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I. INTRODUCTION

Organized molecular films1 fabricated using functional polymers with precisely controlled structures can be developed as candidates for biomimetic models2 and molecular electronic devices,3 which have attracted considerable interest in fundamental science, as well as for their potential applications. Generally, it is well known that crystalline polymers construct hierarchical structures from lamellae on the nanometer scale to spherulite on the mesoscopic scale. 4 Crystals in these crystalline polymers are generally formed by the folding of the main-chain, although there main-chain, although there are two types of structural characteristics for side-chain crystalline ternary comb polymers. It is known that ternary comb polymers, which have long n-alkyl side-chains with crystallization ability attached to an amorphous main-chain, are packed into a layer structure along the c-axis and sub-cell of the side-chains in the ab-plane.5 This "sub-cell" structure6 of the side-chain is formed as a two-dimensional lattice, and the "layer structure" along the c-axis often reflects the long spacing between the main-chains in the accumulated double layer structures. With regard to the industrial application of these type of ternary comb polymers, poly(octadecyl)-based materials that use co-crystallization with another hydrocarbon to incorporate the material into the same crystalline lattice have found numerous applications such as pour-point depressants for lubricating oils or fuels, rheological modifiers, additives in petroleum products, and smart gels.7

On the other hand, many researchers have attempted to utilize poly-N-vinylcarbazole (Poly-NVCz) as organic light emitting diodes, organic transistors, and host compounds for organic electroluminescence8 in recent years, because it is well known that Poly-NVCz exhibits properties identical to those of organic semiconductors.9 Further, it is expected that Poly-NVCz can be used to realize a hologram memory material because of the high refractive index (greater than 1.68) of its monomer.10

As mentioned above, it is essential to control the molecular orientation and the arrangement at the monomolecular level in order to drive the functionality of these organic molecular devices in an efficient manner. However, in many cases, it is difficult to control the molecular arrangement and the homopolymer packing because Poly-NVCz itself easily forms an amorphous polymer.11

In previous study, we have investigated the control of solid-state structures and the formation of organized films for the newly synthesized comb copolymers containing hydrogenated and fluorinated side-chains.12 These comb polymers form a side-chain crystal in the bulk state by van der Waals interaction between the side-chains and the extremely stable condensed monolayers at the air/water interface. If bulky and flat functional groups are incorporated in the main-chains of side-chain crystalline polymers, it will be possible to control the arrangement of bulky groups at

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the molecular level, regardless of the low crystallinity of the polymers.

Recently, the fine structures in the solid-state of the synthesized ternary comb polymers containing N-vinylcarbazole (NVCz) in the main-chains obtained by co-polymerization with both hydrogenated and fluorinated long-chain compounds were investigated by wide-angle X-ray diffraction (XRD). Further, the molecular arrangements of the organized molecular films in ternary comb copolymers containing NVCz units were estimated by in-plane XRD.13

In this study, transition behavior from monolayer on the water surface to single particle layer of ternary comb copolymer containing carbazole ring have investigated by surface pressure-area (*π*-A) isotherm, atomic force microscopy (AFM), out-of-plane XRD.

II. Experimental

a) Materials

The ternary comb copolymers used in this study were obtained by the copolymerization of NVCz with octadecyl acrylate (OA) and 2-(perfluorodecyl)ethyl acrylate (FF10EA) at various monomer ratios. Copolymerizations were carried out in an acetone solution at 50 °C for 48 h using azobisisobutyronitrile (AIBN) as an initiator. These monomers and the initiator were purchased from Tokyo Kasei Co. Ltd. and Daikin Fine Chemicals Co. Ltd., and were used without further purification. The precipitated polymers were washed with acetone until they were free of monomers. The ternary comb copolymer compositions were determined by 1H NMR (Nihon Densi Co. Ltd. EX270 NMR) spectroscopy. The tacticity of fluorinated homopolymer obtained by 1H NMR analysis according to the reference was found to be almost syndiotactic (Diad: 58 %). In this study, we synthesized ternary copolymers with two series of molecular weights estimated to be approximately Mw = 4.43 × 104 and 4.93 × 103 (Mw/Mn ≈ 2.14 and 1.17 respectively) on the basis of GPC (JASCO-860-CO) measurements.

According to the theory of the Q-e scheme proposed by T. Alfrey and C.C. Price,14 these ternary comb polymers form alternating copolymers in the view of relation of NVCz and long-chain acrylates. In this case, the e values of NVCz, OA and FF10EA are –1.40, +1.12 and +0.66 respectively. Thus, it appears that the NVCz : long-chain acrylates copolymers almost form ideal alternating copolymers, especially for the 2:1:1 monomer ratio.

b) Formation of copolymer monolayers on water surface and estimation of molecular arrangement in the films

The monolayers of the ternary comb copolymer with NVCz were spread from the chloroform or chloroform/trifluoroacetic acid = 90/10 (v/v) mixed solutions (about 10–4 M) onto the distilled water (about 18 MΩ•cm). The *π*–A isotherms were measured by a USI-3-22 film balance (USI Co. Ltd.) at 15 °C. These monolayers were transferred onto glass (XRD sample), quartz (UV-vis and fluorescence spectroscopy), and mica (AFM) substrates by the Langmuir-Blodgett (LB) method to obtain alternating Y-type film at 15 °C.

The long spacing between the layer structures along the c-axis estimated by an out-of-plane X-ray diffractometer (Rigaku, Rint-Ultima III, CuKα radiation, 40 kV, 40 mA) equipped with a graphite monochromator.

III. Results and Discussion

Figure 1 shows *π*-A isotherm of "single particle layer" on the water surface and corresponding AFM image of single particle layer on solid substrate of Poly-NVCz. This homopolymer formed single particle layer on the water surface after spreading, immediately. This

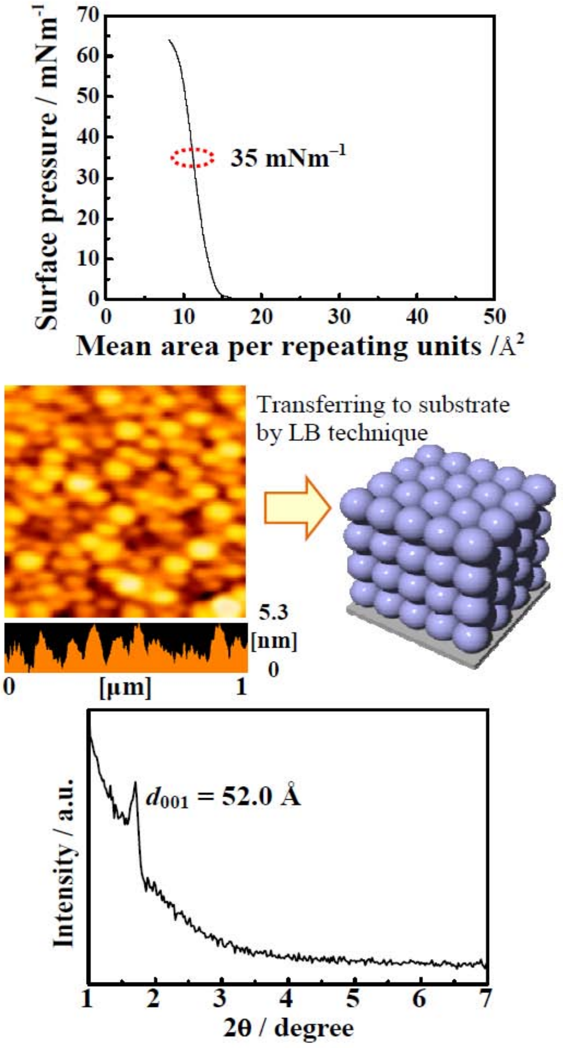

Fig. 1 : *π*-A isotherm of single particle layer on the water surface and AFM images of single particle layer on solid of PNVCz homopolymer, and out-of-plane XRD of multi-particle layers of Poly-NVCz.

figure also shows out-of-plane XRD of multi-particle layers of Poly-NVCz. From the result of this measurement, it is found that inter-particle spacing along the c-axis correspond to 52 Å.

Figure 2 shows π-A isotherm of "monolayer" on the water surface and corresponding AFM image of monolayer on solid substrate of NVCz:FF10EA:OA = 2:1:1 copolymer. This figure also shows out-of-plane XRD of multilayers of this copolymer. This profile clearly indicates higher order reflection of (00l) plane. Therefore, it is found that this LB multilayer formed highly ordered layer structure.

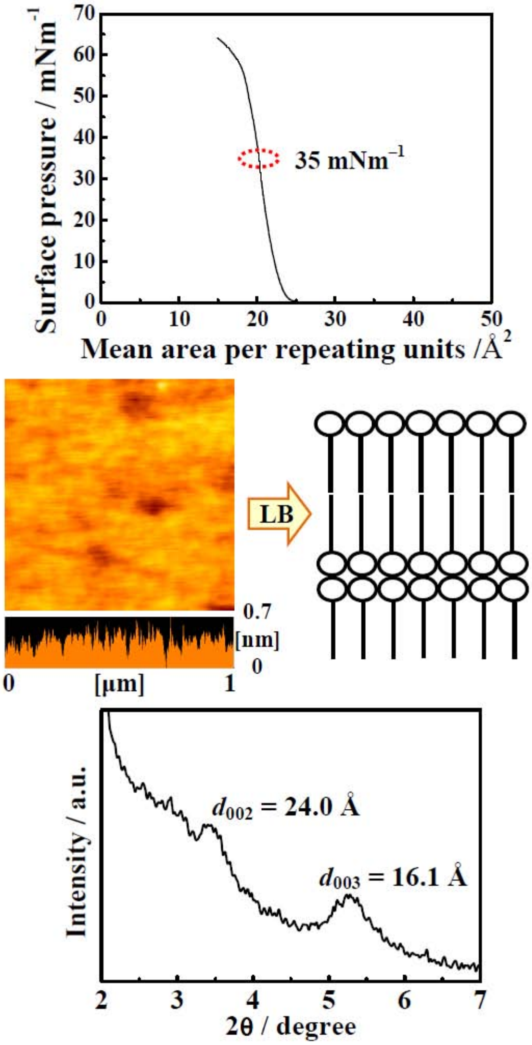

Fig. 2 : π-A isotherm of monolayer on the water surface and AFM images of monolayer on solid of VCz:FF$_{10}$ EA:OA = 2:1:1 copolymer, and out-of-plane XRD of multilayers of this copolymer

Figure 3 shows π-A isotherm of monolayer on the water surface of NVCz:FF10EA:OA = 3:1:1, 4:1:1, and 6:1:1 copolymers. All isotherms indicate an existence of plateau region based on the two-dimensional phase transition.

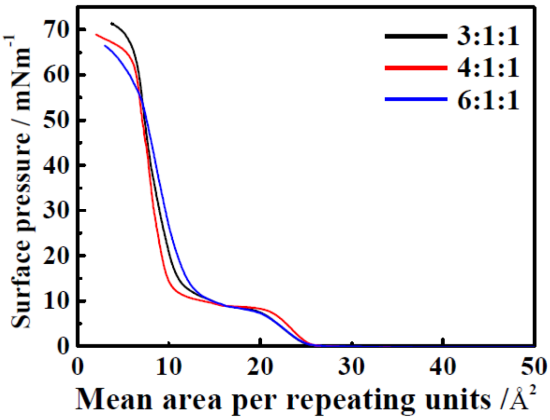

Fig. 3 : π-A isotherm of monolayer on the water surface of NVCz: FF$_{10}$EA:OA = 3:1:1, 4:1:1, and 6:1:1 copolymers

Figure 4 shows AFM images of Z-type monolayer and single particle layer on the water surface NVCz:FF10EA:OA = 3:1:1, 4:1:1, and 6:1:1 copolymers transferred at before and after transition. This figure indicates monolayer of these copolymers on the water surface formed below 10 mN m–1, and this monolayer transited to single particle layer above 15 mN m–1. This figure also means that spontaneous "particulation" behavior is accelerated by incorporation of carbazole units in ternary copolymer films.

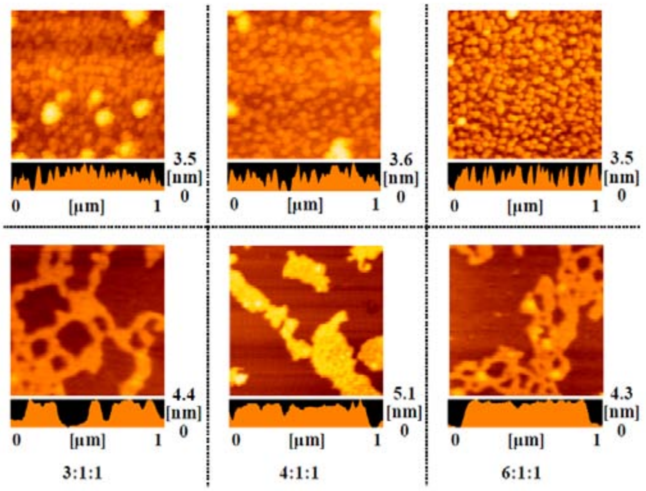

Fig. 4 : AFM images of Z-type monolayers and single particle layers on the water surface of NVCz: FF$_{10}$EA: OA = 3:1:1, 4:1:1, and 6:1:1 copolymers transferred at before (5 mN m^{-1}, lower column) and after (35 mN m^{-1}, upper column) transition.

Figure 5 shows out-of-plane XRD profiles of LB multilayers of NVCz:FF10EA:OA = 4:1:1 copolymer transferred at 35 and 5 mN m–1. It is found that both organizations commonly formed ordered layer structure along the c-axis.

Figure 6 shows schematic illustration of polymer nanosheet and polymer nanosphere layered organization, and their formation mechanism. It seems that polymer particles are formed by piled up molecular chain, like a bilayer structure in high surface pressure region.

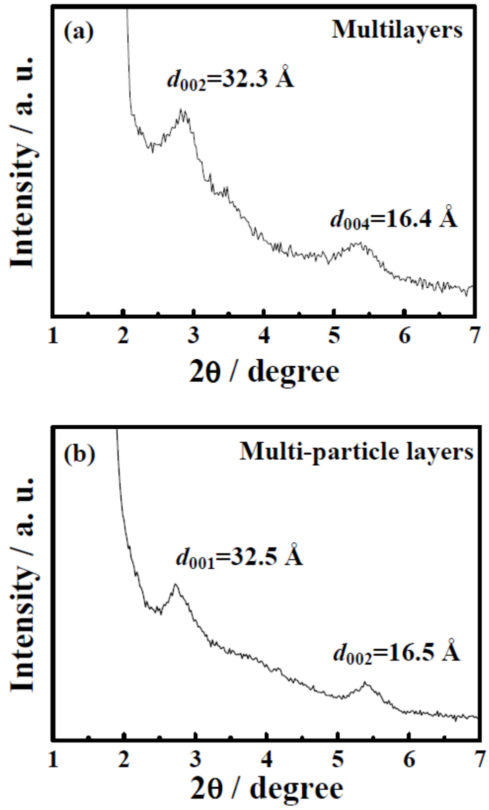

Fig. 5 : Out-of-plane XRD profiles of LB multilayers of NVCz:FF$_{10}$EA:OA = 4:1:1 copolymer transferred at (a) 5 mN m^{-1} and (b) 35 mN m^{-1}.

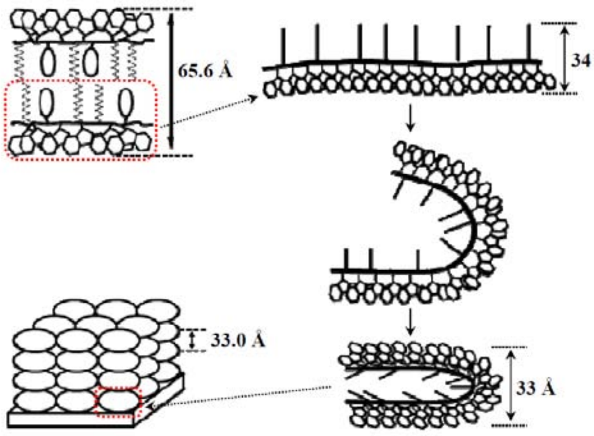

Fig. 6 : Schematic illustration of polymer nanosheet and polymer nanosphere layered organization, and their formation mechanism

Figure 7 shows UV-vis and fluorescence spectra of Poly-NVCz and NVCz:FF10EA:OA = 4:1:1 copolymer in solution. Further, fig. 8 shows ones of multi-particle layered organization of Poly-NVCz and NVCz: FF$_{10}$EA:OA = 4:1:1 copolymer.

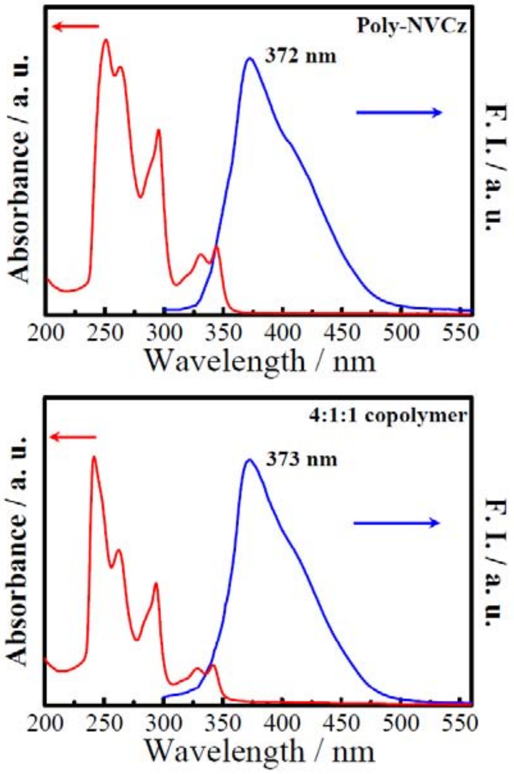

Fig. 7 : UV-vis and fluorescence spectra of Poly-NVCz and NVCz:FF$_{10}$EA:OA = 4:1:1 copolymer in solution

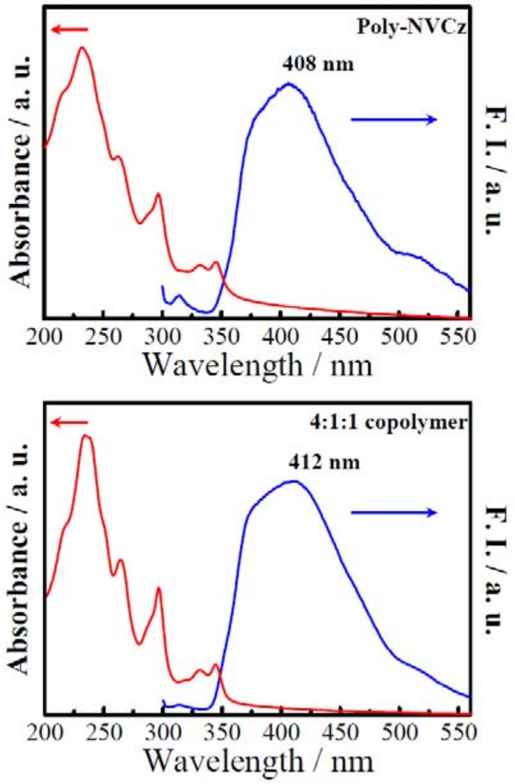

Fig. 8 : UV-vis and fluorescence spectra of multi-particle layered organization of Poly-NVCz and NVCz: FF$_{10}$EA:OA = 4:1:1 copolymer.

multi-particle layered organization of same materials.

The "polymer nanosphere" of these ternary comb copolymers showed the absorption band around 250 nm and emitted fluorescence at 400 nm. The emitted band in fluorescence spectrum showed red-shift to the one of their solution. It is speculated that this result means formation of aggregated structure by π-π stacking of NVCz rings.[15-17]

IV. CONCLUSION

Formation behavior of single particle layer of ternary comb copolymer containing NVCz have investigated. This copolymer monolayer is able to form the "polymer nanosheet" fabricated by a LB technique. Further, single particle layer is able to form the multi-particle layered organization of "polymer nanosphere". This ternary comb copolymer synthesized by radical copolymerization. Spontaneous particle formation is attained by incorporation of hydrophobic carbazole. Monolayer of these copolymers on the water surface transited to single particle layer above 15 mN m–1.

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