THA APPLICATION OF THE SMALL-ANGLE X-RAY SCATTERING BEAMLINE IN THE STRUCTURAL ANALYSIS OF THE POLYMERS *

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Abstract

Small-angle X-ray Scattering (SAXS) is a key technique for analyzing nanometer-scale structures in polymers using synchrotron radiation. In this experiment, we explored the 4C SAXS II Beamline at the Pohang Light Source II (PLS-II), which is optimized for the analysis of polymers, nanomaterials, and biomacromolecules. The beamline consists of a front end with an undulator, an optical hutch for beam shaping, and an experimental hutch where samples are treated. Liquid samples were prepared and measured in both static and flow modes, with background subtraction using reference solutions. We also observed the use of refractive index and light scattering detectors for preparing sample to be measured. This research highlighted how accelerator tools like SAXS contribute in diverse research fields.

INTRODUCTION

A synchrotron light source is utilized to analyze the material structure or the fine processing system by means of the light radiated when the electron in the synchrotron deflects its direction. The synchrotron is made up of a linear accelerator with an electron gun, the storage ring as a radiation source, and the beamline where a variety of experiments are conducted. In the storage ring, multiple beamlines are outstretched to the hutch according to the purpose of the experiment. We, especially, focus on the Small-angle X-ray scattering (SAXS), a universal technique to study the structure of various noncrystalline systems on nanometer scale [1]. When X-rays are irradiated on a target material, they are scattered as they pass through the material, and atoms interfere with one another depending on their relative positions. The location and degree of mutual interference are determined by the type and position of atoms, so information about electron distribution within the material can be obtained from the annihilation or constructive interference of the scattered X-rays. SAXS is becoming a standard tool for structural characterization under carefully controlled conditions, such as pH, ionic strength, chemical reagents, humidity, electric or magnetic field, pressure, and temperature [2].

In this research, we visited the Pohang Light Source II (PLS-II) 4C SAXS II Beamline and looked around the apparatus in the experiment hutch. This line is specialized for the interpretation of the complex structures like polymer, nanomaterials, and biological macromolecules (protein, DNA, and RNA). Accordingly, we made a tour inspection of the specimen preparation facilities followed by the hutch. A sample is, then, analyzed in the experimental stage and this process is divided into the background setting and the actual sample observation. The sample is dissolved in the solvent as a liquid specimen, therby the X-ray diffraction profile image is acquired.

This experiment allowed us to learn the overall layout of the beamline facilities and sample analysis process. In terms of the purpose of the accelerator, how it is applied to the diverse experiments has significant meaning in the development and design of the accelerator. Synchrotron radiation has a wide wavelength range, from low-energy visible light to high-energy X-rays, and can be selected and used according to the experimental purpose. The significance of this study is that we learned how SAXS can observe samples and confirmed that synchrotron radiation can be directly helpful in other scientific fields.

SMALL-ANGLE X-RAY SCATTERING

SAXS is a technique for analyzing the nanometer-sized structure of a sample by irradiating the sample with X-rays and measuring the intensity of the X-rays scattered at small scattering angles of a few milliradians. SAXS is based on the intensity of the scattered X-ray, which is expressed as I, with respect to the scattering angle. The intensities are a summed convolution of the angle-dependent interference of the squared scattering amplitudes of X-ray spherical waves arising from all atoms illuminated within an incident beam. The intensity pattern can be written as follows:

$$\boldsymbol{q} = 4\pi sin\theta/\lambda \tag{1}$$

where 2θ is the scattering angle and λ is the radiation wavelength. The scattering angle is inversely proportional to the probe length of the interior sample, d.

$$d = 2\pi/q \tag{2}$$

It means that the scattering intensities are relate to the structures of the sample. When X-rays encounter nonuniform points within a sample, scattering occurs, and X-rays scattered at small angles are more sensitive to the shape, size, and aggregate structure of the sample than to the overall structure of the sample. Parameters such as the average size and molecular distribution of the sample can be inferred through the measured scattering intensity distribution.

An incident beam k_i travels to the sample and is scattered according to the sample structure in which the small proportion of the beam interacts with atoms to generate scattering events k_s. Then, a detecter installed behind the sample can capture the scattering pattern as the intensity vector, q. The intensity and scattering angle information of the scattered X-rays are recorded as position coordinates (x, y). A smaller

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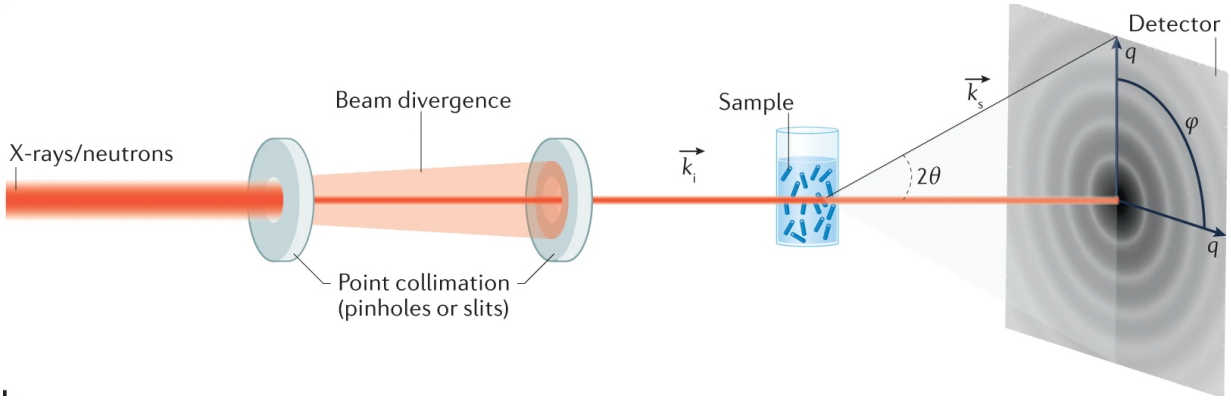

Figure 1: A layout of the SAXS experiment setup.

scattering angle is recorded closer to the center of the detector, and a larger angle is recorded further out. The collected data is stored in the form of 2D images, and the detector plays a key role in obtaining quantitative information about the structure inside the sample by accurately recording the distribution of X-ray scattered intensities [3].

BEAMLINE LAYOUT

At the PLS II, synchrotron radiation spreads out approximately 0.2 mrad when the path changes from the bending magnets located at each 10° angle in the storage ring with a circumference of about 280 m. The undulator, which is the linear magnetic structures, are used to improve the properties of the radiation produced at the front end. Then, the radiation is collimated at the optical hutch before reaching the experimental hutch where the sample is installed.

Front End

The nature of the radiation is determined by the type of magnet such as the bending magnet or the wiggler. In this beamline, the undulator is equipped to produce the X-ray beam. In general, the bending magnet produces the light proportionally to the number of electrons, and it is mainly installed in the storage ring. The zigzag motion in addition to the bending is of importance in determining the intensity of the radiation. The undulator has the following relationship among the number of radiated photons, that of electrons in the beam, and that of undulator periods.

$$N_f \sim N_e \cdot N \tag{3}$$

In this way, the radiation from the undulator passes through maintenance facilities such as beam stoppers and beam diagnostic devices and heads to the hutch.

Optical Hutch

The optical hutch, where where scientists can adjust the light to their experiment's specifications, is another important component to deliver the radiation to the experimental stage. The beam position is controlled by two reflecting mirrors and the beam path is slightly bent, allowing it to head toward the collimator. As additional devices, copper screens and tungsten wire monitors for beam intensity and position monitoring are placed in the optics hutch. However, it has relatively limited space due to its characteristics of the middle stage. Accordingly, a separate diagnostic beam hutch is installed, in which precise optical equipments are assembled [4].

Experimental Hutch

Figure 2: Sample measurements are accomplished inside the hutch. The hard X-rays used in this beamline have high energy and can penetrate samples albeit the sample is placed in the atmosphere. However, due to radiation exposure issues, experiments are conducted inside a shielded hutch.

This hutch is for the main stage where the sample measurement is conducted. The detector collects the imformation of the scattered X-ray about 2 m behind the sample stage. It is enclosed in an experimental hutch and all components can be remotely controlled. Attenuators embracing various aluminum foil thicknesses are also located in front of the vacuum chamber to control the photon flux on the sample. A beam stopper is installed at the end of the vacuum chamber to measure the transmitted X-ray beam intensity, based on the photocurrent transferred from the beam stopper relative to the intensity of the transmitted X-ray beam [5].

SAMPLE MEASUREMENT

Beam users can process a sample into a homogeneous liquid form, place it on the measurement stage, turn on the beam, and obtain a scattered image profile, which can be

viewed in real time outside the hutch. Before analyzing the sample, its processing plays a crucial role in affecting the quality of the profile. Thus, one has to verify the generic condition of the sample before the sample is exposed to the SAXS beam. For instance, it is prohibited to let the bubble exist in the solution because it disturbs and disperses the beam, making noise on the data. Typically, the sample is filtered to remove dust or large particles, and the concentration is adjusted to a measurable level for scattering intensity. A blank sample is also prepared so that measurements can be made under the same conditions, which serves as a reference for removing background scattering. Typically, a refractive index detector is used to determine the content of a substance by the difference in refractive index according to the concentration of the sample. A light scattering detector is used to measure the molar mass and size of macromolecules and nanoparticles present in a solution. Information about the molecular weight and size distribution of the sample can be obtained through the intensity of the scattered light.

Figure 3: Sample is processed by a series of gauging device.

Regardless of the sample quality, the reference background sample is required to be measured by SAXS beam. A solution without the sample has its unique scattering and structure, which is also observed in the sample solution and has to be canceled out. In order to distinguish the background information from the sample dissolved in the solution, the sample and the reference solution is treated in the same duration and condition. This process allows for the subtraction of non-sample-related signals such as optical and electrical noise from sample light scattering during sample measurement, thereby ensuring the accuracy and reliability of measurement results.

Figure 4: Sample stage for solution adsorption.

The sample measurement is divided into two versions: static mode and flow mode. In static mode, the stage keeps the solution stationary during exposure to the beam, providing a simple setup for stable samples. On the other hand, flow mode allows continuous sample circulation, reducing radiation damage and improving measurement reproducibility for sensitive solutions. A very small amount of sample solution is injected into the sample stage through a tube, and scattering data can be obtained when the beam is irradiated. Through these measurements, research results have been achieved in various fields, such as obtaining modeling images of biomacromolecules and analyzing the molecular orientation of the organic solar cell at this beamline.

SUMMARY

This report presents a practical study of the SAXS technique in the field. It enables the structural analysis of various matters like biomolecules at the nanoscale by measuring X-ray scattering at small angles. The beamline has a front-end radiation source using an undulator, an optical hutch with beam reflectors and diagnostic tools, and an experimental hutch equipped with a beam scattering detector and sample stage. Sample preparation included filtration, concentration adjustment, and reference measurement to minimize background noise. The measurements were conducted in both static and flow modes, depending on sample sensitivity and stability. Supporting detectors such as refractive index and light scattering detectors provided complementary information on molecular weight and distribution. This experiment demonstrated how SAXS systems combine advanced beamline optics, sample handling, and data analysis to enable precise structural investigation. Going forward, further development in unmanned control using robot arm and real-time data processing could enhance the accessibility and throughput of SAXS for future scientific applications.

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