



Nanostructure Analysis of Polymer Assembly on Water Surface by X-ray Reflectometry

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Abstract X-ray reflectivity (XR) is an extremely powerful technique to study the fine structure of surface and interface in the order of angstrom. In this study, we have performed systematic XR measurements for monolayers on water surface. The nanostructures of various monolayers were precisely determined, and their changes by surface pressure and photoisomerization were clearly detected. The structure of lipid monolayer and DNA complex at air-water interface was also evaluated.

Introduction

X-ray and neutron reflectivity (XR, NR) measurements have been becoming one of the popular techniques for the study of surfaces, interfaces, and thin film structure. Extensive works have been done especially for polymer thin films under both specular and off-specular conditions, and important and novel aspects have been reported for extremely thin films, and microphase separation systems. As to monolayers on water surface, XR and NR have been also applied for polymer monolayer [1], lipids and its biological complex [2], two dimensional "jelly-fish-like" micelle on water surface [3], and a micelle layer in water subphase under surfactant monolayer at water surface [4]. However, a fatal disadvantage of reflectivity measurement has been so far very limited facility and equipment by which XR or NR measurement can be performed for liquid surface.

We have recently constructed a compact air-water interface X-ray reflectometer for laboratory use [5,6]. This apparatus enables us to detect the *in situ* structural change of samples as a function of surface pressure. The purpose of this paper is to describe the nanostructure analysis of polymer assembly on water surface by using our X-ray reflectometer.

Experimental

The apparatus was constructed by modification of RINT-TTR theta-theta goniometer (Rigaku corporation, Tokyo, Japan). This is so-called "butterfly" type goniometer, and we put some special devices to this original system to make it the reflectivity apparatus. The X-ray generator, which is mounted on one of the goniometer arms, is a rotating anode type with Cu target (60kV, 300mA). A channel-cut Ge single crystal (Ge(111), two bounds) is used as a monochromator. The divergence and receiving slits has 50 micrometer width. At the sample position, a Langmuir-Blodgett trough, which was specially designed only for this apparatus (USI System, Fukuoka, Japan) was attached to change the surface pressure of monolayers. The advantage of this apparatus is that the *in situ* measurement of the monolayer at the air-water interface is possible since the sample stage does not move and is kept horizontal during measurement. All measurements were performed under specular condition. The details of the apparatus and data treatment have been fully explained in the previous papers [5,7].

Results and Discussion

(1) Lipid Monolayer on Water Surface

XR profiles of distearoylphosphatidylcholine (DSPC) monolayer on water surface shows clear fringes. The very large dynamic range of almost 8 decades should be noted since this is as good as that by synchrotron source. The position of the fringe shifted towards lower angles with the increase of surface pressure, indicating the increase of thickness of monolayer. This is reasonable since the lipid molecules in monolayer stand up and are highly aligned with increasing surface pressure. The total thickness of monolayer can be estimated to be 25.5, 25.5, 26.4, and 27.1 Å for surface pressures of 10, 20, 30, and 40 mN/m, respectively. Thus, the extremely small change of monolayer thickness could be precisely evaluated. Similar measurements and analysis were performed also for dibehenoylphosphatidylcholine (DBPC).

(2) Amphiphilic Polymer Monolayer on Water Surface

X-ray reflectivity (XR) measurements were carried out for the spread monolayers of two kinds of amphiphilic block polymers on water surface. In the case of poly(α -methylstyrene)-*block*-poly(*N*-alkyl-4-vinylpyridinium iodide) (alkyl = methyl or decyl), one or two broad Kiessig fringes were observed at higher surface pressure. These fringes became clearer and their positions shifted towards lower angles with increasing the surface pressure [7]. The XR profiles of spread monolayer of poly(1,1-diethylsilabutane)-*block*-poly(2-hydroxyethyl methacrylate) (poly(SB-*b*-HEMA)) on the water surface showed clear Kiessig fringes up to the third order, indicating the smooth-faced monolayer with high uniformity of thickness. The fitting of XR profiles with the two-layer model revealed that the upper layer is formed by the melt of the SB chains and that the lower layer consists of hydrated HEMA chains [8].

(3) Photoisomerization of Polymer Monolayer on Water Surface

XR measurements were performed for monolayers of poly(vinyl alcohol) containing a photochromic azobenzene side chain (6Az10-PVA) [9] on water surface. Since this polymer has azobenzene unit, it shows *cis-trans* isomerization by UV-VIS irradiation (350nm and 440nm). Fig. 1 shows the XR profiles for *cis*- (a) and *trans*- (b) form monolayers of 6Az10-PVA at surface pressure 4mN/m. The Kiessig fringe was clearly observed at the reflection angle θ of about 2 degree. From the comparison between XR profiles for *cis*- and *trans*-form, small but significant difference can be confirmed for θ range from 2 to 3 degree. The solid lines in Fig. 1 are the best fit curves by model fitting, which gave us a structural change as schematically shown in the right of the figure. Since *trans*-form has smaller area per molecule than *cis*-form, the same surface pressure means denser packing of molecules for *trans*-form. Reflecting this situation, the thickness of hydrophobic part (6Az10) is larger for *trans*-form (27.5 Å) than for *cis*-form (24.0 Å). For hydrophilic part (PVA) under water, the similar trend is observed (4.0 and 2.1 Å). Under higher surface pressure at 11mN/m, the same change for *cis-trans* isomerization was observed. However, the thickness changes of both parts were smaller than those at 4 mN/m because of closer packing of side chain. To our knowledge, this is the first *in situ* observation of photoisomerization of monolayer on water surface [10].

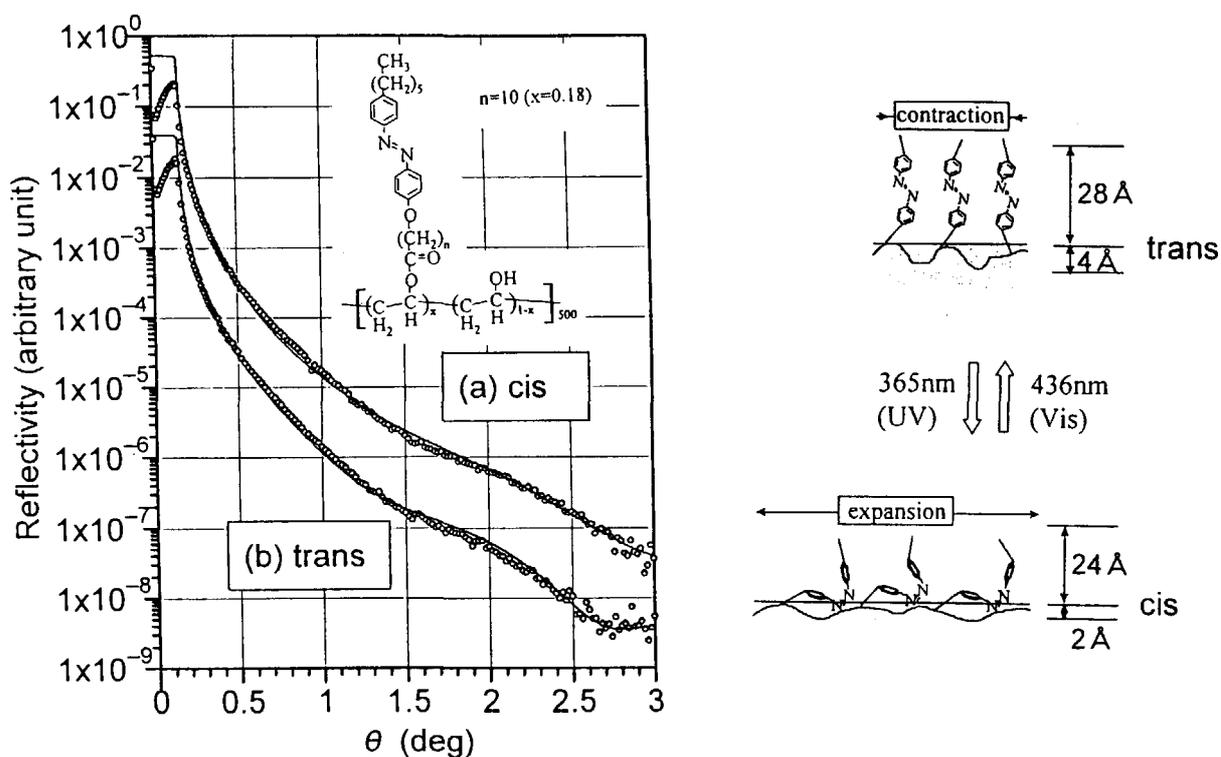


Fig. 1. XR profiles of 6Az10-PVA monolayer on water surface in *cis*- and *trans*-form. By model fitting, the structural change was evaluated as is shown in the right side.

(4) Lipid Monolayer - Biopolymer Complex

The fine structure of DNA-Lipid monolayer complex, which is interesting from the points of view of cell-biopolymer interaction and construction of supramolecular assembly [11], was directly observed by XR technique. A cationic lipid, dimethyldioctadecylammonium bromide and Calf thymous DNA were used. XR profiles for the complex on water surface show the broad Kiessig fringes at about 1 and 2-2.5 degree of the reflection angles. The position of Kiessig fringe moved towards lower reflection angles, indicating the increase of thickness with increasing surface pressure. From the fitting procedure, the three layer model of lipid-DNA (1)-DNA(2) was obtained. This observation can be attributed to the change of molecular arrangement of lipid molecule. The lipid molecules arrange on water surface with some tilting angle which depends on surface pressure. Under the water, DNA molecules are adsorbed to the lipid monolayer to form polyion complex by electrostatic force. The first layer of DNA has thickness of about 20 Å which is comparable to the diameter of cylindrical DNA molecule. Hence the 1st layer can be thought to be DNA layer adsorbed to lipid layer in side-on manner. The thickness of the second layer is about 40 Å. It is obviously hard that the second negatively charged DNA adsorbs on also negatively charged first DNA layer. Therefore, this seems to indicate that the DNA molecules do not adsorb to lipid layer in fully stretched conformation in side-on manner, but have flexible conformation like a wavy form, which results in totally about 40 Å DNA layer under lipid monolayer. By the density obtained by fitting, the volume fraction of DNA in "first layer" was calculated to be ca.70 vol.% and for "second layer" to be ca.30 vol.% [12].

Conclusions

Direct *in situ* evaluation of fine structure of monolayers on water surface has become possible by our XR instrument. It gives us nanoscale structural change of polymer assembly such as lipid monolayer, polymer monolayer and lipid monolayer-biopolymer complex. The XR data obtained provide a lot of highly precise structural parameters for monolayer on water surface. These observations strongly support the importance of *in situ* experiments.

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