

# Solid-state Structure and Molecular Orientation in Organized Films of Ternary Comb Copolymers Containing N-vinylcarbazole

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The fine structures in the solid state and molecular orientation in Langmuir-Blodgett films of newly synthesized ternary comb copolymers with N-vinylcarbazole were investigated by wide-angle X-ray diffraction (XRD), small angle X-ray scattering, in-plane XRD, out-of plane XRD and atomic force microscopy. From the results of XRD in bulk, two kinds of short spacing peaks based on the formation of the sub-cell for fluorinated and hydrogenated side-chains were confirmed. Further, these ternary copolymers formed highly ordered layer structure. In addition, these ternary copolymers formed extremely condensed monolayers on the water surface. From the out-of plane XRD measurements of multilayers, formation of highly ordered layer structure was conformed. From the results of in-plane XRD and AFM, it was found that phase-separated structures between fluorinated and hydrogenated side-chains could not form in two-dimensional films. These structural changes may be cause by the  $\pi$ - $\pi$  interaction between the carbazole rings.

Key words: Organized molecular films, Ternary comb copolymer, Fluorocarbon, Hydrocarbon, N-vinylcarbazole

## 1. INTRODUCTION

The organized molecular films<sup>1</sup> fabricated using functional polymers with precisely controlled structures can be developed as candidates for biomimetic models<sup>2</sup> and molecular electronic devices,<sup>3</sup> which have attracted considerable interest in fundamental science, as well as for their potential applications.<sup>4</sup> Generally, it is well known that crystalline polymers construct hierarchical structures from lamellae on the nanometer scale to spherulite on the mesoscopic scale.<sup>5</sup> Crystals in these crystalline polymers are generally formed by the folding of the 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 crystallizable long n-alkyl side-chains 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.<sup>6</sup> This "sub-cell" structure<sup>7</sup> 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.<sup>8</sup>

On the other hand, many researchers have attempted to utilize poly-N-vinylcarbazole (PNVCz) as organic light emitting diodes, organic transistors, and host compounds for organic electroluminescence<sup>9</sup> in recent years, because it is well known that PNVCz exhibits properties identical to those of organic

semiconductors.<sup>10</sup> Further, it is expected that PNVCz can be used to realize a hologram memory material because of the high refractive index (greater than 1.68) of its monomer.<sup>11</sup>

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 PNVCz itself easily forms an amorphous polymer.<sup>12</sup>

Previously, 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.<sup>13</sup> 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 the molecular level, regardless of the low crystallinity of the polymers.

In this study, 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. Further, the molecular arrangements of the organized molecular films in ternary comb copolymers containing NVCz units were estimated by in-plane X-ray diffraction.

## 2. EXPERIMENTAL

### 2.1 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 (FF<sub>10</sub>EA) 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 syndiotactic poly-FF<sub>10</sub>EA homopolymer was obtained from a 1 M rad <sup>60</sup>Co  $\gamma$ -ray irradiated post-polymerization according to the procedure described in the previous work.<sup>14</sup> The  $\gamma$ -ray irradiation was carried out at the Japan Atomic Energy Institute at Takasaki. The ternary comb copolymer compositions were determined by <sup>1</sup>H NMR (Nihon Densi Co. Ltd. EX270 NMR) spectroscopy. The tacticity of fluorinated homopolymer obtained by <sup>1</sup>H 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  $M_w = 4.43 \times 10^4$  and  $4.93 \times 10^3$  ( $M_w/M_n \approx 2.14$  and 1.17 respectively) on the basis of GPC (JASCO-860-CO) measurements. The molecular weights of fluorinated homopolymers and copolymers at higher ratios of FF<sub>10</sub>EA units were estimated to be above thousand. These values were estimated from the intrinsic viscosity  $[\eta]$ , which is equal to 0.12–0.54, for these trifluoroacetic acid solutions at 30 °C by using the relation  $[\eta] = KM^\alpha$ , where  $K = 0.24\text{--}0.25 \times 10^{-4}$  and  $\alpha = 0.75\text{--}0.78$ . The values of  $K$  and  $\alpha$  were assumed from the results of the viscosity-averaged molecular weight of poly-alkyl acrylate.<sup>15</sup>

According to the theory of the Q-e scheme proposed by T. Alfrey and C.C. Price,<sup>16</sup> 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 FF<sub>10</sub>EA 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.

### 2.2 Structural estimation of bulk copolymers.

The packing modes of several copolymers in the crystalline phases were examined by X-ray powder diffraction measurements using a Rigaku Rad-rA diffractometer, which was equipped with a graphite monochromator, with CuK $\alpha$  radiation at 40 kV and 200 mA.

### 2.3 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 M $\Omega$ -cm). The surface pressure–area ( $\pi$ -A) isotherms of the polymers were measured on a film balance (Kyowa Kaimen Kagaku Co. Ltd., compression speed: 5  $\text{\AA}^2/\text{repeating units} \cdot \text{min}$ ) at 15 °C. These fluorinated ternary comb copolymers formed extremely condensed monolayers. These monolayers were transferred to the solid substrates at 15 °C and at a proper surface pressure (15–25 mNm<sup>-1</sup>) by the Langmuir-Blodgett (LB) method to obtain alternating Y-type film.

The in-plane spacings of the two-dimensional lattice of the films were determined by analyses using an X-ray diffractometer for different geometrical arrangements (Bruker AXS, MXP-BX, CuK $\alpha$  radiation, 40 kV, 40 mA, an instrument specially made to order) equipped with a parabolic graded multilayer mirror.

## 3. RESULTS AND DISCUSSION

Figure 1 shows the WAXD profiles of the low and high molecular weight ternary comb copolymers containing NVCz with various several side-chain ratios. From these profiles, we recognized systematic changes in the short-spacing regions with the monomer ratios. Further, we concluded that PNVCz forms an amorphous polymer judging from the appearance of two types of halos and the absence of any peaks.

In addition, from the profiles of poly-OA and poly-FF<sub>10</sub>EA, short spacing peaks based on the sub-cell formation of side-chains were confirmed at 4.2 and 5.0  $\text{\AA}$ , respectively. According to Platé's review, these peaks correspond to (100) reflections.<sup>17</sup> In the profiles of copolymers with high molecular weight, both short spacing peaks at 4.2 and 5.0  $\text{\AA}$  are commonly confirmed, especially NVCz:OA:FF<sub>10</sub>EA=2:1:1, 3:2:1, 6:5:1, and 9:8:1 copolymers. However, the low molecular weight copolymers with same component show the almost single short spacing

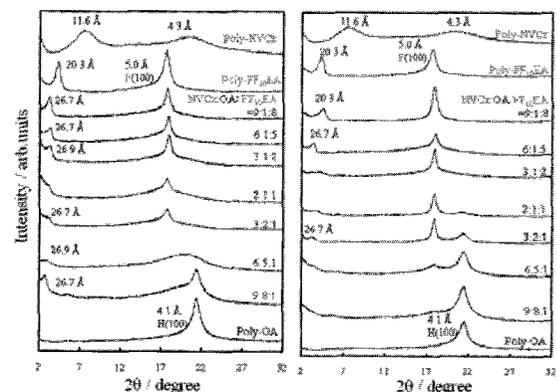
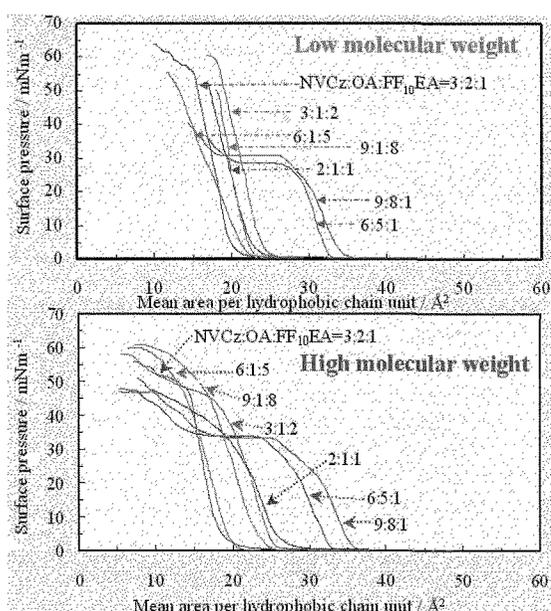


Figure 1 XRD profiles of ternary comb copolymers containing NVCz with several ratios. (left) low and (right) high molecular weights.

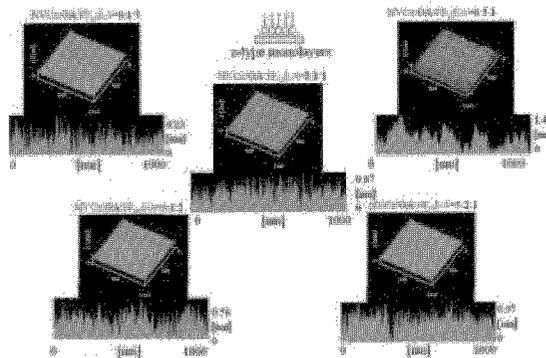


**Figure 2**  $\pi$ -A isotherms of monolayers on the water surface of ternary comb copolymers containing NVCz at 15 °C.

peaks with certain degree halos. This result means higher crystallinity of copolymer with high molecular weight than with low one. In the small angle region, long spacing peaks were clearly observed in the profile of poly-FF<sub>10</sub>EA at approximately 20.3 Å, whereas no peaks were observed in the low angle side in the profile of poly-OA. Poly-FF<sub>10</sub>EA forms a highly ordered layer structure along the direction of the *c*-axis. In accordance with the previous work, it appears that these long spacing peaks are defined at the (002) reflection<sup>18</sup> because poly-FF<sub>10</sub>EA forms a double layer structure and the calculated length of the fluorocarbon side-chain is examined at approximately 20 Å. Based on computer simulation estimations, the *d*-spacing from the (001) reflection peak of poly-OA was expected to be approximately 50 Å (double layer spacing), although poly-OA did not form the layer structure in the bulk state.

These WAXD profiles indicate the possibility of the structural control of bulky functional groups related to the formation of side-chain crystals and their crystallinity reflected on the peak width. These results contain very important and clear information on the formation of side-chain crystalline polymers with two-dimensional sub-cell structures.

On the basis of these experimental results, we attempt to utilize the ternary comb copolymers containing NVCz units as the material for the formation of monolayers on the water surface. Figure 2 show the surface pressure–area ( $\pi$ -A) isotherms for the monolayers of the NVCz:OA:FF<sub>10</sub>EA ternary copolymers with high and low molecular weights on distilled water at 15 °C. It has been observed that these ternary comb polymer monolayers stabilize considerably and form condensed films. In both molecular weights cases, the monolayers of ternary copolymers with high content of OA relatively exhibit lower collapsed surface pressure,



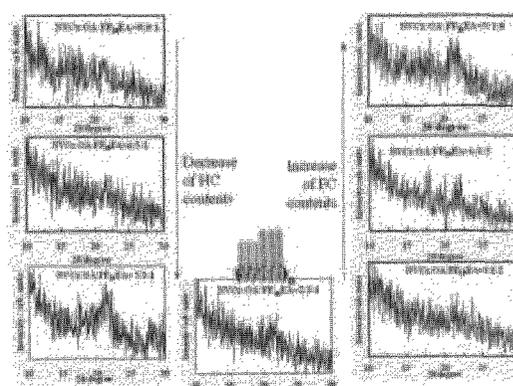
**Figure 3** AFM images of Z-type monolayers of ternary comb copolymers (low molecular weight) containing NVCz.

especially, NVCz:OA:FF<sub>10</sub>EA=6:5:1, and 9:8:1 copolymers. In addition, since distribution of side-chain areas to the monomer ratio was relatively sharp, ternary copolymers with low molecular weight mainly is applied following research of two-dimensional molecular film formation.

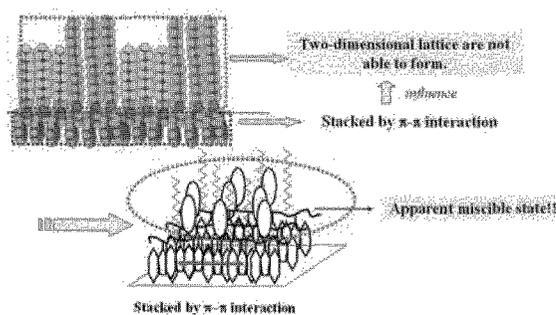
Figure 3 shows the AFM images of Z-type monolayers of ternary comb copolymers with low molecular weight. Generally, hydrogenated and fluorinated component are immiscible with each other. Therefore, these types of copolymer monolayers exhibit the phase-separated surface in many cases.<sup>13</sup> However, monolayers of NVCz:OA:FF<sub>10</sub>EA ternary copolymers show the apparently homogeneous surface.

Figure 4 shows the in-plane X-ray diffraction profiles of LB multilayers (20 layers) of ternary copolymers with low molecular weight containing NVCz. Almost all profiles indicate did not exhibit the clearly peaks. Therefore, it seems that both side-chains do not form the closely packing in the two-dimensional molecular films of the ternary copolymers.

Previously, we reported structural changes in side-chain packing in organized molecular films of NVCz:FF<sub>10</sub>EA binary copolymers.<sup>19</sup> In that case, the spacing of fluorinated side-chains



**Figure 4** In-plane XRD profiles of LB multilayers for ternary comb copolymers (low molecular weight) containing NVCz.



**Figure 5** Schematic models of structural formation for ternary comb copolymers with NVCz.

transit from 5.0 Å to 4.2 Å by the influence of  $\pi$ - $\pi$  stacking of carbazole rings in main-chain. The value of two-dimensional lattice spacing at 4.2 Å is well-corresponding to that of hydrogenated components. One of the origins for immiscibility and phase separation property of hydrogenated and fluorinated component is given as differences in van der Waals forces between each unit although any other reasons maybe exist. Above mentioned binary copolymer case, hydrogenated side-chains packed by strong van der Waals interaction did not receive the  $\pi$ - $\pi$  stacking of carbazole rings in main-chain. The origin of this phenomenon, in this study which indicate formation of apparently homogeneous surface and destruction of two-dimensional lattice in hydrogenated and fluorinated molecular film surface, is caused by  $\pi$ - $\pi$  interaction between carbazole rings to the fluorocarbon units, especially. That is to say, it is suggested that formation of apparently homogeneous surface is brought about by identification of strength for packing forces between hydrogenated and hydrogenated side-chain units. These speculations are shown in Fig. 5.

As mentioned previously, it is possible to control the surface morphologies of the monolayers for copolymers containing functionalised carbazole group arranged by copolymerization with two kinds of long-chain vinyl compounds (resultant ternary comb copolymer) and the method of organized molecular films.

#### 4. CONCLUSION

We investigated the molecular arrangement of mono and multilayers with regard to the three-dimensional crystal structure of newly synthesized ternary comb copolymers with the carbazole group using WAXD,  $\pi$ -A isotherm AFM observation, and in-plane XRD measurements. In the solid state, hydrogenated and fluorinated ternary comb copolymers containing NVCz form side-chain crystals at lattice spacings of 4.2 and 5.0 Å, respectively. It was suggested that the carbazole rings incorporated in the copolymer main-chain were arranged along the *c*-axis as formation of layer structure. The Langmuir monolayers on the water surface of these ternary copolymers formed

extremely condensed monolayers. From the in-plane XRD analysis of multilayers in solids, destruction of two-dimensional lattice is confirmed. AFM images of Z-type monolayer of ternary copolymers show the apparently homogeneous and flat surface. It is suggested that this result is caused by  $\pi$ - $\pi$  stacking of carbazole rings.

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