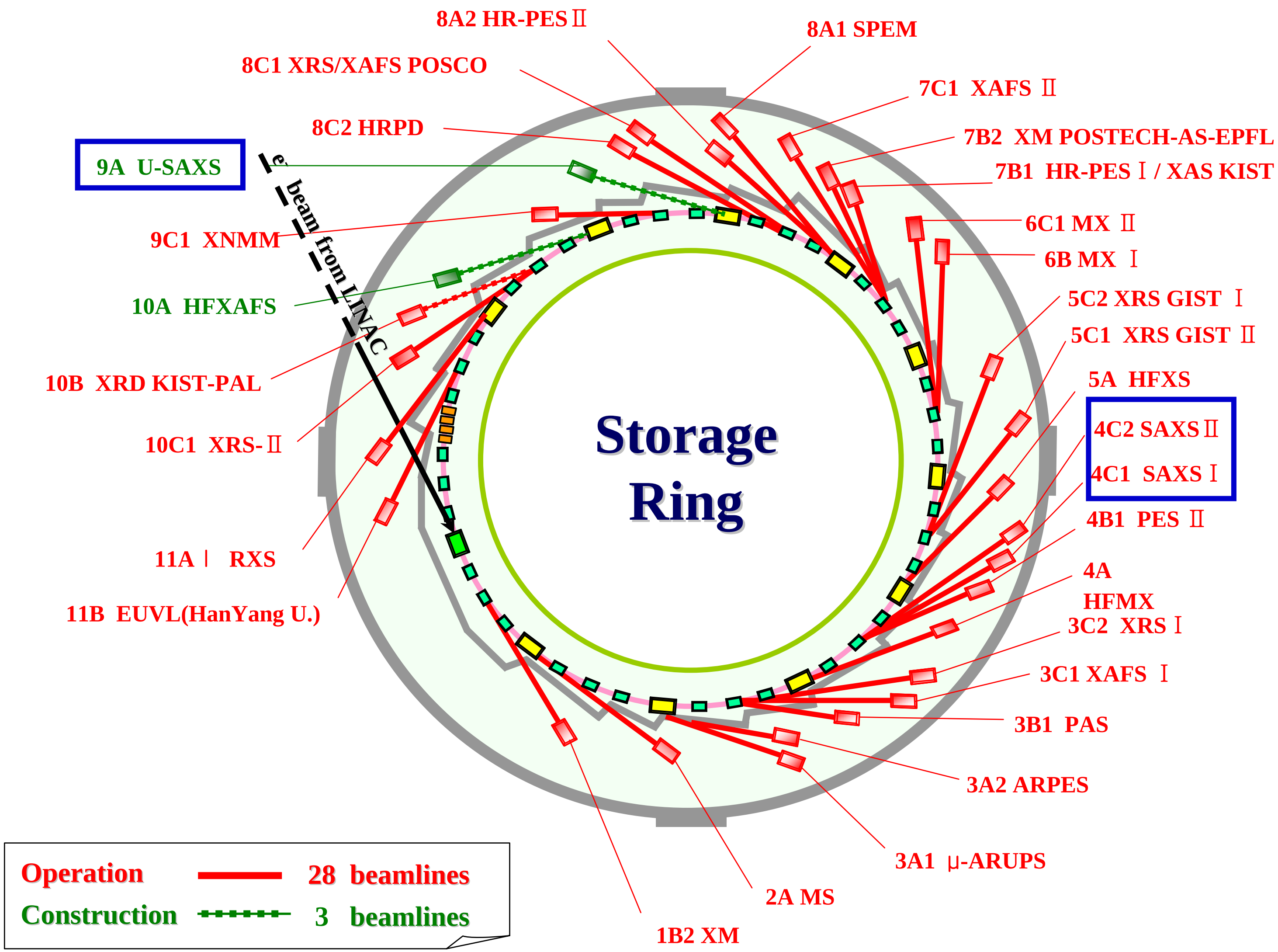


POSTECH CAMPUS


Pohang Light Source
(2.5 GeV: 3rd Generation Facility)
Utilities
E-Gun
LINAC
Storage Ring
Administration
Beam Lines
(Experimental Station)

September 2008

PLS Beamline Status



* fs-THz BL : Technical Building II

Strategy for PLS' Future

1. Current Synchrotron Facility (3rd Generation)

(1) Top-Up Mode Operation (2008-2010)
(2) Major Upgrade -- 100 M$(US) (2009-2011)
- **Smaller Emittance: 5 nm·rad**
- **Higher Beam Flux**
- **More Insertion Device Beam Lines: 20-24**

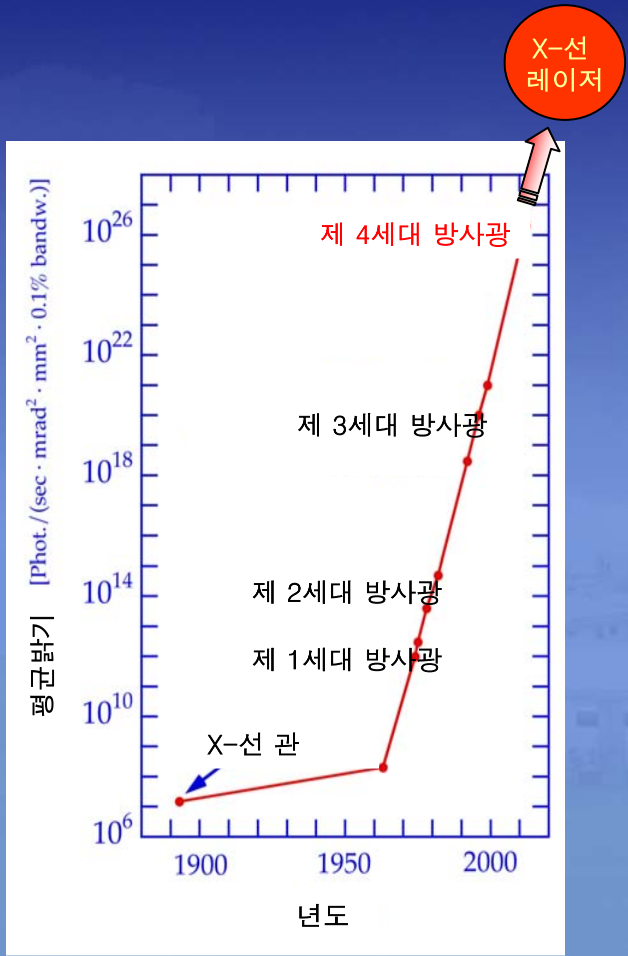
2. XFEL (X-ray Free Electron Laser) Facility (4th Generation)

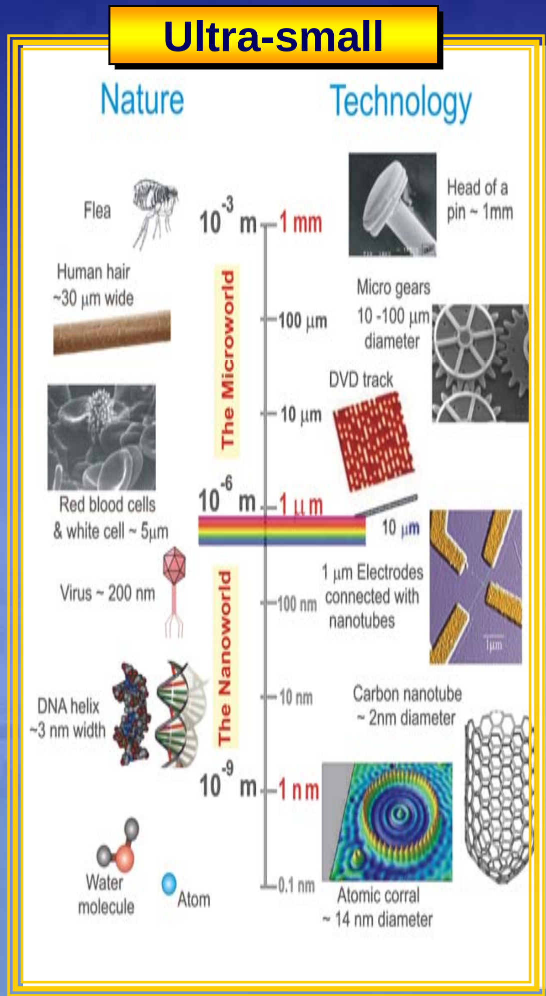
(1) Energy: 10 GeV (0.1 nm λ)
(2) 3 X-ray BLs & 3 VUV BLs
(3) Budget: 400 M$(US)
(2010-2013)

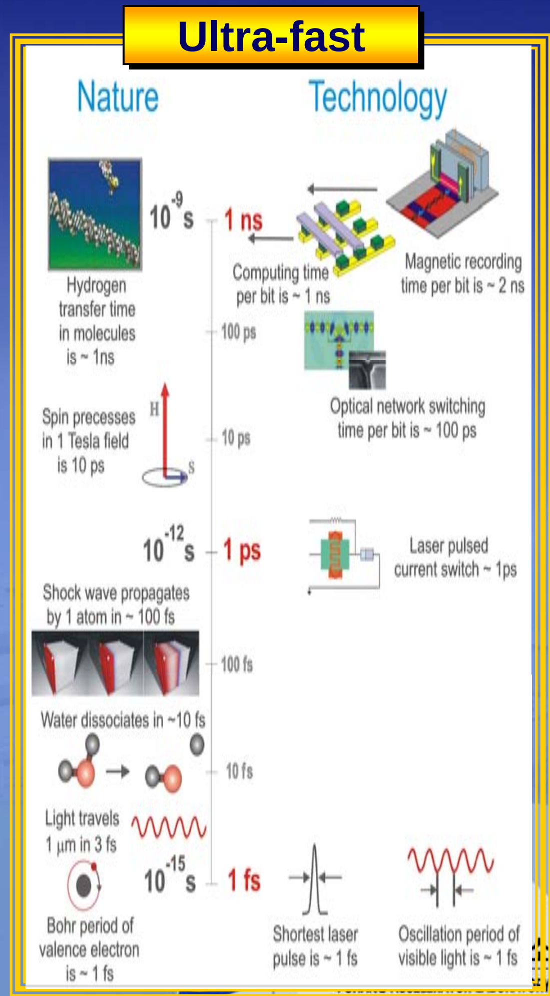
*** Coherent X-ray Beam (X-ray Laser)**
*** Super-high Beam Flux**
*** Nanoscale Beam Size**
*** Femtosecond Pulse X-ray Beam**

Applications of XFEL In Science

XFEL
- Coherent beam source
- Higher flux beam source
- Smaller size beam source
- Pulse beam source (~ fs)







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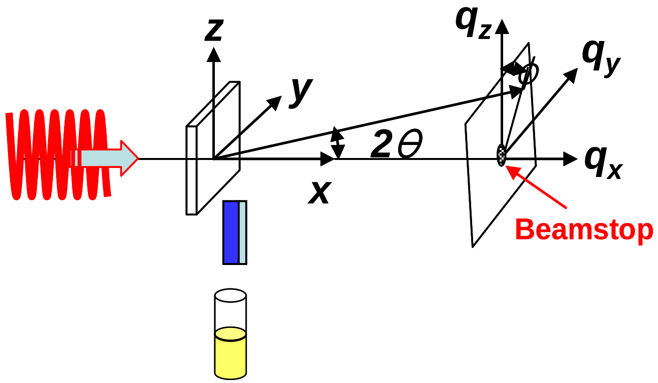
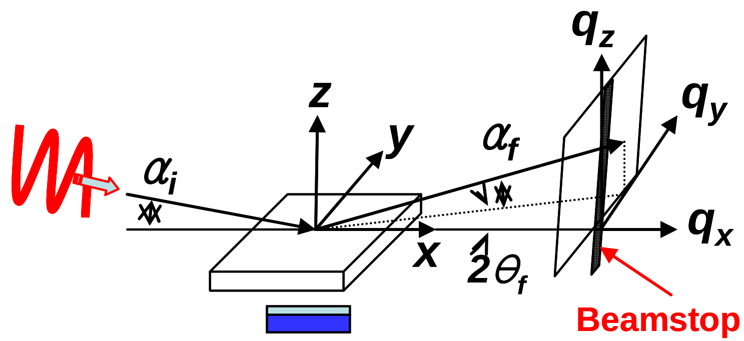
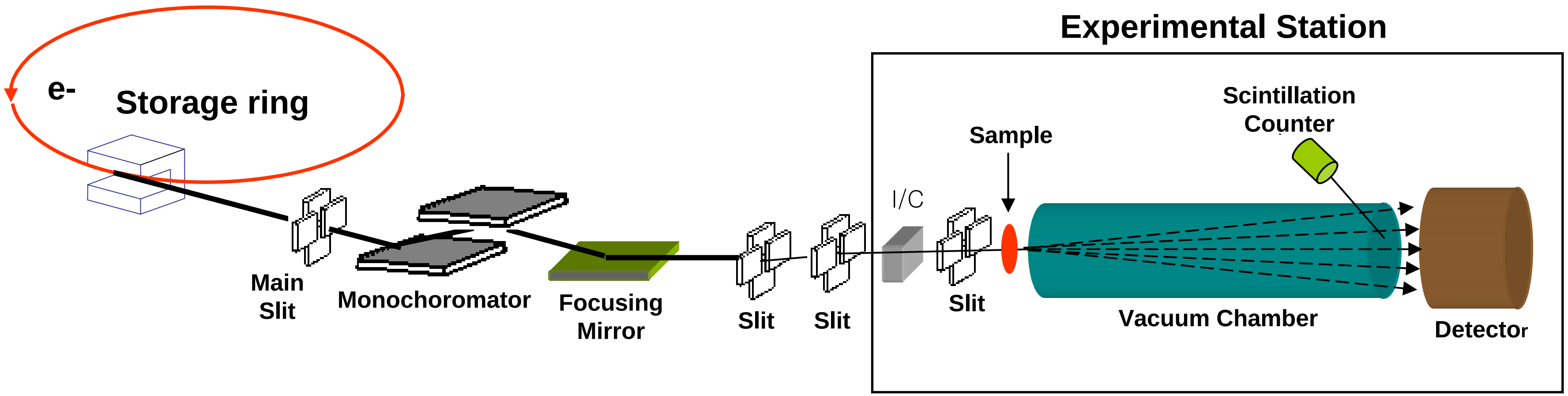
Optics of
Small Angle X-ray Scattering (SAXS)





TSAXS **GISAXS**

SAXS Beamlines



X-rays at the sample

- **Photon flux (monochoromatic, focusing) :**

  10^{11} – 10^{18} photons/sec/mm^2 at 8 keV

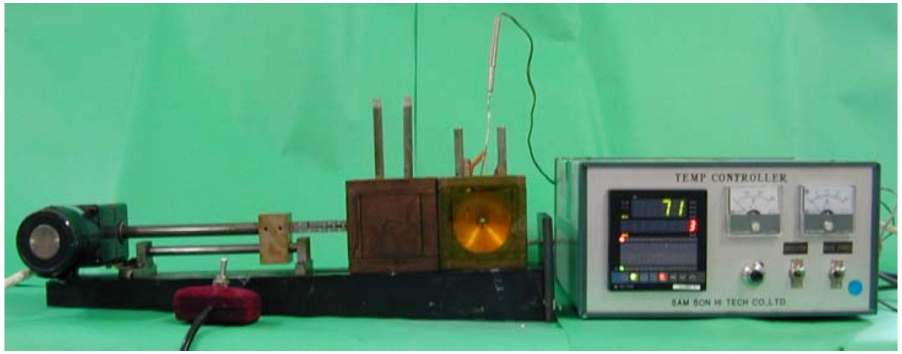
- **Beam size : < 0.8 × 0.8 mm^2**

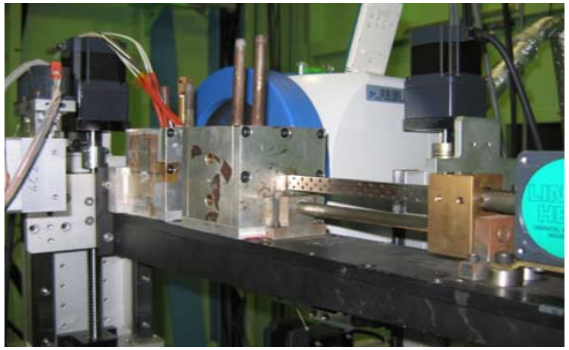
2-D CCD X-Ray Detector

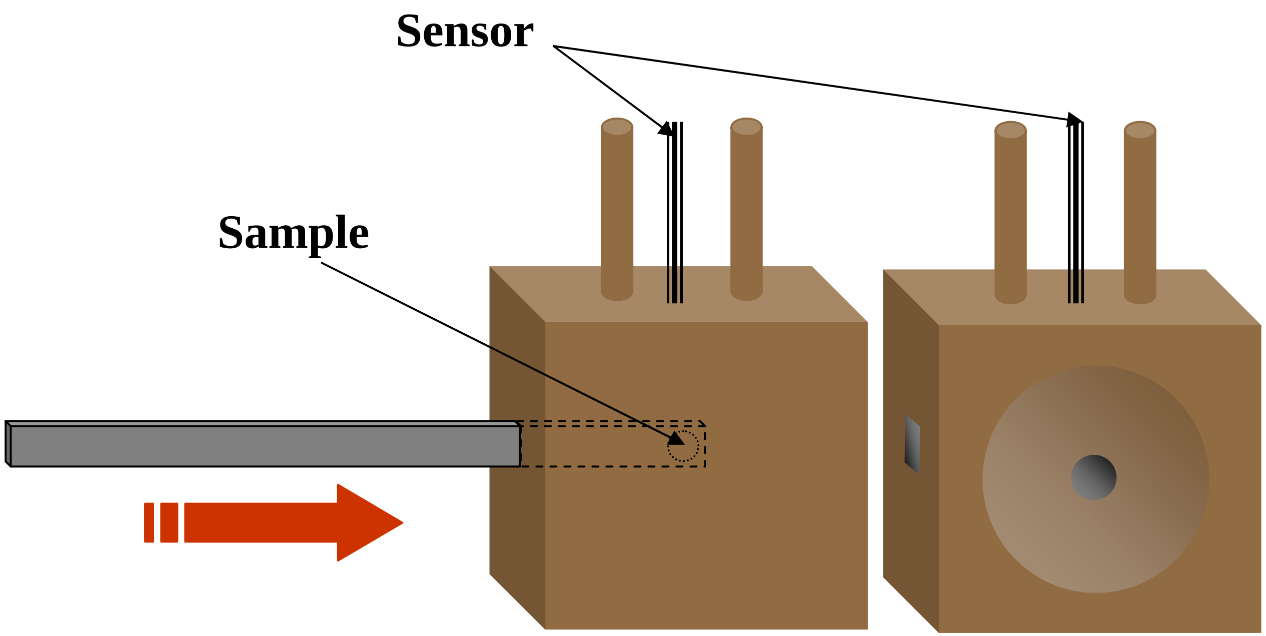
Roper Scientific

MAR research

Device for Temperature Jumping







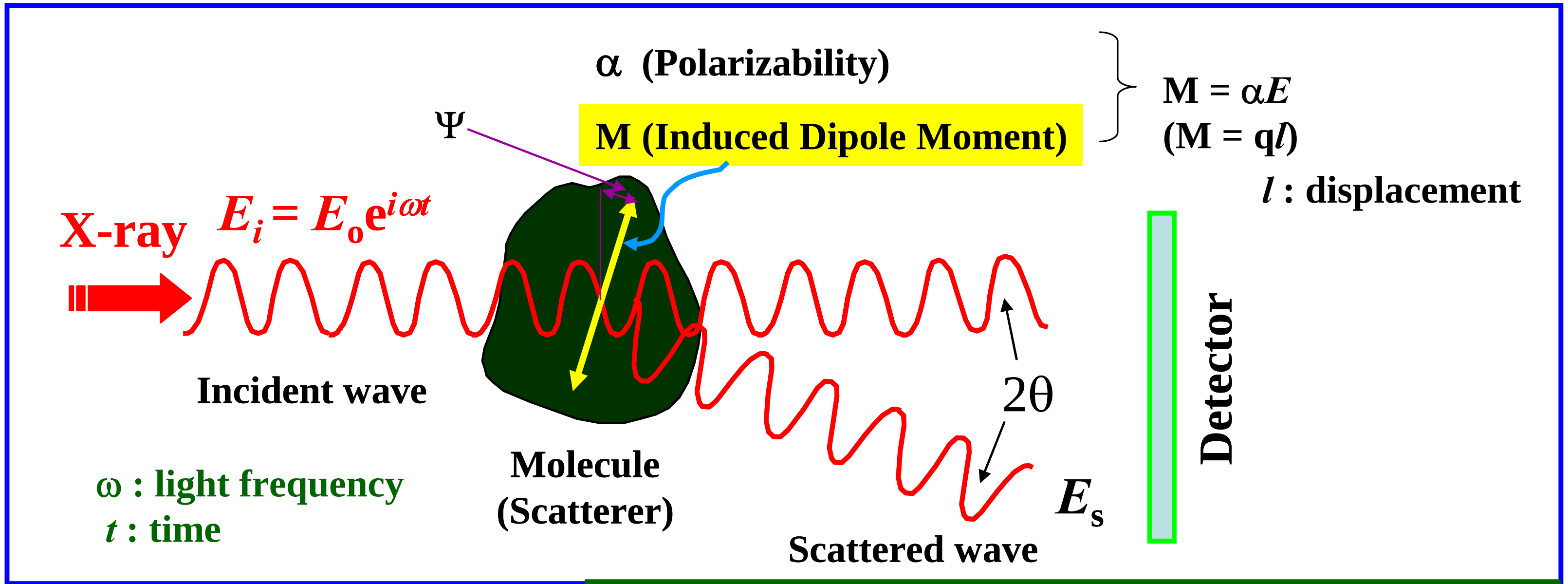
Temperature A Temperature B

Other Devices for Samples

1. Mechanical Tester
2. Rheometer
3. DSC
4. Liquid Cell
5. Liquid Flow Cell
6. Fiber Spinner
7. Magnets
8. Many Other Devices
   depending on what you want

Outline

X-Ray Scattering from One Molecule (Particle)



$$E_s = \frac{(\partial^2 \mathbf{M} / \partial t^2)}{c^2 r} \cos \Psi$$

$$\mathbf{M} = \alpha E = \alpha E_o e^{i\omega t}$$

$$(\partial^2 \mathbf{M} / \partial t^2) = -\alpha \omega^2 E_o e^{i\omega t}$$

$$E_s = \frac{-\alpha \omega^2 E_o e^{i\omega t}}{c^2 r} \cos \Psi$$

c : light speed
r : sample-to-detector distance

$I_s = E_s \cdot E_s^*$ **(scattered wave intensity)**

$I_o = E_o \cdot E_o^* = E_o^2$ **(incident wave intensity)**

LOW FREQUENCY (Rayleigh) CASE, $\omega << \omega_o$ → **Light scattering**

$$\alpha = e^2 / k$$

HIGH FREQUENCY (Thomson) CASE, $\omega >> \omega_o$ → **X-Ray Scattering**

$$\alpha = e^2 / m\omega^2$$

It is independent of k and decreases with ω. **(because ω is very high.)**

e : charge of an electron
k : force constant
m : mass of an electron

Scattering vector

Scattering vector

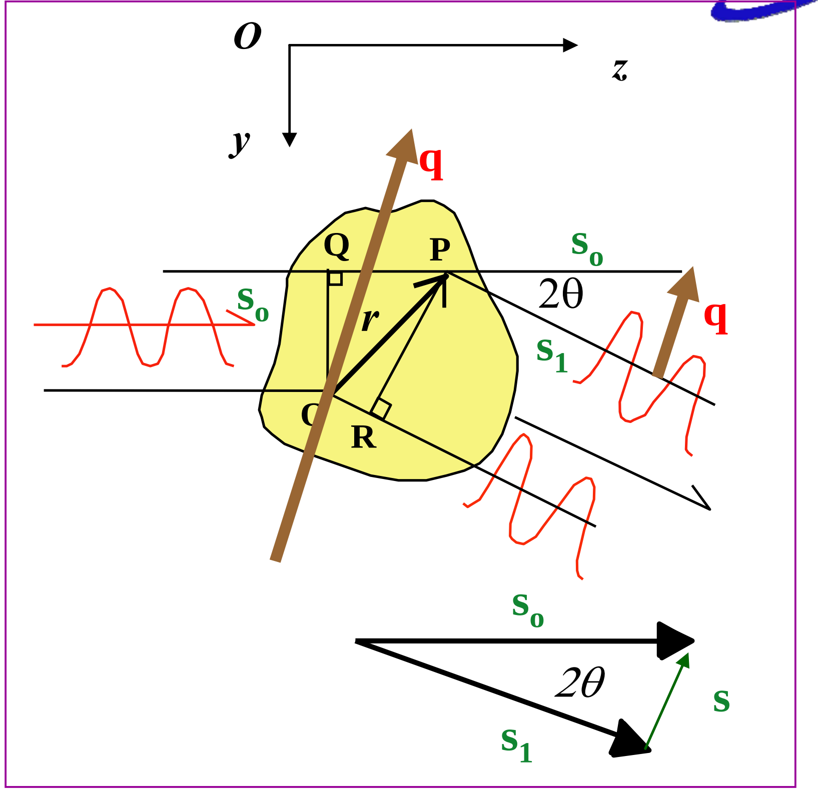
$\mathbf{s_o} = \mathbf{e}_z, \quad \mathbf{s_1} = \mathbf{e}_y \sin 2\theta + \mathbf{e}_z \cos 2\theta$

$\mathbf{s} = \mathbf{s_o} - \mathbf{s_1} = \left[\mathbf{e}_z(1-\cos 2\theta) - \mathbf{e}_y \sin 2\theta\right]$

$k = 2\pi/\lambda$ **Wave number (modulus of wave vector)**

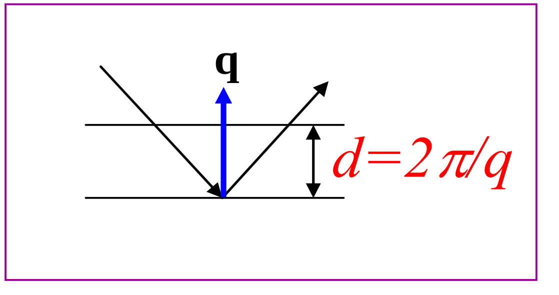
$s = |\mathbf{s}| = \left[(1-\cos 2\theta)^2 + \sin^2 2\theta\right]^{1/2} = 2\sin\theta$

$\mathbf{q} = k\,\mathbf{s} \qquad q = k\,s = \dfrac{4\pi}{\lambda}\sin\theta$



Bragg's eq.: lattice spacing *d*

$$2d\sin\theta = n\lambda(n = 1,2,3...) \Rightarrow d = \frac{n\lambda}{2\sin\theta} = \frac{2\pi}{q}(n = 1)$$



The phase difference δ, from O and P is equal to the inner vector product, q.r.

$$\delta = \frac{2\pi}{\lambda}(\text{QP - OR}) = \frac{2\pi}{\lambda}(\mathbf{s_o}\cdot\mathbf{r} - \mathbf{s_1}\cdot\mathbf{r}) = \mathbf{q}\cdot\mathbf{r}$$

Phase Factor $\delta = \mathbf{q} \cdot \mathbf{r}$

$$E_s = \frac{-\alpha\omega^2 E_o e^{i\omega t}}{c^2 r} \cos \Psi$$

$$E_s = \frac{-\omega^2 E_o e^{i\omega t}}{c^2 r} \cos \Psi \sum_i \alpha_i e^{-ikx_i}$$

$$F = \sum_i \rho_i e^{-ikx_i}$$

$$F(\mathbf{r}_i) = \sum_i \rho_i e^{-i(\mathbf{q}\cdot\mathbf{r}_i)}$$

***F* : Form Factor**

$$E_s = K_s F(\mathbf{r}_i)$$

$$K_s = \frac{-\omega^2 E_o e^{i\omega t}}{c^2 r} \cos \Psi$$

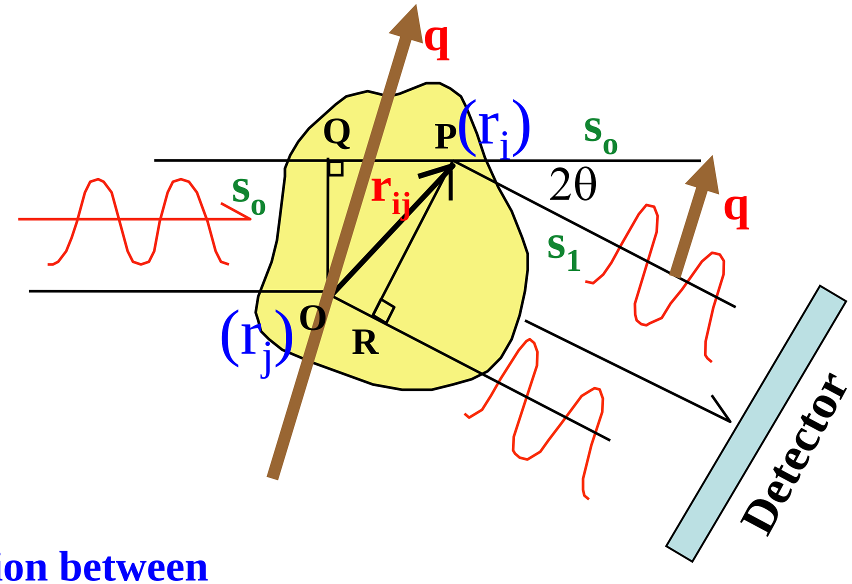
$$I_s = E_s \cdot E_s^*$$

$$I_s = K_s \{F(\mathbf{r}_i) \cdot F^*(\mathbf{r}_i)\}$$

I_s : Scattering Intensity

$$F(\mathbf{r}_i) = \sum_i \rho_i(\mathbf{r}_i) e^{-i(\mathbf{q}\cdot\mathbf{r}_i)} \qquad \rho(\mathbf{r}_i) = \rho_o + \Delta\rho_i$$

$$F(\mathbf{r}_j) = \sum_j \rho_j(\mathbf{r}_j) e^{-i(\mathbf{q}\cdot\mathbf{r}_j)} \qquad \rho(\mathbf{r}_j) = \rho_o + \Delta\rho_j$$



$$I_s = K_s\{F(\mathbf{r}_i)\cdot F^*(\mathbf{r}_i)\}$$

$$= K_s \sum_i \rho_i e^{-i(\mathbf{q}\cdot\mathbf{r}_i)} \sum_j \rho_j e^{i(\mathbf{q}\cdot\mathbf{r}_j)}$$

(no correlation between the fluctuation of a volume element and its distance away from another)

$$= K_s \sum_i \sum_j \{\rho_o^2 e^{-i(\mathbf{q}\cdot\mathbf{r}_{ij})} + \rho_o\Delta\rho_i e^{-i(\mathbf{q}\cdot\mathbf{r}_{ij})} + \rho_o\Delta\rho_j e^{-i(\mathbf{q}\cdot\mathbf{r}_{ij})} + \Delta\rho_i\Delta\rho_j e^{-i(\mathbf{q}\cdot\mathbf{r}_{ij})}\}$$

0 (homogeneous) 0 0

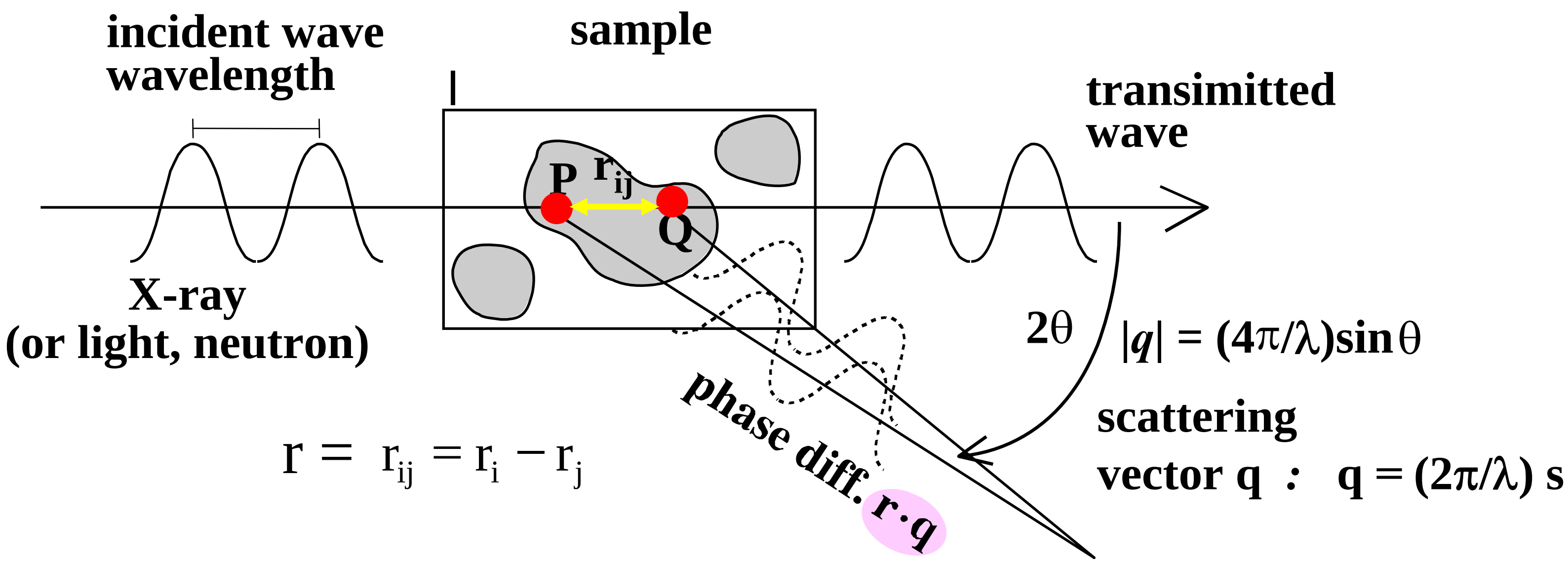
$$I_s = K_s \sum_i \sum_j \Delta\rho_i\Delta\rho_j e^{-i(\mathbf{q}\cdot\mathbf{r}_{ij})}$$

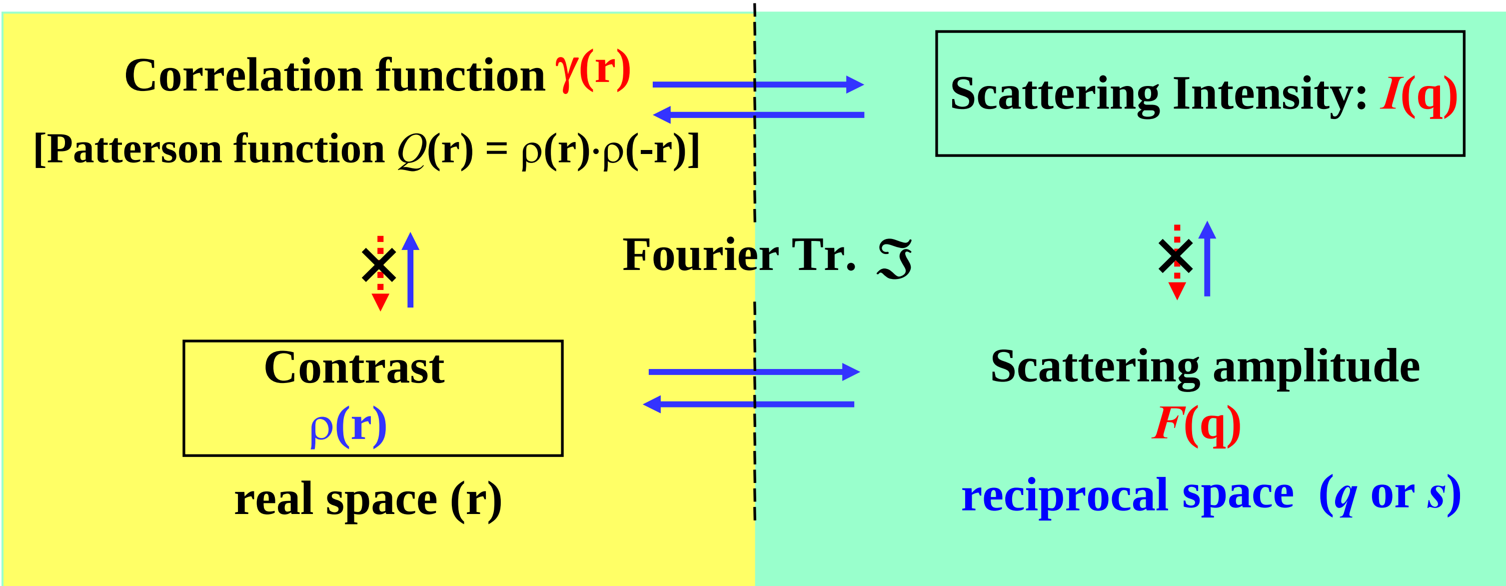
$\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ **(interdistance of a pair of scatters)**

$$I_s(\mathbf{q}) = K_s \sum_i \sum_j \Delta\rho_i(\mathbf{r})\Delta\rho_j(\mathbf{r}) e^{-i(\mathbf{q}\cdot\mathbf{r})}$$

(a generalized scattering equation)

Structure analysis by Scattering and Concept of Real and Reciprocal Spaces





How to find Scattering Amplitude [*F*(r)] from Scattered Intensity?

$$I_s(\mathbf{q}) = K_s \sum_i \sum_j \Delta\rho_i(\mathbf{r})\Delta\rho_j(\mathbf{r}) e^{-i(\mathbf{q}\cdot\mathbf{r})}$$

$$I(\mathbf{q}) = K_s\,[F(\mathbf{r})\cdot F^*(\mathbf{r}')]$$

Correlation function

$\gamma(\mathbf{r})$

(1) Correlation Function Approach

- Correlation function $\gamma(\mathbf{r})$

(2) Fine Structural Model Approach

- sphere
- Gaussian sphere
- core/shell sphere
- rod
- cylinder
- disc

etc

(1) Correlation function Approach

Auto-Correlation Function γ(r) (Patterson Function)

$$\gamma(\mathbf{r}) = \frac{\Delta\rho(\mathbf{r}) * \Delta\rho(-\mathbf{r})}{\int_0^\infty [\Delta\rho(\mathbf{r})]^2 d\mathbf{r}} = \frac{\int_0^\infty \Delta\rho(\mathbf{u})\Delta\rho(\mathbf{r}+\mathbf{u})d\mathbf{u}}{\int_0^\infty \Delta\rho(\mathbf{u})\Delta\rho(\mathbf{u})d\mathbf{u}}$$

$$\gamma(\mathbf{r}) = \Im^{-1}\{I_{obs}(\mathbf{q})\} \cdot \frac{1}{\langle(\Delta\rho)^2\rangle V}$$

$$\Delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_0$$

For an isotropic system $|\mathbf{q}| = q, \ |\mathbf{r}| = r$

$$\gamma(r) = \Im^{-1}\{I_{obs}(q)\} \frac{1}{\langle\{\Delta\rho(u)\}^2\rangle V} = \frac{\int q^2 I_{obs}(q) \frac{\sin qr}{qr} dq}{\int q^2 I_{obs}(q) dq}$$

Pair Distance Distribution Function (PDDF) $p(r) = r^2 \gamma(r)$

Correlation function *versus* Scattering intensity

Density distribution

$$\rho(\mathrm{r}) \longrightarrow \gamma(\mathbf{r})$$ **Correlation of paired scatters**

Correlation function

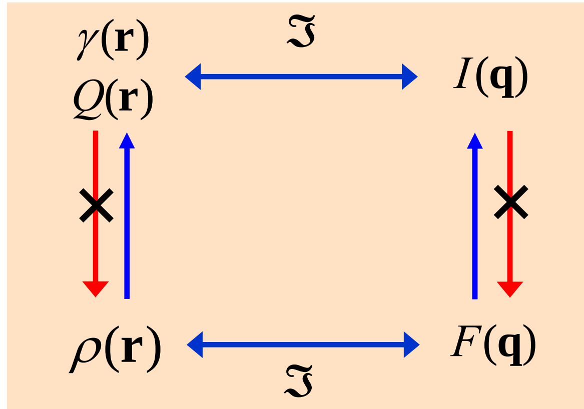
$$\gamma(\mathbf{r}) = \underbrace{\int \rho(\mathbf{r}')\rho(\mathbf{r}-\mathbf{r}')d\mathbf{r}'}\,/\,\underbrace{\int \rho^2(\mathbf{r}')d\mathbf{r}'}$$

Scattering intensity ↕ **Fourier transform**

$$I(q) = \frac{K}{V}\int \gamma(\mathbf{r})\exp(i\mathbf{q}\cdot\mathbf{r})d\mathbf{r}$$

r = r – r'

Patterson Function



$$I(\mathbf{q}) = \Im\{Q(\mathbf{q})\} \qquad Q(\mathbf{r}) = \Im^{-1}\{I(\mathbf{q})\}$$

$$Q(\mathbf{r}) = \rho(\mathbf{r}) * \rho(-\mathbf{r}) = \int \rho(\mathbf{u})\rho(\mathbf{r}+\mathbf{u})\,d\mathbf{u}$$

$$Q(\mathbf{r}) = \int_0^\infty (\Delta\rho(\mathbf{u}) + \rho_0)(\Delta\rho(\mathbf{r}+\mathbf{u}) + \rho_0)\,d\mathbf{u}$$
$$= \int \Delta\rho(\mathbf{u})\Delta\rho(\mathbf{r}+\mathbf{u})\,d\mathbf{u} + C$$

$$\Delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_0$$

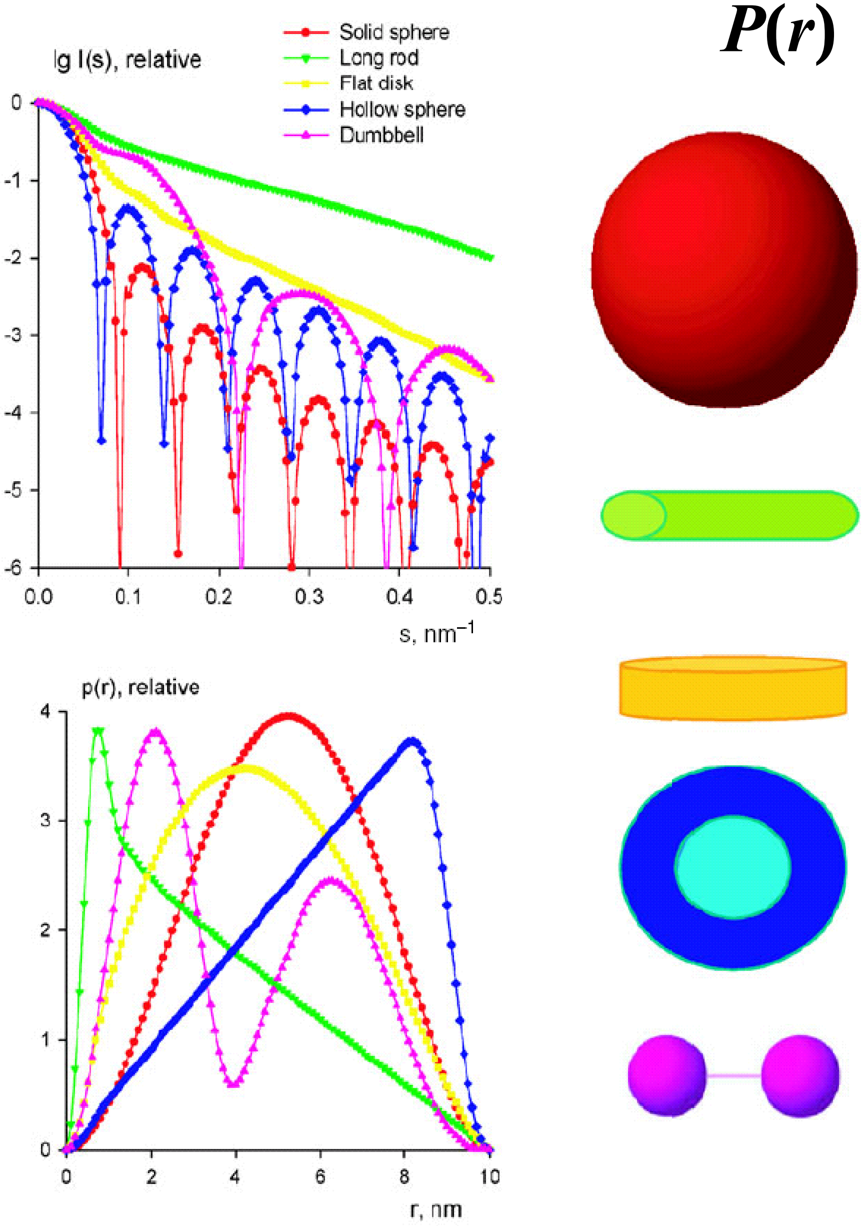
$$I(\mathbf{q}) = \Im\{\Delta\rho(\mathbf{r}) * \Delta\rho(-\mathbf{r})\} + \Im\{C\}$$

$$I_{obs}(\mathbf{q}) = \Im\{\Delta\rho(\mathbf{r}) * \Delta\rho(-\mathbf{r})\}$$

$$I_{obs}(\mathbf{q}) = \Im\left[Q_{\Delta\rho}(\mathbf{r})\right] \Leftrightarrow Q_{\Delta\rho}(\mathbf{r}) = \Im^{-1}\{I_{obs}(\mathbf{q})\}$$

Pair Distance Distribution Function *P*(r)

$$P(r) = r^2\gamma(r) = r^2 \cdot \int \Delta\rho(u)\Delta\rho(r+u)\,du$$



- ✓ Distribution of distances of atoms from centroid
- ✓ 1-D: Only distance, not direction
- ✓ 20:1 ratio $q_{min}(\pi/d_{max}):q_{max}$ usually ok
- ✓ p (r) gives an alternative measure of Rg and also "longest cord"

(2) Fine Structural Model Approach

Scattering amplitude (i.e., Scattering Function = Structure Function);
Scattering intensity

Density distribution

$$\rho(\mathrm{r})$$

Fourier TF = summation with phase difference

$$F(\mathbf{q}) = \frac{K_s}{V}\int \rho(\mathbf{r})\exp(i\mathbf{q}\cdot\mathbf{r})d\mathbf{r}$$

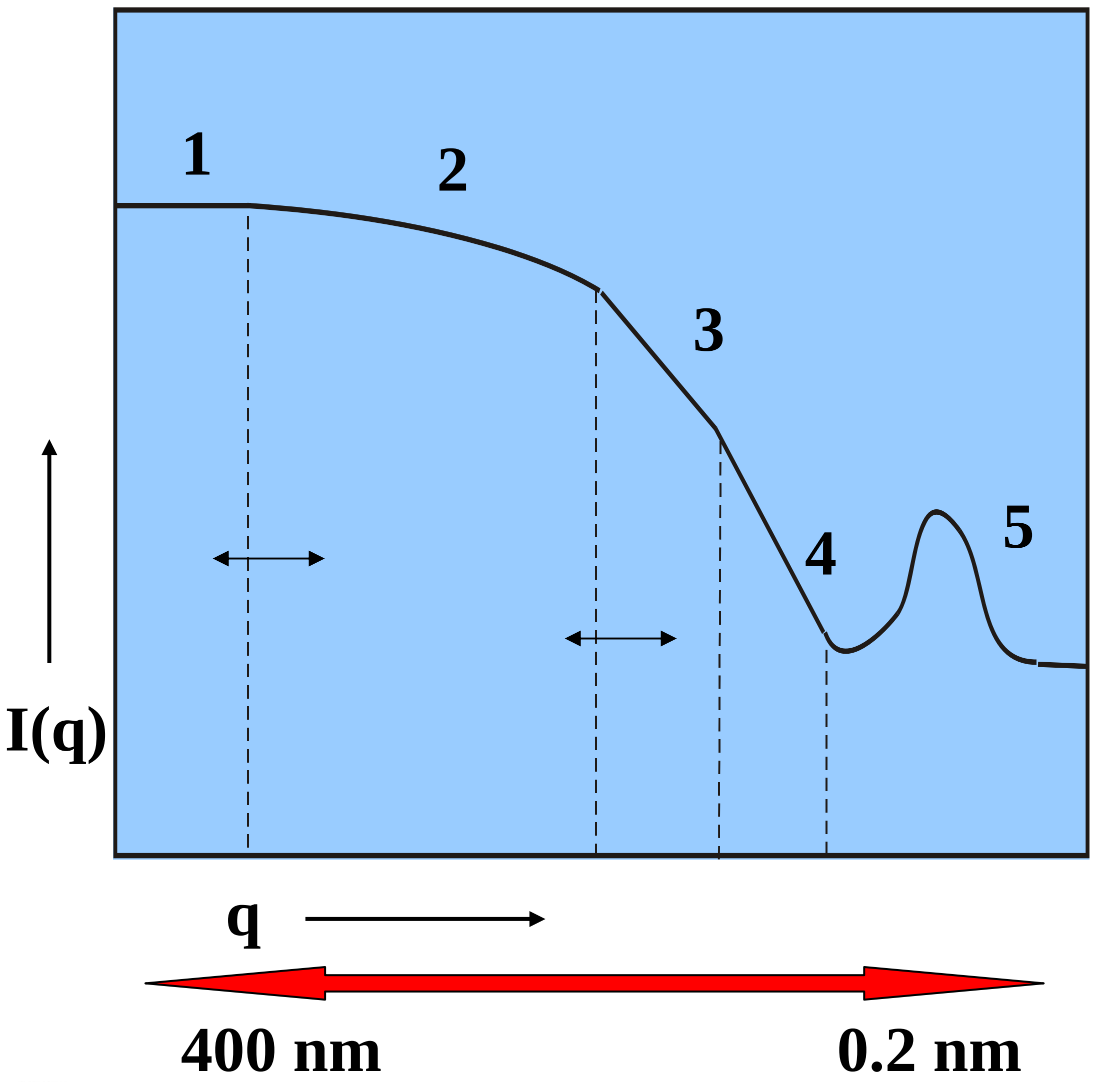
Scatt. amplitude

Scattering intensity

$$I(q) = \frac{K}{V}\iint \rho_{\mathrm{i}}(\mathbf{r})\rho_{\mathrm{j}}(\mathbf{r})\ \exp(i\mathbf{q}\cdot\mathbf{r})d\mathbf{r}$$

r = r – r'

Scattering Angle Region versus Length Scale in Structural Information



1 limit q → 0
electron density contrast
density fluctuations
molecular weights

2 Guinier range
particle size

3 particle shape
large scale structures

4 Porod range
particle surface
Surface/volume

5 Intermolecular
ordering

Various types of plots

Methods to analyze I(q)

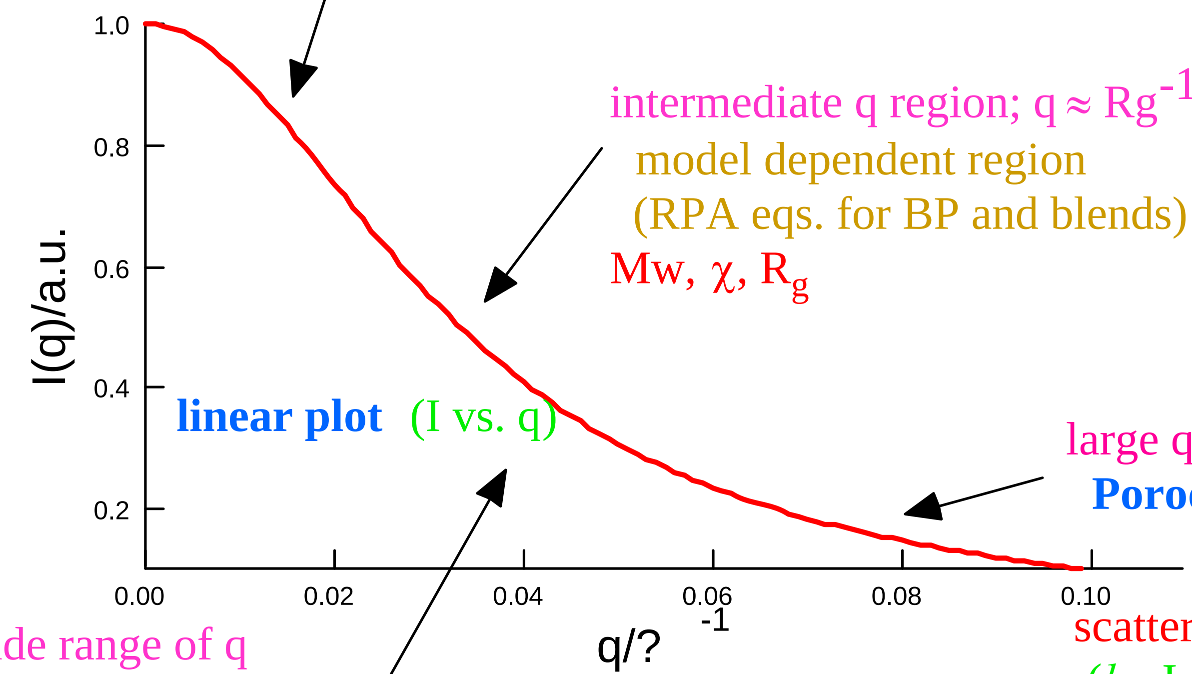
low q region; $q < Rg^{-1}$

Guinier plot ... R_g (*log*I vs. q^2) $$I(q) \sim exp\left[-R_g^2 q^2/3\right]$$

Zimm plot ... R_g, A_2, Mw (I^{-1} vs. q^2) $$KC/I(q) = M^{-1}\left[1 + R_g^2 q^2/3 + ..\right] + 2A_2C$$

Ornstein-Zernike plot ... ξ (I^{-1} vs. q^2) $$I(q) = I(0)/\left[1 + \xi^2 q^2\right]$$

Debye-Bueche plot (two phase) ($I^{-1/2}$ vs. q^2) ... chord length $$I(q) = I(0)/\left[1 + a^2 q^2\right]^2$$



linear plot (I vs. q)

intermediate q region; $q \approx Rg^{-1}$

model dependent region

(RPA eqs. for BP and blends)

Mw, χ, R_g

large q region; $q > Rg^{-1}$

Porod law (two phase) $$I(q) \sim q^{-4}$$

scattering exponent

(*log*I vs. *log*q) $$I(q) \sim q^{-1/\nu}$$

wide range of q

Kratky plot (q^2I vs. q)... segment length, a

$$q^2 I(q) \sim \frac{z}{q^4 R_g^4}\left\{exp\left[-R_g^2 q^2\right] - 1\right\} - \frac{1}{a^2}$$ (Debye fun.)

Invariant

Integration of Intensity

$$\int_0^{\infty} I_{obs}(\boldsymbol{s})d\boldsymbol{s} = \int_0^{\infty} I_{obs}(\boldsymbol{s})e^{2\pi i \boldsymbol{s}\cdot\boldsymbol{r}}d\boldsymbol{s}$$

$$\Im^{-1}\left[I_{obs}(\boldsymbol{s})\right]$$

$$\left\langle(\Delta\rho)^2\right\rangle V \cdot \gamma(0) = \left\langle(\Delta\rho)^2\right\rangle V, \qquad r = 0$$

Integration of intensity =
average density difference * scattering volume

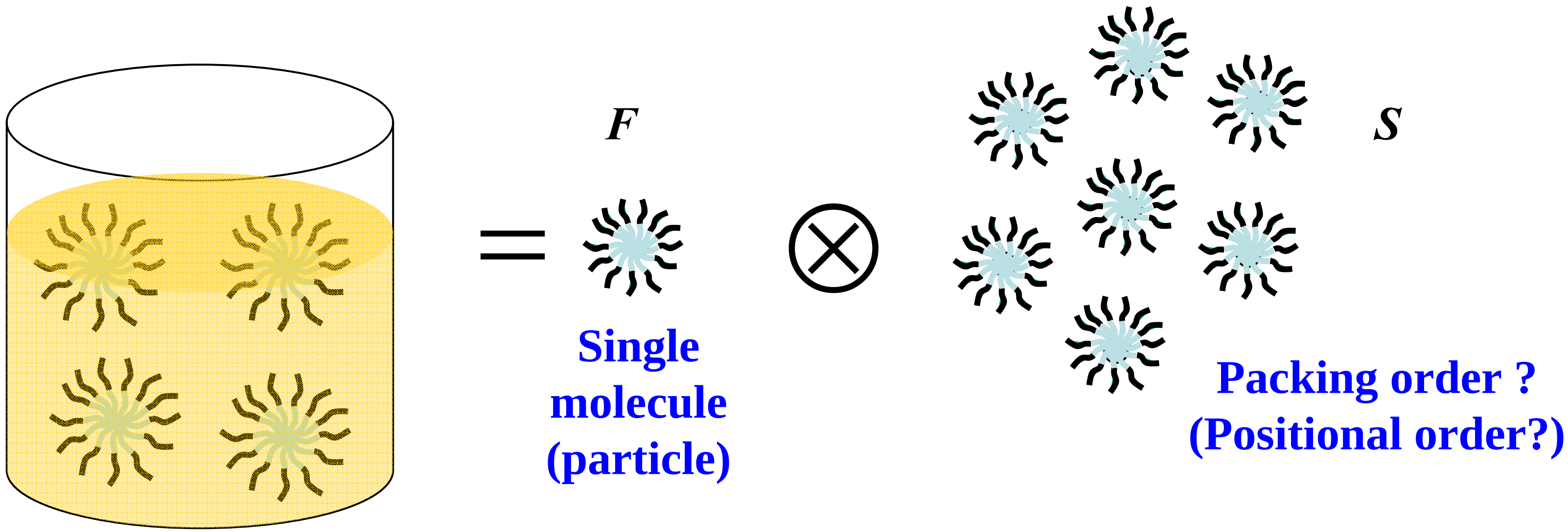
X-Ray Scattering from Multiple Molecules (Particles)

Convolution

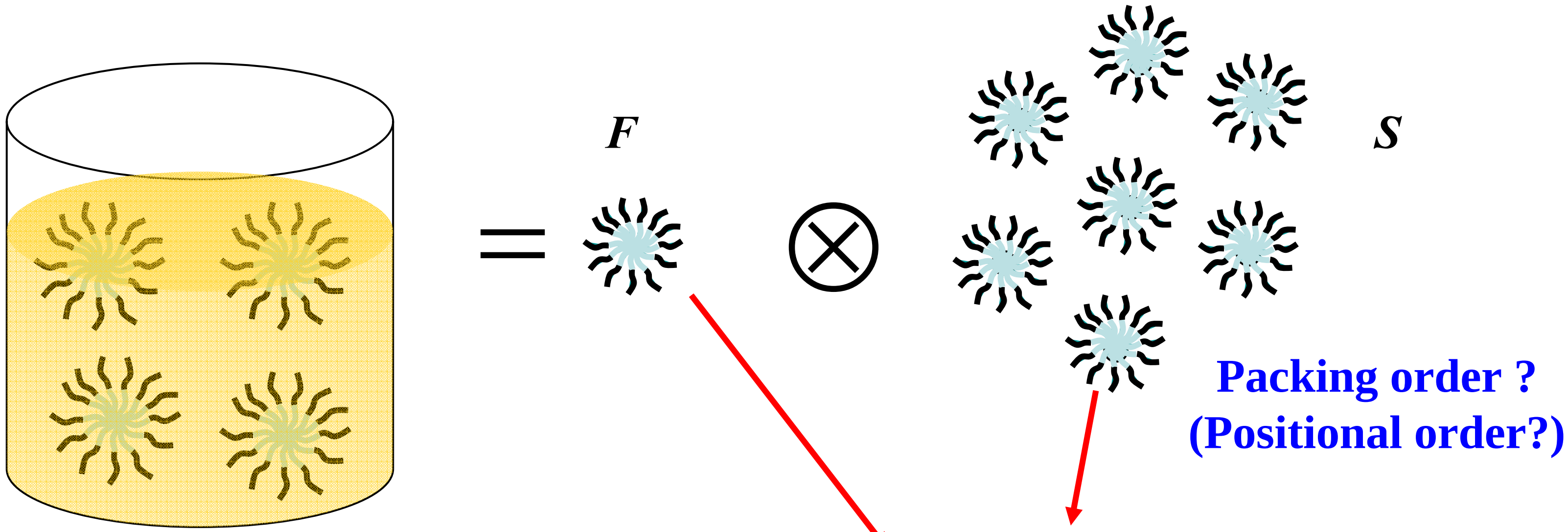
$$\{F * S\}(\mathbf{r}) \equiv \int_{-\infty}^{\infty} F(\mathbf{u}) S(\mathbf{r} - \mathbf{u}) d\mathbf{u}$$

$$\{F * S\}(-\mathbf{r}) \equiv \int_{-\infty}^{\infty} F(\mathbf{u}) S(\mathbf{r} + \mathbf{u}) d\mathbf{u}$$

$$\Im\{F * S\} = \Im\{F\} \cdot \Im\{S\}$$

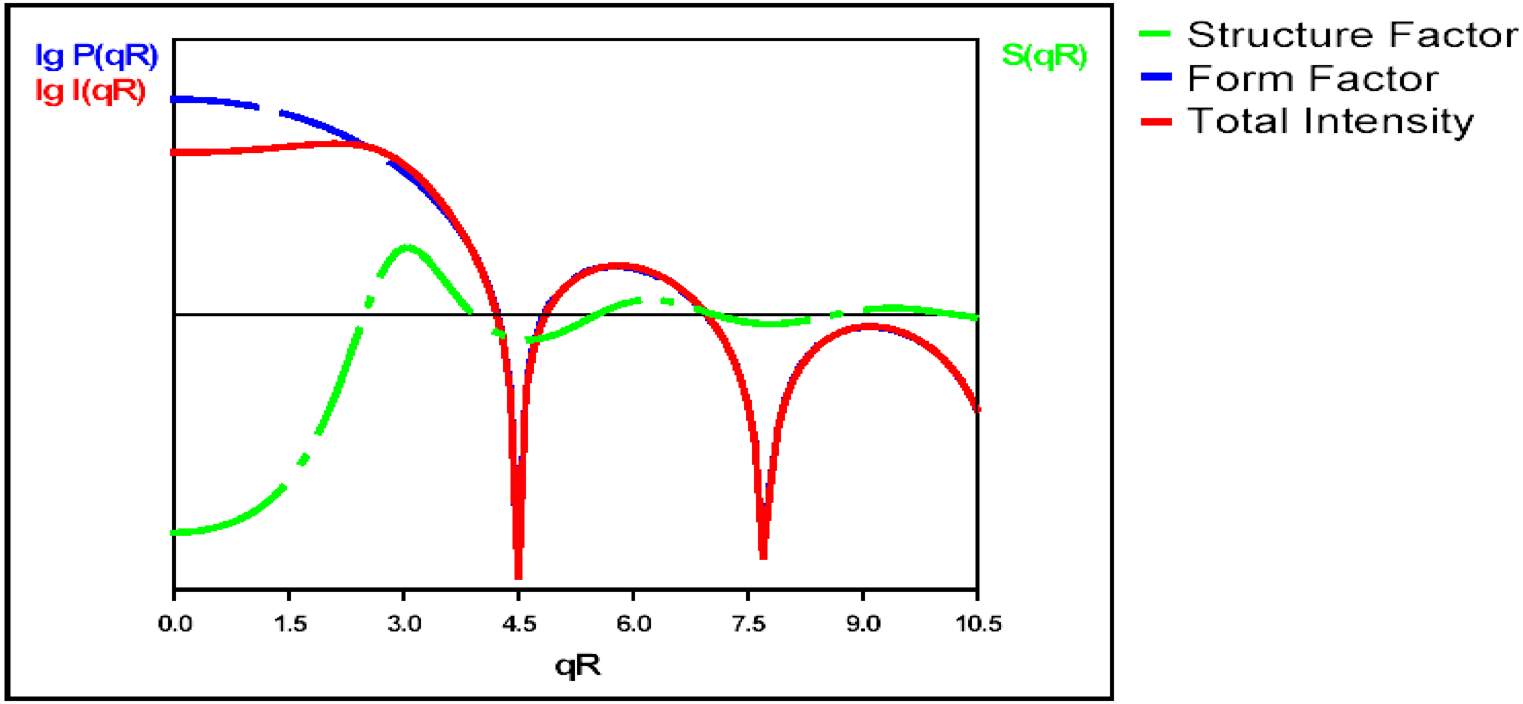


X-Ray Scattering from Multiple Molecules (Particles)



$$I = N_p \left(\Delta\rho_p\right)^2 \underbrace{F^2(q)}_{\textit{Form Factor}} \underbrace{S^2(q)}_{\textit{Structure Factor}}$$

$S(q) \approx 1$ for dilute solution



$$I = N_p \left(\Delta\rho_p\right)^2 \underbrace{F^2\left(q\right)}_{\text{Form Factor}} \underbrace{S^2\left(q\right)}_{\text{Structure Factor}}$$

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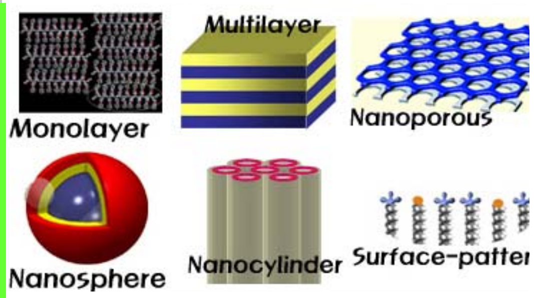
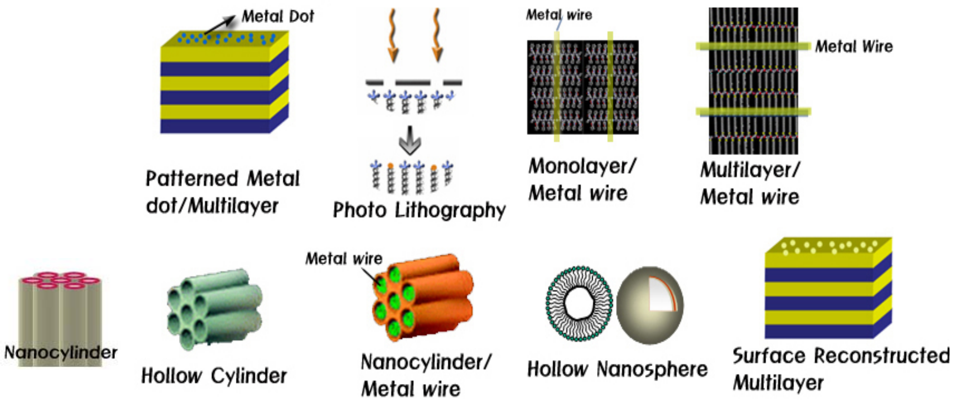
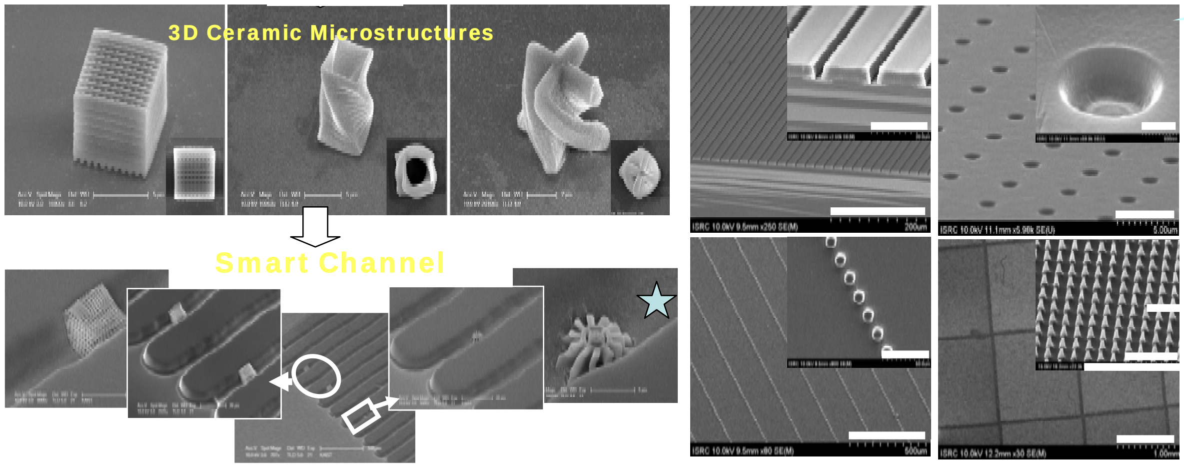
Challenges in Nano-Science & Technology

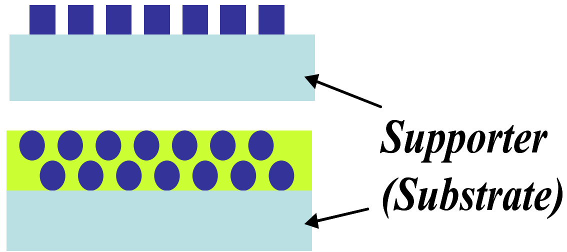
NanoMaterials
NanoFarications
NanoCharacterizations
for Various Nanostructures
(and Building Blocks)







Nanostructures



Nanoscale Specimens

small mass, volume ⇨ weak signal

Analytical Techniques

One of Major Issues:

How to characterize?

Scatterings ? → GIXS, GINS

Reflectivity → X-ray, Neutron

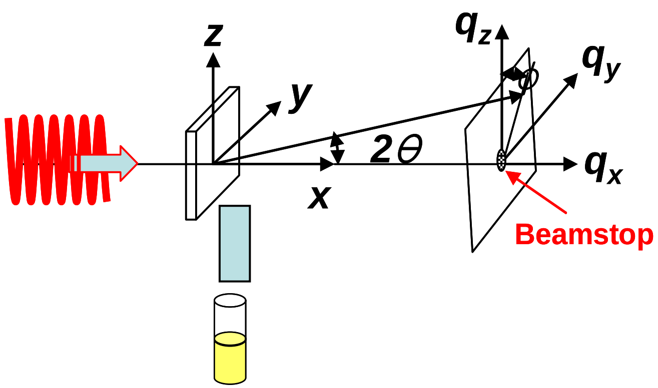
Microscopies ?

Spectroscopies ?

etc.

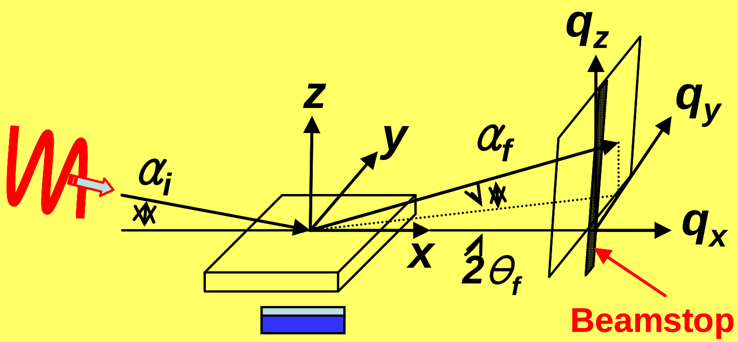
X-ray Scattering Setup

Conventional Transmission X-Ray Scattering (TXS)



Bulk Samples
Solution Samples

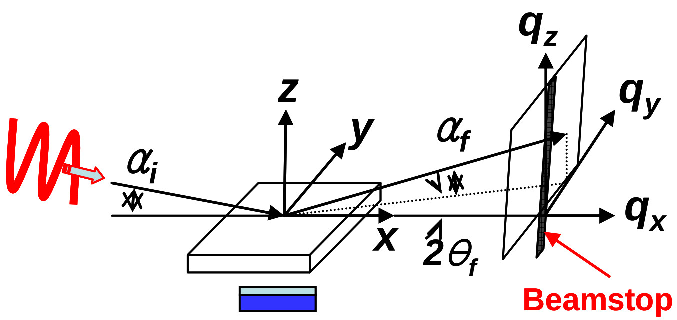
Grazing Incidence X-Ray Scattering (GIXS)



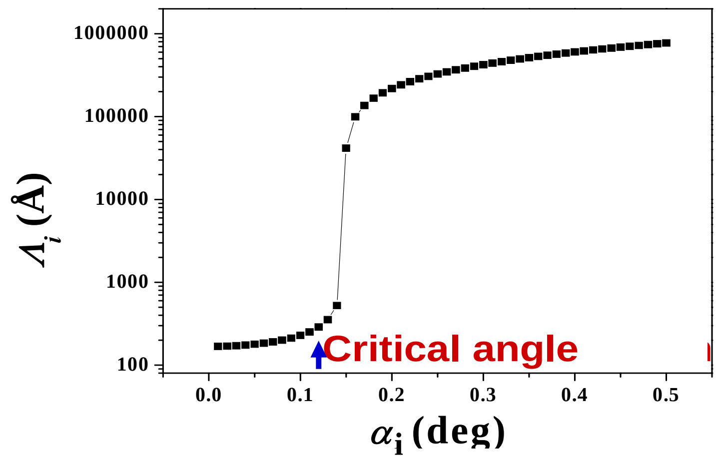
Nanoscale Thin Films
NanoStructured Products
Nanoscale Specimens

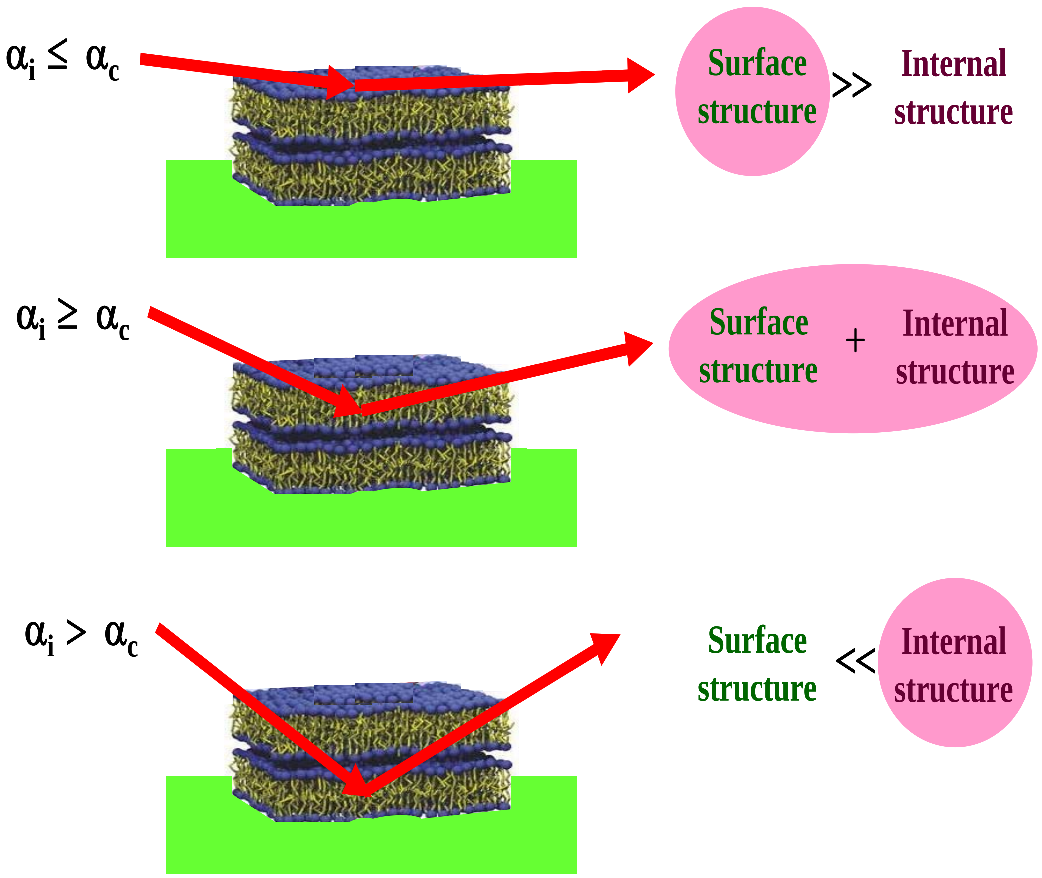
Grazing Incidence X-ray Scattering (GIXS)

GIXS



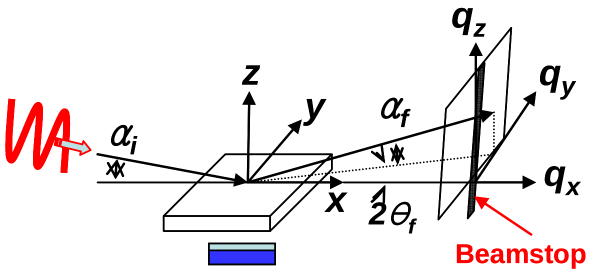
Penetration depth profile





- Surface
- Interfaces
- Sub-layers
- Electron density
- etc.

Nanostructure on Substrate

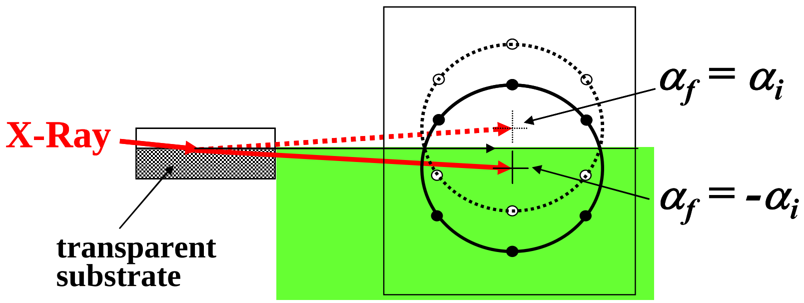


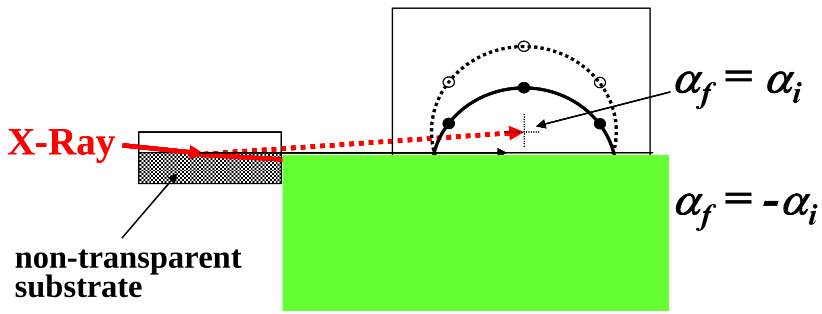
$$\alpha_f = \arccos\left(\sqrt{n_R^2 - \left(\frac{q_{c,z}}{k_o} \pm \sqrt{n_R^2 - \cos^2\alpha_i}\right)^2}\right)$$

$$2\theta_f = \arccos\left(\frac{\cos^2\alpha_i + \cos^2\alpha_f - \left(\frac{q_{c,\parallel}}{k_o}\right)^2}{2\cos\alpha_i\cos\alpha_f}\right)$$

Internal Structure

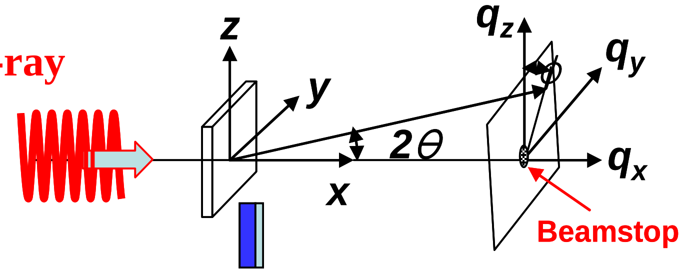
- Scattering from internal structure
  - * Scattering from reflected beam
  - * Scattering from transmitted beam

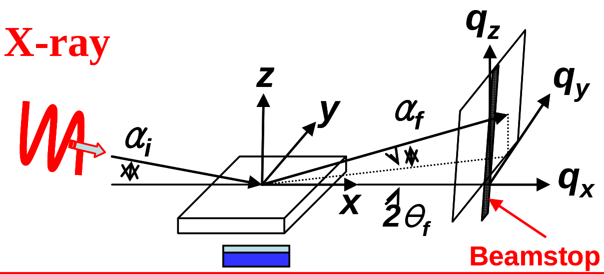


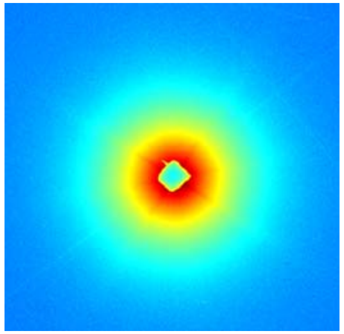


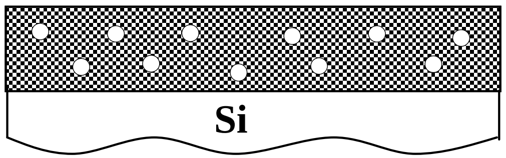
Macomolecules (2005) 39, 3395; (2005) 39, 4311
Nature Materials (2005) 4, 147
Adv. Mater. (2005) 17, 696

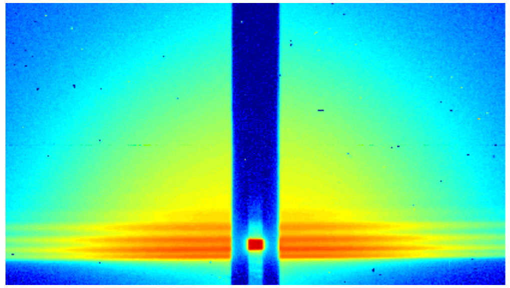
TXS vs GIXS for Characterizing Nanotructure on Substrate











Merit

TXS:
- Easy measurement
- Easy analysis
- In-plane information (q_x, q_y)

GIXS:
- Strong intensity
- Easy preparation of samples
- More information (q_x, q_y, q_z)

Concerns

TXS:
- Any possible scattering from substrate
- Transparency of substrate to X-ray beam
- High energy and high flux X-ray beam

GIXS:
- Scattering from surface structure
- Scattering from internal structure
  - * Scattering from reflected beam
  - * Scattering from transmitted beam
- Refraction effect involved

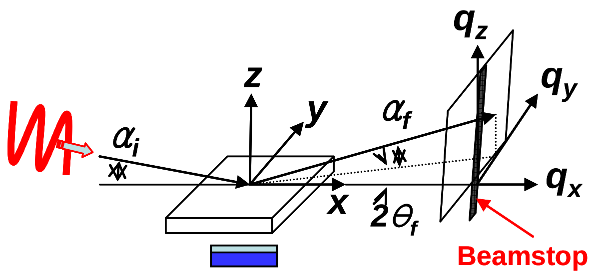
• Need a special setup
• Need new scattering theory

Nanostructure on Substrate

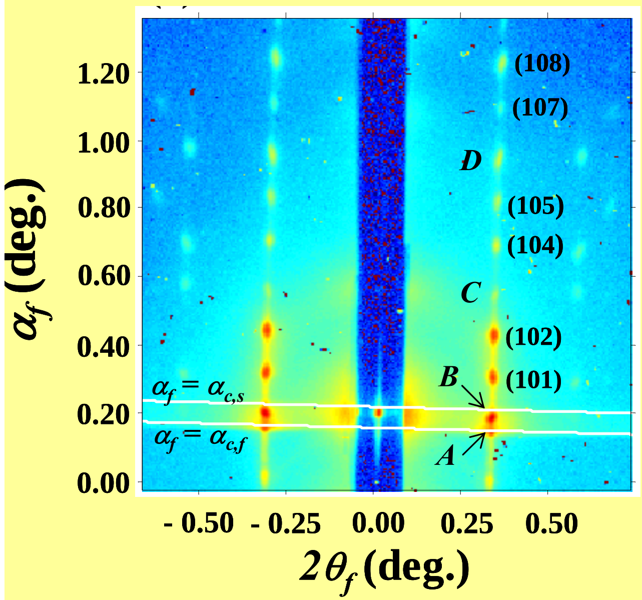
Internal Structure

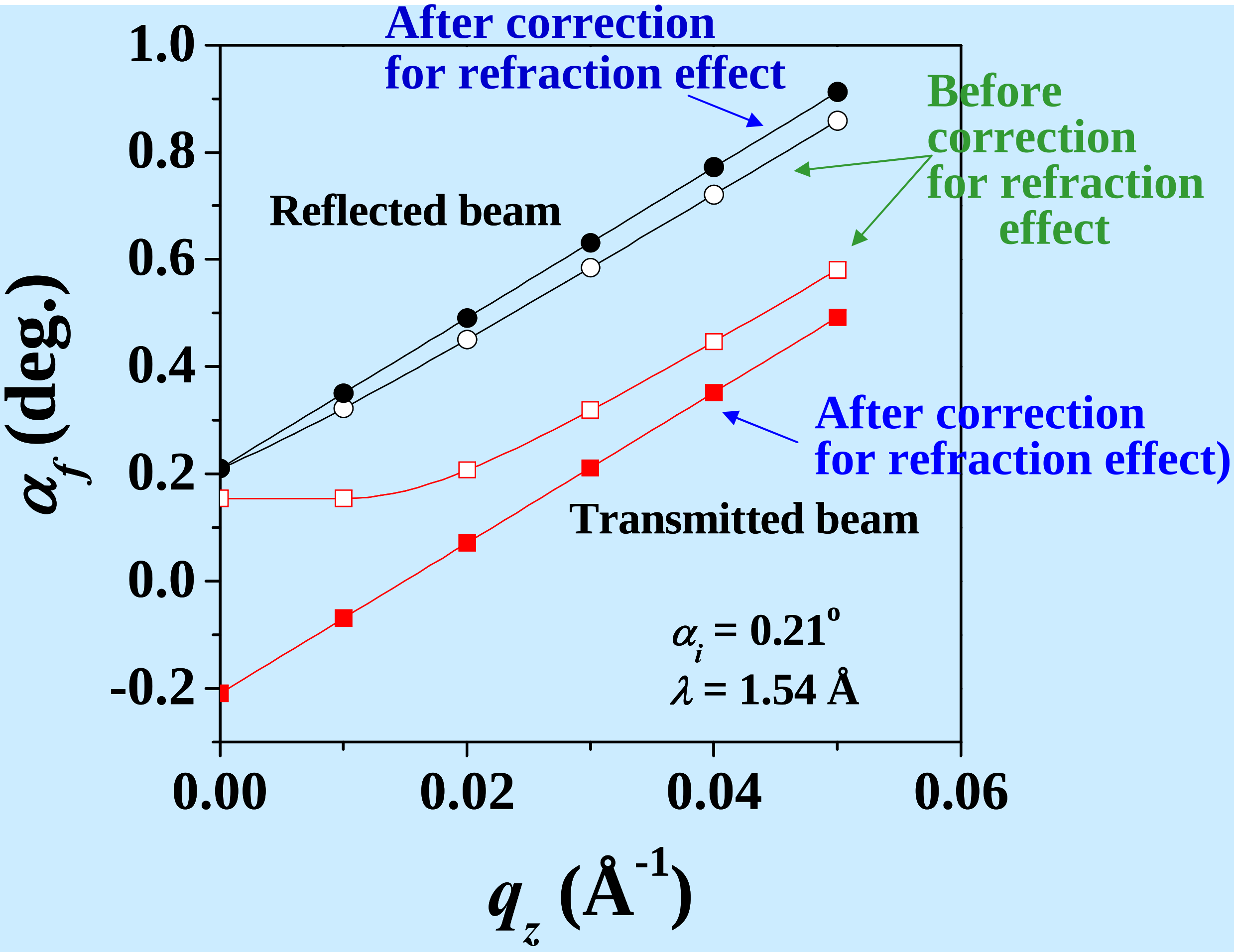
- Scattering from internal structure
  * Scattering from reflected beam
  * Scattering from transmitted beam
  * Refraction effect

GIXS



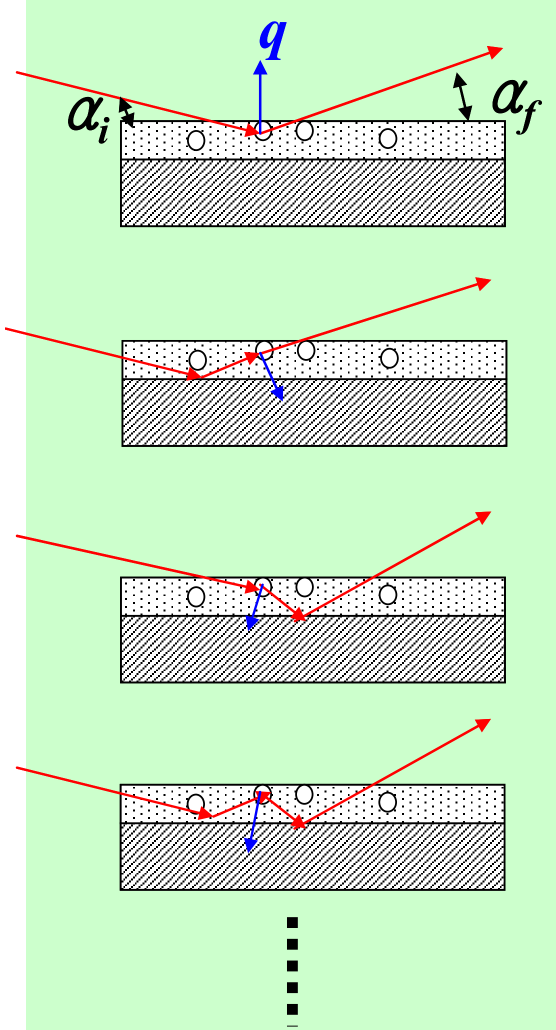
PS-*b*-PI(37/63) film
(HPL; ρ_e = 360 nm^{-3})

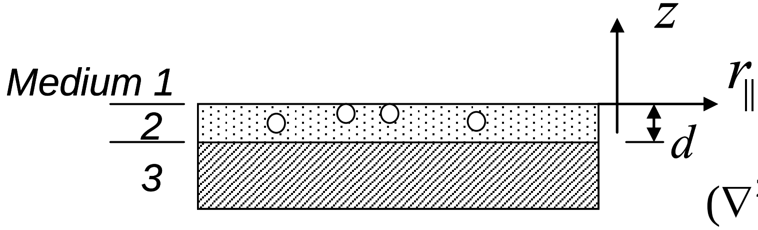




GIXS Intensity : DWBA

Scattering process





$(V = V_1 + V_2)$

$$(\nabla^2 + k_0^2 - V_1)\Psi = 0$$

$$\Psi_{sc}(\mathbf{r}) = -\frac{ik_0 r}{4\pi r}\int d^3 r' \Psi^1(\mathbf{r}', -\mathbf{k_f}) V_2(\mathbf{r}') \Psi^1(\mathbf{r}', \mathbf{k_i})$$

(DWBA)

$$I_{GIXS}(\alpha_f, 2\theta_f) = \frac{1}{16\pi^2}\cdot\frac{1-e^{-2\,\mathrm{Im}(q_z)\cdot \mathbf{d}}}{2\,\mathrm{Im}(q_z)}\cdot\left|\begin{matrix} T_i T_f F(q_\parallel, \mathrm{Re}(q_{1,z})) + \\ T_i R_f F(q_\parallel, \mathrm{Re}(q_{2,z})) + \\ T_f R_i F(q_\parallel, \mathrm{Re}(q_{3,z})) + \\ R_i R_f F(q_\parallel, \mathrm{Re}(q_{4,z})) \end{matrix}\right|^2$$

$$I_{GIXS}(\alpha_f, 2\theta_f) \cong \frac{1}{16\pi^2}\cdot I_{independent}$$

$$= \frac{1}{16\pi^2}\cdot\frac{1-e^{-2\,\mathrm{Im}(q_z)\cdot d}}{2\,\mathrm{Im}(q_z)}\cdot\left[\begin{matrix} |T_i T_f|^2 I_1(q_\parallel, \mathrm{Re}(q_{1,z})) + \\ |T_i R_f|^2 I_1(q_\parallel, \mathrm{Re}(q_{2,z})) + \\ |T_f R_i|^2 I_1(q_\parallel, \mathrm{Re}(q_{3,z})) + \\ |R_i R_f|^2 I_1(q_\parallel, \mathrm{Re}(q_{4,z})) \end{matrix}\right]$$

$q_\parallel = \sqrt{q_x^2 + q_y^2}$

$q_{1,z} = k_{z,f} - k_{z,i}$

$q_{2,z} = -k_{z,f} - k_{z,i}$

$q_{3,z} = k_{z,f} + k_{z,i}$

$q_{4,z} = -k_{z,f} + k_{z,i}$

$k_{z,i} = k_o\sqrt{n^2 - \cos^2\alpha_i}$

$k_{z,f} = k_o\sqrt{n^2 - \cos^2\alpha_f}$

$k_o = 2\pi/\lambda$

R_i , T_i : incoming wave

R_f, T_f: outgoing wave

F : amplitude of scattering from the internal structure

$I_1 = FF^*$; intensity

$$I_{GIXS}(\alpha_f, 2\theta_f) \cong \frac{1}{16\pi^2} \cdot \frac{1 - e^{-2\,\mathrm{Im}(q_z)\cdot \mathbf{d}}}{2\,\mathrm{Im}(q_z)} \cdot \begin{bmatrix} |T_i T_f|^2 I_1(q_\parallel, \mathrm{Re}(q_{1,z})) + \\ |T_i R_f|^2 I_1(q_\parallel, \mathrm{Re}(q_{2,z})) + \\ |T_f R_i|^2 I_1(q_\parallel, \mathrm{Re}(q_{3,z})) + \\ |R_i R_f|^2 I_1(q_\parallel, \mathrm{Re}(q_{4,z})) \end{bmatrix}$$

I_1, scattered intensity from scatters in nanoscales

(1) Spherical structures: (model approach)

$$I_1 = c\int_0^\infty n(r)\upsilon^2(r)\,|F(qr)|^2\, S(qr)\,dr$$

$$n(r) = \frac{1}{\sqrt{2\pi}\, r_o \sigma e^{\sigma^2/2}} e^{\frac{-\ln(r/r_o)^2}{2\sigma^2}}$$

(2) Random two-phase structures: (correlation function approach)

$$I_1 = \frac{8\pi\phi(1-\phi)(\rho_{e(film\ medium)} - \rho_{e(scatter)})^2 \xi^3}{(1+q^2\xi^2)^2}$$

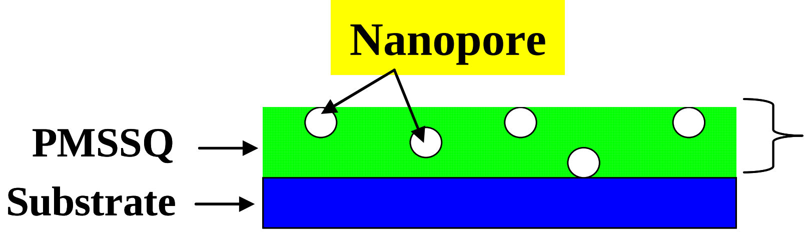
(3) Structures in Crystal lattices: (model approach)

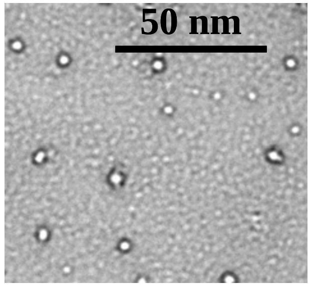
$$I_1(\mathbf{q}) = S(\mathbf{q}) \cdot P(\mathbf{q})$$

Macomolecules **(2005) 38, 3395**
Macromolecules **(2005) 38, 4311**
Nature Materials **(2005) 4, 147**
Adv. Mater. **(2005) 17, 696**

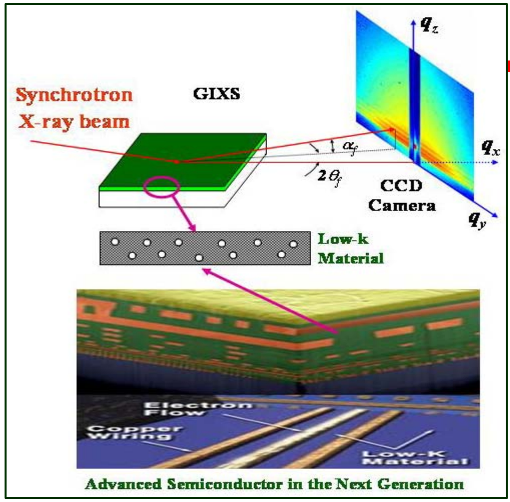
Outline

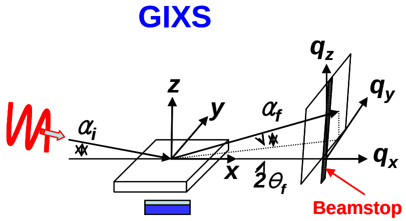
1. GIXS Analysis of NanoPores: Ultralow-k Dielectrics in Nano-Thin-Films



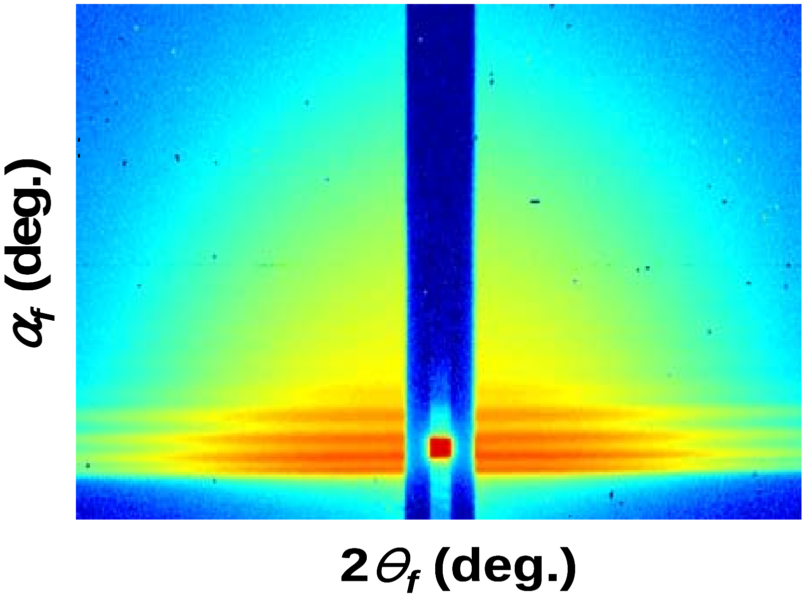


TEM



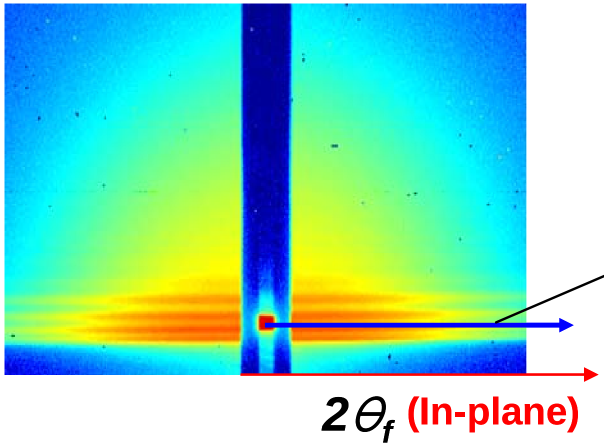


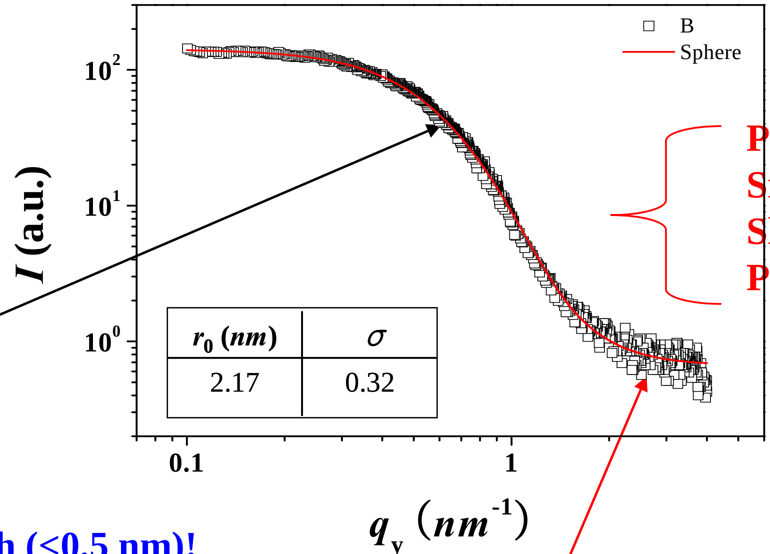
* AFM found: Surface is very smooth (<0.5 nm)!
* Nanospcimen thickness: ca. 100 nm.



2D GIXS Pattern (experimental data)

(1) Data Analysis with GIXS of Spherical Structures (Pores)





- Pore size
- Size distributions
- Shape
- Porosity …

*** AFM found: Surface is very smooth (<0.5 nm)!**

*** Nanospcimen thickness: ca. 100 nm.**

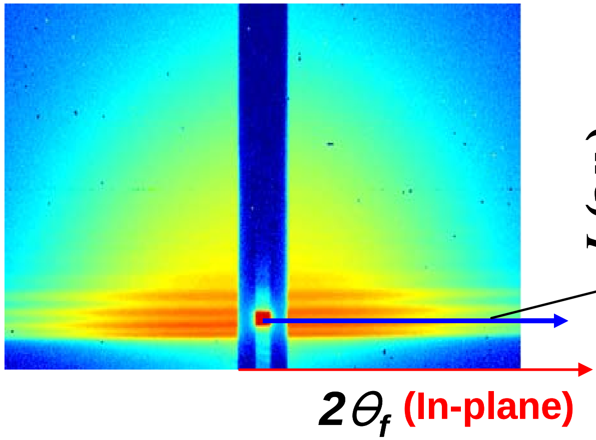
$$I_{GIXS}(\alpha_f,2\theta_f) \cong \frac{1}{16\pi^2}\cdot\frac{1-e^{-2\,\mathrm{Im}(q_z)\cdot d}}{2\,\mathrm{Im}(q_z)}\cdot\begin{bmatrix}|T_iT_f|^2 I_1(q_\parallel,\mathrm{Re}(q_{1,z}))+\\ |T_iR_f|^2 I_1(q_\parallel,\mathrm{Re}(q_{2,z}))+\\ |T_fR_i|^2 I_1(q_\parallel,\mathrm{Re}(q_{3,z}))+\\ |R_iR_f|^2 I_1(q_\parallel,\mathrm{Re}(q_{4,z}))\end{bmatrix}$$

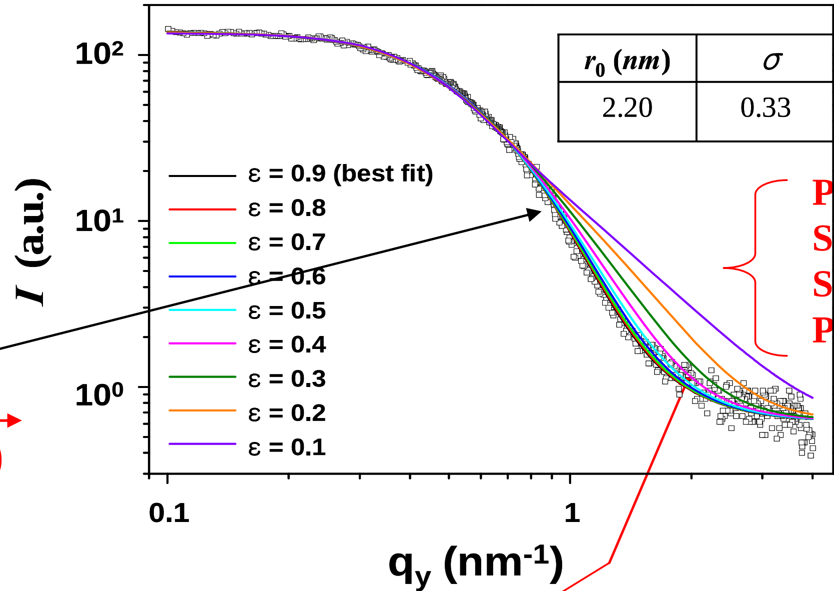
$$I_1 = \int n(r)\left(\frac{4\pi r^3}{3}\right)^2\left(\frac{\sin(qr)-qr\cos(qr)}{(qr)^3}\right)^2 S(qr)\,dr$$

$$n(r) = \frac{1}{\sqrt{2\pi r_0\sigma e^{0.5\sigma^2}}}\,e^{\frac{-\ln(r/r_0)^2}{2\sigma^2}}$$

Sphere Form Factor: $F_{sphere}(q,r) = \frac{3[\sin(qr)-qR\cos(qr)]}{(qr)^3}$

(2) Data Analysis with GIXS of Ellipsoidal Structures (Pores)

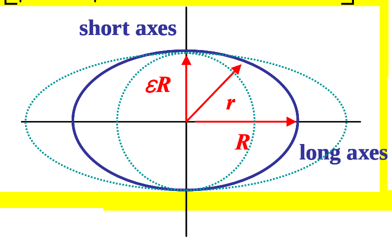




r_0 (nm)	σ	ε
2.20	0.33	0.90

Pore size
Size distributions
Shape
Porosity …

$$I_{GIXS}(\alpha_f, 2\theta_f) \cong \frac{1}{16\pi^2} \cdot \frac{1-e^{-2\,\mathrm{Im}(q_z)\cdot d}}{2\,\mathrm{Im}(q_z)} \cdot \begin{bmatrix} |T_i T_f|^2 I_1(q_{\|}, \mathrm{Re}(q_{1,z})) + \\ |T_i R_f|^2 I_1(q_{\|}, \mathrm{Re}(q_{2,z})) + \\ |T_f R_i|^2 I_1(q_{\|}, \mathrm{Re}(q_{3,z})) + \\ |R_i R_f|^2 I_1(q_{\|}, \mathrm{Re}(q_{4,z})) \end{bmatrix}$$



$$I_1 \quad) = \int n(r) \left(\frac{4\pi r^3}{3} \right)^2 F^2_{ellipsoid}\, S(qr)\, dr$$

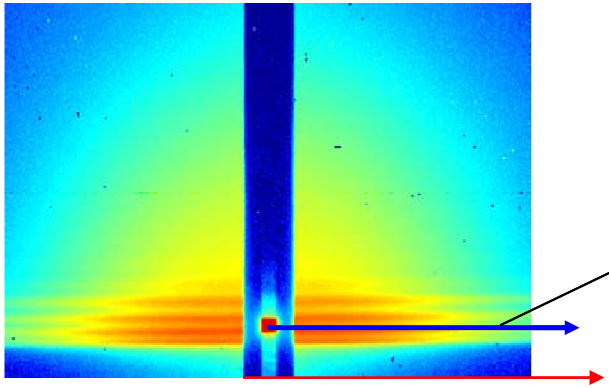
$$n(r) = \frac{1}{\sqrt{2\pi}\, r_0 \sigma e^{0.5\sigma^2}}\, e^{\frac{-\ln(r/r_0)^2}{2\sigma^2}}$$

$$F_{ellipsoid}(q, R, \varepsilon) = \int_0^{\pi/2} F^2_{sphere}\left[q, r(R, \varepsilon, \alpha)\right] \sin\alpha\, d\alpha$$

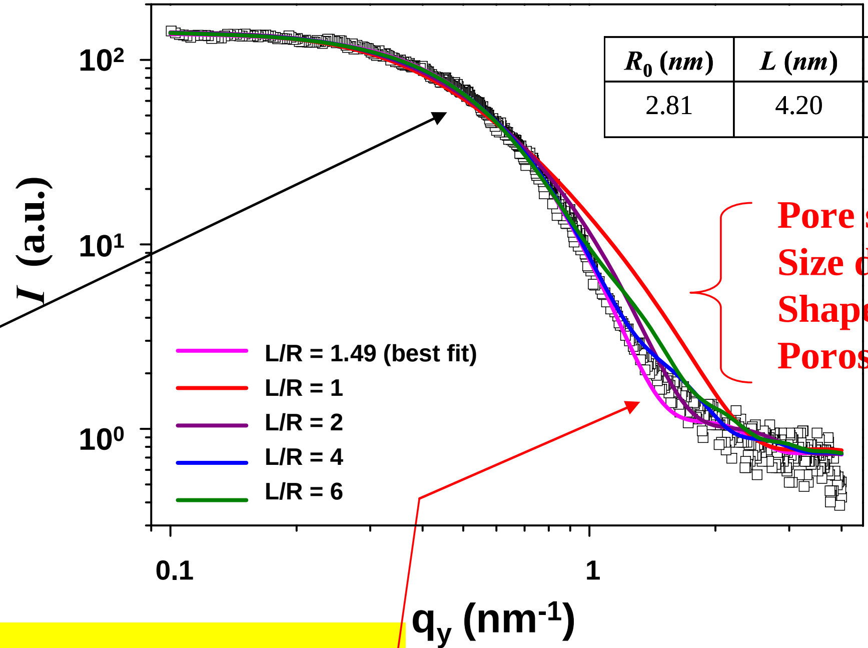
$$r(R, \varepsilon, \alpha) = R\sqrt{\sin\alpha^2 + \varepsilon^2 \cos\alpha^2}$$

(ε : aspect ratio)

(3) Data Analysis with GIXS of Cylindrical Structures (Pores)



$2\theta_f$ (In-plane)



R_0 (nm)	L (nm)	σ
2.81	4.20	0.33

Pore size
Size distributions
Shape
Porosity …

$$I_{GIXS}(\alpha_f, 2\theta_f) \cong \frac{1}{16\pi^2} \cdot \frac{1-e^{-2\,\mathrm{Im}(q_z)\cdot d}}{2\,\mathrm{Im}(q_z)} \cdot \begin{bmatrix} |T_i T_f|^2 I_1(q_\parallel, \mathrm{Re}(q_{1,z})) + \\ |T_i R_f|^2 I_1(q_\parallel, \mathrm{Re}(q_{2,z})) + \\ |T_f R_i|^2 I_1(q_\parallel, \mathrm{Re}(q_{3,z})) + \\ |R_i R_f|^2 I_1(q_\parallel, \mathrm{Re}(q_{4,z})) \end{bmatrix}$$

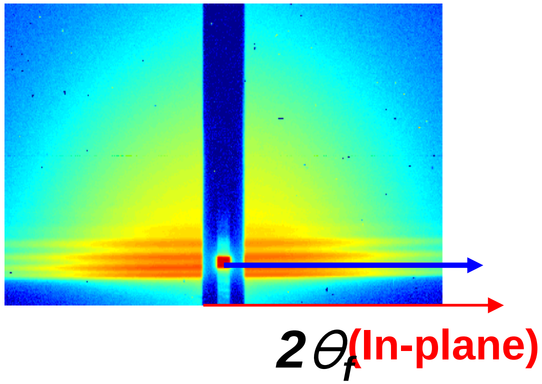
$$I_1 = \int n(R,L) V^2 F_{cylinder}^2 S(qr)\,dr$$

$n(R,L)$: lognormal function

$$F_{cylinder}(q,R,L) = \int_0^{\pi/2} \left[\frac{2B_1(qR\sin\alpha)}{qR\sin\alpha} \frac{\sin(qL\cos\alpha)/2}{qL\cos\alpha/2} \right]^2 \sin\alpha\, d\alpha$$

R : radius, L : length

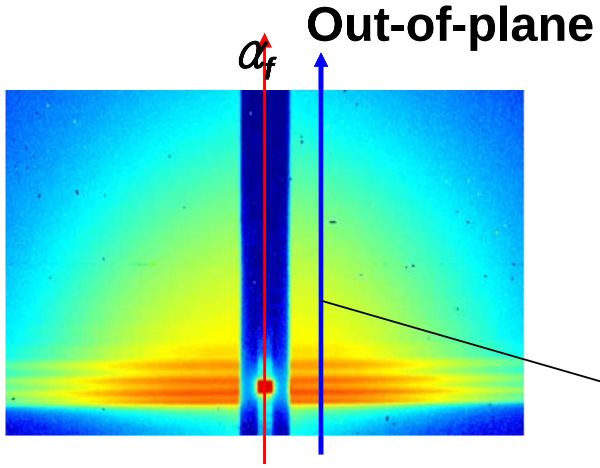
B_1 : first order Bessel function)

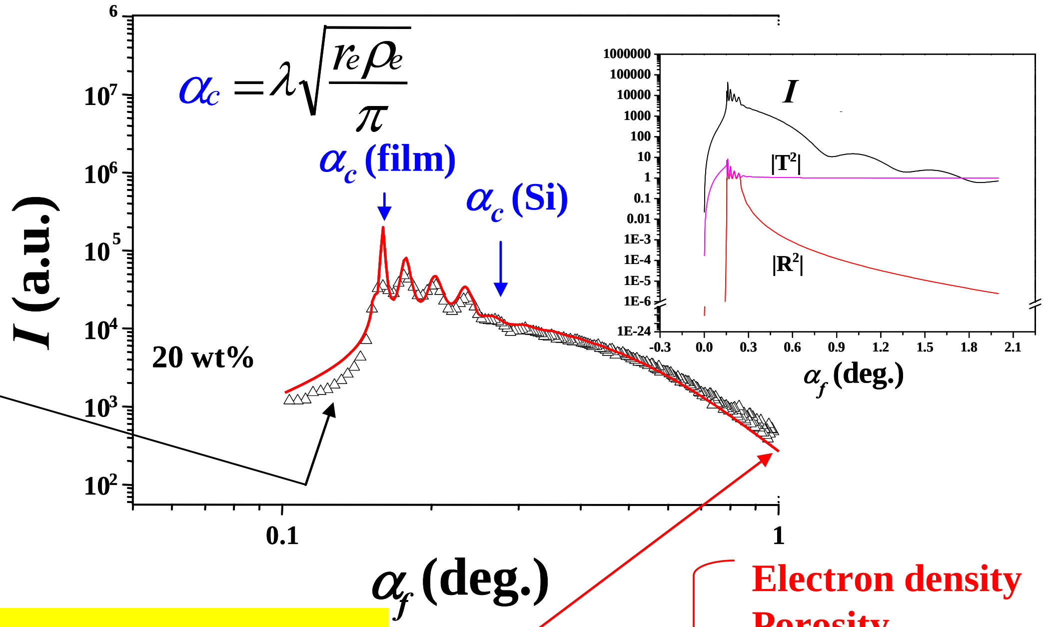


This Series of GIXS Analyses gives Conclusions:

- **Nanopore shape: “Sphere (hard sphere)”**
- **Packing order: “None”**
  (randomly dispersed in the film plane)

(4) Structural Information in the Out-of-Plane





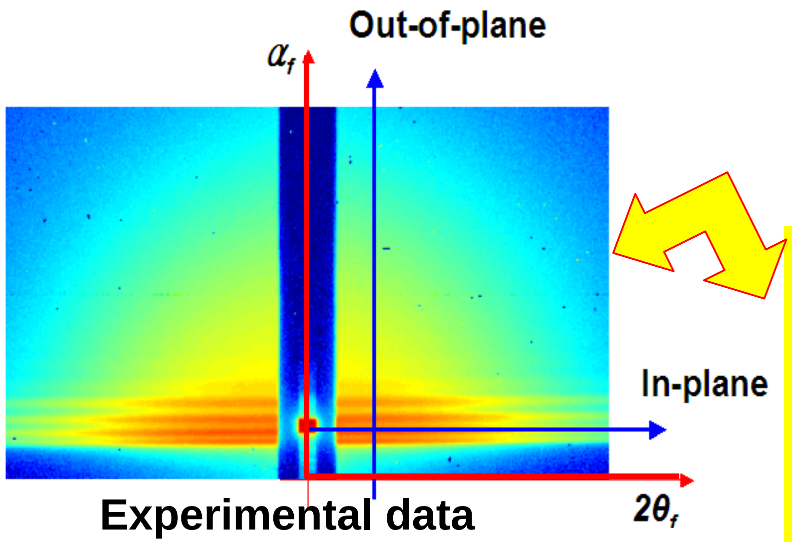
Electron density
Porosity
Thickness
Orientation

$$I_{GIXS}(\alpha_f, 2\theta_f) \cong \frac{1}{16\pi^2}\cdot\frac{1-e^{-2\mathrm{Im}(q_z)\cdot d}}{2\mathrm{Im}(q_z)}\cdot\left[\begin{array}{l} \left|T_iT_f\right|^2 I_1(q_\parallel,\mathrm{Re}(q_{1,z}))+ \\ \left|T_iR_f\right|^2 I_1(q_\parallel,\mathrm{Re}(q_{2,z}))+ \\ \left|T_fR_i\right|^2 I_1(q_\parallel,\mathrm{Re}(q_{3,z}))+ \\ \left|R_iR_f\right|^2 I_1(q_\parallel,\mathrm{Re}(q_{4,z})) \end{array}\right]$$

$$I_1 = \int n(r)\left(\frac{4\pi r^3}{3}\right)^2\left(\frac{\sin(qr)-qr\cos(qr)}{(qr)^3}\right)^2 S(qr)\,dr$$

$$n(r) = \frac{1}{\sqrt{2\pi r_0 \sigma e^{0.5\sigma^2}}}\, e^{\frac{-\ln(r/r_0)^2}{2\sigma^2}}$$

(5) 2D GIXS Simulation

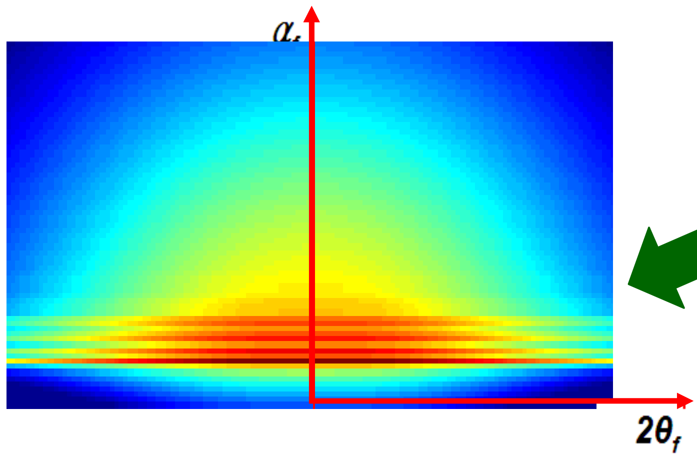


Experimental data

$$I_{GIXS}(\alpha_f, 2\theta_f) \cong \frac{1}{16\pi^2} \cdot \frac{1 - e^{-2\,\mathrm{Im}(q_z)\cdot d}}{2\,\mathrm{Im}(q_z)} \cdot \left[\begin{array}{l} |T_i T_f|^2 I_1(q_\parallel, \mathrm{Re}(q_{1,z})) + \\ |T_i R_f|^2 I_1(q_\parallel, \mathrm{Re}(q_{2,z})) + \\ |T_f R_i|^2 I_1(q_\parallel, \mathrm{Re}(q_{3,z})) + \\ |R_i R_f|^2 I_1(q_\parallel, \mathrm{Re}(q_{4,z})) \end{array} \right]$$

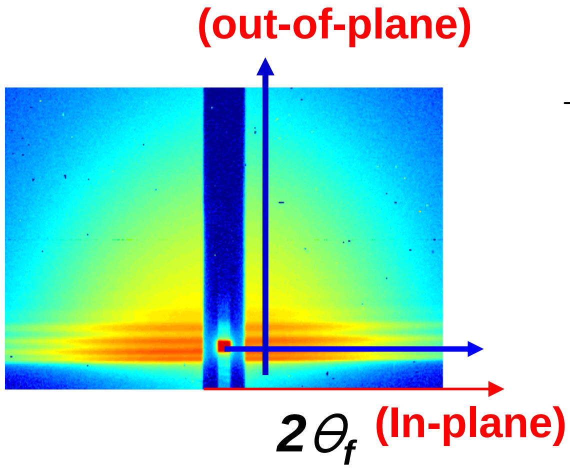
$$\boldsymbol{I_1} = \int n(r) \left(\frac{4\pi r^3}{3} \right)^2 \left(\frac{\sin(qr) - qr\cos(qr)}{(qr)^3} \right)^2 S(qr)\,dr$$

$$n(r) = \frac{1}{\sqrt{2\pi}\, r_0 \sigma e^{0.5\sigma^2}} e^{\frac{-\ln(r/r_0)^2}{2\sigma^2}}$$



Simulated GIXS pattern

Ree et al.,
***Nature Materials* (2005) 4, 147**
***Adv. Mater.* (2005) 17, 696**
Patents filed

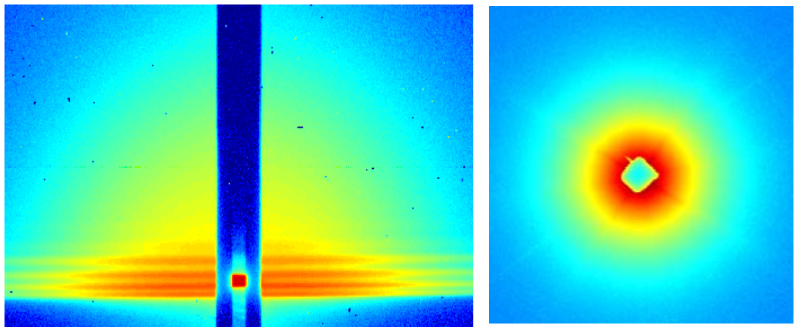


In- and Out-of-Plane GIXS Profiles Analysis

gives Conclusions:

- **Nanopore shape: "Sphere (hard sphere)"**
- **Packing order: "None"**
  (randomly dispersed within the thin film)

*** Further, We have verified these GIXS Analysis Results by the TXS Measurement and Data Analysis!**



GIXS **TXS**

M. Ree et al., *Macromolecules* 39, 8991 (2005)

Comparison of GIXS and TXS Analysis

Pore structures and properties of nanoporous PMSSQ films imprinted with PCL4 porogen

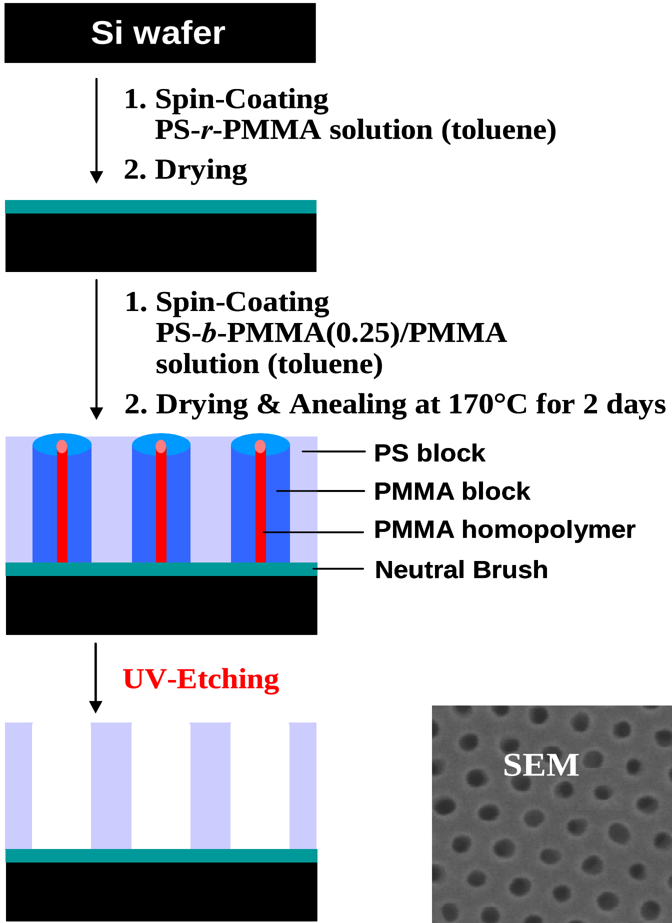
Porogen loading (wt%)	Cure temp. (°C)	$\overline{R_g}$ [a] (nm) GIXS	$\overline{R_g}$ [a] (nm) TXS	ρ_e [b] (nm^{-3})	P [c] (%)	n [d]	k [e]
0	400	-	-	399	-	1.3960	2.70
PCL4							
10	400	5.3(0.01)	4.4 (0.06)	373	6.5	1.3587	2.44
20	400	10.0(0.02)	11.3 (0.10)	338	15.3	1.3207	2.16
30	400	>40 [g]	>40 [g]	302	24.3	1.2795	1.85
30	200	-	>40 [g]	398	-	-	-

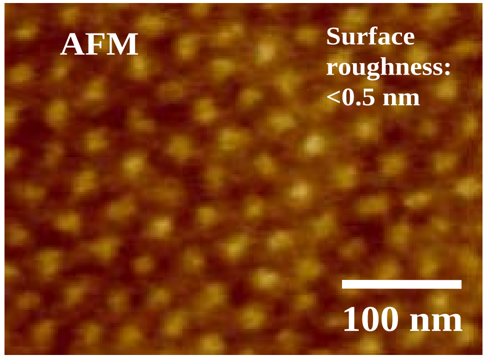
[a] Average radius of gyration estimated from the radius r and number distribution of pores obtained by the analysis of SAXS profile.
[b] Electron density determined from the out-of-plane GISAXS profile.
[c] Porosity estimated from the electron density of the film.
[d] Refractive index measured at 633 nm using spectroscopic ellipsometry.
[e] Dielectric constant measured at 1 MHz using an impedance analyzer.
[f] Standard deviation in the determined $\overline{R_g}$ value.
[g] Not detected due to the out of the detection limit (ca. 40 nm).

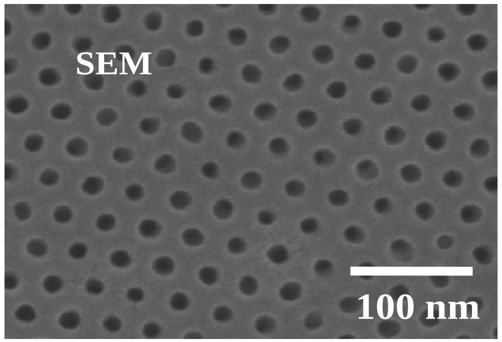
M. Ree et al., *Macromolecules* 39, 8991 (2005)

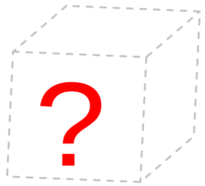
PS-b-PMMA Film (25-90 nm thick)

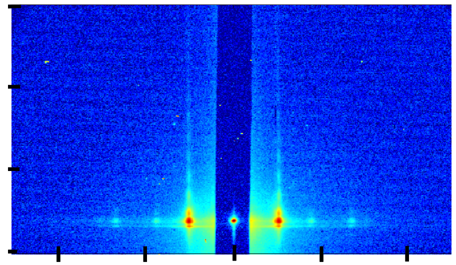
*Co-worked with Prof. Jin Kon Kim (Postech)







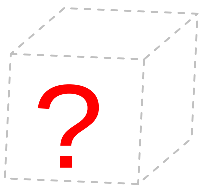


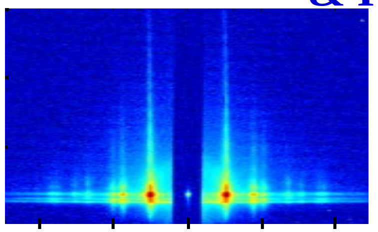


(1) $R_{cylinder}$ & Distribution ?

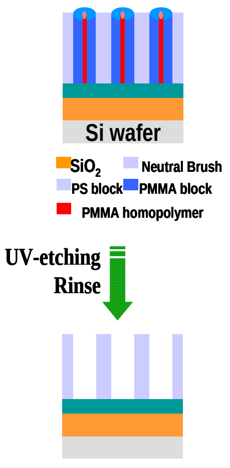
(2) $L_{cylinder}$ & Distribution ?

(3) Cylindrical Pore Depth & Its Quality ?

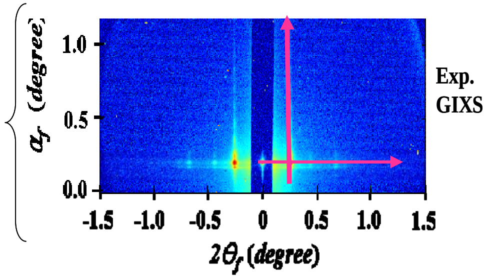


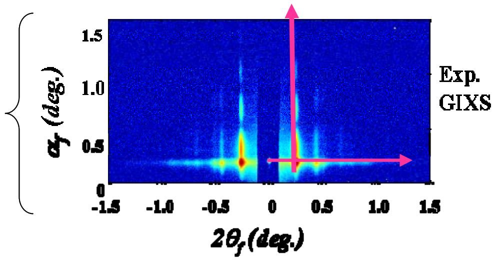


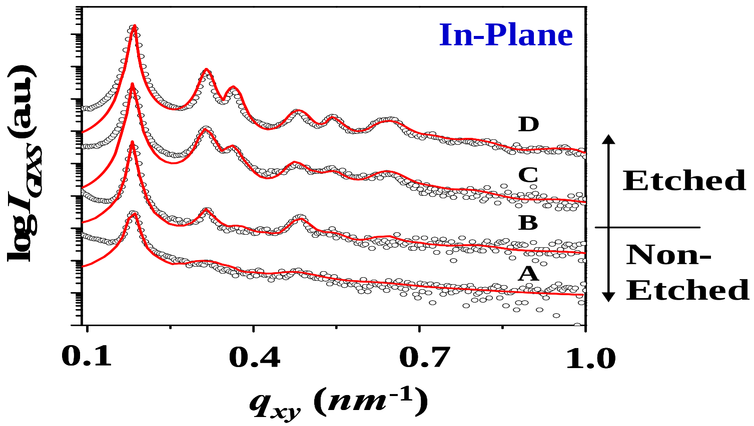
J. Appl. Crystallogr. 40, 305 (2007)
Adv. Funct. Mater. 18, 1371 (2008)

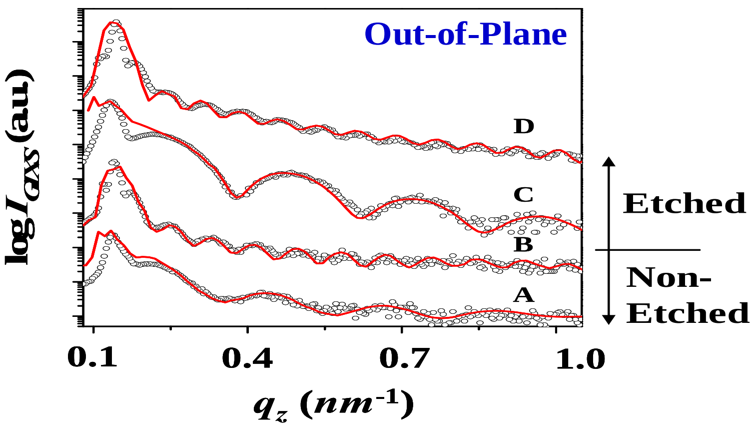


$R_{cylinder}$=? nm
L = ? nm









$$I_{GIXS}(\alpha_f, 2\theta_f) \cong \frac{1}{16\pi^2} \cdot \frac{1-e^{-2\mathrm{Im}(q_z)\cdot d}}{2\mathrm{Im}(q_z)} \cdot \begin{bmatrix} |T_iT_f|^2 I_1(q_\parallel, \mathrm{Re}(q_{1,z})) + \\ |T_iR_f|^2 I_1(q_\parallel, \mathrm{Re}(q_{2,z})) + \\ |T_fR_i|^2 I_1(q_\parallel, \mathrm{Re}(q_{3,z})) + \\ |R_iR_f|^2 I_1(q_\parallel, \mathrm{Re}(q_{4,z})) \end{bmatrix}$$

$$I_1(q) = |F(q)|^2 Z(q)$$

$$F(q,R,L) = 2\pi R^2 L \frac{J_1(qR)}{qR} \sin(qL/2)\exp(-iqL/2)$$

$$G(R) = \frac{1}{\sqrt{2\pi}\sigma_R}\exp\left[-\frac{(R-\bar{R})^2}{2\sigma_R^2}\right]$$

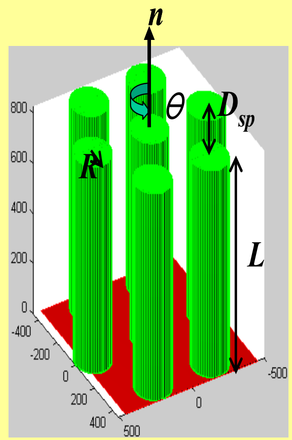
$$Z(q) = \prod_{k=1}^{d} Z_k(q)$$

$$Z(q) = \mathrm{re}\left\{\frac{1+F_k(q)}{1-F_k(q)}\right\} = \frac{1-|F_k|^2}{1-2|F_k|\cos(a_k\cdot q)+|F_k|^2}$$

$$F_k(q) = |F_k(q)|\exp(-iqa_k)$$

$$|F_k(q)| = \prod_{j=1}^{2}\exp\left[-\frac{1}{2}g^2(qa_j)^2\right]$$

$$g^2 = \Delta^2 a_j / a_j^2$$



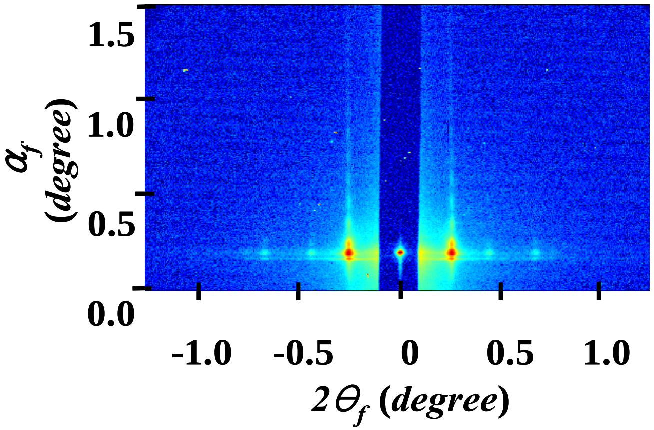
$R_{cylinder}$=11.5 nm
L = 25 – 100 nm

g: paracrystal distortion factor

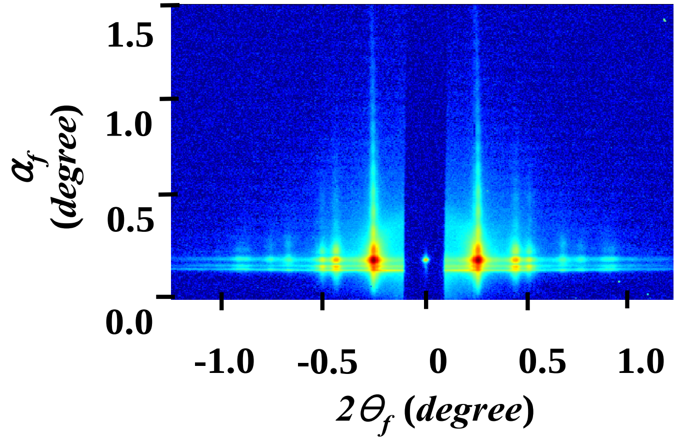
GIXS

Measured

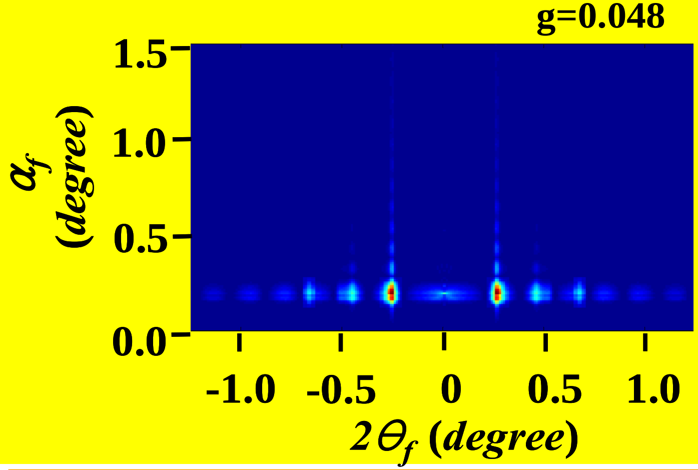
Before UV-Etching

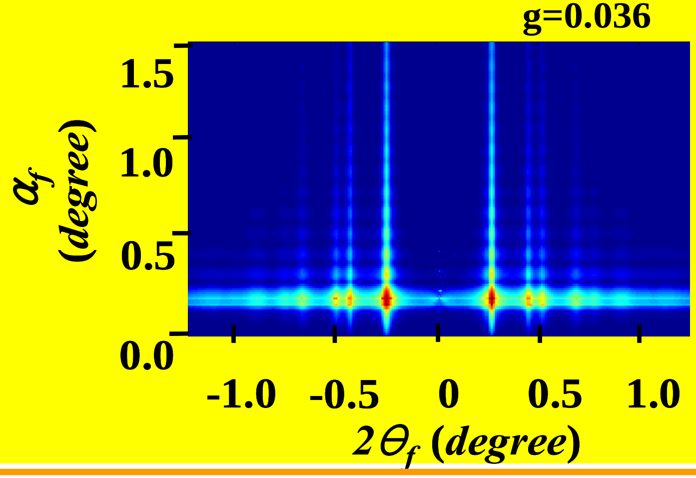


After UV-Etching



Calculated





Parameters in calculating 2D GIXS pattern:

- $\alpha_i = 0.20°$
- $L = 78.8$ nm
- $R = 11.8$ nm
- $\sigma_r = 2.95$ nm
- $D_{sp} = 34.0$ nm ρ_e(film)=348 nm^{-3}

Parameters in calculating 2D GIXS pattern:

- $\alpha_i = 0.20°$
- $L = 86.1$ nm
- $R = 11.7$ nm
- $\sigma_r = 2.90$ nm
- $D_{sp} = 34.0$ nm ρ_e(film)=261 nm^{-3}

J. Appl. Crystallogr. 40, 305 (2007)

Structural and property characteristics of thin films of the PS-*b*-PMMA/PMMA mixtures before and after UV-etching

Sample	t^{a} (nm)	Structural parameters					Properties		
		L^{b} (nm)	$\overline{R}^{c}$ (nm)	$\sigma_R{}^{d}$ (nm)	$d_{sp}{}^{e}$ (nm)	g^{f}	$\alpha_c{}^{g}$ (deg.)	$\rho_e{}^{h}$ (nm^{-3})	$P_e{}^{i}$ (%)
Before etching									
Film-1	28.5	28.5	11.0	3.01	34.0	0.053	0.156	348	–
Film-2	78.8	78.8	11.4	3.00	34.0	0.048	0.156	348	–
After UV-etching									
Film-3	25.0	25.0	11.8	2.95	34.0	0.040	0.136	265	25.3
Film-4	86.1	86.1	11.7	2.90	34.0	0.036	0.135	261	26.6

[a] Film thickness.

[b] Length of the cylindrical pores.

[c] Pore radius determined from the peak maximum of the radius *r* and the number distribution of pores.

[d] Standard deviation of the pore radius.

[e] Center-to-center distance of the cylindrical pores (*d*-spacing of the hexagon).

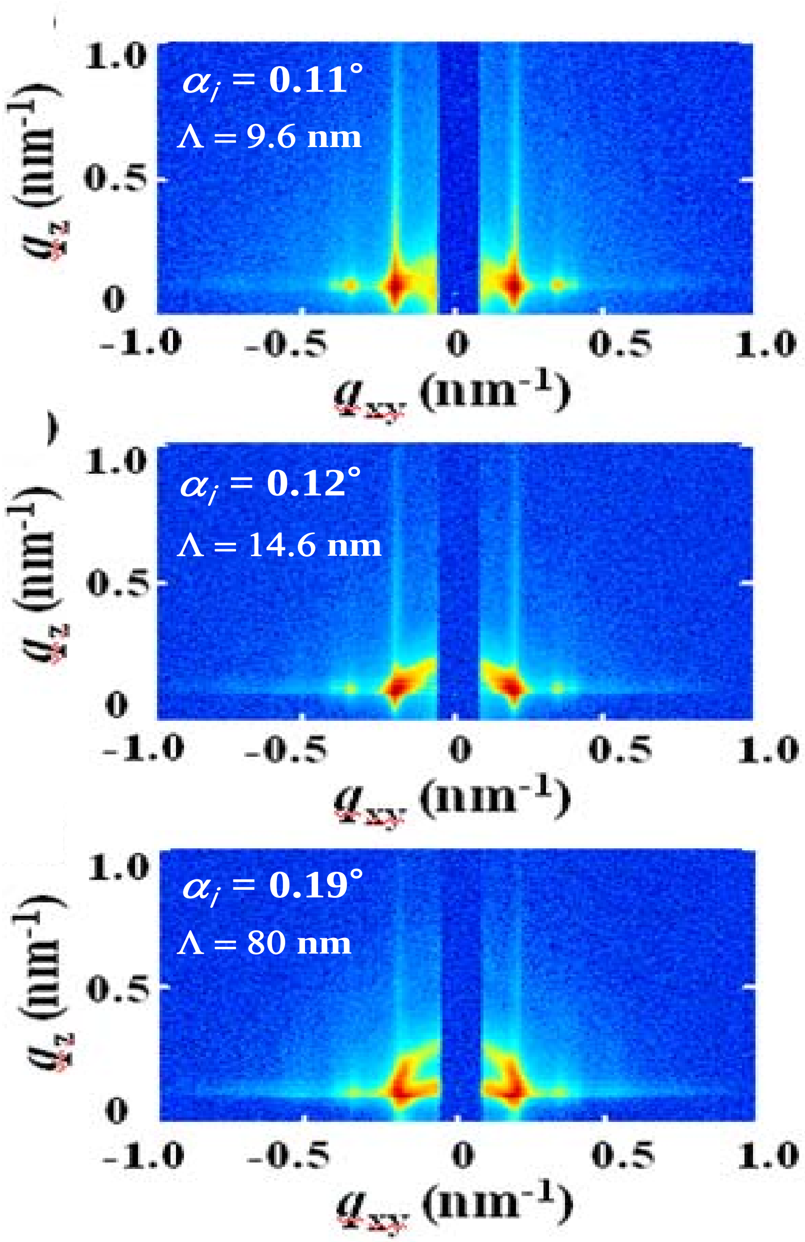
[f] Paracrystal distortion factor

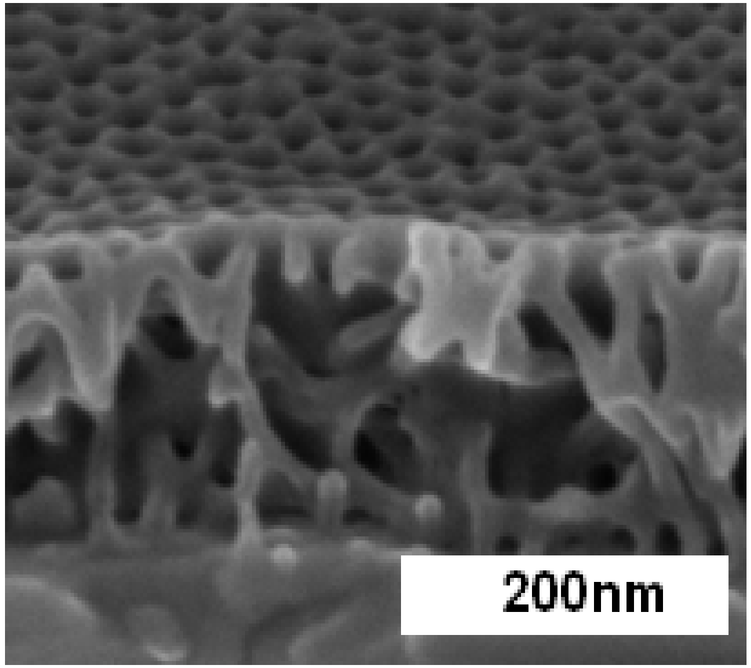
[g] Critical angle of the film determined from the out-of-plane GIXS profile.

[h] Electron density determined from the critical angle of the film.

[i] Porosity estimated from the electron density of the film with respect to the electron density of PS.

Surface/Internal Structure: Surface Structure and Its Depth Variation in Nanotemplates



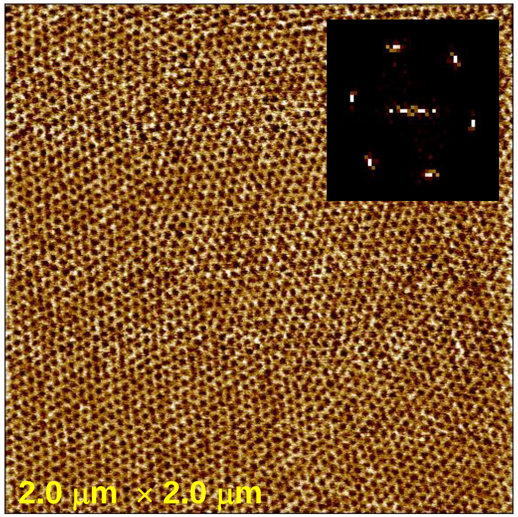


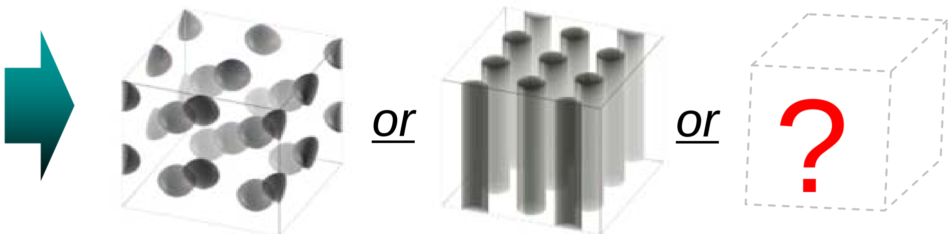
PS-b-PMMA Film (200 nm thick)

rms roughness: 0.1-0.3 nm

***Macromolecules*, 38, 10532 (2005)**

Fractionated (FM)
(wt_{PMMA} = 0.345) *AFM*



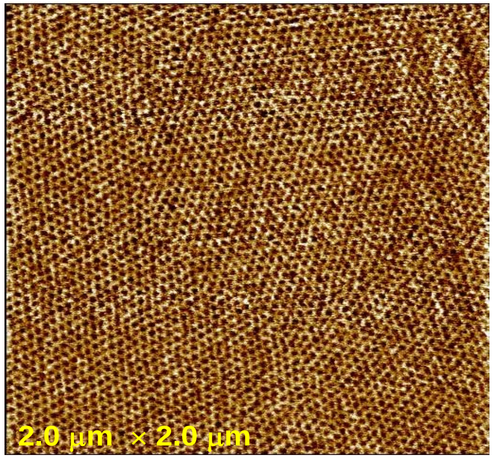


***Co-worked with Prof. Taihyun Chang (Postech)**

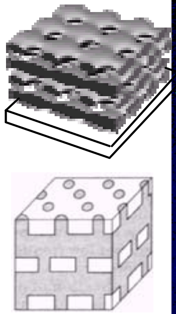
PS-b-PMMA Film (200 nm thick)

Macromolecules, 38, 4311 (2005)
Macromolecules, 38, 10532 (2005)
Macromolecules, 39, 684 (2006)
Macromolecules 40, 2603 (2007)
J. Appl. Crystallogr. 41, 281 (2008)

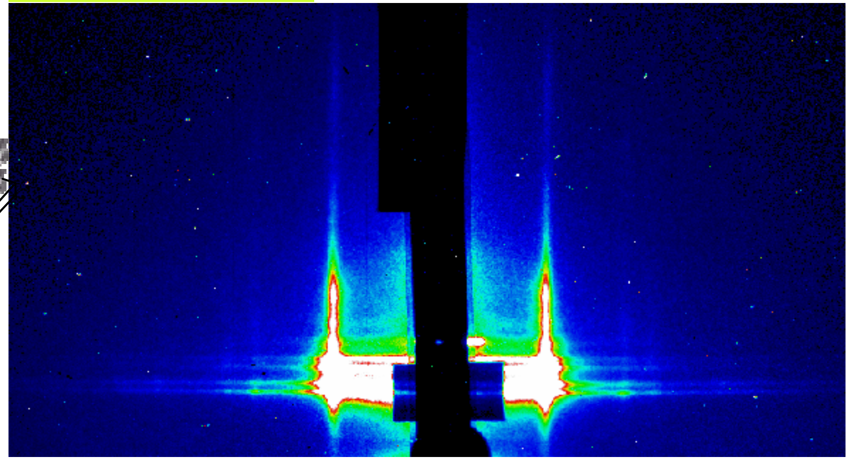
Fractionated (FM)
(wt_{PMMA} = 0.345)



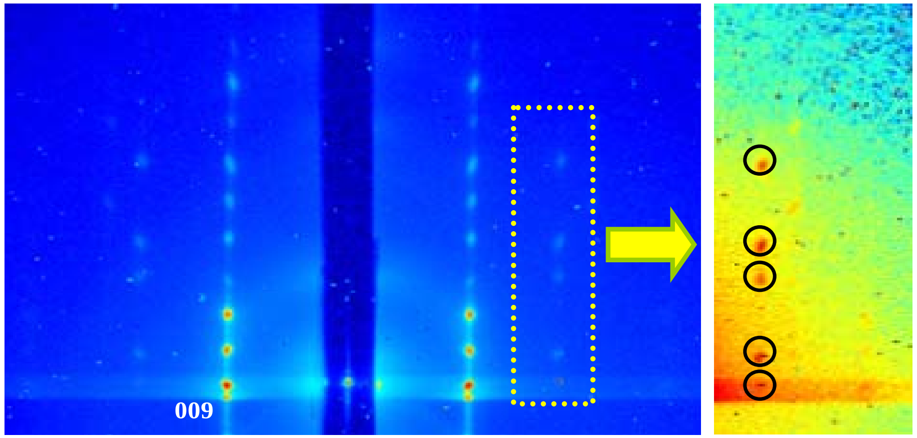
HPL



$\alpha_c \leq \alpha_i \leq \alpha_s$



(Measured)



Co-worked with
Prof. Taihyun Chang (Postech)
Dr. Byeongdu Lee (APL)

$$I_{GIXS}(\alpha_f, 2\theta_f) \cong \frac{1}{16\pi^2} \cdot \frac{1-e^{-2\,\mathrm{Im}(q_z)\cdot \mathbf{d}}}{2\,\mathrm{Im}(q_z)} \cdot \begin{bmatrix} |T_i T_f|^2 I_1(q_\parallel, \mathrm{Re}(q_{1,z})) + \\ |T_i R_f|^2 I_1(q_\parallel, \mathrm{Re}(q_{2,z})) + \\ |T_f R_i|^2 I_1(q_\parallel, \mathrm{Re}(q_{3,z})) + \\ |R_i R_f|^2 I_1(q_\parallel, \mathrm{Re}(q_{4,z})) \end{bmatrix}$$

$$I_1(\mathbf{q}) = P(\mathbf{q}) \cdot S(\mathbf{q})$$

$$P(\mathbf{q}) = F^2(\mathbf{q}, R, L)$$

$$F(\mathbf{q}, R, L) = 2\pi R^2 L \frac{J_1(q_\parallel R)}{q_\parallel R} \frac{\sin(q_z L/2)}{q_z L/2} \exp[-iq_z L/2]$$

$$F(\mathrm{q}, R, L) = F_\perp(q_\parallel, R) \cdot F_\parallel(q_z, L)$$

$$F_\perp(q_\parallel, R) = \frac{2J_1(q_\parallel R)}{q_\parallel R}$$

$$F_\parallel(q_z, L) = \frac{\sin(q_z L/2)}{q_z L/2} \exp[-iq_z L/2]$$

$$\langle F(\mathbf{q}, R, L)\rangle = \langle F_\perp(q_\parallel, R)\rangle \cdot \langle F_\parallel(q_z, L)\rangle$$

$$\langle F_\perp(q_\parallel, R)\rangle = \frac{\int_0^\infty G(R) F_\perp(q_\parallel, R)\, dR}{\int_0^\infty G(R)\, dR}$$

$$\langle F_\parallel(q_z, L)\rangle = \frac{\int_0^\infty G(L) F_\parallel(q_z, L)\, dL}{\int_0^\infty G(L)\, dL}$$

$$G(R) = \frac{1}{\sqrt{2\pi}\sigma_R} \exp\left[-\frac{(R-\bar{R})^2}{2\sigma_R^2}\right]$$

$$G(L) = \frac{1}{\sqrt{2\pi}\sigma_L} \exp\left[-\frac{(L-\bar{L})^2}{2\sigma_L^2}\right]$$

$$S(\mathbf{q}) = \prod_{l=1}^{3} \prod_{k=1}^{3} Z_{lk}(\mathbf{q})$$

$$Z_{lk}(\mathbf{q}) = \frac{1-|F_{lk}(\mathbf{q})|^2}{1-2|F_{lk}(\mathbf{q})|\cos(\mathbf{q}\cdot \mathbf{a}_{lk}) + |F_{lk}(\mathbf{q})|^2}$$

$$F_{lk}(\mathbf{q}) = |F_{lk}(\mathbf{q})| \exp(-i\mathbf{q}\cdot \mathbf{a}_{lk})$$

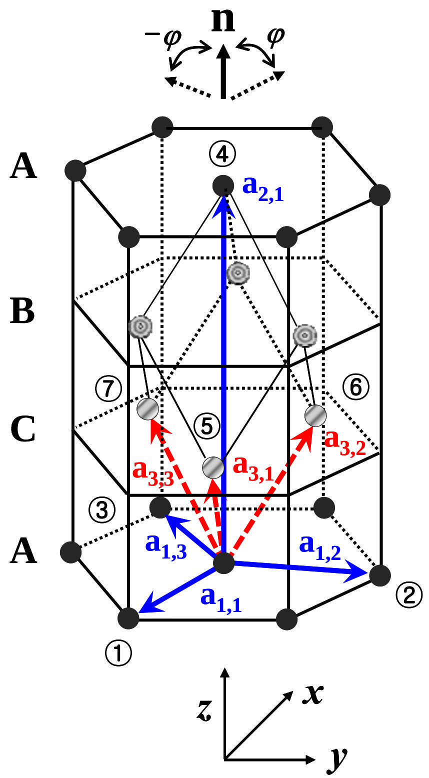
$$|F_{lk}(\mathbf{q})| = \prod_j^7 \exp\left[-\frac{1}{2} g_{lk,j}^2 (\mathbf{q}\cdot \mathbf{a}_{lk,j})\right].$$

$$g_{lk,j}^2 = \Delta^2 \mathbf{a}_{lk,j} / \mathbf{a}_j^2$$

$$I_{\mathrm{GIXS},\varphi}(\mathbf{q}) = \int_{-\pi}^{\pi} I_{\mathrm{GIXS}}(\mathbf{q}) D(\varphi)\, \mathrm{d}\varphi$$

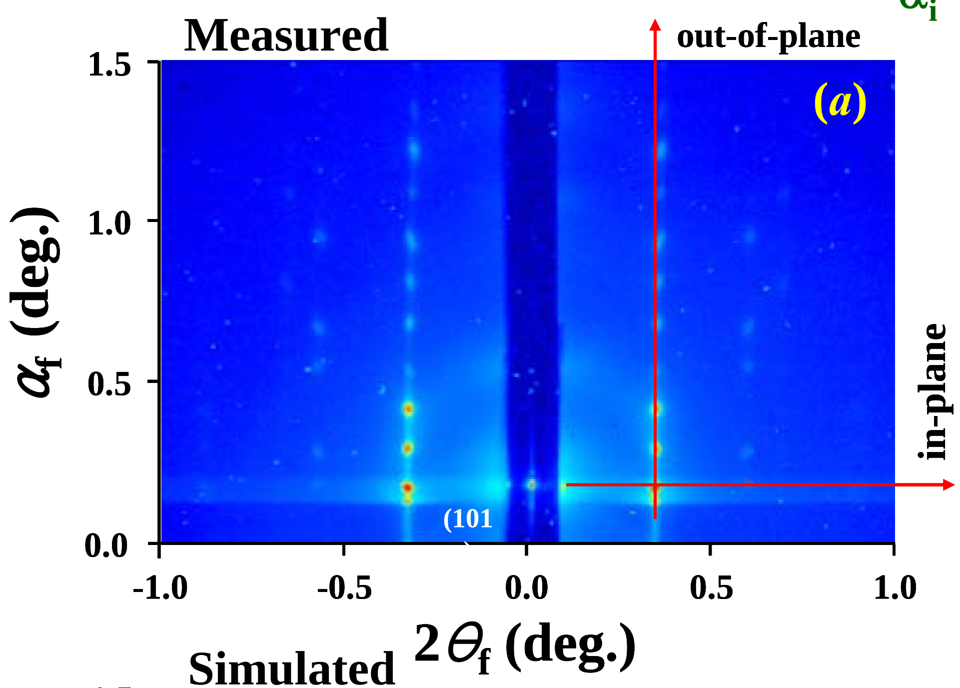
$$O_{\mathrm{s}} = \int D(\varphi) \frac{(3\cos^2\varphi - 1)}{2}\, \mathrm{d}\varphi$$

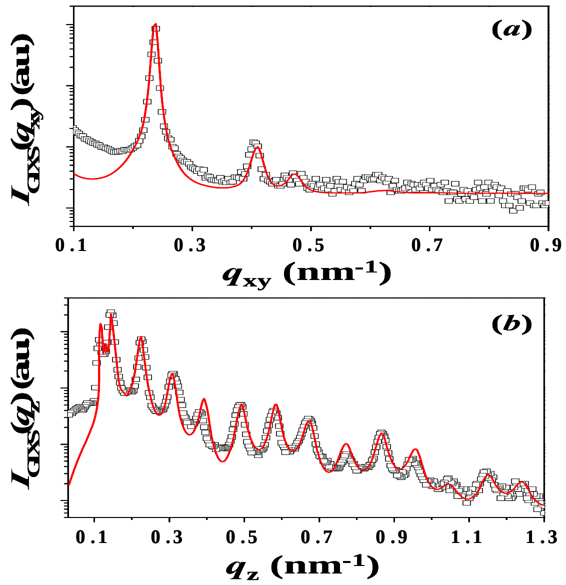
$$D(\varphi) = \frac{1}{\sqrt{2\pi}\sigma_\varphi} \exp\left[-\frac{(\varphi - \bar{\varphi})^2}{2\sigma_\varphi^2}\right]$$

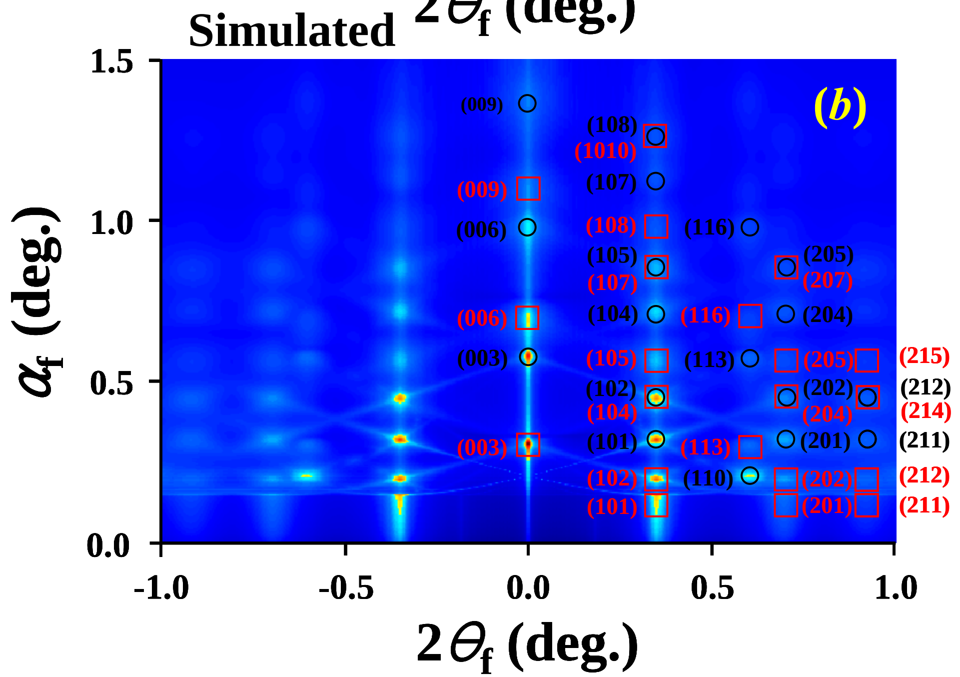


J. Appl. Crystallogr. **41, 281 (2008)**

$\alpha_i = 0.220°$







HPL structure with ABC stacking

Open circles (black color):
due to reflected X-ray beams

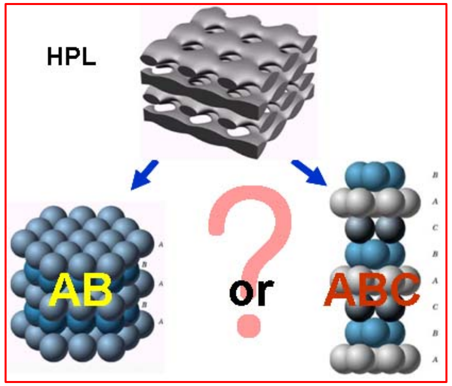
Open squares (red color):
due to transmitted X-ray beams

***J. Appl. Crystallogr.* 41, 281 (2008)**

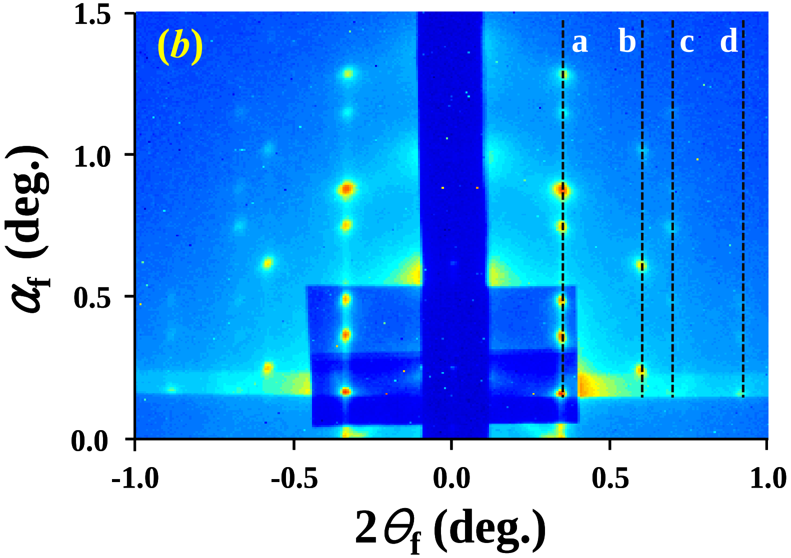
Structural parameters of a PS-*b*-PI diblock copolymer thin film, which were obtained by GIXS measurements and data analysis.

a_H † (nm)	c_H ‡ (nm)	$\overline{R}$ § (nm)	σ_R ¶ (nm)	$\overline{L}$ †† (nm)	σ_L ‡‡ (nm)	Thickness§§ (nm)	$\rho_{e,f}$ ¶¶ (nm^{-3})	$\overline{\varphi}$ †††	σ_φ ‡‡‡	S §§§
30.6	66.1	10.6	4.5	20.2	0.9	1254.0 ± 4.0	360	0	0	1

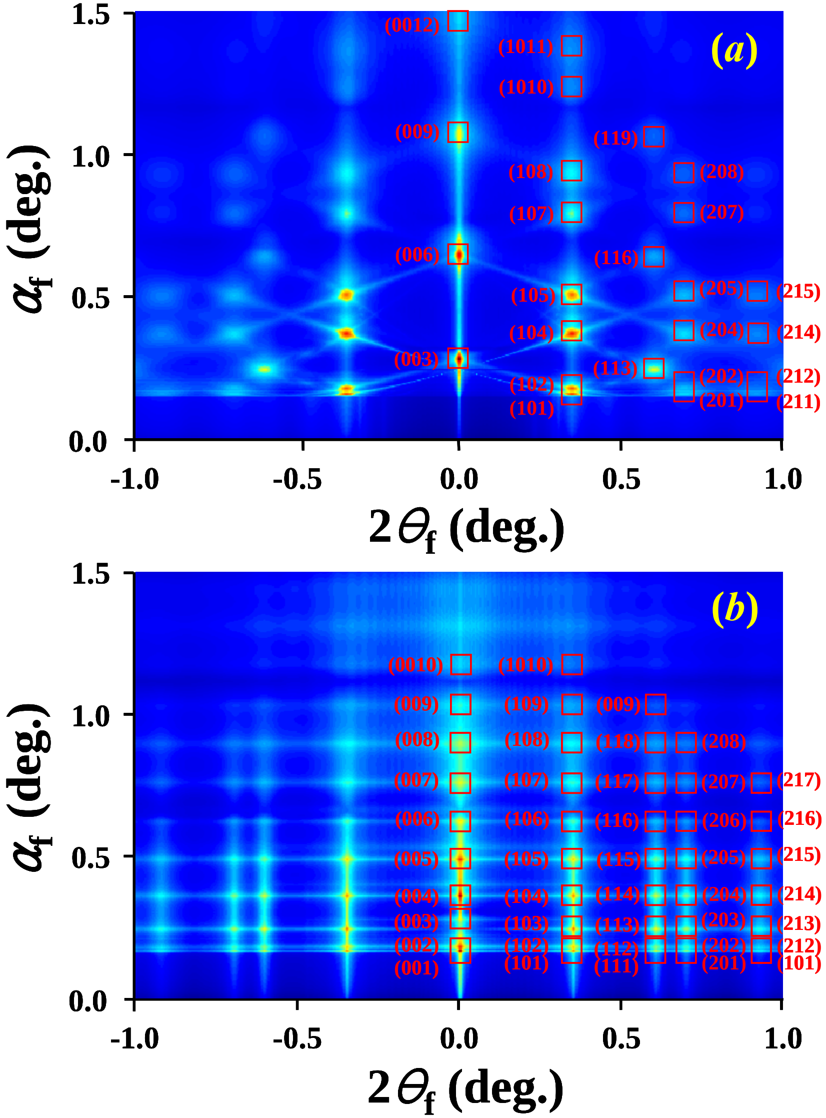
† Hexagonal lattice parameter along the film surface.
‡ Hexagonal lattice parameter along the film thickness direction.
§ Mean radius of cylinder.
¶ Standard deviation of the cylinder radius.
†† Mean length of cylinder.
‡‡ Standard deviation of the cylinder length.
§§ Film thickness measured using spectroscopic ellipsometry.
¶¶ Electron density determined from the critical angle of film.
††† Mean polar angle.
‡‡‡ Standard deviation of polar angle from mean polar angle.
§§§ Second order orienation factor.



Measured $\alpha_i = 0.240°$



Simulated



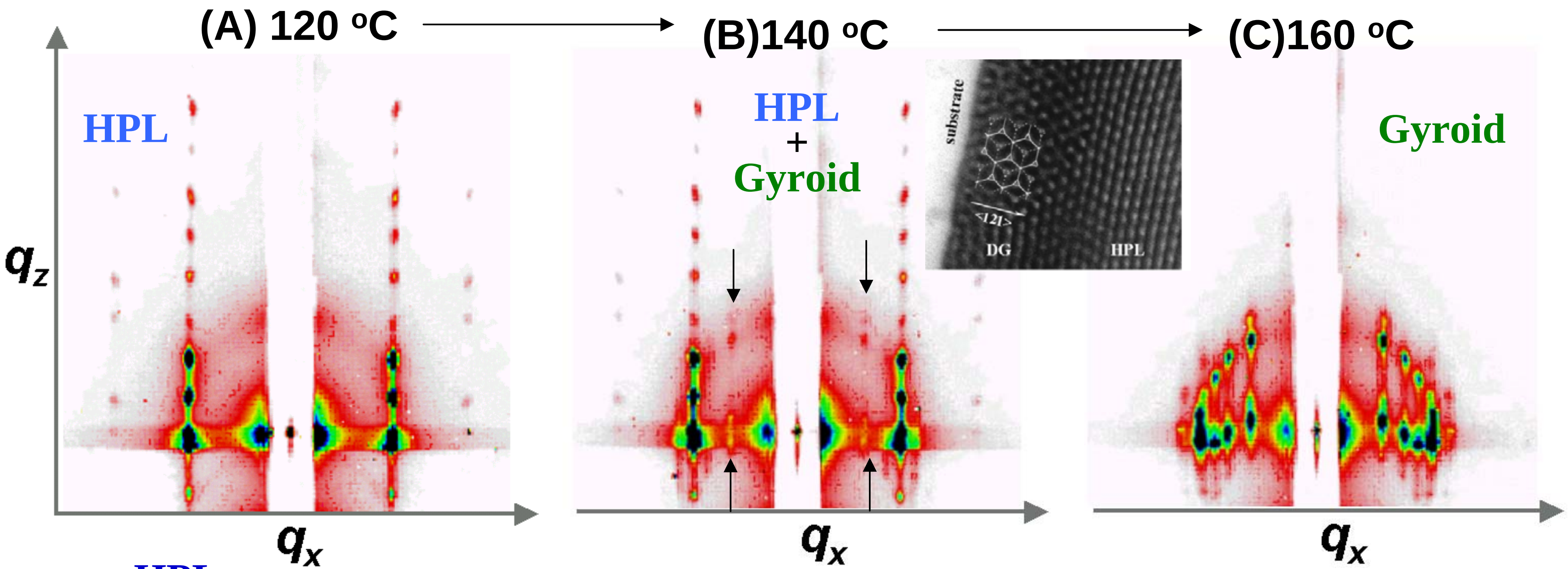
ABC Stacking

AB Stacking

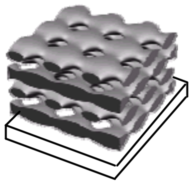
J. Appl. Crystallogr. 41, 281 (2008)

4. Phase Transition of HPL phase to Gyroid

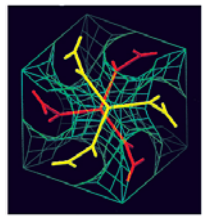
PS-*b*-PI (wt_{PI}=0.634) film (1254 nm thick)   rms roughness: 0.1-0.3 nm



HPL



$$\alpha_c \le \alpha_i \le \alpha_s$$



Gyroid

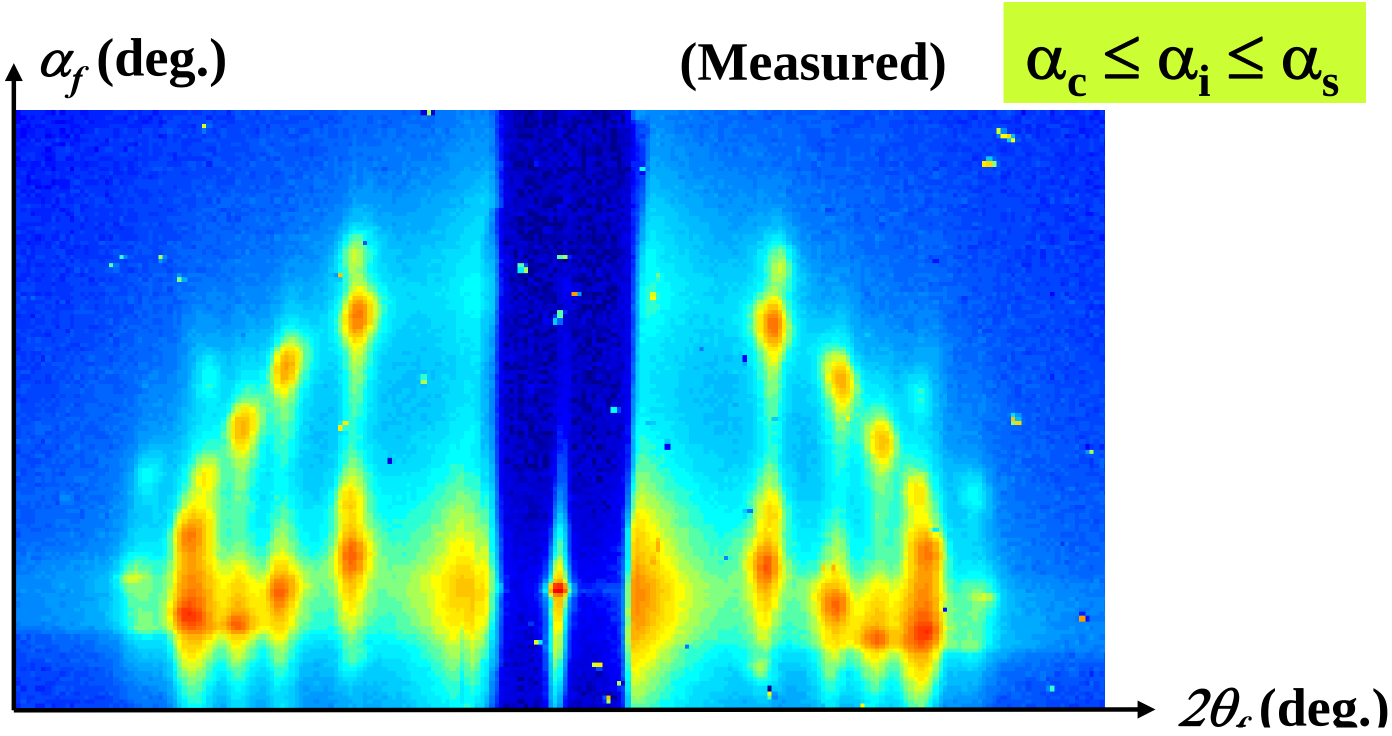
•Gyroid-structured microdomains perfectly oriented along the {121} plane parallel to the in-plane of a film.

Macromolecules, 38, 4311 (2005)
Macromolecules, 38, 10532 (2005)
Macromolecules, 39, 684 (2006)
Macromolecules, 40, 2603 (2007)
J. Appl. Crystal., 40, 950 (2007)
J. Appl. Crystal., 41, 281 (2008)

Co-worked with
Prof. Taihyun Chang (Postech)
Dr. Byeongdu Lee (APL)

5. GIXS Analysis of Gyroid Nanostructures

PS-b-PI Diblock Copolymer Thin Film on Si Substrate



J. Appl. Cryst. **40, 950-958 (2007)**

*** 2008 Cover Page of J. Appl. Cryst.**

$$I_{GIXS}(\alpha_f, 2\theta_f) \cong \frac{1}{16\pi^2} \cdot \frac{1-e^{-2\,\mathrm{Im}(q_z)\cdot \mathbf{d}}}{2\,\mathrm{Im}(q_z)} \cdot \begin{bmatrix} |T_i T_f|^2 I_1(q_\parallel, \mathrm{Re}(q_{1,z})) + \\ |T_i R_f|^2 I_1(q_\parallel, \mathrm{Re}(q_{2,z})) + \\ |T_f R_i|^2 I_1(q_\parallel, \mathrm{Re}(q_{3,z})) + \\ |R_i R_f|^2 I_1(q_\parallel, \mathrm{Re}(q_{4,z})) \end{bmatrix}$$

Paracrystalline system is considered to consist of infinite periodic minimal surfaces (IPMS),
IPMS in the form $h(xyz) = 0$ (von Schnering & Nesper, 1991):

$$h(xyz) = \sin(\frac{2\pi x}{a_\mathrm{G}})\cos(\frac{2\pi y}{a_\mathrm{G}}) + \sin(\frac{2\pi y}{a_\mathrm{G}})\cos(\frac{2\pi z}{a_\mathrm{G}}) + \sin(\frac{2\pi z}{a_\mathrm{G}})\cos(\frac{2\pi x}{a_\mathrm{G}}$$

$h(xyz)$: a trigonometric function, which is given for the gyroid surface, and a_G is the cubic lattice parameter.

$$P(\mathbf{q}) = \left[\sum_{j=1}^{N} s_j \cos(qr_j) \frac{\sin[qn_j(L/2)]}{qn_j(L/2)}\right]^2 + \left[\sum_{j=1}^{N} s_j \sin(qr_j) \frac{\sin[qn_j(L/2)]}{qn_j(L/2)}\right]^2$$

s_j : surface area of the jth minimal surface (MS)
r_j : position of the jth MS's centre
n_j : a unit vector normal to the surface of the jth MS
L : width of PS phase.

$$S(\mathbf{q}) = \prod_{k=1}^{3} Z_k(\mathbf{q})$$

$$Z_k(\mathbf{q}) = 1 + \frac{F_k(\mathbf{q})}{1-F_k(\mathbf{q})} + \frac{F_k^*(\mathbf{q})}{1-F_k^*(\mathbf{q})}$$

$$F_k(\mathbf{q}) = |F_k(\mathbf{q})| e^{-i\mathbf{q}\cdot\mathbf{a}_k}$$

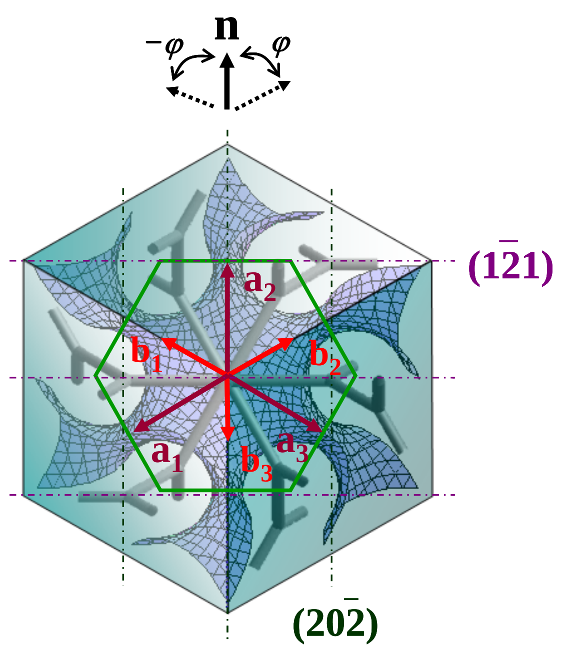
$$|F_k(\mathbf{q})| = \exp\left[-\left(\frac{q_1^2 g_1^2 + q_2^2 g_2^2 + q_3^2 g_3^2}{2}\right)\right]$$

$\mathbf{a}_1 = d(\mathbf{b}_1 + \mathbf{b}_3)$
$\mathbf{a}_2 = d(\mathbf{b}_1 + \mathbf{b}_2)$
$\mathbf{a}_3 = d(\mathbf{b}_2 + \mathbf{b}_3)$
$g_1 = \Delta\mathbf{a}_1/\mathbf{a}_1$
$g_2 = \Delta\mathbf{a}_2/\mathbf{a}_2$
$g_3 = \Delta\mathbf{a}_3/\mathbf{a}_3$

$$I_{\mathrm{GIXS},\varphi}(\mathbf{q}) = \int_{-\pi}^{\pi} I_{\mathrm{GIXS}}(\mathbf{q}) D(\varphi)\,\mathrm{d}\varphi$$

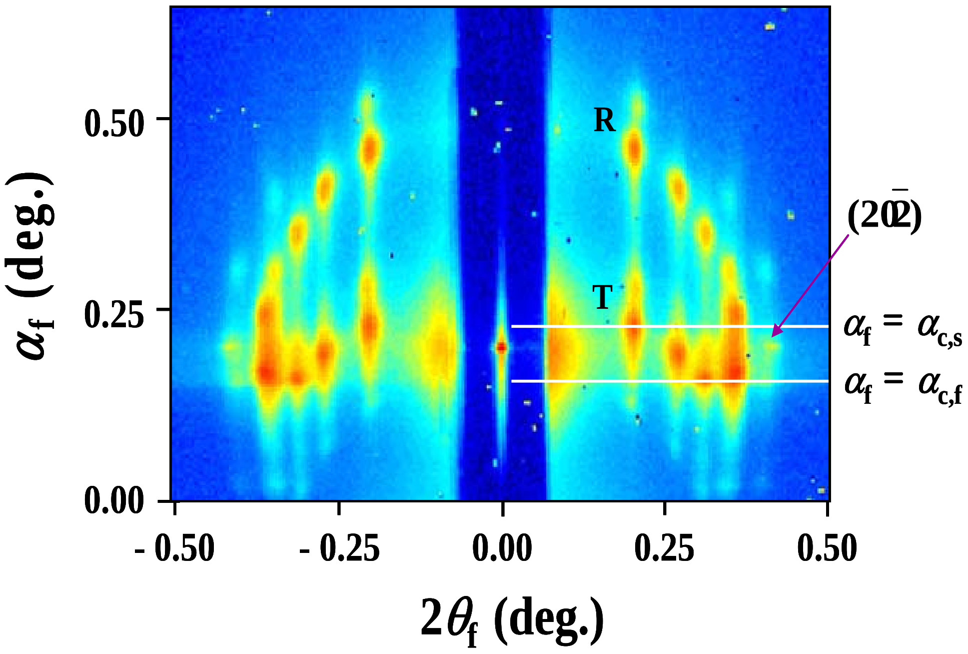
$$O_\mathrm{s} = \int D(\varphi) \frac{(3\cos^2\varphi - 1)}{2}\,\mathrm{d}\varphi$$

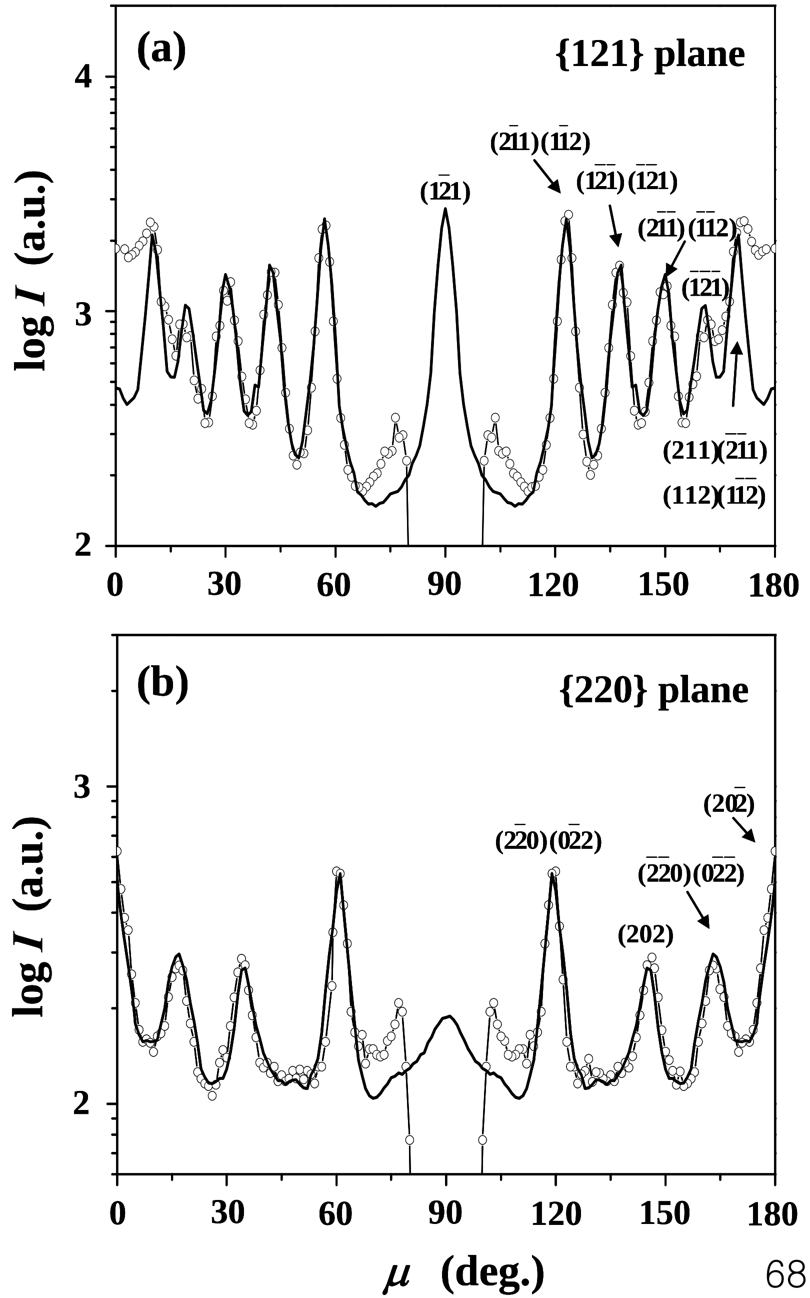
$$D(\varphi) = \frac{1}{\sqrt{2\pi}\sigma_\varphi} \exp\left[-\frac{(\varphi - \bar{\varphi})^2}{2\sigma_\varphi^2}\right]$$

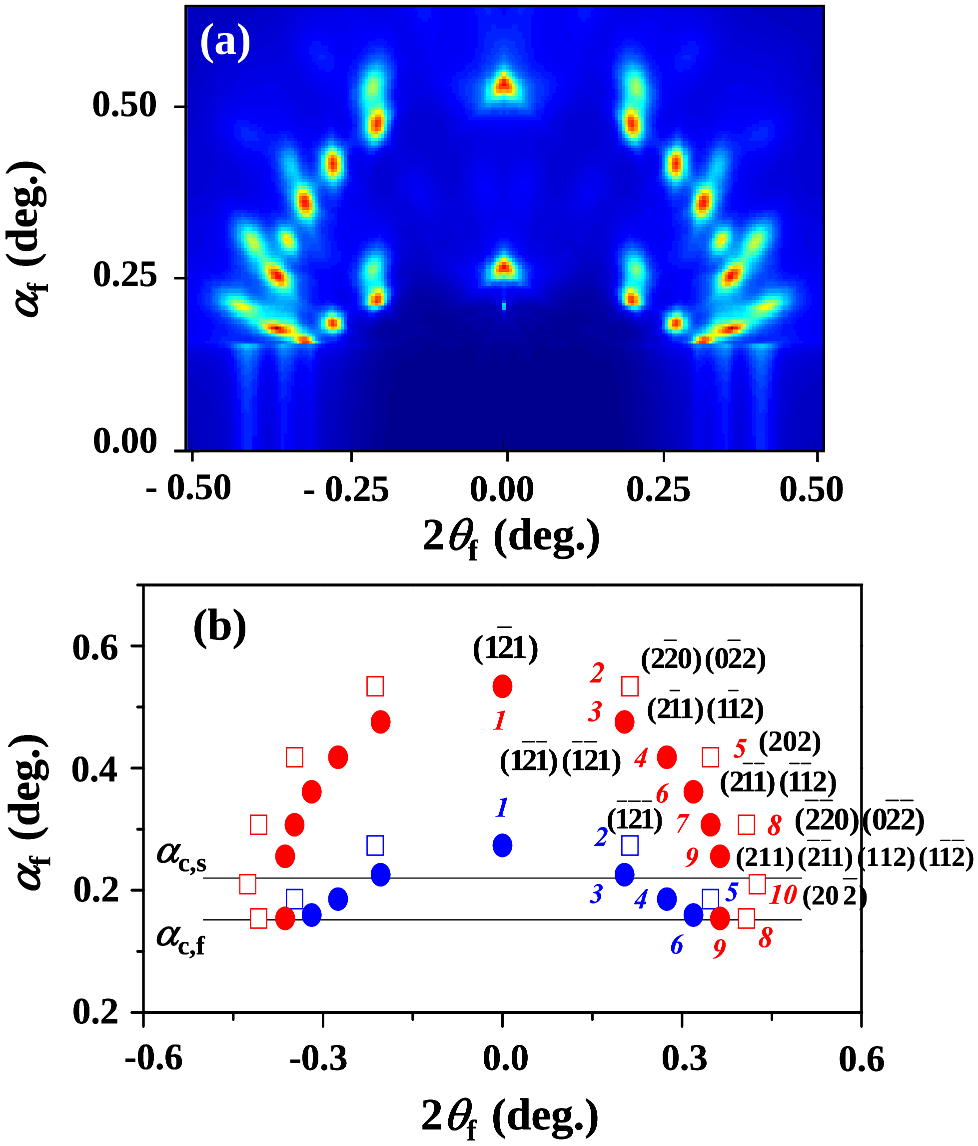


67

***J. Appl. Cryst.* 40, 950-958 (2007)**

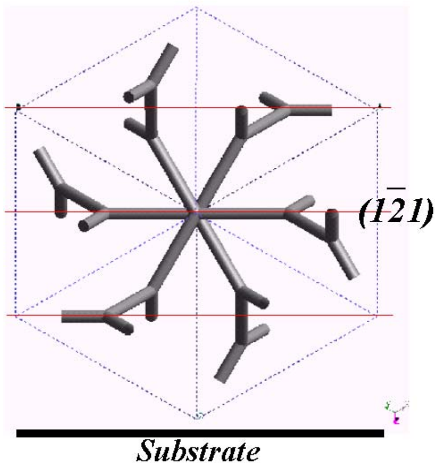

R
T
(20$\bar{2}$)
$\alpha_f = \alpha_{c,s}$
$\alpha_f = \alpha_{c,f}$
0.50
0.25
0.00
- 0.50
- 0.25
0.00
0.25
0.50
α_f (deg.)
$2\theta_f$ (deg.)

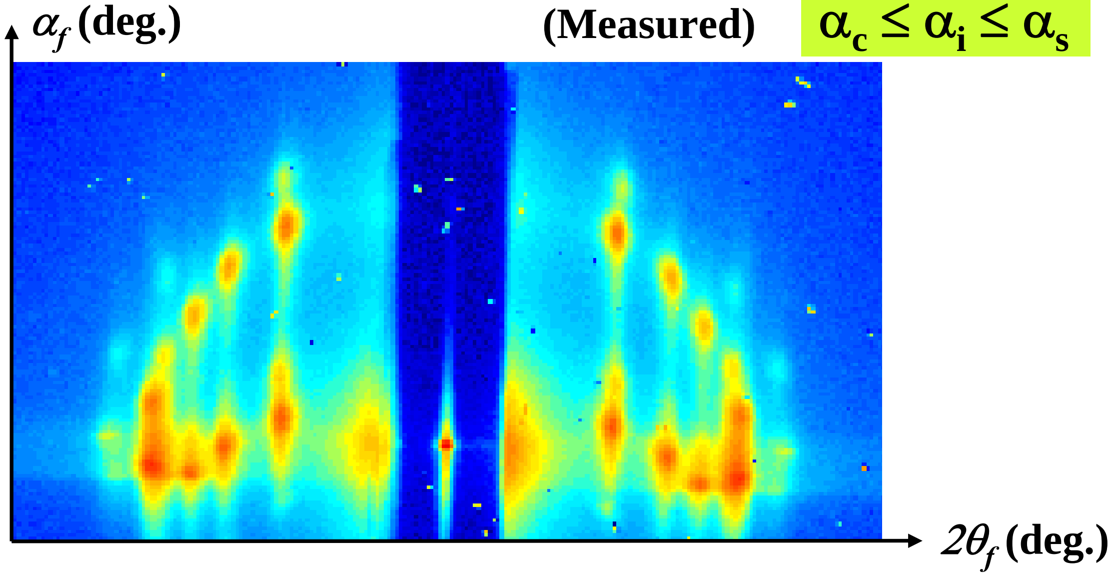

(a)
{121} plane
(1$\bar{2}$1)
(2$\bar{1}$1)(1$\bar{1}$2)
(1$\bar{2}\bar{1}$)($\bar{1}\bar{2}$1)
(2$\bar{1}\bar{1}$)($\bar{1}\bar{1}$2)
($\bar{1}\bar{2}\bar{1}$)
(211)($\bar{2}$1$\bar{1}$)
(112)($\bar{1}$1$\bar{2}$)
log I (a.u.)
(b)
{220} plane
(2$\bar{2}$0)(0$\bar{2}$2)
(20$\bar{2}$)
($\bar{2}\bar{2}$0)(0$\bar{2}\bar{2}$)
(202)
log I (a.u.)
μ (deg.)

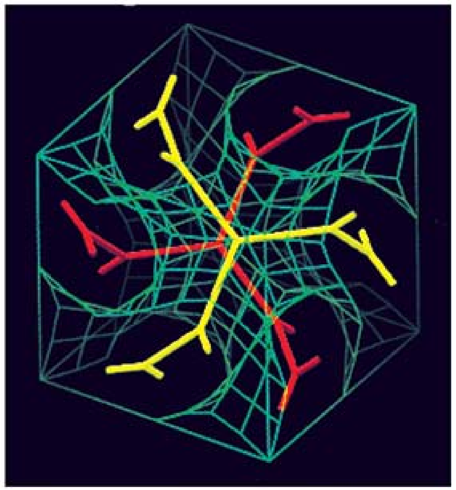


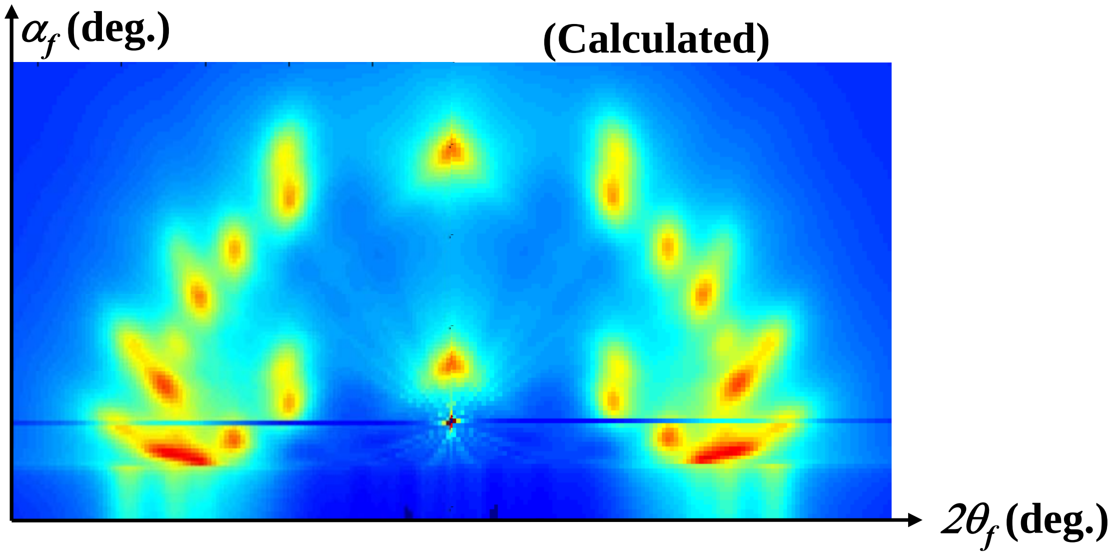
(a)
0.50
0.25
0.00
- 0.50
- 0.25
0.00
0.25
0.50
$2\theta_f$ (deg.)
α_f (deg.)
(b)
0.6
0.4
0.2
0.2
-0.6
-0.3
0.0
0.3
0.6
$\alpha_{c,s}$
$\alpha_{c,f}$
$2\theta_f$ (deg.)
α_f (deg.)

$\alpha_c \leq \alpha_i \leq \alpha_s$









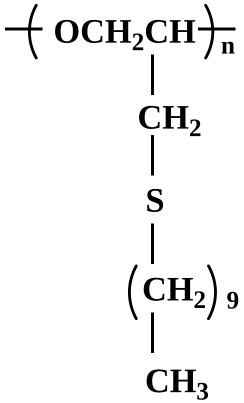
J. Appl. Cryst. **40, 950-958 (2007)**

Structural parameters of gyroid structure of PS-*b*-PI diblock copolymer, which were obtained by GIXS measurement and data analysis

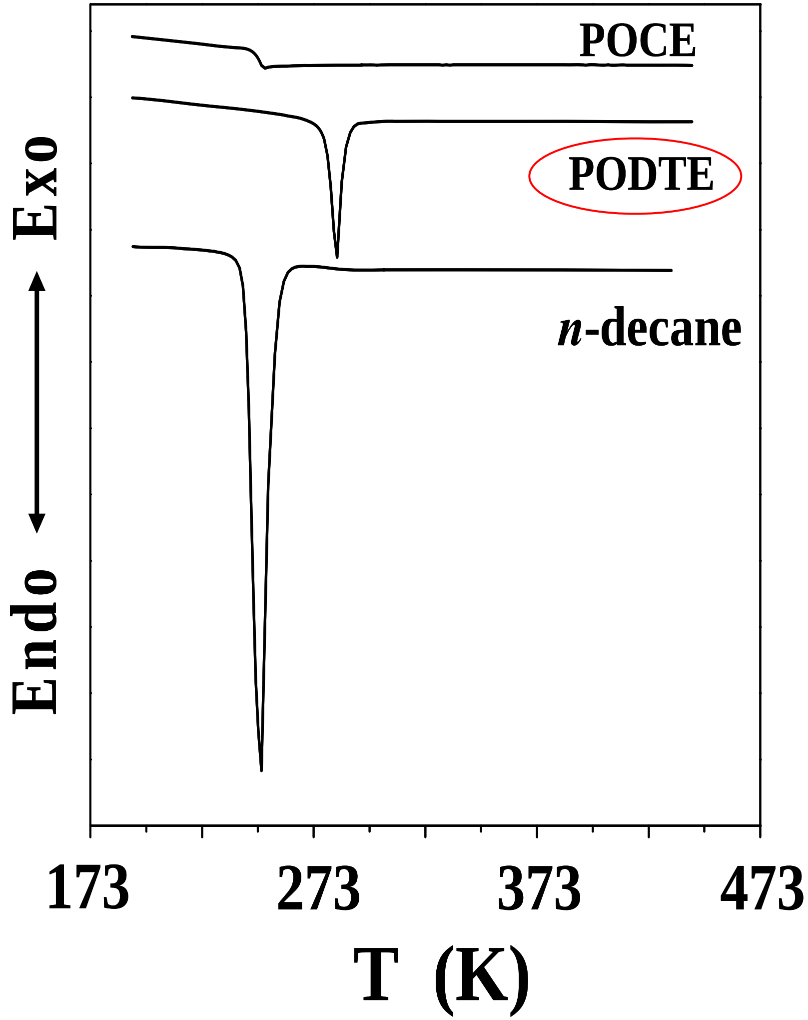
a_G (nm)	L (nm)	{121} plane g_1	{121} plane g_2	{121} plane g_3	{220} plane g_1	{220} plane g_2	{220} plane g_3	φ (deg.)	σ_φ (deg.)	O_s
58.7	14.5	0.03	0.20	0.10	0.07	0.22	0.11	0.0	0.0	1.0

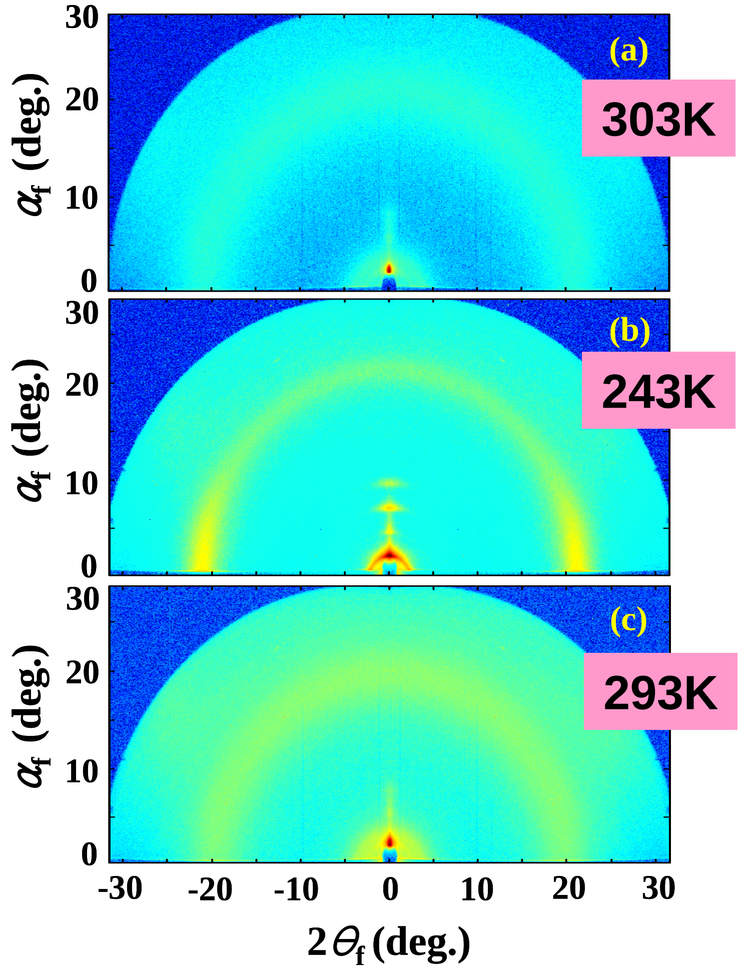
J. Appl. Cryst. **40, 950-958 (2007)**

6. GIXS Analysis of Lamellar Stacks



PODTE





J. Appl. Cryst., **40**, 476 (2007)

$$I_{GIXS}(\alpha_f, 2\theta_f) \cong \frac{1}{16\pi^2} \cdot \frac{1 - e^{-2\,\mathrm{Im}(q_z)\cdot \mathbf{d}}}{2\,\mathrm{Im}(q_z)} \cdot \begin{bmatrix} |T_i T_f|^2 I_1(q_\parallel, \mathrm{Re}(q_{1,z})) + \\ |T_i R_f|^2 I_1(q_\parallel, \mathrm{Re}(q_{2,z})) + \\ |T_f R_i|^2 I_1(q_\parallel, \mathrm{Re}(q_{3,z})) + \\ |R_i R_f|^2 I_1(q_\parallel, \mathrm{Re}(q_{4,z})) \end{bmatrix}$$

$$I_1(\mathbf{q}) = P(\mathbf{q}) \cdot S(\mathbf{q})$$

$$P(\mathbf{q}) = \exp\left\{ \frac{1}{4\pi} \left[L_1^2 (q_x \sin\beta + q_z \cos\beta)^2 + L_2 q_y^2 + L_3 q_z^2 \right] \right\} \sin^2\beta$$

$$S(\mathbf{q}) = \left[\langle |f|^2 \rangle - |\langle f \rangle|^2 \right] + |\langle f \rangle|^2 \left[\prod_{k=1}^{3} Z_k(\mathbf{q}) \right]$$

$L_1 = L_2 = d_r$
$L_3 = h$

$$f = \frac{\sin(q_z h/2)}{q_z h/2} \exp\left(-\sigma_h{}^2 q_z{}^2/2\right)$$

h : one layer thickness
σ_h : deviation in h

$$Z_k(\mathbf{q}) = \frac{1 - |F_k(\mathbf{q})|^2}{1 + |F_k(\mathbf{q})|^2 - 2|F_k(\mathbf{q})|\cos(\mathbf{q}\cdot\mathbf{a_k})}$$

$$F_1(\mathbf{q}) = \exp\left[-\left(\frac{q_r^2 d_r^2 g_{rr}^2 + q_z^2 d_3^2 g_{r3}^2}{2} \right) \right]$$

$$F_2(\mathbf{q}) = \exp\left[-\left(\frac{q_r^2 d_r^2 g_{rr}^2 + q_z^2 d_3^2 g_{r3}^2}{2} \right) \right]$$

$$F_3(\mathbf{q}) = \exp\left[-\left(\frac{q_r^2 d_r^2 g_{3r}^2 + q_z^2 d_3^2 g_{33}^2}{2} \right) \right]$$

$g_{rr} = \Delta a_{rr}/a_r$

$g_{r3} = \Delta a_{r3}/a_r$

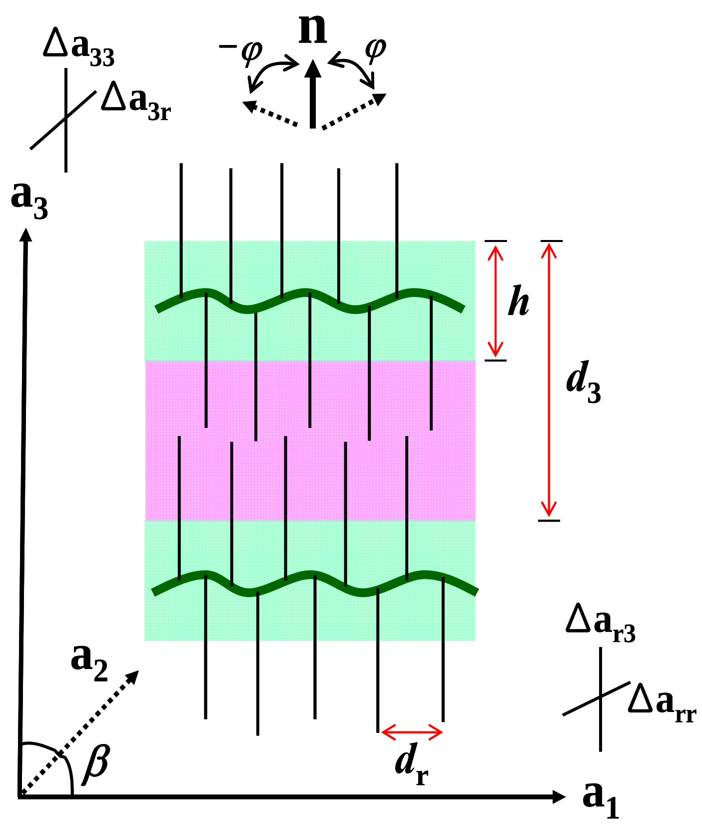
$g_{3r} = \Delta a_{3r}/a_r$

$g_{33} = \Delta a_{33}/a_3$

$$I_{\mathrm{GIXS},\varphi}(\mathbf{q}) = \int_{-\pi}^{\pi} I_{\mathrm{GIXS}}(\mathbf{q}) D(\varphi)\,\mathrm{d}\varphi$$

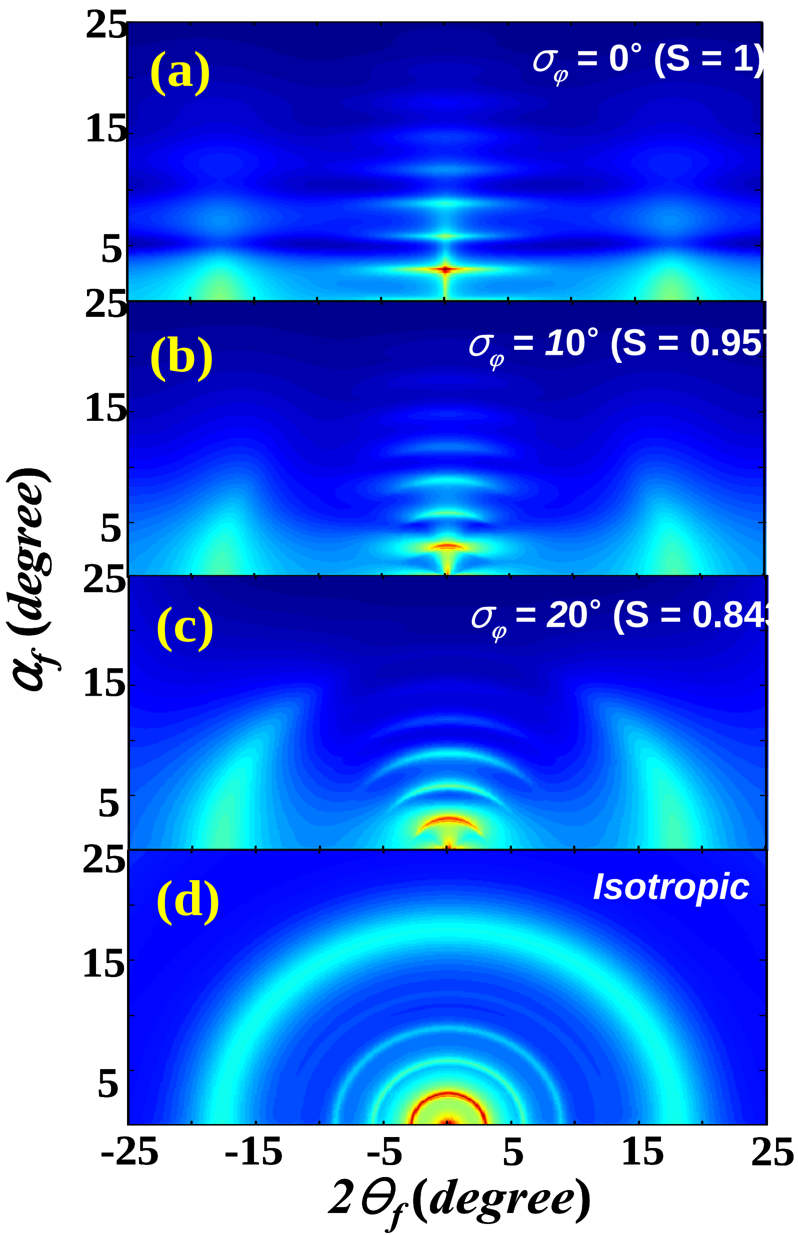
$$O_s = \int D(\varphi) \frac{(3\cos^2\varphi - 1)}{2}\,\mathrm{d}\varphi$$

$$D(\varphi) = \frac{1}{\sqrt{2\pi}\sigma_\varphi} \exp\left[-\frac{(\varphi - \bar{\varphi})^2}{2\sigma_\varphi^2} \right]$$



J. Appl. Cryst., **40**, 476 (2007)

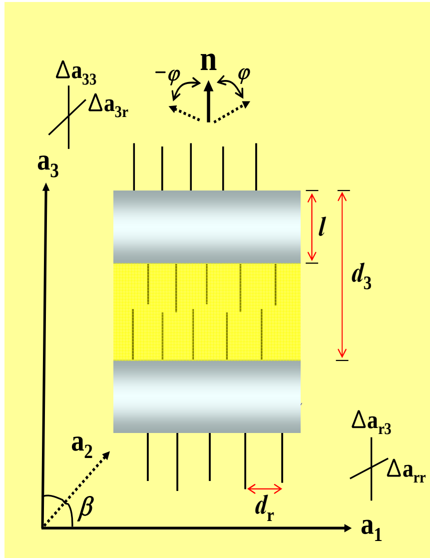
Surface Undulations in Lamellar Structure



Distribution of Orientation

$$D(\varphi) = \frac{1}{\sqrt{2\pi\sigma_\varphi}} \exp\left[-\frac{(\varphi - \bar{\varphi})^2}{2\sigma_\varphi^2} \right]$$

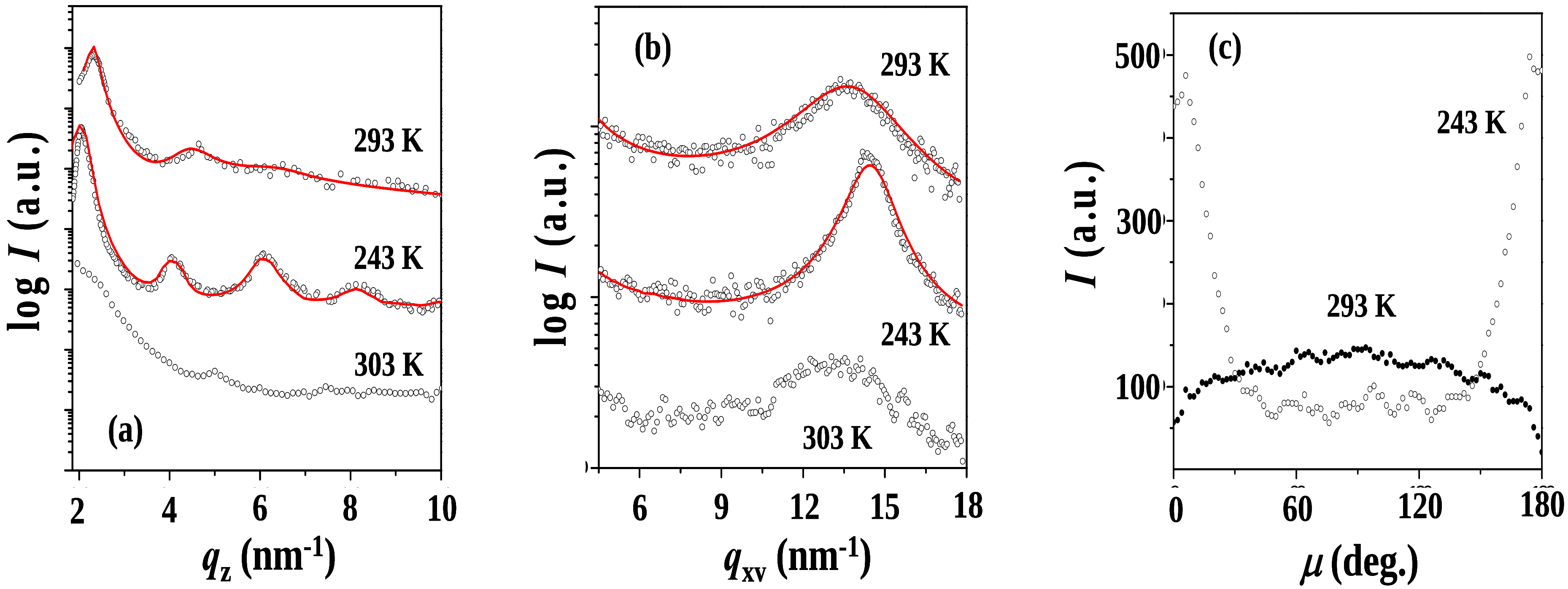
$$I_{GIXS,\varphi}(\mathbf{q}) = \int_{-\pi}^{\pi} I_{GIXS}(\mathbf{q}) D(\varphi) d\varphi$$



Order Parameter

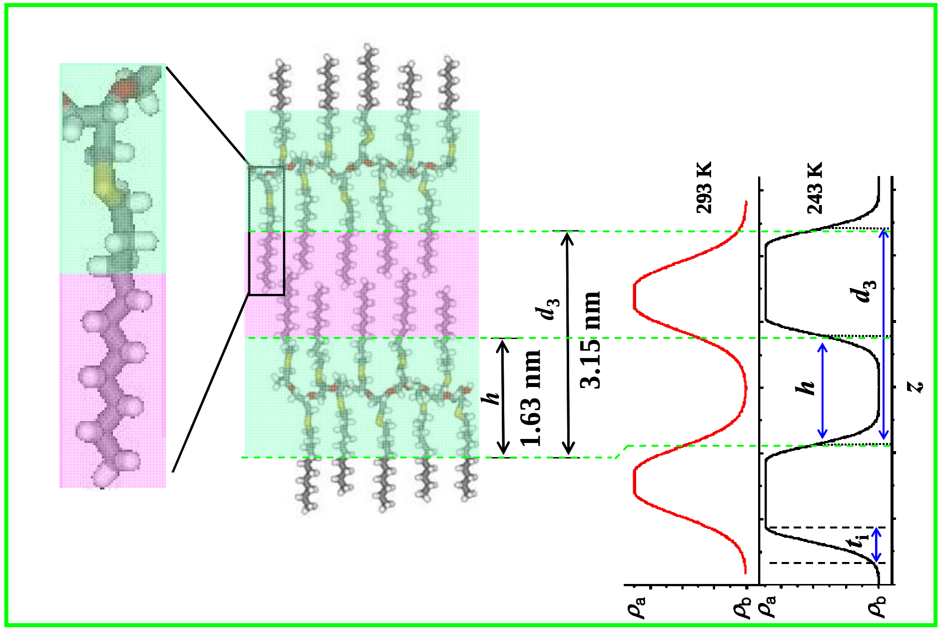
$$S = \int D(\varphi) \frac{(3\cos^2\varphi - 1)}{2} d\varphi$$

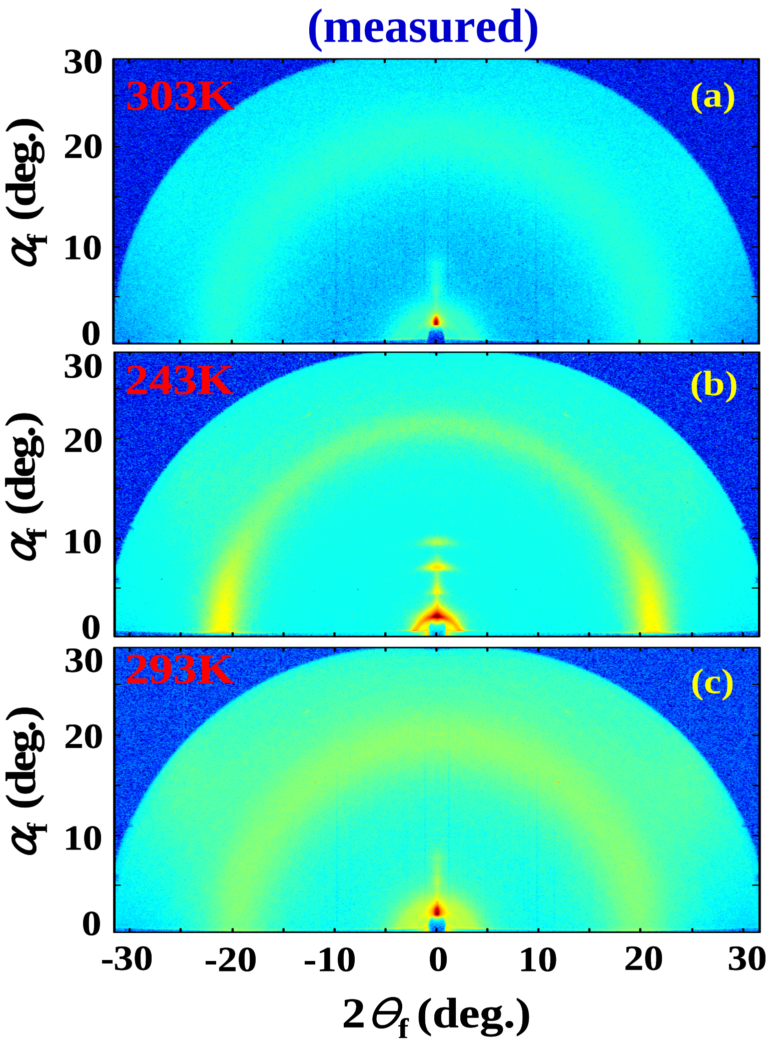
d_3 = 3.0 nm, l = 1.70 nm, σ_l = 0.15 nm, g_{33} = 0.05, g_{3r} = 0.05,
d_r = 0.45 nm, g_{r3} = 0.5, g_{rr} = 0.15, β = 90°, α_i = 0.20°
film thickness = 100 nm
electron density of film = 200 nm^{-3}
electron density of substrate = 699 nm^{-3}

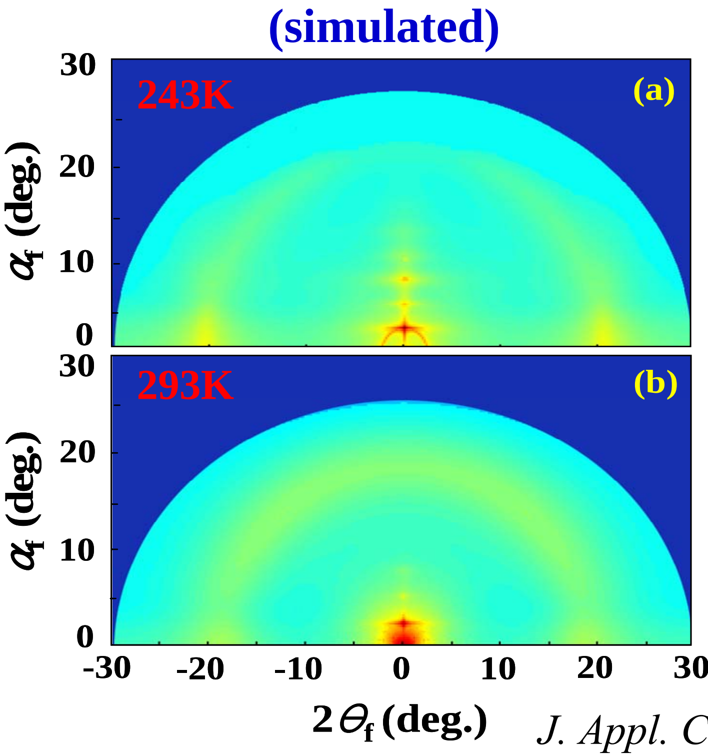


(a)
293 K
243 K
303 K
log I (a.u.)
2
4
6
8
10
qz (nm-1)
(b)
293 K
243 K
303 K
log I (a.u.)
6
9
12
15
18
qxy (nm-1)
(c)
500
300
100
243 K
293 K
I (a.u.)
0
60
120
180
μ (deg.)

T (K)	d_3 (nm)	g_{33}	g_{3r}	d_r (nm)	g_{r3}	g_{rr}	h (nm)	σ_h (nm)	t_i (nm)	β (deg.)	φ (deg.)	σ_φ (deg.)	O_s
243	3.15	0.076	0.061	0.44	0.23	0.145	1.63	0.13	0.33	90	0	2.3	0.997
293	2.82	0.16	0.14	0.47	0.36	0.220	1.60	0.23	0.58	90	0	3.5	0.992

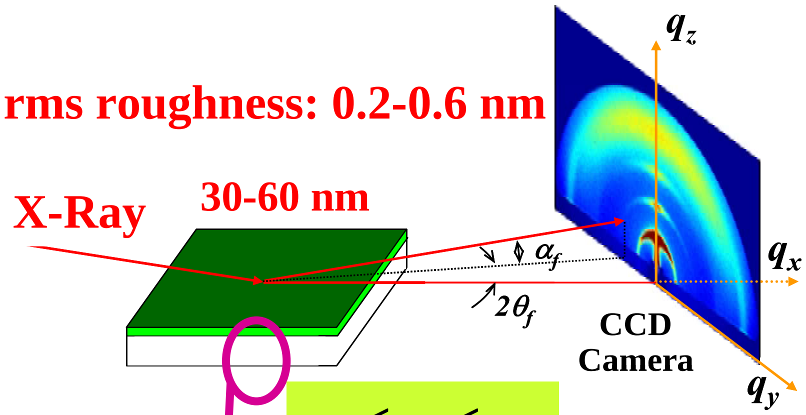




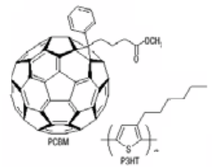


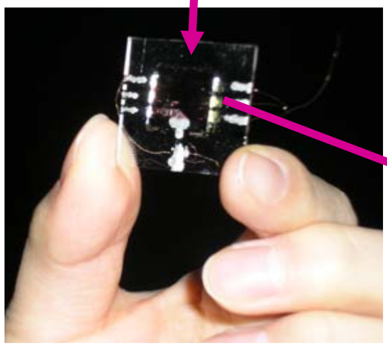
7. Solar Cell : Nanofilms of Poly(3-hexylthiophene)(P3HT)/Fullerene: Lamellar Stacks

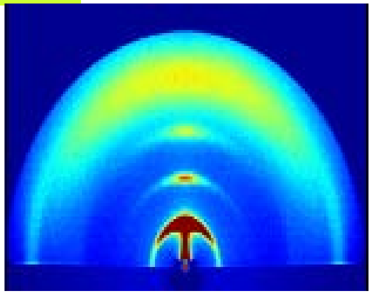
rms roughness: 0.2-0.6 nm

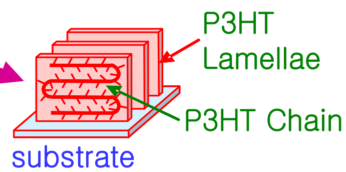


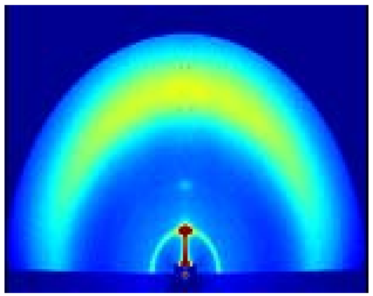
$\alpha_c \leq \alpha_i \leq \alpha_s$



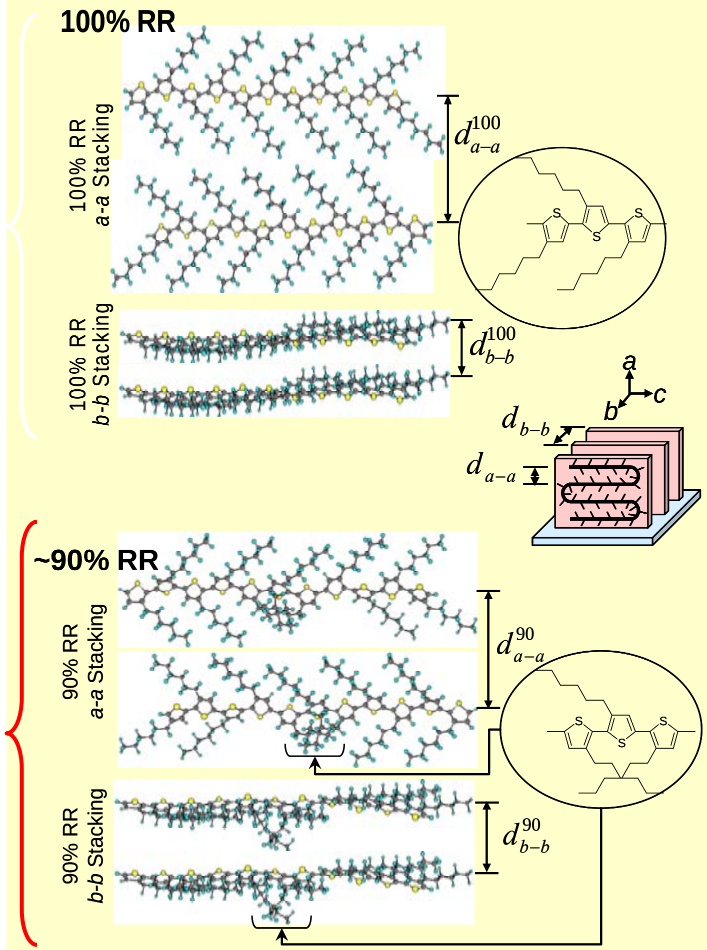








Molecular Orientation in Thin Film

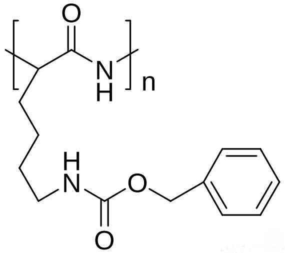


High Quantum Yield Solar Cell

Low Quantum Yield Solar Cell

Nature Materials , 5, 197 (2006)

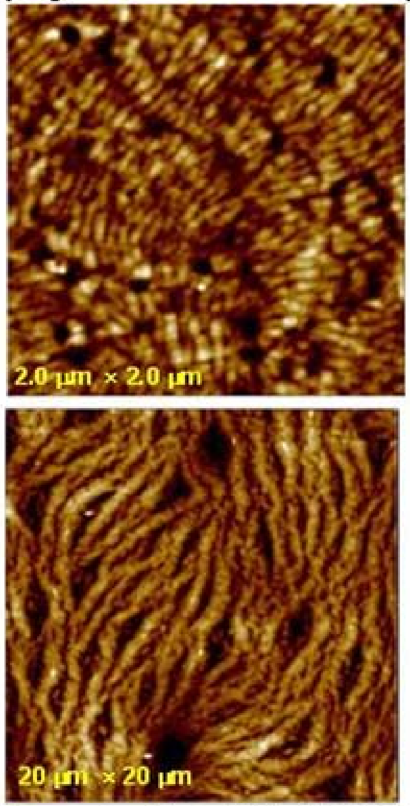
8. Polypeptide – poly(z-lysine) film or fibrils (60 nm thick)



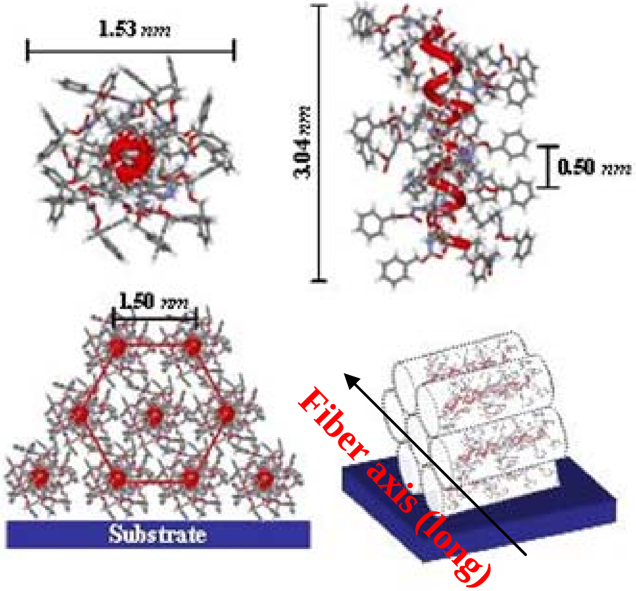
rms roughness: 0.3 – 0.8 nm

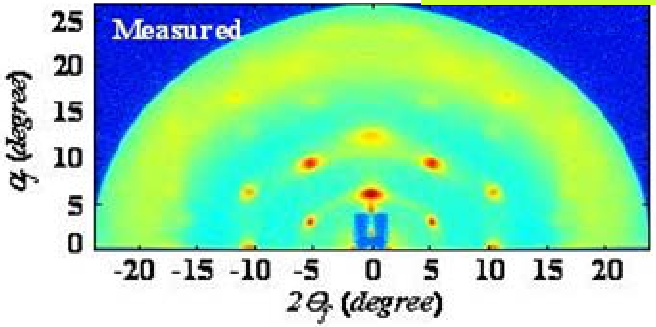
$\alpha_c \leq \alpha_i \leq \alpha_s$

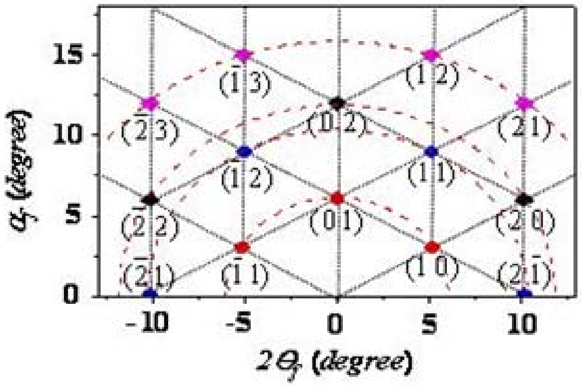
(Prepared with a solution in THF)

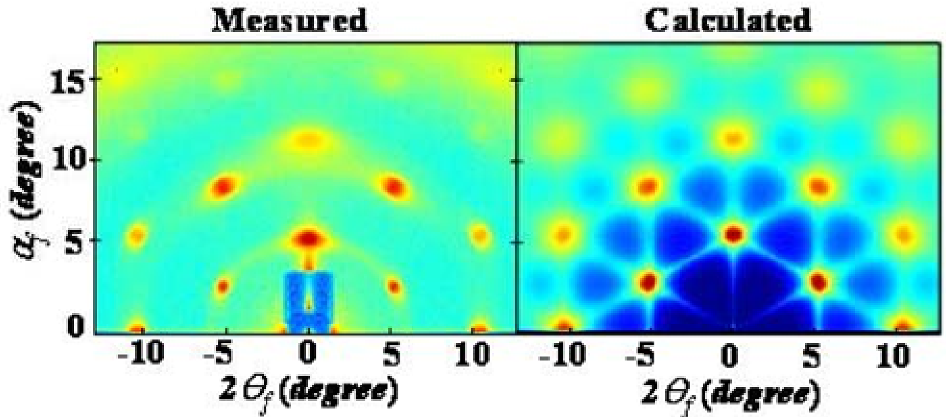


(Prepared with a solution in DMF)



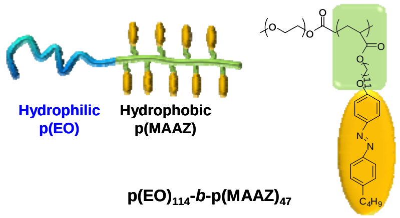


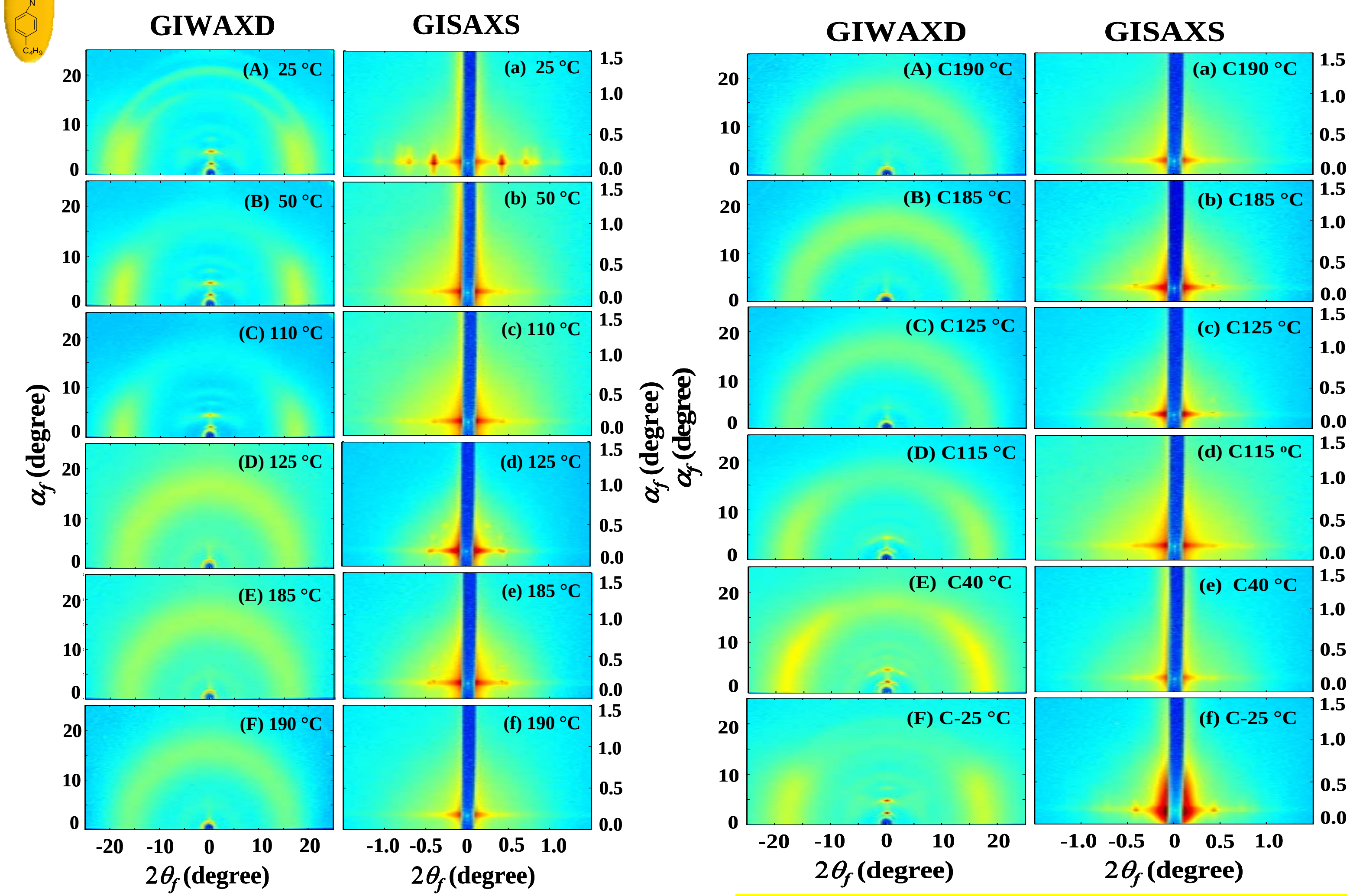




J. Phys. Chem. B. **112, 8868 (2008)**

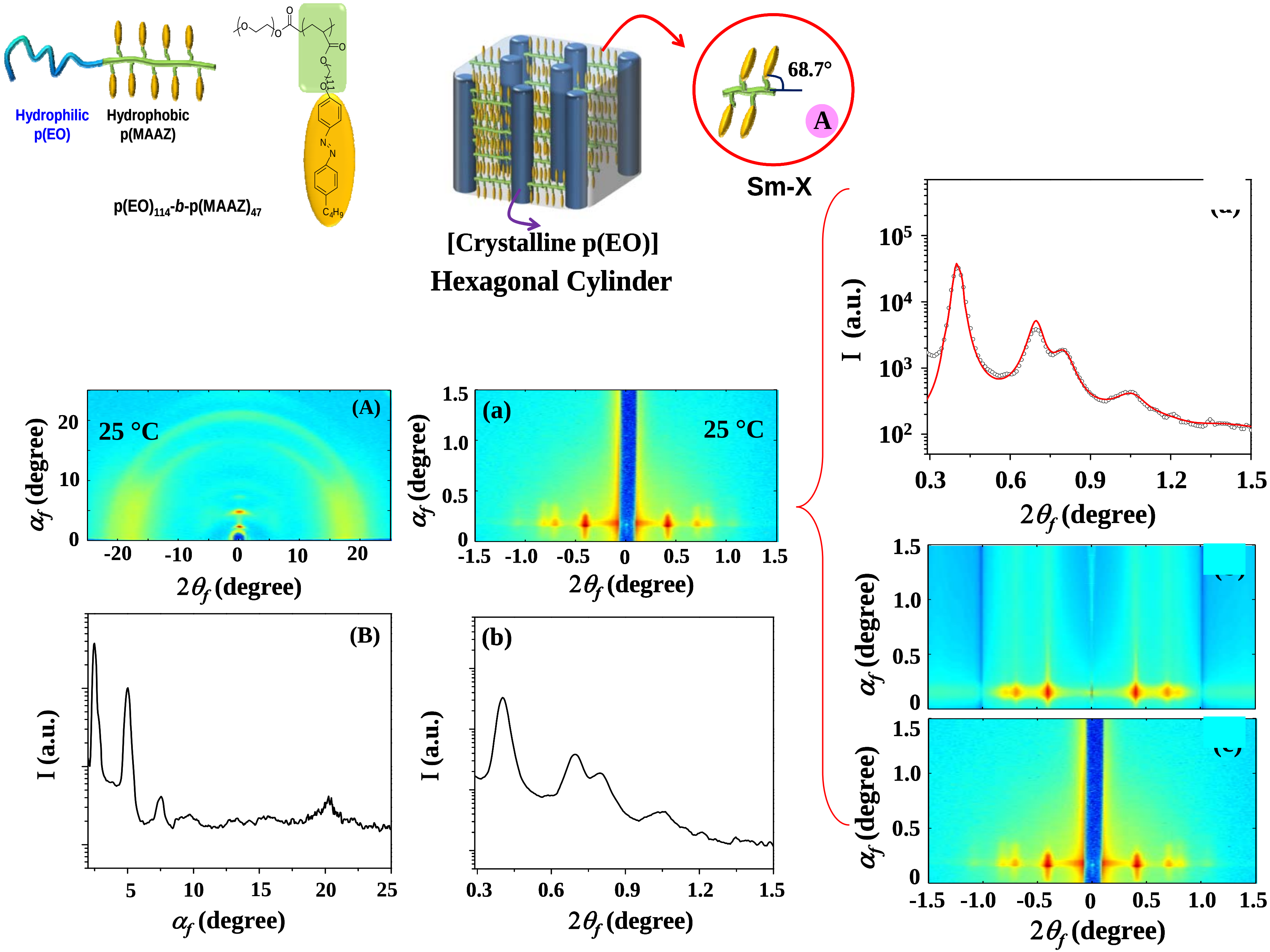
9. GIXS Analysis of Linear-Brush Diblock Copolymer in thin Films (I)



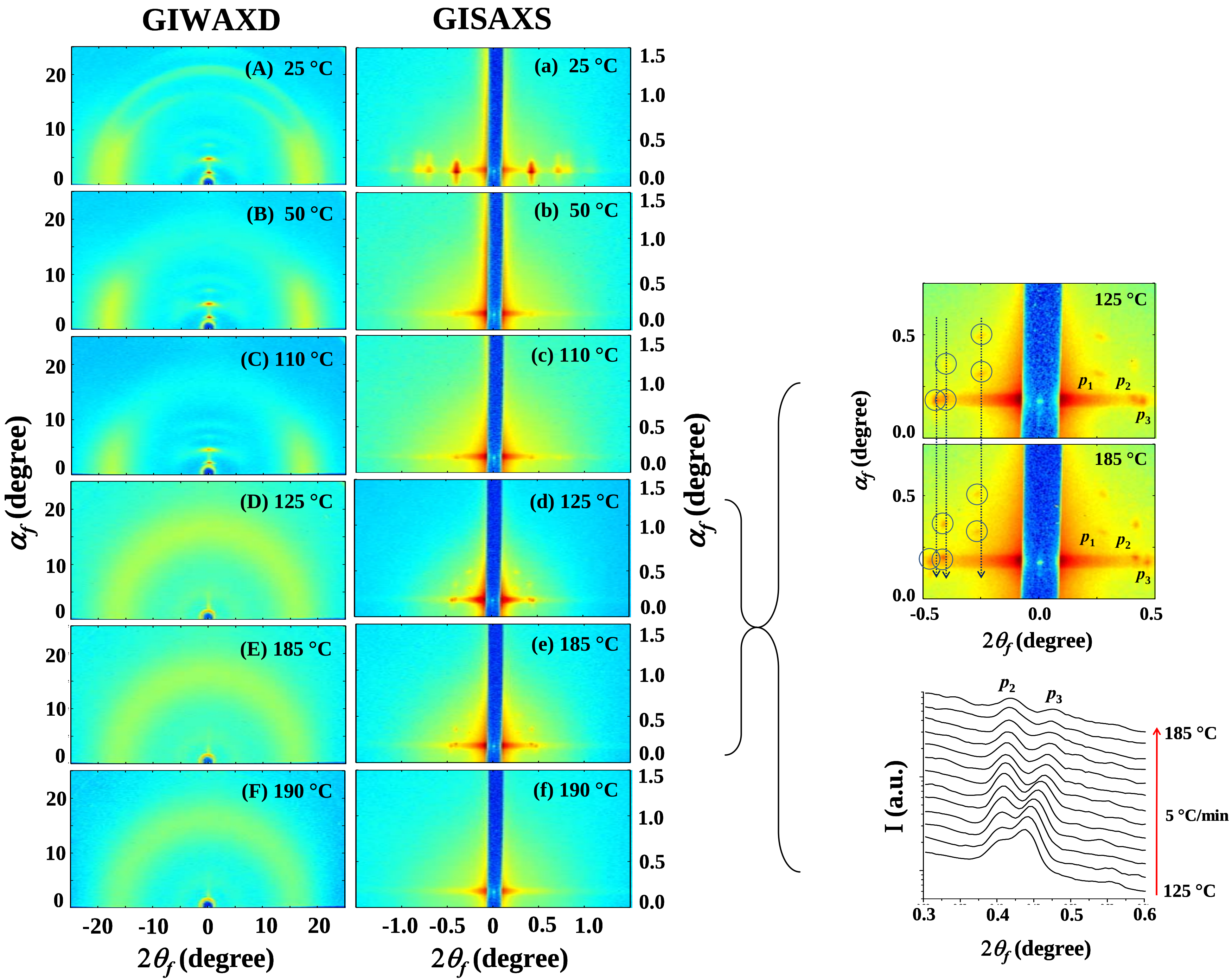


Co-worked with
Prof. Hirohisa Yoshida (Tokyo Metro. U.)
Prof. Tomokazu Iyoda (Tokyo Inst. Tech)

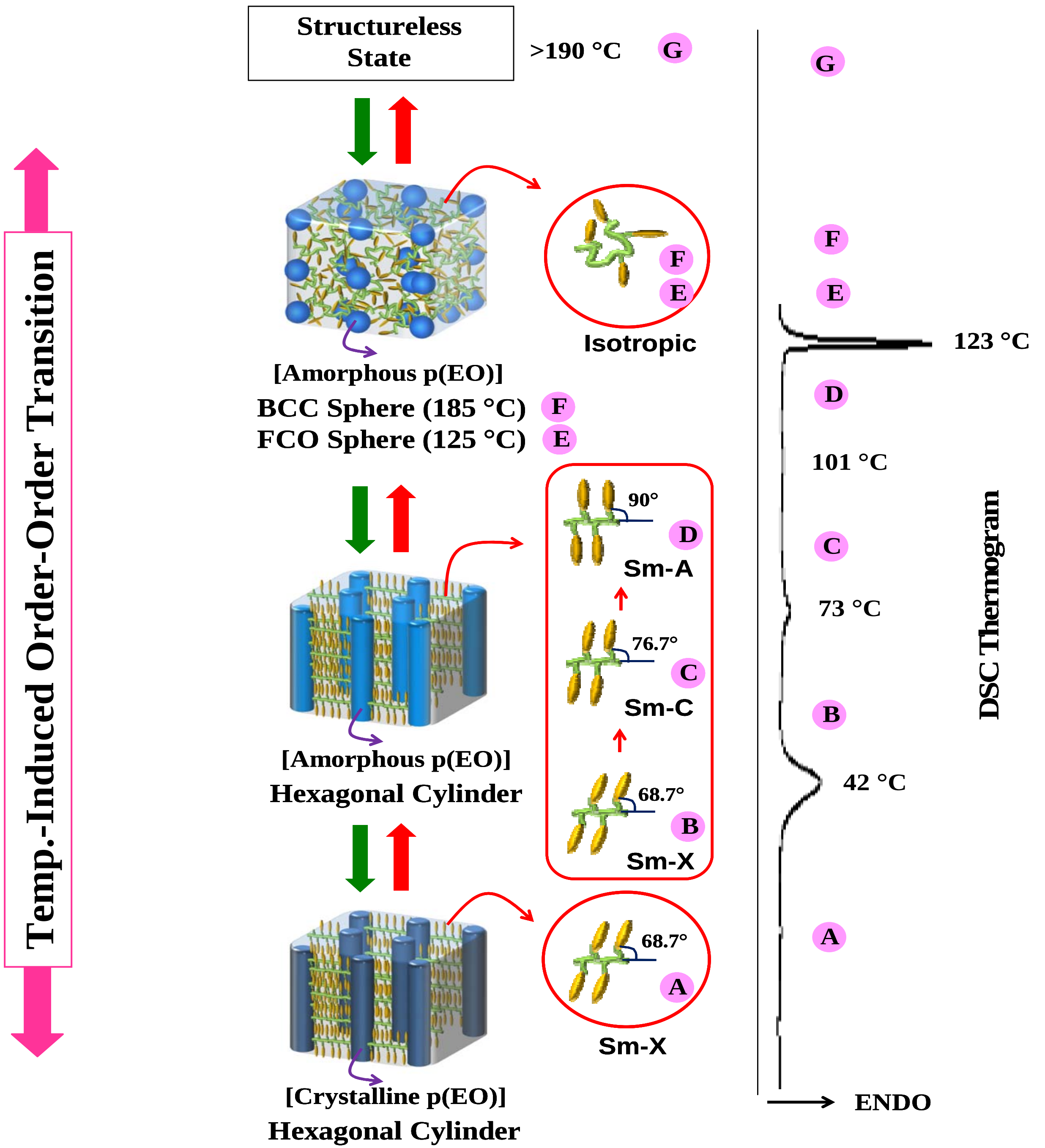
J. Phys. Chem. B. **112, 8486 (2008)**



Hydrophilic p(EO)
Hydrophobic p(MAAZ)
p(EO)$_{114}$-*b*-p(MAAZ)$_{47}$
[Crystalline p(EO)]
Hexagonal Cylinder
68.7°
A
Sm-X
(A)
25 °C
α_f (degree)
$2\theta_f$ (degree)
(a)
25 °C
(B)
I (a.u.)
(b)
10^5
10^4
10^3
10^2

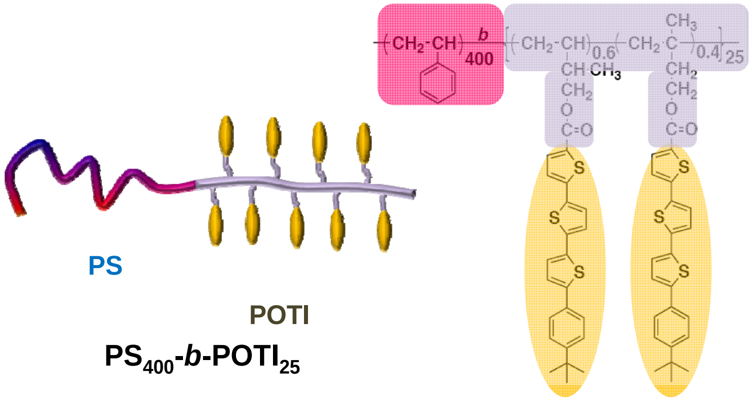


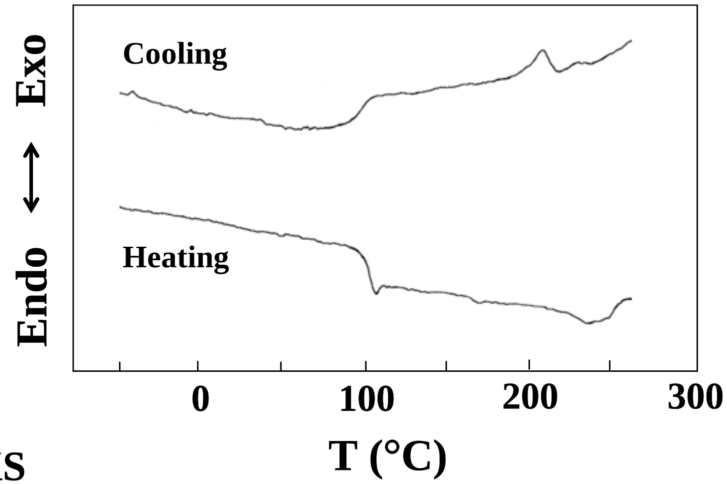
GIWAXD
GISAXS
(A) 25 °C
(B) 50 °C
(C) 110 °C
(D) 125 °C
(E) 185 °C
(F) 190 °C
(a) 25 °C
(b) 50 °C
(c) 110 °C
(d) 125 °C
(e) 185 °C
(f) 190 °C
α_f (degree)
$2\theta_f$ (degree)
125 °C
185 °C
p_1
p_2
p_3
I (a.u.)
185 °C
5 °C/min
125 °C

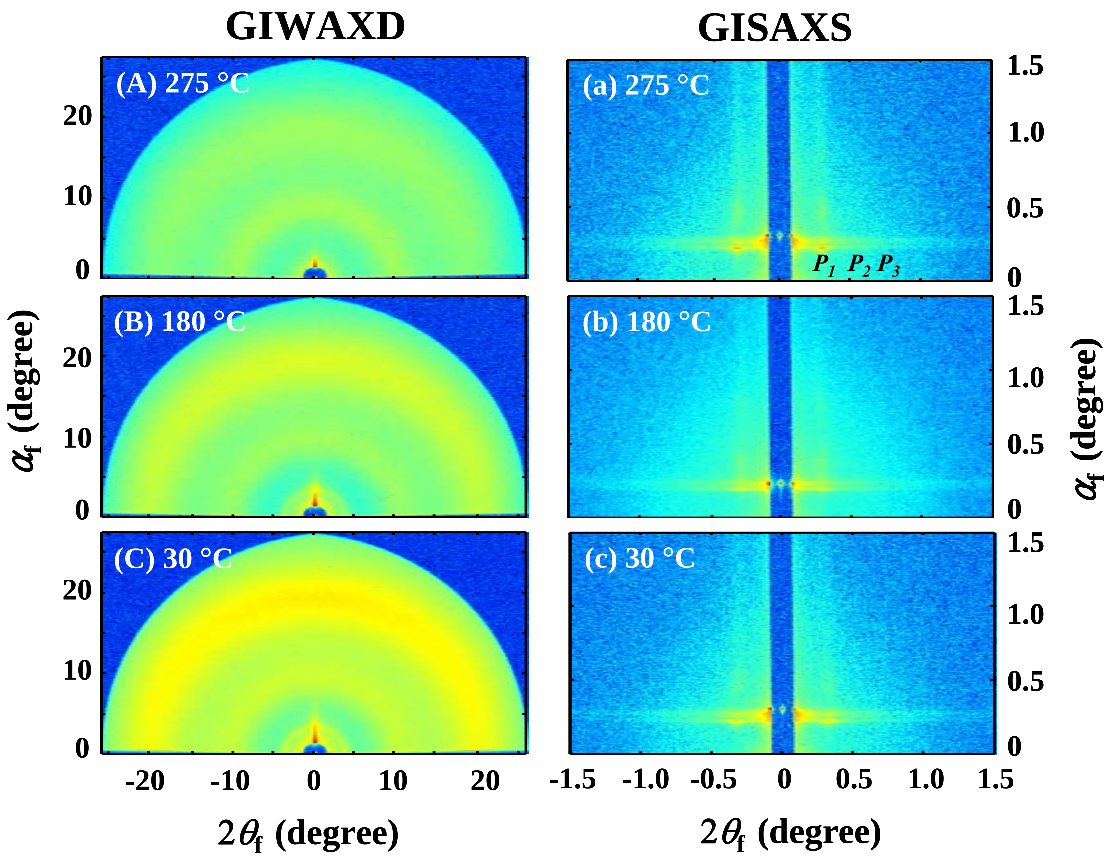


J. Phys. Chem. B. 112, 8486 (2008)

10. GIXS Analysis of Linear-Brush Diblock Copolymer in thin Films (II)

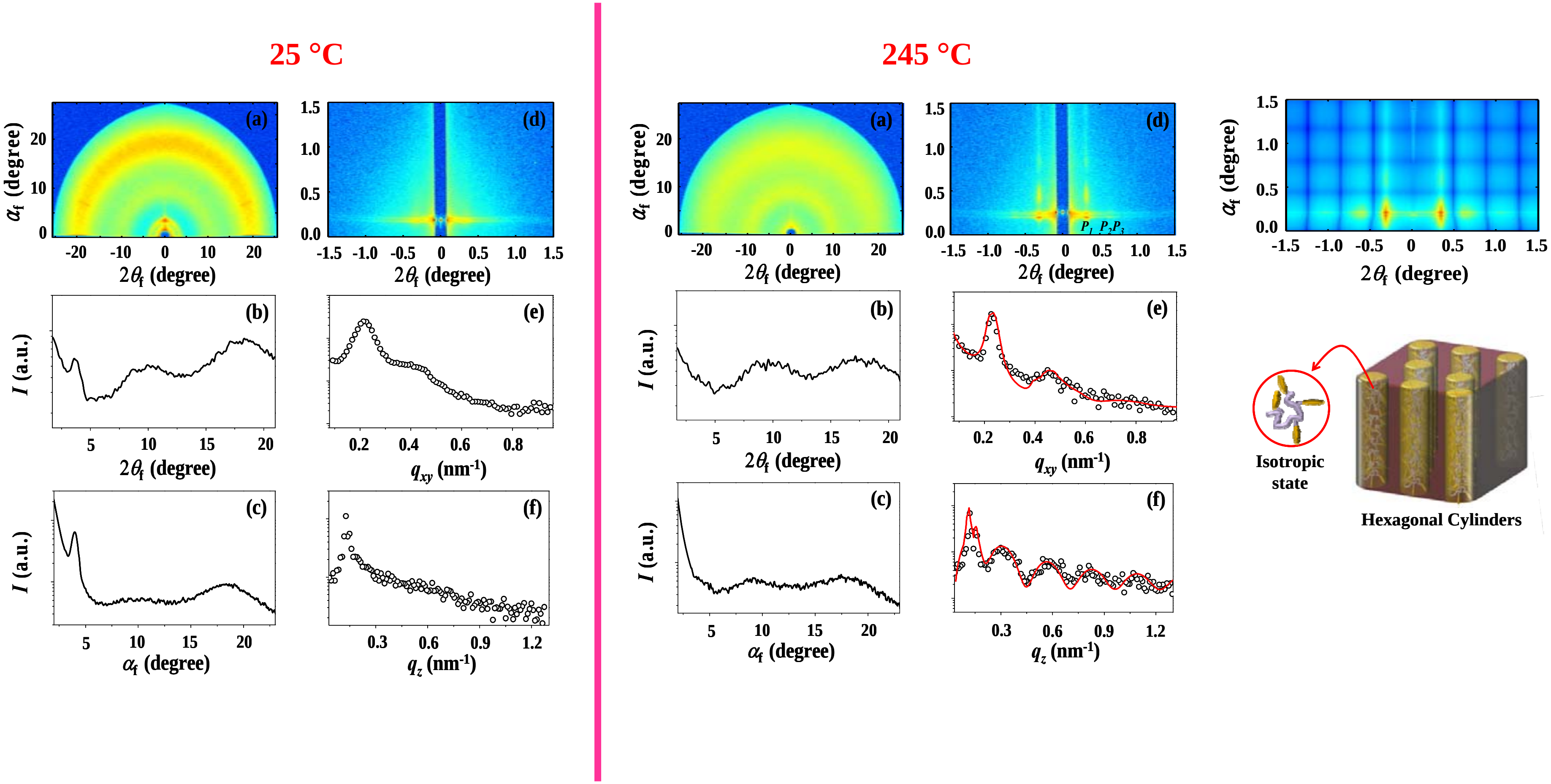




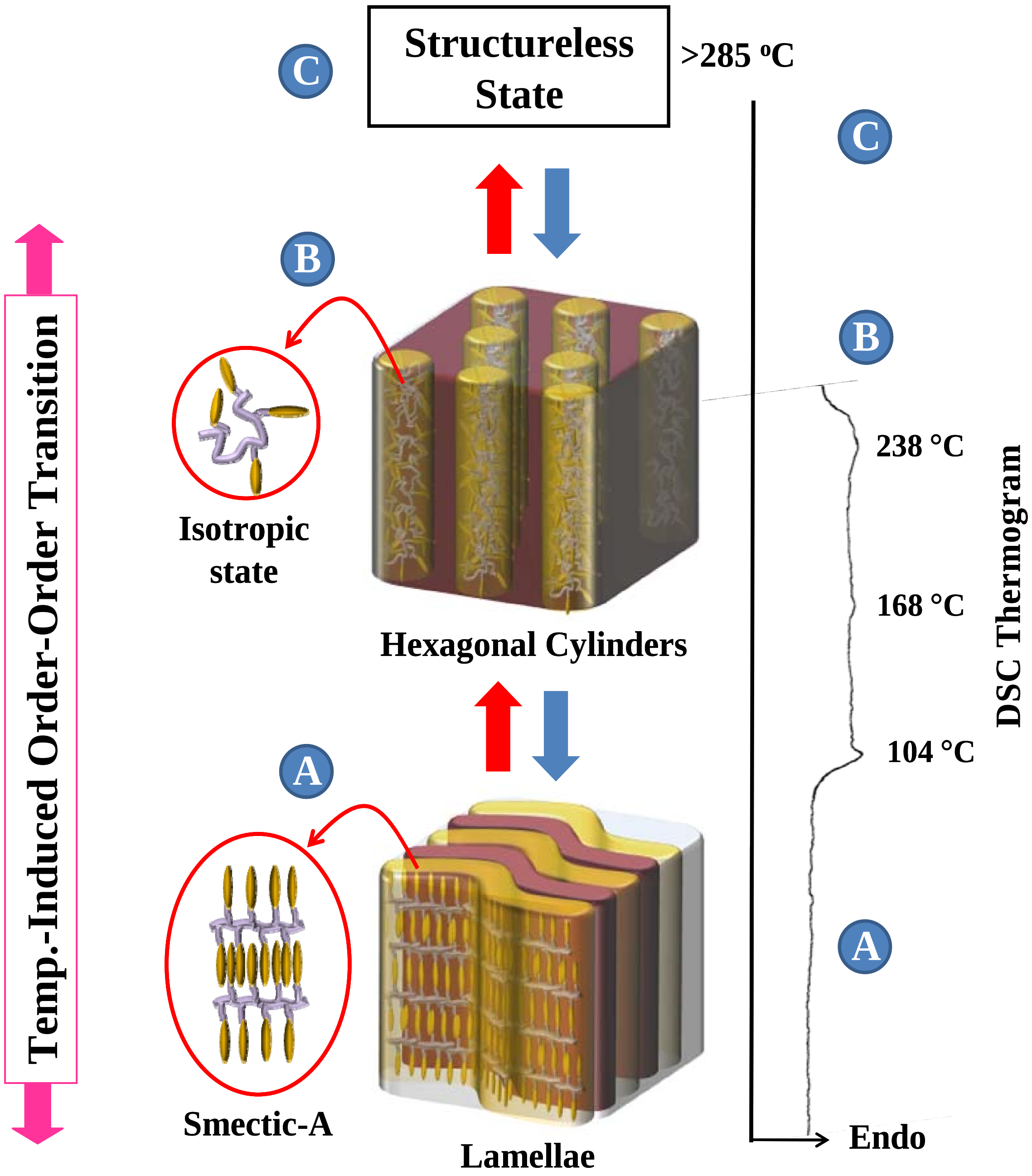


Co-worked with
Prof. Teruaki Hayakawa
(Tokyo Inst. Tech)

Macromolecules (in press)

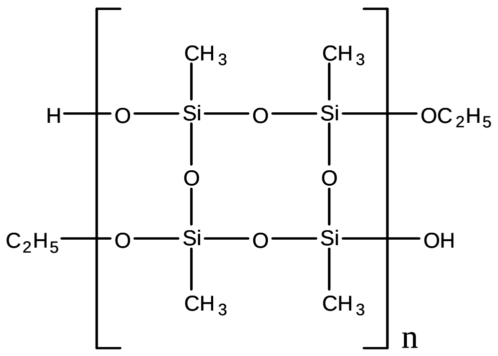


25 °C
245 °C
(a)
(b)
(c)
(d)
(e)
(f)
αf (degree)
2θf (degree)
I (a.u.)
qxy (nm-1)
qz (nm-1)
P1 P2 P3
Isotropic state
Hexagonal Cylinders

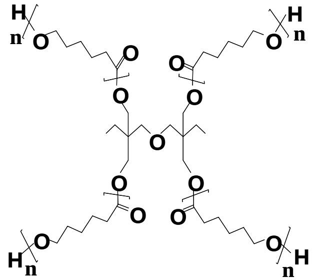

Structureless State
>285 °C
C
B
A
Isotropic state
Hexagonal Cylinders
Smectic-A
Lamellae
238 °C
168 °C
104 °C
Endo
DSC Thermogram
Temp.-Induced Order-Order Transition

11. *In-Situ* GIXS Measurements

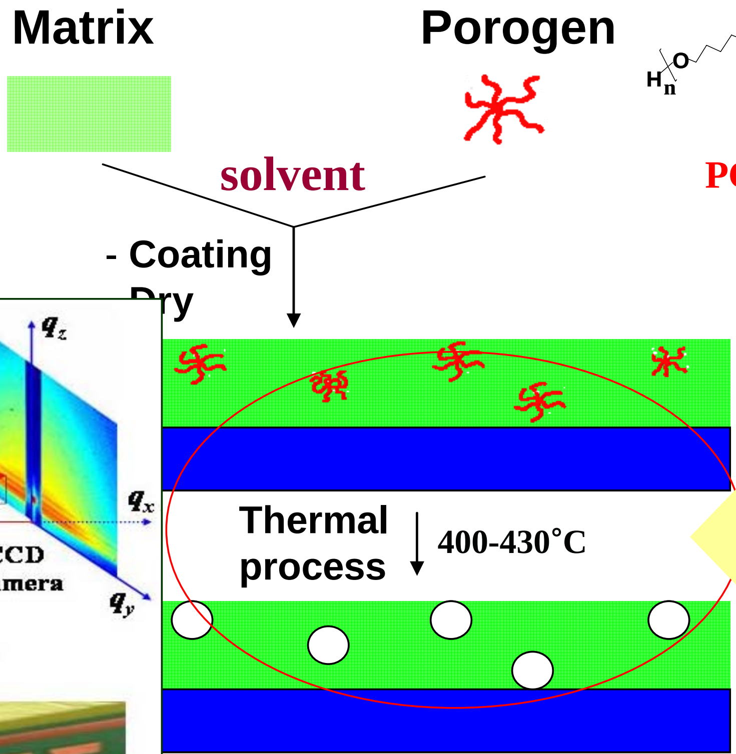
In-situ GIXS - Nanopous dielectric thin films: Low-k nanofilms

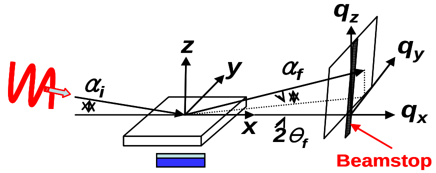


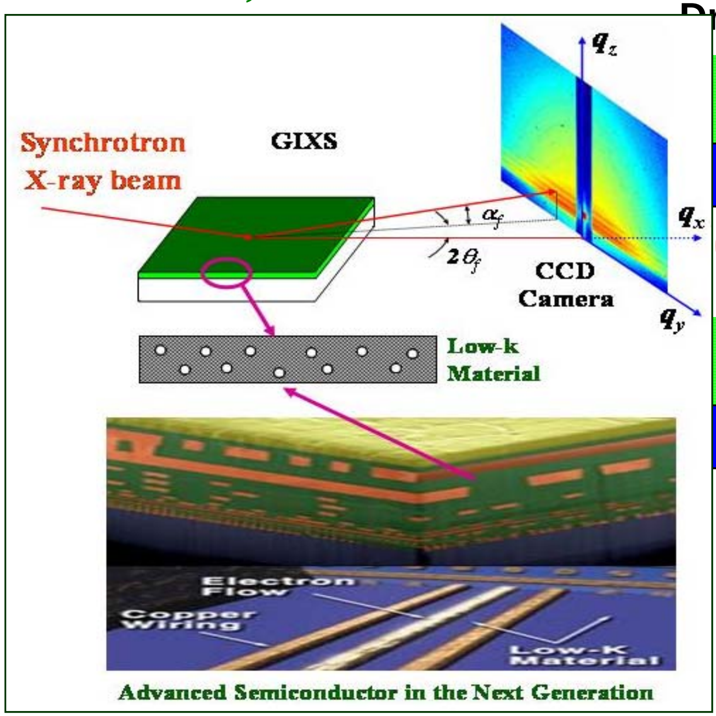
PMSSQ Precursor
10,000 $\overline{M}w$



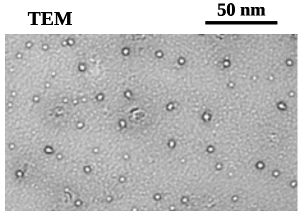
PCL4 Porogen







in-situ GIXS Measurements conducted



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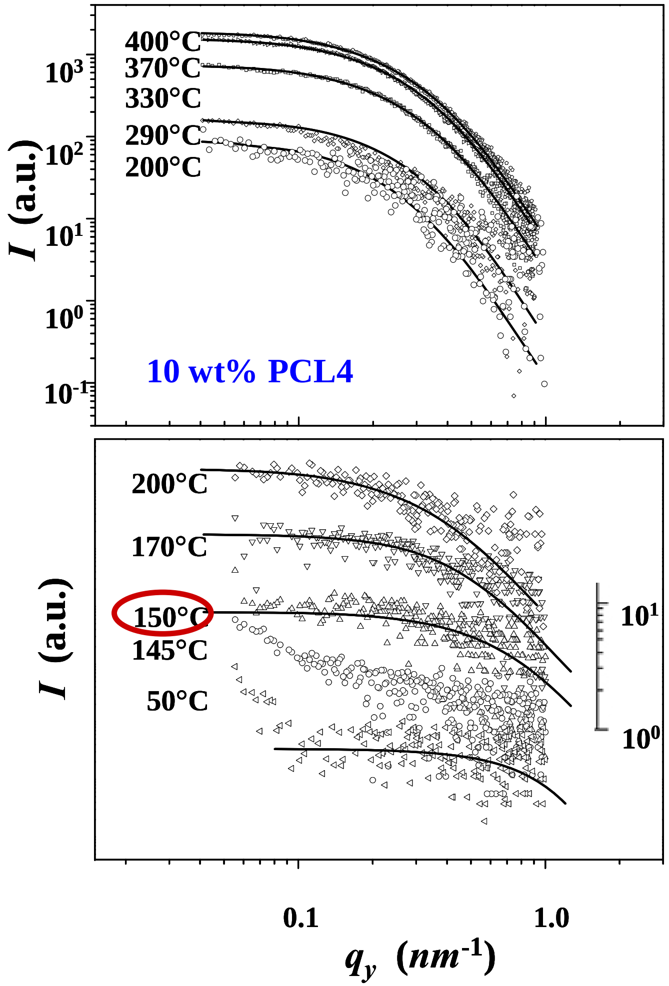
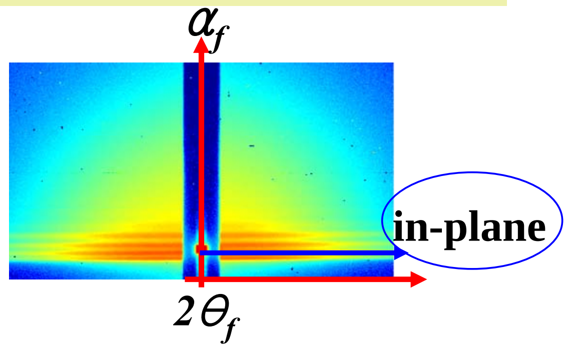
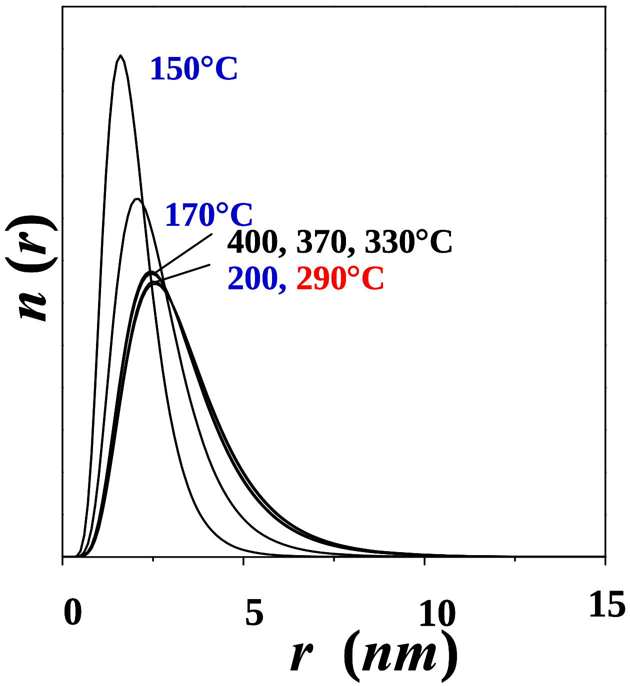
J. Phys. Chem. B, 110, 15887 (2006)
J. Mater. Chem. 16, 685 (2006)
Nanotechnology 17, 3490 (2006)
Macromolecules 38, 8991 (2005)
Macromolecules 38, 3395 (2005)

In-situ GIXS Measurements: PCL4/PMSSQ film

PCL4/PMSSQ precursor Thin Film (25°C) —2°C/min, vacuum→ (400°C) PCL4/PMSSQ Thin Film —2°C/min, vacuum→ (25°C)

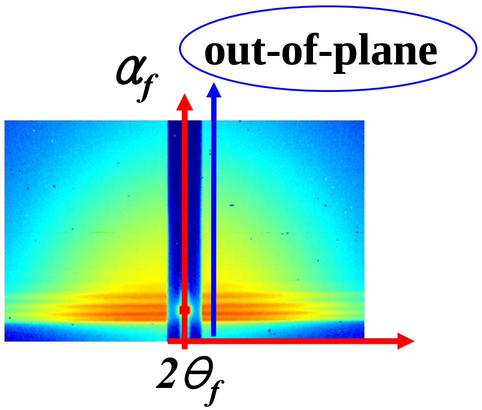


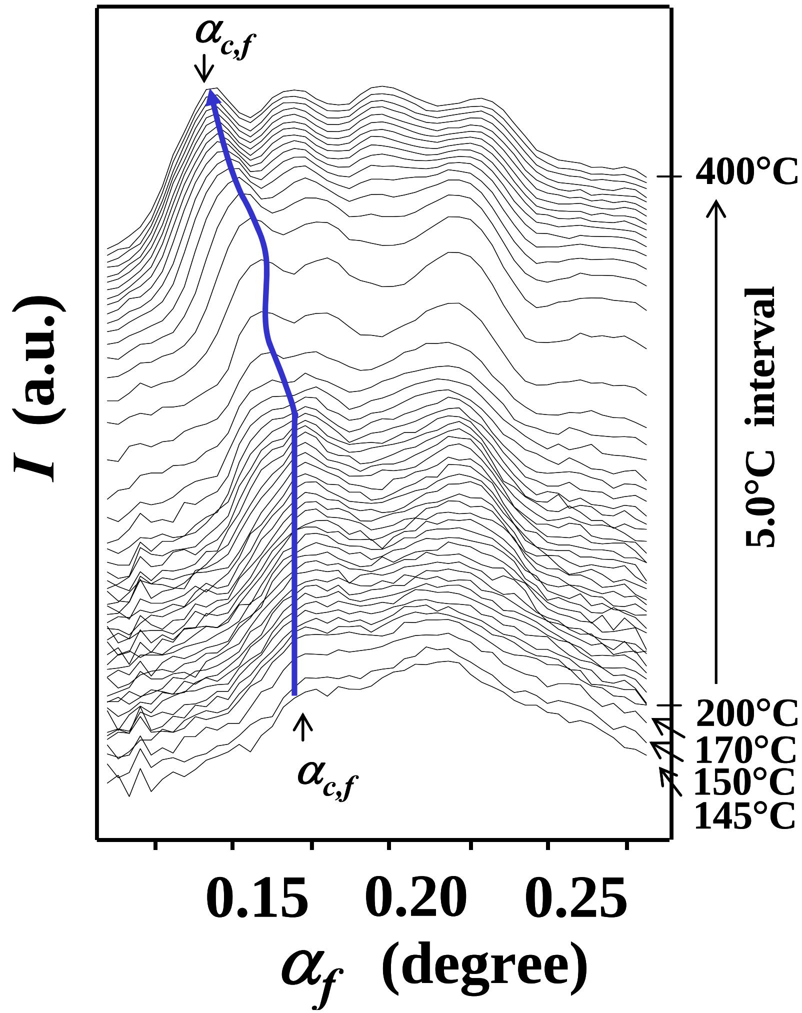




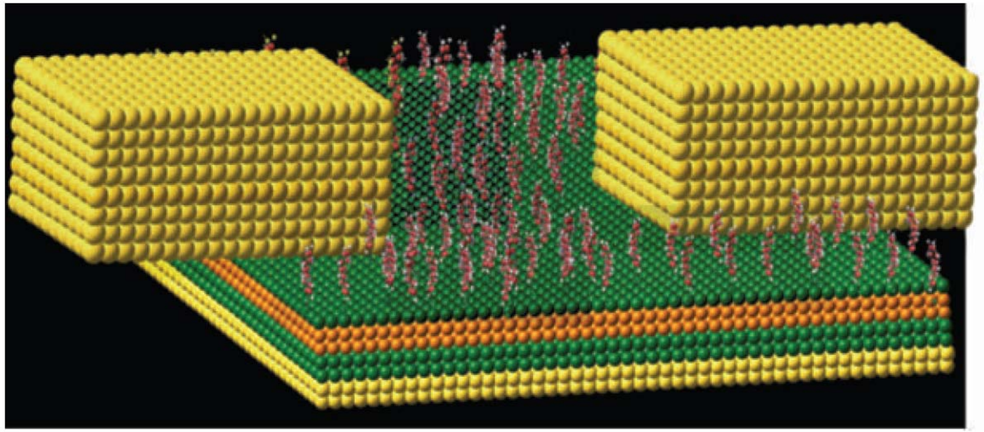
In-situ GIXS Measurements: PCL4/PMSSQ film

PCL4/PMSSQ precursor Thin Film (25°C) —2°C/min, vacuum→ (400°C) PCL4/PMSSQ Thin Film —2°C/min, vacuum→ (25°C)

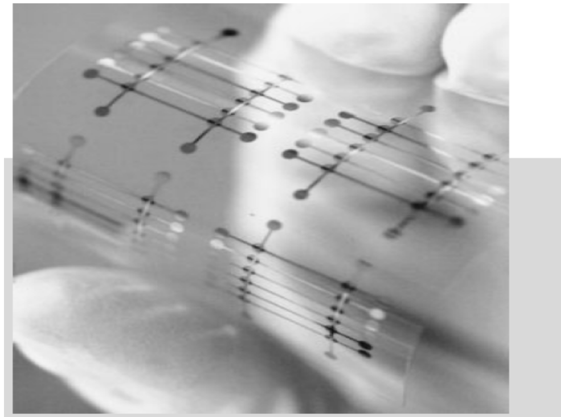


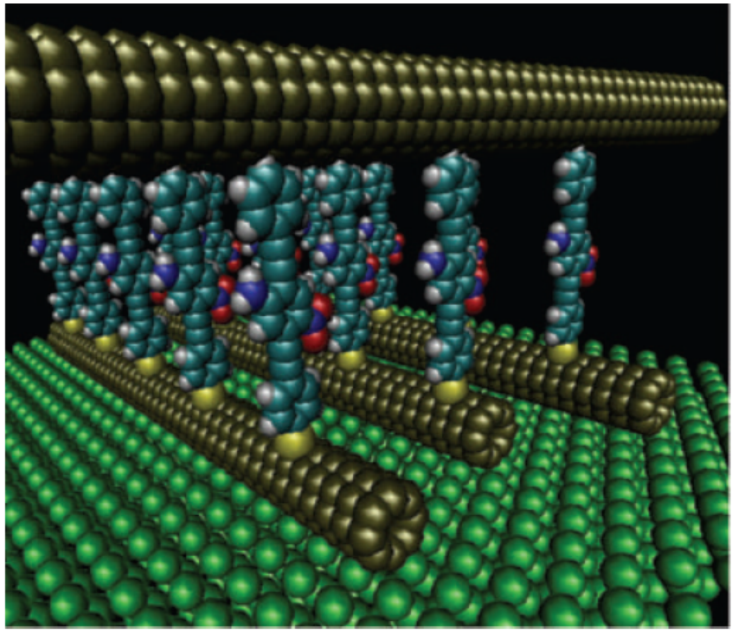


12. Current GIXS Analysis - Organic and Polymeric Electronic Devices (in progress): TFT, FET, MED, LCD, PDP, etc.



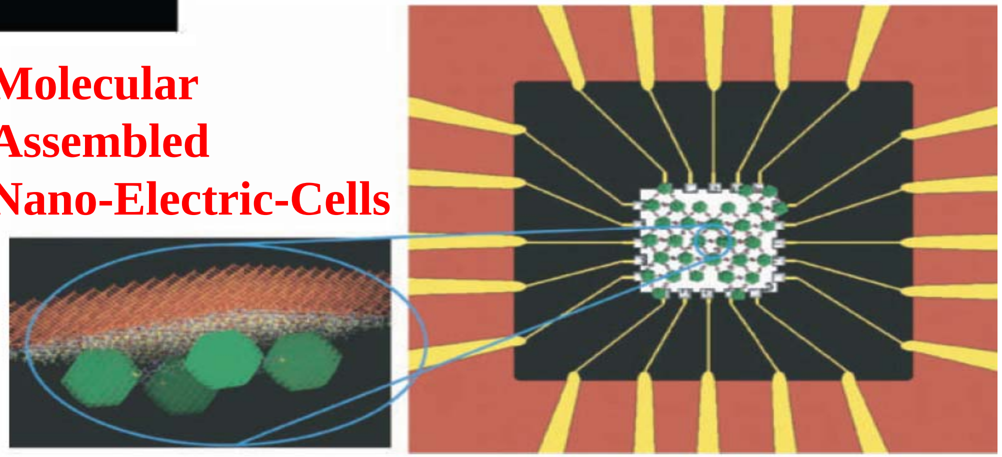
Field Effect Transistor (FET)





Molecular & Carbon Nanotube Wiring

Molecular Assembled Nano-Electric-Cells



Adv. Funct. Mater. 17, 2637 (2007)
Electron Device Letters 28, 967 (2007)
Appl. Phys. Letters 91, 093517 (2007)
Langmuir 23, 9024-9030 (2007)
IEEE Electron Device Lett. 29, 694 (2008)
Appl. Phys. Lett. 92, 243305 (2008)
Adv. Mater. 20, 1766 (2008)
Adv. Funct. Mater. (in press) + More

Outline

A. Introduction – Pohang Light Source & Postech
B. Optics, Beamlines and Equipments of SAXS
C. Fundamentals of SAXS

D. Fundamentals of Grazing Incidence X-Ray Scattering (GIXS)
E. Applications of GIXS in Nano-Science and Technology
12 Examples of Recent Research Results

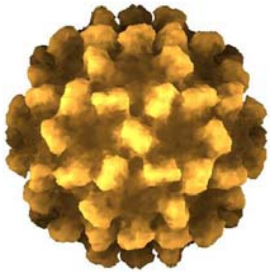
F. Solution X-Ray Scattering

G. Conclusions – I, II
H. References
I. Coworkers
J. M. Ree's Group at Postech

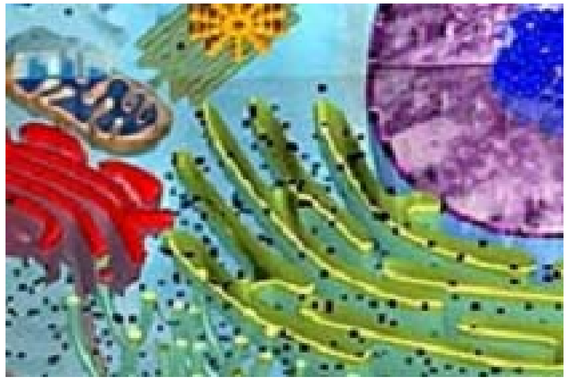
Introduction to
Solution X-Ray Scattering

Biological Systems

Proteins



Viruses



Subcellular structures

crystallography
spectroscopy

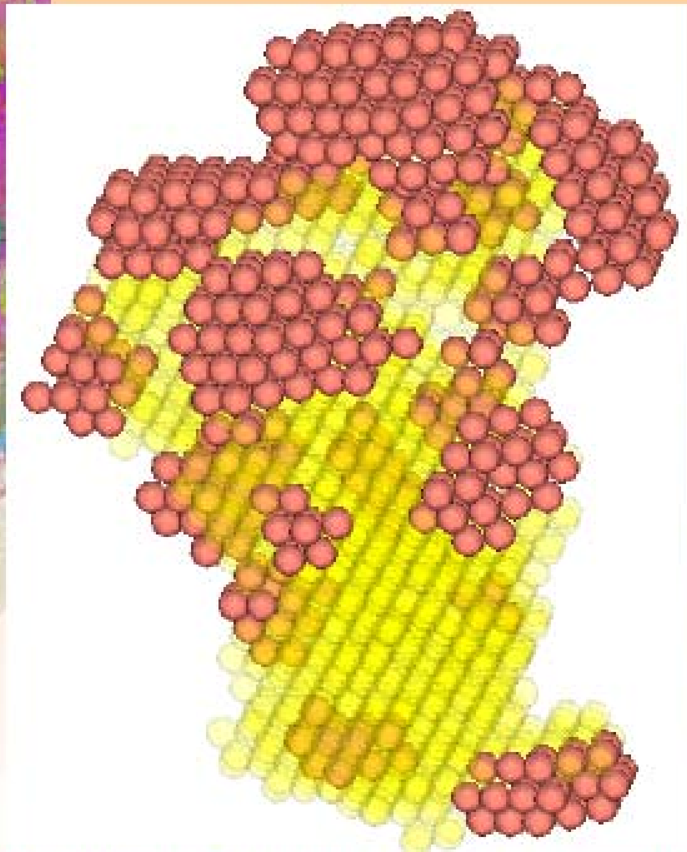
SAXS

imaging technique
microscopy

Å nm µm mm m

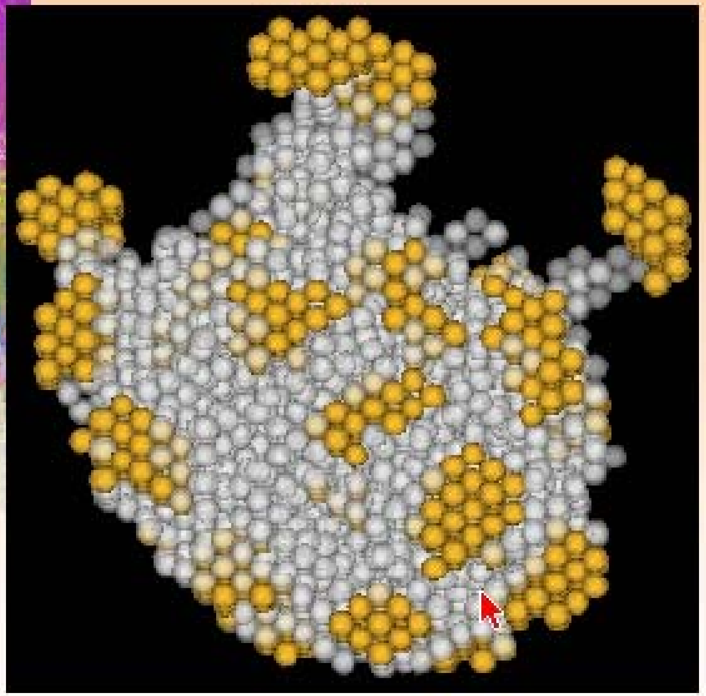
Characteristic length

Solution SAXS *versus* Single Crystallography

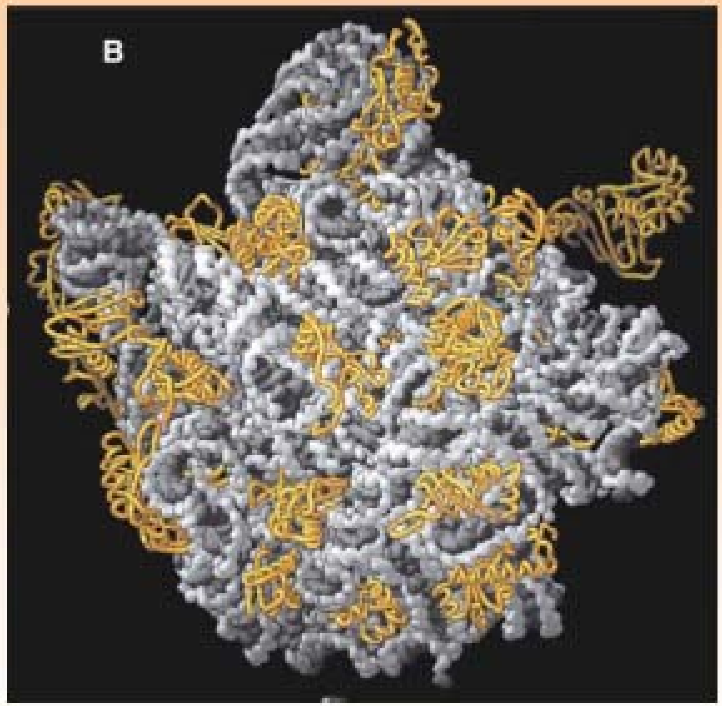


3 nm resolution model of the 30S subuinit in the 70S ribosome *E.coli* (Svergun & Nierhaus, May 2000)

0.33 nm resolution model of the 30S subunit *Th. Thermophilus* (Yonath group, September 2000)

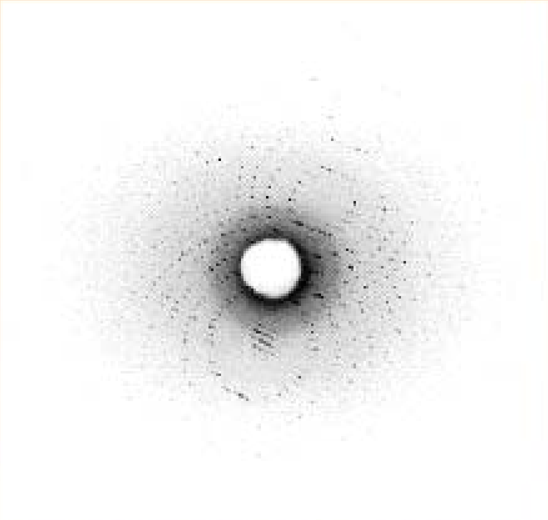


3 nm resolution neutron scattering model of the 50S subunit in the 70S ribosome *E.coli* (Svergun & Nierhaus, May 2000)



0.24 nm resolution crystallographic model of the 50S subunit *H.marismortui* (Steitz group, August 2000)

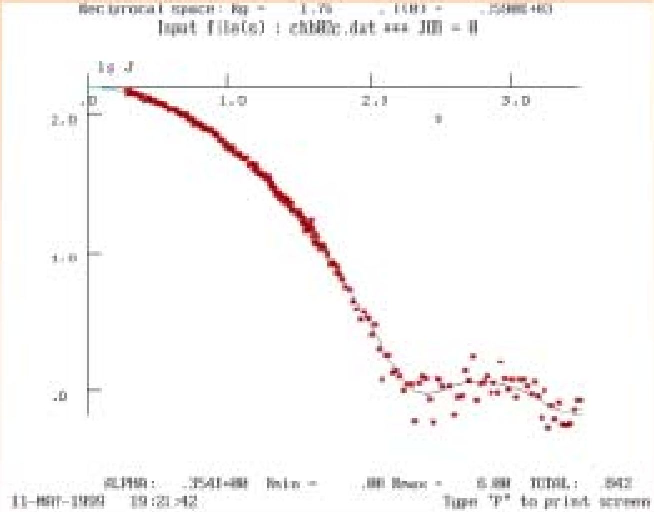
- Thousands of reflections
- 3D, high resolution



- Data undersampled,

  $\Delta s = 2\pi / D$

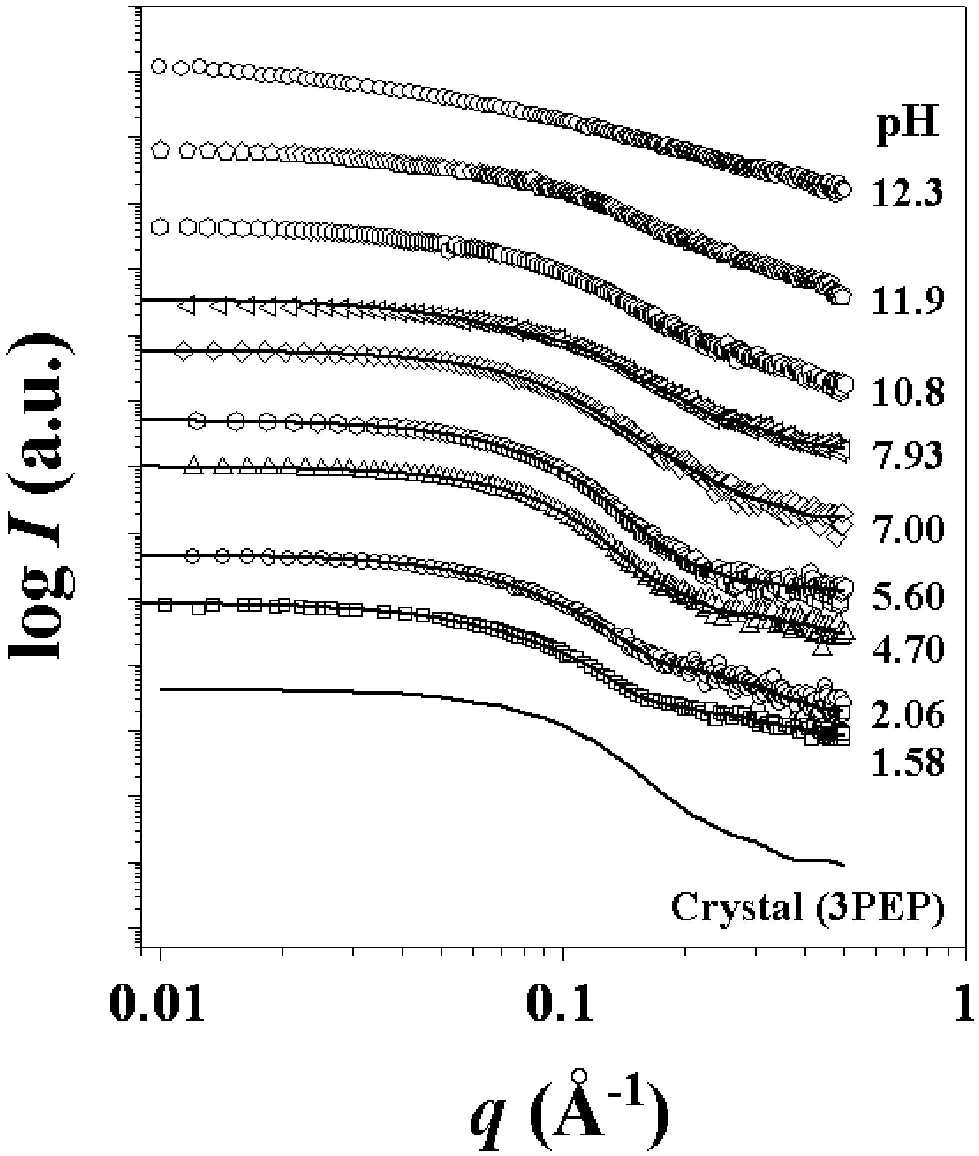
- A few Shannon channels
- 1D, low resolution



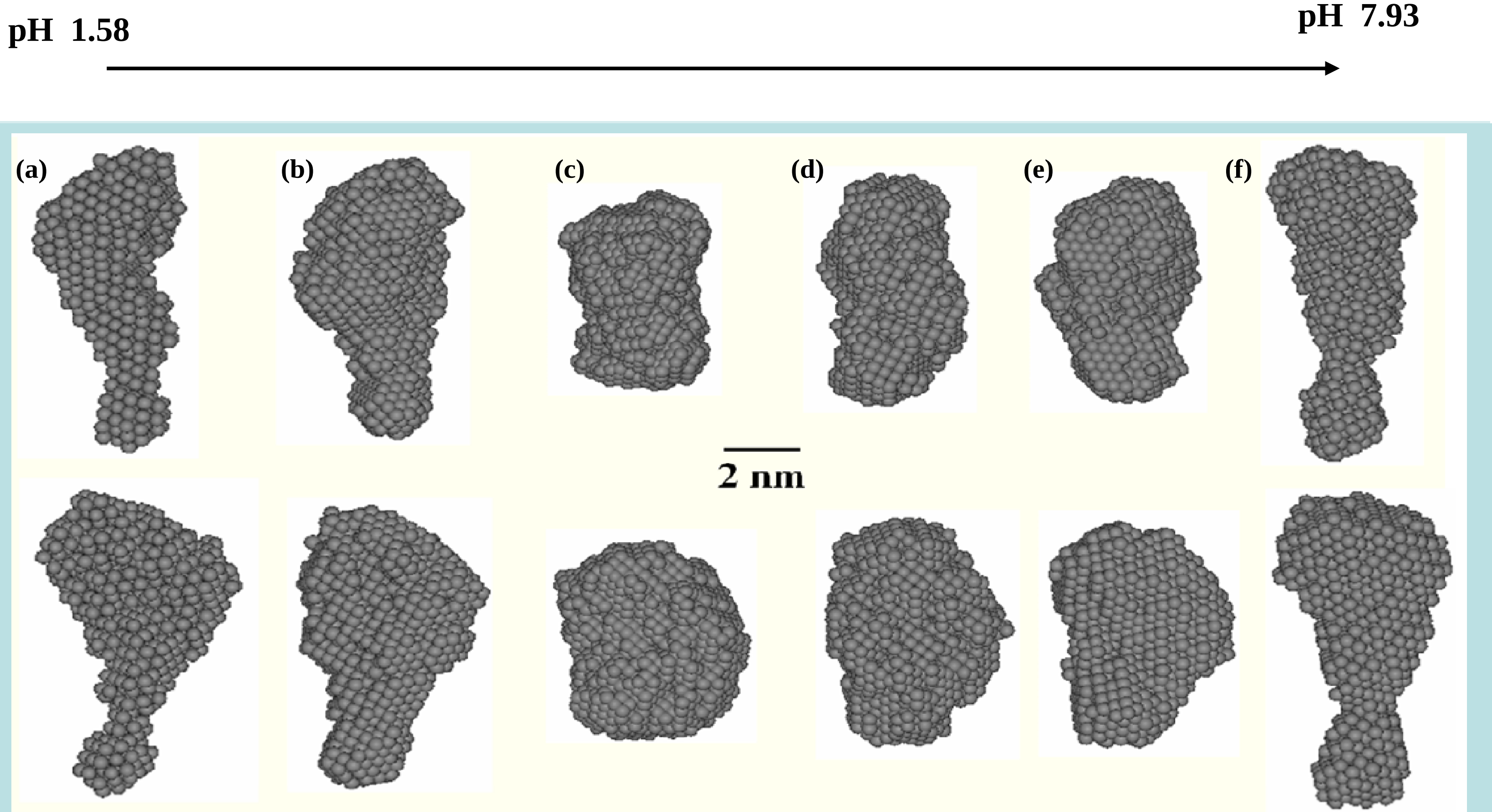
- Data oversampled,

  $\Delta s << \pi / D$

Scattering Profiles of Porcine Pepsin in Various pH Conditions



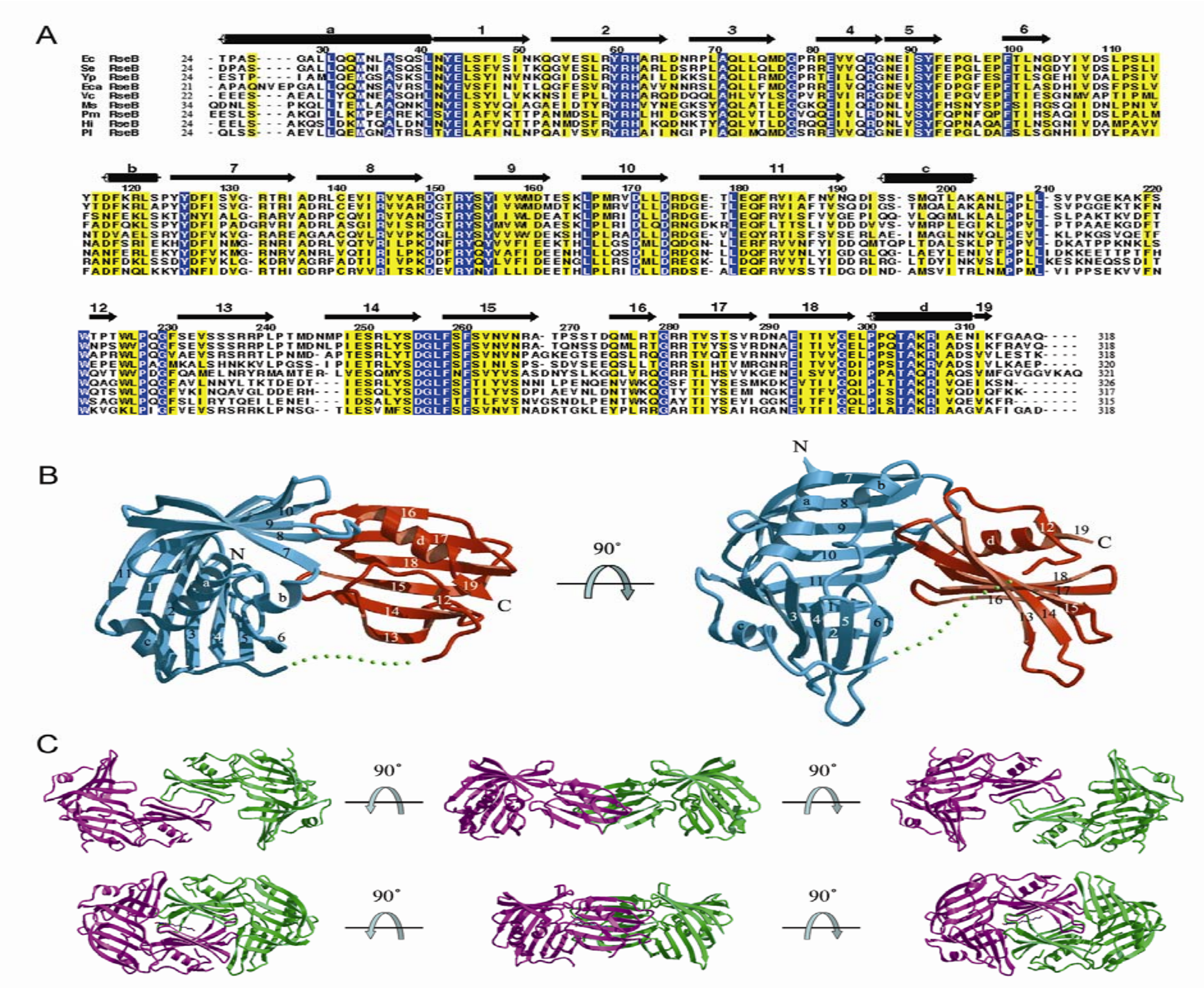
Structure Changes of Porcine Pepsin in Various pH Conditions



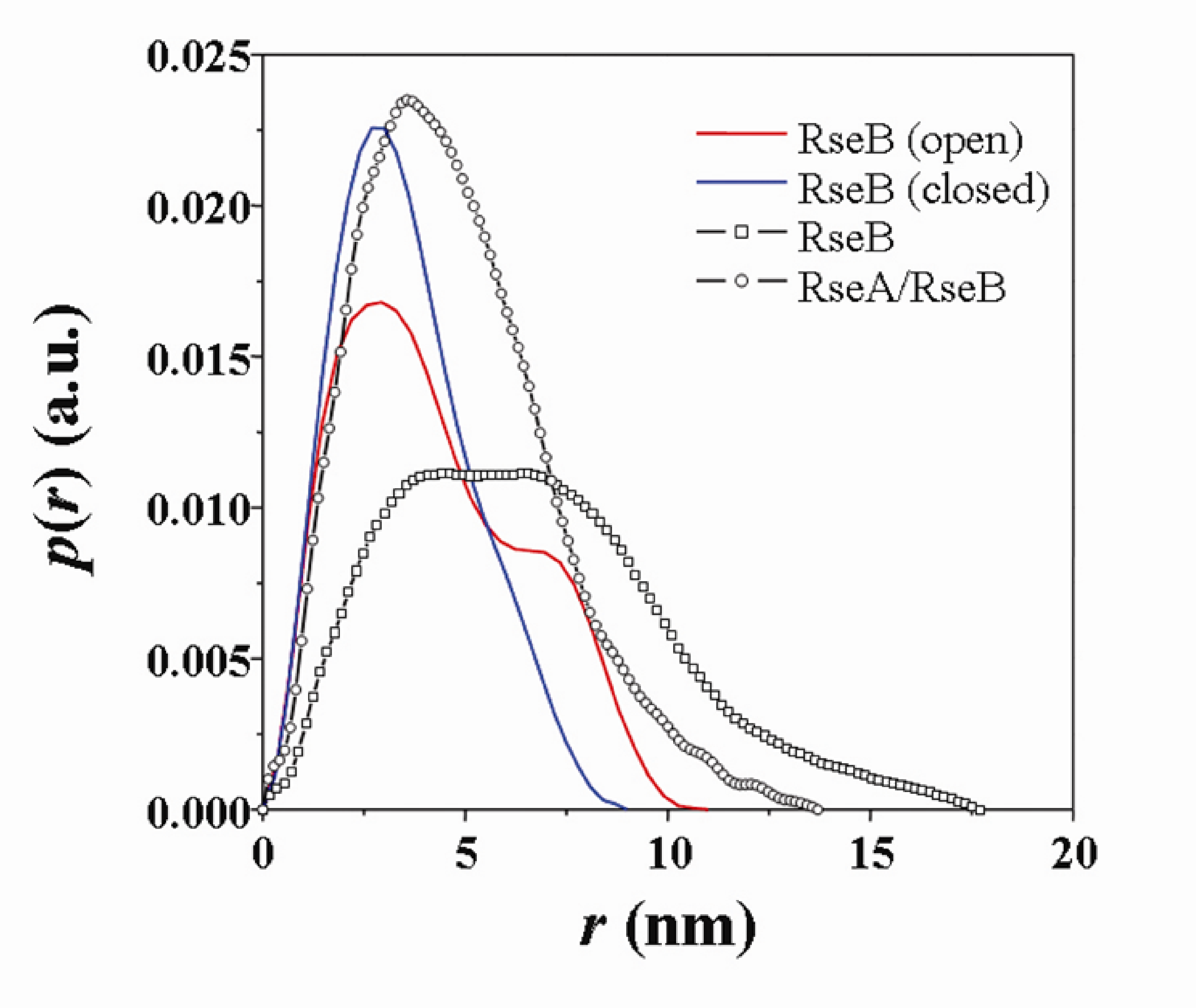
Low resolution structural models of porcine pepsin in solution under several pH conditions: (a) pH 1.58, (b) pH 2.06, (c) pH 4.70, (d) pH 5.60, (e) pH 7.00, and (f) pH 7.93. In each panel, lower orientation is rotated by 90° clockwise around vertical axis.

K.S. Jin, M. Ree et al., J. Phys. Chem. B. (in press)

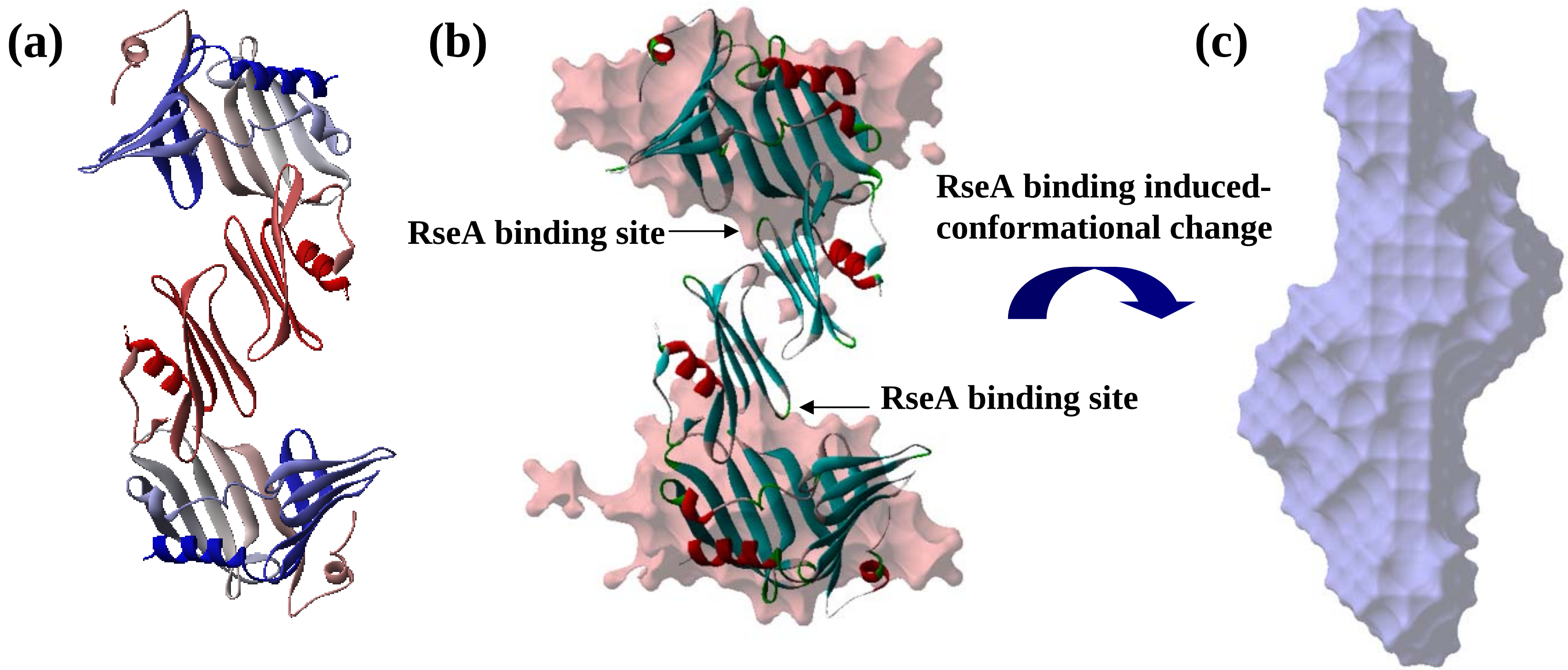
RseA and RseB



p(r) Profiles of RseB and RseA in Solutions (obtained from SAXS Profiles)



Structures of RseB (b) and RseA121–216/RseB complex (c)



(a) Crystal structure of *Escherichia coli* RseB at a resolution of 0.24 nm

The solution models of RseB (b) and RseA$_{121–216}$/RseB complex (c) restored from the SAXS data at a resolution of 1.25 nm. The ribbon diagram of the RseB is overlapped onto the solution model of RseB for the comparison of overall shape and dimension.

D.Y. Kim, K.S. Jin, E. Kwon, M. Ree, K. K. Kim, *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 8779-8

Conclusions – GISAXS

- **GISAXS Optics, Theory and Data Analysis Methods Reviewed.**

- **GISAXS is Very Powerful to Analyze Structures in Nanoscaled Samples and Products.**

- **GISAXS is Very Powerful to Characterize Structural Changes in Time-Resolved Mode.**

- **GISAXS is the Nondestructive analysis technique.**

Conclusions – TSAXS

- **SAXS Optics and Sample Stage Related Equipments Reviewed.**
- **Theoretical Fundamentals of TSAXS Reviewed.**
- **TSAXS is Very Powerful to Analyze Single Particles (Molecules) and Their Assemblies in Solutions and Solids.**
- **TSAXS is Very Powerful to Analyze Proteins and Other Biomacrmolecules in Nature.**

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Dr. Jinhwan Yoon (U. Mass)   Dr. Kyuyoung Heo (RIST)   Dr. Kyung Sik Jin (PLS)
Dr. Byeongdu Lee (APL)   Dr. Yongtaek Hwang (Samsung Elec.)
Prof. Weontae Oh (Dongeui Univ.)   Dr. Young-Hee Park (RIST)
Prof. Seung Woo Lee (YeongNam Univ.)
Prof. Seung Moon Pyo (Konkuk Univ.)
Dr. Youngkyoo Kim (Kyung Pook National Univ)

Prof. Taihyun Chang (Postech)
Prof. Jin Kon Kim (Postech)
Prof. Prof. Hirohisa Yoshida (Tokyo Metropolitan U.)
Prof. Teruaki Hayakawa (Tokyo Inst. Tech)

Prof. Akira Hirao, Prof. Takashi Ishizone
Prof. Toyoji Kakuchi (Hokkaido Univ.)

Dr. Sono Saski, Dr. Osami Sakata, Dr. Kimura, Dr. Masaki Takata (Spring-8)
Dr. Richard Garrett, Dr. Bill Hamilton, Dr. Mike James (ANSTO)

M. Ree's Group

1. Research Fields

<Polymer Physics>
- Polymer chain conformation
- Structures and morphology
- Nanostructuring
- Electric, dielectric, optical, thermal, mechanical properties
- Sensor properties
- Surface, interfaces

<Polymer Synthesis>
- Functional polymers
- Structural polymers
- Polypeptides, DNA, RNA

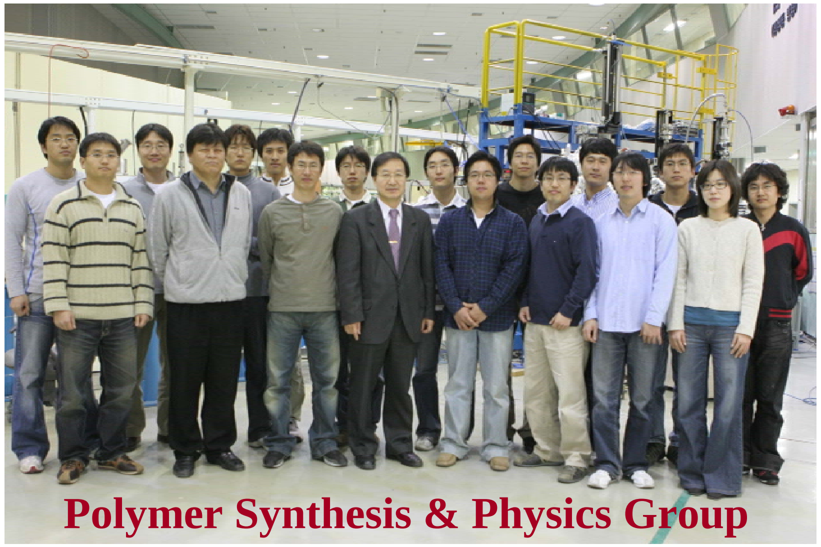
♦ Polymers for Microelectronics, Displays, & Sensors

♦ Polymers for Implants & Biological Systems

♦ Proteins & Polynucleic acids (DNA, RNA)

2. Group Members (25)

2 Postdoctoral Fellows
13 Ph.D. candidates
2 Undergraduates
2 Technicians
2 Secretaries
4 Scientists (PLS: Coworkers)



Polymer Synthesis & Physics Group


Pohang Light Source
Pohang City
POSTECH Campus


Thank you very much
for your attention !!!