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

Studies of the Directional Property on Rubbed Alignment Films by Rubbing Condition

Musun Kwak [a], Daekyung Han [a], Hyukmin Kwon [a], Siehyung Choi [a], Youngseok Choi [a], Dohoi Koo [a], Kijeong Kim [b] & Bongsoo Kim [b]

[a] Panel Technology Department, LG Display CO. Ltd., Paju-si, Gyeonggi-do, Korea

[b] Pohang Accelerator laboratory (PAL), POSTECH, Pohang, Kyongbuk, Korea

Version of record first published: 16 Jun 2011

To cite this article: Musun Kwak, Daekyung Han, Hyukmin Kwon, Siehyung Choi, Youngseok Choi, Dohoi Koo, Kijeong Kim & Bongsoo Kim (2011): Studies of the Directional Property on Rubbed Alignment Films by Rubbing Condition, Molecular Crystals and Liquid Crystals, 546:1, 11/[1481]-16/[1486]

To link to this article: http://dx.doi.org/10.1080/15421406.2011.571590

Mol. Cryst. Liq. Cryst., Vol. 546: pp. 11/[1481]–16/[1486], 2011

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.571590

Taylor & Francis
Taylor & Francis Group

Studies of the Directional Property on Rubbed Alignment Films by Rubbing Condition

MUSUN KWAK,[1] DAEKYUNG HAN,[1] HYUKMIN KWON,[1] SIEHYUNG CHOI,[1] YOUNGSEOK CHOI,[1] DOHOI KOO,[1] KIJEONG KIM,[2] AND BONGSOO KIM[2]

[1]Panel Technology Department, LG Display CO. Ltd., Paju-si, Gyeonggi-do, Korea
[2]Pohang Accelerator laboratory (PAL), POSTECH, Pohang, Kyongbuk, Korea

The near-edge X-ray absorption fine structure(NEXAFS) and its polarization dependence on Carbon(C) K-edge, is used to obtain information on the molecular orientation at the polyimide(PI) surface. Rubbed PI alignment layer was controlled the pile contact impression and stage speed. We could estimate the alignment angle α of the molecules with the surface normal of the PI molecules through the intensity change of C=C π^* in NEXAFS C K-edge spectrum, depending on the photon incident angle $\theta = 20°$, 55° and 90°. As increasing the depth of the pile contact, the angle α was linearly decreased. The stage speed dependency was shown an irregular pattern.

Keywords Alignment; NEXAFS; polyimide; rubbing

1. Introduction

The rubbed PI films are widely used as an alignment film (AF) in practical applications. And, the alignment mechanism of liquid crystal (LC) molecules in contact with a rubbed PI film is very important not only of scientific interest, but also of technological importance. Through the previous studies [1–5], now it is understood that for rubbed PI films the intermolecular interaction plays a more important role in LC alignment than the elastic interaction. The importance of alignment of the conjugated main chain is widely recognized for enhancing specific electronic properties such as the photon absorption and charge transport of these devices. Higher carrier mobility and polarized photon emission are usually obtained when the conjugated polymer films are macroscopically ordered. Even though evidence of bulk polymer alignment on rubbed PI of AFs exists, we do not know whether this alignment persists throughout the film to the surface. Also, polymers are being developed

Address correspondence to Kijeong Kim, Pohang Accelerator laboratory (PAL), POSTECH, Pohang, Kyongbuk 790-784, Korea. Tel.: +82-54-279-1554; Fax: +82-54-279-1599; E-mail: kjkim@postech.ac.kr or Musun Kwak, Panel Technology Department, LG Display Company Ltd., 1007 Deogeun-ri, Wollong-Myeon, Paju-si, Gyeonggi-do, Korea. E-mail: musunkwak@lgdisplay.com

increasingly as functional materials to be applied in low cost, large-scale, and flexible organic electronic devices including organic thin film transistors (OTFTs), photovoltaics, and organic light-emitting diodes (OLEDs) [6,7]. So, it is important to understand the nature of molecular orientation on the polymer surface [8,9].

In this paper, we introduced the analysis of near edge X-ray absorption fine structure (NEXAFS) and its polarization dependence on carbon K-edge to obtain information on the molecular orientation at the polymer surface. When the soft X-ray radiation is polarized in the direction of the transition dipole moment of the electron orbital of the molecule, the probability of the adsorptions will be increased and the absorption results in the excitation of an electron from the core shell to an excited state. When the core hole fills, either an X-ray photon (fluorescence) or an Auger electron is emitted. The emitted Auger electrons are detected by channel electron detector and they come dominantly from the top ~1 nm of the thin film [10]. Therefore, the purpose of this paper is to examine the effects of various rubbing conditions, such as the roll speed, the stage speed, and the pile contact compression using NEXAFS.

2. Experiments

The samples of rubbed PI (SE20 series, Nissan CO., Ltd.) thin film with a thickness of 80 nm on ITO substrate were supplied by LG Display. These polyamic acid (PAA) films were pre-bake at the temperature of 80°C for 150 sec and then post-bake at the temperature of 230°C for 1000 sec. The rubbing strength (RS) has been defined in previous paper [11]. To examine the alignment property changes caused by rubbing conditions, we controlled the pile contact impression, the roll speed and the stage speed. And rubbing cloth was rayon. The pile contact impression is the measured value of width that glass contact with rubbing cloth to determine the frictional force and intensity. At this experiment, the value of pile contact impression; 14, 16, 18 mm can be convert into the value of M; 0.3.0.4.0.5 mm, respectively. Each rubbing parameter of samples was appeared on the Table 1.

Table 1. Rubbing parameter for the examined 11 samples

Sample number	Contact impression [mm]	Roll speed [rpm]	Stage speed [mm/s]
1	14	1100	30
2	16	1100	30
3	18	1100	30
4	14	1300	30
5	16	1300	30
6	18	1300	30
7	14	1500	30
8	16	1500	30
9	18	1500	30
10	16	1300	40 [ref.]
11	16	1300	50

NEXAFS spectra were measured at the end station on the 2B1 beam-line in the Pohang Light Source (PLS) [12]. The partial electron yield (PEY) mode and the total electron yield (TEY) NEXAFS spectra were collected using a channel electron multiplier that has an adjustable entrance grid bias and by measuring the sample current. For the PEY detection mode, -210 V of retarding voltage and 1.6 kV of accelerating voltage were impressed [13,14]. The carbon K-edge NEXAFS spectra were recorded at the angle of $\theta = 20°$, 55°, and 90°, where θ is the angle between the electric field vector (**E**) of the polarized soft X-rays and the sample normal as well as the angle between the incident photon beam and the sample surface (inset of Fig. 2). The data were first normalized by the current of the clean Au mesh to remove the monochromator structure due to adsorbed carbon on the optical elements of the beam-line. Secondly, the edge jump was set to 1 for all spectra to remove contributions from the emission angle, beam decay, and effective spot size on the sample. The polarization dependence of the π^*(C=C) resonance was then analyzed. The photons showed a polarization of 85% with an incident photon energy resolution of 350 meV near the carbon K-edge region.

3. Result and Discussion

Figure 1 shows the PI molecular, PAA type [15], structure. PI molecules are a linear structure, consisted with dianhydride and diamine. After preparing the thickness of 80 nm PI thin film on the ITO glass, each sample was rubbed with the different rubbing condition, as can be seen the table 1. The uniform alignments of nematic liquid crystals(NLCs) on solid surfaces is an important matter and the unidirectional rubbing of polymer-coated substrates with fabric is almost exclusively used in industrial production of liquid crystal displays (LCDs). For rubbing the PI, the rotating rubbing wheels with a fur on its surface are rolling on the PI surface with contact compression during the sample plate moving to defined direction.

Figure 2 shows an example of NEXAFS spectra of PI using the partial electron yield (PEY) mode for the rubbing condition of 1300 rpm of roll speed, 40 mm/sec of stage speed and 16 mm of pile contact depth. The thickness of PI was 80 nm. Two peaks were observed at the position of 285.5 eV (A) and 288.2 eV (B) from each spectrum. Each peak was assigned as C=C π^* of benzene and C=O, respectively. These two peaks also showed good angle dependency, and the intensities of the dominant benzene π^* resonance at 285.5 eV changed with the polarization direction. Changes were also observed in the resonances at 288.2 eV (C=O). TEY and PEY showed a difference intensity at the C=O π^* resonance (not shown here). From the intensity of C=O bond was enhanced on the PEY mode indicated that the C=O molecular bonding is more prominent on the surface. And there were the broad two peaks between 290 and 310 eV which were originated from the σ^* states of C=C, C-C, C-N and C=O.

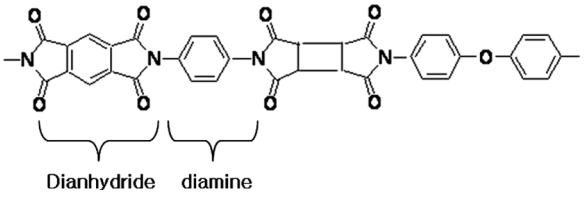

Figure 1. Molecular structure of polyimide (PI), consisted with dianhydride and diamin.

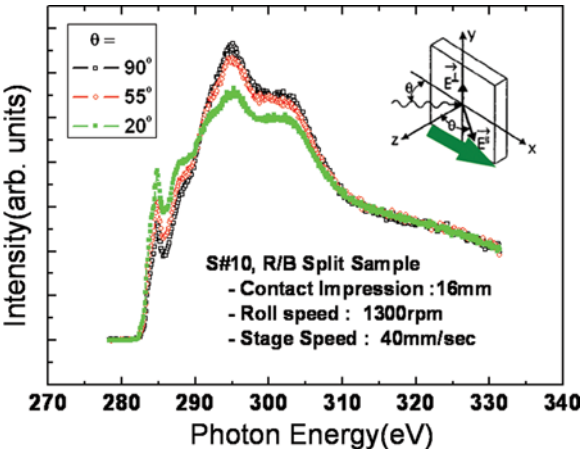

Figure 2. NEXAFS spectra of the rubbed PI at the roll speed of 1300 rpm, the stage speed of 40 mm/sec and the pile contact impression of 16 mm. Inset shows the experimental geometry for the measurement of incident angle dependence of NEXAFS, θ is the angle of incident photon and the green arrow shows rubbing direction.

To determine the alignment angle α between the double bonds of the degree of alignment of the surface molecule to the polarization of the X-ray beam, we used an analytical solution of the NEXAFS intensity problem [10]. The relationship between the photoelectron intensity and the incident photon beam angle can be expressed as $I_v \propto \frac{P}{3}\{1+\frac{1}{2}(3\cos^2\theta-1)(3\cos^2\alpha-1)\}+\frac{(1-P)}{2}\sin^2\alpha$, where α and θ are the angle between the molecular axis and the surface normal and the angle between the light polarization vector (E-vector) and the surface normal, respectively, and P is the degree of polarization. For this experiment, we assumed a polarization factor of $P = 0.85$ [14]. The π^* resonance intensity was strong when the photon beam was

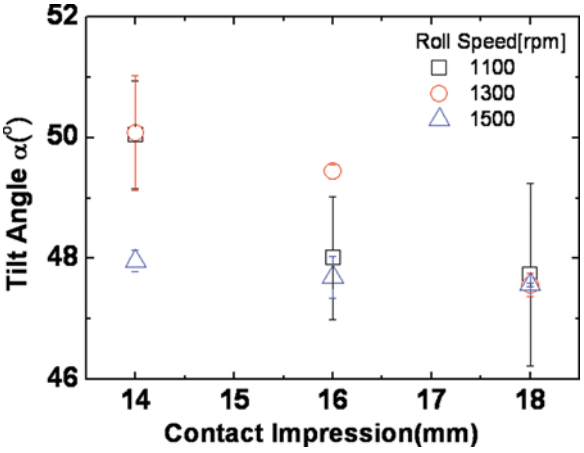

Figure 3. Relation between the pile contact impression and the tilt angle α of the PI molecules at the rolling speed of 1100 (black square), 1300 (red circle) and 1500 (green triangle) rpm. (Figure appears in color online.)

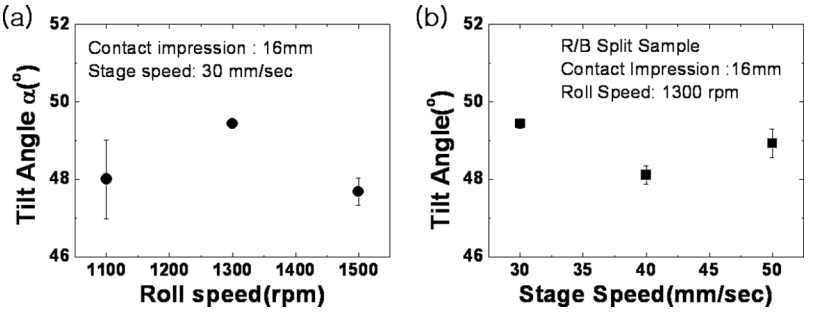

Figure 4. (a) The relation between the roll speed and the tilt angle of PI at the contact impression of 16 mm and the stage speed of 30 mm/sec. (b) The relation between the stage speed and the tilt angle of PI at the contact impression of 16 mm and the roll speed of 1300 rpm.

incident with an angle of $\theta = 20°$ (glancing incidence), whereas it was weak when the incident photon angle was $\theta = 90°$ (normal incidence). We calculated the alignment angle α of the PI films by using the experimentally measured variation of the relative intensity for the 285.5 eV π^* (C=C) resonance with the polarization vector angle. These values were obtained by measuring the height of the π^* (C=C) resonance intensity.

Figure 3 shows the α change of the PI molecules at the rolling speed of 1100 (black square), 1300 (red circle) and 1500 (green triangle) rpm. At the rolling speed of 1100 rpm, the α of PI was decreased as increasing the contact impression. This phenomenon was similar at the rolling speed of 1300 rpm and 1500 rpm. Even though we changed the roll speed from 1100 rpm to 1500 rpm, the tilt angle converges to 47.7° at the pile contact impression of 18 mm. This explains that the PI molecules are inclined to the surface as increasing the pile contact impression.

Figure 4(a) shows the relation between the roll speed and the angle α of PI at the contact impression of 16 mm and the stage speed of 30 mm/sec. As can be seen in Figure 4(a), the roll speed dependence was not shown regular dependency. But the α angle reached to 48°. The stage speed was also shown irregular pattern. Figure 4(b) shows the relation between the stage speed and the tilt angle of PI at the contact impression of 16 mm and the roll speed of 1300 rpm.

4. Conclusion

We examined the effects of various rubbing condition on the PI by using NEXAFS spectra. We controlled the pile contact impression and stage speed. We could estimate the average tilt angle α of the PI molecules through the measured intensity change of C=C π^* in NEXAFS C K-edge spectrum, depending on the photon incident angle $\theta = 20°$, 55° and 90°. As increasing the depth of the pile contact to 18 mm, the molecular tilt angle α was linearly decreased to 47.7° at the roll speed of 1100, 1300 and 1500 rpm. But, there is no the roll speed and the stage speed dependency.

Acknowledgments

The experiments at PLS were supported in part by MEST and POSTECH. This research was supported by the LG Display through the grant of 4.0003497.01 and

National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (2009-0087138).

References

[1] Pidduck, A. J., Bryan-Brown, G. P., Haslam, S., Bannister, R., Kitely, I., McMaster, T. J., & Boogaard, L. (1996). *J. Vac. Sci. Technol.*, *A14*, 1723.
[2] Lee, E. S., Saito, Y., & Uchida, T. (1992). *Jpn. J. Appl. Phys.*, *2*(32), L1822.
[3] Berreman, D. W. (1972). *Phys. Rev. Lett.*, *28*, 1683.
[4] Geary, J. M., Goodby, J. W., Kmetz, A. R., & Pastel, J. S. (1987). *J. Appl. Phys.*, *62*, 4100.
[5] Arafune, R., Sakamoto, K., Ushioda, S., Tanioka, S., & Murata, S. (1998). *Phys. Rev.*, *B58*, 5914.
[6] Chen, X. L., Lovinger, A. J., Bao, Z., & Sapjeta, J. (2001). *Chem. Mater.*, *13*, 1341.
[7] Garnier, F., Yassar, F., Hajlaoui, A., Horowitz, R., Deloffre, G., Servet, F., Ries, B., & Alnot, S. (1993). *J. Am. Chem. Soc.*, *115*, 8716.
[8] Pattison, Lisa R., Alexander, Hexemer, Edward Kramer, J., Sitaraman Krishnan, Pierre Petroff, M., & Daniel Fischer, A. (2006). *Macromolecules*, *39*, 2225.
[9] Cheun, H., Liu, X., Himpsel, F. J., Knaapila, M., Scherf, U., Torkkeli, M., & Winokur, M. J. (2008). *Macromolecules*, *14*, 6463.
[10] Stohr, J., Samant, M. G., Favre, A. C., Díaz, J., Momoi, Y., Odahara, S., & Nagata, T. (1998). *Macromolecules*, *31*, 1942.
[11] Seo, D. S., Muroi, K., & Kobayashi, S. (1992). *Mol. Cryst. Liq. Cryst.*, *213*, 223.
[12] Kim, K. J., Kang, T. H., Kim, B. S., Bang, J. H., & Lee, M. H. (1997). *J. Kor. Phys. Soc.*, *30*, 148.
[13] Kim, K. J., Lee, H. G., Choi, J. H., Lee, H. K., Kang, T. H., Kim, B., & Kim, S. (2008). *J. Phys. Condens. Matter.*, *20*, 225017.
[14] Lee, H. K., Kim, K. J., Han, J. H., Kang, T. H., Chung, J. W., & Kim, B. (2008). *Phys. Rev.*, *B77*, 115324.
[15] Kwak, M. S., Chung, H. R., Choi, J. H., Kwon, H. M., Kim, J. Y., Han, D. K., Park, C. H., Lee, S. M., Lee, C. G., & Cha, S. Y. (2009). *Mol. Cryst. Liqu. Cryst.*, *507*, 129.