# SAXS Research at NSRRC

*The thriving small-angle X-ray scattering (SAXS) activities at NSRRC in the couple years are briefly reviewed. A planned SAXS beamline at NSRRC for soft matter and nanostructures is introduced.*

**Beamline**

17B3 Small Angle X-ray Scattering beamline
23A1 Small Angle X-ray Scattering beamline (under construction)

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Small-angle X-ray scattering (SAXS), a scattering tool of atomic spatial resolution and high penetration power, provides a non-destructive scattering tool in structural characterization for surfaces, interfaces, as well as bulks, and is an decent complimentary technique to the direct imaging tools such as the SEM, TEM, and AFM in nanostructure research. Capable in probing structural information (electron density fluctuations) in a wide range of length scales spanning from sub-nanometer to submicron, SAXS has been employed regularly in many fields where nanostructure and/or mesomorphous structure take a decisive role in determining phases, functions, and/or performances of devices.

The merits of using SAXS in structural characterization have been recognized by many research groups in Taiwan. Several SAXS instruments equipped with in-house X-ray sources have been installed in recent years, with fruitful results. Nevertheless, with limited flux ($10^6$ photon/s) and fixed energy (mainly 8 keV) of the in-house X-ray sources, many advanced researches are frustrated, especially in time-resolved structural transitions and low-density contrast systems such as protein folding dynamics or polymer morphology in solutions. Anomalous SAXS for multiphase structures, like core-shell bimetallic nanoparticles in quantum dots or catalyst applications, is hopeless with an in-house X-ray source.

With five orders of magnitude higher photon flux ($10^{11}$-$10^{12}$ photon/s) and a wide tuneable energy range (5-23 keV), an advanced synchrotron radiation X-ray source apparently can cover a wide range of SAXS needs in Taiwan. In the past few years, limited SAXS measurements were conducted on a temporary setup modified from the 8-circile diffractometer by Drs. C. H. Hsu and H. Y. Lee at BL17B1. In 2004 summer, a temporary BL01B SAXS endstation operated for a short moment then was replaced by the current X-ray microscopy endstation. In the period of test run at BL01B, many advanced SAXS measurements were explored, including the anomalous SAXS, temperature-dependent SAXS, time-resolved SAXS, simultaneous SAXS/WAXS measurement, SAXS/DSC, and SAXS for protein solutions, etc.. The fruitful results, to be briefly reviewed below, were presented in the SAXS workshop and the NSRRC user meeting in 2004. Afterwards, a SR SAXS interest group was shaped and organized.

On the basis of the active science projects and interests of the SAXS interest group, a survey of NSRRC for potential SR SAXS users during the past couple years, and most of all, the requests from many enthusiastic research group leaders, NSRRC has lunched a SAXS research program for soft matter and nanostructures, including the construction of a dedi-

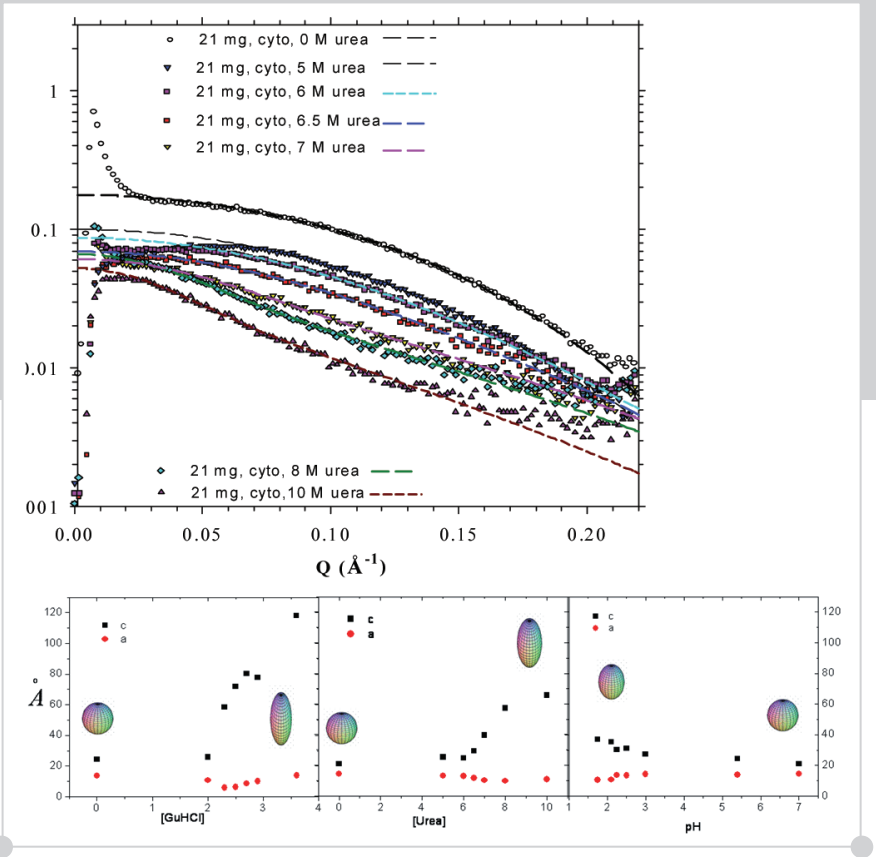


**Fig. 1:** Up, the SAXS data for the protein cytochrome *c* are fitted (dashed curve) using an ellipsoidal shape for the protein morphology in the solutions, where *Q* is scattering wavevector transfer of photons. Down, the cartoons illustrate graphically the unfolded and folded protein shapes with different denaturants and pH values in the cytochrome *c* solutions. *a* and *c* denote the semi-major and semi-minor axes of the ellipsoid shape. (Shiu *et al.*)

cated, state-of-art SAXS beamline with an advanced X-ray source at the new beamline BL23A within two years. In the transition time before the commission of the dedicated SAXS beamline and endstation, we have also installed a SAXS endstation at beamline BL17B3 for the urgent needs requested from the SAXS interest group. The BL17B3 SAXS endstation shares the 17B X-ray source with the BL17B1 X-ray scattering endstation for material research. Below, we detail the SAXS-related research activity in Taiwan and report the status of the dedicated SAXS beamline under construction.

## SAXS activities at NSRRC

The recent SAXS activities at NSRRC are briefed with a focus on soft matter.

### (1) Biomolecules in solutions and membranes.

Presently in Taiwan, there are growing activities in experimental study of protein folding. For instance, Drs. Y. J. Sheu and I. R. Sheu are interested in using extended X-ray absorption fine structure (EXAFS) combining with SAXS, at NSRRC, to study the folding of cytochrome-c and lysozyme, influenced by temperature, solvent, and pH values (Fig. 1). The results reveal the global and local morphology changes of the protein in solutions during unfolding.

**Interactions of biomacromolecules with membranes.** Other than aqueous solutions, membranes can also provide an environment for protein and enzymes in actions, including the tunnelling of membranes by antimicrobial peptide. In the therapy gene delivery into cells, Safynia et al. have succeed in

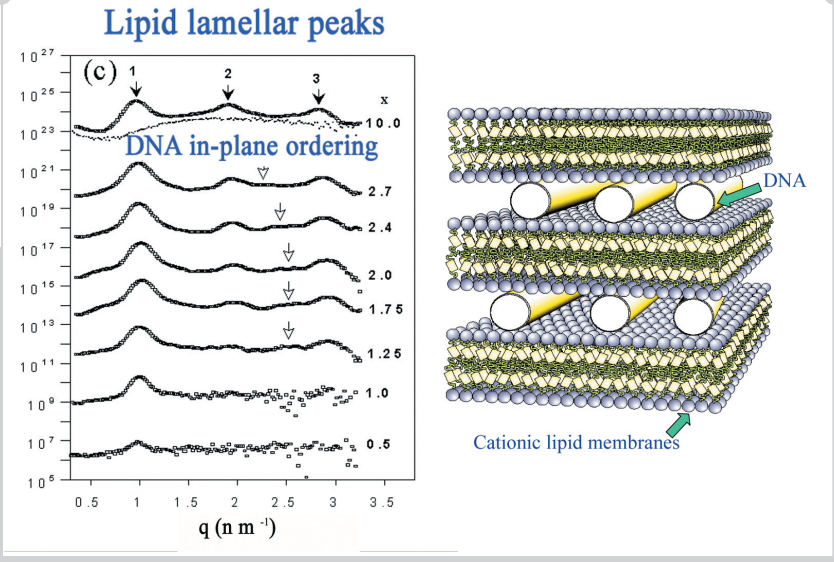


**Fig. 2:** Multilamellar structure consisting of alternating lipid bilayer and DNA in-plane monolayers in DNA/cationic lipid complex. The DNA chains confined between the lipid bilayers adopt a smectic order. The SAXS data show the in-plane DNA ordering peaks shifts as the DNA concentration increases (smaller x value) (provided by H. L. Chen and C. M. Wu).

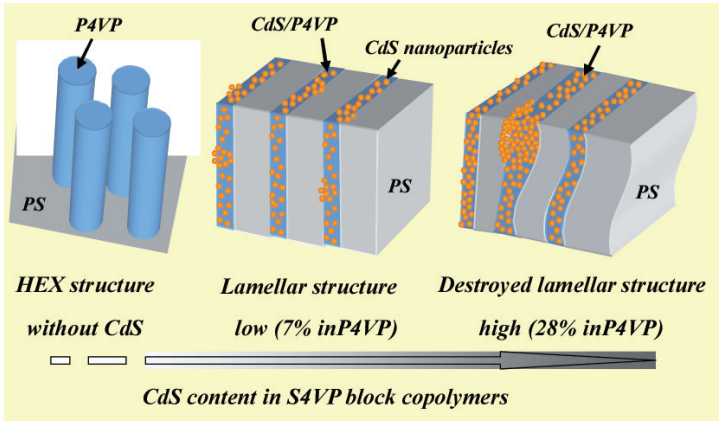


**Fig. 3:** (Left) Hydrogen bonding induces the morphological transformation from the HEX structure of pure Poly(styrene-b-4-vinylpyridine) (S4VP) block copolymers to lamellar CdS/S4VP composites upon selective segregation of CdS nanoparticles into the P4VP phase. (Right-hand-side) SAXS data (triangles) for the sample of 7% CdS. The form factor $P(Q)$ of the composite is a summation of the scattering contributions of the CdS nanoparticles of an average radius of 17.5 Å and a polydispersity of 50% and the P4VP slabs (of a slab thickness 112 Å) in the PS matrix. The extracted structure factor $S(Q)$, = $I(Q)/P(Q)$, for the composite fitted suggest a lamellar spacing of 43.9 nm. (Yeh *et al.*)

using SAXS to observe the structural transition of a complex of charged lipid membranes and DNA. Domestic researcher Prof. H. L. Chen (NTHU) has also conducted studies in the charged cholesterol and DNA using SAXS (Fig. 2), with fruitful results.

**(2) Polymer and polymer complex.**

Polymer is one of the most important soft materials, with a very broad spectrum of application ranging from commodity to high-tech areas. Structural polymer research in Taiwan is growing rapidly in recent years, due to the advances in imaging (TEM, SEM, etc.) and scattering (light scattering, X-ray scattering) tools. Especially, in the polymer nanocomposites with controlled order, SAXS can conveniently differentiate the structural characteristics of the ordered copolymer matrix and nanoparticles in a complex system, as shown in a recent study of Yeh *et al.* (Fig. 3).

Polymer structures in solutions or molten states are extremely soft, and easy to be manipulated by, for instance, temperature or shearing force, for a controlled alignment or phase separation. This type of study is important in identifying or creating intermediate structural patterns under the influence of processing procedure (solvent or external shear) for preferred structural characteristics that can be kinetically trapped in the bulk states, after cast from the controlled solutions or molten states for practical devices. An example in this field of research deals with the kinetics of the phase separation during melting. Figure 4 shows the simultaneous SAXS and DSC measurement conducted on a SAXS setup at BL01B for the study of the kinetics of PCL/PEG copolymer, with a time resolution of 3 min.

On the other hand, simultaneously SAXS/WAXS measurement has been explored at NSRRC. Figure 5 shows the simultaneously observed WAXS peak and SAXS peak, when the sample temperature ramped to 100˚C, ~ the liquid crystal transition temperature of the peptide. The simultaneously appeared SAXS/WAXS peaks correlate the stacking order (phase separation) of the additional planar hexagonal-packing of the diblock copolymer after α-CD inclusion with the channel crystallization, and indicates the formation of juxtaposed bilayer-like nanostructure featuring hexagonally packed PBLG stacks and channel-type polypseudorotaxane moieties.

**The status of the SAXS beamline and endstation**

A dedicated small-angle X-ray scattering (SAXS) beamline BL23A using a new X-ray source generated from an In-Acromat superconducting wiggler (IASW6)

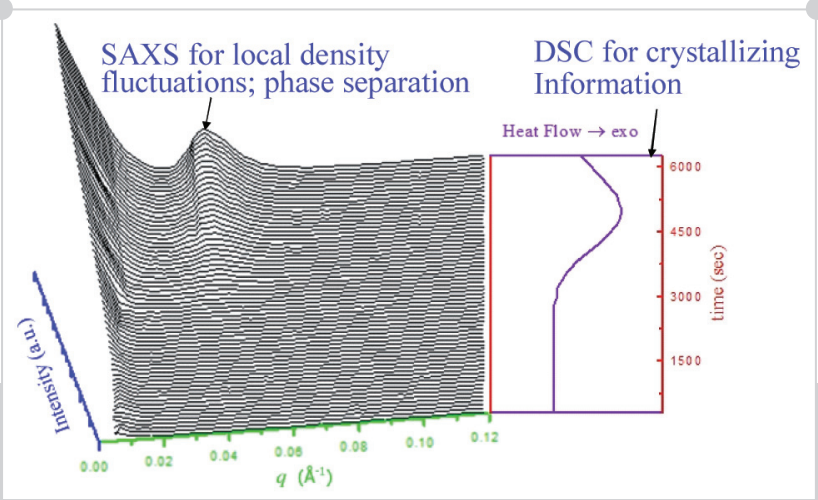


**Fig. 4:** Phase separation kinetics of PCL/PEG copolymer studied by simultaneously SAXS/DSC setup at NSRRC (Chuang *et al.*)

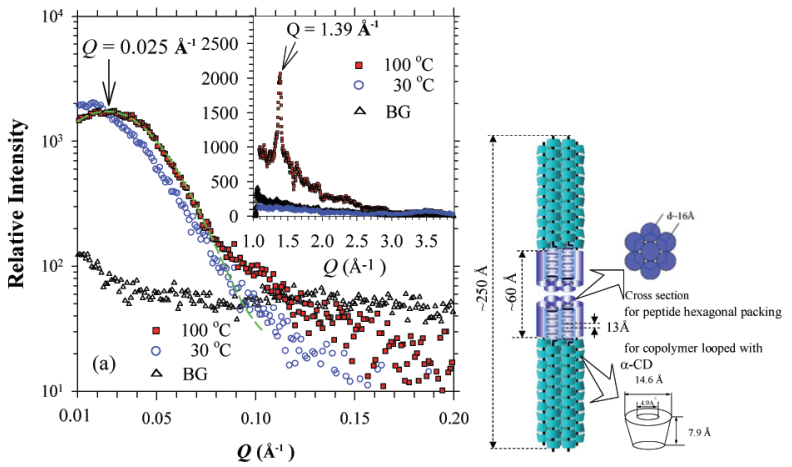


**Fig. 5:** Simultaneous SAXS and WAXS (inset) data for the α-CD · $P(EO_{19}$-*r*-$PO_3)$-*b*-$PBLG_{20}$ complex at 30 and 100°C. Note, the peak at $Q$ = 1.39 $Q^{-1}$ (WAXS) corresponds to the channel crystallization of α-CD, which signifies the formation of hexagonal structure of the α-CD-copolymer complex. Cartoon (right) for the hexagonal-within-lamellar mesomorphic structure of the complex (Lee *et al.*).

insertion device is under construction. The IASW6 with peak magnetic field of 3.1 T, magnet period of 6 cm, and total magnetic length of 96 cm, can provide a photon flux ~$10^{12}$ - $10^{13}$ photons/s in the energy range of 5-23 keV. Taking 0.2 mard radiation fan from the source of a beam divergence of 200 and 392 μrad in the vertical and horizontal directions, respectively, the dedicated SAXS beamline aims at expanding the current SAXS scope in Taiwan, especially in soft matter as well as in nanoparticles, ceramic, and alloys. The monochromator of the SAXS beamline integrates double Si(111) crystals (DCM) and double Mo/$B_4C$ multilayers (DMM) into one cradle for a fast exchange between these two modes. With a collimating mirror and a toroidal focusing mirror (FM) of 1:1 focusing ratio (equal distances between the photon source to FM and FM to detector), this beamline can provide two operation modes of high-*Q* resolution and high flux, respectively, by selectively using the DCM or DMM mode. The SAXS beamline allows energy scan with an energy resolution within 5-10 eV for anomalous SAXS measurements. With a reflecting mirror of special coating to scan the incident angle, grazing incident SAXS for liquid surfaces is possible. Ray tracing simulation result shows that at 8 keV, a high quality beam of small beam size (0.5 mm) and beam divergence (50 μrad) at the detector position, 26.5 m from the photon source, is achievable with a flux of ~$10^{11}$ photons/s for high-Q resolution SAXS measurements. With a maximum sample-to-detector distance of 6 m, the minimum Q achievable will be 0.002 $Å^{-1}$. The flux can be more than one order of magnitude higher when the DMM is used with slightly broadened beam size and beam divergence. The realization of the dedicated BL23A SAXS beam line at NSRRC in 2007 should provide a world-competing SAXS instrument for SAXS-related researches in Taiwan.

In the meanwhile, the BL17B3 small-angle and wide-angle X-ray scattering (SWAXS) instrument is operational since Feb. 2006. Couple improvements on GISAXS and shear device are under ways. A MARCCD165 area detector especially for polymer research will be expected on the instrument at the end of 2006 or the beginning of 2007. The current position sensitive gas proportional area detector will still be used for time-resolved SWAXS measurements and protein solution measurements, of a low scattering intensity, therefore, requires a high accuracy of background measurement. Currently, the 17B3 SWAXS beam time requested exceeds much more than that available. The author will like to thank Drs. Y. J. Shiu, C. M. Wu, S. W. Yeh, W.-T. Chuang, and H.-F. Lee for providing the experimental results in this article.

## Publications


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