微小角入射 X 線回折法と X 線／中性子反射率法による高分子薄膜の表面・界面構造解析

Surface and Interface Characterization of Polymer Thin Films by Grazing Incidence Wide Angle X-ray Diffraction and X-ray/Neutron Reflectivity

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Polymer thin films have numerous technical applications as functional coatings, the most typical example is fluoropolymer coatings for wettabitily, friction and adhesion control. Polymer blends and polymer brushes can be tailored for functional properties.　X-ray reflectivity (XR), grazing incidence wide angle X-ray diffraction(GIWAXD)/small angle X-ray scattering scattering (GISAXS)　and neutron reflectivity(NR)　are powerful nondestructive analytical tools in order to characterize surface and buried interface of polymer thin films on various substrates.　The perpendicular density profile of thin films has been studied with XR. GIWAXD refers to an x-ray diffraction method based on the grazing incident geometry is perfectly suited for the investigation of the crystalline state of surfaces and thin films. On the other hand, NR is a technique for measuring the structure of thin films, similar to the often complementary techniques of　XR and ellipsometry.　NR is advantageous in a few significant ways. Most notably, since the technique probes nuclear contrast, rather than electron density, it is more sensitive for measuring some elements, especially lighter elements.　In the case of polymers, deuterium labeling is used in order to make a contrast of the certain component.　In this presentation, several examples of surface and interface analysis of polymer thin films will be introduced.

The molecular aggregation states of poly(fluoroalkyl acrylate) [PFA-C_y, where y is the fluoromethylene number of the fluoroalkyl (R_f) groups] thin films were characterized by GIWAXD.　In-plane diffractions corresponding to the hexagonal packing of the R_f groups were observed for PFA-C_y with $y \geq 8$ in the surface and bulk regions.　In the case of our-of-plane diffraction, the peaks　attributed to the lamellae structure in which FA-C8 groups ordered like a multilayer. GIXD study of PFA-C8 revealed that the FA-C8 side chain tend to orient perpendicular to the outer-most surface　in order to minimize the surface free energy.　The orientation fluoroalkyl group is closely related to the wettability of surfaces.

NR is suitable for the analysis of buried interfaces.　Polystyrene (PS) blend thin films　with polyhedral oligomeric silsesquioxane (POSS) and organic-inorganic hybrid polymers (PS-POSS), which are PS with a POSS end group, were prepared. Surface and interface structure of PS/POSS and PS/PS-POSS blend thin films were characterized by neutron reflectivity. POSS was enriched at the surface and interface of PS thin films and inhibited dewetting. However, increase in surface roughness was observed due to the crystallization of POSS.　On the other hand, PS-POSS were well dispersed in PS thin films and provided thermal stability to films against dewetting

Furthermore, NR was applied to characterize the D_2O/polymer brush interface. The zwitterionic polyelectrolyte brushes on the quartz plates were prepared by surface-initiated atom transfer radical polymerization of 2-methacryloyloxyethyl phosphorylcholine (MPC). NR was measured by irradiation of neutron beam from the quartz plate, which was contacted with water trough, to the interface between liquid phase and immobilized polyelectrolyte brush. NR profiles of polyelectrolyte brush/D_2O interface indicated that the PMPC chains exhibited a stretched conformation and formed concentration gradient of D_2O under swelling states. The effect of ionic strength on PMPC brush conformation was analyzed by NR. The difference between reflectivity of PMPC brushes in D_2O and in salt solution was negligible. The authors supposed that hydrated ion could not diffuse in the brush layer because of the presence of a densely grafted polyelectrolyte with local high ion concentration.