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Simultaneous Fabrication of an Alignment Layer and a Wall Structure for a Liquid Crystal Display by Solvent-Assisted Micromolding

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Abstract: Patterning and aligning are the most distinctive research areas in surface science. In this paper, we demonstrate a fabrication method for the simultaneous formation of a wall-structured surface relief and a molecular aligning region between the walls. A photoreactive polymer, poly(vinyl cinnamate) (PVCi), was used as the matrix; it was coated either onto a rigid glass substrate or a flexible plastic substrate. We used a solvent-assisted micro-molding poly(dimethylsiloxane) stamp to form 10-μm-wide and 10-μm-high walls every 100 μm on the matrix. The direction of the molecular alignment in the region between the walls was perpendicular to the direction of the walls; this finding was confirmed by the subsequent liquid crystal (LC) alignment investigation. The alignment of this wide region between the wall structures is uncommon and differs from the molecular alignment induced by the micro-groove topology due to the patterning. Additionally, the application of linearly polarized ultraviolet irradiation onto the photoreactive PVCi improved the molecular alignment either on the region between the walls or on the lateral side of the walls; this finding was confirmed by polarized light microscopy imaging. The simultaneous formation of the wall support in the molecular aligning region can be used in flexible LC displays, in which the maintenance of cell gaps and the aligning of the LC material play a critical role in display performance.

Keywords: liquid crystal display, alignment, pattern, spacer, flexible.

Introduction

There is increasing demand for flexible displays for up-and-coming flexible electronic devices such as wearable computers. Flexible display electronic devices offer many advantages, such as light weight, durability, and portability.[1] Liquid crystal displays (LCDs) which use liquid crystals as optical switches are now widely used because of the technology is mature. Thus, a number of studies have focused on using LCDs as a platform technology to achieve flexible displays.[1-3]

The most prominent change required for the shift of technology from conventional LCDs to flexible LCDs is that the display must adjust itself to bending stress, and it also must maintain a constant gap between two active layers under various external conditions to provide stable and uniform operation.[4-7] Previous studies suggested substituting the glass substrate by a flexible plastic substrate[8] and using the wall structure between the upper and lower electrode substrate to withstand the bending stress that is normally encountered in flexible LCD applications.

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In addition to the wall structure formation, the conventional rubbing method for fabricating the alignment layer in the liquid crystal should be replaced because of an inherent problem in the rubbing method, namely static electricity build up leading to dust accumulation and electrical failure. The problem of electrical buildup on the surface becomes particularly serious when a plastic substrate is used. Thus, alternative methods such as imprinting,[9,10] oblique sputtering,[11] and photoalignment from UV exposure,[12-14] have been intensively studied for providing a liquid crystal (LC) alignment layer for flexible LCDs. As the alignment layer is closely related to the optical efficiency of the LCD, our group has thoroughly investigated photoreactive oligomeric materials using a linearly polarized UV light (LPUV) aligning mechanism, and reported our results regarding the pretilt angle evolution of the photoalignment layer, the biodegradable photoalignment layer, and the enhanced contrast near the pixels from the incorporation of oligomeric cinnamates.[2,15-17]

To date, the processes of forming an alignment layer and a wall structure have been performed separately using different materials. Although attempts to remove the alignment layer to reduce the fabrication step have been reported,[18] there have been few reports on simultaneously forming a wall structure and a molecular alignment region that can provide a facile and economical fabrication procedure.

Here, we propose a new fabrication method that can reduce the number of steps for the wall and alignment formation using a single photoreactive material by solvent-assisted micromolding (SAMIM). The approach was first applied to a rigid glass substrate and subsequently extended to flexible plastic substrates.

Experimental

The wall structure and alignment layer of the flexible LCD were fabricated simultaneously. Three different steps were followed to investigate their influence on the aligning of LCs. The steps are summarized in Figure 1.

First, the master pattern of the poly(dimethylsiloxane) (PDMS) stamp was fabricated, following previous work.[19,20] A PDMS mold with patterns was prepared from a commercially available liquid prepolymer mixture of a silicon elastomer base and curing agent (Sylgard 184, Dow Corning). The mixture of base and curing agent (ratio 10:1) was stirred at 350 rpm for 40 min to mix completely. Any bubbles generated during mixing were removed by repeatedly evacuating and purging the mixtures in a vacuum oven. A PDMS rubber stamp with patterns was obtained by thermal curing of the prepolymer mixture on a photoresist master at 80 °C for 5 h. The cured PDMS was then peeled off from the master.

Poly(vinyl cinnamate) (PVCi, average M_w ~200,000 by GPC, powder, Sigma Aldrich) was dissolved in tetrahydrofuran (Junsei Chem.) to prepare a 20 wt% solution. The solution was spin-coated onto either a glass plate or an optical-grade poly(ethylene terephthalate) (PET) film at 550 rpm for 45 s. The coated substrate was prebaked at 45 °C for 1 h before use. On the prepared PVCi film, the wall structure was formed from a patterned PDMS stamp using SAMIM.[21,22] The height and width of the wall were each 10 μm and the length was fully extended to the end of the PDMS mold. The wall patterns were repeated every 100 μm, considering the pixel size of a normal LCD. The solvent used for the SAMIM procedure was ethanol and a limestone block was applied on the PDMS mold (2.5 cm×2.5 cm) to secure good patterning over the pattern area (1.5 cm×1.5 cm), using a pressure of 1.81 kPa. The fabricated PDMS stamp and patterned PVCi were examined by HR-SEM (MIRA LMH, TESCAN) to confirm the surface morphology. Three different approaches were followed, based on the wall-patterned films. First, the cells were prepared without any treatment (Figure 1(a)). Secondly, linearly polarized UV light (a 500 W high-pressure mercury lamp) was irradiated on the wall-patterned glass plate or PET film through a UV linear dichroic polarizer (27320, Oriel) and a UV filter (59800, Oriel) for 12 min. The intensity of the irradiated UV light was measured to 4 mW/cm^2 with a UV detector (UTT-150, Ushio). The direction of the UV light passing the polarizer was parallel to the direction of the wall pattern. The UV light was applied from the normal direction of the coated films. In the third approach, and in addition to the second, the wall-patterned substrate was successively rotated to +45° and -45° from the normal direction for extra irradiation by the linearly polarized UV light. This was intended to irradiate the

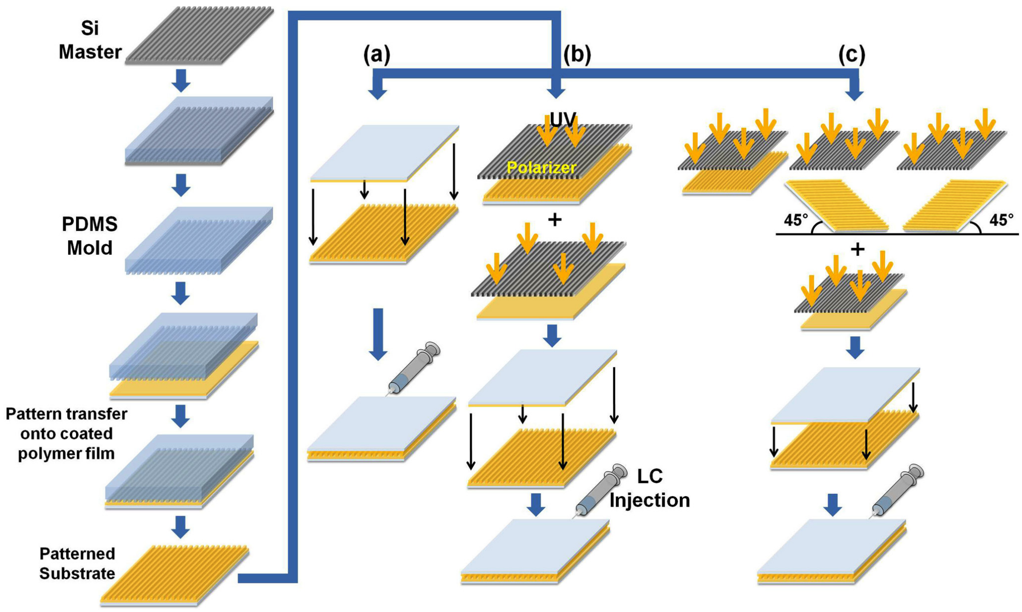

Figure 1. Schematic diagram illustrating the fabrication process of the wall structure and LC alignment layer. Different routes for cell fabrication based on (a) a patterned substrate, (b) LPUV irradiation onto a patterned substrate, and (c) additional LPUV irradiation of (b) with rotation of ±45° to the normal direction.

lateral face of the wall. All the LC cells were fabricated by sandwiching two glass plates using epoxy bond. The resulting cell gap was that of the wall height of the patterned PVCi, which is 10 μm. We used a nematic LC (E7) that could align in an in-plane orientation. A mixture of LC and blue dye (methyl blue) was injected into the cell gap to probe the LC's orientation, followed by baking at 65 ^{o}C for 10 min. Unlike rigid glass plates, the plastic film deformed easily, so a flat glass plate was used to support the PET films during cell fabrication and was removed at the end of fabrication. The orientation of the LC induced by the PVCi alignment layer was observed by rotating the cells in a polarized filter equipped with a UV-Vis spectrometer at a wavelength of 653 nm, to detect the methyl blue dye incorporated in the LC. The observed results are summarized in polar plots.

Results and Discussion

The structure with a wall and an alignment layer is fabricated simultaneously as shown in Figure 1. The differences in Figure 1(a) to (c) are no UV treatment, LPUV treatment, and additional oblique LPUV irradiation, respectively. A wall structure supporting a cell gap and an alignment layer that generates optical anisotropies through the LC orientation are essential structures of the flexible LCD. Generally, wall structures have been formed on the alignment layer. However, these separate processes use different materials and a wall structure lacking an LC alignment can lead to poor contrast and a complicated procedure. PVCi is a well-known alignment layer for nematic LCs. Because the cinnamoyl group of PVCi undergoes an anisotropic [2+2] photocycloaddition reaction when irradiated by LPUV, a noncontact method, rather than a rubbing procedure, can be used to form a photoaligning layer.[4] We successfully prepared wall patterns, as shown in Figure 2, using coated PVCi. The reversed pattern of the PDMS stamp was clearly expressed, and the surface wall pattern and the surface of the PVCi patterned by SAMIM is illustrated in Figure 2. The figure clearly shows a constant distance in the wall pattern that corresponds to the PDMS stamp with the linear wall structure repeated every 100 μm. Moreover, the wall height of the patterned PVCi was formed by the PDMS stamp at 10 μm.

Since the coated PVCi acts as an alignment layer under LPUV irradiation, cells are prepared with the PVCi-coated glass substrates with LC incorporation. Polar plots for cells containing LC using only wall patterns (Figure 1(a)), LPUV irradiation on wall patterned film (Figure 1(b)), and LPUV irradiation in the normal direction and 45^{o} oblique irradiation onto a patterned film (Figure 1(c)) were investigated for LC alignment. To investigate the alignment, LC containing a small amount of dichroic dye was placed between the two substrates and the surfaces were prepared for the three different cases.

The LC alignments on the wall-patterned photoreactive films on glass substrates with different treatments are shown in Figure 3. Interestingly, the LC alignments, which can be generated by LPUV irradiation, were also observed in the wall-patterned film without UV treatment (Figure 3(b)). In the polar plots, the pattern and linearly polarized UV light demonstrated a synergistic effect (Figure 3(c)). In contrast, the additional oblique irradiation intended for alignment on the lateral side of the wall showed little effect on the substrate molecular alignment (Figure 3(d)).

To investigate the underlying mechanism of the molecular alignment in a patterned cell without LPUV irradiation, we explored the possibility of interaction between the PVCi and the PDMS stamp, material effects, and the SAMIM conditions. First, a flat PDMS stamp without a pattern was used to investigate the interaction between the PVCi and PDMS. The results show that there is no peculiar trace of anisotropy in the polar plot (Figure 4(a)); this suggests that the molecular orientation of the wall-patterned PVCi layer is not from the flat PDMS stamp itself. We also varied the applied pressure by changing the weight of the block on the patterned PDMS stamp during the SAMIM and examining the orientation, but no trend related to the amount of pres-

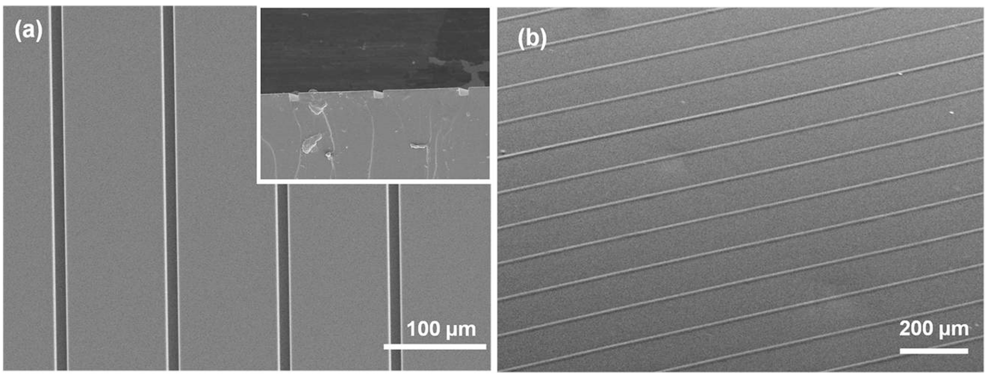

Figure 2. (a) SEM image of the fabricated PDMS stamp (inset image shows the cross-sectional SEM image of the PDMS stamp) and (b) SEM image of the patterned PVCi layer.

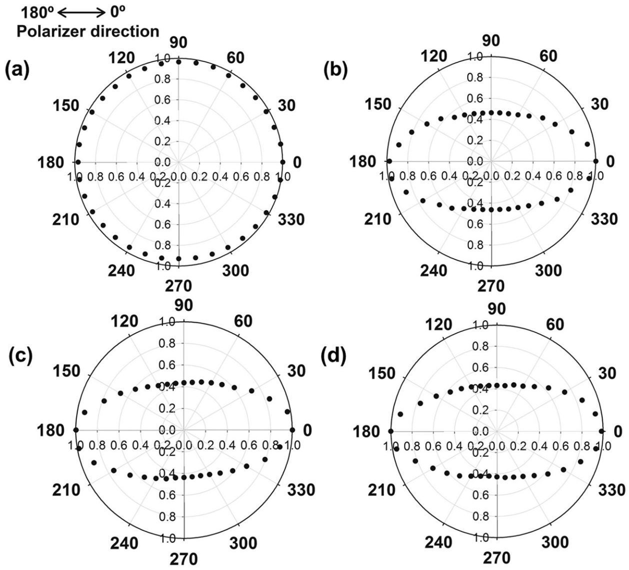

Figure 3. Polar plots of liquid crystal orientation on the in-plane alignment layer of PVCi coated onto glass plate after cell fabrication: (a) spin-coated PVCi, (b) patterned PVCi substrate, (c) LPUV irradiation onto a patterned substrate, and (d) additional LPUV irradiation of (c) at ±45° from the normal direction.

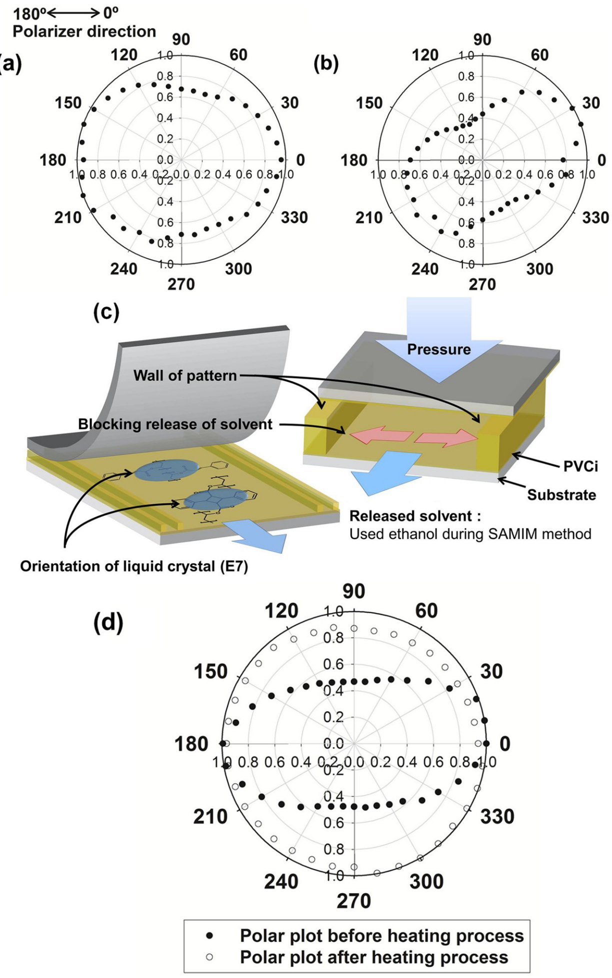

Figure 4. Polar plots of coated PVCi after the SAMIM process using (a) a flat PDMS stamp, (b) a poly(vinyl alcohol) (PVA)-coated substrate with a patterned PDMS stamp, (c) schematic illustration of the proposed mechanism for the PVCi layer, showing molecular alignment during the SAMIM procedure, and (d) polar plots of the patterned PVCi before and after heat treatment.

sure was observed. Instead of the photoreactive material PVCi, poly(vinyl alcohol) (PVA), which provides the aligning layer in the rubbing process, was used as the coating and wall patterns were prepared by the same procedure. It was observed that although the direction differed from the case of PVCi, it also showed anisotropy, which indicates molecular in-plane alignment of the wall-patterned sample (Figure 4(b)). The comparison between PVCi and PVA, indicated that the capacity for molecular orientation is related to chemical composition, and the benzene ring on the PVCi seems to enhance molecular orientation. The results reflect the fact that the orientation may differ because of the material orientation and not because of the PVCi characteristics.

We finally focused on the possibility of directional removal of the solvent used in the SAMIM. Compared to the patternless PDMS stamp, the solvents of the wall-patterned structure should diffuse or leave the surface parallel to the wall, as shown in Figure 4(c). Thus, the main chain aligns with the direction of solvent escape, resulting in alignment of the LC to the mesogenic side chain direction (cinnamoyl groups), which is perpendicular to the wall structure. Because the alignment does not originate from the photocycloaddition reaction induced by the LPUV irradiation, it can be easily assumed that the aligning property would deteriorate by the thermal treatment near the glass-transition temperature. Figure 4(d) illustrates the removal of the cell anisotropy after heat treatment at slightly below glass-transition temperature (65 ºC) for 10 min.

It was reported that evaporation-induced flow in a solvent-cast block copolymer can be produced with a high degree of in-plane orientation and lateral ordering.[23,24] Control of the evaporation rate affects the alignment,[25] and the contact of the PVCi and PDMS stamp enabled slow evaporation, so the wall structure is the reason for the directional solvent concentration gradient leading to the orientation of the polymer chain. In this study, an important difference from previous systems is that the polymer was a homopolymer and the wall pattern was responsible for the solvent evaporation direction.

Based on the results of simultaneous wall pattern and alignment layer formation on the glass substrate, we repeated the work with a flexible optical-grade PET film as the substrate for a truly flexible display. Since long UV irradiation might affect the plastic substrate, the oblique irradiation procedure was omitted. The polar plots of the cells from the

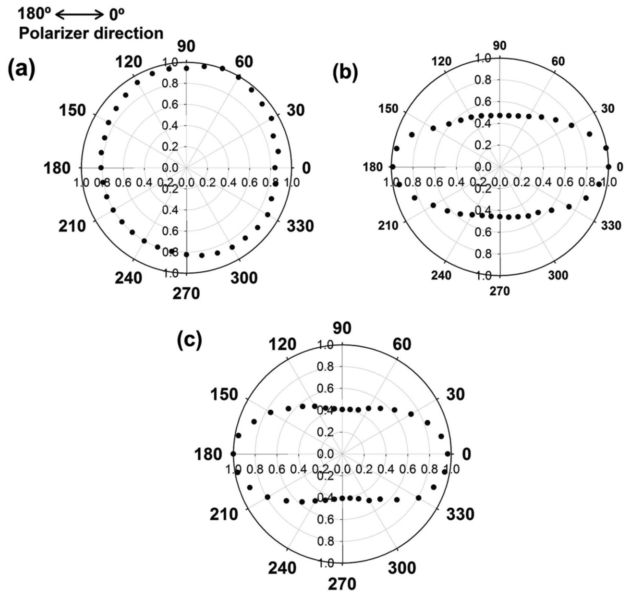

Figure 5. Polar plots of the liquid crystal orientation on the in-plane alignment layer of PVCi coated onto the flexible PET film after cell fabrication: PVCi-coated layer without any treatment, (b) patterned substrate only, and (c) LPUV irradiated onto a patterned substrate.

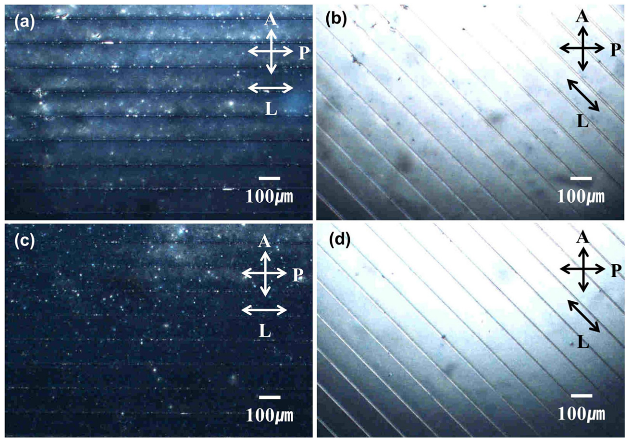

Figure 6. Polarized optical microscopy image of the liquid crystal cell prepared with a patterned PVCi substrate on glass: (a) and (b) show images of the cell from the pattern with normal direction LPUV irradiation at 0º and 45º rotation between the perpendicular polarizers, respectively; (c) and (d) show images of the cell from the pattern with normal and oblique LPUV irradiation at 0º and 45º rotation between the perpendicular polarizers, respectively. The direction of the polarizers (A and P) and the in-plane orientation of the liquid crystals are denoted as arrows in the image. The image was observed by rotating the LC containing the alignment layer sample, which is located between the two perpendicular polarizers.

plastic substrate are shown in Figure 5. The polar plots clearly revealed alignment of the LCs in the direction parallel to the polarization of the UV light. When comparing the polar plots of the glass substrate and polymeric films, the wall-patterned structure showed similar alignment and order parameter values (0.2797 and 0.2829 for the glass substrate and plastic film, respectively). When LPUV was applied, a better order parameter value was obtained for the plastic substrates (0.3016 and 0.3344 for the glass substrate and plastic film, respectively).

Our previous study showed that addition of an oligomeric photoreactive material in a pixel-isolated flexible display improved the contrast as a result of the LC aligning near the wall.[2] We considered that oblique LPUV irradiation followed by LPUV irradiation in the normal direction would induce lateral fraction in the wall alignment, thus, affecting the contrast near the wall. The transmitted intensity of the planar cell between crossed polarizers can be expressed with the equation $I/I_0=\sin^2(2\chi)\times\sin^2(\delta/2)$, where χ is the angle between the polarizer and the optical axis of the LC and δ represents the phase shift. Since the phase shift is constant, the variation in intensity is only governed by the angle between the optical axis and the polarizer (χ).[26] We examined the cells by polarized optical microscopy (POM). The cells were placed between two polarizers arranged perpendicular to each other; the results are shown in Figure 6. With the rotation of the LC cell, the cell showed alternating bright and dark images. The image shows that light leakage near the wall can be improved by oblique LPUV irradiation. This work suggests that the wall structure and the aligning layer could be achieved in a single step using PVCi. Additional LPUV could enhance the structural integrity by reaction with cinnamoyl groups and improve contrast near the wall structures.

Conclusions

We successfully prepared a wall and an alignment layer, which are the fundamental structures in flexible LCDs, by SAMIM with a single photoreactive material either on glass or on a flexible plastic substrate. The fabricated wall structure could support the cell gap, and this is confirmed by the cell fabrication and LC alignment investigations. In addition, it was found that the alignment and patterning can be obtained without additional UV treatment, through solvent evaporation, by regulating the evaporation direction.

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References

(1) J. Jang, *Mater. Today,* **9**, 46 (2006).
(2) S. J. Sung, E. A. Jung, D. H. Kim, D. H. Son, J. K. Kang, and

K. Y. Cho, *Opt. Express,* **18**, 11737 (2010).
(3) Y. T. Kim, J. H. Hong, T. Y. Yoon, and S. D. Lee, *Appl. Phys. Lett.,* **88**, 263501 (2006).
(4) V. Vorflusev and S. Kumar, *Science,* **283**, 1903 (1999).
(5) H. Hah, S. J. Sung, M. Han, S. S. Lee, and J. K. Park, *Displays,* **29**, 478 (2008).
(6) Y. Kim, J. Francl, B. Taheri, and J. L. West, *Appl. Phys. Lett.,* **72**, 2253 (1998).
(7) S. J. Jang, J. H. Kim, J. H. Bae, Y. Choi, H. R. Kim, S. I. Kim, J. H. Souk, and J. H. Kim, *Mol. Cryst. Liq. Cryst.,* **470**, 191 (2007).
(8) A. Hellemans, *IEEE Spectr.,* **37**, 18 (2000).
(9) T. Scharf, A. Shlayen, C. Gernez, N. Basturk, and J. Grupp, *Mol. Cryst. Liq. Cryst.,* **412**, 135 (2004).
(10) H. Hah, S. J. Sung, M. Han, S. Lee, and J. K. Park, *Mater. Sci. Eng. C,* **27**, 798 (2007).
(11) H. Vithana, D. Johnson, and P. Bos, *Jpn. J. Appl. Phys.*, **35**, L320 (1996).
(12) M. Schadt, K. Schmitt, V. Kozinkov, and V. Chigrinov, *Jpn. J. Appl. Phys.,* **31**, 2155 (1992).
(13) M. Schadt, H. Seiberle, and A. Schuster, *Nature,* **381**, 212 (1996).
(14) K. Ichimura, Y. Akita, H. Akiyama, K. Kudo, and Y. Hayashi, *Macromolecules,* **30**, 903 (1997).
(15) S. J. Sung, D. H. Kim, M. R. Kim, and K. Y. Cho, *Macromol. Res.,* **18**, 614 (2010).
(16) J. Lee, S. Lee, Y. C. Jeong, K. Y. Cho, and J. K. Park, *Opt. Express,* **17**, 23565 (2009).
(17) S. J. Sung, J. H. Yun, S. Lee, J. K. Park, D. H. Kim, and K. Y. Cho, *React. Funct. Polym.,* **70**, 622 (2010).
(18) T. C. Lin, S. C. Yu, P. S. Chen, K. Y. Chi, H. C. Pan, and C. Y. Chao, *Curr. Appl. Phys.,* **9**, 610, (2009).
(19) H. Hah, S. J. Sung, and J. K. Park, *Appl. Phys. Lett.,* **90**, 063508 (2007).
(20) J. S. Choi, K. Y. Cho, and J. H. Yim, *Eur. Polym. J.,* **46**, 389 (2010).
(21) N. Y. Lee, J. R. Lim, M. J. Lee, J. B. Kim, S. J. Jo, H. K. Baik, and Y. S. Kim, *Langmuir,* **22**, 9018 (2006).
(22) J. A. Rogers, Z. N. Bao, and L. Dhar, *Appl. Phys. Lett.,* **73**, 294 (1998).
(23) J. Hahm and S. J. Sibener, *Langmuir,* **16**, 4766 (2000).
(24) M. Kimura, M. J. Misner, T. Xu, S. H. Kim, and T. P. Russell, *Langmuir,* **19**, 9910 (2003).
(25) S. H. Kim, M. J. Misner, T. Xu, M. Kimura, and T. P. Russell, *Adv. Mater.,* **16**, 226 (2004).
(26) J. Naciri, J. Y. Fang, M. Moore, D. Shenoy, C. S. Dulcey, and R. Shashidar, *Chem. Mater.,* **12**, 3288 (2000).