Transactions of the Materials Research Society of Japan 33[1] 75-78 (2008)

Structural Control of Functionalized Groups in Organized Molecular Films of Comb Copolymers

Atsuhiro Fujimori*, Hiroko Hoshizawa, Ryoko Kobayashi and Natsuki Sato
Graduate School of Science and Engineering., Yamagata University, Yonazawa, Yamagata, 992-8510, Japan
Fax: +81-238-26-3073, e-mail: fujimori@yz.yamagata-u.ac.jp

Orientation for functional carbazole groups in comb copolymers were controlled using co-polymerization with long-chain vinyl compounds and the method of organized molecular films. Their structures were estimated using in-plane X-ray diffraction (XRD) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. In the bulk state, fluorinated comb copolymers form side-chain crystal at a two-dimensional lattice spacing of 5.0 Å. From the in-plane XRD measurements of multilayers on solids, the two-dimensional lattice structures of fluorinated comb copolymer films containing NVCz units were different from those in their bulk states. Polarized NEXAFS measurements showed highly ordered orientation of carbazole groups in the films. This well-ordered arrangement of functional groups should be caused by the π–π interaction between the carbazole rings.

Key words: Organized molecular films, Comb copolymer. N-vinylcarbazole, in-plane X-ray diffraction, NEXAFS spectroscopy

1. INTRODUCTION

Many researches have attempted to utilize poly-N-vinylcarbazole (poly-NVCz) as organic light emitting diodes, organic transistors, and host compounds for organic electroluminescence[1-3] in recent years because poly-NVCz exhibits properties identical to those of organic semiconductors.[4] Undoubtedly, poly-NVCz is an excellent functional polymer with abilities of blue fluorescence based on carbazole excimer, high hole mobility, high refractive index of its monomer unit and so on.

It is essential to accurately control the molecular alignment at the molecular 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 orientation of functional groups in the homopolymer because poly-NVCz itself easily forms an amorphous polymer.[5] If bulky and flat functional groups such as carbazole rings are incorporated in the amorphous main-chains of side-chain crystalline polymers, it will be possible to control the arrangement of bulky functional groups at the molecular level. In this study, we try to arrange the bulky carbazole groups in the organized films of comb copolymers. Fine structures in the solid-state of newly synthesized comb copolymers containing N-vinylcarbazole (NVCz) in the main-chains obtained by co-polymerization with fluorinated long-chain compounds were investigated by X-ray diffraction (XRD) in both three-dimensional crystals and two-dimensional molecular films. Further, the arrangement of carbazole rings of comb copolymers in two-dimensionally organized molecular films were estimated by polarized near-edge X-ray absorption fine structure (NEXAFS) spectroscopy.

2. EXPERIMENTAL

The comb copolymers used in this study were obtained by the co-polymerization of NVCz with 2-(perfluorodecyl)ethyl acrylate ($FF_{10}EA$) at various monomer ratios. Co-polymerization was carried out in an acetone solution at 50 °C for 48 h using 1.0 mol% azobisisobutyronitrile as an initiator. The comb copolymer compositions were determined by ^{1}H NMR spectroscopy. The tacticity of fluorinated homopolymer obtained by ^{1}H NMR analysis according to the reference was found to be almost syndiotactic (Diad: 58 %).[6] The average molecular weights of several copolymers were estimated to be approximately $Mw = 4.65 \times 10^4$ ($Mw/Mn \approx 1.96$) on the basis of GPC measurements. According to the theory of the Q-e scheme proposed by Alfrey and Price,[7] these comb polymers form alternating copolymers. The packing modes of several copolymers in the bulk state were examined by powder XRD measurements. At the air/water interface, these fluorinated comb copolymers formed extremely condensed monolayers.[8] These monolayers were transferred to the solid substrates at 15 °C and at a proper surface pressure by the Langmuir-Blodgett (LB) method to obtain alternating Y-type films. The in-plane spacings of the two-dimensional lattices of the films were determined by analyses using an in-plane XRD diffractometer equipped with a parabolic graded multilayer mirror.[9,10] NEXAFS spectra[11] were measured on the BL-7A soft X-ray beamlines in the National Laboratory for High-Energy Accelerator Research Organization (KEK-PF) with synchrotron radiation from a bending-magnet source.[12-14]

3. RESULTS AND DISCUSSION

Figure 1 shows the powder XRD profiles

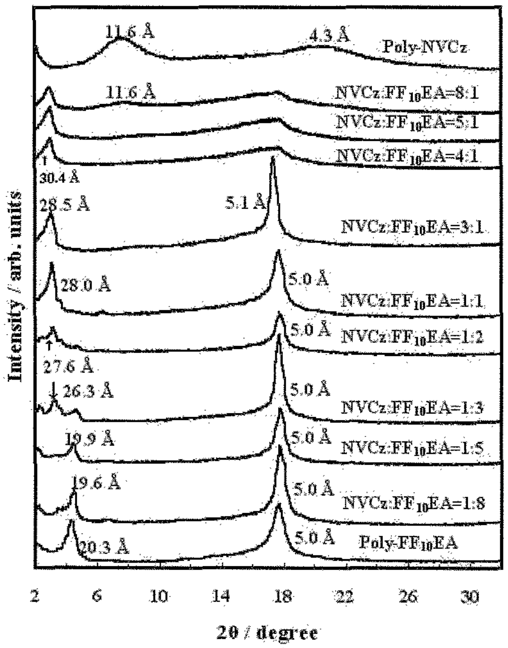

Figure 1 WAXD profiles of fluorinated comb copolymers.

of NVCz:$FF_{10}EA$ copolymers in bulk. From the result of this measurement, it is concluded that PNVCz forms an amorphous polymer judging from the appearance of two types of halos and the absence of any peaks. We consider that the halo around 4.3 Å corresponds to the distance between carbazole rings, and the one around 11.6 Å to the distance between two carbazole units along the ring diameter direction in the atactic PNVCz.

Further, from the profiles of poly-$FF_{10}EA$, short spacing peaks based on the sub-cell formation of side-chains were confirmed at 5.0 Å. According to Platé's review, these peaks correspond to the (100) reflections.[15] These reflections around 20 degrees indicate the presence of two-dimensional lattices formed by side-chains.[16,17] NVCz:$FF_{10}EA$ = 1:1 copolymer also shows a (100) reflection. These findings indicate that these comb copolymers including NVCz unit form side-chain crystals in bulk.

Figure 2 shows the in-plane XRD profiles of the LB films (20 layers) of comb copolymers containing NVCz. These profiles indicate the packing mode of side-chains in the two-dimensional films of the copolymer systems. Organized molecular films of almost all NVCz:$FF_{10}EA$ copolymers show packing modes different from those in their bulk states. In the case of copolymers at high $FF_{10}EA$ ratios, hexagonal packing was formed at a lattice spacing of 5.0 Å. However, the in-plane XRD profile of an NVCz:$FF_{10}EA$ = 1:1 copolymer film exhibits two kinds of short spacing peaks at 4.2 and 5.0 Å. From these results, it is inferred that a distorted orthorhombic packing of a side-chain lattice is formed. At high NVCz ratios, isotropic hexagonal packing at a two-dimensional lattice spacing of 4.2 Å is constructed although the value of 4.2 Å is generally too small to pack fluorocarbons in lattice.

In order to interpret these phenomena, we propose models schematically shown in Fig. 2. we assume that the structural changes in fluorocopolymers are caused due to the competition between the forces that are effective in two- and/or three-dimensional crystals, namely, the "weak van der Waals interaction between fluorocarbons" and the "relatively strong π–π interaction between carbazole rings."[8] In the monolayers of amphiphiles having fluorocarbon as hydrophobic chains, the van der Waals force is relatively weak. Therefore, these polymer molecules should be rearranged by the π–π interaction between the carbazole rings at the air-water interface or during the transfer to the solid substrates, especially at high NVCz rates. The side-chain packing should change with the

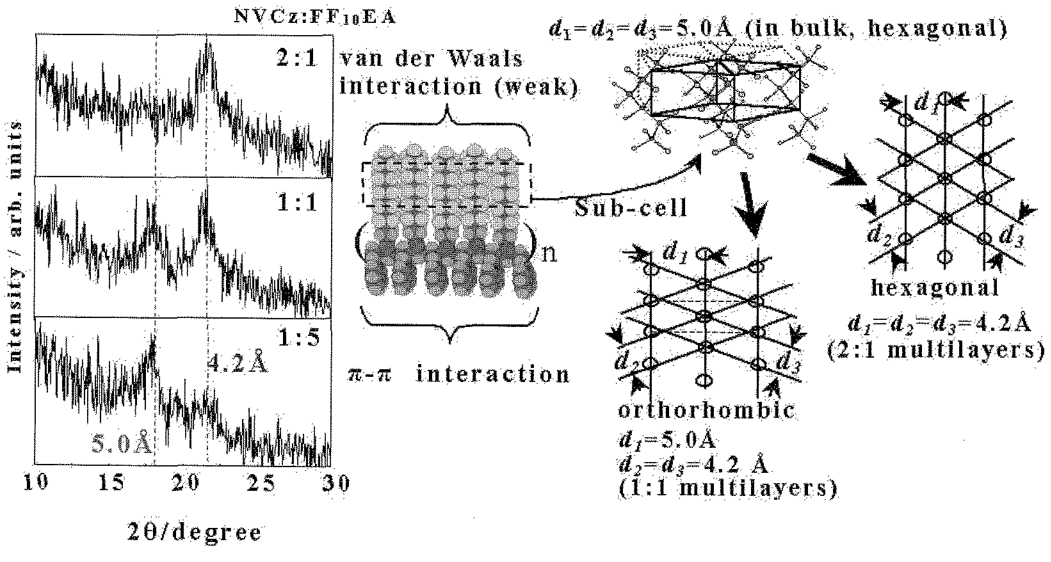

Figure 2 In-plane XRD profiles of the LB films of comb copolymers and schematic models of changes in two-dimensional lattices of their side-chains.

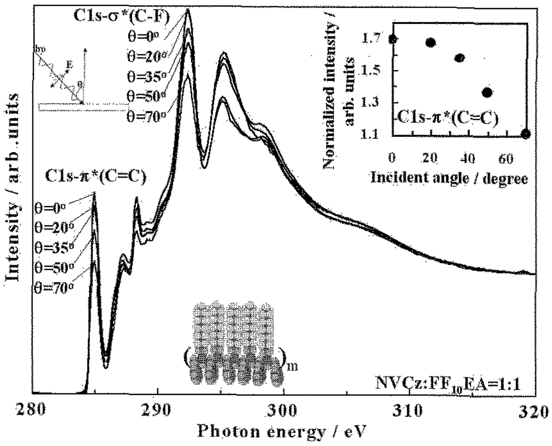

Figure 3 Polarized NEXAFS spectra of the LB film of NVCz: $FF_{10}EA$ = 1:1 copolymer (inset; plots of normalized intensity *vs*. incident angle).

rearrangement of the carbazole groups. The spacing between the carbazole groups most suitable for the π–π interaction should be 4.2~4.3 Å, which is supported by XRD in bulk.

Figure 3 shows the dependence of the angle of incidence on the C K-edge NEXAFS spectra of the LB film of NVCz: $FF_{10}EA$=1:1 copolymer in order to directly examine the orientation of carbazole rings. The NEXAFS spectra of the C1s to π*(C=C) transition strongly depend on the incident angle. Since the C=C bond exists in only the carbazole rings, the dependence of this transition reflects regular arrangement of the carbazole rings. This peak at 285.5 eV reachs a maximum at the grazing incidence and is weakened at normal incidence. This clear dependence of the C1s to π* transition indicates highly ordered orientation of the carbazole groups with a nearly perpendicular orientation of the π* orbital. The inset in the upper right of Figure 3 shows the plots of the normalized peak intensity *vs*. the incident angle. Regular arrangement of the functional group is evident.

Figure 4 shows the estimation of the orientation angles of the carbazole group and fluorinated side-chains in an NVCz:$FF_{10}EA$=1:1 copolymer monolayer from the polarized C K-edge NEXAFS spectra. Assuming the uniaxial orientation, the orientation angle of the carbazole group is determined by fitting the dependence of the normalized intensity (Fig. 4(a)). Assuming also the tilt angle 14.3° of the $-CF_2$ plane with respect to the perpendicular direction of the molecular axis of the fluorocarbon (resultant 13/6 helical conformation), the orientation angle of the fluorinated side-chains is determined (Fig. 4(b)). The carbazole group and the fluorinated side-chains in this copolymer LB film should be tilted about by 15° and 45° with respect to we can the surface normal, respectively.

As mentioned previously, we can control the orientation of the functionalized carbazole group using co-polymerization with long-chain vinyl compounds (resultant comb copolymer) and the method of organized films. The methods used in this study lead directly to control of both chemical and crystal structures from the sub-nanometer size. Refer to our other reports related to morphology of this film and results of hydrogenated comb polymer films.[8] From experimental results in these studies, these copolymers and their organized films are expected to be used as a new functional polymer nano-material.

CONCLUSION

Molecular arrangement of monolayers and multilayers related to three-dimensional crystal structures of newly synthesized comb copolymers having carbazole groups was investigated by in-plane XRD, and NEXAFS spectroscopy. In the solid-state, hydrogenated and fluorinated comb copolymers containing NVCz have formed side-chain crystals at 4.2 and 5.0 Å lattice spacings, respectively. The incorporated carbazole rings in main-chain were arranged perpendicularly to the film plane. LB films of these copolymers consist of extremely condensed monolayers except for a fluorocarbon : NVCz = 1:1 copolymer. From the in-plane XRD of multilayers on solids, two-dimensional lattice structures of fluorinated comb copolymers containing NVCz units were different from those in the bulk states. These structural changes should be caused by the π–π interaction between the carbazole rings than the van der Waals interaction between the fluorocarbon side-chains.

ACKNOWLEDGEMENTS

The authors thank Prof. K. Seki of Nagoya Univ. and Prof. K. Amemiya of KEK-PF for help in NEXAFS measurements. This work was performed under approval of the Photon Factory Program Advisory Committee (proposal No. 2004G322 and 2006G060).

REFERENCES

[1] H. Hoegl and *J. Phys. Chem.*, **69**, 755 (1965).
[2] J. M. Pearson, M. Stolka, "*Poly(N-vinylcarbazole)*" in Polymer monograph, vol. 6, New York: Gordon and Breach, 1981.
[3] R. Ragni, E. A. Plummer, K. Brunner, J. W. Hofstraat, F. Babudri, G. M. Farinola, F. Naso and L. De Cola, *J. Mater. Chem.*, **16**, 1161 (2006).
[4] V. N. Mylnikov, *Adv. Polym. Sci.*, **115**, 1 (1994).
[5] C. Maertens, P. Dubois, R. Jerome, P. A. Blanche and P. C. Lemaire, *J. Polym. Sci., Part B, Polym. Phys.*, **38**, 205 (2000).
[6] K. Yamada, T. Nakano and Y. Okamoto, Y., *Polym. J.*, **30**, 641 (1998).
[7] T. Alfrey and C. C. Price, *J. Polym. Sci.*, **2**, 101 (1947).
[8] H. Hoshizawa, R. Masuya, T. Masuko and A. Fujimori, *Polym. Adv. Technol.*, **18**, 353 (2007).
[9] A. Fujimori, Y. Sugita, H. Nakahara, E. Ito, M. Hara, N. Matsuie, K. Kanai, Y. Ouchi and K. Seki, *Chem.*

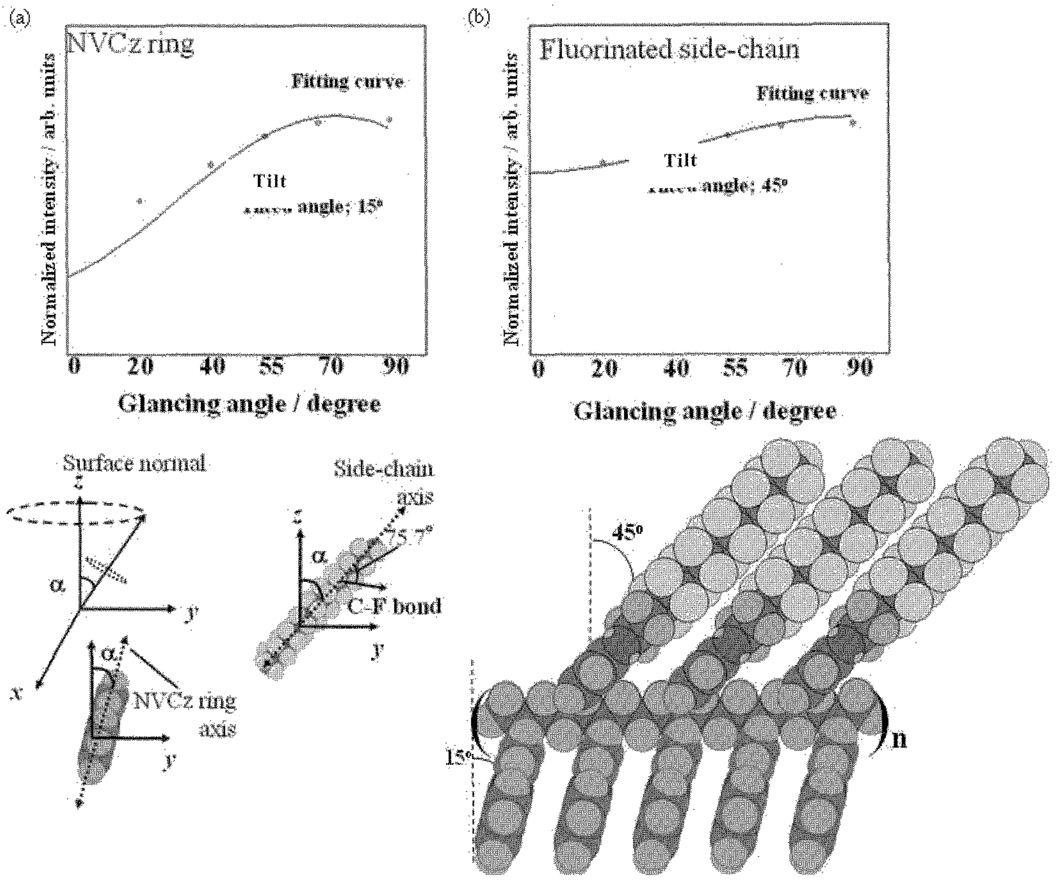

Figure 4 **Estimation of orientation angle for (a) carbazole group and (b) fluorinated side-chains in monolayer of NVCz: $FF_{10}EA$ = 1:1 copolymer, and schematic illustration.**

Phys. Lett., **387**, 345 (2004).
[10] A. Fujimori, T. Araki, H. Nakahara, E. Ito, M. Hara, K. Kanai, Y. Ouchi and K. Seki, *Chem. Phys. Lett.*, **349**, 6 (2001).
[11] J. Stöhr, "*NEXAFS Spectroscopy*", Springer, Berlin, 1992.
[12] K. Seki, R. Matsumoto, E. Ito, T. Araki, T. Sakurai, D. Yoshimura, H. Ishii, Y. Ouchi, T. Miyamae, T. Narita, S. Nishimura, Y. Takata, T. Yokoyama, T. Ohta, S. Suganuma, F. Okino and H. Touhara, *Mol. Cryst. Liq. Cryst.*, **355**, 247 (2001).
[13] A. Fujimori, T. Araki, H. Nakahara, E. Ito, M. Hara, N. Matsuie, H. Ishii, Y. Ouchi and K. Seki, *Bull. Chem. Soc. Jpn.*, **76**, 663 (2003).
[14] A. Fujimori, T. Araki, H. Nakahara, E. Ito, M. Hara, H. Ishii, Y. Ouchi and K. Seki, *Langmuir*, **18**, 1437 (2002).
[15] N. A. Platé and V. P. Shibaev, *J. Polym. Sci., Macromol. Rev.*, **8**, 117 (1974).
[16] K. Inomata, Y. Sakamaki, T. Nose and S. Sasaki, *Polym. J.*, **28**, 986 (1996).
[17] A. Fujimori, H. Saitoh and Y. Shibasaki, *J. Therm. Anal.*, **57**, 631 (1999).

(Received December 5, 2007;Accepted Febrary 15, 2008)