SAXS/WAXS Capability and Absolute Intensity Measurement Study at the SAXS Beamlne of the Siam Photon Laboratory

Rarm Phinjaroenphan$^1$, Siriwat Soontaranon$^2$, Prae Chirawatkul$^2$, Jitrin Chaiprapa$^2$, Wutthikrai Busayaporn$^2$, Surachai Pongampai$^2$, Supanan Lapboonreung$^2$ and Supagorn Rugmai$^{1,2}$

$^1$ School of Physics, Suranaree University of Technology, Muang, Nakhon Ratchasima 30000, Thailand
$^2$ Synchrotron Light Research Institute, Muang, Nakhon Ratchasima 30000, Thailand
E-mail: supagorn@slri.or.th

Abstract. A Small Angle X-ray Scattering (SAXS) beamline has been constructed at the Siam Photon Laboratory of the Synchrotron Light Research Institute (SLRI), Thailand. The beamline was commissioned and opened for users in March 2011. In order to maximize the photon flux, a Double Multilayer Monochromator was adopted to monochromatize synchrotron x-rays within the energy range of 6-9 keV. The experimental station is equipped with a CCD detector for SAXS measurements and an Image Plate for wide angle x-ray scattering (WAXS) measurements. Apparatus for in-situ measurements have been developed to enable studies of nano structural changes during temperature and tensile variation. Capability for scattering measurements in absolute unit has been investigated. This work reports the current status of the beamline and results from dispersed Au nanoparticles measurements.

1. Introduction
SAXS [1, 2] is an important tool for nano scale material characterizations. The information obtained from the SAXS data includes the nano scale structural orderings and, for dilute systems, the sizes and shapes of nanoparticles. Moreover, if the measured intensity is calibrated to the absolute unit (cm$^{-1}$), additional information such as specific surface areas and molecular weights can be determined [2, 3] and data taken from different instruments can be quantitatively compared [4]. Because the SAXS technique allows structural characterization without the requirement for crystallinity, it has been widely used in polymer science and biology [5, 6]. The technique is also useful for materials science [7] including the growing field of nanomaterials such as studies of magnetic nanoparticles [8] and semiconductor thin films [9].

2. SAXS beamline at the SLRI
The setup of the beamline has previously been described [10]. For the experimental station, depending on the chosen sample-to-detector distance, the SAXS measurement using the CCD camera offers the scattering vector, $q$, range from 0.1 to 2 nm$^{-1}$ and the WAXS measurement using the image plate offers the $q$ range from 1.5 to 40 nm$^{-1}$. The availability of the SAXS and WAXS techniques from the two detectors provides an opportunity for structural information
Figure 1. The WAXS profiles of normal rice starch and potato starch. The A-type structure of the normal rice starch and B-type structure of the potato starch could be identified.

Figure 2. The SAXS profiles of normal rice starch and potato starch. The d-spacings for the lamellar structure of 9.17 nm for the normal rice starch and 9.23 nm for the potato starch were determined.

... to be collected in two length scales. The various applications utilizing these complementary information include the study of molecular and lamellar structures of starch during gelatinization [11] or the study of nano and atomic scale orderings during a nucleation process in polymer crystallization [12]. An example of SAXS and WAXS measurements performed at the beamline is shown in figures 1 and 2. For this experiment, structures of several types of starch were probed. Both the SAXS and WAXS measurements were performed using the exposure time of 240 s and the q ranges of 0.16 to 2.07 nm\(^{-1}\) for the SAXS measurements and 1.80 to 19.81 nm\(^{-1}\) for the WAXS measurements. From figure 1, the Bragg’s peaks corresponding to the A-type structure of the normal rice starch and those corresponding to the B-type structure of the potato starch [13] can be identified. The d-spacing values of 9.17 and 9.23 nm for the normal rice starch and the potato starch, respectively, obtained from the SAXS profiles in figure 2 can give quantitative information about the starch’s lamellar structures and relate to its amylose and amylopectin contents and defects in the structures.

At this beamline, samples can be measured in a transmission geometry. Holders for powder and liquid samples are available. Moreover, the experimental station can be mounted with a heating/cooling stage with the temperature range from -196 to 600 °C. A tensile stage with the maximum applied force of 200 N and a heating/cooling capability in the temperature range from -196 to 350 °C can also be mounted.

3. Absolute intensity measurements of Au nanoparticles
The dispersed Au nanoparticles are commercially available from Corpuscular. Two samples with the particle diameters of 30 and 60 nm dispersed in water were measured at room temperature. The measurements of water were also made at room temperature for the background subtraction and the absolute intensity calibration. All the measurements were performed with the x-ray energy of 8 keV, the exposure time of 100 s and the q range from 0.10 to 1.09 nm\(^{-1}\).

The scattering profiles of the samples were normalized and corrected for background scattering using the in-house developed software S AXSIT [14]. The profiles were then calibrated to an absolute intensity scale using water as a primary standard [15, 16]. As the differential scattering cross-section, \(d\Sigma/d\Omega(q)\), of water at \(q = 0\) is solely dependent on its isothermal compressibility [17], the \(d\Sigma/d\Omega_{\text{water}}(0)\) can be calculated and the value is \(1.633 \times 10^{-2}\) cm\(^{-1}\). Thus the absolute intensity of Au nanoparticles was determined from

\[
\frac{d\Sigma}{d\Omega}(q) = CF \times \frac{I_q(q)}{d_s t_s},
\]
where $I_s(q)$, $d_s$ and $t_s$ are the measured intensity, the thickness and the transmission of the sample, respectively, and $CF = \left( \frac{dS}{dt} \right)_{water} (0) \frac{d_{water} \cdot t_{water}}{I_{water}(q)}$ is the calibration factor.

The $I_{water}(q)$ used to calculate $CF$ was an average of the mean values of $I_{water}(q)$ functions from each water measurement. The obtained $I_{water}(q)$ are shown as a dashed line in figure 3 and the value of $CF$ is $1.83(7) \times 10^7$. The information readily available from the data is the radius of gyration, $R_g$, and the Porod’s constant, $K$. By extrapolating the data to the low $q$ region using the Guinier approximation and to the high $q$ region using the Porod’s law, the Porod’s invariant, $Q_p$, [3] were determined from the data. The obtained values for $R_g$, $K$ and $Q_p$ are summarized in table 1. For the 60 nm diameter sample, the value of $R_g$ could not be estimated as the deviation from the Guinier’s approximation is large when $q_1R_g$, where $q_1$ is the maximum $q$ value used in the approximation, is large [2].

Because the form factor of the Au nanoparticles is known, a model of a dispersed spherical nanoparticles with a Gaussian distributed radii was built and refined to the experimental data using SASFIT [18]. From the model, the mean radii and the corresponding standard deviation of the distribution are 14(2) nm and 1.531(1) nm for the 30 nm diameter sample and 28(3) nm and 2.483(2) nm for the 60 nm diameter sample. The data and the fit for the 60 nm diameter sample are shown in figure 4. The values of $K$ and $Q_p$ determined from the fits are similar to those obtained from the data as shown in table 1. Also shown in table 1 are the $R_g$ obtained from the model which, for a spherical particle, are related to the mean radius of the sphere, $R$, by $R_g = \sqrt{3/5}R$. As can be seen from the table, for the 30 nm diameter sample, the value of $R_g$ obtained from the data is similar to that obtained from the model.

If the scattering intensity is in absolute unit, the specific surface area, $S_v$, can be calculated from $K$ [3]. If the form factor and its distribution is known, $S_v$ can also be calculated from a model. For this work, the values of $S_v$ determined from the data and those determined from the model are shown in table 1. As seen from the table, the values obtained from the model and from the data are 22% and 13% difference for the 30 and 60 nm diameter samples, respectively. It has been shown that absolute unit data can be used to determine $S_v$ regardless of the knowledge of the form factor. And, for the current data, the values of $S_v$ were obtained with around 20% errors. Moreover, if the density of the solution is known the molecular weight of the dispersed particles can be determined from the $I(0)$ values in the absolute unit [15].
Table 1. Integral parameters of Au nanoparticles obtained from the measured data in the absolute unit and those obtained from the model.

|          | $R_g$ (nm) | $K$ (cm$^{-5}$) | $Q_p$ (cm$^{-4}$) | $S_v$ (cm$^{-1}$) |
|----------|------------|-----------------|-------------------|-------------------|
| data (30 nm) | 10.8(1)    | 2.02(5) × 10$^{24}$ | 3.78(2) × 10$^{18}$ | 0.216(5) |
| model (30 nm) | 11(1)      | 2.59(3) × 10$^{24}$ | 3.576 × 10$^{18}$  | 0.277(4) |
| data (60 nm)  | -          | 9.4(2) × 10$^{23}$ | 2.044 × 10$^{18}$  | 0.100(2) |
| model (60 nm) | 22(2)      | 8.31(6) × 10$^{23}$ | 2.37(5) × 10$^{18}$ | 0.0887(7) |

4. Conclusion
The current status of the SAXS beamline at the SLRI is described. The results from the two detectors for SAXS and WAXS measurements are shown. Water was used as a primary standard to calibrate the scattering profiles of dispersed Au nanoparticles to an absolute intensity scale. The $S_v$ values obtained from the absolute unit data are comparable to those obtained from the model. It has been shown that absolute intensity measurement data can be collected at the beamline and $S_v$ values can be determined with around 20% error.

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