# Reflectometric Investigation of Hybrid Langmuir Films Consisting of a Perfluorinated Fatty Acid and a Block Copolymer with Hydrophobic and Perfluoroalkyl Side Chains

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Controlling morphology of a thin film is indispensable for optimizing physical characters such as wetting and tribology of the film. A block copolymer, poly (3,5-bis(3,5-bis(benzyloxy) -benzyloxy)benzyl methacrylate-random-methacrylic acid)-block-poly(2-perfluorooctylethyl acrylate) (M2den3) form spherical micelles in solutions.[1)] However, its Langmuir film at air/water interface displays unique morphology of the strip-like aggregates, because the polymer consists of hydrophobic and solvophobic side chains.[2)] If an amphiphile familiar to both polymer and water is mixed the polymer, the modification of the film morphology can be expected. In the present work, hybrid Langmuir films of a M2den3 and a perfluorooctadecanoic acid at different mixing ratios were investigated by neutron reflectometry, and the structures of the hybrid films were examined.

At air/water interface, a perfluorooctadecanoic acid arranges with the molecular orientation, where hydrophilic carboxylic acid moiety anchors in water and alkyl chain moiety locates at air phase owing to its solvohobicity.[3)] Then the perfluorinated block in M2den3 is expected to localize in the perfluolinated alkyl chain domain of fatty acids. Thus, the hybrid Langmuir films should consist of three layers, that is, layers of hydrophobic (dendron), solvophobic (perfluorinated) and hydrophilic (carboxylic acid) moieties, as inserted in Fig 1.

Neutron reflectivity measurement was carried out on an ARISA of KEK in Tsukuba, Japan. Hybrid Langmuir monolayers prepared at air/$D_2O$ interface was compressed up to a surface pressure of 15 mN/m and used for the measurement. Based on the Fresnel equation and the five layer (including air and water layers) model, the carve fitting of calculated one with observed one was carried out, and the optimum set of the parameters was determined. Depth – scattering length density (SLD) profile at a mixing ratio 4 of fatty acid to M2den3, which was illustrated from the parameters at optimum condition, is shown in Figure 1. It was referred from the obtained depth - density curve that the monolayers were explicitly separated into dendron block, perfluorinated, and carboxyl acid layers. Furthermore, the SLD of dendron layer was decreased with increasing the mixing ratio of perfluorooctadecanoic acid, indicating the decrease in the occupation of dendron moiety. These experimental facts are consistent with the expectation of layer model described above and supported the structure of longitudinally phase-separated hybrid film. The layer formation is resulted not only from the intermolecular interaction between perfluorinated fatty acids and block copolymers but also from the geometry or shape of the molecules.

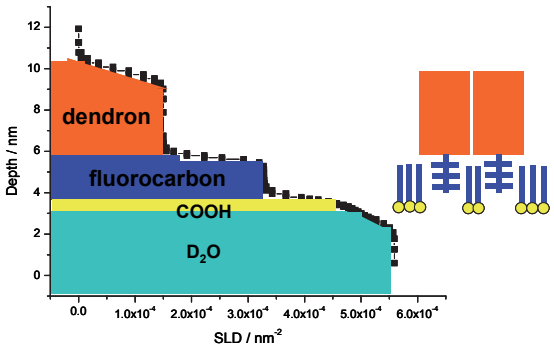


Fig.1. The depth – SLD profile where a mixing ratio of perfluorinated fatty acid to M2den3 is 4. Insert: illustration of phase-separated hybrid Langmuir film structure.

References

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