

Total reflection and SAXS studies on multilayers of amphiphilic block copolymer

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Introduction

We have reported the nano-scale ordered structure change of amphiphilic di-block copolymers consisted of hydrophilic poly(ethylene oxide) (PEO) and hydrophobic poly(methacrylate) derivatives PMA(Az) containing liquid crystalline azobenzene unit as an ester, PEO_m-b-PMA(Az)_n, by blend [1,2]. The surface structure of Langmuir-Blodgett (LB) membrane of PEO_m-b-PMA(Az)_n was also investigated by the total X-ray reflectivity (TXR), the grazing incidence X-ray analysis (GISAXS) and SAXS [3]. In this study, LB films of PEO₄₀-b-PMA(Az)₃₉ with various layers were investigated by SAXS and TXR measurements.

Experiments

Materials

LB membranes of PEO₄₀-b-PMA(Az)₃₉ with various layers from 2 to 10 used through experiments were prepared at 24 mNm⁻¹, which corresponded to two-dimensional solid state, using surface pressure vs. surface area (π -A) curve measurement

Methods

The SAXS and TXR measurements [4] were performed by SAXS optics at BL-10C, PF, KEK. The wavelength of X-ray and the measurement range of scattering vector were 0.1488 nm and $0.8 \text{ nm}^{-1} < q (=4\pi\sin\theta/\lambda) < 4.5 \text{ nm}^{-1}$, respectively. The incident angle of X-ray was 0.5°.

Results

Total X-ray reflectivity

SAXS profiles of amphiphilic di-block copolymer PEO₄₀-b-PMA(Az)₃₉ LB films with various layers were shown in Fig. 1.

The oscillating peaks shown in Fig. 1 indicated that PEO₄₀-b-PMA(Az)₃₉ LB films had the flat surfaces at each layers and the interface between LB film and substrate. The thickness of LB films obtained by TXR profiles were 18.4, 23.1, 29.9, 42.7, 55.2 and 67.9 nm for 2, 3, 4, 6, 10 and 20 layers, respectively. Two types of relationship between the total thickness and layer numbers below and above 8 layers indicated that the density of LB layers was influenced by layer number. Comparing with the thickness of monolayer, the thickness of LB membranes lower than 8 layers was higher than the expected value, in other words, the density of each layers was lower than those of monolayer and LB membranes over 8 layers.

Small Angle X-ray Scattering

The SAXS profiles of LB membrane consisted of 6 layers showed diffraction peaks of (001) plane in addition to the oscillated refractivity. The space distance of lamellar ordering in 6-layers LB membrane was 3.2 nm from the diffraction peaks corresponding to (001) plane. The 10-layers LB membrane showed two diffraction peaks corresponding to (001) and (002) plane, the space distance of lamellar ordering of 3.2 nm. With increasing layer number, the order of LB membranes increased. The SAXS diffraction peak corresponding to the stacked layers was required the ordered structure at least 6 layers.

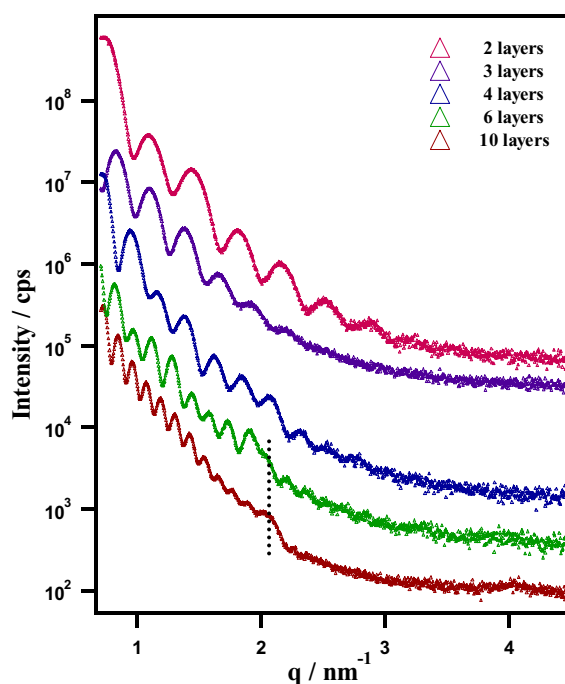


Fig. 1 SAXS profiles of amphiphilic di-block copolymer PEO₄₀-b-PMA(Az)₃₉ Langmuir-Blodgett films with various layers.

References

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