

Fabrication and Structural Estimation of "Polymer Nanosphere Multilayered Organization"

Atsuhiko Fujimori

Graduate School of Science and Engineering, Saitama University,
Shimo-okubo 255, Sakura-ku, Saitama, 338-8570, Japan

Abstract. We have newly constructed "multi-particle layered organization" of aromatic polyamide (poly-(*N*-alkylated benzamide), *abbrev.* PABA_n, *n*: carbon number of side-chains) derivatives having both a rigid main chain and a flexible side chains by a Langmuir-Blodgett (LB) technique. This organization is composed of the build-up particle layers with highly regular arrangement along the *c*-axis. The particle arrangement of this organization of polymer nanosphere was estimated by performing out-of plane X-ray diffraction (XRD), and atomic force microscopic (AFM) observation. In addition, it is also proposed that ternary comb copolymers with carbazole units and both hydrogenated and fluorinated side-chains are candidates of newly typed "polymer nanosheet" material. These copolymers with high hydrophobic carbazole contents also formed single particle layer at air/water interface and "multi-particle layered organization" was constructed by a LB technique. Therefore, it was found that "multi-particle layered organization of polymer nanosphere" and "polymer nanosheet" are simultaneously formed by same component copolymer materials with hydrophobic carbazole units.

1 Introduction

It is possible for "layered organization", such as graphite, alminosilicate, biological membrane, cell membrane, Langmuir-Blodgett (LB) film¹, β -sheet in protein, and lamella structure² of crystalline polymer to regard as key material throughout organic, inorganic, and bio-substances. Exfoliation, intercalation, deintercalation, electron transfer between layers, and so on are representative excellent functions of "layered organization". Hence, these type organizations have attracted considerable interests in fundamental science; further, these structural materials have several potential applications.

By the way, collapsed mechanism of monolayer on the water surface is possible to produce a newly construction of molecular assembly.³ One of the important candidate is nanoparticles of organic polymers. Previously, we have reported a formation mechanism of a single particle layer on the water surface of hydrophobic polymers and fabrication of multi-particle layers by the LB technique.⁴ The main objective of this paper is to generalize nanoparticle formation of hydrophobic polymers at air/water interface. These nanoparticles produced at air/water interface were able to form the layered organization by a bottom-up method. The structure of "polymer nanosphere multilayered organizations" are similar to that of colloidal crystal.⁵ Colloidal particles are small objects with at least one characteristic dimension in the range of 1 nm to 1 μ 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, such as their use 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, or fluid dynamics. However, colloidal crystals were generally composed of micro scale order particles and the particles were usually expensive metals or inorganic materials.

Previously, aromatic polyamides with a rigid main-chain and flexible side-chain having various length (poly-(*N*-alkylated benzamide), *abbrev.* PABA_n, *n*: the number of carbon atoms in the side-chains) were synthesized by direct condensation polymerization^{4,6}. Figure 1(a) shows structure of "polymer nanosphere multilayered organization" of aromatic polyamide with pentyl side-chain (PABA₅). Atomic force microscopy (AFM) image shows formation of single particle layer of PABA₅^{4,6}. Out-of-plane XRD profile of LB multi-particle layers of PABA₅ indicates higher order reflections of the (00*l*) plane. In addition, structural color of step-wise multi-particle layers of PABA₅ are clearly appeared.³ The crystal distortion was obtained by the result of paracrystal analysis to this LB multi-particle layers. The *g* value⁷ of 0.52 was defined by $g = d_k / \Delta d_k$. The $g = 0$ for the ideal lattice (no distortion) and $g = 1.0$ for the "completely" distorted crystal. (In other words, the material is no longer crystal.) It is expected that these layered organizations of inexpensive soft materials at nano-meter size show wavenumber selectivity at several tens of angstrom, such as vacuum ultraviolet or far-ultraviolet light.

Further, surface morphology of PABA_n systematically varied by method of monolayer on the water surface of

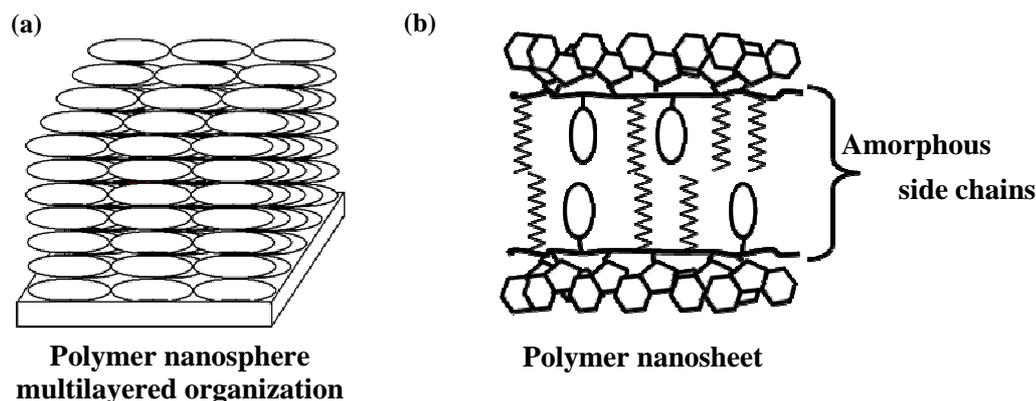


Figure 1. Structural models of (a) “polymer nanosphere multilayered organization” of aromatic polyamides and (b) “polymer nanosheet” of ternary comb copolymers with N-vinyl carbazole (NVCz) units.

these polyamide derivatives. The PABA_n with relatively short alkylated side chain have indicated characteristic particle formation.

In this study, the formation mechanism and functionality of multi-particle layered organization of aromatic polyamides, and other hydrophobic polymers were investigated by surface pressure - area (π -A) isotherms and AFM observation. These hydrophobic polymers correspond to ternary comb copolymer containing hydrophobic N-vinyl carbazole (NVCz) unit. In the previous study, we have constructed a new type of “polymer nanosheets” with a highly ordered layer structure containing amorphous side chains and π - π stacking of NVCz in these ternary comb copolymers (Fig. 1(b)).⁸

In the present work, formation behavior of nanoparticles of ternary comb copolymers with high NVCz content was also investigated at air/water interface. In other words, it was attempted generalization of formation of “polymer nanosphere multilayered organizations” for other hydrophobic polymers.

2 EXPERIMENTAL

2.1 Polymerization.

PABA_n compounds used in this study were synthesized by the direct condensation polymerization of N-alkylated aminobenzoic acid from methyl to heptadecyl substituents ($n=1 \sim 17$).⁶ The average molecular weights, M_w , of these aromatic polyamides were 20,000-90,000. The ternary comb copolymers used in this study were obtained through copolymerization of NVCz with octadecyl acrylate (OA) and 2-(perfluorodecyl)ethyl acrylate (FF₁₀EA) at various monomer ratios. Copolymerization was carried out in an acetone solution at 50 °C for 48 h using azobisisobutyronitrile (AIBN) as an initiator ($M_w=4.93 \times 10^3$, $M_w/M_n=1.17$).⁸

2.2 Formation of polymer monolayers on water surface.

Monolayers of polymers prepared from chloroform solutions (about 10^{-4} M) were formed on distilled water (about 18 M Ω -cm). The π -A isotherms were measured by a USI-3-22 film balance (USI Co. Ltd.) at 15 °C. These aromatic polyamides formed highly condensed monolayers. These monolayers were transferred onto

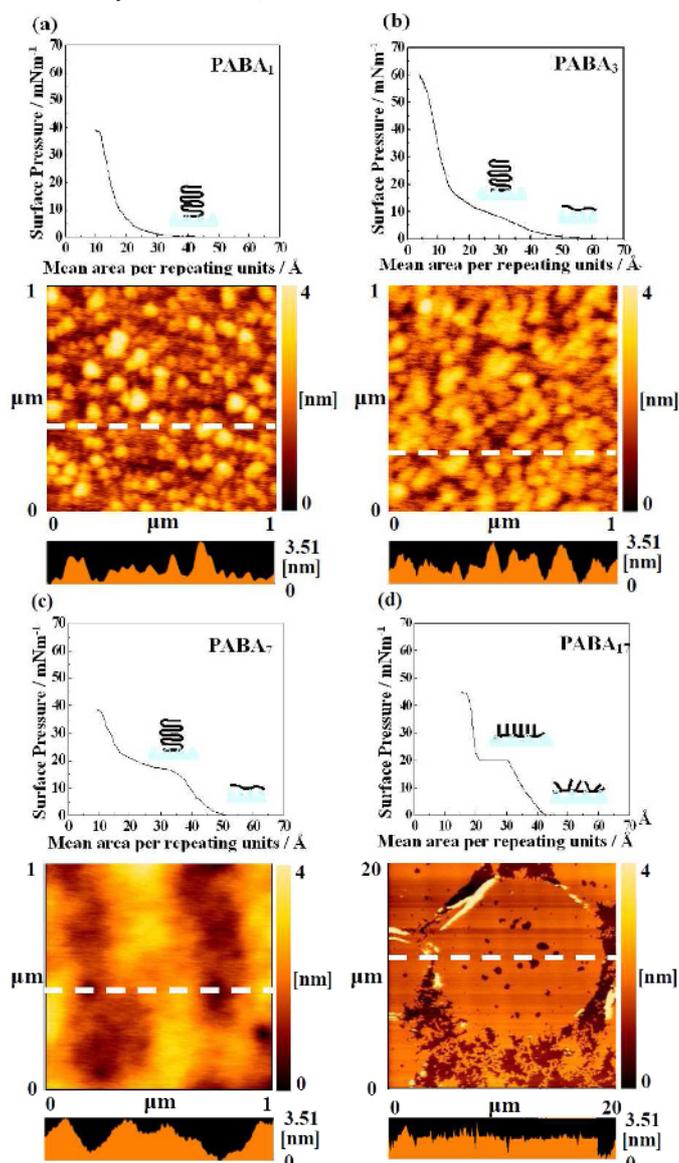


Figure 2. Surface pressure–area isotherms and AFM images of monolayers or single particle layers aromatic polyamides; (a) PABA₁ (b) PABA₃ (c) PABA₇ and (d) PABA₁₇.

solid substrates at 15 or 25 °C, and an appropriate surface pressure (15–25 mNm⁻¹) was applied to obtain alternating

Y-type films by the Langmuir–Blodgett (LB) method. Hydrophobic side-chains on the outermost surface of Z-type films transferred onto solid substrates were exposed to air.

2.3 Observation of surface morphology in organized molecular films

The surface morphologies of the transferred films were observed using a scanning probe microscope (Seiko Instrument, SPA300 with SPI-3800 probe station, tapping mode AFM) and microfabricated rectangular Si cantilevers with integrated pyramidal tips by applying a constant force of 1.4 Nm^{-1} .

3 RESULTS and DISCUSSION

Figure 2 shows π -A isotherms and corresponding AFM images of monolayers or piled up monolayers on the water surface of PABA₁, PABA₃, PABA₇, PABA₁₇. In this case, these isotherms indicate plateau regions that mean formation of collapsed monolayer with increase in surface pressure. From the results of AFM images of Fig. 2(a) and (b), it is supposed that films transferred at 25 mNm^{-1} indicate formation of particle layer. At the high surface pressure region, collapsed monolayers of PABA₁ and PABA₃ might be formed nanoparticles. This result supported by analysis of out-of-plane XRD. Regularity of particle formation was depended on the side-chain length. The plateau part of Fig.2 (b) only, is corresponded to the transition to the single particle layer from monolayer. In other words, the region mean that a point from monolayer to single particle layer occurs at that surface pressure.

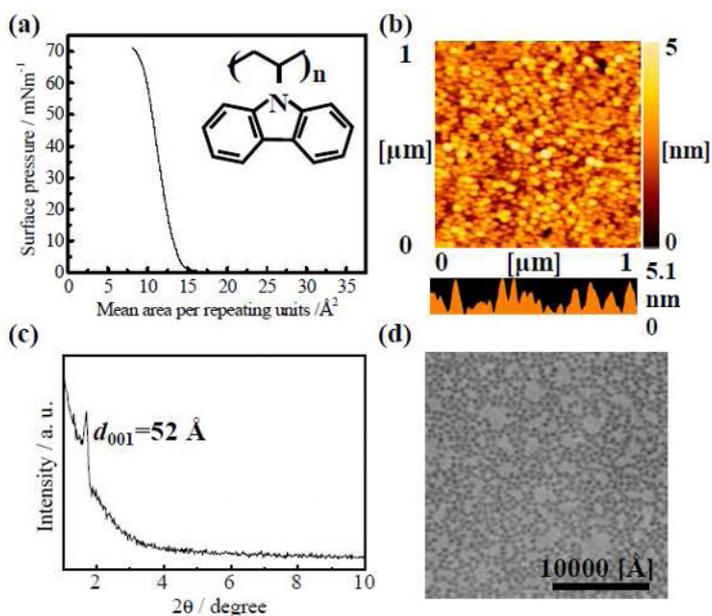


Figure 3. Formation of single particle layers of other polymers; (a) surface pressure–area isotherm of single particle layer on the water surface of N-vinylcarbazole. (b) AFM image of single particle layer of N-vinylcarbazole. (c) Out-of-plane XRD profiles of LB multi-particle layers of N-vinylcarbazole. (d) TEM image of single particle layer of polystyrene quoted by reference.⁹

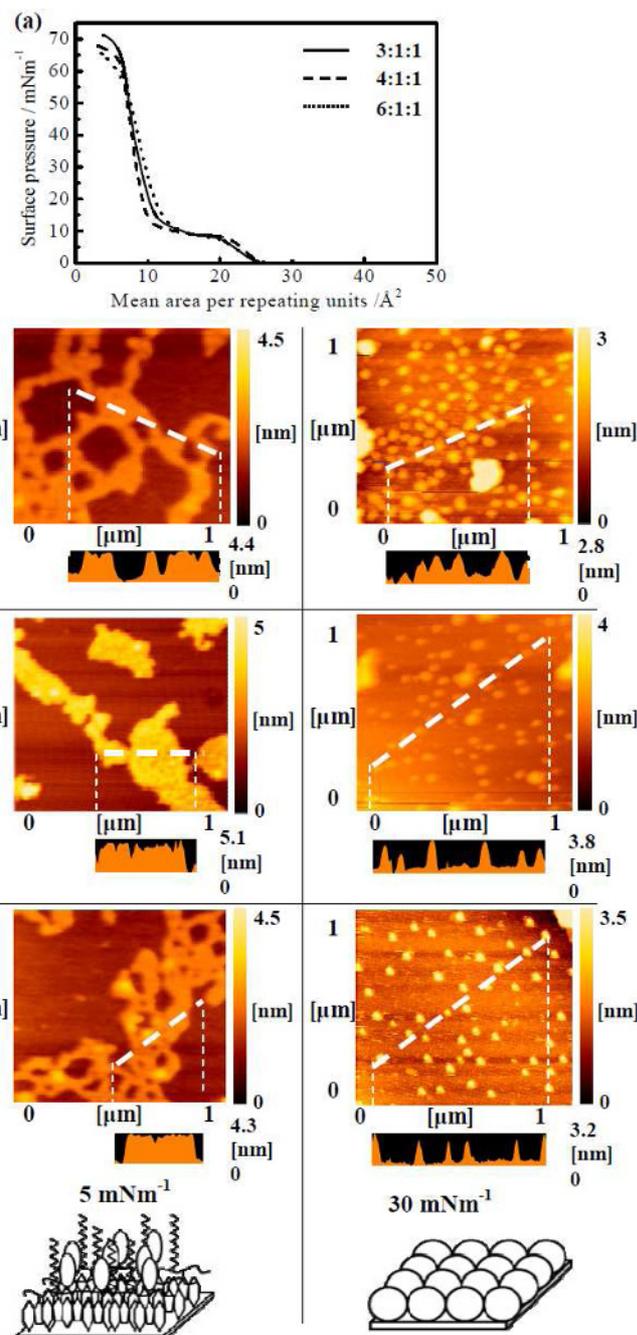


Figure 4. (a) Surface pressure–area isotherm and (b) AFM images of Z-type monolayers and single particle layers of NVCz : OA: FF₁₀EA=3:1:1, 4:1:1, and 6:1:1 copolymers. The cross section is shown in the white dashed line.

Similarly at the high surface pressure region, the presence of a shapeless domain was recognized in the case of the PABA₇ collapsed monolayer. According to the in-plane and out-of plane XRD and polarized IR spectroscopy results, the molecular arrangement in these shapeless domains was almost random^{5, 7}. PABA₁₇ molecules were closely packed, and they formed a side chain hexagonal lattice in a giant flat domain in the monolayer at the high surface pressure region. This hypothesis was supported by both the in-plane and out-of-plane XRD measurement and AFM observation

results^{5, 7}. The polydispersity of the domain was significant in a large scan area of $30 \times 30 \mu\text{m}^2$. The PABA₁₇ monolayer was an assembly of circular domains with different sizes.

Figure 3 indicates formation of single particle layers of other hydrophobic polymers. Figure 3(a) shows the π -A isotherm of a single particle layer of NVCz on the water surface. Judging from the corresponding AFM image, this polymer immediately formed the particles after spreading. Out-of-plane XRD profile of LB multi-particle layers of poly-NVCz indicated a sharp diffraction peak of (001) plane. In other words, the multi-particle layers of poly-NVCz have ordered layer structure although polymer nanosphere is strictly ellipsoid. Therefore hydrophobic poly-NVCz were constructed and also form “polymer nanosphere multilayered organizations” when Langmuir and Langmuir-Blodgett method were used. Generally, hydrophobic polymers formed easily the nanoparticles with regular height at air/water inter face. Previously, Kumaki reported formation of polystyrene particle at air/water interface by transmission electron microscopy.⁹ Therefore, construction of “polymer nanosphere multilayered organizations” by several hydrophobic polymers may be universal.

Previously, we have reported highly ordered and stable layered “Polymer nanosheets” constructed with amorphous side chains and π - π stacking of NVCz in ternary comb copolymers. High hydrophobicity add to the polymers when content of NVCz unit is high in these ternary comb copolymers.¹ Figure 4(a) shows π -A isotherms of NVCz:OA:FF₁₀EA=3:1:1, 4:1:1, and 6:1:1 copolymers. In this case, the plateau region of isotherms also corresponds to collapsed surface pressure. At the high surface pressure region, collapsed monolayers of these copolymers formed nanoparticles. On the other hand, monolayers with a network structure are formed at the low surface pressure region. Hence, these-type ternary comb copolymers are able to form both polymer nanosheet and polymer nanosphere controlled by surface pressure.

As mentioned above, formation mechanism and structure of multi-particle layered organization of aromatic polyamides, Poly-NVCz, polystyrene, and ternary polymers with NVCz units were discussed in this paper. Formation of “polymer nanosphere” with a regular height at an air/water interface may be universal in the hydrophobic polymers.

4 REFERENCE

- [1] G. L. Gaines, Jr., *Insoluble Monolayers at Liquid Gas Interfaces*; Wiley: New York, (1966).
- [2] A. Keller, *Phil. Mag.*, **2**, 1171 (1957).
- [3] A. Fujimori, *Kobunshi Ronbunshu*, **68**, 579 (2011).
- [4] A. Fujimori, S. Chiba, N. Sato, Y. Shibasaki, Y. Abe, *J. Phys. Chem. B*, **114**, 1822 (2010)
- [5] (a) G. Riess, G. Hurtrez, P. Bahadur, “In Encyclopedia of Polymer Science and Engineering” H. F. Mark, J. I. Kroschwitz, Eds, Wiley, New York, 1985, vol. 2, p 324. (b) I. W. Hamley, “The Physics of Block Copolymers” Oxford University Press, New York, 1998.

- [6] Y. Shibasaki, Y. Abe, N. Sato, A. Fujimori and Y. Oishi, *Polym. J.*, **42**, 72 (2010).
- [7] T. Harada, H. Matsuoka, H. Yamaoka, *Langmuir*, **15**, 573-577 (1999)
- [8] A. Fujimori, H. Hoshizawa, S. Kobayashi, N. Sato, K. Kanai, Y. Ouchi, *J. Phys. Chem. B*, **144**, 2100-2110 (2010).
- [9] J. Kumaki, *Macromolecules*, **19**, 2258 (1986).