Formation Mechanism and Functionality of Multi-particle Layers of Aromatic Polyamides

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We constructed two-dimensional integrated single particle layer on the water surface of aromatic polyamides (poly-(N-alkylated benzamides) *abbrev.* PABA_n, n: carbon number of side-chains) having both a rigid main-chain and a flexible side-chain with different lengths. Further, the build-up particle layers with highly regular arrangement along the *c*-axis are formed by Langmuir-Blodgett (LB) method. Molecular orientation and surface morphology of organized particle films of PABA_n were investigated by performing surface pressure-area (π -A) isotherm, in-plane and out-of plane X-ray diffraction (XRD), and atomic force microscopy (AFM) measurements. These single particle layers of several aromatic polyamides on the water surface were highly condensed at 15 °C. Results of out-of plane XRD measurement of multi-particle layers showed that the PABA₅ particle layers showed large periodicities of 50–60 Å at 15 °C. From these experimental findings, it was concluded that the polymer synthesis method employed in the present study can be directly used to control their surface morphologies, behavior of two-dimensional integration and multi-particle layer formation.

Key words: Aromatic Polyamides, Organized molecular films, Single particle layer, Multi-particle layers, Formation mechanism

1. INTRODUCTION

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, drinks, inks, paints, toners, coatings, papers, cosmetics, photographic films, and rheological fluids. In addition, colloidal crystals,¹ 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. But colloidal crystals were composed of micro scale order particles and the particles are almost expensive metals or inorganic materials.

By the way, comb polymers are useful materials because of the different solid-state natures of the main-chains and the side-chains, which generally afford long-range phase-segregated structures.¹ Crystalline main-chain with amorphous side-chain² and amorphous main-chain with crystalline side-chain³ comb polymers have been studied extensively and reviewed in terms of their chemistry⁴ and physical properties.⁵ The movement of the crystalline segments is variably inhibited by the amorphous portion; thus, various segregated structures are formed from similar

materials. The “crystalline-crystalline” comb polymers,⁶ especially those with aromatic main-chain polymers,⁷ are of interest because packing of the bulky aromatic polymer main-chain can be changed by varying the crystallinity of the side-chains. Kevlar, poly(*p*-phenylene terephthalamide) (PPTA), was first functionalized with linear hydrocarbons of 3, 4, 7, 12, and 18 carbons through metalation of PPTA using sodium hydride [degree of substitution (DS) was 86 to 99%, inherent viscosity (η_{inh}) 0.06 to 0.14] and the packing mode was investigated for the resulting comb polymers, which were all amorphous except for the polymer with C₁₈H₃₇ side-chains.⁸ Poly(3-*n*-alkyl-4-oxybenzoate)s (PAOBA)s with alkyl side-chains varying from 1 to 18 carbons were prepared and their phase properties fully investigated.⁹ The structure and thermal transition from crystalline to mesophase of PAOBA with short alkyl chains, such as propyl groups, was controlled by the rigid-rod main-chain, while those of PAOBA having longer alkyl chains were controlled by the nature of the side-chains. N-Alkylated poly(*p*-benzamide) (PABAn, DS > 96%) (from 10 to 18 carbons) also was prepared by the metalation method, and their packing structure investigated.¹⁰ In contrast to the high crystallinity of PAOBA, all PABA_n

polymers, except for the one with the 18-carbon alkyl chain, were amorphous, due to the bulky aromatic rings and relatively sparse semi-crystalline alkyl chains. We expect that well-defined PABA_n should pack easily in a different form upon polymerization of a completely alkylated monomer with a side-chain containing a number of carbons ranging from 1 to 17.

In our previous study, aromatic polyamides with a rigid main-chain and flexible side-chain having various length (poly-(N-alkylated benzamide), *abbrev.* PABA_n, n: carbon number of side-chains) were synthesized by direct condensation polymerization.^{11,12} In the case of using of method of monolayer on the surface of these polyamides, surface morphology of PABA_n systematically varied.¹¹ In this study, formation mechanism and functionality of multi-particle layers of aromatic polyamides.

2. EXPERIMENTAL

2.1 Direct polycondensation of PABA_n.

PABA_n compounds used in this study were synthesized by the direct condensation polymerization of N-alkylated aminobenzoic acid with pentyl, heptyl, and heptadecyl substituents (n=5, 7, and 17).¹² The PABA_n compounds were prepared by the same method, as described above. The average molecular weights, *M_w*, of these aromatic polyamides were 20,000–90,000. N-Methylaminobenzoic acid (4.55 g, 30.1 mol), triphenylphosphine (9.44 g, 36.0 mmol), and pyridine (30 mL) were then added to the flask. The mixture was stirred until the solid was dissolved. Hexachloroethane (8.52 g, 36.0 mmol) was then added to this solution, and the mixture was refluxed for 24 h. After the solution was cooled to room temperature, methanol/hydrogen chloride was added and stirred for 5 h. The PABA_n compounds were prepared by the same method, as described above. The average molecular weights, *M_w*, of these aromatic polyamides were 20,000–90,000.

2.2 Formation of polymer monolayers on water surface.

Monolayers of aromatic polyamides prepared from chloroform solutions (about 10⁻⁴ M) were formed on distilled water (about 18 MΩ·cm). The surface pressure–area (π–A) isotherms of the polyamide monolayers were measured on a film balance (Kyowa Kaimen Kagaku Co. Ltd., compression speed: 1.25 or 10 cm² / min) at 15 or 25 °C. These aromatic polyamides formed highly condensed monolayers. These monolayers were transferred onto 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 1 shows out-of plane XRD profile (2θ layers) and AFM image of multi- and single particle layers of PABA₅. These molecules form the particle with 3 nm height on the water surface because of their low hydrophilicity. The multilayers transferred by Langmuir–Blodgett method, indicate the formation of highly order layer structure estimated by out-of plane XRD. In this case, out-of plane XRD profile shows second and third order reflection. Further, value of first order diffraction is about 6 nm. This value is almost corresponding to height double-particles. Therefore, it is suggested that polar groups in hydrophilic ones are localized in the bottom of particle.

Figure 2 shows occurrence of structural colors for stepping transferred Langmuir–Blodgett films of PABA₅ deposited particle layer up to visible light region. In spite of the layered organization of sphere, construction of highly order layer structure is induced by deposition.

In order to discuss the formation mechanism for single particle layer on the water surface, figure 3 shows schematic illustration of transition behavior from monolayer to particle layer. From the results of π–A isotherm at 15 °C, PABA₅ shows phase transition in two-dimensional plane. In this case, it seems that monolayer is formed at lower surface pressure region (Fig. 3(a)) and particles appear after

Figure 1 Out-of plane XRD profile and AFM image of multi- and Z-type single particle layers of PABA₅

Figure 2 Occurrence of structural colors; Photograph of stepping transferred Langmuir-Blodgett films of PABA₅.

transition (Fig. 3(b)). In the case of PABA₇, single particle layer can not be formed on the water surface at 15 °C. However, at 25 °C, single particle layer of PABA₇ can be formed with increase of molecular mobility on the water surface. On the other hand, PABA₁₇ having longer side-chain form the homogeneous monolayer over the almost all subphase temperature.

Figure 4 shows models of formation of lamella-like folded chain structure in the particle with regular height. Indeed, average transfer ratio of monolayers of PABA₅ at high surface pressure region is 1.4 (over 1.0) whereas that of PABA₁₇ monolayer exhibit almost 1.0. A reason of this result may indicate that individual particles are formed by multilayers of folded polymer-chain. This result also supported formation of particle of PABA₅. The length of

Figure 4 Models of formation of lamella-like folded chain structure in the particle with regular height.

polymer main-chain inferred from molecular weight ($M_w=20,000-90,000$) exhibit the range from 25 to 75 nm. Height of formed nanoparticles is about 3 nm. In the case of length of polymer main-chain of 50 nm and thickness of a polymer-chain of 0.5 nm (calculated by a simple molecular modeling), polymer main-chain fold at 5-6 times and the length of this folded unit indicate the 8-10 nm in order to exhibit 2.5-3.5 nm height of nanoparticles. Generally, it is well-known that lamellae thickness of crystalline polymer converges to about 10 nm size.⁷⁻⁹ This analogy may suggest to dependency on molecular weight related to the size of nanoparticles. The origin of small dispersion of particle height in this study may be based on the use of relative low molecular weight polymers.

In addition, the functionality of multi-particle layer of aromatic polyamides also estimated in this study. Figure 5 shows optical properties of LB multi-particle layers of PABA₅ and their solution one. In the case of solution, broaden fluorescence band around 538 nm appears by excitation wavelength of 260 nm. On the other hand, sharper fluorescence band at 523 and 536 nm are confirmed in their multi-particle layers transferred both high and low surface pressures, respectively. In the case of high transferring surface pressure, intensity of fluorescence band remarkable is enhanced and shift to the long emission wavelength region. It seems that this phenomenon induce the changes in effective conjugation length of aromatic polyamides with transition from monolayer to single particle layers.

4. CONCLUSIONS

In this paper, we discussed formation mechanism of single particle layer of aromatic polyamides with relative short alkyl side-chain. In addition, the optical properties for occurrence of structural colors and emission of fluorescence are also estimated. It is suggested that single particle layer is corresponding to an assembly of lamella-like folded polymer chains. Quite regular arrangement of polymer particles in

Figure 3 Models of formation mechanism from monolayer to single particle layer: (a) large surface area (low surface pressure region), and (b) small surface area (high surface pressure region).

Figure 5 UV-vis and fluorescence spectra of PABA₅ in (a) chloroform solution, and (b) multilayers (···: transferred at low surface pressure (before phase transition), and —: transferred at high surface pressure (after transition)).

layered organization induces the structural color of the film. Further, changes in effective conjugation length cause the shift of the maximum fluorescence wavelength and enhancement of intensity.

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