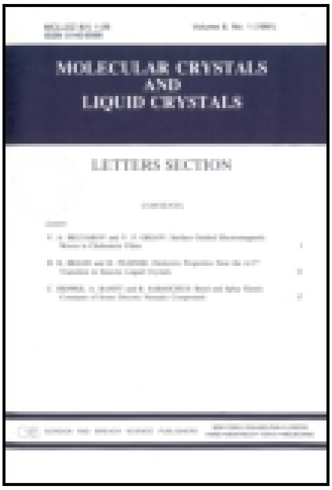
This article was downloaded by: [University Of Gujrat]
On: 11 December 2014, At: 13:55
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

NEXAFS Study on Photoalignment of Liquid Crystalline Polymeric Films

Nobuhiro Kawatsuki[a], Yonosuke Inada[a], Kohei Goto[a], Mizuho Kondo[a], Yuichi Haruyama[b] & Shinji Matsui[b]

[a] Department of Materials Science and Chemistry, Graduate School of Engineering, University of Hyogo, Hyogo, Japan

[b] Laboratory of Advanced Science and Technology for Industry, University of Hyogo, Kamigori, Ako, Hyogo, Japan

Published online: 06 Dec 2014.

To cite this article: Nobuhiro Kawatsuki, Yonosuke Inada, Kohei Goto, Mizuho Kondo, Yuichi Haruyama & Shinji Matsui (2014) NEXAFS Study on Photoalignment of Liquid Crystalline Polymeric Films, Molecular Crystals and Liquid Crystals, 601:1, 49-56, DOI: 10.1080/15421406.2014.940492

To link to this article: http://dx.doi.org/10.1080/15421406.2014.940492

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Mol. Cryst. Liq. Cryst., Vol. 601: pp. 49–56, 2014
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2014.940492

NEXAFS Study on Photoalignment of Liquid Crystalline Polymeric Films

NOBUHIRO KAWATSUKI,[1,*] YONOSUKE INADA,[1]
KOHEI GOTO,[1] MIZUHO KONDO,[1] YUICHI HARUYAMA,[2]
AND SHINJI MATSUI[2]

[1]Department of Materials Science and Chemistry, Graduate School of Engineering, University of Hyogo, Hyogo, Japan
[2]Laboratory of Advanced Science and Technology for Industry, University of Hyogo, Kamigori, Ako, Hyogo, Japan

Polarization-dependent near-edge X-ray absorption fine structure (NEXAFS) measurement is performed to investigate orientation structures of the near-surface of the reoriented photo-cross-linkable liquid crystalline polymer (PMCB6M) films, which are applicable to liquid crystal (LC) alignment layer. The 3D orientation parameter at the near-surface of the reoriented PMCB6M film is ∼0.7, which is similar to the results obtained by a polarization absorption spectroscopy that evaluates the reorientation behavior in bulk. Furthermore, more preferable in-plane orientation is observed at the nearest surface of the film, and the phenyl rings in the reoriented mesogenic side groups show slightly perpendicular orientation to the surface normal.

Keywords Photoalignment; NEXAFS; photoinduced orientation; liquid crystals; LC alignment

Introduction

The photoalignment technique has received much attention in liquid crystal display (LCD) industries because of its free of dust and static electricity, and patternable ability, and it can replace conventional mechanical rubbing and stretching method [1–3]. For the photoalignment layer for low-molecular-weight LCs, photosensitive polymeric films are generally irradiated with linearly polarized (LP) light to accomplish a small optical anisotropy based on an axis-selective photoreaction [4]. Many photosensitive materials including cinnamate ester [4–8], cinnamic acid [9, 10], and azobenzene-containing polymers [11–13] have been investigated for the LC alignment layers.

For the uniaxial LC alignment on the photoalignment layer, an anisotropic interaction at an interface between LC molecules and the photoalignment layer determines the LC orientation direction. Namely, the photoinduced small optical anisotropy controls the LC alignment behavior. However, most of the photoalignment layers do not exhibit

---

[*] Address correspondence to Nobuhiro Kawatsuki, Department of Materials Science and Chemistry, Graduate School of Engineering, University of Hyogo, 2167 Shosha Himeji, Hyogo, 671-2280, Japan. Tel.: +81-79-267-4886; Fax: +81-79-267-4885. E-mail: kawatuki@eng.u-hyogo.ac.jp

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

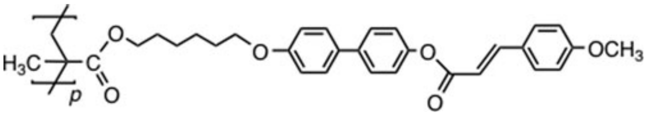


Figure 1. Chemical structure of PMCB6M.

molecular orientation of the film. Therefore, the azimuthal LC anchoring on the common photoalignment film such as poly(vinyl cinnamate) is much smaller than that of conventional rubbed polyimide film [14]. In contrast, we have carried out systematic studies on thermally enhanced photoinduced molecular reorientation in photosensitive liquid crystalline polymeric materials based on the axis-selective photoreaction combined with the thermal self-organization [15–18]. Among them, a polymethacrylate comprised of cinnamate derivative side groups (PMCB6M; Fig. 1) exhibited sufficient photoinduced molecular reorientation, and was applicable to photoalignment layer for LCs with larger azimuthal LC anchoring [19].

Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy provides an elucidation of the near-surface ($<$10 nm) structure of polymeric films, which evaluates resonances from transitions from the 1s core revel to π^* and σ^* orbitals. Carbon 1s NEXAFS spectra of several kinds of polymeric films, including polyurethanes [20], polyesters [21], and conjugated polymers [22], were investigated to determine the composition of materials. Furthermore, the orientation structure of near-surface structure

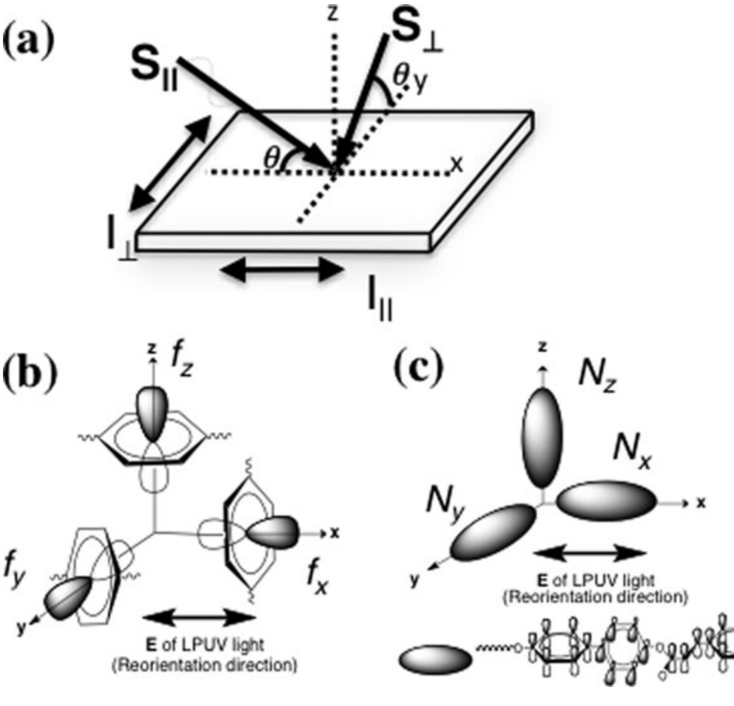


Figure 2. (a) Experimental geometry for measurement of angular dependence of NEXAFS. (b) Illustration of orientation factors (f_x,f_y,f_z), that show orthogonally located phenyl rings. (c) Illustration of fractional number of side group segments N_x, N_y, and N_z derived from three orientation factors.

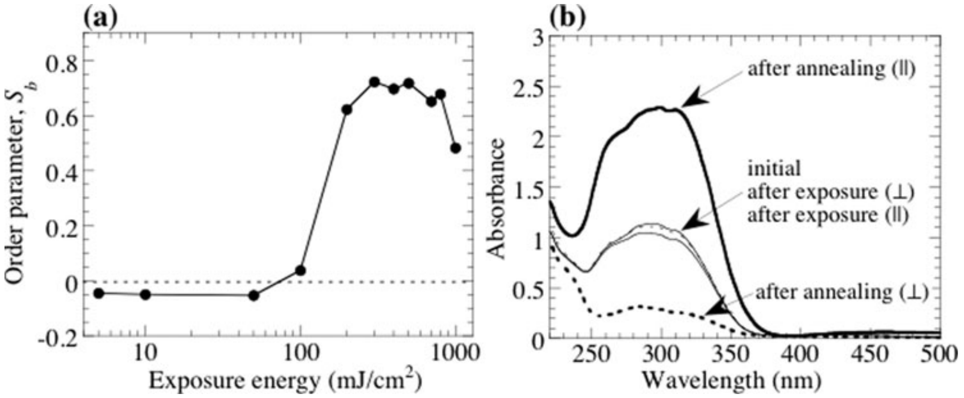


Figure 3. (a) Thermally enhanced S_b values of PMCB6M films as a function of exposure energy. Annealing temperatures: 180°C. (b) Change in the polarization UV-vis polarization spectrum of a PMCB6M film before photoirradiation for 300 mJ/cm^2 after subsequent annealing at 180°C for 10 min (thick lines). Solid line represent $A_{\parallel}$, while dotted lines show $A_{\perp}$.

in an oriented film can be evaluated because the resonances depend on the polarization and incident angle of the X-ray, where the synchrotron radiation X-ray is linearly polarized [22–25].

In case of the LC alignment, a near-surface structure of the alignment layer is most important because the LC alignment ability depends on the interaction at the interface. Several studies have been carried out to determine a molecular orientation at the surfaces of the rubbed polyimide and polystyrene films using NEXAFS spectroscopy, where the near-surface of the rubbed film reveals high orientation structure [23–25]. For the photoalignment layer of PVCi film, molecular orientation of the film was scarcely observed [26]. In contrast, the reoriented PMCB6M film exhibits an improved azimuthal anchoring for the LC alignment as compared to the conventional PVCi photoalignment film due to its molecularly oriented structure [17, 19]. However, the reoriented structure of the film near-surface of reoriented PMCB6M films have yet to be investigated. In this context, NEXAFS spectroscopy was performed to evaluate the near-surface orientation of molecularly reoriented PMCB6M films.

Experimental

Materials and Film Preparation

PMCB6M ($M_n = 39{,}000$, $M_w/M_n = 2.8$) was synthesized according to the literature [17]. Thin films were prepared by spin-coating a methylene chloride solution of PMCB6M (1 wt/wt-%) onto quartz or ITO-coated glass substrates. The film thickness was approximately 170 nm. The film was irradiated with a linearly polarized (LP) UV light from a high-pressure Hg lamp with a cut-off filter under 300 nm that was passed through Gran-Taylor polarizing prisms. The light intensity was 50 mW/cm^2 at 365 nm. For the thermally enhanced molecular reorientation, the irradiated film was annealed at 180°C for 10 min [16, 17]. The generated optical anisotropy of the film was measured by polarization UV-vis

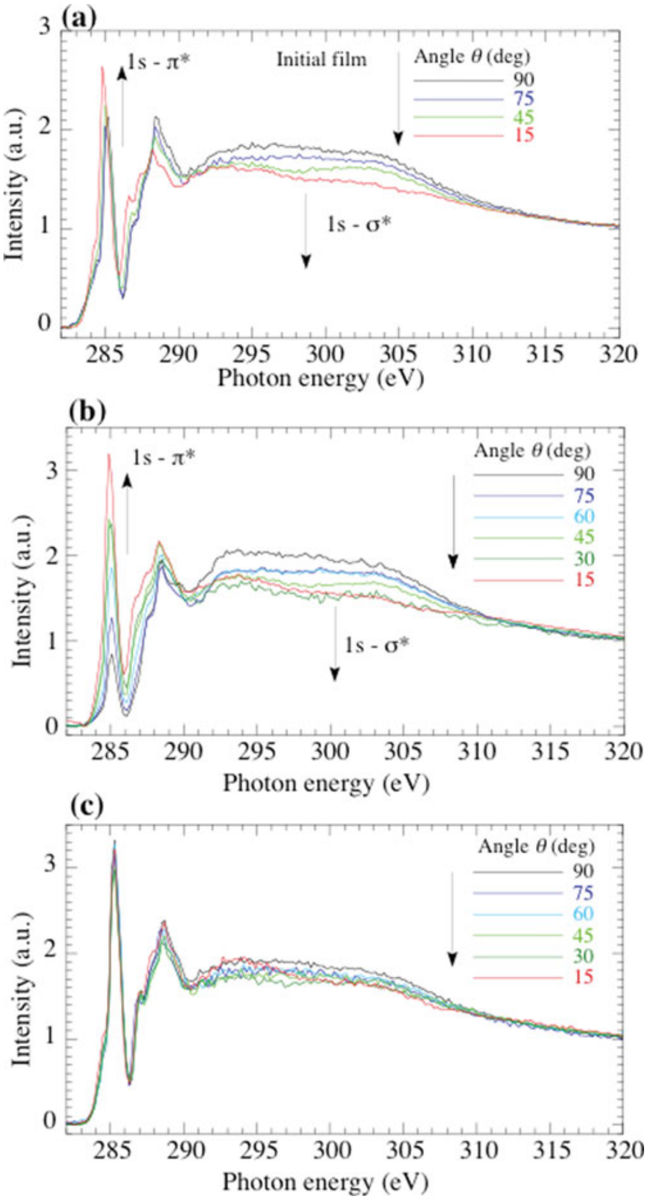


Figure 4. (a) Carbon K-edge NEXAFS spectra for an as-coated PMCB6M film as a function of the X-ray incident angles. (b) and (c) Carbon K-edge NEXAFS spectra for a reoriented PMCB6M film as a function of the X-ray incident angles from surface parallel. **E** of X-ray is (b) parallel and (c) perpendicular to the orientation direction, respectively (Fig. 2a).

spectroscopy. The in-plane order parameter in bulk film, S_b, is expressed in the form of equation 1;

$$S_b = \frac{A_{||} - A_{\perp}}{A_{||} + 2A_{\perp}}, \tag{1}$$

where $A_{\parallel}$ and $A_{\perp}$ are the absorbances parallel and perpendicular to polarization (**E**) of the LPUV light.

NEXAFS Spectroscopy

The NEXAFS measurements were performed at NewSUBARU Synchrotron Radiation Facility on beam line 7B (University of Hyogo), which delivers soft X-ray radiation undulator equipped with a plane grating monochromater (slits; 150 μm). The radiation energy resolution was 300 meV at 280 eV. The NEXAFS spectra were recorded using PMCB6M films on ITO/glass substrates at 77 K to prevent damage of the specimen. The total electron yield (TEY) detection was using an electrometer apparatus, while the partial electron yield (PEY) was measured with photoelectron energy analyzer. Angular dependences of both TEY and PEY detection were obtained by rotating a sample film with parallel and perpendicular to **E** of LPUV light, where the reorientation direction is parallel to x axis (Fig. 2a).

The three molecular orientation factors (f_x,f_y,f_z), that show orthogonally located phenyl rings (Fig. 2b), are calculated from the angular dependence of the NEXAFS intensity of the carbon 1s to π^* transition at 285 eV [20–25]. Using the f_x, f_y, and f_z values, the fractional number of side group segments N_x, N_y, and N_z (Fig. 2c) are estimated using the three permutations of the expression $2f_i = N_j + N_k$ where i, j, and k reflect three axes [23]. The x-y plane and 3D in-plane order parameters, S_{xy} and S_{3D}, are expressed in the form of equations 2 and 3, respectively;

$$S_{xy} = \frac{N_x - N_y}{N_x + 2N_y} \tag{2}$$

$$S_{3D} = \frac{N_x - N_y}{N_x + N_y + N_z} \tag{3}$$

Results and Discussion

Thermally Enhanced Photoinduced Orientation of PMCB6M Film

As previously reported, PMCB6M films reveal molecular reorientation parallel to **E** after annealing the exposed films at elevated temperature when degree of the axis-selective photoreaction of the side groups is approximately 10% [17]. Figure 3a plots thermally amplified S_b values of PMCB6M films as a function of exposure doses when the exposed films are annealed at 180°C. It shows sufficient molecular reorientation parallel to **E** is observed when the exposure energy was 200 – 700 mJ/cm^2, where DP is 5 – 20%. Axis-selectively photo-cross-linked side groups act as anchors to thermally reorient whole mesogenic side groups parallel to **E** [16, 17].

Figure 3b show polarization absorption spectrum change in a PMCB6M film before and after exposure to LPUV light for 300 mJ/cm^2, and subsequent annealing at 180°C for 10 min. The S_b value is 0.76, showing in-plane molecular reorientation parallel to **E** in bulk. Additionally, mesogenic groups in the out-of-plane direction thermally reoriented to the in-plane direction because $A_{\parallel}+A_{\perp}$ value after the reorientation is larger than $A_{\parallel}+A_{\perp}$ after the exposure.

NEXAFS Spectroscopy of Reoriented PMCB6M Film

NEXAFS provides the near-surface (<10 nm) molecular orientation structure in detail by evaluating the angular dependency of the resonance intensity [23–25]. Both as-coated and

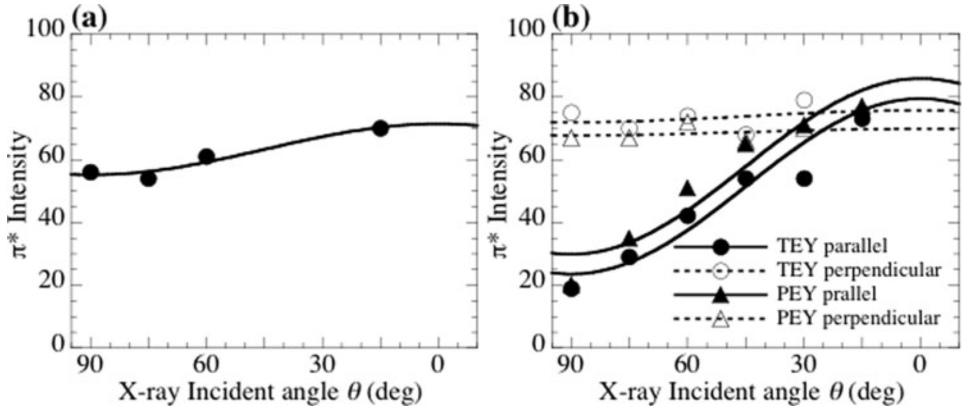


Figure 5. (a) Angular dependence of the 1s-π^* intensity of the as-coated PMCB6M film. (b) Polarization dependence of the 1s-π^* intensity of the reoriented PMCB6M film. The angular dependence for the electric field vector rotated within the *x-z* plane parallel to the reoriented direction (closed points), while within the *y-z* plane perpendicular to the reoriented direction (open points) (Fig. 2a).

reoriented PMCB6M films fabricated on ITO-glass substrate were subjected to NEXAFS spectroscopy. Figure 4a plots angular dependency of normalized TEY intensity of NEXAFS data of the as-coated PMCB6M film. It shows that the intensity of the 1s to π^* transition at 285 eV gradually increases as decreasing polar angle (θ), while that of the 1s to σ^* transition at 300 eV revealed an opposite tendency. This means that phenyl rings (Ph) in the mesogenic side groups preferentially oriented within the sampled subsurface layer. Similar angular dependency was observed in unrubbed polyimide and polystyrene films, which was due to the steric effects and the minimization of the surface energy [24, 25].

In contrast, larger angular dependency was observed in the reoriented film. Figures 4b and c plot angular dependency of normalized TEY intensity of the reoriented PMCB6M film, which was prepared by exposing to LPUV light for 300 mJ/cm^2, and subsequent annealing at 180°C for 10 min. It shows that the angular dependency both 1s to π^* and 1s to σ^* transitions in the parallel configuration are much larger than that for the as-coated film (Fig. 4b). On the other hand, the intensity of whole region in the perpendicular

Table 1. Order parameter derived by polarized UV-vis spectrum, molecular distribution factors (f_x, f_y, and f_z, and N_x, N_y, and N_z), *x-y* plane distribution ratio (D_{xy}), and order parameters (S_{xy} and S_{3D}) of initial and reoriented PMCB6M films

	UV-vis		NEXAFS								
Film	S_b a)	mode	f_x	f_y	f_z	N_x	N_y	N_z	D_{xy} b)	S_{xy}	S_{3D}
Oriented	0.76	TEY	0.12	0.43	0.45	0.76	0.13	0.10	4.5	0.62	0.63
Oriented	0.76	PEY	0.08	0.45	0.47	0.84	0.10	0.06	7.8	0.71	0.74
Initial	0	TEY	0.30	0.30	0.39	0.39	0.39	0.21	1.9	0	0

a) at 314 nm. b) $D_{xy} = (N_x + N_y)/2N_z$.

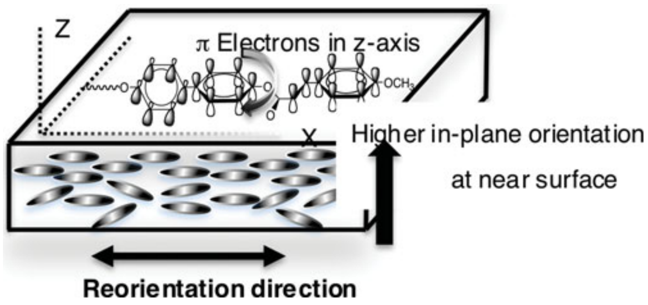


Figure 6. Schematic illustration of uniaxial oriented PMCB6M film.

configuration shows much less angular dependency (Fig. 4c). This indicates the uniaxial in-plane orientation of the mesogenic side groups parallel to **E** of LPUV light.

For a quantitative estimation of the molecular orientation, Figs. 5a and b respectively plot the NEXAFS intensity of the 1s to π^* transition of as-coated and reoriented PMCB6M films as a function of incident angle of the X-ray, which derives three orientation factors f_x, f_y, and f_z (Fig. 2b) by employing the same procedure in oriented polymeric films [23, 24]. Then the number of molecular distributions in three axes (N_x, N_y, and N_z in Fig. 2c) is obtained, and the calculated data are summarized in Table 1.

For the non-exposed film, distribution of Ph rings in x-y plane is larger than that in z-direction because f_z is larger than f_x and f_y as mentioned above. This means that distribution of the mesogenic groups in x-y plane (in-plane orientation) is larger than that in z-direction, where the x-y plane distribution ratio, D_{xy} ($= (N_x+N_y)/2N_z$), is 1.9 (Table 1). After the thermally enhanced molecular reorientation, angular dependency in the parallel configuration became much greater, while that in the perpendicular configuration became smaller (Fig. 5b). The 3D order parameter S_{3D} is 0.63 for TEY, and 0.74 for PEY, respectively. Additionally, the D_{xy} value increased after the thermally generated reorientation process, ($D_{xy} = 4.5$ for TEY, 7.8 for PEY) indicating that the in-plane orientation became predominant similar to the result obtained by polarized UV-vis spectroscopy. Additionally, by considering the result that the S_{3D} value for PEY is larger than that for TEY, and D_{xy} value increased after the reorientation, the in-plane uniaxial orientation is more preferential at the nearer surface of the reoriented film. Furthermore, the phenyl rings in the reoriented mesogenic side groups show slightly perpendicular orientation to the surface normal because f_z values are slightly larger than f_y, as illustrated in Fig. 6.

Conclusion

A polarization-dependent near-edge X-ray absorption fine structure (NEXAFS) measurement demonstrated a preferred uniaxial orientation of the mesogenic side groups at the near-surface of the PMCB6M films; The mesogenic side groups of the non-exposed film preferentially oriented within the sampled subsurface layer, while this tendency enhanced when the thermally enhanced molecular reorientation was conducted. The 3D orientation parameter of the reoriented film at the near-surface is ~0.7. Furthermore, more preferential in-plane reorientation at the nearer surface was observed by comparing the TEY and PEY NEXAFS spectra. The sufficient molecular orientation at the near surface of reoriented PMCB6M film plays an important role in the effective azimuthal anchoring for LC molecules in LCDs.

References

[1] Yaroshchuk, O., & Reznikov, Y. (2012). *J. Mater. Chem.*, *22*, 286.
[2] O'Neill, M., & Kelly, S. M. (2000). *J. Phys. D: Appl. Phys.*, *33*, R67.
[3] Schadt, M., Seiberle, H., & Schuster, A. (1996). *Nature*, *381*, 212.
[4] Schadt, M., Schmitt, K., Kozinkov, V., & Chigrinov, V. (1992). *Jpn. J. Appl. Phys.*, *31*, 2155.
[5] Ibn-Elhaj, M., Chappellet, S., & Linker, F. (2012). *Solid State Phenom.*, *181–182*, 3.
[6] Iimura, Y., Saitoh, T., Kobayashi, S., & Hashimoto, T. (1995). *J. Photopolym. Sci. Tech.*, *8* 257.
[7] Chrzanowski, M. M., Zielinski, J., Olifierczuk, M., Kedzierski, J., & Nowinowski-Kruszelnicki, E. (2011). *J. Achiev. Mater. Manufact. Eng.*, *48*, 7.
[8] Kawatsuki, N., Ono, H., Takatsuka, H., Yamamoto, T., & Sangen, O. (1997). *Macromolecules*, *30*, 6680.
[9] Uchida, E., & Kawatsuki, N. (2006). *Macromolecules*, *39*, 9357.
[10] Kawatsuki, N., Kawanishi, T., & Uchida, E. (2008). *Macromolecules*, *41*, 4642.
[11] Usami, K., Sakamoto, K., Yokota, J., Uehara, Y., & Ushioda, S. (2008). *Thin Solid Films*, *516*, 2652.
[12] Usami, K., Sakamoto, K., Uehara, Y., & Ushioka, S. (2005). *Appl. Phys. Lett.*, *86*, 211906.
[13] Sakamoto, K., Usami, K., Kikegawa, M., & Ushioka, S. (2003). *J. Appl. Phys.*, *93*, 1039.
[14] Li, X. T., Pei, D. H., Kobayashi, S., & Iimura, Y. (1997). *Jpn. J. Appl. Phys.*, *36*, L432.
[15] Kawatsuki, N. (2011). *Chem. Lett. 40*, 548.
[16] Kawatsuki, N., Kawakami, T., & Yamamoto, T. (2001). *Adv. Mater.*, *13*, 1337.
[17] Kawatsuki, N., Goto, K., Kawakami, T., & Yamamoto, T. (2002). *Macromolecules*, *35*, 706.
[18] Kawatsuki, N., Uchimura, H., Hosoda, R., & Kondo, M. (2013). *Macromolecules*, *46*, 2092.
[19] Kawatsuki, N., Hamano, K., Ono, H., Sasaki, T., & Goto, K., (2007). *Jpn. J. Appl. Phys.*, *46*, 339.
[20] Urquhart, S. G., Smith, A. P., Ade, H. W., Hitchcock, A. P., Rightor, E. G., & Lidy, W. (1999). *J. Phys. Chem.*, *103*, 4603.
[21] Okajima, T., Teramoto, K., Mitsumoto, R., Oji, H., Yamamoto, Y., Mori, I., Ishii, H., Ouchi, Y., & Seki, K. (1999). *J. Phys. Chem. A 102*, 7093.
[22] Watts, B., Swaraj, S., Nordlund, D., Lüning, J., & Ade, H. (2011). *J. Chem. Phys.*, *134*, 024702.
[23] Cheun, H., Liu, X., Himpsel, F. J., Knaapila, M., Scherf, U., Torkkeli, M., & Winokur, M. J. (2008). *Macromolecules*, *41*, 6463.
[24] Samant, M. G., Stöhr, J., Brown, H. R., Russel, T. P., Sands, J. M., & Kumar, S. K. (1996). *Macromolecules*, *29*, 8334.
[25] Stöhr, J., Samant, M. G., Cossy-Favre, A., Díaz, J., Momoi, Y., Odahara, S., & Nagata, T. *Macromolecules* (1998). *31*, 1942–1946.
[26] Weiss, K., Wöll, C., Böhn, E., Fiebranz, B., Forstmann, G., Peng, B., Scheumann, V., & Johannsmann, D. (1998). *Macromolecules*, *31*, 1930.
[27] Barachevsky, V. A. (1991). *Proc SPIE*, *1559*, 184.