# Phase transitions in polymeric and micellar systems

*Group B*

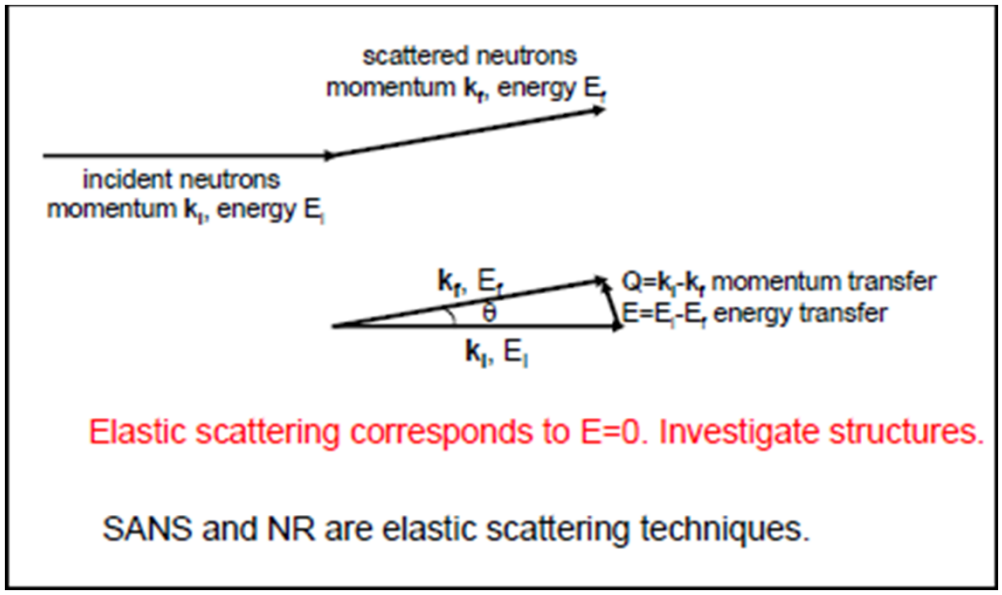
NCNR Summer School on
Methods and Applications of Small
Angle Neutron Scattering

*June 13-16, 2011*

# INTRODUCTION

SANS is a useful tool of the structure and dynamics of materials on large range length scales of 1 – 500 nm.

**Neutron Scattering**



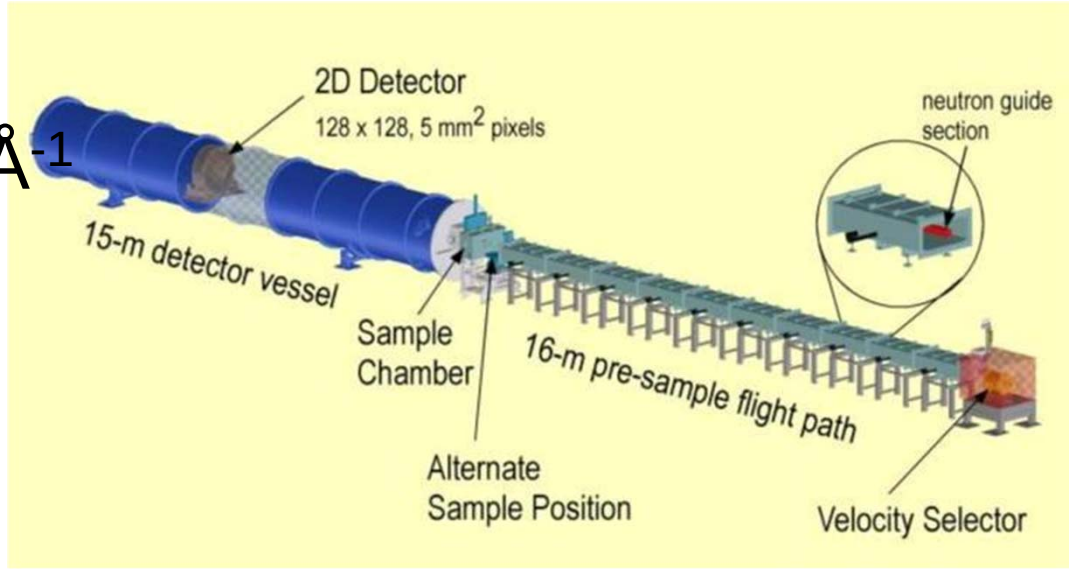

$$I(Q) = \frac{d\Sigma_{coh}(Q)}{d\Omega} + \frac{d\Sigma_{incoh}}{d\Omega}$$

~ Contrast factor = $(\rho_A-\rho_B)^2$
- Info. about structure

- Q-independent
- no info. about structure

# Experimental Apparatus

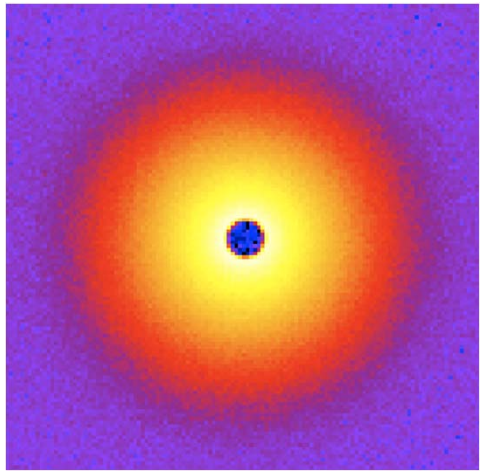
- Experiments were “performed” on the NG-7 SANS instrument
- Three detector positions were used:
  - 14, 4 and 1 m
  - Total q-range: ~$3.5 \times 10^{-3}$ – 0.51 $Å^{-1}$
  - Transmission measured at 4 m

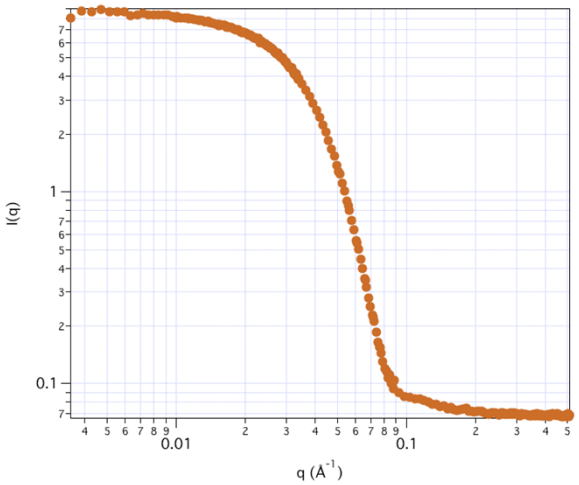



http://www.ncnr.nist.gov/instruments/ng7sans/

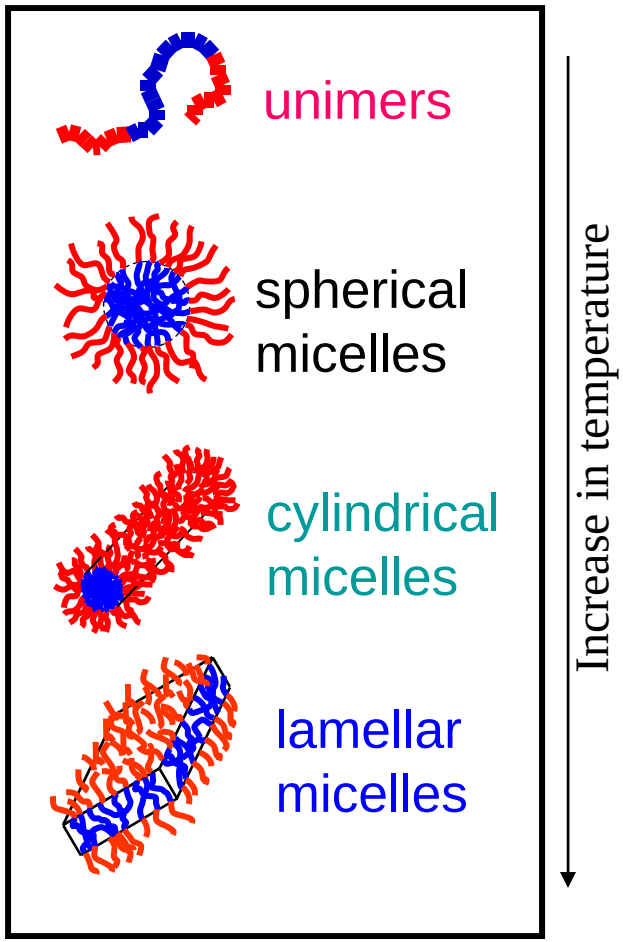
# Data Reduction

- Results were corrected by the standard analysis procedure by:
  - Pixel efficiency, cell blank, and background
- Absolute scaling was achieved by measuring sample transmission



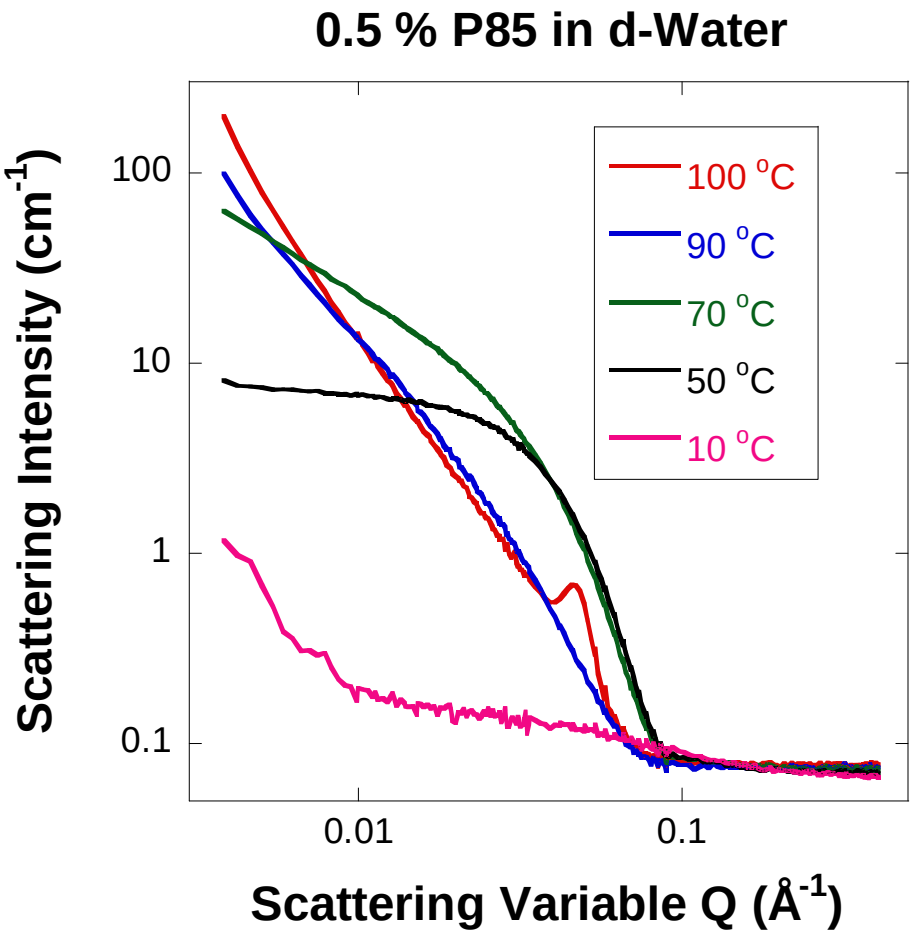


# Experiment: Evolution of Pluronic-85 Micelles

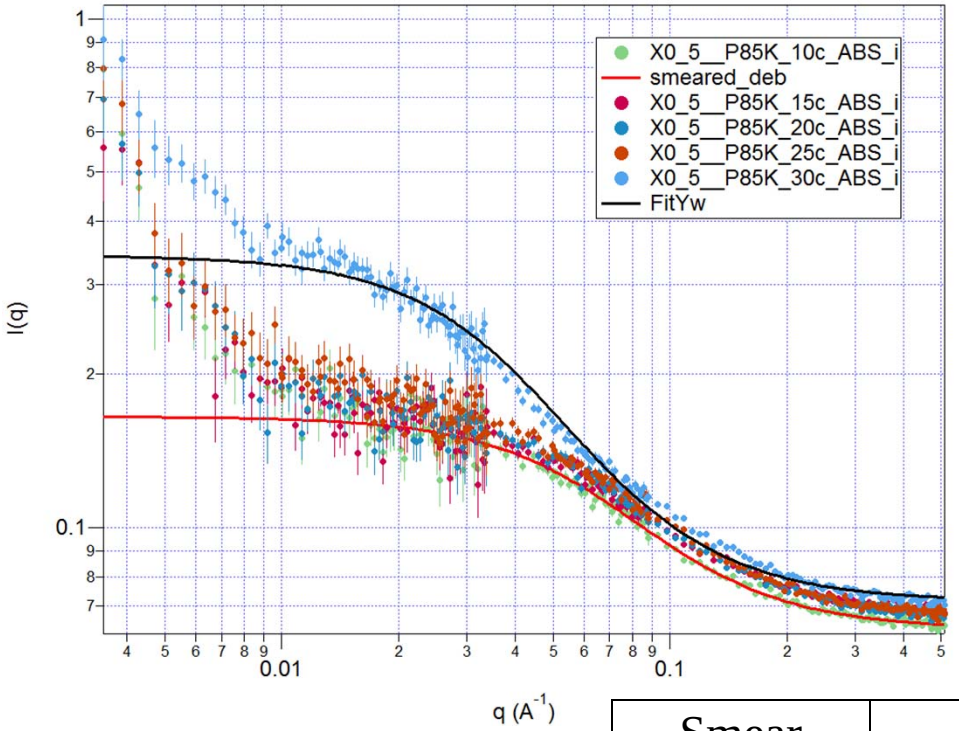



- Looking at the temperature dependence on phase behavior of P85.
- Using Appropriate models to interpret the data.

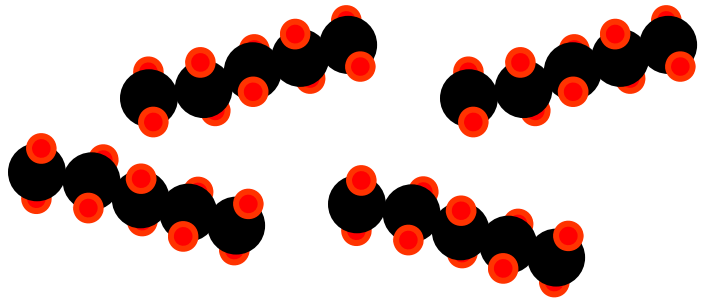
# SANS Data


0.5 % P85 in d-Water
Scattering Intensity (cm-1)
100
10
1
0.1
0.01
0.1
Scattering Variable Q (Å-1)
100 °C
90 °C
70 °C
50 °C
10 °C

# Fit to Smeared Debye Model




Pluronic P85 unimers



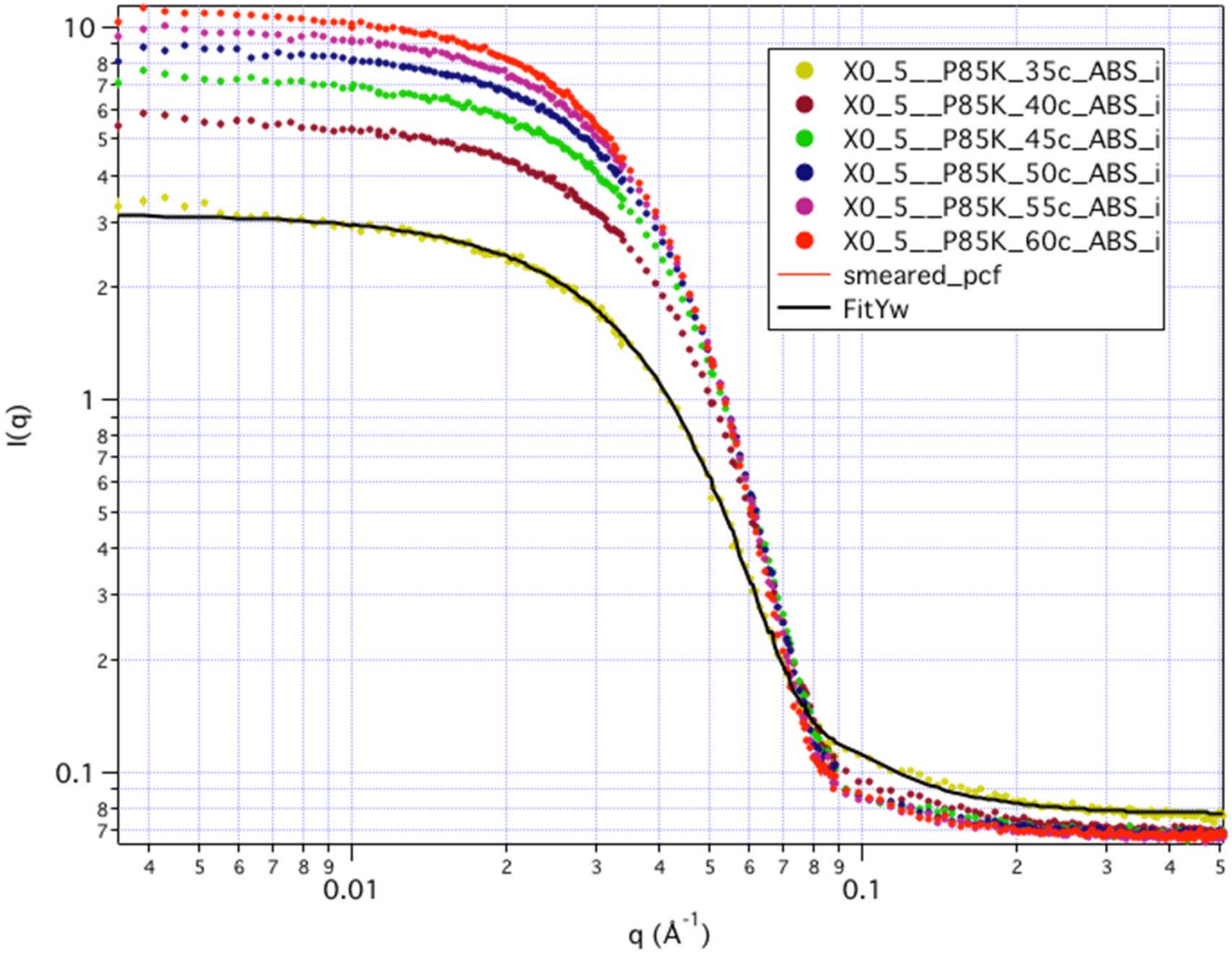
Fit parameters

***Debye Model***

$$I(Q) \approx \frac{2}{QR_g^4}\left[\exp(-Q^2R_g^2) - 1 + Q^2R_g^2\right]$$

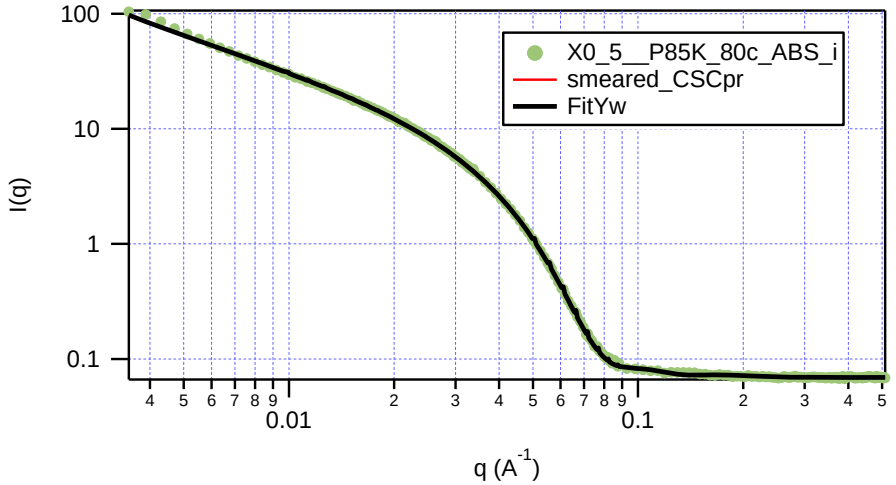
| Smear model | 10°C | 15°C | 20°C | 25°C | 30°C |
|---|---|---|---|---|---|
| Scale | 0.103 | 0.105 | 0.110 | 0.116 | 0.259 |
| Rg (Å) | 24.392 | 23.497 | 23.540 | 23.910 | 40.126 |
| Bkg ($cm^{-1}$) | 0.063 | 0.067 | 0.066 | 0.067 | 0.072 |

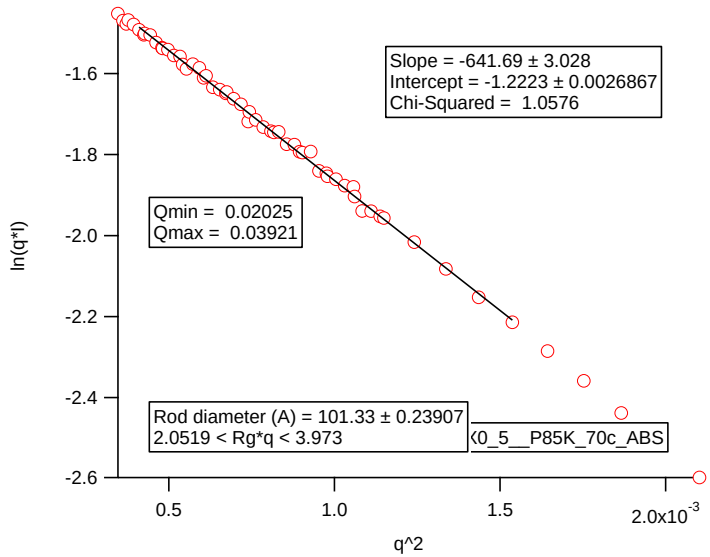
Core Shell poly dispersed Sphere:



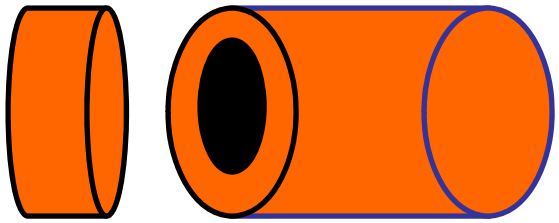
| | 35° | 40° | 45° | 50° | 55° | 60° |
|---|---|---|---|---|---|---|
| Scale | 1.0e-2 ± 5.0e-4 | 9.7e-3 ± 6.5e-4 | 1.0e-2 ± 2.9e-4 | 9.9e-3 ± 2.6e-4 | 9.5e-3 ± 1.7e-4 | 9.5e-3 ± 2.0e-4 |
| Avg Core Rad (Å) | 55.5 ± 0.2 | 47.7 ± 0.2 | 46.5 ± 0.16 | 47.2 ± 0.06 | 48.2 ± 0.14 | 49.2 ± 0.1 |
| Core Polydisp | 0.20 ± 7.3e-4 | 0.17 ± 1.2e-3 | 0.14 ± 2.1e-3 | 0.14 ± 1.6e-3 | 0.14 ± 1.3e-3 | 0.14 ± 1.3e-3 |
| Shell Thickness (Å) | 8.5 ± 0.7 | 28.4 ± 1.8 | 25.3 ± 0.6 | 23.5 ± 0.5 | 22.7 ± 0.3 | 22.9 ± 0.4 |
| PPO SLD: 4e-7 | 3.3e-6 ± 9.6e-8 | 3.4e-7 ± 1.5e-8 | 4.6e-7 ± 3.0e-8 | 3.8e-7 ± 1.4e-8 | 3.3e-7 ± 1.2e-8 | 3.1e-7 ± 7.9e-9 |
| PEO SLD: 6e-7 | 8.5e-6 ± 1.9e-7 | 6.2e-6 ± 1.6e-8 | 5.8e-6 ± 2.8e-8 | 5.6e-6 ± 2.4e-8 | 5.5e-6 ± 2.5e-8 | 5.4e-6 ± 3.4e-8 |
| Solvent SLD ($Å^{-2}$) | 6.3e-6 | 6.3e-6 | 6.3e-6 | 6.3e-6 | 6.3e-6 | 6.3e-6 |
| Bkg | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 |

# P85 at 70 and 80 C




- Qualitative picture
  - Low Q region $I(Q) \propto Q^{-1.14}$ => Cylinder
- Modified Guiner
  - Cylinder Rg
    - 107.15 ± 0.22746 (80 C)
    - 101.33 ± 0.23907 (70 C)

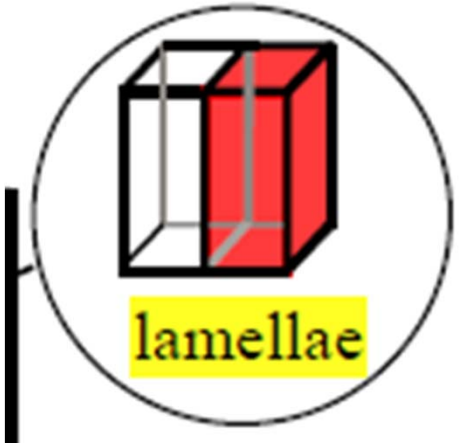
# Model

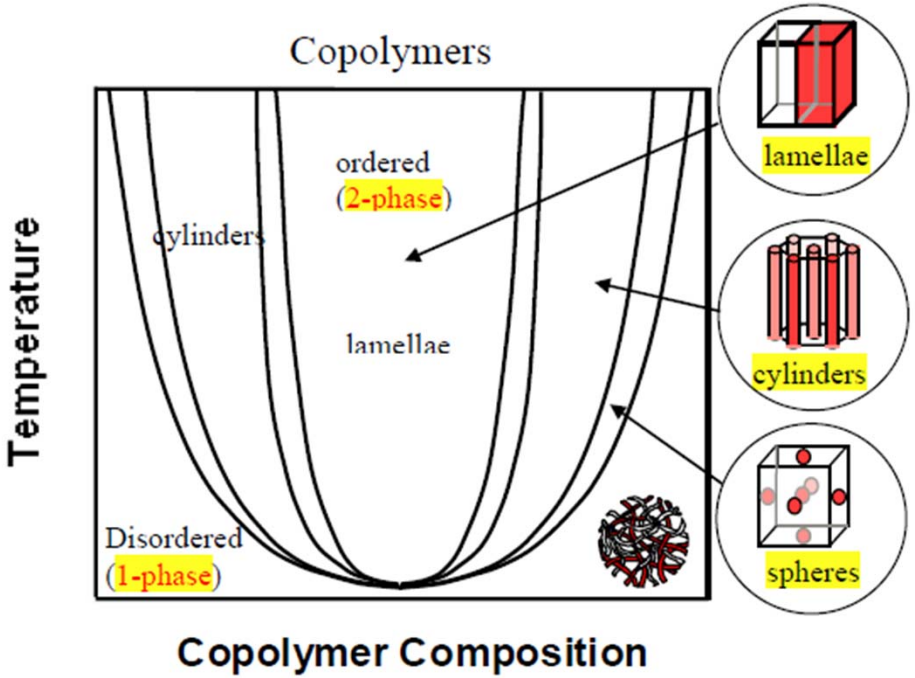
- Form factor
  - Poly-dispersed Core-Shell cylinder

| | 70 C | 80 C |
|---|---|---|
| scale | 0.012866 | 0.01378 |
| mean CORE radius (A) | 19.5407 | 20.0765 |
| radial polydispersity (sigma) | 0.330847 | 0.34089 |
| CORE length (A) | 5210.51 | 6079.28 |
| radial shell thickness (A) | 30.3771 | 28.1016 |
| face shell thickness (A) | 2243.11 | 1643.7 |
| SLD core (A^-2) | 1.67E-07 | 1.67E-06 |
| SLD shell (A^-2) | 3.80E-06 | 3.74E-06 |
| SLD solvent (A^-2) | 6.36E-06 | 6.36E-06 |
| incoh. bkg (cm^-1) | 0.069013 | 0.068943 |

# Lamellar Structure Model

- Assumes a stack of lamellae with very large disk radius and alternating lamellae

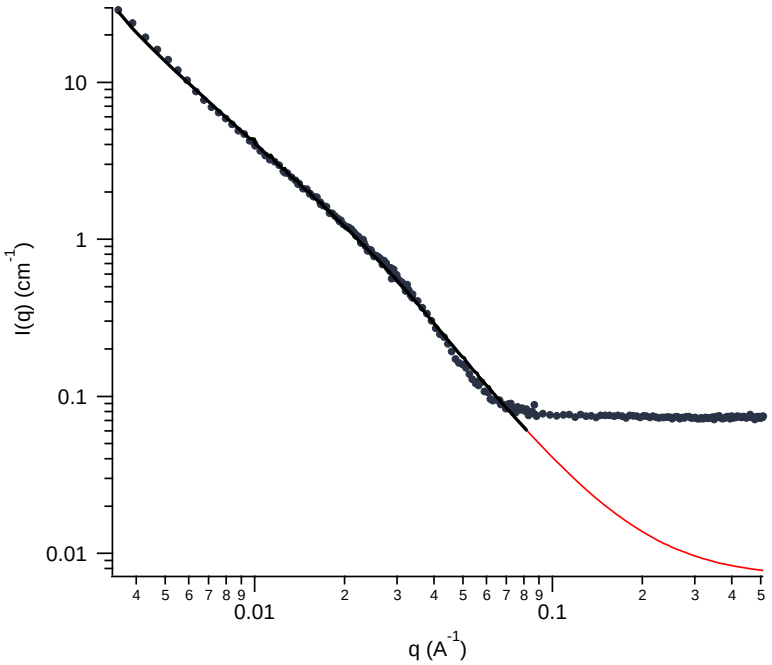


# Lamellar Structure Model

- 90°C
  - Stacked Disk Model
  - Guinier-Porod Model –WORKED!

- Lamella not fully developed
  - Looking at low Q value, the power rule is between -1 and -2 which indicates a transition between cylindrical micelle to lamella

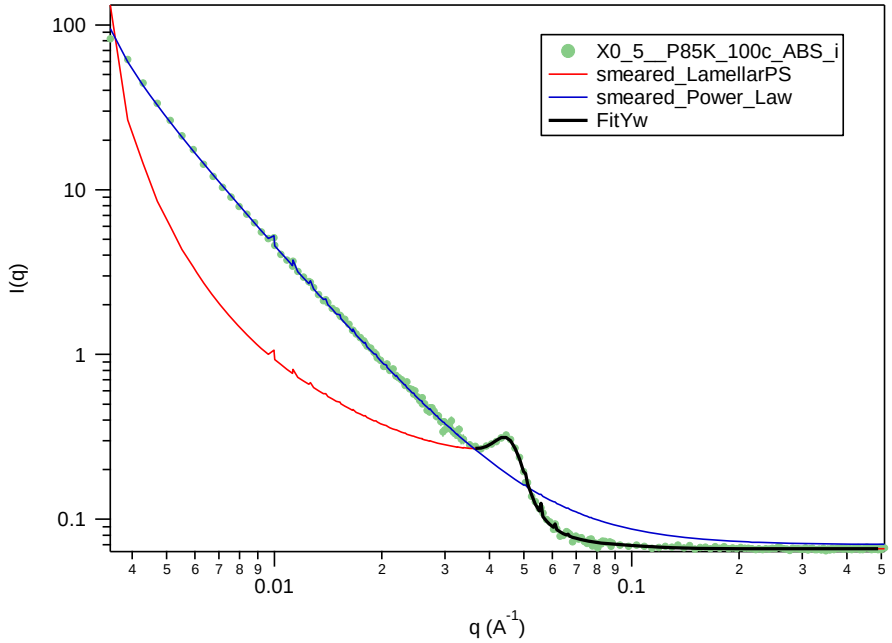



Guinier Scale: 0.00226157
Dimension Variable, s: 1.62924
Rg [A]: 19.3604
Porod Exponent: 2.32079
Bgd [cm-1]: 0.007

# Lamellar Structure Model

- 100°C
  - Lamellar Paracrystal Stacked Model (Peak) and Power Law

- Does not adequately fit fully developed lamellar structure as seen by peak
  - This is a demixed lamellae phase consisting of lamellar stacks separated by pockets of solvent



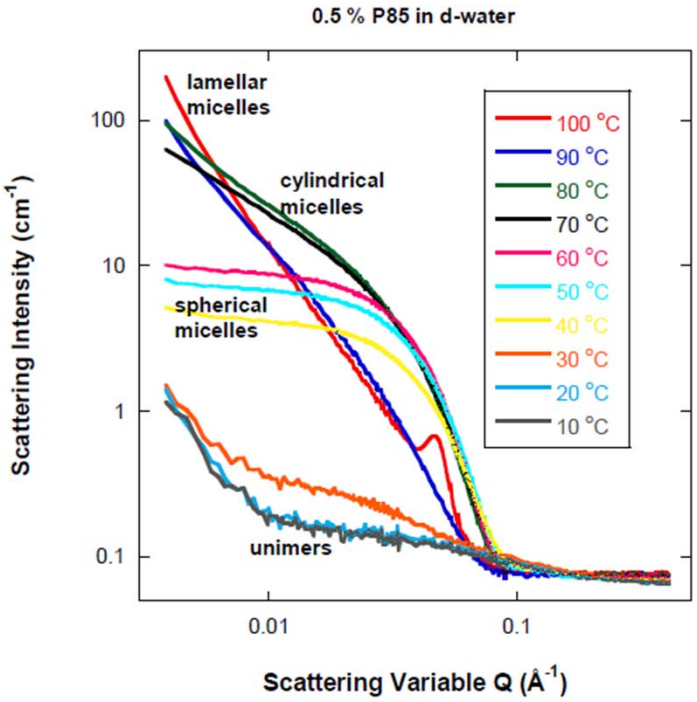

**Lamellar Paracrystal Stacked Model**

Scale: 0.00101
Lamellar spacing, D (A): 137.48
Thick (delta) (A): 76.08
polydisp of Bilayer Thickness: 0.29
SLD bilayer (A^-2): 5e-07
SLD solvent (A^-2): 6.3e-06
# of Lamellar plates: 55
Caille parameter: 0.67
Incoherent Bgd (cm-1): 0.066

**Power Law**

Coefficient, A :6.53e-05
(-)Power: 2.41131

# Summary




- As temperature increases the micelle structure changes from:
  - Unimers (10°C) → spherical (40°C) → cylindrical (70°C) → lamellar (90°C)