

## Structural estimation of organized molecular films for comb copolymer containing N-vinylcarbazole

Atsuhiko Fujimori\*, Hiroko Hoshizawa, Ryosuke Masuya, Toru Masuko

Department of Polymer Science and Engineering, Faculty of Engineering, Yamagata University, Yonazawa 992-8510, Japan  
Fax: +81-238-26-3073, e-mail: fujimori@yz.yamagata-u.ac.jp

Molecular orientation in Langmuir-Blodgett (LB) films of newly synthesized ternary comb copolymers with N-vinylcarbazole (NVCz) and fluorinated side-chain was investigated using X-ray diffraction (XRD), differential scanning calorimetry (DSC) surface pressure-area ( $\pi$ -A) isotherm, out-of plane and in-plane XRD, and atomic force microscopy (AFM). The results were compared with those of three-dimensional crystals. In the bulk state, these ternary comb copolymers formed side-chain crystals, which exhibited two-dimensional lattice spacing of 4.2 and 5.0 Å. From the results of the DSC measurements, sharp melting peaks appeared in the relatively lower temperature side in the thermograms. This result supported the formation of side-chain crystals in the synthesized ternary comb copolymers. These copolymers formed extremely condensed monolayers on the water surface. From the out-of plane XRD measurements of multilayers on solids, formation of highly ordered layer structure were confirmed. From the in-plane XRD measurements of these multilayers, the two-dimensional lattice structures of ternary comb copolymer films containing NVCz units were different from that of their bulk state. These structural changes may be caused by the  $\pi$ - $\pi$  interaction between the carbazole rings comparable with the van der Waals interaction between fluorocarbons.

Key words: N-vinylcarbazole, Ternary comb copolymer, Organized molecular film, Molecular orientation, Out-of plane and In-plane X-ray diffraction

### 1. INTRODUCTION

Micro lithography technique at nanometer scale using organic molecules<sup>1</sup> is an important subject for development of new molecular devices. It is well known that characteristic phase separation occurs in the mixed materials containing fluorocarbons and hydrocarbons because of the lack of miscibility.<sup>2</sup> Since Güntherodt, *et al.* reported studies on mixed monolayer system containing fluorinated compounds using friction force microscopy,<sup>3</sup> several mixed systems of fluorinated and hydrogenated compounds in the three-dimensional composites and two-dimensional organized molecular films were widely examined by many investigators. However, it is impossible to pattern the surface on the nanometer length scale in phase-separated systems on this kind, because the hydrogenated domains in the phase-separated structures are generally on the size of a few  $\mu\text{m}$ .<sup>4</sup> This may be caused by co-existence of condensed and expanded phases (island and sea regions) formed by oriented hydrocarbons and unoriented fluorocarbons, respectively, because of the difference in van der Waals interaction between the chains. If this phase separation was available for the surface patterning on the nanometer length scale by changing the monomer ratios on the co-polymerization, it is interesting in the scopes of not only basic science but also nano-technology. Hence, we tried to form monolayers of binary copolymer containing both hydrogenated and fluorinated side-chains in a previous study.<sup>5</sup> These monolayers constructed the surface pattern of the size of a few tens of nanometers. The surface morphologies depended on the side-chain content and mobility

of main-chain.<sup>6</sup>

In addition, many investigators have attempted to utilize poly-N-vinylcarbazole (PNVCz) as organic light emitting diodes, organic transistors, and host compounds for organic electro luminescence<sup>7</sup> because PNVCz exhibits a property identical to that of organic semiconductors.<sup>8</sup> Further, it is expected that PNVCz can be used to realize a hologram memory material because of the high refractive index (1.68) of its monomer.<sup>9</sup>

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 carbazole ring arrangement and packing because PNVCz itself easily forms an amorphous polymer.<sup>10</sup>

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>5</sup> These comb polymers form a side-chain crystal in the bulk state by van der Waals interaction between the side-chains and extremely stable condensed monolayers at the air/water interface.<sup>6</sup> If bulky and flat functional groups are incorporated in the main chain of side-chain crystalline polymers, it may be possible to control the arrangement of bulky groups at the molecular level in spite of the low crystallinity of the polymers.

In this study, fine structures in the solid-state of the synthesized ternary comb polymers containing N-vinylcarbazole (NVCz) in the main-chain obtained by co-polymerization with hydrogenated and fluorinated long-chain

vinyl compounds were investigated by wide-angle X-ray diffraction (WAXD). Further, the molecular arrangement of the organized molecular films in the comb copolymers containing NVCz units were estimated by out-of-plane and in-plane X-ray diffraction (XRD), and atomic force microscopy (AFM).

## 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 several monomer ratios. Copolymerizations were carried out in solutions of acetone at 50 °C for 48 h using 1.0 mol% 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>11</sup> The  $\gamma$ -ray irradiation was carried out at the Japan Atomic Energy Institute at Takasaki. The comb copolymer compositions were determined by <sup>1</sup>H NMR (Nihon Densi Co. Ltd. EX270 NMR) spectroscopy. The tacticity of the fluorinated homopolymer was obtained by <sup>1</sup>H NMR analysis according to the reference and was found to be almost syndiotactic (Diad: 61 %). The molecular weights of several copolymers with higher ratios of OA units were estimated to be approximately  $M_w = 3.39 \times 10^4$  ( $M_w/M_n \approx 1.18$ ) on the basis of GPC (JASCO-860-CO) measurement. The molecular weights of the fluorinated homopolymers and the copolymers with higher ratios of FF<sub>10</sub>EA units were estimated to be above a 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>12</sup>

According to the theory of the Q-e scheme proposed by T. Alfry and C.C. Price,<sup>13</sup> these comb polymers form alternating copolymers. In this case, the  $e$  values of NVCz and OA are  $-1.40$  and  $+1.12$ , respectively. Thus, the NVCz:long-chain acrylate copolymers form almost ideal alternating copolymers, especially at the 1:1 monomer ratio.

### 2.2 Structural estimation of bulk copolymers.

Thermal analyses were carried out by using a Seiko Instruments model DSC200 differential scanning calorimeter (DSC). The DSC measurements were performed at a standard scanning rate of 10.0 °C min<sup>-1</sup>.

The packing modes of several copolymers in the crystalline phase 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 ternary comb copolymer with NVCz were spread from the chloroform or chloroform/trifluoroacetic acid = 90/10 (v/v) mixed solutions (about 10<sup>-4</sup> 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 Å<sup>2</sup>/repeating units. min) at 15 °C. These fluorinated 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), and surface lowering method (SLM) to obtain alternating Y-type films and nonalternating Z-type films, respectively.

The in-plane spacing of the two-dimensional lattice of the films was determined by analysis using an X-ray diffractometer for different geometrical arrangements<sup>14</sup> (Bruker AXS, MXP-BX, CuK $\alpha$  radiation, 40 kV, 40 mA, an instrument specially made to order) equipped with a parabolic graded multilayer mirror. The monomolecular level resolution of this in-plane XRD apparatus was realized by applying the X-ray at an incident angle of 0.2° and by slow scanning at 0.05°/20 s.

## 3. RESULTS AND DISCUSSION

### 3.1 Estimation of fine structures for ternary comb copolymers in bulk state.

Figure 1 shows the WAXD profiles of the ternary comb copolymers containing NVCz with several side-chain ratios. From these profiles, interesting systematic changes were confirmed in the short-spacing region, which depended on the

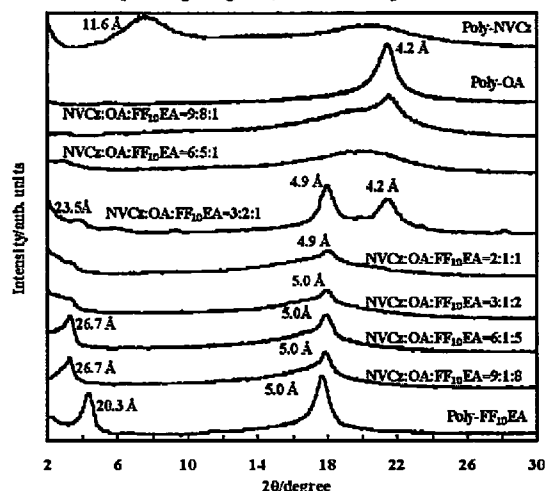


Figure 1 WAXD profiles of ternary comb copolymers containing NVCz with several ratios.

side-chain ratios. We concluded that PNVCz forms an amorphous polymer because of the appearance of two types of halos and the absence of a peak.

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 Å, respectively. According to Platé's review, these peaks correspond to (100) reflection.<sup>15</sup> In the case of copolymers, especially NVCz:OA:FF<sub>10</sub>EA=3:2:1, two kinds of short spacing peaks of side-chains were commonly confirmed at 4.2 and 5.0 Å. In the present work, these peaks were defined as H(100) and F(100) reflections. These peaks should be assigned to the structure in the different region of ternary copolymer crystal because these values agree well with the in-plane lattice spacings of sub-cells for the homopolymers. This means that fluorinated and hydrogenated side-chains are separately packed in the phase-separated domains.

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, these long spacing peaks are defined at the (002) reflection<sup>11</sup> because poly-FF<sub>10</sub>EA forms a double layer structure and the calculated length of the fluorocarbon side-chain is approximately 20 Å. Although computers suggest that the d-spacing from the (001) reflection peak of poly-OA should be approximately 50 Å (double layer spacing), poly-OA did not form a layer structure. Further, the intensity of the H(100) reflection (4.2 Å) gradually decreased with an increase in the OA ratio, and the intensity of the F(100) reflection (4.9 ~ 5.0 Å) gradually decreased with an increase in the FF<sub>10</sub>EA ratio. In the case of the NVCz:OA:FF<sub>10</sub>EA=3:2:1 ternary copolymers, both of the (100) reflections appeared in the profile. Both hydrogenated and fluorinated side-chain crystals in these copolymers form closest packing structures in all the copolymers used in this study.

These XRD profiles indicate the possibility of structural control of bulky functional groups using the crystallization of side-chains, with their crystallinity reflected in 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.

### 3.2 Molecular arrangement of organized molecular films for ternary comb copolymers.

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 water. Figure 2 show the surface  $\pi$ -A isotherms for the copolymer monolayers, on distilled water at

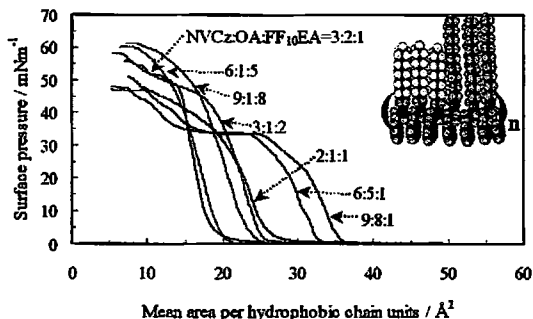


Figure 2  $\pi$ -A isotherms of monolayers on the water surface of ternary comb copolymers at 15 °C.

15 °C. It has been observed that these ternary comb copolymer monolayers are stabilized considerably and form condensed films.

Figure 3 shows the out-of plane X-ray diffraction profiles of several transferred films (20 layers) of ternary comb copolymers containing NVCz. These profiles indicate the formation of layer structure in the organized molecular films of the copolymer systems. The LB films of these ternary copolymers formed highly order layer structure. In the case of fluoro-side-chain rich region in Fig. 3(a), peak intensity and values of (001) spacing (in other words, "c-axis length" or "long spacing") decreased with a decrease in fluorocarbon content. In the case of hydrocarbon rich region in Fig. 3(b), long spacing peaks shifted to the lower angle side with increasing hydrogenated side-chain ratio.

On the other hand, from the result of in-plane XRD measurements, only one short spacing peak was confirmed at 4.2 Å, which in usual casts suggest the formation of hydrogenated hexagonal sub-cell. In addition, surface morphologies of these copolymer monolayers

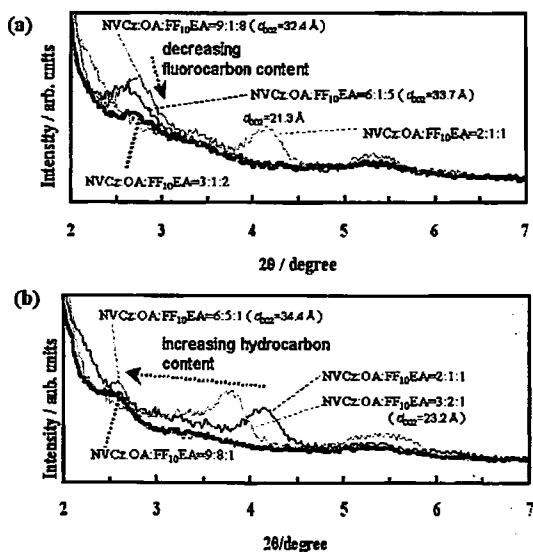


Figure 3 Out-of plane XRD profiles of multilayers for NVCz : OA : FF<sub>10</sub>EA ternary copolymers transferred by Langmuir-Blodgett method (20 layers). (a) NVCz : OA : FF<sub>10</sub>EA = 2 : 1 : 1, 3 : 1 : 2, 6 : 1 : 5, 9 : 1 : 8, (b) NVCz : OA : FF<sub>10</sub>EA = 2 : 1 : 1, 3 : 2 : 1, 6 : 5 : 1, 9 : 8 : 1.

observed by AFM did not exhibit phase-separated structures, but relatively flat and homogenous surface.

In order to interpret these phenomena, we referred to example of NVCz:FF<sub>10</sub>EA binary copolymer LB films.<sup>16</sup> In the case of a copolymers with high FF<sub>10</sub>EA ratios in this system, hexagonal packing was formed at a lattice spacing of 5.0 Å. The in-plane XRD profile of the NVCz:FF<sub>10</sub>EA=1:1 copolymer films exhibits two kinds of short spacing peaks at 4.2 and 5.0 Å. From this result, it is inferred that distorted orthorhombic packing of a side-chain lattice is formed. Further, in the case of high NVCz ratios, an isotropic hexagonal packing for a in-plane lattice spacing of 4.2 Å is constructed although the value of 4.2 Å is generally too narrow to pack fluorocarbons in lattice.

It is assumed that the structural changes in fluoro-copolymer are caused due to the competition between the forces formed in a two- or three-dimensional crystal, namely, the "weak van der Waals interaction between fluorocarbons" and the "relatively strong  $\pi$ - $\pi$  interaction between carbazole rings." Binary fluoro-copolymer molecules are rearranged by the  $\pi$ - $\pi$  interaction between the carbazole rings at the moment when a transfer to the solid substrate occurs. Consequently, it appears that the side-chain packing changes with the rearrangement of the carbazole groups. The most suitable spacing between the carbazole groups for the  $\pi$ - $\pi$  interaction to work is probably 4.2 Å, which is identical to the value of the spacing between the hydrogenated side-chain crystals.

Hence, in the case of NVCz:OA:FF<sub>10</sub>EA ternary copolymers, the value of in-plane spacing is 4.2 Å only, and phase-separated structures of hydrogenated and fluorinated regions do not form. We assume that van der Waals interaction between hydrocarbons,  $\pi$ - $\pi$  interaction between the carbazole rings and van der Waals interaction between fluorocarbons are comparable with each other. This may be the reason of the formation of flat and homogeneous surface.

In Fig. 4, we summarized our interruptions as the schematic models.

#### 4. CONCLUSION

We investigated the molecular arrangement of mono and multilayers of newly synthesized ternary comb copolymers with the carbazole group using WAXD,  $\pi$ -A isotherm, out-of and in-plane XRD, and AFM. The structures were compared with those of three-dimensional crystals. In the solid state, ternary comb copolymers containing NVCz form side-chain crystals. The Langmuir monolayers on the water surface of these copolymers formed extremely condensed monolayers. From the out-of plane XRD analysis of multilayers in solids, formation of highly ordered layer structure were confirmed. These copolymer monolayers form the relatively homogenous surface with in-plane lattice spacing of 4.2 Å (hexagonal),

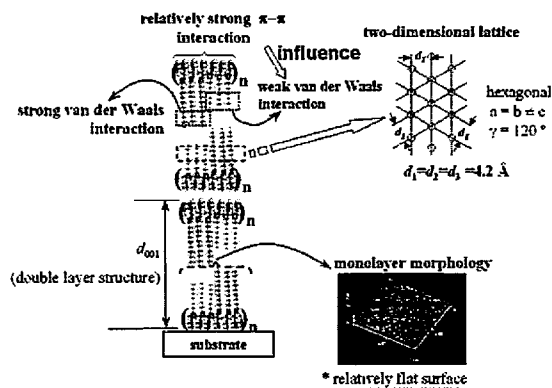


Figure 4 Schematic models of structural formation for ternary comb copolymers with NVCz.

which may be due to the  $\pi$ - $\pi$  interaction between the carbazole rings comparable with the van der Waals interaction between the fluorocarbon side-chains.

#### REFERENCES

- [1] V. K. Gupta, N. L. Abbott, *Science*, **6**, 276 (1997).
- [2] R. M. Overney, E. Meyer, J. Frommer, H. -J. Güntherodt, *Langmuir*, **10**, 1281 (1994).
- [3] R. M. Overney, E. Meyer, J. Frommer, D. Brodbeck, R. Luthi, L., Höwald, L., H. -J. Güntherodt, H. Fujihira, H. Takano, Y. Gotoh, *Nature*, **359**, 133 (1992).
- [4] T. Imae, T. Takeshita, M. Kato, *Langmuir*, **16**, 612 (2000).
- [5] R. Masuya, N. Ninomiya, A. Fujimori, H. Nakahara, T. Masuko, *J. Polym. Sci., Part B, Polym. Phys.*, **44**, 416 (2006).
- [6] A. Fujimori, R. Masuya T. Masuko, E. Ito, M. Hara, K. Kanai, Y. Ouchi, K. Seki, H. Nakahara, *Polym. Adv. Technol.*, **17**(9-10), 653 (2006).
- [7] J. M. Pearson, M. Stolka, "Poly(*N*-vinylcarbazole)" in Polymer monograph, vol. 6, New York: Gordon and Breach, (1981).
- [8] K. R. Choudhury, M. Samoc, A. Patra, P. N. Prasad, *J. Phys. Chem. B*, **108**(5), 1556, (2004).
- [9] M. T. R. Laguna, J. Gallego, F. Mendicuti, E. Saiz, M.P. Tarazona, *Macromolecules*, **35**(20), 7782, (2006).
- [10] C. Maertens, P. Dubois, R. Jerome, P.A. Blanche, P.C. Lemaire, *J. Polym. Sci., Part B, Polym. Phys.*, **38**(1), 205, (2000).
- [11] A. Fujimori, H. Saitoh, and Y. Shibasaki, *J. Thermal. Anal.*, **57**, 631, (1999).
- [12] J. G. Fee, W. S. Port, L. P. Witnauer, *J. Polym Sci.*, **33**, 95, (1958).
- [13] T. Alfrey, C. C. Price, *J. Polym. Sci.*, **2**, 101, (1947).
- [14] A. Fujimori, Y. Sugita, H. Nakahara, E. Ito, M. Hara, N. Matsuie, K. Kanai, Y. Ouchi, K. Seki, *Chem. Phys. Lett.*, **387**, 345, (2004).
- [15] N. A. Platé, V. P. Shibaev, *J. Polym. Sci., Macromol. Rev.*, **8**, 117, (1974).
- [16] H. Hoshizawa, R. Masuya, T. Masuko, A. Fujimori, *Trans. Mater. Res. Jpn*, **32**, (2007) to be submitted for publication.