An Advanced Instrument for Small- and Wide-angle X-ray Scattering

At the National Synchrotron Radiation Research Center (NSRRC), an advanced small/wide-angle X-ray scattering (SAXS/WAXS) instrument has been installed on the BL23A beamline of online beam position monitors. The corresponding BL23A SWAXS endstation is featured in simultaneous, time-resolved SAXS/WAXS with DSC, shear, temperature jump, or stretching device for polymers and liquid crystals; stopped-flow SAXS as well as general solution SAXS for colloidal particles, proteins, and biomacromolecules for in situ structural changes can be conducted. With the double multilayer monochromator (DMM) mode for a high flux beam of ~ $10^{11}$ photons/s, scattering time resolution can be within a second for structural dynamics studies with polymer crystallization; with the double crystal monochromator (DCM) mode for a beam of an energy resolution of few eVs, anomalous scattering is also available for multiphase nanoparticles, composites, and alloys, containing elements of characteristic X-ray absorptions in the energy region between 5-23 keV. Grazing incidence SAXS/WAXS for polymer, lipid or nanoparticle thin films/monolayers on solid substrates can be performed. With a deflecting mirror for a precise beam incidence on liquid surfaces, GISAXS studies with monolayers or mesostructured thin films in situ formed at the air-liquid interface are realized. The instrument performance is illustrated via SAXS/WAXS measurements covering a wide range of applications.

Small-angle X-ray scattering (SAXS) is increasingly more popular in nanostructure characterization, as illustrated by the quickly multiplied SAXS beamlines in synchrotron radiation facilities worldwide. With a superconducting wiggler source at the beamline 23A of the National Synchrotron Radiation Research Center (NSRRC), having a 1.5 GeV electron storage ring operated at a constant current mode of 300 mA, we recently have installed a dedicated small/wide angle X-ray scattering (SWAXS) instrument located at the BL23A beamline for structural characterization with soft matter and nanoparticles. The performance of the SWAXS instrument (Fig. 1) has been illustrated via several measurements of different classes, including: (1) simultaneous measurements with SAXS, WAXS, and differential scanning calorimetry (DSC) for correlated changes of crystalline structures and nanostructures in polymer crystallization, (2) structural evolution over a large length scale of ~ 250 nm in a supramolecular complex of a diblock copolymer grafted with amphiphilic mesogens, (3) SAXS for polymer blends under in-situ drawing with a tensile stress tester, (4) SAXS and ASAXS for unilamellar lipid vesicles and metalloprotein solutions, (5) anomalous GISAXS for oriented membranes of Br-labeled phosphatidylcholine lipids embedded with peptides, and finally (6) GISAXS for surfactant-templated silicate films in situ formed at the air-water interface.

Fig. 1: An overview of the BL23A SAXS/WAXS instrument.
Located inside the BL23A experimental hutch (10 m in length and 4 m in width) is the SAXS/WAXS instrument comprised of the collimation, sample, and post-sample stages (Fig. 2). The collimation stage consists of a 10-ms beam shutter, two pinhole-slit systems, two beam intensity monitors, two sets of attenuators, a laser alignment system and a rotary disk. All these components are situated on the 1-m long motorized optical table, allowing motion in 6 degrees of freedom (6 DoF); this mechanism provides synchronized tilting of the whole collimation system with the deflected beam in the case of GISAXS measurements for air-liquid interfaces, where several selected incident angles are usually needed.

Following the collimation stage is the 6 DoF motorized sample stage for sample alignments, sample oscillation during measurements, and sample changing. Vacuum-tight sample cells for solid and solution samples of various thicknesses between 1.2 to 5 mm are available for simultaneous SAXS/WAXS measurements; three-way flow cells allow circulation of sample solutions or gas flow for solid samples during time-resolved SAXS/WAXS measurements. For protein solution SAXS, high energy X-rays such as 14 keV are advantageous due to lower X-ray absorption and hence decreased protein radiation damage. A Mettler Toledo FP84 differential scanning calorimeter, a Linkam CSS450 shear stage, a Linkam TST350 tensile stress tester, and a BioLOGIC SFM-400 4-syringe stopped-flow system have been respectively modified for simultaneous SAXS/WAXS measurements.

The post sample stage consists of the WAXS section, vacuum bellows, two-beamstop system, and two area detectors, all situated on a 6 DoF motorized optical table 7 x 4 x 1 m³ (length x width x height) in dimension, allowing for systematic alignment of the whole post-sample section with the X-ray beam. The two-section vacuum bellows provides convenient and continuous changes, under vacuum, in the sample-to-detector (SD) distance from 2.2 to 5.2 m (or 1.7 to 3.2 m, when only one section of the bellows is used).

We have performed several measurements to illustrate the various aspects of the SAXS/WAXS instrument, as described below. With a time resolution of 5 s, the measured SAXS and WAXS spectra concomitantly capture the evolution of nanostructure and crystalline structure of syndiotactic polystyrene (sPS). The SAXS/WAXS/DSC results simultaneously collected over a single sample provide excellent correlations between the development of nano/crystalline structures and the observed thermal events. To capture rapid nanostructural changes with SAXS, both high X-ray flux and fast data collection are indispensable. With the frame-shift mode of MAR165 CCD for sub-second data collection, it is possible to capture structural evolution details in the early stage of polymer crystallization with the new SAXS instrument of 2 x 10¹¹ photons/s under DMM mode. Also, the spatial resolving power of the SAXS/WAXS instrument critically depends on the minimum q value available. A test of the instrument q-minimum using a supramolecular complex of a

![Fig. 2: A schematic drawing of the BL23A SAXS/WAXS instrument: beam intensity monitors (BM1 and BM2), attenuators (ATT1 and ATT2), pinhole-slit P1 and P2, and a rotary disk containing a photodiode detector and 9 standard metal foils for beam energy calibration. WAXS-V and WAXS-H are linear gas detectors.](image-url)
diblock copolymer grafted with amphiphilic mesogens polystyrene-block-poly(4-vinylpyridine) can evaluate a large length scale of ~ 250 nm in a supramolecular complex of a diblock copolymer grafted with amphiphilic mesogens. Furthermore, the BL23A SAXS/WAXS instrument can provide a high-energy beam (e.g. 14 keV) to reduce X-ray absorption for protein solution SAXS. And a wide X-ray energy range (5-23 keV) is available for anomalous SAXS (ASAXS) which has been shown to be particularly useful in revealing the composition and/or distribution of heavy atoms (ions) enclosed in metallo-proteins or lipid membranes.

To probe structural characteristics of oriented thin films on solid substrate, it is necessary to perform SAXS in grazing incidence geometry. Equipped with the pin-hole-slit collimation system for a flexible choice of beam size and the two independent beamstops respectively for blocking the direct beam and the specular beam from substrate, the BL23 SAXS/WAXS instrument can be easily converted to the GISAXS mode from the transmission SAXS mode. The SWAXS instrument in BL23A is also capable of performing anomalous GISAXS. Recently, a sophisticated methodology with anomalous GISAXS has been developed to resolve the pore phase structure of peptide-lipid mixtures; in which energy scan near (and below) the absorption edge of the labeling atoms of the lipids were used to reveal the phase information of the small-angle diffractions from the mixture via the intensity changes of the diffraction peaks with beam energy.

In the BL23A SWAXS endstation, we have especially designed a plane mirror which is installed after FM to provide a possibility to bend the beam downwards for GISAXS on liquid surfaces. Air-water interface connects two highly unsymmetrical environments, which is advantageous in orientating amphiphilic molecules to form highly ordered films of small surface roughness. Probing in-plane as well as normal-to-plane structures of such films grown on the gravity levelled air-water interface of atomic smoothness, however, requires a deflectable beam for a selectable incident angle. With a Si-based plane mirror installed to the BL23A SAXS/WAXS beamline, the beam incident angle on water surface can be freely tuned to the critical angle for total reflection for improved sensitivity to nanostructures at/near the air-water interface. We demonstrate below such a GISAXS application for the growth of a surfactant-templated silicate film in-situ formed at the air-water interface.

The sample solution was prepared by adding tetraethyl orthosilicate (TEOS) into a surfactant solution of cetyltrimethylammooium bromide (CTAB) of pH < 1, with molar composition H₂O : HCl : CTAB : TEOS = 100 : 2 : 0.11 : 0.7. The mixture was filled into a Teflon trough 100 x 100 mm² in area and 0.7 mm in depth, which was inserted in an Al box with Kapton windows for GISAXS at ambient temperature (298 K). GISAXS images (Fig. 3) were collected with an imaging rate of 2 frames per min, using a 10 keV beam and a grazing incident angle of 0.15°. Within the first 1200 s, the GISAXS patterns were relatively featureless (Fig. 3(a)). At the end of this induction stage, the first faint lamellar peak appeared, followed by emergence of second- and third-order lamellar peaks. These peaks, signifying the formation of lamellae at the air-water interface, intensified with time and became eminent around t = 2820 s (Fig. 3(b)). At t = 4620 s, two side peaks by the meridian lamellar peaks were clearly observable (Fig. 3(c)), implying a transition of the layer structure to a hexagonal structure in the surface film. Presumably, the polymerization of TESO initiated an in-plane rearrangement for the 3-D ordered structure. The GISAXS image taken at the end of the 2-hr observation exhibits single-crystal-like reflections (Fig. 3(d)), indicating a surface film of a highly ordered structure of hexagonal packing. The detailed formation process thus recorded greatly facili-

![Fig. 3: Representative GISAXS 2-D images taken at (a) 0 s, (b) 2820 s, (c) 4620 s, and (d) 6540 s, of the formation of a free standing CTAB-silicate film of hexagonally packed channel structure at the air-water interface. Note the in situ lamellar-to-hexagonal transformation revealed by (b) and (c).](image-url)
tates the understanding of the formation mechanism of the CTAB-silicate film at the air-water interface.

It would not be difficult to extend the study of the air-water interface to liquid-liquid interfaces with the SAXS/WAXS instrument, as there are high energy X-rays available up to 23 keV for adequate penetration of the beam through the top fluid phase. For instance, with a beam of 22 keV and an incident angle of 0.15°, the beam can penetrate a thick hexane film (with an X-ray path length up to 25 mm) on top of water substrate and reach the hexane-water interface with >75% residual beam intensity.

With the illustrated performance, the BL23A SAXS/WAXS instrument at NSRRC proves to be versatile for a wide range of applications in structural characterization of soft matter and nanomaterials, covering a length scale from 0.1 to 300 nm and a time resolution down to 100 ms. The tunable beam energy from 5 to 23 keV renders anomalous SAXS and GISAXS feasible for multiphase/hierarchical systems containing various heavy atoms such as core-shell bimetallic nanoparticles and semiconductor quantum dots, metalloproteins, and metal-labeled lipid/peptide complexes. In particular, the deflectable beam design allows for GISAXS characterization of air-liquid/liquid-liquid interfaces. Measurements are greatly facilitated by the ease and stability in beam energy change as well as the fast switch between the two monochromators of DCM and DMM for either high energy resolution or high flux. The large vacuum bellows provides convenient and continuous changes in the sample-to-detector distance under vacuum. The rigorous and efficient data reduction routines provide support to the processing of a large quantity of SAXS/WAXS data collected from time-resolved measurements. Currently, the instrument is being used for a variety of projects including ongoing studies for the systems mentioned above.

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**References**

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