

## Fabrication and structure of “polymer nanosphere multilayered organization”



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### ABSTRACT

We constructed a multiparticle layered organization of aromatic polyamides with rigid main chains and flexible side chains by the Langmuir–Blodgett (LB) technique, which resulted in a highly regular arrangement along the *c*-axis. The particle arrangement was estimated by performing out-of-plane X-ray diffraction (XRD) analysis and atomic force microscopic (AFM) observation. The results suggest that a double-particle layered structure (Y-type) is formed by the LB technique, forming amphiphilic particles at the air/water interface. Copolymers with highly hydrophobic carbazole contents and both hydrogenated and fluorinated side-chains also formed a single-particle layer at the air/water interface and exhibited multiparticle layers by a LB technique. Therefore, it is possible to control the formation of single- and double-particle layered structure using these techniques. Further, it was found that multiparticle layered organization of polymer nanospheres and polymer nanosheets could be formed simultaneously with the same component material.

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## 1. Introduction

Materials with a layered organization such as graphite, aluminosilicate, biological membranes, cell membranes, Langmuir–Blodgett (LB) films [1–5],  $\beta$ -sheets in proteins [6–8], and lamella structures [9–11] of crystalline polymers are regarded as key materials in the organic/inorganic and biochemistry fields. Exfoliation [12–14], intercalation [15–17], deintercalation [18–20], electron transfer between layers [21–23], and so on are representative functions of this type of layered organization, which has thus attracted considerable interest in fundamental science.

By collapsing a monolayer consisting of organic polymer nanoparticles on the surface of water, it is possible to produce new molecular assemblies [24]. Fig. 1a shows single-particle and multiparticle layers of hydrophobic polymers on a water surface fabricated by the LB technique. These nanoparticles form a layered organization by the bottom-up method. These multilayered polymer nanospheres are similar to colloidal crystals [25]. Colloidal particles are small objects with at least one characteristic dimension in the range of 1 nm to 1  $\mu$ m. They have long been used as major components of various industrial products such as foods, inks, paints, toners, coatings, papers, cosmetics, photographic films,

and rheological fluids. Further, colloidal crystals, which comprise three-dimensional periodic arrays of submicron particles, have attracted considerable attention because of their novel photonic applications in the form of photonic crystals. They have also been extensively studied in the context of materials science, chemistry, biology, condensed matter physics, applied optics, and fluid dynamics. Generally, it is well known that photonic crystals are nanostructures that exhibit periodic changes in refractive index. Fig. 1b shows that the construction of a multiparticle layered organization such as that found in photonic crystals is possible by using the LB method. The LB method can alternately transfer particles with different refractive indices, similar to the formation of hetero film. However, colloidal crystals are generally composed of micro-sized particles and the particles are frequently expensive metals or inorganic materials.

Polymer nanospheres are a viable alternative to colloidal crystals. Fig. 2 shows the formation, structure, and function of multilayered polymer nanospheres of aromatic polyamides. The atomic force microscopic (AFM) image shows the formation of a single-particle layer of an aromatic polyamide with a pentyl side chain (PABA<sub>5</sub>) [26,27] (Fig. 2a). The out-of-plane XRD profile of the LB-fabricated multiparticle layers of PABA<sub>5</sub> indicates higher-order reflection of the (00 $l$ ) plane (Fig. 2b). By applying of three-dimensional paracrystal analysis, [28] a *g* value, which is a measure of crystal distortion, of 0.52 was calculated from the result of out-of-plane XRD of this LB multiparticle layers (Fig. 2c). The interference

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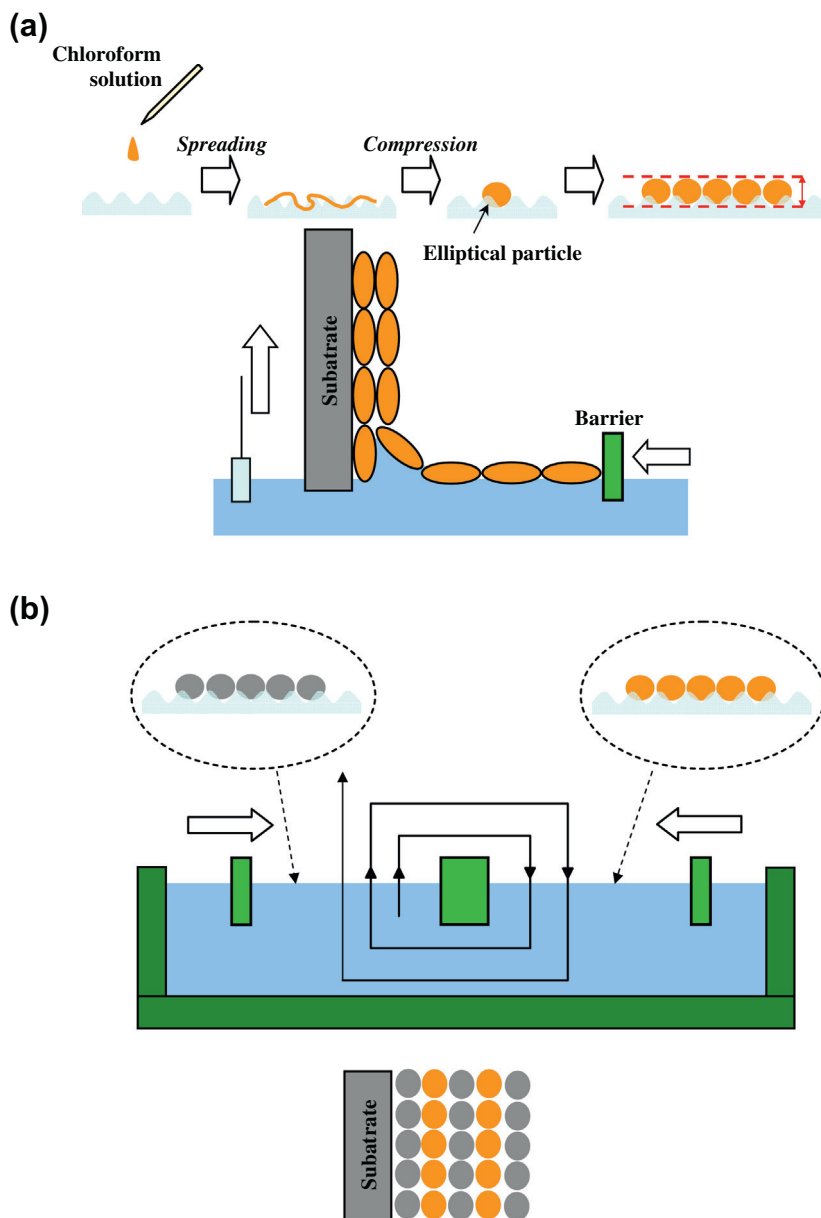


Fig. 1. Formation mechanism of: (a) single-particle layer on the water surface of hydrophobic polymers and (b) multiparticle layers by the LB technique.

colors resulting from the difference in layer thickness of the step-wise multiparticle layers of PABA<sub>5</sub> are easily visible (Fig. 2d). In addition, it is expected that fabrication of inexpensive, nanometer-size, soft material multiparticle layers by hybridization of particles with different refractive indices. This layered organization may show wave number selectivity at several tens of angstroms, such as in the region of vacuum ultraviolet or far-ultraviolet light (Fig. 2e). Further, surface properties of polymers are important for understanding adhesion, friction, and wear-resistance characteristics [29–32]. For example, wettability of LB films is sensitive to the flatness or roughness of these surfaces. It is expected application of multiparticle layers for various devices.

In a previous study, aromatic polyamides with a rigid main chain and flexible side chains of various lengths [poly-(*N*-alkylated benzamide), *abbrev.* PABA<sub>*n*</sub>, *n*: number of carbon side chains] were synthesized by direct condensation polymerization [33,34]. In the case of using of method of monolayer on the water surface of these

polyamides, the surface morphology of PABA<sub>*n*</sub> systematically varied depending on the side-chain length [35–39]. In this study, the formation mechanism and functionality of the multiparticle layered organization of aromatic polyamides and other hydrophobic polymers were investigated by surface pressure-area ( $\pi$ -A) isotherms and AFM observation. These hydrophobic polymers correspond to ternary comb copolymers containing hydrophobic *N*-vinyl carbazole (NVCz) units. Previously, we constructed novel polymer nanosheets with a highly ordered layer structure with amorphous side chains and  $\pi$ - $\pi$  stacking of NVCz in the form of ternary comb copolymers [40]. Therefore, the formation behavior of particles of these type ternary comb copolymers with highly hydrophobic NVCz content was also used. In addition, organo-modified zirconia and clay as particles of different refractive indices were used. As the first attempt on this study, multiparticle layered organization consisting of such particles was prepared and corresponding particle arrangement was investigated.

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